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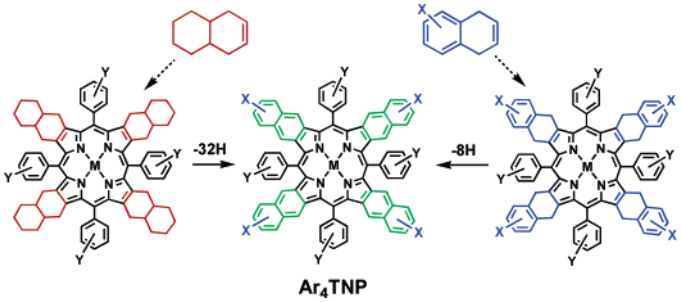
Synthesis of Symmetrical Tetraaryltetranaphtho[2,3]porphyrins

Olga S. Finikova,[†] Sergei E. Aleshchenkov,[‡] Raymond P. Briñas,[†] Andrei V. Cheprakov,*[,‡] Patrick J. Carroll,[§] and Sergei A. Vinogradov*[,†]

Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, Department of Chemistry, Moscow State University, Moscow 119899, Russia, and Department of Chemistry, Crystallographic Laboratory, University of Pennsylvania, Philadelphia, Pennsylvania 19104

avchep@elorg.chem.msu.ru; vinograd@mail.med.upenn.ed

Received December 24, 2004



A new method of synthesis of *meso*-tetraaryltetranaphtho[2,3]porphyrins (Ar_4TNP) has been developed. Ar_4TNPs with peripheral functional groups are obtained by oxidative aromatization of *meso*-tetraarylporphyrins in which pyrrole units are fused with either octahydro- or dihydronaphthalene moieties. These precursor porphyrins are synthesized in four to five steps from readily available starting materials, such as naphthalene or 1,4-benzoquinone. The pathway originating in dihydronaphthalene, i.e., the "dialine" route, was found to be superior to the alternative "octaline" route in that it (1) enables the shortening of the overall reaction sequence, (2) has a broader scope in terms of the peripheral substitution in Ar_4TNPs, and (3) affords higher yields of the target porphyrins. Pd complexes of the synthesized Ar_4TNPs exhibit remarkably strong absorption bands at 710−720 nm ($\epsilon \sim 200\,000\ M^{-1}\ cm^{-1}$) and phosphoresce at room temperature with moderate quantum yields ($\phi = 2-3\%$, $\lambda_{max} = 900-1000$ nm). The absorption maxima of naphthoporphyrins substituted with eight methoxy groups ($Ar_4TNP(OMe)_8$) were found to be about 15−20 nm red shifted compared to the corresponding maxima of unsubstituted Ar_4TNPs. The X-ray crystallographic data suggest that these spectral shifts are caused not by the differences in nonplanar distortions of the macrocycles but by the purely electronic effects of the substituents.

Introduction

In the past two decades, the interest in tetrapyrrolic chromophores with enhanced absorption in the far-red region of the spectrum has been steadily on the rise. Beginning with singlet oxygen sensitization and tumor therapy (PDT),[1] the usefulness of near-infrared-absorbing porphyrinoids has been evidenced in biomedical imaging[2] and in the development of nonlinear optical materials.[3] In addition, these compounds frequently demonstrate intriguing electrochemical[4] and acid−base properties,[5] suggesting applications in small molecule and ion sensing. Shifting of the absorption bands of porphyrinoids into the lower energy region can be approached in different ways, which include expanding the basic tetrapyrrolic macrocycle by adding extra pyrrolic fragments,[6] manipulating porphyrin planarity,[7] as well as extending the porphyrin core by fusing it with external aromatic fragments.[8] The latter approach leads to the so-called "π-

* To whom correspondence should be addressed. (S.A.V.) Phone: (215) 898-6382. Fax: (215) 573-3787.
† Department of Biochemistry, University of Pennsylvania.
‡ Department of Chemistry, Moscow State University.
§ Department of Chemistry, Crystallographic Laboratory, University of Pennsylvania.

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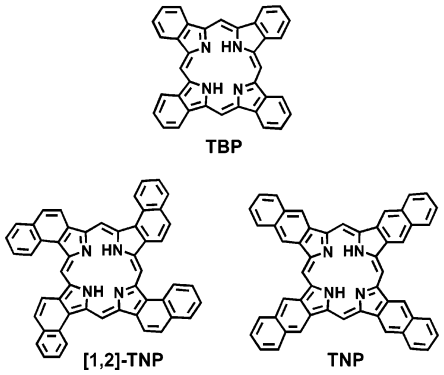
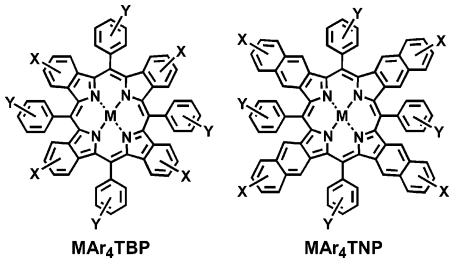
10.1021/jo047741t CCC: $30.25
Published on Web 05/07/2005

CHART 1



extended porphyrins," which, though studied relatively little, have already proven attractive for a variety of applications. For example, the simplest π-extended porphyrins, i.e., tetrabenzoporphyrins (TBP; Chart 1), appear to be useful in biological oxygen imaging,[2b,9] PDT,[10] and have shown potential in optical limiting.[3a,11] At the same time, tetranaphthoporphyrins (TNP; Chart 1), which possess even stronger near-infrared bands, have been explored only minimally,[12] mainly because of their limited synthetic availability.

CHART 2



The extension of all four porphyrin pyrroles by fused naphthalene fragments leads to a number of isomeric tetranaphthoporphyrins (Chart 1). Symmetrical tetranaphtho[2,3]porphyrins (TNPs)[13] stand out in this group because they possess the highest order of molecular symmetry and, consequently, exhibit the strongest and most narrow spectral transitions. The zinc complex of *meso*-unsubstituted TNP was originally synthesized by Lukyanets and co-workers in 1979 by condensing 3-carboxymethyl-5,6-benzophthalimidine with zinc acetate at high temperature.[14] Originating from phthalocyanine chemistry, this approach had been used before in the synthesis of tetrabenzoporphyrins.[15] Later, other naphthoporphyrins, such as [1,2]-TNP (Chart 1) and a number of peripherally substituted TNPs, were synthesized from the corresponding benzophthalimidines or naphthalenedicarboximides[16,12b] by similar methods.

In terms of practical handling, *meso*-tetraaryl-substituted TNPs (Ar_4TNP) (Chart 2) offer an important advantage over their *meso*-unsubstituted analogues due to improved solubility. It is known that laterally extended porphyrins in general and tetranaphthoporphyrins in particular present considerable solubility problems, which can be, at least in part, circumvented by introducing *meso*-aryl substituents into the porphyrin macrocycle.[17] The above-mentioned template condensation approach has been applied by the same group (Lukyanets and coworkers) to synthesize Ar_4TNPs from [2,3]naphthalenedicarboximide and arylacetic acids in the presence of zinc acetate at 350−400 °C.[16a] Though it did allow initial screening of the physical properties of TNPs,[12] this method appeared to be quite impractical due to the extremely low yields and laborious chromatographic purifications required for isolation of the final products. In addition, extremely harsh reaction conditions prohib-

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ited the introduction of functional groups into the TNP macrocycle.

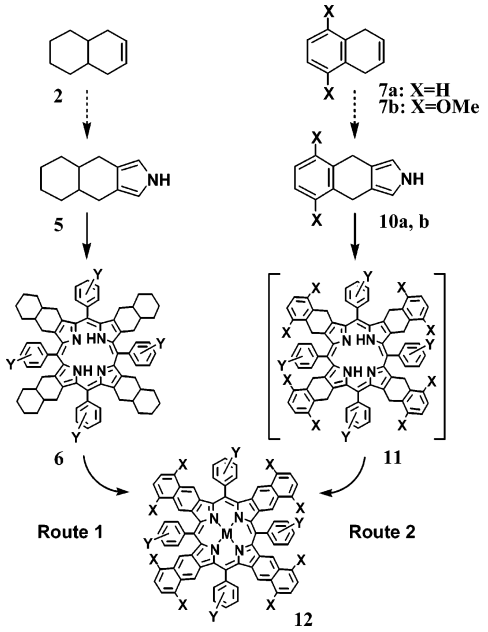
Over the past decade, a different approach to tetranaphthoporphyrins, as well as to the other aromatically extended porphyrins, has emerged from the works of the Ono[18] and Lash[8,17b,19] groups. Their methodology is based on pyrroles already fused with aromatic rings, from which the target porphyrins are assembled in standard ways. Such pyrroles can be prepared from the corresponding nitroarenes and isocyanoacetates under Barton−Zard conditions.[20] A number of extended porphyrins, including tetranaphtho[1,2]porphyrins,[18] were synthesized using this method, but naphtho[2,3]porphyrins remained an inaccessible target, as only [1,2]-naphtho-fused pyrroles could be produced from either 1-nitro- or 2-nitronaphthalene.[18,21]

In more recent years, Ono and co-workers proposed another pathway to laterally extended porphyrins based on the retro-Diels−Alder reaction.[22] This approach has been successfully implemented in the synthesis of both TNPs and Ar_4TNPs (Ar = Ph).[23] According to the Ono's method, TNPs are obtained from the precursor porphyrins, in which all four pyrroles are fused with bicyclic fragments, by simply heating these porphyrins under reduced pressure. Thermal extrusion of ethylene induced in this manner results in a clean and quantitative aromatization; however, the synthesis of the precursors themselves is rather complicated. In addition, the method is inappropriate for synthesizing porphyrins containing substituents in the naphtho rings.

In the course of our own work on the synthesis of π-extended porphyrins, we recently came across a useful strategy based on the direct *oxidative aromatization* of porphyrins annealed with nonaromatic saturated hydrocarbon rings. This approach enabled us to obtain a variety of polyfunctionalized tetraaryltetrabenzoporphyrins (Ar_4TBPs) in good yields from readily available starting materials.[24] The oxidative aromatization method also proved to be quite applicable to the synthesis of Ar_4TNPs.[25] Herein, we report the optimized synthesis, novel structural data, and some basic photophysical properties of two classes of Ar_4TNPs with and without substituents in the naphtho rings.

Two synthetic routes to Ar_4TNPs, both relying on the oxidative aromatization approach, are shown in Scheme 1.

SCHEME 1



The routes differ in terms of the types of fused porphyrins (**11** vs **6**) which precede the target Ar_4TNPs (**12**) in Scheme 1. In route 1, further referred to as the "octaline" route, the starting material is Δ^2-octaline **2**. The sequence of transformations leading first to the octaline-fused porphyrins of type **6** and then to Ar_4TNPs (**12)** is very similar to our earlier published approach to Ar_4TBPs, in which cyclohexene-fused porphyrins served as nonaromatized precursor porphyrins.[24] Aromatization of octahydronaphthalene rings in porphyrins **6** required strong oxidative conditions and was possible only for copper and palladium complexes of **6**.

The alternative route (route 2, Scheme 1) starts with 1,4-dihydronaphthalene derivatives **7a**,**b** and will be further termed as the "dialine" route. The basic strategy, i.e., the oxidative aromatization at the last step of the sequence, remains the same; however, the aromatization of precursor porphyrins **11** requires the removal of only 8 hydrogens, as opposed to the 32 which must be removed in the "octaline" route. Accordingly, the aromatization proceeds much more easily, making the "dialine" route advantageous in a number of ways. A discussion of both routes, as well as of the spectroscopic and structural properties of the obtained Ar_4TNPs, is presented below.

Results and Discussion

The synthesis of Pd complexes of Ar_4TNPs (**Pd-12a,b)** via the "octaline" route is outlined in Scheme 2.[26]

cis-Δ^2-Octaline **2** was prepared from the Diels−Alder adduct of butadiene and 1,4-benzoquinone **1** using a published procedure (**a1**).[27] Compound **2** was further transformed into vinyl sulfone **3** via the sequence of published reactions (**b1, c1**).[28] Vinyl sulfone **3** was reacted

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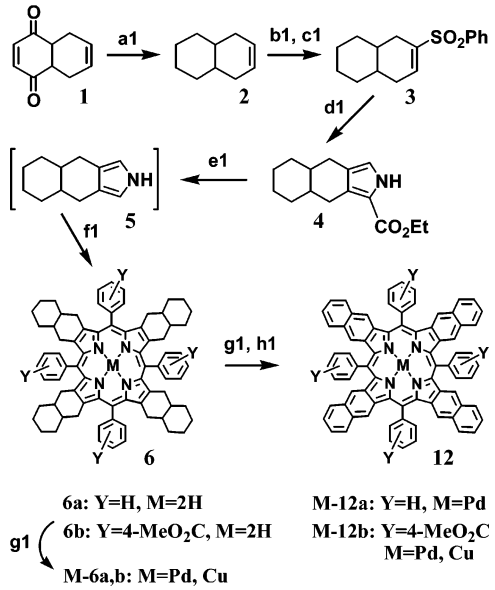
SCHEME 2[a]

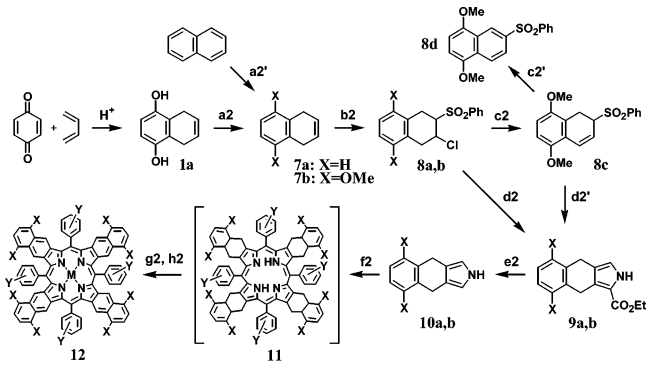


[a] Key: **a1,** (1) Zn dust, AcOH−H_2O, reflux, 30 min, (2) $NH_2NH_2{\cdot}H_2O$, KOH, ethylene glycol (50%); **b1,** (1) PhSCl, CH_2Cl_2; (2) *m*-CPBA; **c1,** DBU, CH_2Cl_2 (80% for **b1** + **c1**); **d1,** $CNCH_2CO_2Et$, ^{t}BuOK, THF, 0 °C to rt (88%); **e1,** KOH, $(CH_2OH)_2$, reflux, 30 min; **f1**, (1) ArCHO, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 1.5 h, rt, (2) DDQ (40−45% for **e1** + **f1**); **g1**, $PdCl_2$, MeCN−THF, Et_3N, reflux, 15 min (95−97%), or $Cu(OAc)_2{\cdot}2H_2O$, CH_2Cl_2−MeOH, reflux, 10 min (99%); **h1**, DDQ, toluene, reflux, 5 min (40−46% for **Pd-12a,b**); or in the presence of $Sc(OTf)_3$ (20% for **Cu-12b**).

with ethyl isocyanoacetate in the modified Barton−Zard synthesis[29,30] (**d1**) to yield pyrrole ester **4**, which was converted into pyrrole **5** upon reflux with KOH in ethylene glycol (**e1**). Pyrrole **5** without isolation was introduced into the Lindsey condensation with aromatic aldehydes (**f1**), yielding porphyrins **6a**,**b**. *meso*-Tetraarylated cycloalkene-fused porphyrins possess very high basicities[5e] and easily form dications upon treatment with DDQ. These dications have been shown to be completely inert in aromatization;[23] therefore, octaline-fused porphyrins **6** had to be converted into appropriate metal complexes **M-6**. The best results were obtained with Pd derivatives **Pd-6a**,**b**, which were oxidized by DDQ (**h1**) in refluxing toluene, affording **Pd-12a**,**b** in 40−45% yield. Aromatization of copper complexes appeared to be much less effective (2−3% yield) but could be improved in the presence of $Sc(OTf)_3$,[31] giving **Cu-12b** in 20% yield. Attempts to oxidize nickel complexes of **6** under a variety of conditions proved unsuccessful as complete decomposition of porphyrins was observed. In the case of zinc complexes, aromatization was impeded due to the rapid demetalation of **Zn-6** upon treatment with DDQ, which resulted in the formation of dications.

The "octaline" synthesis of Ar_4TNPs turned out to be much less efficient than the analogous synthesis of Ar_4-TBPs from cyclohexene-fused porphyrins.[24] In the latter, both copper and palladium complexes of Ar_4TBPs could

SCHEME 3[a]



[a] Key: **a2**, Me_2SO_4, K_2CO_3, acetone, reflux, 36 h (98%); **a2′**, Na, EtOH, 3 h (80%); **b2**, (a) PhSCl, CH_2Cl_2; (b) *m*-CPBA (83−90%); **c2**, DBU, CH_2Cl_2, −10 °C−rt, 5 min (60% for **8c**); **c2′**, ^{t}BuOK, THF, rt, 2h (90% for **8d**); **d2**, **d2′**, $CNCH_2CO_2Et$, ^{t}BuOK, THF, reflux 30 min (70−80%); **e2**, KOH, $(CH_2OH)_2$, reflux, 30 min (90−97%); **f2**, (1) ArCHO, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 1.5 h, rt; **g2**, DDQ, rt of reflux 30 min (35−49%); **h2**, $PdCl_2$ or $Zn(OAc)_2{\cdot}2H_2O$, PhCN/pyridine, reflux, 1−5 min (80−95%).

be obtained at the oxidation step in 60−95% yields, while the maximal yield achieved in the case of $PdAr_4$TNP **12b** was only 46%. This lower efficiency of the aromatization is likely to be caused by poor stability of the resulting metal complexes of Ar_4TNPs, which decompose quickly under strongly oxidative conditions. Indeed, the literature data point to the fact that the oxidation potentials of TNPs are quite low.[12b,d] At the same time, milder oxidants, such as *p*-chloranil or *o*-chloranil, appeared to be inefficient and failed to induce the aromatization.

The intrinsic limitations of the "octaline" route prompted us to search for an alternative method of synthesis of Ar_4-TNP. Decreasing the degree of saturation of the fused rings in the precursor porphyrins seemed like a feasible way to facilitate the aromatization, avoiding harsh oxidative conditions at the final step of the sequence. Indeed, replacing the precursor octaline-fused porphyrins **6** with dihydronaphthalene-fused porphyrins **11** (Scheme 1) proved to have a pronounced effect on the aromatization reaction. The details of the corresponding "dialine" route are shown in Scheme 3.

The key starting material, 1,4-dihydronaphthalene (1,4-dialine) **7a**, can be conveniently prepared in bulk quantities from naphthalene.[32] Similarly, other 1,4-disubstituted dialines, e.g., 1,4-dialkyl-1,4-dihydronaphthalene[33] and 1,4-dicarboxy-1,4-dihydronaphthalene,[34] which in principle are suitable precursors in this route, also can be synthesized from naphthalene. Another useful starting material, 5,8-dihydroxy-1,4-dihydronaphthalene **1a**, can be prepared in one step from butadiene and 1,4-benzoquinone.[35] This compound can be readily converted into a variety of useful derivatives by means of the Williamson alkylation. In this work, the dimethoxy derivative **7b** was employed.

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(30) Arnold, D. P.; Burgess-Dean, L.; Hubbard, J.; Abdur Rahman, M. *Aust. J. Chem.* **1994**, *47*, 969.
(31) The use of $Sc(OTf)_3$ was proposed by Osuka et al. to facilitate oxidative coupling of porphyrins into conjugated multiporphyrin arrays: Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79.
(32) Hückel W.; Schlee R. *Chem. Ber.* **1955**, *88*, 346.
(33) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283.
(34) Lyssy, T. M. *J. Org. Chem.* **1962**, *27*, 5.
(35) Rama Rao, A. V.; Yadav, J. S.; Bal Reddy K.; Mehendale, A. R. *Tetrahedron* **1984**, *40*, 4643.

The transformations following the initial syntheses are very similar for compounds **7a** and **7b**. Both **7a** and **7b** were first converted (**b2**) into the corresponding α-chlorosulfones **8a**,**b** using a published procedure.[28] The subsequent synthesis of pyrrole-esters **9a** and **9b**, however, required slightly different protocols due to the differences in the reactivity of the substrates, as well as to some unforeseen side reactions (vide infra).

Pyrrole esters with fused nonaromatic rings, such as **9a**,**b**, are usually synthesized from the corresponding cyclic α-vinyl sulfones by the modified Barton−Zard method, in which an α-vinyl sulfone is typically added to an equimolar mixture of an alkyl isocyanoacetate and a base (usually ^{t}BuOK).[24,29] On the other hand, conversion of the α-chlorosulfone into the α-vinyl sulfone, which usually precedes the Barton−Zard synthesis, also requires 1 equiv of a base.[28] It seemed, therefore, sensible to combine these two steps into one by simply adding the α-chlorosulfone to a mixture of 2 equiv of the base and 1 equiv of the isocyanoacetate (**d2**). In this case, the first equivalent of, e.g., ^{t}BuOK would be spent to eliminate HCl, while the second would generate anionic species from ethyl isocyanoacetate for the Barton−Zard synthesis.

As expected, treatment of α-chlorosulfone **8a** with a mixture of 2.2 equiv of ^{t}BuOK and 1.2 equiv of ethyl isocyanoacetate in THF at 0 °C followed by a 30 min reflux afforded pyrrole ester **9a** in 70% yield (**d2**). However, under the same conditions, dimethoxy derivative **8b** gave the target pyrrole ester **9b** in about a 1:1 molar ratio with the side product, naphthyl sulfone **8d**. Further, it was found that naphthyl sulfone **8d** readily forms upon treatment of **8b** with an excess of a strong base, such as ^{t}BuOK or DBU, and that the reaction involves the initial elimination of HCl. For example, the reaction between α-chlorosulfone **8b** and 1 equiv of DBU (**c2**) afforded allyl sulfone **8c**, and treatment of the latter with an excess of ^{t}BuOK at rt gave **8d** almost quantitatively (**c2′**). It is known that aromatization of cyclohexadienes can be, in principle, incurred by strong bases.[36] In this respect, it is interesting that sulfones **8a** and **8b** behave so differently under basic conditions: in the case of unsubstituted sulfone **8a** aromatization via the elimination of the phenylsulfonyl group, leading to the formation of naphthalene, is the predominant pathway.

Allyl sulfone **8c** appeared to be active as a substrate in the Barton−Zard reaction (**d2′**), since under basic conditions it exists in equilibrium with the corresponding vinyl sulfone.[37] When reacted with an equimolar mixture of ^{t}BuOK and ethyl isocyanoacetate in refluxing THF, **8c** gave **9b** in 80% yield. On the other hand, avoiding the side reaction (i.e., formation of **8d**) and thus keeping the synthesis of **9b** from **8b** a one-pot procedure could be done by simply using 2 M excess of isocyanoacetate. In this case, α-chlorosulfone **8b** had to be added to the mixture of equal amounts of ^{t}BuOK and ethyl isocyanoacetate (2.2 mol of each per 1 mol of **8b**), affording **9b** as a sole product in 77% yield. Apparently, the potassium derivative of isocyanoacetate, capable of driving the initial elimination of HCl from **8b**, is more active in the Barton−Zard reaction than in the subtraction of another proton and the following aromatization.

Esters **9a**,**b** were further converted (**e2**) into pyrroles **10a**,**b**, which reacted with aromatic aldehydes under Lindsey conditions (**f2**). In the latter syntheses, the mixtures were either allowed to stir overnight at room temperature (**12c**,**d**) or refluxed for 30−60 min (**12a**,**b**) following the addition of DDQ. In either case, intermediate porphyrins of type **11** were not isolated; instead, the free bases Ar_4TNPs **12a**,**b** and Ar_4TNP$(OMe)_8$'s **12c**,**d** were obtained in 35−50% yield. Spectroscopic analysis of samples taken at different times during the syntheses of porphyrins **12a**,**b**, however, suggests that under optimized conditions porphyrins **11** can be obtained as individual compounds. Ar_4TNPs **12a**,**b** were further reacted with zinc acetate or palladium chloride in appropriate solvents, yielding the corresponding metal complexes **M-12**.

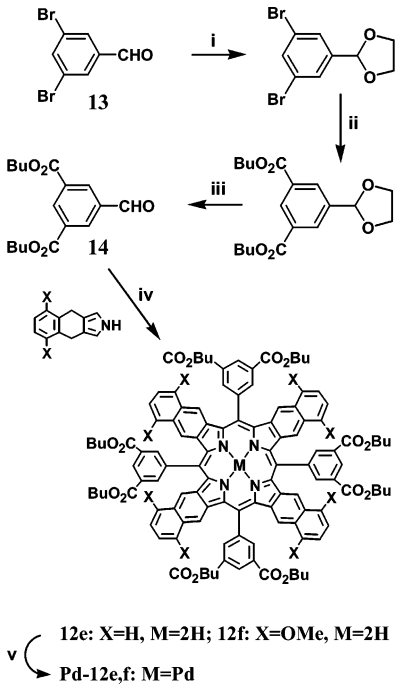
Unexpectedly, naphthoporphyrins **12a**,**b** and **12c**,**d** exhibit large differences in solubility. Unsubstituted Ar_4TNPs **12a**,**b**, and their metal complexes are soluble in most organic solvents (e.g., CH_2Cl_2, THF). Porphyrins **12c**,**d** (Ar_4TNP$(OMe)_8$), on the other hand, are practically insoluble at room temperature, despite multiple peripheral substituents; these porphyrins can, however, be dissolved to moderate concentrations in hot benzonitrile and nitrobenzene. The broadening of aromatic resonances in ^{1}H NMR spectra of both Ar_4TNPs and Ar_4TNP$(OMe)_8$ suggests that these porphyrins aggregate in solution. It was possible to improve the resolution of the proton spectra of metal complexes **M-12a**−**d** using polar solvents, such as pyridine-d_5, $PhNO_2$-d_5, or dmso-d_6, and performing measurements at elevated temperatures. However, except for **Zn-12d**, ^{13}C NMR spectra of compounds **12c**,**d** and **M-12c**,**d** could not be recorded with satisfactory resolution. NMR spectra of free base porphyrins **12a**−**d**, which are less soluble and more likely to aggregate than the metal complexes, could not be fully resolved either, even if measurements were done in polar solvents at high temperatures (>100 °C). In contrast, the dications of **12a**−**d** (trifluoroacetates or chlorides) were found to be easily soluble in $CDCl_3$, although in some cases aggregation still presented a problem. For example, good-quality ^{1}H and ^{13}C spectra of the dications of Ar_4TNPs **12a**,**b** were easily recorded for concentrated solutions of trifluoroacetates, while the spectra of Ar_4TNP$(OMe)_8$ **12d** could be obtained for chlorides only in very diluted (∼0.1 mg/mL) solutions.

As shown above, low solubility and strong aggregation often make handling of naphthoporphyrins very difficult. Although *meso*-arylation in many cases improved solubility, aggregation of both Ar_4TNPs and Ar_4TNP$(OMe)_8$ still imposed significant difficulties on the spectroscopic measurements. To overcome this problem, we synthesized Ar_4TNPs in which each *meso*-aryl ring was substituted with two butoxycarbonyl groups in the 3,5-positions. The butyl ester substituents not only improved the solubility of Ar_4TNPs (**12e,f)** but also considerably prevented their aggregation. The synthesis of octabutoxycarbonyl-Ar_4TNPs is shown in Scheme 4.

(36) Pines, H.; Stalick, W. M. *Base-catalyzed reactions of hydrocarbons and related compounds*; Academic Press: New York, 1977; p 483.

(37) Allyl sulfones are known to exist in equilibrium with the corresponding vinyl sulfones in the presence of strong bases, such as DBU or ^{t}BuOK. For examples, see: (a) Savoia, D.; Trombini C.; Umani-Ronci, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 123. (b) Inomata, K.; Hirata, T.; Kinoshita, H.; Kotake H.; Senda, H. *Chem. Lett.* **1988**, 2009.

SCHEME 4[a]



[a] Key: **i**, $(CH_2OH)_2$, PhH, *p*-TosH·H_2O, reflux, 8 h; **ii**, (1) CO, BuOH, Pd[$(PPh_3)_4$], Et_3N, 36 h, 80 °C; **iii,** HCl_{aq}, THF, reflux 40 min (**i**−**iii**) 77%); **iv**, (1) BF_3·Et_2O, CH_2Cl_2, 1.5 h, rt; (2) DDQ, rt or reflux 30 min (40−45%); **v**, $PdCl_2$, PhCN, reflux, 20−30 min (**12e**, 80%) or $PdCl_2$, PhCN/pyridine, reflux, 3−5 min (**12f**, 85%).

The precursor aldehyde, dibutyl 5-formylisophthalate **14**, was prepared in the total yield of 77% from the commercially available 3,5-dibromobenzaldehyde **13** in three steps: (1) protection of the carbonyl group, (2) Pd-catalyzed butoxycarbonylation, and (3) deprotection. Aldehyde **14** reacted with pyrroles **9a**,**b** (Scheme 4) affording porphyrins **12e**,**f** in 30−40% yields. Palladium complexes of these porphyrins were prepared by reacting the free bases with $PdCl_2$ in refluxing PhCN (**12e**) or in PhCN−pyridine mixture (**12f**). Both the free bases and palladium complexes of octabutoxycarbonyl porphyrins **12e**,**f** are very easily soluble in most organic solvents and much less prone to aggregation.

Although detailed examination of the photophysical properties of Ar_4TNPs calls for a special investigation, we performed an initial analysis of their absorption and, in some cases, their emission characteristics, as well as some structural studies. The original driving force behind our work in the area of extended porphyrins is their potential use as functional elements for biological oxygen sensors.[9,12f] In this respect, examining the phosphorescent characteristics of Pd complexes presents to us a special interest. On the other hand, there are a number of questions in the current porphyrin literature associated with the effects of nonplanar distortion and π-extension on the spectra of porphyrins.[38] Following tetraaryltetrabenzoporphyrins (Ar_4TBP), Ar_4TNPs continue the row of laterally extended porphyrins, in which the influences of distortion and extended π-conjugation on the red shifts

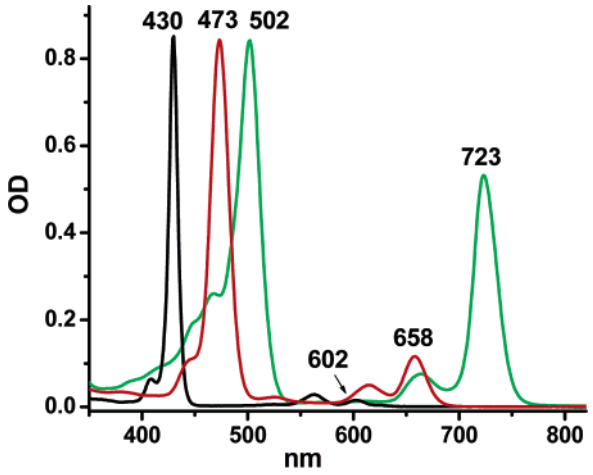


FIGURE 1. Absorption spectra of ZnTPP (black line), $ZnPh_4$-TBP (red line), and $ZnPh_4$TNP (green line) in pyridine.

of optical transitions and other photophysical properties can be assessed systematically. A comparative photophysical study as well as some theoretical calculations have been recently published for Zn and Pd complexes of symmetrically extended porphyrins.[11c,12g] One of the main conclusions made was that the influence of nonplanar distortion on the red shifts of the optical transitions of Ar_4TNPs, as compared to Ar_4TBPs, is much smaller than that of the π-conjugation. These results were based on the analysis of the computationally obtained structures, since no experimental data on Ar_4-TNPs was available. Herein we present new X-ray data and some additional photophysical measurements, further supporting the above-mentioned conclusion.

Compared to the regular *meso*-tetraarylporphyrins (Ar_4P), which possess nearly ideally planar structures, Ar_4TNPs exhibit large red shifts of the absorption bands. For example, in the case of zinc complexes these shifts reach about 70 nm for the Soret bands and up to 120 nm for the Q-bands (Figure 1). In addition, relative intensities of the Q-band maxima increase greatly upon extension of the macrocycle π-system, e.g., as much as about 15−20 times for Zn complexes.

The Q-bands of Ar_4TNPs are significantly red-shifted in respect to the Q-bands of Ar_4TBPs as well, while the positions the Soret maxima are shifted notably less (Figure 1). For example, the Q-bands of the homologous complexes $ZnPh_4$TNP (**Zn-12a**) and $ZnPh_4$TBP[39] differ by 65 nm ($\lambda_Q^{\mathbf{Zn-12a}} = 723$ nm vs $\lambda_Q^{\mathbf{ZnPh4TBP}} = 658$ nm). At the same time, the Soret bands differ by no more than 30 nm ($\lambda_{Soret}^{\mathbf{Zn-12a}} = 473$ nm vs $\lambda_{Soret}^{\mathbf{ZnPh4TBP}} = 502$ nm) (Figure 1). The oscillator strengths of the Q-bands of Ar_4-TNPs are about 3−4 times larger than those of the similar Ar_4TBPs. A question arises whether the differences in these basic photophysical properties of Ar_4TNPs vs Ar_4TBPs are caused by stronger nonplanarity of the former, by the electronic effects of naphtho vs benzo groups or by a combination of both of these factors.

It has been shown that the classic Gouterman's four-orbital model[40] cannot adequately explain the absorption properties of Ar_4TNPs.[11c] In these porphyrins, HOMOs

(38) Haddad, R. E.; Gazeau, S.; Pecaut, J.; Marchon, J. C.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 1253 and references therein.

(39) Cheng, R. J.; Chen, Y. R.; Chuang, C. E. *Heterocycles* **1992**, *34*, 1.

(40) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.

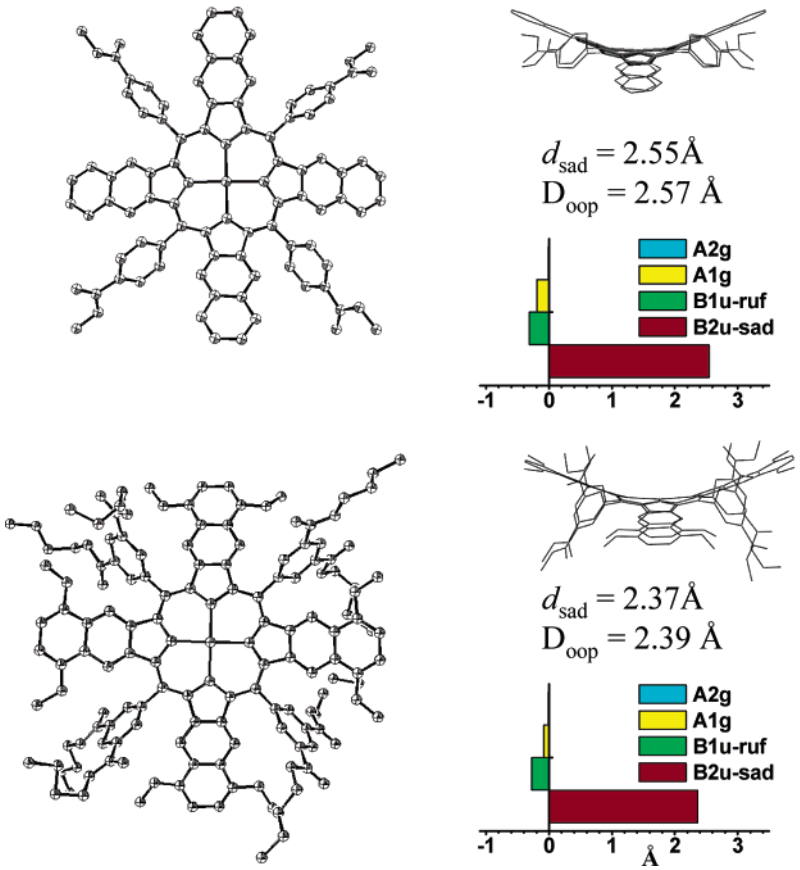


FIGURE 2. X-ray crystal structures of **Pd-12b** ($PdAr_4TNP$) and **Pd-12f** ($PdAr_4TNP(OMe)_8$). The diagrams on the right depict the results of the NSD analysis,[41] showing only two main out-of-plane (oop; B1u-ruffling and B2u-saddling) and two in-plane (ip; A1g and A2g) distortion modes. The parameter D_{oop} is a measure of the total distortion of the core tetrapyrrole macrocycle, which takes into account all out-of-plane distortion modes. The parameter d_{sad} quantifies the B1u saddling distortion only.

are not far enough separated from the other MOs, which also participate in the configuration interaction defining the properties of the ground and excited states. Therefore, the spectra of Ar_4TNPs are complicated by extra transitions in the Soret-band region. The lower energy bands of both Ar_4TBPs and Ar_4TNPs, however, still can be formally traced to the transitions involving HOMO-1 (b_1) and the LUMO pair.[11c] Since HOMO-1 is largely localized on the α- and β-carbons of the pyrrole rings,[40] π-conjugation, which can be viewed for this purpose as a substitution of the of β-pyrrole carbons, should affect mostly the Q-band transitions. This notion manifests itself in larger red shifts of the Q-bands of Ar_4TNP's vs their Soret bands (Figure 1).

The recently obtained structural data[25] suggest that the degrees of nonplanarity of MAr_4TNPs and MAr_4TBPs[39] are very close, implying that the red shifts of the absorption bands of Ar_4TNPs are caused mainly by the extended π-conjugation. In this work, we show that the additional side substitution in naphtho rings, which in principle could have influenced the Ar_4TNP geometry, has, in fact, no structural effect, but yet causes an extra red shift of optical transitions. The X-ray crystallographic structures of Pd complexes of two types of Ar_4TNPs, **Pd-12b** and **Pd-12f**, are shown in Figure 2 together with their NSD (normal-coordinate structural decomposition) analyses.[41] NSD analysis is a very helpful tool for comparing nonplanar distortions in different types of porphyrins and for presenting their differences in a graphical mode.

The analysis of the X-ray data collected from a crystal of **Pd-12f** revealed that the side Bu groups and the cocrystallized solvent (Et_2O) molecules were severely disordered, which lowered the quality of the overall crystal structure determination (see the Supporting Information). Nevertheless, the structure of the core tetrapyrrole macrocycle was determined with adequate quality, so that only small variations in distortion modes would be expected should the NSD analysis be performed on an overall better resolved structure.

The main distortion mode in both **Pd-12b** ($PdAr_4TNP$) and **Pd-12f** ($PdAr_4TNP(OMe)_8$) is saddling (B2u), although there are small contributions of ruffling (B1u) and two in-plane distortions A1g and A2g. The same modes were found to be dominant in the other reported structures of extended porphyrins: $ZnPh_4TBP{\cdot}THF$,[39] $H_2Ph_4TBP(CO_2Me)_8$,[5e] and $NiPh_4TBP(CO_2Me)_8$.[24b] Despite eight methoxy groups in **Pd-12f** its degree of nonplanarity (D_{oop} = 2.38Å) is very close to that of **Pd-12b** (D_{oop} = 2.57Å), and in fact, **Pd-12f** is even slightly less distorted than **Pd-12b**. At the same time, for the pair of porphyrins with the same substituents in the *meso*-aryl rings (**Pd-12e** and **Pd-12f**), the absorption bands of **Pd-12f**, which contains

(41) (a) Jentzen, W.; Song, X.-Z.; Shelnutt, J. A. *J. Phys. Chem. B* **1997**, *101*, 1684. (b) Jentzen, W.; Ma, J. G.; Shelnutt, J. A. *Biophys. J.* **1998**, *74*, 753.

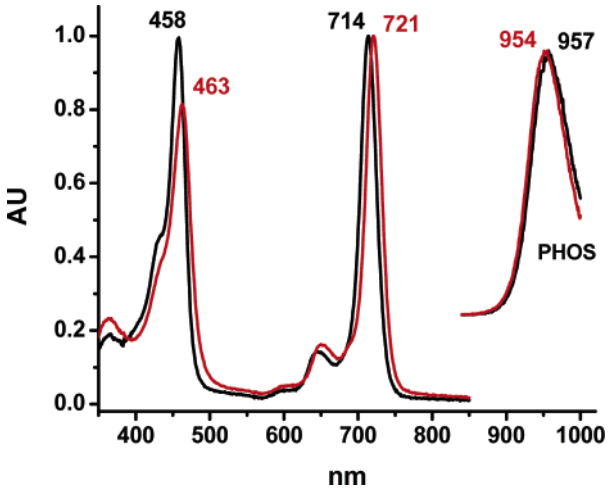


FIGURE 3. Absorption and phosphorescence (designated as PHOS) spectra of **Pd-12e** (black) and **Pd-12f** (red) in deoxygenated toluene solutions.

eight methoxy substituents, are notably red-shifted relative to those of the unsubstituted **Pd-12e**: $\lambda_Q^{\mathbf{Pd-12e}} = 714$ nm vs $\lambda_Q^{\mathbf{Pd-12f}} = 721$ nm and $\lambda_{Soret}^{\mathbf{Pd-12e}} = 458$ nm vs $\lambda_{Soret}^{\mathbf{Pd-12f}} = 463$ nm) (Figure 3).

The red shift, therefore, is most probably caused exclusively by the electronic effect of eight methoxy groups in **Pd-12f**, which are likely to raise the energy of its HOMO, narrowing the HOMO−LUMO gap. A more detailed understanding of the effects of peripheral substitution in extended porphyrins would require spectroelectrochemical measurements,[4] which would help to track down changes in HOMOs and LUMOs upon substitution individually.

Ar_4TNPs free bases exhibit strong fluorescence (e.g., **12e**: $\phi = 0.063$, $\lambda_{max} = 767$ nm (DMF); **12f**: $\phi = 0.132$, $\lambda_{max} = 769$ (DMF); compare to $\phi_{H2TPP} = 0.11$ (C_6H_6)[42]), which is somewhat unexpected considering their high nonplanarity.[43] The observed fluorescence quantum yields are much higher than those of other saddled porphyrins, e.g., $\phi_{H2OETPP} = 0.005$ (H_2OETPP = octaethyltetraphenylporphyrin),[43] suggesting that the extended π-conjugation causes a decrease in either the probability of the internal conversion of $^1(\pi, \pi^*)$ state or of the intersystem crossing from $^1(\pi, \pi^*)$ state, or both.

The presence of extremely powerful near infrared bands in the absorption spectra of Ar_4TNPs ($\epsilon_Q \approx 200\,000$ M^{-1} cm^{-1}) automatically draws attention to these porphyrins as potential PDT sensitizers and in vivo optical imaging probes, e.g., for oxygen.[9] For these applications, it is necessary that porphyrins possess stable, long-living triplet states, which are normally generated via the intersystem crossing from the first excited singlet states. The efficiency of intersystem crossing is substantially increased in the presence of heavy metal ions, e.g., Pt and Pd,[44] and therefore, the corresponding complexes are especially interesting. It was found that Pd complexes of Ar_4TNPs exhibit relatively strong phosphorescence in deoxygenated solutions at room temperature upon excitation at either Q or Soret bands. The phosphorescence maxima are at about 955 nm and the Stokes shifts relative to the Q-bands are in the order of 240−250 nm, which is substantially larger than for PdTPP (166 nm)[11c] and $PdPh_4$TBP (172 nm).[9b] Measuring absolute quantum efficiencies above 850 nm is intrinsically difficult because of the rapidly falling sensitivity of detection systems (PMT) in this wavelength range and the absence of good reference points for actinometry measurements. Due to these complications, the reported values should be considered as only approximate. The phosphorescence quantum yields were found to be 1.8% for **Pd-12e** and 2.5% for **Pd-12f**,[45] which is lower than the values obtained for $PdAr_4P$ ($\phi = 4.5\%$) and for $PdAr_4$TBP ($\phi = 6.7\%$) (Ar = 4-$MeO_2C-C_6H_4$) using the same conditions, i.e., in deoxygenated toluene at rt. Consistent with quantum yields, the phosphorescence lifetimes ($\tau_0 = 48$ μs and $\tau_0 = 38$ μs) are also shorter than those of the reference porphyrins ($\tau_0^{PdAr4P} = 385$ μs, $\tau_0^{PdAr4TBP} = 205$ μs). More rapid nonemissive deactivation of the triplet states of Ar_4TNPs is most probably caused by their very low energy levels, which further increase the probability of internal conversion into the ground states common among nonplanar porphyrins.[46] Other spectroscopic features of $PdAr_4$TNPs are similar to those reported earlier

Phosphorescence of **Pd-12f** was found to be very sensitive to oxygen having the Stern−Volmer quenching constant K_q in DMF of about 20 000 $mmHg^{-1}s^{-1}$. This value is more than two times higher than K_q's of $PdAr_4P$[47] or of $PdAr_4$TBP (Ar = $HO_2CC_6H_4$), which in DMF at rt are about 10 000 and 7000 $mmHg^{-1}s^{-1}$, respectively. Such high sensitivity to oxygen makes $PdAr_4$TNPs quite potent as phosphors for in vivo oxygen measurements and also as PDT agents, despite their moderate emission quantum yields and lifetimes. In addition, large gaps between the Q and Soret bands ($\Delta\lambda > 250$ nm) and rather large T^0-T^1 extinction coefficients[11c] place $PdAr_4$TNPs among the most promising dyes for optical limiting. On the other hand, for this and other applications, chemical and photochemical stability of Ar_4TNPs will be of crucial importance. Improving it by a different macrocycle substitution will be the next synthetic challenge in this area of porphyrin synthesis.

In conclusion, a method of synthesis of Ar_4TNPs based on oxidative aromatization has been developed. Two variants of the method, the "dialine" and the "octaline" routes, have been compared, revealing the former's numerous advantages. The "dialine" route employs readily available 1,4-dihydronaphthalene derivatives as starting

(42) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.
(43) Gentemann, S.; Medforth, C. J.; Forsyth, T. P.; Nurco, D. J.; Smith, K. M.; Fajer, J.; Holten, D. *J. Am. Chem. Soc.* **1994**, *116*, 7363.
(44) Eastwood, D.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *35*, 359.

(45) In our preliminary communication,[25] we reported a different, probably exaggerated value for the phosphorescence quantum yield of the compound **Pd-12b**, i.e., 6.5%. This was probably a result of an inaccurate calibration curve used for the PMT (Hamamatsu R2685) correction. Having said that, an error of 5−10% is rather expected for the measurements in the wavelength range where detector sensitivity drops by a factor of 10 per each 50 nm. A different detector (photodiode or an APD) would be required to measure quantum yields of the naphthoporphyrin's luminescence more accurately.
(46) (a) Gentemann, S.; Medforth, C. J.; Ema, T.; Nelson, N. Y.; Smith, K. M.; Fajer, J.; Holten, D. *Chem. Phys. Lett.* **1995**, *245*, 441. (b) Gentemann, S.; Nelson, N. Y.; Jaquinod, L.; Nurco, D. J.; Leung, S. H.; Medforth, C. J.; Smith, K. M.; Fajer, J.; Holten, D. *J. Phys. Chem. B* **1997**, *101*, 1247. (c) Chirvony, V. S.; van Hoek, A.; Galievsky, V. A.; Sazanovich, I. V.; Schaafsma, T. J.; Holten, D. *J. Phys. Chem. B* **2000**, *104*, 9909.
(47) (a) Vinogradov, S. A.; Lo, L. W.; Wilson, D. F. *Chem. Eur. J.* **1999**, *5*, 1338. (b) Rozhkov, V. V.; Wilson, D. F.; Vinogradov, S. A. *Macromolecules* **2002**, *35*, 1991.

materials and makes it possible to obtain the target porphyrins in five to six steps, with up to 20% overall yield. The efficiency and versatility of this method has been demonstrated by synthesizing a variety of Ar_4TNPs and their metal complexes, including polyfunctional derivatives with substituents in the fused naphtho rings and/or in the *meso*-aryl rings.

Experimental Section

Ethyl isocyanoacetate was prepared from glycine ethyl ester hydrochloride according to the published method.[48] 1,4-Dihydronaphthalene **7a**,[32] 5,8,9,10-tetrahydro-1,4-naphthoquinone **1**, 5,8-dihydroxy-1,4-dihydronaphthalene **1a**, and 5,8-dimethoxy-1,4-dihydronaphthalene **7b**[35] were synthesized as described previously. Octaline **2** was obtained from **1** in 40% yield according to the published procedure.[27] Sulfone **3** was prepared from **2** in 80% yield following the standard method.[28] The equipment used for analytical characterization of the compounds has been described elsewhere.[24,25] Melting points are uncorrected.

Pyrrole Ester 4. Synthesis of **4** followed a general protocol described earlier.[29] A solution of ethyl isocyanoacetate (565 mg, 5.0 mmol) in 15 mL of dry THF was added to a suspension of 90% ^{t}BuOK (620 mg, 5.0 mmol) in 25 mL of THF at 0 °C under Ar. A solution of sulfone **3** (1.1 g, 4.1 mmol) in 30 mL of THF was added dropwise to the mixture and left to react at rt under continuous stirring. After 4 h, the volume of the mixture was reduced to about 10 mL by rotary evaporation. CH_2Cl_2 (100 mL) was added to the mixture, and the resulting solution was washed with water and then with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was dried in a vacuum to remove the excess isocyanoacetate, and the product was purified on a silica gel column (eluent: CH_2Cl_2). After evaporation of the solvent, the product was crystallized from CH_2Cl_2−hexane or ethyl alcohol. **4**: yield 890 mg, 88%, colorless crystals; mp 114−116 °C; TLC, CH_2Cl_2, $R_f \sim 0.6$, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ 8.74 (broad s, 1H), 6.60 (d, 1H, $J = 3$ Hz), 4.29 (m, 2H), 3.05 (dd, 1H, $J_1 = 17$ Hz, $J_2 = 5$ Hz), 2.61 (dd, 1H, $J_1 = 15$ Hz, $J_2 = 4$ Hz), 2.23 (dd, 1H, $J_1 = 17$ Hz, $J_2 = 10$ Hz), 2.10 (dd, 1H, $J_1 = 16$ Hz, $J_2 = 11$ Hz), 1.85 (m, 2H), 1.75 (m, 2H), 1.28−1.35 (ovrlap t + m, 3 + 4H), 1.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 161.6, 128.2, 122.2, 118.0, 117.3, 59.8, 39.0, 34.5, 34.4, 30.9, 29.8, 26.6, 26.4, 14.7. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.59; H, 8.65; N, 5.67.

Porphyrins 6a,b. Pyrrole ester **4** (890 mg, 3.60 mmol) was refluxed under Ar with an excess of NaOH (1.2 g, 30 mmol) or KOH (1.9 g, 30 mmol) in ethylene glycol (30 mL) for 20 min. The mixture was rapidly cooled on an ice bath. CH_2Cl_2 (60 mL) was added, and the mixture was thoroughly washed with water (2 × 100 mL; brine was added to reduce the emulsion). The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed in a vacuum. The resulting material was purified on a short (2 × 10 cm i.d.) silica gel column (eluent: CH_2Cl_2). The solvent was removed under vacuum, and the remaining material (560 mg) was dissolved in 320 mL of CH_2Cl_2. Benzaldehyde (in the case of **6a**: 345 mg, 3.25 mmol) or methyl 4-formylbenzoate (in the case of **6b**: 533 mg, 3.25 mmol) was added, and the mixture was kept under continuous stirring in the dark under Ar for 10 min. $BF_3{\cdot}Et_2O$ (90 mg, 0.64 mmol) was added in one portion, and the mixture was left to react at rt under Ar for 1.5 h. DDQ (900 mg, 4 mmol) was added, and the mixture was allowed to stir for another 1 h. The resulting green solution was washed with 10% aq Na_2SO_3 (2 × 100 mL), then with 10% aq Na_2CO_3 (100 mL) and finally with 5% aq HCl, after which it was dried over Na_2SO_4. The solvent was removed in a vacuum, and the remaining material was purified on a silica gel column twice (eluent: CH_2Cl_2, then CH_2Cl_2−THF, 10:1). Each time a bright green band eluting with CH_2Cl_2−THF was collected and the solvent was removed in a vacuum. The remaining green solid was purified by repetitive precipitation from CH_2Cl_2 with hexanes−ether mixture (4:1) and dried in a vacuum. To obtain porphyrins **6a,b** as free bases, the CH_2Cl_2 solutions of the corresponding dications were thoroughly washed with 10% aq Na_2CO_3, dried over K_2CO_3, and evaporated.

6a, as dication dichloride: yield 450 mg, 45%, green powder; ^{1}H NMR ($CDCl_3$−TFA-*d*) δ 8.3 (br, 8H), 7.8 (br s, 12H), 2.2−0.0 (m, 56H), −1.6 (br s, 4H); MALDI-TOF *m/z* 1048.7, calcd 1046.6; UV−vis for dication dichloride, CH_2Cl_2; λ_{max} nm (ϵ) 462 (185 000), 610 (92 000), 666 (16 600).

6b, as dication dichloride: yield 485 mg, 40%, green powder; ^{1}H NMR ($CDCl_3$−TFA-*d*) δ 8.4−8.6 (m, 16H), 4.2 (s, 12H), 2.4−0.3 (m, 56H), −1.3 (br s, 4H); MALDI-TOF *m/z* 1280.2, calcd 1279.6; UV−vis for dication dichloride, CH_2Cl_2, λ_{max} nm (ϵ) 474 (190 000), 620 (98 200), 677 (18 400).

Pd−Porphyrins (Pd−6a,b). An excess of $PdCl_2$ (20 mg, 0.11 mmol) was added to a solution of porphyrin **6a** (90 mg, 0.08 mmol) or **6b** (110 mg, 0.08 mmol) in CH_3CN−THF (**6a**: 30 mL, 1:2; **6b**: 20 mL, 1:1) or dioxane (30 mL), and the mixture was refluxed for 10−15 min. Et_3N (0.5 mL) was added, and the mixture was refluxed for an additional 5 min. The conversion was monitored by UV−vis spectroscopy (solvent $CHCl_3$−AcOH), and the reaction was stopped when the porphyrin−dication band at around 470 nm disappeared. The mixture was evaporated to dryness, and the remaining material was purified on a silica gel column (eluent: CH_2Cl_2) to give the product as a red amorphous solid.

Pd-6a: yield 87 mg, 95%; ^{1}H NMR ($CDCl_3$) δ 8.2−7.5 (m, 20H), 2.2−0.7 (m, 56H); MALDI-TOF *m/z* 1153.6, calcd 1150.5; UV−vis, CH_2Cl_2, λ_{max} nm (ϵ) 424 (200 000), 536 (20 200), 570 (15 300).

Pd-6b: yield 107 mg, 97%; ^{1}H NMR ($CDCl_3$) δ 8.5−7.9 (m, 16H), 4.1 (s, 12H), 2.4−0.6 (m, 56H); MALDI-TOF *m/z* 1382.2, calcd 1384.0; UV−vis, CH_2Cl_2, λ_{max} nm (ϵ) 429 (210 000), 539 (20 600), 576 (16 000).

Cu−Porphyrin (Cu−6b). An excess of $Cu(OAc)_2{\cdot}2H_2O$ (20 mg, 0.11 mmol) was added to a solution of porphyrin **6b** (100 mg, 0.074 mmol) in CH_2Cl_2−MeOH (20 mL, 10:1), and the mixture was refluxed for 15 min. The conversion was monitored by UV−vis spectroscopy (solvent $CHCl_3$−AcOH). The reaction was stopped when the Soret absorption of the porphyrin dication disappeared. The mixture was evaporated to dryness, and the remaining material was purified on a silica gel column (eluent: CH_2Cl_2) to give the product as red amorphous solid. Porphyrin **Cu−6b**: yield 100 mg, 99%; MALDI-TOF *m/z* 1307.5, calcd 1307.3; UV−vis CH_2Cl_2, λ_{max} nm (ϵ) 428 (172 000), 559 (14 800).

Pd−Tetranaphthoporphyrins (Pd−12a,b). Pd−6a (80 mg, 0.07 mmol) or **Pd−6b** (93 mg, 0.067 mmol) was dissolved in 50 mL of dry toluene under Ar. DDQ (365 mg, 1.61 mmol) was added, and the mixture was refluxed for 3−5 min. The color of the solution changed from red to brown and the product precipitated as a dark green powder. The mixture was allowed to cool, and the solvent was removed in a vacuum. The resulting solid was dissolved in CH_2Cl_2 (several drops of EtOH were added to dissolve the remaining residue), washed with 10% aq Na_2SO_3 (2 × 50 mL), 10% aq Na_2CO_3 (50 mL), water, and brine, and dried over Na_2SO_4. The solvent was removed in a vacuum, and the solid was purified on a silica gel column (eluent: CH_2Cl_2, then CH_2Cl_2−THF, 30:1). The bright green band was collected. The volume of the solution was reduced to ~1 mL by rotary evaporation; it was layered over with diethyl ether and left in a closed vessel overnight. The product precipitated as a dark green solid (**6a**) or dark-green crystals (**6b**).

(48) Tietze, L. F.; Eicher, T. *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*; Georg Thieme Verlag: New York, 1991.

Pd−12a: yield 31 mg, 40%; ^{1}H NMR (pyridine-d_5) δ 8.48−8.07 (m, 20H), 7.96 (br s, 8H), 7.89 (br, 8H), 7.6 (8H, overlap with solvent); ^{13}C NMR (pyridine-d_5) δ 144.1, 138.9, 136.8, 136.2 (overlap with solvent), 134.7, 131.9, 130.7, 130.2, 129.9, 126.9, 117.8; MALDI-TOF *m/z* 1120.5, calcd 1119.6; UV−vis, pyridine, λ_{max} nm (ϵ) 462 (190 000), 642 (27 600), 706 (204 200).

Pd-12b: yield 54 mg, 46%; ^{1}H NMR ($CDCl_3$−pyridine-d_5) δ: 8.8−8.6 (m, aa′bb′, 16H), 7.7−7.8 (overlap s+m, 8+8H), 6.6 (m, 8H, overlap with solvent), 4.3 (s, 12H); ^{13}C NMR ($CDCl_3$-pyridine-d_5) δ 165.9, 145.6, 137.0, 134.5 (overlap with solvent), 133.4, 130.05, 130.0, 129.9, 128.2, 125.3, 115.1, 51.5; MALDI-TOF *m/z* 1351.9, calcd 1351.7; UV−vis, pyridine, λ_{max} nm (ϵ) 462 (190 000), 647 (25 000), 713 (179 500). Anal. Calcd for $C_{84}H_{52}N_4O_8Pd$: C, 74.64; H, 3.88; N, 4.14. Found: C, 74.30; H, 3.97; N, 4.11.

Cu−Tetranaphthoporphyrin (Cu−12b). Porphyrin **Cu−6b** (30 mg, 0.023 mmol) was dissolved in 30 mL of freshly distilled dry toluene under Ar. DDQ (120 mg, 0.54 mmol) and $Sc(OTf)_3$ (100 mg, 0.2 mmol) were added, and the mixture was refluxed for 20 min. The color of the solution changed from red to brown-green, and a dark precipitate formed. The mixture was allowed to cool, and CH_2Cl_2 (50 mL) was added. The solution was washed with 10% aq Na_2SO_3 solution (2 × 50 mL), water (100 mL), and brine (100 mL) and dried over Na_2SO_4. The solvents were removed in a vacuum, and the remaining solid was purified on a silica gel column (eluent: CH_2Cl_2−THF, 30:1). The first green fraction contained a mixture of porphyrins which were poorly separated and eluted in the following order: **6b**, partially oxidized **6b**, **Cu−12b**. **Cu−12b** was collected, the solvent was evaporated in a vacuum and the remaining green solid was dried in a vacuum. **Cu−12b**: yield 6 mg, 20%; MALDI-TOF *m/z* 1308.9, calcd 1308.1; UV−vis, CH_2Cl_2, λ_{max} nm (ϵ) 478 (170 000), 665 (20 400), 731 (154 000). Anal. Calcd for $C_{84}H_{52}CuN_4O_8$: C, 77.08; H, 4.00; N, 4.28. Found: C, 77.58; H, 4.68; N, 4.47.

α-Chlorosulfones (8a,b). Synthesis of compounds **8a**,**b** generally followed the published method.[28] To a stirred solution of PhSCl (50 mmol) in 50 mL of CH_2Cl_2, prepared as described in ref 28, was added dropwise a solution of **7a** (6.51 g, 50 mmol) or **7b** (9.5 g, 50 mmol) in 20−30 mL of dry CH_2Cl_2 at 0 °C under Ar. The mixture was allowed to warm to rt with stirring and under Ar for 1−2 h. The mixture was kept in a freezer at −18 °C overnight, and the precipitated succinimide was removed by filtration. The remaining solution was diluted with CH_2Cl_2 to ∼200 mL total volume and cooled to 0 °C on an ice bath. Solid *m*-CPBA (77%, 30 g, 125 mmol) was gradually added to the stirred solution in ∼1−2 g portions. The ice bath was removed, and the mixture was left to stir at rt for 1 h. An ice-cold 10% aq Na_2SO_3 solution (250 mL) was added, and the resulting mixture was allowed to stir for another 1 h. Aqueous Na_2CO_3 solution (10%, 100 mL) was added to the mixture, and it was transferred into a separatory funnel. The organic phase was separated, washed with 10% aq Na_2SO_3 solution (100 mL) and 10% aq Na_2CO_3 solution (100 mL), dried over K_2CO_3, and evaporated to dryness. The resulting material was recrystallized from ethyl alcohol to give the product as a colorless solid.

8a: 12.75 g, 83%, colorless crystals; mp 117−118 °C; TLC, CH_2Cl_2: moves with solvent front, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ 7.92−7.57 (m, 5H), 7.20−7.17 (m, 2H), 7.13−7.09 (m, 2H), 4.83 (m, 1H), 3.73−3.70 (m, 1H), 3.48−3.44 (dd, 1H, J_1 = 16 Hz, J_2 = 5 Hz), 3.32−3.27 (dd, 1H, J_1 = 15 Hz, J_2 = 6.5 Hz), 3.18−3.13 (dd, 1H, J_1 = 6.5 Hz, J_2 = 16 Hz), 3.07−3.06 (dd, 1H, J_1 = 16 Hz, J_2 = 4 Hz); ^{13}C NMR ($CDCl_3$) δ 138.2, 134.4, 132.8, 132.1, 129.7, 129.1, 128.9, 128.3, 127.4, 127.3, 66.6, 52.8, 37.3, 26.4. Anal. Calcd for $C_{16}H_{15}ClO_2S$: C, 62.64; H, 4.93. Found: C, 62.48; H, 4.90.

8b: 16.50 g, 90%, colorless crystals; mp 117−118 °C; TLC, CH_2Cl_2, R_f ∼ 0.9, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ: 7.92−7.53 (m, 5H), 6.64 (s, 2H), 4.82 (m, 1H), 3.76 (s, 3H), 3.74−3.70 (s+m, 3H+1H), 3.40−3.33 (dd, 1H, J_1 = 4.5 Hz, J_2 = 18 Hz), 3.20−3.17 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 151.2, 150.9, 138.4, 134.2, 129.4, 129.0, 122.2, 121.9, 108.2, 107.9, 64.6, 55.8, 55.7, 52.1, 30.7, 20.3. Anal. Calcd for $C_{18}H_{19}ClO_4S$: C, 58.93; H, 5.22. Found: C, 58.85; H, 5.29.

Allyl Sulfone 8c. A stirred solution of **8b** (1.78 g, 4.85 mmol) in CH_2Cl_2 (15 mL) was cooled to 0 °C on an ice bath, and the solution of DBU (0.75 g, 4.95 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The ice bath was removed, and the mixture was stirred at rt for 1−2 h. Diethyl ether (10 mL) was added to the mixture, and the resulting solution was washed with 5% aq HCl and then with brine and dried over Na_2SO_4. The solvent was removed in a vacuum, and the resulting material was purified on the silica gel column twice to give the product as a colorless solid. **8c**: yield 0.96 g (60%); mp 155−156 °C; TLC, CH_2Cl_2, R_f ∼ 0.5, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ 7.7−7.2 (m, 5H), 6.94 (d, 1H, J = 10 Hz), 6.56 (d, 1H, J = 8.5 Hz), 6.43 (d, 1H, J = 8.5 Hz), 5.99 (dd, 1H, J_1 = J_2 = 10 Hz), 3.91 (m, 1H), 3.75 (s, 3H), 3.65 (dd, 1H, J_1 = 18 Hz, J_2 = 4 Hz), 3.60 (s, 3H), 2.96 (dd, 1H, J_1 = 18 Hz, J_2 = 8 Hz); HR-MS 353.0830 (M^+ + Na), calcd 353.0824.

Naphthyl Sulfone 8d. A solution of **8c** (430 mg, 1.3 mmol) or **8b** (477 mg, 1.3 mmol) in 25 mL of THF was added dropwise to stirred solution of 90% ^{t}BuOK (500 mg, 4 mmol) in dry THF (50 mL) at 0 °C. The ice bath was removed, and the mixture was stirred at room temperature for 2−3 h or until the red color disappeared. The solvent was removed in a vacuum, and the resulting material was dissolved in 50 mL of CH_2Cl_2. The solution was washed with 10% aq HCl (2 × 50 mL) and then with brine, dried over Na_2SO_4, and chromatographed on a short (2×5 cm i.d.) silica gel column, eluting with CH_2Cl_2. The first light-yellow fraction was collected (TLC, CH_2Cl_2, R_f ∼ 0.8, fluorescent blue spot in UV light). The product was isolated as yellow oil upon removal of the solvent. The oil crystallized upon addition of ethyl alcohol and it was dried in a vacuum. **8d**: yield 390 mg (90%), light-yellow solid; mp 156−158 °C; ^{1}H NMR ($CDCl_3$) δ 8.92 (s, 1H), 8.26 (d, 1H, J = 9 Hz), 7.98+7.44−7.52 (m, 2+3H), 7.86 (d, 1H, J = 9 Hz), 6.82 (d, 1H, J = 8.5 Hz), 6.76 (d, 1H, J = 8.5 Hz), 3.95 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 150.3, 149.3, 142.1, 138.4, 133.2, 129.4, 128.1, 127.9, 125.5, 123.9, 123.8, 122.9, 107.0, 105.1, 56.1, 55.9; HR-MS 351.0656 (M^+ + Na), calcd 351.0667.

Pyrrole Ester 9a. A solution of ethyl isocyanoacetate (1.4 g, 12.4 mmol) in 10 mL of dry THF was added to a stirred suspension of 90% ^{t}BuOK (3.1 g, 24.8 mmol) in 30 mL of dry THF at rt under Ar. A solution of α-chlorosulfone **8a** (3.2 g, 10.3 mmol) in 25 mL of THF was quickly added to the mixture, which was stirred under Ar for 10 min at rt and then refluxed under Ar for 40 min. The mixture was cooled to rt, and its volume was reduced to about 15 mL by rotary evaporation. CH_2Cl_2 (100 mL) was added to the mixture, and the resulting solution was washed with water (100 mL) and then with brine (50 mL) and dried over K_2CO_3. After evaporation of the solvent, the residue was recrystallized from hexane and/or ethyl alcohol to give the ester **9a** as pale yellow crystals. **9a**: yield 1.6 g, 65%; mp 155−156 °C; TLC, CH_2Cl_2, R_f ∼ 0.6, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ 9.2 (broad s, 1H), 7.4 (m, 1H), 7.3 (m, 1H), 7.28−7.20 (m, 2H), 6.86 (d, 1H, J = 2.5 Hz), 4.42 (q, 2H, J = 7 Hz), 4.23 (s, 2H), 3.95 (s, 2H), 1.46 (t, 3H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 161.7, 135.3, 135.1, 129.4, 129.1, 126.4., 126.2, 126.1, 120.6, 118.3, 117.6, 60.2, 28.4, 27.1, 14.8. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.44; H, 6.27; N, 5.75.

Pyrrole Ester 9b. Method A. A solution of ethyl isocyanoacetate (2.4 g, 21.2 mmol) in 30 mL of dry THF was added to a stirred suspension of 90% ^{t}BuOK (2.4 g, 19.3 mmol) in 50 mL of dry THF at rt under Ar. A solution of α-chlorosulfone **8b** (3.5 g, 9.5 mmol) in 40 mL of THF was added dropwise to the mixture, and the mixture was refluxed under Ar for 1 h. The mixture was cooled to rt, and the volume of the solvent was reduced to about 20 mL by rotary evaporation. CH_2Cl_2 (150 mL) was added to the mixture, and the resulting solution was washed with water (2 × 100 mL) and brine (100 mL) and dried over K_2CO_3. The resulting solution was passed through

a short (ø2×5 cm) silica gel column, eluting with CH_2Cl_2–THF (20:1). After evaporation of the solvents, the residue was crystallized from ethyl alcohol to give the ester **9b** as pale-yellow crystals. **9b**: yield 2.2 g, 77%.

Pyrrole Ester 9b. Method B. A solution of allyl sulfone **8c** (2.74 g, 8.3 mmol) in 10 mL of dry THF was added dropwise to a stirred mixture of 90% ^{t}BuOK (1.20 g, 10 mmol) and ethyl isocyanoacetate (1.20 g, 10.6 mmol) in 50 mL of dry THF at rt under Ar. The resulting mixture was refluxed for 1 h, cooled, and worked up as described above. **9b**: yield 1.92 g, 80%; mp 157–158 °C; TLC, CH_2Cl_2, $R_f \sim 0.4$, dark spot in the UV light; ^{1}H NMR ($CDCl_3$) δ 8.92 (broad s, 1H), 6.80 (d, 1H, $J = 2$ Hz), 6.69 (s, 2H), 3.36 (q, 2H, $J = 7$ Hz), 4.06 (s, 2H), 3.82–3.83 (ovrlapping s+d, 6H+2H), 1.49 (t, 3H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) δ 161.4, 151.8, 151.5, 125.3, 124.8, 119.5, 118.2, 117.6, 107.1, 106.9, 59.9, 55.8, 55.7, 22.4, 20.9, 14.6. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.67; H, 6.37; N, 4.56.

Pyrroles 10a,b. A stirred mixture of pyrrole ester **9a** (2.41 g, 10 mmol) or **9b** (3.01 g, 10 mmol) and NaOH (2.0 g, 50 mmol) was refluxed under Ar in ethylene glycol for 20–30 min. The resulting solution was rapidly cooled on an ice bath and diluted with CH_2Cl_2 (100 mL). The mixture was thoroughly washed with water (2 × 100 mL; brine was added to reduce the emulsion), and the aqueous phase was extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed in a vacuum, and the resulting material was purified on a short (2 × 10 cm i.d.) silica gel column, eluting with CH_2Cl_2. The solvent was evaporated, and the resulting colorless solid was introduced into the following porphyrin synthesis immediately.

10a: yield 1.7 g, 97%; ^{1}H NMR ($CDCl_3$) δ 7.97 (broad s, 1H), 7.35 (m, 2H), 7.25 (m, ovlpd. w/solv, 2H), 6.67 (d, 2H, $J = 2.5$ Hz), 3.99 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 136.7, 129.3, 125.9, 118.7, 112.8, 27.8.

10b: yield 2.06 g, 90%; ^{1}H NMR ($CDCl_3$) δ 8.06 (broad s, 1H), 6.70 (s, 2H), 6.66 (d, 2H, $J = 2.5$ Hz), 3.88 (s, 4H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 151.8, 126.5, 117.5, 113.0, 107.1, 56.0, 21.3.

Tetranaphthoporphyrins (12a–f). Pyrrole **10a**,**b** (2.5 mmol) was dissolved in CH_2Cl_2 (250 mL), aryl aldehyde (2.5 mmol) was added, and the stirred mixture was kept in the dark under Ar for 10 min. $BF_3{\cdot}Et_2O$ (71 mg, 0.5 mmol) was added in one portion, and the mixture was allowed to react at rt for 1.5 h. DDQ (2.3 g, 10 mmol) was added to the mixture in one portion, and the mixture was stirred at rt overnight (**12c**,**d**,**f**) or refluxed for 30–60 min (**12a**,**b**,**e**). The resulting mixture was washed with 10% aq Na_2SO_3 (2 × 30 mL) and with water (2 × 100 mL). The following workup procedures for the individual porphyrins are described below.

12c,d. The organic phase, containing a fine suspension of green particles, was evaporated in a vacuum. The remaining green solid, insoluble in most organic solvents, was repeatedly washed with water, with THF, and with CH_2Cl_2–py (10:1) and recrystallized from hot PhCN. The resulting green precipitate was washed with CH_2Cl_2–py (10:1) and dried in a vacuum. Porphyrins **12c**,**d** are poorly soluble in pyridine and DMF, moderately soluble in hot benzonitrile and nitrobenzene, and well soluble in acids (AcOH, TFA).

12a,b and 12e,f. The organic layer was dried over K_2CO_3, the solvent was evaporated in a vacuum, and the remaining solid was washed with MeOH (**12a**) or with CH_3CN (**12b**,**e**,**f**), dried,and purified by chromatography on a silica gel column (eluent: CH_2Cl_2, then CH_2Cl_2–THF 30:1–10:1). The green band was collected and reduced to a small volume, and the porphyrin was precipitated by addition of about 20-fold excess volume of methanol (**12a**) or CH_3CN (**12b**,**e**,**f**). The precipitate was dried in a vacuum. The trifluoroacetates of dications of porphyrins **12a**,**b**,**e**, were prepared by dissolving the free base porphyrins in TFA and evaporating the solutions in a vacuum.

12a: yield 49%, shiny green plates; ^{1}H NMR (as dication ditrifluoroacetate, $CDCl_3$) δ 8.63–7.97 (s+m, 8+20H), 7.72 (m, 8H), 7.50 (m, 8H), 2.63 (br s, 4H); ^{13}C NMR (as dication ditrifluoroacetate, $CDCl_3$) δ 140.9, 139.7, 135.6, 132.9, 130.6, 130.2, 129.9, 129.5, 127.5, 125.4, 112.6; MALDI-TOF *m/z* 1017.2, calcd 1015.2; UV–vis, pyridine, λ_{max} nm (ϵ) 503 (220 000), 680 (24 000), 731 (104 000). Anal. Calcd for $C_{76}H_{46}N_4$: C, 89.91; H, 4.57; N, 5.52. Found: C, 88.88; H, 4.23; N, 5.40.

12b: yield 45%, bluish green crystals; ^{1}H NMR (as dication ditrifluoroacetate, $CDCl_3$) δ 8.80–8.64 (m, aa′bb′, 16H), 7.90 (s, 8H), 7.66 (m, 8H), 7.47 (m, 8H), 4.19 (s, 12H), 3.77 (br s, 4H); ^{13}C NMR (as dication ditrifluoroacetate, $CDCl_3$, 40°C) δ 167.1, 143.8, 141.4, 136.3, 133.1, 131.8, 131.2, 129.9, 129.5, 127.5, 125.8, 111.7, 52.8; ^{1}H NMR (as free base, 1,1,2,2-tetrachloroethane-d_2, 90 °C) δ 8.66–8.56 (m, aa′bb′, 8H), 7.70 (s, 8H), 7.67 (m, 8H), 7.46 (m, 8H), 4.41 (s, 12H), 2.27 (br s, 2H); MALDI-TOF: *m/z* 1246, calcd 1246.4; UV–vis, pyridine, λ_{max} nm (ϵ) 500 (207 700), 672 (26 100), 732 (111 000); as dication ditrifluoroacetate, CH_2Cl_2, λ_{max} nm (ϵ) 530 (186 900), 800 (75 300). Anal. Calcd for $C_{84}H_{54}N_4O_8$: C, 80.88; H, 4.36; N, 4.49. Found: C, 88.51; H, 4.24; N, 4.40.

12c: yield 40%, green powder; NMR spectra of **12c** could not be recorded due to its very low solubility and strong aggregation; MALDI-TOF *m/z* 1017.2, calcd 1015.2; UV–vis, pyridine, λ_{max} nm (ϵ) 509 (200 000), 683 (30 700), 750 (98 400). Anal. Calcd for $C_{84}H_{62}N_4O_8$: C, 80.36; H, 4.98; N, 4.46. Found: C, 79.90; H, 4.57; N, 4.33.

12d: yield 44%, green powder; ^{1}H NMR (as dication dichloride, $CDCl_3$)[49] δ 8.69–8.62 (m, aa′bb′, 16H), 8.32 (s, 8H), 6.64 (m, 8H), 4.16 (s, 12H), 3.78 (s, 12H); MALDI-TOF *m/z* 1486.5, calcd 1487.5; UV–vis, pyridine, λ_{max} nm (ϵ) 508 (220 000), 685 (26 100), 754 (135 000). Anal. Calcd for $C_{92}H_{70}N_4O_{16}$: C, 74.28; H, 4.74; N, 3.77. Found: C, 73.55; H, 4.56; N, 3.97.

12e: yield 35%, dark green powder; ^{1}H NMR (as dication ditrifluoroacetate, $CDCl_3$) δ 9.52 (s, 8H), 9.38 (s, 4H), 7.85 (s, 8H), 7.70 (m, 8H), 7.51 (m, 8H), 4.42–4.51 (m, 16H), 3.79 (br s, 4H), 1.82 (m, 16H), 1.41 (m, 16H), 0.88 (t, 24H, $J = 7$ Hz); ^{13}C NMR (as dication ditrifluoroacetate, $CDCl_3$) δ 165.6, 141.2, 140.3, 139.9, 133.2, 133.0, 132.4, 129.7, 129.6, 127.9, 125.6, 111.0, 66.1, 30.8, 19.4, 13.8; MALDI-TOF *m/z* 1818.36, calcd 1816.13; UV–vis, pyridine, λ_{max} nm (ϵ) 501 (200 000), 685 (24 300), 740 (95 500). Anal. Calcd for $C_{116}H_{110}N_4O_{16}$: C, 76.71; H, 6.10; N, 3.08. Found: C, 76.45; H, 5.68; N, 3.03.

12f: yield 39%, dark green powder; ^{1}H NMR (as free base, $CDCl_3$) δ 9.46 (d, 4H, $J = 2$ Hz), 9.24 (d, 8H, $J = 1.5$ Hz), 8.10 (br, 8H), 6.65 (s, 8H), 4.38 (t, 16H, $J = 7$ Hz), 3.86 (s, 12H), 1.69 (m, 16H), 1.34 (m, 16H), 0.82 (t, 24H, $J = 7$ Hz); ^{13}C NMR (as free base, pyridine-d_5) δ 166.5, 150.8, 144.6, 139.4, 139.0, 134.1, 132.3, 131.8, 125.5, 119.8, 114.1, 104.7, 66.1, 56.2, 31.2, 19.6, 14.0; MALDI-TOF *m/z* 2054.8, calcd 2056.3; UV–vis, pyridine, λ_{max} nm (ϵ) 505 (225 000), 686 (29 500), 758 (162 900). Anal. Calcd for $C_{124}H_{126}N_4O_{24}$: C, 72.43; H, 6.18; N, 2.72. Found: C, 72.10; H, 6.12; N, 2.85.

Tetranaphthoporphyrin (12b) from Cu–12b. Cu–12b (6 mg, 0.0045 mmol) was dissolved in 5 mL of polyphosphoric acid and stirred in a closed vessel for 4–5 h at 50 °C, then at rt overnight. MeOH (10 mL) and H_2SO_4 (2 mL) were added to the mixture, and it was left to stir for 24 h. CH_2Cl_2 (50 mL) was added, and the organic phase was washed with water, with 10% aq $NaHCO_3$ solution, and then 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 (eluent: CH_2Cl_2–THF, 30:1). The green fraction was collected, and the solvent was evaporated in a vacuum. **7a**: yield 4 mg, 72%.

Pd–Tetranaphthoporphyrins (Pd–12) from Free Bases (12). A solution of porphyrin **12** (0.04 mmol) in PhCN (5–7 mL) was brought to boiling, and an excess of $PdCl_2$ (10 mg, 0.06 mmol) was added to the mixture in one portion. In the

(49) The NMR sample was obtained by dissolving ~0.5 mg of **12d** free base in $CDCl_3$ contaminated with traces of HCl, which formed in $CDCl_3$ upon prolonged storage. The solution of the dication had a deep purple color.

case of porphyrins **12a**,**b**,**e**, the mixture was refluxed for 20−30 min until the conversion was complete (controlled by UV−vis spectroscopy). For porphyrins **12d**,**f**, the mixture was refluxed for 3−5 min, after which a few drops of pyridine were added. The mixtures containing the individual Pd porphyrins were worked up as described below.

Pd−12a,b,e. PhCN was removed in a vacuum (0.5 mmHg), and the remaining solid was purified on a silica gel or neutral alumina column (eluent: CH_2Cl_2, then CH_2Cl_2−THF, 30:1). The bright green band was collected. The solvent was evaporated in a vacuum, and the remaining material was dissolved in a minimal volume of warm CH_2Cl_2. The solution was layered over with an excess (∼10-fold) of acetonitrile (**12a**,**e**) or ether (**12b**) and left in a closed vessel overnight. The products precipitated as dark-green crystals.

Pd−12a: yield 85%; see above. **Pd−12b**: yield 87%; see above.

Pd−12e: yield 80%; ^{1}H NMR (pyridine-d_5) δ 10.02 (s, 4H), 9.78 (s, 8H), 7.98 (s, 8H), 7.71 (m, 8H), 7.38 (m, 8H), 4.45 (t, 16H, J = 6.5 Hz), 1.60 (m, 16H), 1.26 (m, 16H), 0.82 (t, 24H, J = 7 Hz); ^{13}C NMR (pyridine-d_5) δ 166.4, 144.1, 140.1, 138.9, 136.5, 134.2, 132.2, 131.9, 129.9, 127.3, 124.5 (overlap with solvent), 116.0, 66.5, 31.2, 19.3, 14.1; MALDI-TOF *m/z* 1921.5, calcd 1920.5; UV−vis, pyridine, λ_{max} nm (ϵ) 459 (195 000), 647 (25 500), 715 (195 800). Anal. Calcd for $C_{116}H_{108}N_4O_{16}Pd$: C, 72.54; H, 5.67; N, 2.92. Found: C, 72.40; H, 5.63; N, 2.88.

Pd−12d. The hot mixture (see above) was filtered through Celite, the solution was diluted with THF, and the precipitate was collected by centrifugation, repeatedly washed with THF−pyridine (20:1), and dried in a vacuum. Yield of **Pd-12d**: 80%, green powder, insoluble in most organic solvents, moderately soluble in hot pyridine, PhCN, and hot $PhNO_2$. ^{1}H NMR ($PhNO_2$-d_5/DMSO-d_6, 1:1, 80 °C) δ 8.75−8.52 (m, aa′bb′, 16H), 8.20 (s, 8H), 6.77 (s, 8H), 4.25 (s, 12H), 3.87 (s, 24H); MALDI-TOF *m/z* 1590.7, calcd 1591.9; UV−vis, pyridine, λ_{max} nm (ϵ), 465 (170 000), 653 (31 000), 720 (183 000). Anal. Calcd for $C_{92}H_{68}N_4O_{16}Pd$: C, 69.41; H, 4.31; N, 3.52. Found: C, 67.96; H, 3.91; N, 3.27.

Pd−12f. The mixture was cooled, PhCN was removed in a vacuum (0.5 Torr), and the resulting solid was purified on a neutral alumina column (eluent: CH_2Cl_2). The bright green band was collected. The solvent was evaporated, and the remaining material was dissolved in the minimal volume of warm CH_2Cl_2, layered over with an excess volume of ether (∼10-fold), and left in a closed vessel overnight. The product precipitated as dark-green crystals. **Pd−12f**: yield 85%; ^{1}H NMR (pyridine-d_5) δ 10.10 (t, 4H, J = 1.5 Hz), 9.74 (d, 8H, J = 2 Hz), 8.61 (s, 8H), 6.73 (s, 8H), 4.44 (t, 16H, J = 6.5 Hz), 3.93 (s, 12H), 1.59 (m, 16H), 1.26 (m, 16H), 0.71 (t, 24H, J = 7 Hz); ^{13}C NMR (pyridine-d_5) δ 166.6, 150.8 (overlap with solvent), 144.2, 139.2, 138.3, 136.4 (overlap with solvent), 134.4, 132.0, 125.1, 119.3, 115.9, 104.5, 66.2, 56.3, 31.3, 19.7, 14.0; MALDI-TOF *m/z* 1259.9, calcd 1260.7; UV−vis, pyridine, λ_{max} nm (ϵ) 463 (170 000), 654 (31 200), 725 (220 600). Anal. Calcd for $C_{124}H_{124}N_4O_{24}Pd$: C, 68.93; H, 5.78; N, 2.59. Found: C, 68.45; H, 5.74; N, 2.55.

Zn−Tetranaphthoporphyrins (Zn−12) from Free Bases (12). A solution of porphyrin **12** (0.04 mmol) in PhCN (5−7 mL) was brought to boiling, and an excess of $Zn(OAc)_2 \cdot 2H_2O$ (10 mg, 0.06 mmol) was added to the mixture. In the case of porphyrins **12a**,**b**, the mixture was refluxed for 15−20 min until the conversion was complete (controlled by UV−vis spectroscopy). In the case of porphyrins **12d**,**f**, the mixture was refluxed for 3−5 min, after which time a few drops of pyridine were added and the mixture was allowed to cool to rt. The mixture was diluted with methanol (50−100 mL), and the green precipitate was collected by centrifugation, repeatedly washed with methanol−pyridine mixture (50:1), and dried in a vacuum. **Zn−12**: yield 85−95%. **Zn−12a**: as described in ref 12g. **Zn-12c**: ^{1}H NMR (pyridine-d_5, 70 °C) δ 8.80−8.60 (br, 8H), 8.56−8.11 (m, 20H), 8.82 (br s, 8H); ^{13}C NMR spectra of **Zn−12c** could not be recorded due to its very low solubility and strong aggregation; MALDI-TOF *m/z* 1320.0, calcd 1318.8; UV−vis, pyridine, λ_{max} nm (ϵ) 504 (290 000), 667 (23 600), 730 (171 100). Anal. Calcd for $C_{84}H_{60}N_4O_8Zn$: C, 76.50; H, 4.59; N, 4.25. Found: C, 75.66; H, 4.54; N, 4.31. **Zn-12d**: ^{1}H NMR (pyridine-d_5) δ 8.97−8.68 (m, aa′bb′, 16H), 8.65 (s, 8H), 6.80 (s, 8H), 4.26 (s, 12H), 3.93 (s, 24H); ^{13}C NMR (pyridine-d_5, 50 °C) δ 168.6, 151.3, 144.5, 137.9, 134.9, 131.8, 131.7, 125.3, 119.6, 116.5, 104.1, 56.3, 52.7; MALDI-TOF *m/z* 1549.4, calcd 1550.9; UV−vis, pyridine, λ_{max} nm (ϵ), 503 (280 000), 669 (24 700), 732 (166 100). Anal. Calcd for $C_{92}H_{68}N_4O_{16}Zn$: C, 71.25; H, 4.42; N, 3.61. Found: C, 70.91; H, 4.38; N, 3.60.

Dibutyl 5-Formylisophthalate (14). 3,5-dibromobenzaldehyde **13** (6.0 g, 22.73 mmol), ethylene glycol (20 mL), and *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol) were refluxed in benzene (100 mL) with a Dean−Stark refluxing condenser for 5 h. After cooling, the solution was transferred into a separatory funnel, washed with 10% aq $NaHCO_3$ (100 mL) and water (100 mL), and dried over Na_2SO_4. The solvent was evaporated, and the resulting oil (7.0 g; ^{1}H NMR ($CDCl_3$) δ 7.54 (d, 1H, J = 1.5 Hz), 7.44 (d, 2H, J = 1.5 Hz), 5.64 (s, 1H), 3.89−3.98 (m, 4H)) was placed in a pressure-resistant vessel for carbonylation. Triethylamine (10 mL), PPh_3 (100 mg), and Pd(0)[(PPh_3)]$_4$ (100 mg) were added, and the mixture was heated to 90 °C on an oil bath in CO atmosphere. The carbonylation was carried out at 90 °C for 48 h under 2 atm of CO (for details of the carbonylation procedure see refs 47b and 50]). The mixture was allowed to cool, and the vessel was opened and left under the fume hood for another 1 h. $Et_3N \cdot$HBr, formed as a white precipitate, was removed by filtration, and the filtrate was dried on a rotary evaporator at 0.5 mmHg. The remaining oil [8.7 g; ^{1}H NMR ($CDCl_3$) δ 8.66 (s, 1H), 8.30 (d, 2H, J = 0.5 Hz), 5.88 (s, 1H), 4.34 (t, 4H, J = 7 Hz), 4.15−4.04 (m, 4H), 1.76 (m, 4H), 1.47 (m, 4H), 0.97 (t, 6H, J = 8 Hz)] was dissolved in THF (25 mL), concd HCl (4 mL) and water (15 mL) were added, and the mixture was refluxed for 1.5 h. CH_2Cl_2 (150 mL) was added to the mixture, and the organic phase was washed with 10% aq Na_2CO_3 (100 mL) and then with brine (100 mL) and dried over Na_2SO_4. The solvent was removed in a vacuum, and the resulting oil was purified on a neutral alumina column (3 × 20 cm i.d., eluent: CH_2Cl_2−THF, 20:1−10:1). The first fraction (TLC, CH_2Cl_2−THF, 20:1, R_f ∼ 0.75, dark spot in the UV light) was collected, and the solvent was evaporated in a vacuum to give the product as a light-yellow oil. **14**: yield 5.4 g, 77%; ^{1}H NMR ($CDCl_3$) δ 10.13 (s, 1H), 8.88 (d, 1H, J = 1.5 Hz), 8.67 (d, 2H, J = 1.5 Hz), 4.39 (t, 4H, J = 7 Hz), 1.79 (m, 4H), 1.49 (m, 4H), 0.99 (t, 6H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 190.6, 164.9, 136.9, 135.8, 134.2, 132.3, 65.8, 30.8, 19.3, 13.8; HR-MS 329.1370 (M^+ + Na), calcd 329.1365.

Acknowledgment. Support from the NIH (Grant No. EB003663-01), Anteon, Inc. (Contract No. 02-5403-21-2), the Russian Foundation for Basic Research (Grant No. RFBR 04-03-32650-a), and a grant from the Russian Academy of Sciences to A.V.C. is gratefully acknowledged. We thank Ms. Natalie Kim for proofreading the manuscript.

Supporting Information Available: Details of X-ray structure determination, NSD (Normal-Coordinate Structural Decomposition), and 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.

JO047741T

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