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Synthesis and Luminescence of Soluble *meso*-Unsubstituted Tetrabenzo- and Tetranaphtho[2,3]porphyrins

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Abstract

Syntheses of soluble tetrabenzoporphyrins (TBP) and tetranaphtho[2,3]porphyrins (TNP), with multiple substituents in the conjugated aromatic rings but bearing no substituents in the *meso*-positions, is reported. Both types of porphyrins were obtained by direct aromatization of precursor porphyrins, annealed with either cyclohexene or dihydronaphthalene fragments. TBPs and TNPs possess powerful absorption bands in the near-infrared (λ 610-710 nm, ϵ = 100,000-300,000 M^{-1} cm^{-1}) and exhibit strong luminescence. Free bases and Zn complexes fluoresce with quantum yields of up to 50%, whereas Pd and Pt complexes phosphoresce in solutions at ambient temperatures. Remarkably, the phosphorescence quantum yields of Pd and Pt TBPs reach as high as 20-50%, which places them among the brightest near-infrared phosphors known to date.

Introduction

Porphyrins extended via conjugation with exocyclic aromatic rings form a large group of tetrapyrroles that have received much attention in the recent years.[1] This interest is explained primarily by the photophysical effect of the π-conjugation, known to induce red shifts in the absorption spectra of porphyrins. Absorption in the red region of the spectrum is generally useful for those biomedical applications, which rely on exogenous dyes and/or contrast agents, e.g., PDT,[2] in vivo optical sensing and imaging.[3] Potential applications of π-extended porphyrins, therefore, exist primarily in the biomedical field[3b,4,5] but also include the design of optical limiters[6] and other nonlinear optical materials,[7] as well as the development organic semiconductors,[8] sensitizers for photovoltaic cells[9] and fluorescent STM enhancers.[10]

Our interest in π-extended porphyrins stems from their usefulness as probes for biological oxygen measurements using phosphorescence quenching.[11] Pt and Pd porphyrins show high rates of intersystem crossing from their excited singlet states to the triplet states, from which they decay by emitting phosphorescence.[12] The triplet lifetimes of Pt and Pd porphyrins in solutions at ambient temperatures are usually in the order of tens to hundreds of microseconds, which makes their phosphorescence extremely sensitive to oxygen. For biomedical applications, such as oxygen imaging in tissue in vivo,[3b,13] it is crucial that the absorption bands of the phosphorescent sensors overlap minimally with those of endogenous tissue chromophors (e.g., hemoglobin, myoglobin, cytochromes, etc.). Accordingly, dyes with absorption in the near-infrared and with strong oxygen-dependent phosphorescence have been the focus of our interest. While a large number of porphyrinoids with absorption in the infrared

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Supporting Information Available: Copies of the NMR spectra of newly synthesized porphyrins and metalloporphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

are known to date (e.g., chlorophylls, expanded porphyrins, phthalocyanines, etc.), the list of compounds that simultaneously possess strongly emissive triplet states is very short.[14] Some metal complexes of symmetrically π-extended porphyrins, i.e., tetrabenzoporphyrins (TBPs) and tetranaphtho[2,3]porphyrins (TNPs) (Chart 1), apparently combine both of these properties and, in fact, are superior to the other chromophors due to their particularly intense and narrow transitions in the near-infrared window of tissue.[15]

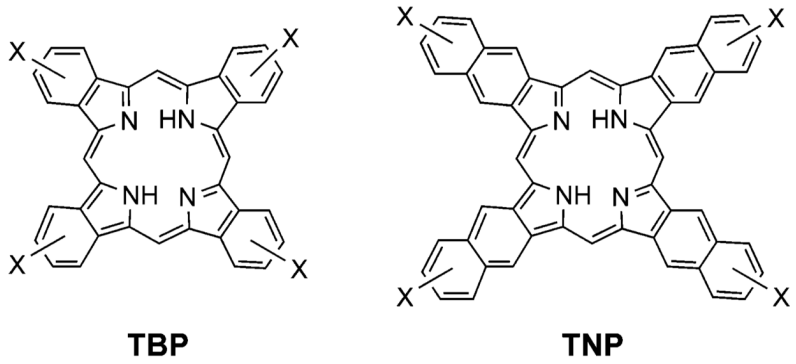

CHART 1.

Some water-soluble Pd *meso*-tetraaryltetrabenzoporphyrins (Ar_4TBP) indeed have been shown to be effective as in vivo phosphorescent oxygen indicators.[3b,15a,b,16] *meso*-Tetraarylated TNPs (Ar_4TNP), although studied much less,[17] also revealed potential in the oxygen-sensing application.[15b,c] At the same time, *meso*-unsubstituted TBPs and TNPs (Chart 1) and their metal complexes have remained practically unexplored in this, as well as in many other, areas of research. This is due largely to the difficulties in their synthesis, their extremely poor solubility and strong aggregation.

Metal complexes of *meso*-unsubstituted TBPs and TNPs, if made adequately soluble, are on the other hand likely to be very potent luminescent chromophores. Core macrocycles in their *meso*-tetraarylated analogues (Ar_4TBPs and Ar_4TNPs), which already exhibit quite strong luminescence, are severely nonplanar.[18,40b,41] Nonplanarity is known to dramatically affect photophysical properties of porphyrins[19] by shifting their absorption bands to the red[20] and by reducing their luminescence quantum yields.[21] According to both the X-ray data[8b,c] and the computational studies,[22] TBPs and TNPs possess nearly ideally planar geometries. Therefore, it would be reasonable to expect that the luminescence quantum yields of TBPs and TNPs would be considerably higher than those of nonplanar Ar_4TBPs and Ar_4TNPs. Given that the absorption Q-bands of TBPs and TNPs are already positioned in the red as a consequence of the π-conjugation, these porphyrins should be superior as biological luminescent sensors.

Understanding the effects of nonplanarity is interesting not only for practical reasons. The interplay between the porphyrin structure and porphyrin photophysics has been intensely discussed in the recent literature.[19,20,23] Not surprisingly, only a few experimental studies address the effects of nonplanarity in π-conjugated porphyrins,[6d,15c,24,25] which is explained by their limited synthetic availability. In the past several years considerable progress has been made in the synthesis of *meso*-tetraarylated extended porphyrins (vide infra), and some of studies of their photophysical properties have been conducted. At the same time, soluble, nonaggregating planar TBPs and TNPs still remain a much less accessible target. Synthesis of these molecules constitutes the main focus of the present work.

Synthesis of *meso*-unsubstituted tetrabenzoporphyrin (TBP) was originally described by Helberger and co-workers[26] and later by Linstead and co-workers.[27] The TBP macrocycle was assembled by self-condensing *o*- cyanoacetophenone in the presence of metal salts at high temperature,[26] an approach resembling classic phthalocyanine chemistry. A number of similar precursors, such as *o*-acetylbenzoic acid,[28] phthalimides,[29] phthalimidines,[26,27,30] isoindoles[31] and isoindoline,[32] were used later to prepare differently substituted TBPs. The first synthesis of tetranaphtho[2,3]porphyrin (TNP) also relied on the "template condensation" method.[33] TNP was synthesized by condensing 3-carboxymethyl-5,6-benzophthalimidine with Zn acetate at high temperature. Several peripherally substituted TNPs, as well as isomeric tetranaphtho[1,2]porphyrins, were later prepared by similar methods from the corresponding benzophthalimidines or naphthalenedicarboximides.[34]

Aside from low yields and the large number of side products, the template condensation approach suffers because of the extremely harsh conditions required for the macrocycle assembly (i.e., fusion at 350-400 °C). Only a few TBPs and TNPs with inert substituents could be synthesized using this method.[29b,30b,31,32] Over the past decade, several new approaches to π-extended porphyrins have emerged, all of them relying on more traditional porphyrin chemistry. A number of π-extended porphyrins were synthesized by Lash and co-workers and Ono and co-workers from the corresponding porphyrinogenic pyrroles, annealed with external aromatic rings.[1b,35,36] Applying the same methodology to tetrabenzo- and tetranaphtho[2,3] porphyrins, however, was impossible because of the very low stability of the required isoindoles.[37] As a result, approaches based on the use of masked isoindole moiety received increasing attention. Two methods of synthesis of the TBP system have been subsequently devised by Cavaleiro's[38] and Ono's groups.[39] In the first method, TBP was synthesized form the precursor cyclohexenoporphyrin by base-catalyzed elimination of sulfinate, followed by oxidation with DDQ.[38] In the second, TBP, TNP and their *meso*-arylated analogues were synthesized by thermal extrusion of ethylene from porphyrins fused with bicyclo[2.2.2] octadiene fragments.[39] A recent version of the latter approach makes it possible to synthesize polyfunctionalized TBPs at low temperatures;[39e] however, the synthesis of bicyclo-fused pyrroles themselves is rather complicated, and no TNPs with substituents in the fused aromatic rings could be produced by this method.

In the course of our own work on the synthesis of polyfunctionalized π-extended porphyrins we came across a useful strategy based on the direct oxidative aromatization of precursor porphyrins, annealed with nonaromatic hydrocarbon rings.[5,40,41,42] Using this method, a variety of Ar_4TBPs[5,40] and Ar_4TNPs[41] were synthesized in good yields from readily available starting materials. In the present paper we extend our methodology on the synthesis of soluble *meso*-unsubstituted TBPs and TNPs and report their basic photophysical properties.

Results and Discussion

Synthesis of *meso*-Unsubstituted Tetrabenzoporphyrins (TBPs)

Synthesis of TBP-octaesters **6a,b** is shown in Scheme 1. Esters **1a,b** were obtained from commercially available 1,2,3,6-tetrahydrophthalic anhydride using standard procedures. Conversion of **1a** (R = Me) into sulfone **2a** and then into pyrroles **3a** and **4a** followed the published method.[40b] The same general procedures were used in the case of dibutoxycarbonyl derivatives, although both sulfone **2b** and pyrrole ester **3b** (X = Bn) were isolated as oils. To allow adequate characterization, these oils could be purified by simple flash chromatography (90-95% purity). Benzyl ester **3b** was subjected to Pd-catalyzed hydrogenolysis, followed by decarboxylation of the pyrrole acid to give pyrrole **4b** in 82% overall yield. Alternatively, *tert*-butyl ester **3c** could be used as a precursor to **4b**. **3c** has an advantage of being a solid compound, and its conversion into **4b** could be accomplished in a single step by being treated with TFA. However, the yield of **4b** in this case was only 30-40%.

Syntheses of tetracyclohexenoporphyrins (TCHPs) **5a,b** from pyrroles **4a,b** followed the classic synthesis of octaethylporphyrin (OEP).[43] Porphyrin **5b** with eight butoxycarbonyl groups was obtained in a higher yield (40-45%) than its octamethoxycarbonylated analogue **5a** (30-40%). The increase in the yield was probably caused by the better solubility of the reaction intermediates, containing multiple butoxycarbonyl residues. Similarly, porphyrin **5b** is very well soluble in most organic solvents (CH_2Cl_2, THF, diethyl ether), whereas porphyrin **5a** is only moderately soluble.

TCHPs **5a,b** were oxidized into the corresponding TBPs **6a,b** by DDQ. The aromatization required substantially longer reaction times than did the recently reported aromatization of *meso*-tetraarylated TCHPs (Ar_4TCHPs).[5,40] However, the processes could be driven to completion, and the products were isolated in moderate (**6a**) to quantitative (**6b**) yields. The most striking difference between the reactivities of *meso*-unsubstituted TCHPs and Ar_4TCHPs was that in the latter case it was necessary to preconvert Ar_4TCHPs into their Cu, Ni or Pd complexes,[5,40] whereas **5a,b** could be oxidized into TBPs directly as free bases. Removing the metalation/demetalation step is obviously an advantage from the practical point of view but is also curious mechanistically.[40b] Metal assistance in the case of Ar_4TCHPs was necessary because when these porphyrins, taken as free bases, were subjected to aromatization, they instantaneously formed dications, completely inert with respect to the oxidation. We have speculated that the protonation of the free bases occurred either directly, due to the acidification of the medium, or via the hydrogen abstraction from the solvent by an intermediate free-base cation radical.[40b] The fact that the rate of the aromatization appears to be reciprocal to the proton affinities of the free bases argues for the former pathway. The basicities of nonplanar Ar_4TCHPs are much higher than those of their planar counterparts TCHPs,[18b] and the latter, as evidenced by our present results, can be aromatized as free bases.

Overall, more soluble octabutoxycarbonyl-TCHP **5b** performed much better in the aromatization than its octamethoxycarbonyl analogue **5a**, whose oxidation was additionally complicated by side reactions. For example, the oxidation of **5b** and **Zn-5b** in toluene was completed after 4 h and required a 1.5- to 2-fold excess of DDQ. Under the same conditions, oxidation of **5a** gave only undefined insoluble green solids, possibly products of the oxidative oligomerization. Aromatization of both **5a** and **Zn-5a** could be accomplished in dioxane, but required a larger excess of DDQ (5- to 6-fold) and longer reaction times. Notably, neither Cu (II) nor Ni(II) nor Pd(II) complexes of **5a** gave metallo-TBPs in good yields, whereas these metals have proven to be the best in the aromatization of Ar_4TCHPs.[40b]

TBP **6b** was further used to synthesize its Pd, Pt and Fe complexes, all of which showed excellent solubility in most common organic solvents. The structure and purity of the newly synthesized complexes were confirmed by ^{1}H and ^{13}C NMR, MALDI-TOF spectrometry and elemental analysis. Pd and Pt derivatives were obtained by refluxing **6b** with the corresponding chlorides in benzonitrile. For insertion of Fe, **6b** was refluxed with a large excess of $FeCl_2$ in propionic acid in the presence of iron wire. The UV-vis spectrum of the resulting **Fe-6b** was very similar to that of Fe(II) (bis)pyridine TBP.[28a] **Fe-6b** was stable on air for days both in the solid state and in solution when stored in the dark. A well-resolved NMR spectrum of **Fe-6b** suggests that this compound is a diamagnetic complex.[44]

Synthesis of *meso*-Unsubstituted Tetranaphtho[2,3]porphyrins (TNP)

TNPs **13a,b** were synthesized as shown in Scheme 2. The starting materials and reagents used in these syntheses were similar to those employed in the synthesis of the *meso*-tetraarylated analogues of porphyrin **13a** (X = OMe), reported recently.[41] The key starting material, 5,8-dihydroxy-1,4-dihydronaphthalene **7**, was prepared from butadiene and 1,4-benzoquinone[45] and converted into its alkoxy derivatives using Williamson alkylation. Dimethoxy derivative **8a** was prepared as described previously,[45] whereas dialkoxy derivatives **8b** and **8c**, terminated

with ester groups, were prepared from **7** and ethyl bromoacetate or ethyl 4-bromobutyrate, respectively.

α-Chlorosulfone **9a** (X = OMe) was obtained from **8a** following the published method.[41] Synthesis of pyrrole **11a** from **9a** was performed as described earlier.[41] **9a** was introduced into the modified Barton-Zard reaction with ethyl isocyanoacetate to give pyrrole ester **10a**, which was further converted into 2,5-unsubstituted pyrrole **11a** upon refluxing with KOH in ethylene glycol.

α-Chlorosulfones **9b,c** were prepared from alkenes **8b,c** by the same method as **9a**.[41] However, because both **9b** and **9c** contained ethyl ester groups, which were intended to be kept intact throughout the rest of the transformations, the use of ethyl isocyanoacetate in the subsequent Barton-Zard synthesis (step c in Scheme 2) was not feasible. Indeed, hydrolytic cleavage of the pyrrole-ethyl ester in the following step (step d in Scheme 2) would require heating this compound with KOH, and that would simultaneously destroy the peripheral ethyl ester groups. Consequently, we turned our attention to isocyanoacetates containing selectively cleavable benzyloxycarbonyl and *tert*-butoxycarbonyl groups. To our surprise, benzyl isocyanoacetate did not react with chlorosulfones **9a-c** at all. *tert*-Butyl isocyanoacetate, on the other hand, reacted readily with sulfone **9c** (X = $O(CH_2)_3CO_2Et$, Scheme 2), giving pyrrole ester **10b** in 70-80% yield, but did not react with **9b** (X = OCH_2CO_2Et, Scheme 2). Only trace amounts of the corresponding pyrrole ester could be isolated, and there was a similar result when **9b** reacted with ethyl isocyanoacetate.

The reasons for the unexpected behavior of benzyl isocyanoacetate is not well understood. In our past experience, benzyl isocyanoacetate did consistently show a somewhat lower reactivity in the Barton-Zard synthesis than did ethyl and *tert*-butyl isocyanoacetates but still usually gave pyrrole esters in reasonably good yields.[40] Lash and co-workers, who originally introduced benzyl isocyanoacetate,[46] used it successfully in many different syntheses;[1b] however, they also commented on its lower reactivity.[46] On the other hand, for **9a-c** the equilibrium between the vinyl sulfone[47] and allyl sulfone forms[48] is most certainly shifted toward the latter. Allyl sulfones are inactive in the Barton-Zard reaction, and thus, reduction in the concentration of the substrate (vinyl sulfone), combined with less active reagent (benzyl isocyanoacetate), led to such a dramatic decrease in the reaction rate, that virtually no condensation could be observed.

One possible explanation of the low reactivity of **9b** is that this chlorosulfone, as well as the corresponding vinyl sulfone, possesses relatively easily ionizable CH_2 groups in the side chains (-O**CH**$_2$$CO_2$R). Abstraction of a proton from one of these groups, under conditions of the Barton-Zard condensation[49] would produce an anionic species, which is likely to be inert in the condensation with isocyanoacetates.

Pyrrole ester **10b**, synthesized from sulfone **9c** and *tert*-butyl isocyanoacetate, was cleaved and decarboxylated by TFA to give **11b** in 98% yield. Pyrroles **11a** (vide supra) and **11b** were further reacted with formaldehyde under conditions similar to those used in the synthesis of **5a,b** (Scheme 1). The UV-vis spectra of the reaction mixtures after the condensation closely resembled the spectra of OEP, evidencing formation of the intermediate octahydro-TNPs of type **12** (Scheme 2). These porphyrins, however, were not isolated. Instead, the mixtures were treated with DDQ or *p*-chloranil, and within minutes the conversion of **12** into TNPs was complete.

Octamethoxy-TNP **13a** appeared to be insoluble in most organic solvents. It was purified by washing it with pyridine and THF, followed by recrystallization from refluxing benzonitrile. Porphyrin **13b**, on the contrary, is very well soluble in many organic solvents, and it was purified by repetitive precipitation from CH_2Cl_2 by acetonitrile. Porphyrins **13a,b** were

isolated in 25-33% yields and converted into their Zn and Pd complexes by being reacted with the corresponding metal salts in refluxing pyridine or benzonitrile-pyridine mixtures.

NMR characterization of porphyrins **13a** and **Pd-13a** was impossible due to their extremely low solubilities. The solubility of **13b** and its complexes was significantly higher, but at the level of concentrations required for the NMR analysis aggregation still presented a considerable problem, especially for the Pd complex. Consequently, the aromatic signals in the spectra of **Pd-13b** appeared to be severely broadened. At the same time, the spectra of the free base **13b** and of **Zn-13b** were quite well resolved, with aromatic resonances appearing at 11-12 ppm.

Photophysical Properties of *meso*-Unsubstituted TBPs and TNPs

Original photophysical studies of tetrabenzoporphyrin and its metal complexes were performed by Soloviev and co-workers[50] and by Gouterman and co-workers.[30c,51] Later, a number of investigators studied metallo-TBPs, primarily with respect to their applications.[4a,15a,52] The photophysics of the TNP system,[34a,17d,53] however, remains seriously understudied. Just the basic photophysical characteristics of Ar_4TNPs have been recently reported,[6d,15c,17g,41] whereas the properties of *meso*-unsubstituted TNPs have not yet been explored.

We have measured the absorption and emission characteristics of TBPs **M-6b** and TNPs **M-13b** and have compared them with those of Ph_4TBPs[5,40] and Ph_4TNPs,[41] substituted with similar functional groups in the fused aromatic rings. In this way, the influence of the side substituents on the photophysical properties can be excluded, whereas the effects of the nonplanar deformation and/or extra π-conjugation involving *meso*-aryl rings can be emphasized. The data are summarized in Table 1, and some absorption and emission spectra are shown in Figures 1 and 2.

The absorption bands of *meso*-unsubstituted TBPs and TNPs are blue-shifted by about 20-40 nm compared to the corresponding bands of Ar_4TBPs and Ar_4TNPs. This reflects the severe nonplanarity of the latter, confirmed earlier by both computational[6d,15c] and X-ray data.[18, 40b,41] Along with its own effect on the absorption spectra,[20,21] the nonplanar deformation causes the *meso*-aryl rings in Ar_4TBPs and Ar_4TNPs to be partially drawn into the π-conjugation, which additionally contributes to the red shifts of the absorption bands.[6d] Consistent with flat structures of porphyrins of **M-6b** and **M-13b**, their Q-bands are much narrower and generally more intense than those of Ar_4TBPs and Ar_4TNPs. The emission bands of **M-6b** and **M-13b** are also much sharper and in some cases (e.g., fluorescence of **6b** and **13b**, Figure 1) display relatively well resolved vibronic structures. The Stokes shifts of the fluorescence of free bases **6b** and **13b** are very small (66 cm^{-1} for **6b**; 94 cm^{-1} for **13b**), whereas the Stokes shifts of the fluorescence of Ar_4TBP free bases are typically in the order of several thousands of cm^{-1} (Table 1). All together, these facts consistently point toward the greatly increased rigidity of planar *meso*-unsubstituted porphyrins and suggest an increase in their radiative transitions.

Indeed, the values of the fluorescence quantum yields of *meso*-unsubstituted TBPs and TNPs free bases are in the range of 15-50%, which is significantly higher than for the analogous $Ar_4TBP(CO_2Me)_8$'s and $Ar_4TNP(OMe)_8$'s (Table 1). As expected, Pd and Pt complexes of either TBPs or TNPs do not show fluorescence, which is due to a dramatic enhancement of their intersystem crossing. Instead, they emit from their triplet states. The quantum yields of the phosphorescence of TBPs **Pd-6b** and **Pt-6b** were found to be as high as 25% and 51% respectively, placing these metalloporphyrins among the brightest near-infrared phosphors known to date. The phosphorescent quantum yields of these porphyrins, as well as their triplet lifetimes are considerably larger than those of Ar_4TBPs.

Based on the trends observed for TBPs and because of the high fluorescence quantum yield of **13b** (45%), a similarly high quantum yield of the phosphorescence of Pd-TNP was expected. To our surprise, the phosphorescence of **Pd-13b** appeared to be quite moderate (ϕ = 4%), resembling that of Pd-Ph_4TNP$(OMe)_8$ (ϕ = 2.5%).[54] It is possible that the lower emission yield of **Pd-13b** is due to the very low energy of the triplet band itself (λ_{max} = 923 nm). Such a low energy triplet state is probably effectively overlapped by many ground-state vibrations, which enhance the rate of its internal conversion and cause the decrease in the emission quantum yield. Nevertheless, the phosphorescence quantum yield of **Pd-13b**, although below expected, is still entirely adequate for considering this chromophor in practical biological applications.

In conclusion, a convenient method of synthesis of *meso*-unsubstituted tetrabenzo- (TBP) and tetranaphtho[2,3]porphyrins (TNP) with solubilizing groups at the periphery is described. The porphyrins were synthesized in 33-45% yields from readily available precursors. TBPs and TNPs and their metal complexes exhibit powerful absorption bands in the red region of the spectrum and luminesce with quantum yields of up to 50%. This places them among the brightest near-infrared absorbing luminescent tetrapyrroles known to date. Because of their exceptionally strong phosphorescence in solutions at ambient temperatures, Pd and Pt complexes of *meso*-unsubstituted π-extended porphyrins show great promise as luminescent probes for biological applications.

Experimental Section

Ethyl isocyanoacetate,[55] benzyl isocyanoacetate[46] and *tert*- butyl isocyanoacetate[56] were prepared according to the published methods. Dimethyl 1,2,3,6-tetrahydrophthalate **1a** was obtained from 1,2,3,6-tetrahydrophthalic anhydride as described previously.[57] 5,8-Dihydroxy-1,4-dihydronaphthalene **7**[45] and 5,8-dimethoxy-1,4-dihydronaphthalene **8a**[45] were synthesized as reported previously. Vinyl sulfone **2a**[40b] and α-chlorosulfone **9a**[41] were prepared following the published methods. Pyrrole esters **3a**[40b] and **10a**[41] and pyrroles **4a**[40b] and **11a**[41] were synthesized according to the published procedures. The equipment used for the analytical characterization of the compounds was described elsewhere.[40b,41] Melting points are reported uncorrected.

Dibutyl 1,2,3,6-Tetrahydrophthalate (1b)

1b was obtained from 1,2,3,6-tetrahydrophthalic anhydride by a standard esterification method. 1,2,3,6-Tetrahydrophthalic anhydride (15 g, 99 mmol), butyl alcohol (40 mL), benzene (100 mL) and $TsOH{\cdot}H_2O$ (0.1 g, 0.53 mmol) were refluxed with a Dean-Stark refluxing condenser until the separation of water stopped. $NaHCO_3$ (0.5 g, 5.95 mmol) was added to the mixture and the excess of butyl alcohol was removed in a vacuum. The resulting material was dissolved in diethyl ether (100 mL), washed with 10% aqueous Na_2CO_3 (100 mL) and dried over K_2CO_3. After evaporation of the solvent, **1b** was obtained as a colorless oil. Yield: 21.1 g, 75%. ^{1}H NMR ($CDCl_3$) δ 5.65 (s, 2H), 4.07 (t, 4H, J = 6.5 Hz), 3.02 (m, 2H), 2.56-2.31 (m, 4H) 1.58 (m, 4H), 1.34 (m, 4H), 0.91 (t, 6H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 173.3, 125.2, 64.42, 39.8, 30.6, 25.9, 19.2, 13.7.

Vinyl Sulfone (2b)

Synthesis of sulfone **2b** from the ester **1b** followed the general procedure described previously.[58] The product was purified by flash chromatography on a short silica gel column (eluent CH_2Cl_2) and isolated as a yellow oil. Yield: 83%. ^{1}H NMR ($CDCl_3$) δ 7.85-7.50 (m, 5H), 7.06 (d, 1H, J = 2 Hz), 4.03-3.86 (m, 4H), 3.10 (m, 1H), 3.00 (m, 1H), 2.90 (m, 1H), 2.60 (m, 3H), 1.45 (m, 4H), 1.28 (m, 4H), 0.88 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 172.1, 171.8, 139.2, 138.5, 136.8, 133.5, 129.3, 128.3, 128.2, 65.1, 39.7, 39.0, 30.7, 30.6, 26.6, 24.4, 19.3, 13.9.

Pyrrole Esters (3b,c)

Esters **3b,c** were synthesized from vinyl sulfone **2b** and the corresponding alkyl isocyanoacetates following the published method,[49d] used previously to synthesize pyrrole **3a** from sulfone **2a** and alkyl isocyanoacetates.[40b]

Benzyl ester **3b** was purified by chromatography on a silica gel column (eluent CH_2Cl_2) and isolated as a yellow oil. Yield of **3b**: 65%. ^{1}H NMR ($CDCl_3$) δ 8.89 (br s, 1H), 7.42-7.31 (m, 5H), 6.67 (d, 1H, J = 1.5 Hz), 5.29 (m, 2H), 4.06 (m, 4H), 3.41-2.83 (m, 6H), 1.56 (m, 4H), 1.32 (m, 4H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 174.5, 173.3, 170.3, 136.6, 128.7, 128.3, 128.2, 127.3, 119.8, 119.3, 117.8, 65.9, 64.8, 64.7, 41.2, 41.1, 30.7, 24.1, 22.6, 19.6, 16.3, 13.9.

tert-Butyl ester **3c** was purified by flash chromatography on a short silica gel column (eluent CH_2Cl_2-THF, 30:1), followed by recrystallization from methanol. Yield of **3c**: 60%, colorless crystals, mp 88-90 °C. ^{1}H NMR ($CDCl_3$) δ 8.96 (br s, 1H), 6.63 (d, 1H, J = 3 Hz), 4.07 (m, 4H), 3.32-2.82 (m, 6H), 1.59-1.55 (s+m, 9+4H), 1.34 (m, 4H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 173.5, 173.4, 161.6, 124.5, 119.5, 119.4, 118.4, 80.7, 64.74, 64.69, 41.23, 41.19, 30.8, 28.7, 24.1, 22.9, 19.3, 13.8. Anal. Calcd for $C_{25}H_{35}NO_6$: C, 65.53; H, 8.37; N, 3.32. Found: C, 65.42; H, 8.33; N, 3.44.

Pyrrole 4b

4b was synthesized from either benzyl ester **3b** or *tert*-butyl ester **3c** following the procedures described earlier for the synthesis of pyrrole **4a**.[40b] **4b** was purified by flash chromatography on a short silica gel column (eluent CH_2Cl_2). Yield: 82% (from **3b**) or 35% (from **3c**), colorless oil. ^{1}H NMR ($CDCl_3$) δ 8.32 (br s, 1H), 6.37 (d, 2H, J = 2 Hz), 3.97 (m, 4H), 3.10-2.80 (m, 6H), 1.50 (m, 4H), 1.25 (m, 4H), 0.83 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 173.7, 116.6, 113.5, 64.6, 41.7, 30.7, 22.8, 19.2, 13.7.

Tetracyclohexenoporphyrins (5a,b)

Syntheses of porphyrins **5a,b** followed the procedure described for the synthesis of OEP.[43] The pyrrole (**4a** or **4b**, 1.6 mmol) was dissolved in benzene (90 mL), the reaction flask was flushed with Ar and shaded from light by a piece of aluminum foil. Formaldehyde (37% aqueous solution, 0.18 mL) and $TsOH\cdot H_2O$ (10 mg, 0.05 mmol) were added, and the mixture was refluxed with a Dean-Stark condenser for 6-8 h under Ar. The mixture was cooled to room temperature, and the flow of air was passed through the mixture overnight under continuous stirring. The solvent was evaporated, and the remaining material was purified on a silica gel column (eluent CH_2Cl_2-THF; **5a**, 20:1-10:1; **5b**, 100:1-50:1). The red fraction was collected, evaporated to dryness, dissolved in a small volume of THF, layered over with ~20-fold excess volume of MeOH-H_2O (3:1) and left overnight in a closed vial. The resulting precipitate was collected by centrifugation and dried in a vacuum. Yield of **5a**: 30-40%, red powder. ^{1}H NMR ($CDCl_3$) δ 9.98-9.85 (m, 4H), 4.70-3.60 (m, 48H), -3.80 (br, 4H); MALDI-TOF: *m*/*z* 990.82, calcd 990.35; UV-vis, CH_2Cl_2, λ_{max} nm (ϵ) 399 (185,000), 498 (14,300), 533 (13,000), 566 (7,000), 620 (5,000). Anal. Calcd for $C_{52}H_{54}N_4O_{16}$: C, 63.02; H, 5.49; N, 5.65. Found: C, 62.28; H, 5.31; N, 5.51. Yield of **5b**: 40-45%, red powder. ^{1}H NMR ($CDCl_3$) δ 9.95-9.80 (m, 4H), 4.50-3.80 (m, 40H), 1.90-0.80 (m, 56H), -3.85 (br, 4H); MALDI-TOF: *m*/*z* 1329.02, calcd 1326.73; UV-vis, CH_2Cl_2, λ_{max} nm (ϵ) 400 (180,000), 498 (14,000), 533 (13,000), 566 (7,000), 620 (5,000). Anal. Calcd for $C_{76}H_{102}N_4O_{16}$: C, 68.75; H, 7.74; N, 4.22. Found: C, 68.37; H, 7.57; N, 4.19.

Zn Tetracyclohexenoporphyrins (Zn-5a,b)

An excess of $Zn(OAc)_2\cdot 2H_2O$ (100 mg, ~0.5 mmol) was added to a solution of porphyrin **5a** or **5b** (0.1 mmol) in THF (20 mL), and the mixture was refluxed for 15-20 min. The conversion

was monitored by UV-vis spectroscopy (solvent THF). The reaction was stopped when the absorption band of the free base porphyrin (λ_{max} = 620 nm) disappeared. The mixture was evaporated to dryness, and the remaining material was purified on a silica gel column (eluent CH_2Cl_2-THF, 20:1). The first pink fraction was collected and evaporated to dryness to give the product as a red amorphous solid. Yield of **Zn-5a**: 95-97%. ^{1}H NMR (DMSO-d_6) δ 9.95-9.80 (m, 4H), 4.80-3.60 (m, 48H); MALDI-TOF *m*/*z* 1054.05, calcd 1052.27; UV-vis, CH_2Cl_2, λ_{max} nm (ϵ) 402 (240,000), 533 (16,000), 568 (12,000). Anal. Calcd for $C_{52}H_{52}N_4O_{16}Zn$: C, 59.23; H, 4.97; N, 5.31. Found: C, 58.80; H, 4.96; N, 5.20. Yield of **Zn-5b**: 95-97%. ^{1}H NMR (DMSO-d_6) δ 9.89 (s, 4H), 4.60-4.40 (m, 16H), 4.2-4.0 (m, 24H), 1.60 (m, 16H), 1.36 (m, 16H0, 0.85 (m, 16H); MALDI-TOF *m*/*z* 1405.51, calcd 1403.67; UV-vis, CH_2Cl_2, λ_{max} nm (ϵ) 402 (220,000), 533 (16,000), 568 (12,000). Anal. Calcd for $C_{77}H_{103}N_4O_{16}Zn$: C, 65.77; H, 7.38; N, 3.98. Found: C, 65.25; H, 7.45; N, 3.60.

Tetrabenzoporphyrins (6a,b and Zn-6a,b)

To synthesize porphyrins **6a** and **Zn-6a**, **5a** or **Zn-5a** (0.1 mmol), respectively, was dissolved in dioxane (75 mL), DDQ (450 mg, 2.0 mmol) was added, and the mixture was refluxed under Ar for 3 h. An extra portion of DDQ (450 mg, 2.0 mmol) was added and the mixture was refluxed for additional 2-3 h. The conversion was monitored by UV-vis spectroscopy (solvent CH_2Cl_2-pyridine).[39d] If required, more DDQ was added and the refluxing was continued until the conversion was complete. In the case of **6b** or **Zn-6b**, **5b** or **Zn-5b** (0.1 mmol), respectively, was dissolved in toluene (100 mL), DDQ (363 mg, 1.6 mmol) was added, and the mixture was refluxed under Ar for 4-5 h, after which the conversion (monitored by UV-vis spectroscopy) was complete.

The workup in all the cases, i.e., **6a**, **Zn-6a**, **6b** and **Zn-6b**, followed the same protocol. The mixture was reduced to a small volume (5-10 mL), CH_2Cl_2 (150 mL) was added, and the resulting solution was washed with 10% aqueous Na_2SO_3 and 10% aqueous Na_2CO_3 and dried over K_2CO_3. After evaporation of the solvent, the resulting material was purified on a silica gel column (eluent CH_2Cl_2-THF, 20:1). The bright green fraction was collected, its volume was reduced down to about 5 mL, and the solution was layered over with methanol and left in a closed vial overnight. The resulting green precipitate was collected by centrifugation and dried in a vacuum. Yield of **6a**:[39f] 20-30%, green powder. Yield of **Zn-6a**:[39d] 96%, green powder. Yield of **6b**: 95%, green powder. ^{1}H NMR ($CDCl_3$) δ 9.55 (s, 4H), 9.22 (s, 8H), 4.74 (t, 16H, *J* = 7 Hz); 2.08 (m, 16H), 1.74 (m, 16H), 1.19 (t, 24H, *J* = 7.5 Hz), -5.06 (br, 2H); ^{1}H NMR (TFA-*d*) δ 11.99 (s, 4H), 10.52 (s, 8H), 4.90 (t, 16H, *J* = 7 Hz); 2.13 (m, 16H), 1.75 (m, 16H), 1.20 (t, 24H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 168.1, 131.7, 122.1, 94.0, 66.4, 31.2, 19.7, 14.3; MALDI-TOF *m*/*z* 1311.54, calcd 1310.60; UV-vis, DMF, λ_{max} nm (ϵ) 404 (46,500), 432 (240,000), 447 (325,000), 579 (20,000), 617 (66,500), 626 (70,000), 673 (46,000). Anal. Calcd for $C_{76}H_{86}N_4O_{16}$: C, 69.60; H, 6.61; N, 4.27. Found: C, 69.19; H, 6.66; N, 4.54. Yield of **Zn-6b**: 97%, green powder. ^{1}H NMR (pyridine-d_5, 50 °C) δ 11.25 (s, 4H), 10.26 (s, 8H), 4.85 (t, 16H, *J* = 7 Hz); 2.05 (m, 16H), 1.69 (m, 16H), 1.11 (t, 24H, *J* = 7.5 Hz); ^{13}C NMR (pyridine-d_5, 50 °C) δ 169.5, 144. 9, 140.6, 132.2, 97.6, 66.5, 31.6, 20.1, 14.4; MALDI-TOF *m*/*z* 1373.11, calcd 1372.52; UV-vis, pyridine, λ_{max} nm (ϵ) 433 (55,-400), 460 (434,000), 589 (22,200), 647 (139,000). Anal. Calcd for $C_{76}H_{84}N_4O_{16}Zn$: C, 66.39; H, 6.16; N, 4.08. Found: C, 66.20; H, 6.19; N, 4.19.

Pd and Pt Tetrabenzoporphyrins (Pd-6b and Pt-6b)

Free base tetrabenzoporphyrin **6b** (35 mg, 0.027 mmol) was dissolved in PhCN (5 mL), $PdCl_2$ (10 mg, 0.053 mmol) or $PtCl_2$ (15 mg, 0.053 mmol) was added, and the mixture was refluxed under Ar. The metal insertion required 5-10 min in the case of Pd complex and 8 h in the case of Pt complex. The conversion was monitored by UV-vis spectroscopy (solvent DMF), and the reaction was stopped when the free-base Q-band (λ_{max} = 673 nm) disappeared. The

mixture was evaporated to dryness at 0.1 mmHg, and the remaining material was washed with methanol, dried, and purified on a silica gel column (eluent CH_2Cl_2-THF, 20:1) to give the product as a blue-green amorphous solid. Yield of **Pd-6b**: 90%. ^{1}H NMR (pyridine-d_5, 70 °C) δ 9.74 (br s, 4H), 9.33 (s, 8H), 4.95 (t, 16H, J = 7 Hz); 2.20 (m, 16H), 1.83 (m, 16H), 1.28 (t, 24H, J = 7.5 Hz); ^{13}C NMR (pyridine-d_5, 70 °C) δ 168.7, 137.3, 135.1., 132.4, 124.2, 97.3, 66.7, 31.6, 20.1, 14.4. MALDI-TOF m/z 1413.33, calcd1414.49; UV-vis, DMF, λ_{max} nm (ϵ) 426 (305,000), 565 (17,000), 618 (160,000). Anal. Calcd for $C_{76}H_{84}N_4O_{16}Pd$: C, 64.47; H, 5.98; N, 3.96. Found: C, 64.29; H, 5.62; N, 4.03. Yield of **Pt-6b**: 84%. ^{1}H NMR (pyridine-d_5, 80 °C) δ 9.99 (s, 4H), 9.46 (s, 8H), 4.92 (t, 16H, J = 7 Hz); 2.16 (m, 16H), 1.80 (m, 16H), 1.23 (t, 24H, J = 7.5 Hz); ^{13}C NMR (pyridine-d_5, 50 °C) δ 168.8, 137.3, 134.8, 132.6, 122.6, 98.1, 66.8, 31.8, 20.2, 14.5; MALDI-TOF m/z 1503.49, calcd 1503.55; UV-vis, pyridine, λ_{max} nm (ϵ) 416 (170,000), 557 (19,000), 609 (165,000). Anal. Calcd for $C_{76}H_{84}N_4O_{16}Pt$: C, 60.67; H, 5.63; N, 3.72. Found: C, 59.84; H, 5.23; N, 3.92.

Fe tetrabenzoporphyrin (Fe-6b)

Porphyrin **6b** (27 mg, 0.02 mmol) was dissolved in propionic acid (10 mL). $FeCl_2 \cdot 4H_2O$ (100 mg, 0.5 mmol) and iron wire (~100 mg) were added, and the mixture was refluxed under Ar for ~1 h. The conversion was monitored by UV-vis spectroscopy (solvent DMF), and the reaction was stopped when the free-base Q-band (λ_{max} = 673 nm) disappeared. The mixture was filtered, the filtrate was evaporated to dryness, and the remaining material was washed with methanol-pyridine mixture and dried in a vacuum. The product was isolated as a blue-green amorphous solid. Yield of **Fe-6b**: 20 mg, 74%. ^{1}H NMR (pyridine-d_5) δ 11.38 (s, 4H), 10.12 (s, 8H), 4.72 (t, 16H, J = 7 Hz); 1.92 (m, 16H), 1.59 (m, 16H), 1.02 (t, 24H, J = 7.5 Hz); ^{13}C NMR (pyridine-d_5) δ 169.5, 143.2, 143.3, 131.2, 121.7, 98.3, 66.4, 31.5, 19.9, 14.2; MALDI-TOF m/z 1365.17, calcd 1364.52; UV-vis, pyridine, λ_{max} nm (ϵ) 422 (110,000), 446 (99,500), 613 (100,000). Anal. Calcd for $C_{76}H_{84}N_4O_{16}Fe$: C, 66.86; H, 6.20; N, 4.10. Found: C, 66.29; H, 6.45; N, 3.98.

5,8-Dialkoxy-1,4-dihydronaphthalenes (8b,c)

Synthesis of compound **8b** generally followed the procedure described for the synthesis of 5,8-dimethoxy-1,4-dihydronaphthalene **8a**.[45] Ethyl bromoacetate was used in the present synthesis instead of dimethyl sulfate. Yield of **8b**: 85%, colorless solid, mp 117-118 °C. ^{1}H NMR ($CDCl_3$) δ 6.50 (s, 2H), 5.87 (s, 2H), 4.56 (s, 4H), 4.24 (q, 4H, J = 7.5 Hz), 3.35 (s, 4H), 1.28 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.2, 169.4, 125.7, 123.5, 108.5, 66.2, 61.3, 24.4, 14.3. Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.50; H, 6.58. Compound **8c** was synthesized using a similar procedure. A mixture of 5,8-dihydroxy-1,4-dihydronaphthalene **7** (3.24 g, 20 mmol), ethyl 3-bromobutirate (11.7 g, 9.0 mL, 60 mmol), NaI (1.5 g, 10 mmol) and K_2CO_3 (15 g) was refluxed in acetone (100 mL) for 48-60 h. The solid was filtered off, washed with CH_2Cl_2 (100 mL), and the filtrate was evaporated under reduced pressure. The resulting material was recrystallized from ethyl alcohol to afford **2c** as a cream-colored solid. Yield of **8c**: 5.45 g, 69%, mp 117-118 °C. ^{1}H NMR ($CDCl_3$) δ 6.58 (s, 2H), 5.86 (s, 2H), 4.13 (q, 4H, ^3J(H,H) = 6.5 Hz), 3.93 (t, 4H, J = 6 Hz), 3.25 (s, 4H), 2.51 (t, 4H, J = 7.5 Hz), 2.10 (m, 4H), 1.25 (t, 6H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 173.5, 150.4, 124.9, 123.8, 108.2, 67.2, 60.6, 31.2, 25.1, 24.5, 14.5. Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.52; H, 7.77.

α-Chlorosulfones (9b,c)

Synthesis of compounds **9b,c** generally followed the procedure described earlier for the synthesis of α-chlorosulfone **9a**.[41] The products were purified by flash chromatography on a silica gel column (eluent **9a**, CH_2Cl_2-THF, 20:1; **9b**, CH_2Cl_2) with subsequent crystallizations from ether-petroleum ether mixtures. Yield of **9b**: 65%, yellowish solid, mp 111-112 °C. ^{1}H

NMR ($CDCl_3$) δ 7.95-7.53 (m, 5H), 6.53 (s, 2H), 4.85 (m, 1H), 4.85 (m, 1H), 4.57 (s, 2H), 4.53 (s, 2H), 4.23 (m, 4H), 3.74 (m, 1H), 3.48-3.26 (m, 4H), 1.26 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 174.3, 169.1, 150.4, 150.1, 138.2, 134.2, 129.4, 129.1, 123.4, 122.7, 109.8, 109.5, 66.5, 66.3, 64.4, 61.4, 51.8, 30.5, 24.6, 20.2, 14.3. Anal. Calcd for $C_{24}H_{27}ClO_8S$: C, 56.41; H, 5.33. Found: C, 56.46; H, 5.27. Yield of **9c**: 75%, yellowish solid, mp 86-87 °C. ^{1}H NMR ($CDCl_3$) δ 7.92-7.55 (m, 5H), 6.60 (s, 2H), 4.86 (m, 1H), 4.13 (m, 4H), 3.90 (m, 4H), 3.70 (m, 1H), 3.38-3.15 (m, 4H), 2.47 (m, 4H), 2.10 (m, 4H), 1.25 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 173.5, 173.4, 150.4, 150.1, 138.4, 134.3, 129.5, 129.1, 122.3, 121.5, 109.2, 108.9, 67.4, 67.2, 64.5, 60.7, 52.0, 31.2, 31.1, 30.7, 25.0, 20.4, 14.5. Anal. Calcd for $C_{28}H_{35}ClO_8S$: C, 59.30; H, 6.22. Found: C, 59.27; H, 6.18.

Pyrrole Ester (10b)

Compound **10b** was prepared from α-chlorosulfone **9c** and *tert*-butyl isocyanoacetate following the procedure described previously for the synthesis pyrrole ester **10a**.[41] The product was purified by flash chromatography on a short silica gel column (eluent CH_2Cl_2-THF, 20:1), followed by recrystallization from methanol. Yield of **10b**: 77%, light yellow crystals, mp 103-104 °C. ^{1}H NMR ($CDCl_3$) δ 8.92 (br s, 1H), 6.81 (d, 1H, J = 2.5 Hz), 6.64 (s, 2H), 4.14 (m, 4H), 4.03 (m, 2H), 3.98 (t, 4H, J = 6 Hz), 3.80 (m, 2H), 2.55 (m, 4H), 2.13 (m, 4H), 1.57 (s, 9H), 1.25 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 173.6, 173.5, 161.7, 151.1, 150.8, 125.7, 125.3, 124.2, 119.3, 119.2, 118.1, 108.0, 107.9, 80.6, 67.3, 67.2, 60.6, 60.5, 31.3, 31.2, 28.7, 25.2, 25.1, 23.0, 21.2, 14.4, 14.3. Anal. Calcd for $C_{29}H_{39}NO_8$: C, 65.77; H, 7.42; N, 2.64. Found: C, 65.71; H, 7.29; N, 2.66.

Pyrrole (11b)

tert-Butyl ester **10b** (300 mg, 0.57 mmol) was dissolved in CH_2Cl_2 (15 mL), and the solution was flushed with Ar for 5 min under stirring. The mixture was cooled on an ice bath, TFA (10 mL) was added, and the mixture was refluxed for 30 min. CH_2Cl_2 (20 mL) was added to the mixture, after which it was poured into a beaker with ice-cold solution of Na_2CO_3 (10% aqueous, 100 mL). The resulting mixture was transferred into a separatory funnel, the organic layer was separated, the water phase was additionally extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic solutions were washed with 10% aqueous Na_2CO_3 (50 mL). After drying over K_2CO_3, the solution was passed through a short silica gel column (eluent CH_2Cl_2-THF, 20:1), and the solvent was evaporated to yield the product as a colorless solid. Yield of **11b**: 255 mg, 98%. ^{1}H NMR ($CDCl_3$) δ 8.09 (br s, 1H), 6.67 (d, 2H, J = 2 Hz), 6.63 (s, 2H), 4.14 (q, 4H, J = 8 Hz), 3.98 (t, 4H, J = 6 Hz), 3.85 (s, 4H), 2.56 (t, 4H, J = 7 Hz), 2.14 (m, 4H), 1.26 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 173.7, 151.0, 126.8, 117.4, 113.1, 108.2, 67.4, 60.6, 31.5, 25.2, 21.2, 14.3.

Tetranaphtho[2,3]porphyrins (13a,b)

The syntheses of porphyrins **13a,b** from pyrroles **11a**,**b** generally followed the procedure, described above for the synthesis of TCHPs **5a,b**. The pyrrole (**11a** or **11b**, 1.2 mmol) was dissolved in benzene (60 mL), and the solution was flushed with Ar. Formaldehyde (37% aqueous solution, 0.11 mL) and $TsOH{\cdot}H_2O$ (30 mg, 0.16 mmol) were added to the mixture under vigorous stirring, and the mixture was refluxed for 4-5 h under Ar and then stirred overnight on air. The solvent was evaporated, and the remaining material was treated with DDQ (100 mg, 4 mmol). In the case of **13a**, the reaction was performed in refluxing dioxane, whereas in the case of **13b**, DDQ was added to the solution in CH_2Cl_2 at room temperature. In the latter case, the oxidation also could be done using *p*-chloranil (100 mg, 4 mmol) in refluxing toluene. The progress of the reaction was monitored by UV-vis spectroscopy (**13a** in DMF; **13b** in CH_2Cl_2). The spectrum changed gradually from the etio type, corresponding

to the porphyrins of type **12** (Scheme 2) to characteristic TNP spectrum with an intense Q-band at ~720 nm.

In the case of **13a**, a green residue precipitated from the reaction mixture. It was collected by centrifugation and washed with pyridine and THF. For further purification, it was recrystallized from refluxing PhCN and dried in a vacuum. Yield of **13a**: 25%, dark green powder. MALDI-TOF *m*/*z* 949.07, calcd 950.33; UV-vis, pyridine, λ_{max} nm (ϵ) (86500), 471 (198,000), 656 (29,500), 721 (191,000). Anal. Calcd for $C_{60}H_{46}N_4O_8$: C, 75.77; H, 4.88; N, 5.89. Found: C, 75.24; H, 4.99; N, 5.75.

In the case of **13b**, the reaction mixture was washed with 10% aqueous Na_2SO_3, with 10% aqueous Na_2CO_3, dried over K_2CO_3 and reduced in volume of about 5 mL. Acetonitrile (60 mL) was added, resulting in formation of a green precipitate. The precipitate was collected by centrifugation, washed with acetonitrile and methanol and dried in a vacuum. Yield of **13b**: 33%, green powder. ^{1}H NMR (pyridine-d_5-PhNO$_2$-d_5, 1:1, 50 °C) δ 11.51 (s, 4H), 10.92 (s, 8H), 4.71 (br t, 16H), 4.56 (q, 16H, J = 7 Hz), 3.23 (t, 16H, J = 7 Hz), 2.88 (m, 16H), 1.35 (t, 24H, J = 7 Hz), -1.27 (br s, 2H); MALDI-TOF *m*/*z* 1752.66, calcd 1750.75; ^{13}C NMR (pyridine-d_5-PhNO$_2$-d_5, 1:1, 80 °C) δ 174.4, 151.2, 127.6, 115.9, 105.6, 93.6, 69.5, 61.2, 32.6, 26.2, 15.0; UV-vis, pyridine, λ_{max} nm (ϵ) 441 (90,000), 471 (205,000), 656 (31,500), 721 (199,500). Anal. Calcd for $C_{100}H_{110}N_4O_{24}$: C, 68.56; H, 6.33; N, 3.20. Found: C, 67.29; H, 6.02; N, 3.03.

Zn Tetranaphtho[2,3]porphyrin (Zn-13b)

An excess of $Zn(OAc)_2 \cdot 2H_2O$ (30 mg, 0.16 mmol) was added to a solution of porphyrin **13b** (17 mg, 0.01 mmol) in pyridine (20 mL), and the mixture was refluxed for 15-20 min. The conversion was monitored by UV-vis spectroscopy (solvent pyridine). The reaction was stopped when the absorption band of **13b** (λ_{max} = 722 nm) disappeared. The mixture was diluted with water, the green precipitate was collected by centrifugation, washed with methanol and dried in a vacuum. Yield of **Zn-13b**: 16 mg, 95%, green solid. ^{1}H NMR (pyridine-d_5) δ 11.80 (br s, 4H), 11.10 (br, 8H), 7.22 (br, 8H, ovlpd. w/solv), 4.60-4.53 (ovlpd. t+q, 16+16H), 3.15 (t, 16H, J = 7 Hz), 2.77 (m, 16H), 1.16 (t, 24H, J = 7 Hz); ^{13}C NMR (pyridine-d_5) δ 174.5, 151.1, 146.2, 138.2, 127.2, 115.5, 104.8, 92.6, 69.2, 61.1, 32.5, 25.6, 14.7; MALDI-TOF *m*/*z* 1815.50, calcd 1812.66; UV-vis, pyridine, λ_{max} nm (ϵ) 439 (11,500), 467 (270,000), 645 (32,000), 674 (32,000), 708 (320,000). Anal. Calcd for $C_{100}H_{108}N_4O_{24}Zn$: C, 66.16; H, 6.00; N, 3.09. Found: C, 65.73; H, 5.90; N, 3.04.

Pd Tetranaphtho[2,3]porphyrin (Pd-13b)

Free-base porphyrin **13b** (17 mg, 0.01 mmol) was dissolved in PhCN (5 mL), $PdCl_2$ (5 mg, 0.028 mmol) was added, and the mixture was refluxed under Ar for 1-3 min. A few drops of pyridine were added, and the mixture was allowed to cool to room temperature. The solvents were removed in a vacuum (0.1 mmHg), and the remaining material was washed with methanol, dried and purified on a silica gel column (eluent CH_2Cl_2-THF, 20:1) to give the product as a green amorphous solid. Yield of **Pd-13b**: 82%. ^{1}H NMR (pyridine-d_5, 100 °C) δ 9.71 (br s, 4H), 9.02 (br, 8H), 4.71 (br, 16H), 4.50 (br, 16H), 3.17 (br, 16H), 2.84 (br, 16H), 1.37 (br, 24H); ^{13}C NMR (pyridine-d_5, 80 °C) δ 174.0, 69.4, 60.8, 32.3, 26.0, 14.7; MALDI-TOF *m*/*z* 1856.58, calcd 1854.64; UV-vis, pyridine, λ_{max} nm (ϵ) 428 (140,000), 633 (34,000), 665 (44,000), 696 (315,000). Anal. Calcd for $C_{100}H_{108}N_4O_{24}Pd$: C, 64.70; H, 5.86; N, 3.02. Found: C, 63.77; H, 5.42; N, 3.54.

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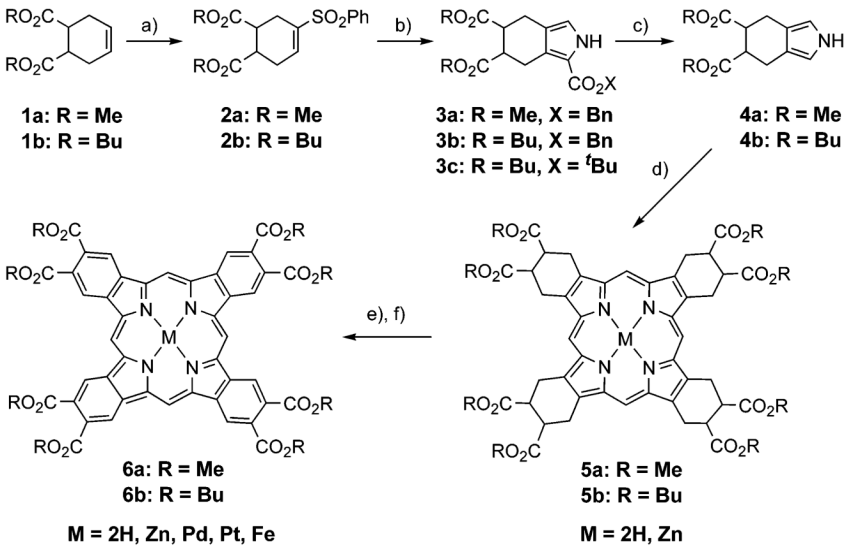
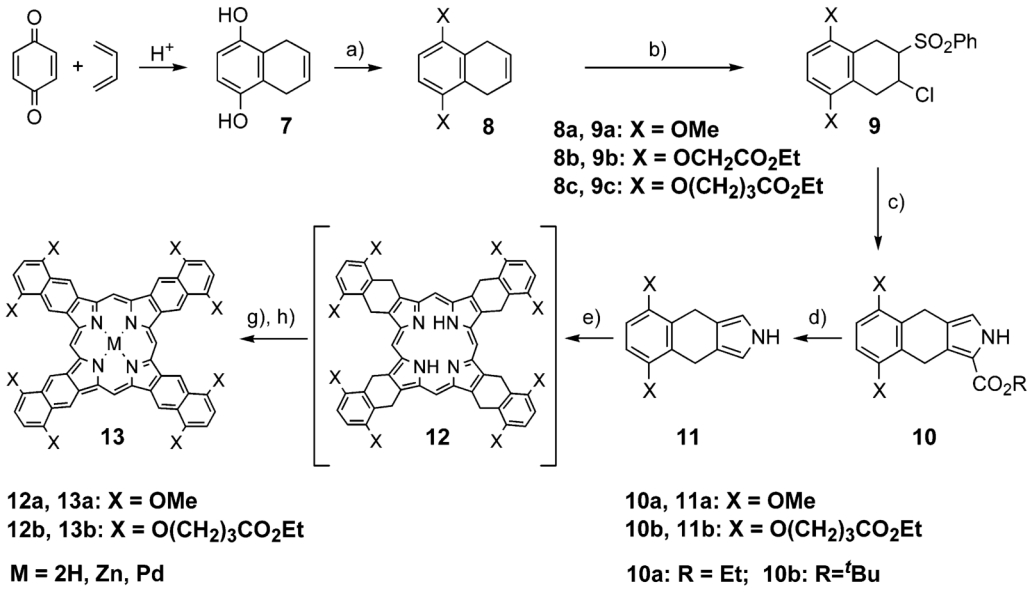


SCHEME 1a. [a] **Reagents and conditions**

(a) (i) PhSCl, CH_2Cl_2, rt; (ii) MCPBA, CH_2Cl_2; (iii) DBU (80-85% for 3 steps); (b) $CNCH_2CO_2X$, *t*BuOK, THF, 0 °C (60-95%); (c) for R = Bn: (i) H_2, Pearlman catalyst, THF-MeOH-Et_3N, rt; (ii) $(CH_2OH)_2$, reflux, 30 min (82-90% for 2 steps); for R = *t*Bu: TFA-CH_2Cl_2, Ar, rt, 30 min (30-40%); (d) (i) $(CH_2O)_n$, PhH, $TsOH{\cdot}H_2O$, Ar, reflux, 6-8 h, then air, (rt), overnight (30-45%); (ii) for M = Zn: $Zn(OAc)_2{\cdot}2H_2O$, THF, reflux, 15 min (95-97%); (e) R = Bu: DDQ, toluene, reflux (95-97%); R = Me: DDQ, dioxane, reflux (20-96%); (f) $PdCl_2$ or $PtCl_2$, PhCN, reflux, Pd: 5-10 min, Pt: 7-8 h (84-90%), or $Fe/FeCl_2{\cdot}4H_2O$, $CH_3CH_2CO_2H$, Ar, reflux 1 h (74%).



SCHEME 2a. [a] **Reagents and conditions**

(a) Me_2SO_4 (for **8a**), or $BrCH_2CO_2Et$ (for **8b**), or $Br(CH_2)_3CO_2Et$-NaI (for **8c**), K_2CO_3, acetone, reflux, 1-3 days (70-98%); (b) PhSCl, CH_2Cl_2, then MCPBA, CH_2Cl_2 (65-85%); (c) $CNCH_2CO_2R$, *t*BuOK, THF, reflux 30 min. (70-80%); (d) for R = Et: KOH, $(CH_2OH)_2$, reflux, 30 min (90-97%); for R = *t*Bu: TFA-CH_2Cl_2, Ar, rt, 30 min (98%); (e) $(CH_2O)_n$, PhH, $TsOH{\cdot}H_2O$, Ar, reflux, 5 h, then air, rt, overnight; (g) DDQ, rt of reflux 30 min (e + g: 25-33%); (h) $PdCl_2$ or $Zn(OAc)_2{\cdot}2H_2O$, pyridine or PhCN/pyridine, reflux (80-95%).

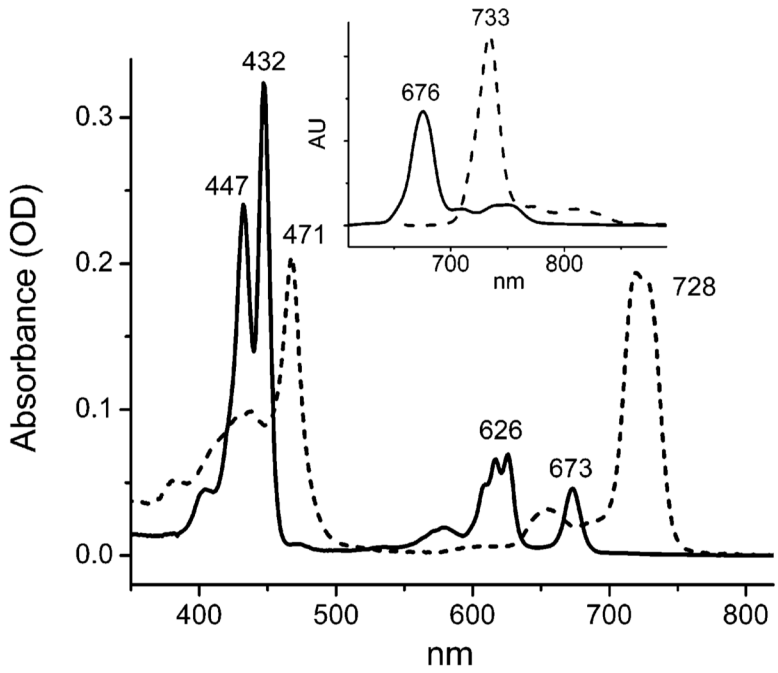


FIGURE 1.

Absorption and fluorescence (inset) spectra of **6b** (–) and **13b** (- - -) in DMF. The spectra are scaled to reflect the relative extinction coefficients (absorption) and quantum yields (fluorescence).

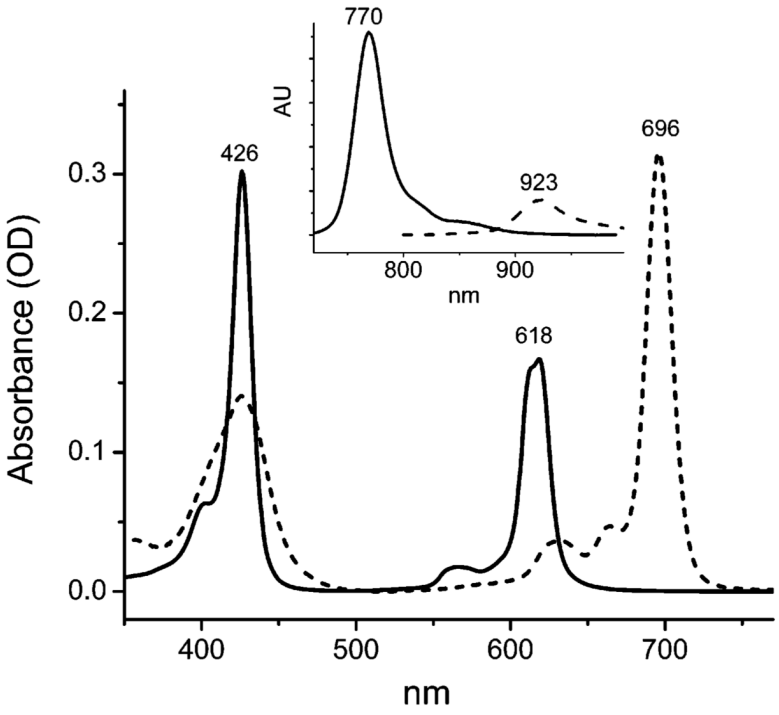
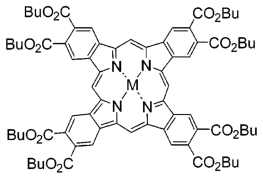
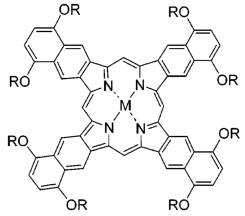
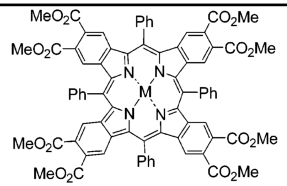
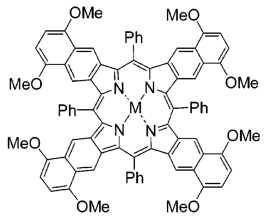


FIGURE 2.

Absorption and phosphorescence (inset) spectra of **Pd-6b** (–) and **Pd-13b** (- - -) in deoxygenated DMF. The spectra are scaled to reflect the relative extinction coefficients (absorption) and quantum yields (phosphorescence).

TABLE 1

Selected Photophysical Data of *meso*-Unsubstituted TBPs and TNPs

Porphyrin[e]	M	Absorption[a]		Emission[b]	
		Soret-band nm (lg ε)	Q-band nm (lg ε)	λ_{max}, nm	Emission type,[c] ϕ (%)/τ (μs)[d]
 **6b**	2H	432 (5.40), 447 (5.51)	626 (4.85), 673 (4.66)	676, 748	f, 27
	Zn	460 (5.64)	647 (5.14)	647, 710	f, 15
	Pd	426 (5.48)	618 (5.20)	770	p, 23/400
	Pt	416 (5.23)	609 (5.22)	745	p, 51/50
 R = -$(CH_2)_3CO_2Et$ **13b**	2H	471 (5.31)	721 (5.30)	733, 810	f, 45
	Zn	467 (5.43)	708 (5.51)	708, 781	f, 18
	Pd	429 (5.15)	696 (5.50)	923	p, 4/75
 **M-Ph_4TBP(CO_2Me)$_8$** [e]	2H	483 (5.36)	639 (1.37)	733, 820	f, 1.8
	Zn	487 (5.59)	668 (4.67)	677, 746	f, 3
	Pd	460 (5.40)	636 (4.94)	787	p, 3/62
 **M-Ph_4TNP(OMe)$_8$** [e]	2H	509 (5.30)	750 (5.00)	957	f, 13
	Zn	504 (5.46)	730 (5.23)	-	-
	Pd	465 (5.23)	720 (5.26)	954	p, 2.5/38

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Porphyrin[e]	M	Absorption[a]		Emission[b]	
		Soret-band nm (lg ε)	Q-band nm (lg ε)	λ_{max}, nm	Emission type,[c] ϕ (%)/τ (μs)[d]

[a] Solvent: pyridine for **Zn-6b, Pt-6b, M-13b** and for all M-Ph$_4$TNP(OMe)$_8$; DMF for **6b, Pd-6b** and for all M-Ph$_4$TBP(CO$_2$Me)$_8$.

[b] Solvent: DMF, deoxygenated by Ar for the phosphorescence measurements.

[c] f = fluorescence, p = phosphorescence.

[d] ϕ = emission quantum yield, τ = phosphorescence lifetime. Lifetime was not measured for fluorescence.

[e] Syntheses and photophysical properties of M-Ph$_4$TBP(CO$_2$Me)$_8$ and M-Ph$_4$TNP(OMe)$_8$ were reported previously.[5,40,41]