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Synthesis of Phosphorescent Asymmetrically π-Extended Porphyrins for Two-Photon Applications

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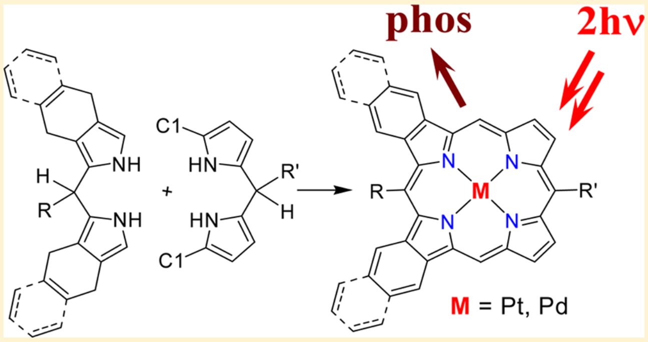
Supporting Information



ABSTRACT: Significant effort has been directed in recent years toward porphyrins with enhanced two-photon absorption (2PA). However, the properties of their triplet states, which are central to many applications, have rarely been examined in parallel. Here we report the synthesis of asymmetrically π-extended platinum(II) and palladium(II) porphyrins, whose 2PA into single-photon-absorbing states is enhanced as a result of the broken center-of-inversion symmetry and whose triplet states can be monitored by room-temperature phosphorescence. 5,15-Diaryl-*syn*-dibenzoporphyrins (DBPs) and *syn*-dinaphthoporphyrins (DNPs) were synthesized by [2 + 2] condensation of the corresponding dipyrromethanes and subsequent oxidative aromatization. Butoxycarbonyl groups on the *meso*-aryl rings render these porphyrins well-soluble in a range of organic solvents, while 5,15-*meso*-aryl substitution causes minimal nonplanar distortion of the macrocycle, ensuring high triplet emissivity. A *syn*-DBP bearing four alkoxycarbonyl groups in the benzo rings and possessing a large static dipole moment was also synthesized. Photophysical properties (2PA brightness and phosphorescence quantum yields and lifetimes) of the new porphyrins were measured, and their ground-state structures were determined by DFT calculations and/or X-ray analysis. The developed synthetic methods should facilitate the construction of π-extended porphyrins for applications requiring high two-photon triplet action cross sections.

INTRODUCTION

In the past two decades, interest in porphyrins with aromatically extended π-systems has been steadily on the rise.[1−4] Today areas of their application encompass optical limiting,[5,6] organic light-emitting diodes (OLEDs)[7−9] and other electronic devices,[10−13] upconversion by sensitized triplet−triplet annihilation (TTA),[14−19] phototherapy,[20−23] and biomedical optical imaging and sensing.[24−28] Progress in all of these areas depends on the availability of molecules with different functional groups, optimal solubility, and tailored photophysical properties, warranting continuous development and optimization of synthetic methods.

Among π-extended porphyrins, fully symmetrical molecules such as tetrabenzoporphyrins, tetranaphthporphyrins, and tetraanthraporphyrins[29] captured the most attention, in part because their synthetic chemistry has been most thoroughly developed.[2,4] These chromophores are characterized by strong and narrow absorption bands in the red spectral region[6,29,30] and form brightly phosphorescent complexes with Pd and Pt[31−35] that are of interest for OLED and imaging applications. In contrast, asymmetrically π-extended porphyrins, which also have been known for a long time,[36−47] have been studied only occasionally.[48] Structural asymmetry generally causes broadening of the porphyrin optical spectra, which may be seen as a disadvantage from the applications' point of view. In addition, asymmetrical porphyrins are usually more laborious to synthesize. However, for technologies that rely on nonlinear optical properties, asymmetrical π-extension may bring about unique possibilities, for example, as a method to increase two-photon absorption (2PA) cross sections.[49]

A number of porphyrin-based systems with enhanced 2PA have been designed in the past, and in some cases 2PA cross sections of several thousand GM units have been reported.[50−57] However, in only a few cases have triplet states of these systems been evaluated in parallel.[52,57] Triplet states, on the other hand, are central to several key applications of porphyrins, including two-photon photodynamic therapy (2P PDT)[58−60] and two-photon phosphorescence lifetime microscopy (2PLM) of oxygen.[61−63] In those cases when evaluation of the triplet states of 2P-absorbing porphyrins has been attempted, measurements have been performed by indirect methods, such as quantification of singlet oxygen (a product of the triplet quenching reaction) or measuring downstream effects of singlet oxygen itself.[59] Such methods, however, can be subject to major errors due to a large number of interfering parameters.[64] At the same time, it is quite possible that modifications of porphyrins leading to an increase in 2PA can simultaneously cause severe

Received: July 21, 2014
Published: August 26, 2014

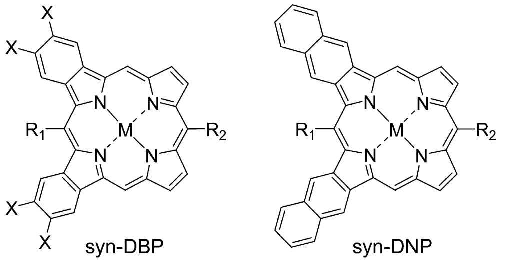
dx.doi.org/10.1021/jo501521x | J. Org. Chem. 2014, 79, 8812−8825

triplet quenching effects, e.g., via formation of low-lying charge transfer states and/or by influencing the vibrational dynamics of the macrocycle, enhancing its nonradiative triplet decay.[34,35] As a result, while gaining in 2PA, these porphyrins could lose their other critical property, i.e., the ability to form long-lived triplet states.

Our goal was to develop 2P-absorbing porphyrins whose triplet states can be monitored directly by emission. The selection rules determining linear one-photon (1P) and 2P transition probabilities in centrosymmetrical molecules, such as regular metalloporphyrins, are mutually exclusive.[65] Consequently, strongly allowed 1P transitions into B (Soret) and Q states,[66] which are states of *ungerade* symmetry, are not allowed for 2PA. On the other hand, *gerade* states, which can be accessed via 2PA, lie at much higher energies,[66] and their 2P spectra overlap with linear transitions (e.g., Q bands), causing the 2P excitation pathway to be overshadowed by 1P absorption. The above selection rules, however, should be relaxed if there is no center-of-inversion symmetry in a porphyrin molecule, causing 1P states to become accessible by 2PA.

Given that Pt and Pd complexes of π-extended porphyrins exhibit strong phosphorescence and that asymmetric π-extension significantly affects the electronic structure of porphyrins,[30,48] we set out to examine whether asymmetrically π-extended Pt and Pd porphyrins can act as efficient triplet chromophores with intrinsically enhanced 2PA. Here we present syntheses of nonfully symmetrical π-extended *syn*-dibenzo- and *syn*-dinaphthoporphyrins (DBPs and DNPs, respectively; Chart 1) and their phosphorescent Pt(II) and Pd(II) complexes. Rational approaches to a number of related tetrapyrroles have been explored previously.[36−47,67,68] In particular, there is an example of a 5,15-*meso*-diaryl DBP, reported by Smith et al.,[46] that is very similar to one of our compounds (porphyrin **20**) but was obtained via different route, i.e., from a sulfolenoporphyrin precursor by the Diels−Alder reaction. The methodology explored in our synthesis is based on the oxidative aromatization method[69−71] and its 4,7-dihydroisoindole variant,[72−75] developed by Cheprakov and coworkers. Preliminary photophysical measurements showed that all of the synthesized Pt porphyrins exhibit very bright phosphorescence at ambient temperatures and increased 2PA compared with nonextended porphyrins. The 2PA is especially enhanced in the case of porphyrins bearing alkoxycarbonyl substituents on the fused benzo rings. The developed methods should facilitate the construction of nonfully symmetrical π-extended porphyrins for applications requiring enhanced 2PA/triplet action cross sections, such as 2P PDT and 2PLM.

Chart 1. Structures of the Target Porphyrins



RESULTS AND DISCUSSION

Synthesis. The π-extended porphyrins synthesized in this study are shown in Chart 1. Two adjacent pyrrole rings in each macrocycle are fused with external aromatic fragments through the β-carbon atoms, forming *syn*- (or *adj*-) dibenzo- and dinaphtho[2,3]porphyrins. If *meso*-aryl substituents are disregarded, these macrocycles belong to the C_{2v} symmetry group, unlike regular metalloporphyrins, which have D_{4h}-type symmetry and thus possess a center of inversion.

Previous studies have shown that planar *meso*-unsubstituted π-extended porphyrins are significantly more emissive than their nonplanar *meso*-tetraarylated analogues.[34,71] However, *meso*-unsubstituted porphyrins are prone to aggregation and often pose serious solubility problems. On the other hand, *meso*-5,15-diarylporphyrins[73] offer a useful compromise between emissivity and solubility. Nonplanar distortions in porphyrins are usually caused by steric repulsion between β-pyrrolic substituents (e.g., fused benzo rings) and *meso*-aryl groups. Placing only two *meso*-aryls opposite to each other allows the macrocycle to evade the strain by undergoing in-plane as opposed to out-of-plane deformation and thus preserve planarity.[34] Moreover, in *syn*-DBPs and *syn*-DNPs (Chart 1), aromatic rings are appended to pyrroles only on "one side" of the molecule, while the dipyrromethene fragment on the opposite side remains strain-free. *mono*-Aryl-substituted DBP **21** lacking a *meso*-aryl group between the two benzo substituents was also synthesized. To improve the solubility, the *meso*-aryl substituents in the majority of the synthesized porphyrins were supplemented by *meso*-dialkoxycarbonyl groups. In all cases, DFT ground-state calculations (B3LYP/6-31G*) confirmed planar macrocycle structures (Figure S1 in the Supporting Information).

The saturated precursor porphyrins for *syn*-DBPs and *syn*-DNPs may be obtained from dipyrromethanes bearing C1 synthons at the 1- and 9-positions and appropriate unsubstituted counterparts (Scheme 1). Following the methods developed by Lindsey and co-workers,[76−79] we chose to use bis(*N*,*N*-dimethylaminomethyl)[76] and bis-(propyliminomethyl)[77,79] derivatives (Chart 2), which have been shown to minimize scrambling in the condensation reaction. Route A was selected because of easier accessibility and higher stability of C1-dipyrromethanes derived from unsubstituted pyrrole.

Generally, 1,9-bis(*N*,*N*-dimethylaminomethyl)-dipyrromethanes such as **1** (Chart 2) are simpler to synthesize, and they lead to excellent results when condensations are carried out in alcohols.[76] For example, in our case **1** was successfully employed in the synthesis of porphyrin **13** in MeOH (see Scheme 3). However, in nonpolar solvents (e.g., toluene, benzene), which appeared to favor syntheses of the majority of our porphyrins (see below), 1,9-bis-(propyliminomethyl)dipyrromethane **2** allowed us to achieve significant improvements in the yield. Dipyrromethanes **1** and **2** (Chart 2) were prepared in 50−70% yield from pyrrole and the corresponding aldehydes.

Cyclohexadieno- (**3** and **4**), cyclohexeno- (**5** and **6**), and tetrahydronaphthaleno-fused (**7**) dipyrromethane esters were synthesized in 70−90% yield from the respective pyrroles[69,71,80,81] and aldehydes (or dimethoxymethane) following the previously developed procedures (Scheme 2).[73,75,82] In the case of sterically more hindered structures **5** and 7, longer times (up to 72 h) were required to complete the condensations.

Scheme 1. Synthetic Approach to *syn*-DBPs and *syn*-DNPs via Oxidative Aromatization

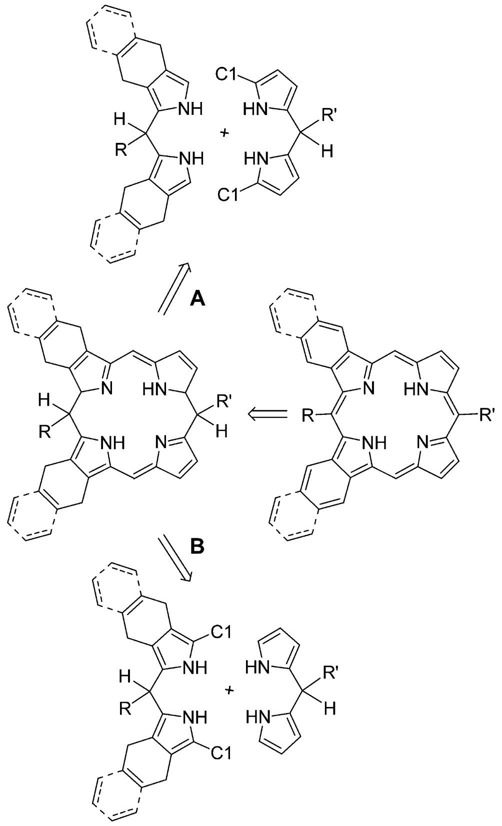
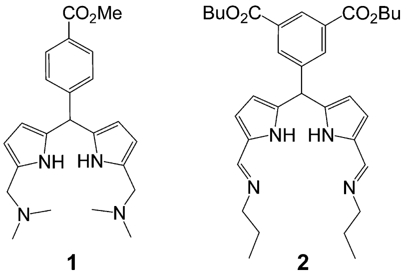


Chart 2. Dipyrromethanes with C1 Synthons at the 1- and 9-Positions



Generally, using acetic acid as the solvent, as opposed to dichloromethane, was found to speed up the reactions by factors of ∼2. The cyclohexadieno- (3 and 4) and tetrahydronaphthaleno-fused (7) dipyrromethane esters were unstable at room temperature and degraded rapidly during purification. These compounds were introduced into subsequent transformations without isolation. (Only compounds that were isolated and fully characterized are identified in the text by bold numbers). Dipyrromethane esters 3, 4, and 5 were de-esterified and decarboxylated in a one-pot reaction upon treatment with TFA, while benzyl esters **6** and 7 were first converted to carboxylic acids by reduction on Pearlman's catalyst ($(Pd(OH)_2/C)$)[83] and then introduced into the TFA-mediated decarboxylation without isolation. De-esterification/decarboxylation was carried out immediately prior to the porphyrin synthesis, since α,α'-unsubstituted dipyrromethanes are even more unstable than their ester precursors and degrade rapidly in air, presumably as a result of oxidation and/or oligomerization. Dipyrromethane 12 was the least stable in the series, and it had to be handled especially promptly. On the basis of analyses of the crude reaction mixtures, the yields of the dipyrromethanes (starting with esters 3−7) ranged from 30 to 65%.

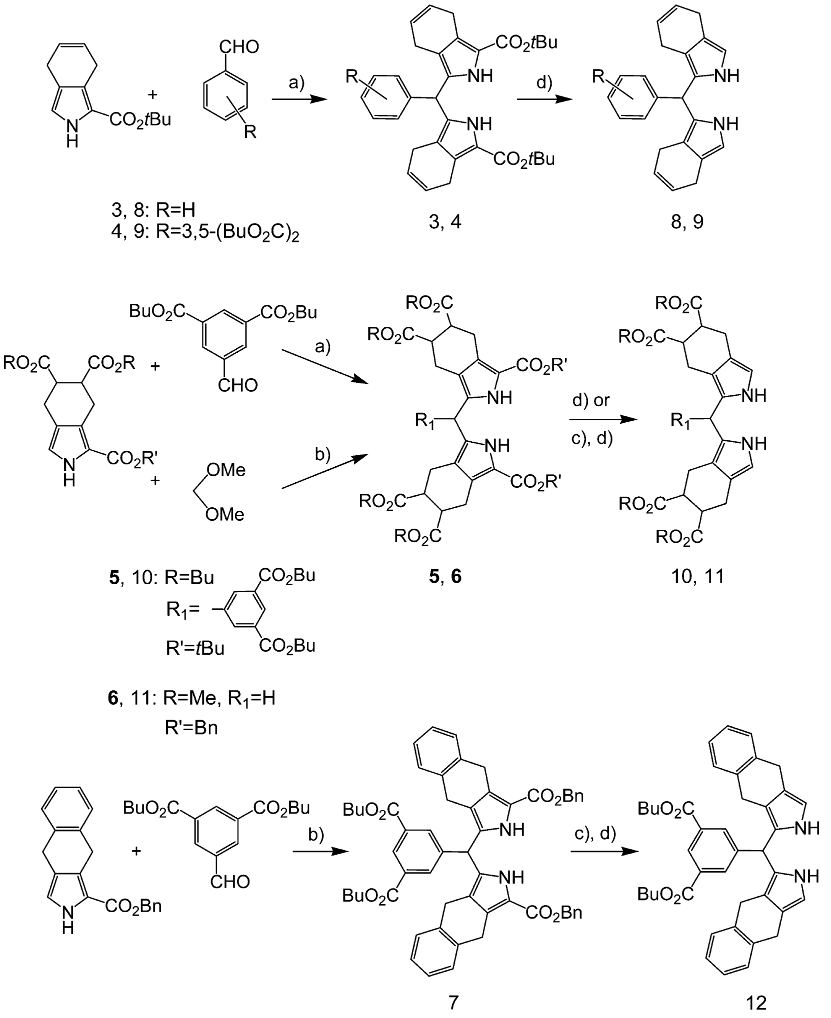
The [2 + 2] assembly leading to the target porphyrins is shown in Scheme 3. According to the original procedures, condensation of 1,9-bis(*N*,*N*-dimethylaminomethyl)- or 1,9-bis(*N*-propyliminomethyl)dipyrromethanes (Chart 2) with 1,9-unsubstituted dipyrromethanes is carried out optimally in refluxing methanol in the presence of a 10-fold molar excess of $Zn(OAc)_2$.[76−79] In cases when the reactants bear functional groups sensitive to solvolysis, methanol may be substituted by toluene, also under reflux, in which case 1,9-bis(*N*-propyliminomethyl)dipyrromethanes are the substrates of choice.[77]

Following the original method,[76] reaction of dipyrromethane 8 with **1** in MeOH in the presence of $Zn(OAc)_2$ gave the Zn complex of porphyrin 13 (Zn−13) in 13% yield. However, applying the same conditions directly to the rest of our substrates proved inefficient. For example, condensation of dipyrromethanes 10 and **2** in MeOH gave Zn−**15** in a rather low 8% yield, and when the reaction was attempted in toluene, the yield dropped below 5%. Other dipyrromethanes showed similar results. On the basis of UV−vis spectra, we concluded that at least in part the low yields were caused by competing oxidation of dipyrromethanes into dipyrromethenes (dipyrrins), whose formation could be easily detected by characteristic optical absorption.[84] Dipyrrins are inert in the condensation.

In order to prevent premature oxidation of dipyrromethanes and establish overall milder conditions for the synthesis, the reaction was attempted as a two-step process using dipyrromethane **2** as a reactant. In the first step, dipyrromethanes 9−12 were condensed with **2** under an inert atmosphere (Ar) in the presence of $Zn(OAc)_2$ in refluxing benzene. The latter has a lower boiling point than toluene, helping to avoid side reactions and decomposition of the sensitive dypyrromethanes. The formation of the corresponding dehydroporphyrinogens and depletion of the starting materials was monitored by MALDI-TOF analysis. Once the concentration of the dehydroporphyrinogens stopped changing, usually after 2−3 h, the mixtures were flushed with air and left to react for an additional 8−16 h (second step). At this stage, the reaction progress was monitored by UV−vis spectroscopy, and the refluxing was continued until the ratio of the intensity in the Soret band region (∼350−400 nm) to the absorption by the side products (dipyrrins) near 500−600 nm was at its maximum. It should be noted that not all of the dipyrromethanes were converted into dehydroporphyrinogens in the first step, but the mixtures were simply allowed to reach their respective steady states. Subsequent oxidation by air apparently was mild enough to prevent fast oxidation of dipyrromethanes but effective in converting dehydroporphyrinogens into porphyrins. The dipyrromethanes in the meantime continued to undergo condensation to generate new dehydroporphyrinogens for oxidation. These conditions allowed us to obtain cyclohexadieno- (14) and cyclohexenoporphyrins (**15** and **16**) in 20−30% yield and the least stable porphyrin 17 in 13% yield. In all cases, the porphyrins were isolated as Zn complexes.

Aromatization of precursors 13−17 into the target dibenzo- (**18**−**21**) and dinaphthoporphyrins (**22**) requires the removal of either two (13, 14, 17) or four (**15**, **16**) hydrogens from each

Scheme 2. Synthesis of β-Substituted Dipyrromethanes[a]



[a]Reagents and conditions: (a) p-TsOH, NBu_4Cl, CH_2Cl_2, r.t., 24 h (**3**), 48 h (**4**), 72 h (**5**). (b) p-TsOH, AcOH, 24 h (**6**), 48 h (**7**). (c) H_2/$Pd(OH)_2$/C,[83] THF, r.t., 24−48 h. (d) (i) TFA/CH_2Cl_2 1:1, 20 °C, 1 h; (ii) $NaHCO_3$.

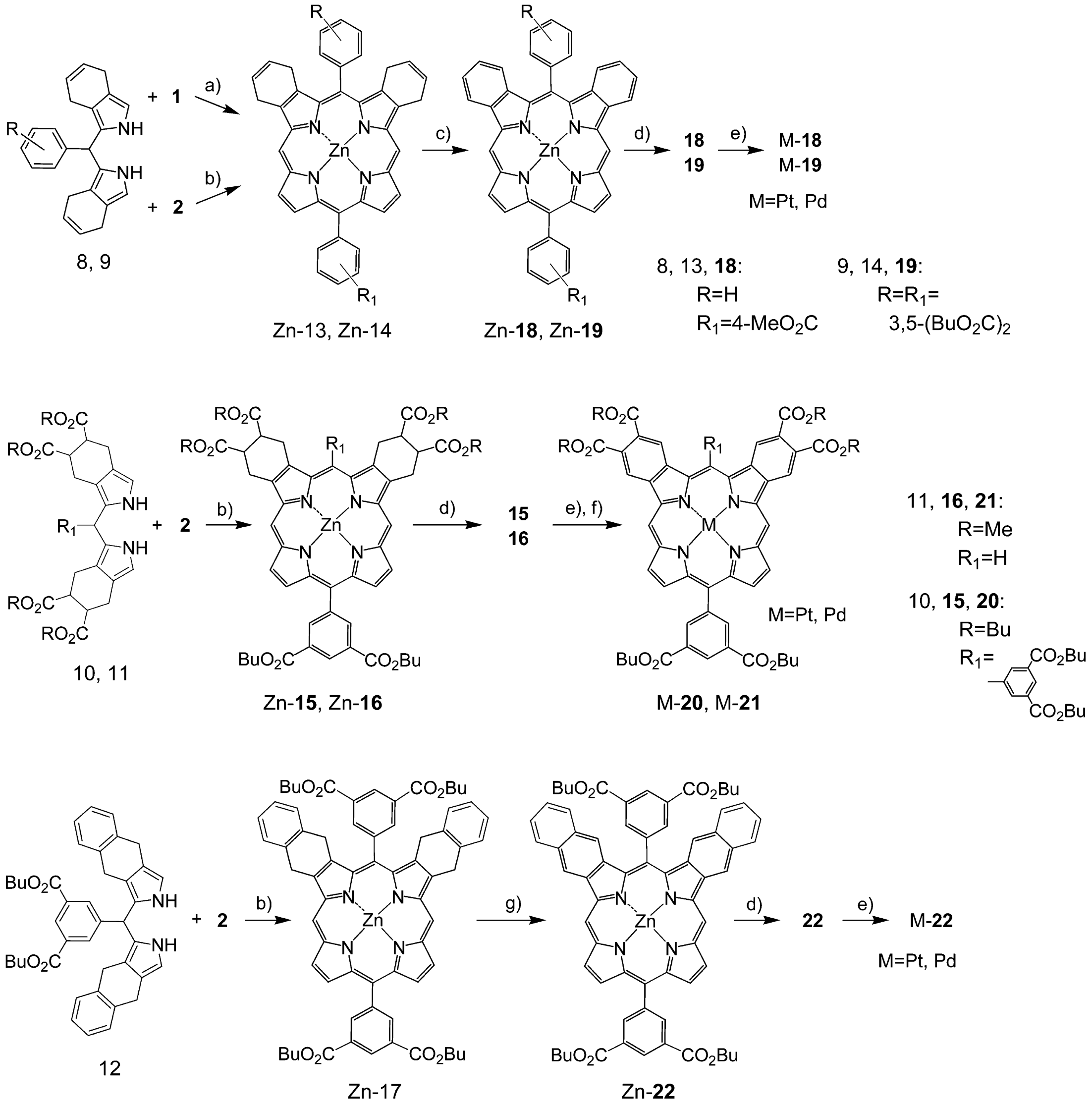
exocyclic ring annealed with the macrocycle, whereas dehydrogenation of less-saturated rings generally occurs much more easily.[2,75] The most common oxidant for aromatizations is DDQ. Aromatizations may be inhibited by the formation of porphyrin dications if the basicities of the corresponding free bases are high.[69] The latter is typical of highly nonplanar porphyrins, which must be converted into stable metal complexes (e.g., with Pd, Pt, or Cu) prior to oxidation.[69] Planar *meso*-unsubstituted[71] and 5,15-diarylporphyrins[72,73] may be oxidized directly as free bases, although metalation usually facilitates the reaction.

Porphyrin 17 was the easiest to aromatize in our series. The transformation of Zn−17 into Zn−**22** could be observed immediately upon addition of DDQ, even at room temperature, by the change of the color of the mixture from red to deep green. Similarly, aromatization of porphyrins Zn−13 and Zn−14 occurred when they were treated with DDQ in THF for just 30−40 min, although heating was required. The Zn complexes of **18**, **19**, and **22** were isolated in almost quantitative yields. The corresponding free-base porphyrins were obtained by facile demetalation with HCl.

The aromatization of tetraalkoxycarbonylporphyrins **15** and **16**, however, proved to be much more difficult. For example, treatment of **15** as either the free base or the Zn complex (Zn−**15**) with excess DDQ in refluxing THF for 14 h did not show any sign of conversion, while the oxidation in refluxing toluene produced mixtures of aggregated inseparable products. Our final targets in this study were phosphorescent Pt and Pd complexes, and therefore, we turned our attention to the methods developed earlier for the synthesis of similar Pt and Pd tetraaryltetrabenzo- and tetranaphthoporphyrins.[69,70] Prior to oxidation, Zn−**15** and Zn−**16** were demetalated and then converted into Pt and Pd complexes (see below). The latter were smoothly oxidized using excess DDQ in toluene over 10 h, yielding the desired complexes M−**20** and M−**21** (M = Pt, Pd) in ~79−92% yield.

Insertion of Pt(II) into the precursor porphyrins **15** and **16** and the target porphyrins **18**, **19**, and **22** was performed either in benzoic acid melt[85] or using the microwave-assisted method.[86] In the former approach, the free-base porphyrins were heated with a 3−4-fold molar excess of $Pt(acac)_2$ in benzoic acid at 130−135 °C for 2−6 h. Subsequent methanol workup, chromatographic purification, and reprecipitation from CH_2Cl_2/MeOH (1:50) afforded the Pt(II)−porphyrin complexes in 20−56% yield. In spite of the moderate yields, the benzoic acid method[85] in our hands has proved to be general

Scheme 3. Synthesis of Target Porphyrins[a]



[a]Reagents and conditions: (a) (i) $Zn(OAc)_2{\cdot}2H_2O$ (10 equiv), MeOH, reflux, 2 h; (ii) DDQ (3 equiv), r.t., 2 h. (b) (i) $Zn(OAc)_2{\cdot}2H_2O$ (10 equiv), C_6H_6, Ar, reflux, 2 h; (ii) air, reflux, 12−18 h. (c) DDQ (3 equiv), THF, reflux, 30−40 min. (d) HCl conc./CH_2Cl_2. (e) Pt insertion: (method 1) $Pt(acac)_2$/benzoic acid, 130−135 °C, 2−6 h; (method 2) $Pt(acac)_2$/PhCN, microwave, 250 °C (~200 kPa, 105−145 W), 40 min. Pd insertion: $Pd(Ac)_2$/PhCN, microwave, 250 °C (~200 kPa, 105−145 W), 40 min. (f) DDQ (5 equiv), toluene, reflux, 10 h. (g) DDQ (3 equiv), THF, r.t., 10 min.

and frequently leads to success when other methods, such as commonly used refluxing in benzonitrile, fail. However, in this particular instance, the best results were achieved using the microwave-assisted insertion, developed by Bruckner and co-workers.[86] Microwave treatment of mixtures of the free-base porphyrins and $Pt(acac)_2$ (3−4 equiv) in benzonitrile for 40 min gave the corresponding Pt complexes in 92% to quantitative yield. Similarly, the Pd complexes were obtained in nearly quantitative yield.

Overall, the developed reaction sequences allowed us to prepare the target Pt and Pd porphyrins in yields of 5−15% relative to the starting pyrrole esters (Scheme 2). The methods do not require expensive reagents and can be scaled to gram quantities.

Photophysical Properties. This section provides a brief overview of the photophysical properties of the newly synthesized porphyrins, while leaving the detailed analysis for a separate account. Because of the presence of *meso*-aryl substituents and alkoxycarbonyl groups, all of the porphyrins were found to be well-soluble in a range of organic solvents (e.g., toluene, CH_2Cl_2, THF, DMF, and DMA), where they showed no signs of aggregation at the concentrations required for optical measurements and above (up to 10^{-5} M). The measurements were performed in dimethylacetamide (DMA). This solvent is especially convenient because of its high boiling point (165 °C), making it possible to deoxygenate solutions by inert gas bubbling (Ar or N_2) at room temperature without experiencing significant losses in the solution volume.

The optical absorption features of the Pt and Pd complexes of the synthesized porphyrins are very similar to each other, with the bands of the Pd porphyrins being red-shifted by 5−15 nm relative to the Pt complexes. The triplet lifetimes of the Pd complexes Pd−**19** through Pd−**22** are 8−10 times longer than those of the respective Pt porphyrins, while their phosphorescence quantum yields are about 2 times lower (Table 1). These trends are common for Pt and Pd porphyrins,[87] and below we discuss only Pt complexes Pt−**18** through Pt−**22**, while the properties of the Pd complexes can be inferred by analogy.

Table 1. Selected Photophysical Parameters for Pt and Pd Complexes of the Synthesized Porphyrins in DMA

	absorption λ_{max} (nm)		phosphorescence	
complex	B band	Q band	λ_{max} (nm)	Φ_{ph}, τ (μs)[a]
Pt−**18**	401	556	685	0.31, 90
Pt−**19**	402	559	686	0.34, 92
Pt−**20**	412	568	680	0.37, 80
Pt−**21**	405	562	675	0.37, 83
Pt−**22**	423	593	753	0.11, 49
Pd−**19**	417	570	706	0.15, 850
Pd−**20**	427	581	702	0.16, 730
Pd−**21**	421	574	696	0.16, 730
Pd−**22**	435	605	774	0.04, 410

[a] The phosphorescence quantum yields (Φ) and lifetimes (τ) were measured at 22 °C in deoxygenated solutions. The fluorescence of rhodamine 6G in EtOH (Φ_{fl} = 0.95) was used as a standard.[88] For comparison, under these conditions the fluorescence quantum yield of tetraphenylporphyrin (H_2TPP) in deoxygenated C_6H_6 is 0.055, and the phosphorescence quantum yield of Pt *meso*-tetraphenyltetrabenzoporphyrin (Ph_4TBP) in deoxygenated DMF is 0.085.

The linear absorption and phosphorescence emission spectra of porphyrins Pt−**18** through Pt−**22** are shown in Figure 1, and the relevant data are compiled in Table 1. Similar graphs for the Pd complexes are shown in Figure S2 in the Supporting Information. It should be noted that the absorption features of ZnDBPs Zn−**18** and Zn−**19** (Figure S3 in the Supporting Information) correspond well with the literature data on similar Zn complexes.[48]

The absorption spectra of all of the synthesized Pt porphyrins exhibit well-defined, narrow bands, resembling in that way the spectra of the fully symmetrical Pt tetrabenzoporphyrins (PtTBPs) (D_{4h} symmetry).[25,32,35,71] The Soret (or B) (S_2), Q (S_1), and phosphorescence (T_1) bands of porphyrins Pt−**18** through Pt−**21** occupy somewhat intermediate positions between the bands of regular nonextended Pt porphyrins (PtPs)[87,89,90] and those of PtTBPs.[25,32,35,71] The Q band of Pt−**22** (λ_{max} = 593 nm) is bathochromically shifted, approaching the Q bands of PtTBPs (~605−615 nm),[32,71] while its B band is also red-shifted, but broadened similar to the B bands of tetranaphthoporphyrins.[71] These observations can be rationalized, at least to a first approximation, by recalling that Q and B bands in regular symmetrical porphyrins are composed of orthogonally polarized transitions (Q_x and Q_y, B_x and B_y) that are formed by configuration interaction involving single-electron excitations between pairs of nearly degenerate HOMOs and LUMOs.[66] π-Extension lifts the degeneracy of one of the HOMOs (a_{2u}), leading to a spectral red shift as well to an increase in the oscillator strength of the Q band.[6,91] Just as in fully symmetrical PtTBPs, the orthogonal transition dipoles in Pt *syn*-DBPs and Pt *syn*-DNPs are identical to each other. Consequently, the *x* and *y* bands are fully superimposed, giving rise to narrow spectral lines, similar to those of PtTBPs. In contrast, in *anti*-DBPs, the *x* and *y* dipoles are not equivalent, resulting in multiple spectral lines in both the Q- and B-band regions.[48]

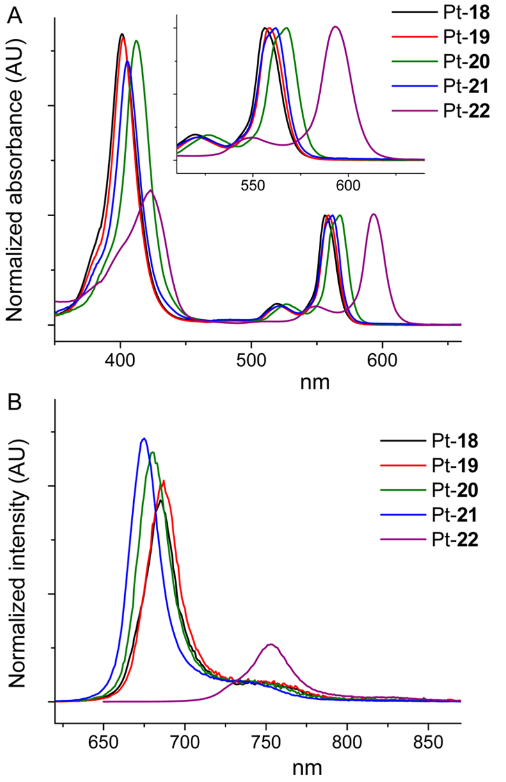


Figure 1. (A) Absorption and (B) phosphorescence spectra of porphyrins Pt−**18** through Pt−**22** in DMA. The absorption spectra were normalized by the corresponding Q-band maxima; the inset shows the zoomed Q-band region. The phosphorescence spectra were normalized by the respective phosphorescence quantum yields (Table 1).

The transitions in Pt−**18** through Pt−**21** are polarized in the directions in which the *syn*-DBP molecules have diameters larger than those of regular Pt porphyrins but smaller than those of PtTBPs. In *syn*-DNP Pt−**22**, on the other hand, the macrocycle diameter along the polarization axes is similar to that of PtTBPs. The energies of the spectral bands generally follow this simple relationship: the "longer" the dipole, the lower the energy of the absorption band. Of course, for accurate quantitative interpretation of the spectroscopic data, a detailed computational/photophysical study such as that performed recently for Zn benzoporphyrins[48] will be required.

In the series of synthesized *syn*-DBPs, porphyrins Pt−**20** and Pt−**21** exhibit the most bathochromically shifted Q and B bands, while their phosphorescence maxima are the most hypsochromically shifted. With the assumption that the phosphorescent triplet states (T_1) in all of these porphyrins are derived from the same electronic configurations as the S_1 (or S_2) states, the data for Pt−**20** and Pt−**21** appear to be consistent with the expansion of the π-conjugation onto the carbonyl groups in the benzo rings in the macrocycles. This expansion further destabilizes one of the HOMOs, causing a red shift in the absorption, but at the same time decreases the exchange energy (2*J*) because of the increase in the size of the π-system,[92] narrowing the S_1−T_1 gap and raising the energy of the T_1 state. Between these two porphyrins, Pt−**20** exhibits more bathochromically shifted bands than Pt−**21**, which is consistent with the presence of only one *meso*-aryl substituent in the latter. The *meso*-aryl groups in 5,15-diarylporphyrins (see the X-ray structure in Figure 2 and the computed structures in

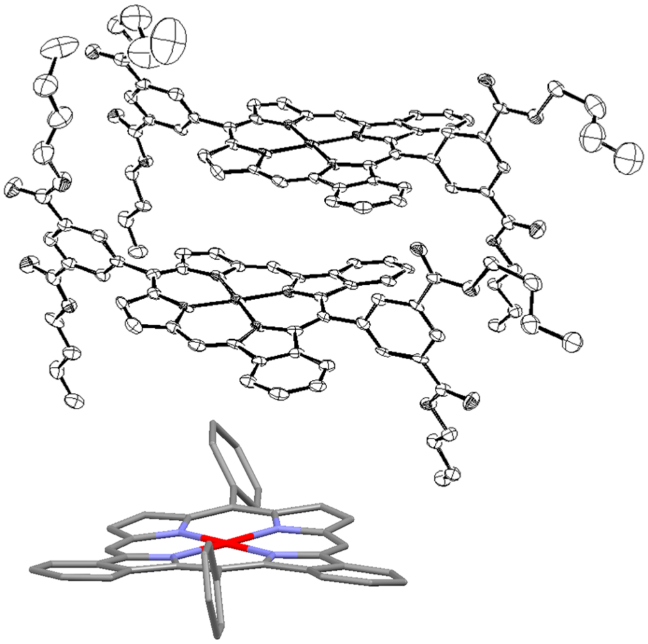


Figure 2. (top) ORTEP view of the X-ray crystallographic structure of porphyrin Pt−**19** (50% thermal ellipsoids) with two stacked nonidentical porphyrin molecules in the cell. All of the hydrogen atoms have been omitted for clarity. (bottom) View of the plain porphyrin skeleton of Pt−**19**, showing the small nonplanar distortion of the macrocycle and tilts of the two *meso*-aryl substituents. The aryl group between the two benzo rings is rotated by 83° relative to the porphyrin mean-square plane.

Figure S1 in the Supporting Information) are almost perpendicular to the porphyrin plane,[34] and yet they participate in the conjugation with the macrocycle, thereby inducing small red shifts in the absorption spectra.[93]

The phosphorescence quantum yields of Pt *syn*-DBPs ($\Phi_{ph} \approx 0.35$) were found to be among the highest reported to date for phosphorescent tetrapyrroles. The quantum yields were measured against the fluorescence of rhodamine 6G in EtOH ($\Phi_{fl} = 0.95$),[88] and the emission spectra were corrected for the wavelength dependences of the detector, excitation source, and monochromators. It should be noted that under the same conditions the phosphorescence quantum yield of Pt *meso*-tetraphenyltetrabenzoporphyrin (Ph_4TBP) in deoxygenated DMF was determined to be 0.085, which is substantially lower than reported previously.[7,35] The high emission yields of Pt *syn*-DBPs are in line with their relatively planar structures (Figure 2 and Figure S1 in the Supporting Information), in accordance with the previously observed correlation between nonplanarity of *π*-extended porphyrins and enhanced nonradiative triplet decay.[34] On average only ~60% of the triplet state in Pt−**18** through Pt−**21** decays via the nonradiative channel (Table S1 in the Supporting Information), while in, e.g., highly nonplanar $PtPh_4TBPs$ this fraction is larger than 90%. In DNP Pt−**22**, the proportion of the $T_1 \rightarrow S_0$ intersystem crossing is also increased to ~90% because of the narrower T_1−S_0 gap.

In order to estimate the performance of porphyrins Pt−**18** through Pt−**22** under 2P excitation, we compared their phosphorescence outputs to that of a regular symmetrical Pt porphyrin, i.e., Pt tetracyclohexenoporphyrin (PtTCHP),[71] which possesses D_{4h} symmetry (Figure S4 in the Supporting Information). The phosphorescence quantum yield of PtTCHP in deoxygenated DMA at 22 °C is 0.42. Our setup allows time-resolved acquisition of phosphorescence upon excitation by trains of femtosecond pulses from a tunable Ti:sapphire laser (see the Supporting Information for details). In Pt porphyrins, because of the ultrafast $S_1 \rightarrow T_1$ intersystem crossing and therefore nearly quantitative formation of the triplet state,[87,90,94] the corrected integrated intensity of the phosphorescence (normalized by the phosphorescence quantum yield and plotted against the excitation wavelength) is directly suitable for comparisons of 2PA cross sections of different porphyrins. To ensure the 2P excitation regime, the signal in all cases was confirmed to exhibit a strictly quadratic power dependence (slope of the log−log plot = 2.00 ± 0.05). The results are summarized in Figure 3 (for the numerical data, see Table S2 in the Supporting Information).

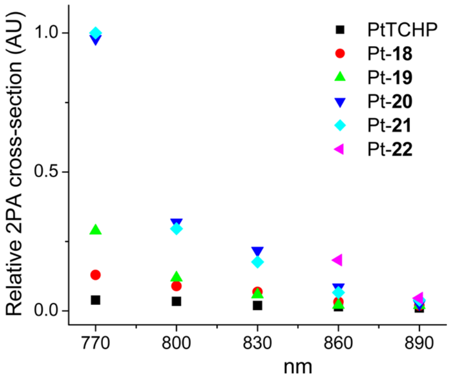


Figure 3. Relative 2PA cross sections (integrated intensities of 2P-excited phosphorescence normalized by the phosphorescence quantum yield) of PtTCHP (D_{4h}) and the synthesized Pt porphyrins. The data are scaled in such a way that the relative 2PA cross section of the most absorbing porphyrin, Pt−**21**, equals 1.0 at 770 nm.

It can be seen that the apparent 2PA cross sections of Pt *syn*-DBPs and *syn*-DNPs are indeed larger than that of the reference PtTCHP. In the case of Pt−**22**, measurements could not be conducted at wavelengths shorter that 860 nm because of the interfering linear excitation into the triplet state ($S_0 \rightarrow T_1$) by the femtosecond pulses. (It should be kept in mind that in Pt porphyrins, because of the very strong spin−orbit coupling, spin-forbidden $S_0 \rightarrow T_1$ transitions may gain significant dipole strength.[95,96]) The most striking enhancement occurs in the case of porphyrins Pt−**20** and Pt−**21** in which the benzo rings contain alkoxycarbonyl groups, as their apparent 2PA cross sections near 770 nm are ~25-fold larger than that of PtTCHP (Table S2 in the Supporting Information). However, it is also clear that in all of the porphyrins the 2PA continues to rise past 800−810 nm, i.e., twice the maximum of the Soret band. Apparently, breaking the center-of-inversion symmetry is not the dominant factor in the enhancement of the 2PA, and the most strongly absorbing 2PA states in these porphyrins are still not the same as their linear 1P states.

These preliminary findings raise the following questions: what are the 2P-absorbing states in *π*-extended Pt porphyrins, and why do alkoxycarbonyl groups cause such a pronounced enhancement of the 2PA? One obvious notion is that the alkoxycarbonyl groups in porphyrins Pt−**20** and Pt−**21** significantly polarize these molecules. For example, on the basis of DFT calculations (B3LYP/6-31G*), the ground-state dipole moment of a Zn porphyrin analogous to Zn−**20** is 6.12 D, whereas for the analogue of Zn−**19** it is only 0.85 D (Figure

S1 in the Supporting Information). Such polarization could in principle lead to an enhancement of 2PA, assuming that in the excited state the dipole moment increases (or changes sign).[97] These and other pertinent photophysical questions should be addressed in a separate study, for which the present work sets the necessary synthetic stage.

■ CONCLUSION

We have developed a synthesis of Pt and Pd complexes of nonfully symmetrical *syn*-DBPs and *syn*-DNPs with solubilizing substituents. These macrocycles possess nearly planar structures and phosphoresce in solutions at ambient temperatures with exceptionally high quantum yields. Preliminary evaluation showed that structural asymmetry causes an increase in the 2PA into 1P-allowed states; however, much stronger 2P-absorbing states are positioned at higher energies. Detailed photophysical studies of the newly synthesized porphyrins are in progress.

■ EXPERIMENTAL SECTION

Descriptions of materials, equipment, and general protocols are provided in the Supporting Information. HRMS data are reported for the highest-intensity peak in the isotope mass distribution and compared to the corresponding peak in the distribution simulated by the mass spectrometer software. The abbreviations used in the ^{1}H NMR peak assignments are shown on p S20 in the Supporting Information.

1,9-Bis(*N*,*N*-dimethylaminomethyl)-5-(4-methoxycarbonylphenyl)dipyrromethane (1). 4-Methoxycarbonylbenzaldehyde (2.40 g, 15 mmol) and pyrrole (100 g, 1.5 mol) were mixed together and purged with Ar for 10 min. $InCl_3$ (0.3315 g, 1.5 mmol) was added, and the reaction mixture was stirred under Ar at room temperature for 1.5 h. NaOH (1.8 g, 43.5 mmol) was added to the mixture, and stirring was continued for additional 45 min. The precipitates were removed by filtration, and pyrrole was removed by distillation in vacuum (~1 mmHg, 18−20 °C); the remaining traces of pyrrole were removed by washing the residue with hexane (3 × 30 mL). The remaining material was dissolved in hot MeOH (100−150 mL). 5-(4-Methoxycarbonylphenyl)dipyrromethane (**1a**) precipitated from solution as pale-yellow crystals upon cooling of the mixture to 0 °C. It was collected by filtration and dried in vacuum. Pale-yellow crystalline powder (mp 153−154 °C). Yield: 0.82 g (62%). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.07 (12H, s, $-NCH_3$), 3.26 (4H, d, $^3J = 2.51$ Hz, $-CHN(CH_3)_2$), 3.81 (3H, s, $-OCH_3$), 5.37 (1H, s, $-CH-$), 5.53 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.54 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.72 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.73 (1H, d, $^3J = 2.8$ Hz, Pyr), 7.23 (2H, d, $^3J = 8.3$ Hz, Ar), 7.85 (2H, d, $^3J = 8.3$ Hz, Ar), 10.51 (2H, s, $-NH$).

To a solution of **1a** (0.9468 g, 2.9 mmol) in CH_2Cl_2 (50 mL), *N*,*N*-dimethylethyleneiminium iodide (Eschenmoser's salt) (1.3871 g, 6.4 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and then diluted with CH_2Cl_2 (350 mL), and K_2CO_3 (10% aq., 350 mL) was added. The organic layer was separated, washed with K_2CO_3 (10% aq., 3 × 350 mL), dried over Na_2SO_4, and concentrated in vacuum. The title compound was precipitated from CH_2Cl_2 upon addition of hexanes, collected by filtration, and dried in vacuum. Pale-yellow crystalline powder (mp 111−113 °C). Yield: 0.8223 g (62%). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.07 (12H, s, $-NCH_3$), 3.26 (4H, d, $^3J = 2.51$ Hz, $-CHN(CH_3)_2$), 3.81 (3H, s, $-OCH_3$), 5.37 (1H, s, $-CH-$), 5.53 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.54 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.72 (1H, d, $^3J = 2.8$ Hz, Pyr), 5.73 (1H, d, $^3J = 2.8$ Hz, Pyr), 7.23 (2H, d, $^3J = 8.3$ Hz, Ar), 7.85 (2H, d, $^3J = 8.3$ Hz, Ar), 10.51 (2H, s, $-NH$). ^{13}C NMR ($CDCl_3$) δ (ppm): 44.2, 44.9, 52.0, 56.6, 107.1, 107.5, 107.6, 128.4, 128.6, 128.9, 129.0, 129.8, 131.70, 131.74, 147.65, 147.67, 167.0. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{31}N_4O_2$ 395.24413, found 395.24368.

1,9-Bis(*N*-Propyliminomethyl)-5-(3,5-dibutoxycarbonylphenyl)dipyrromethane (2). 3,5-Dibutoxycarbonylbenzaldehyde (3.06 g, 10 mmol) and pyrrole (66 g, 1.0 mol) were mixed together and purged with Ar for 10 min. $InCl_3$ (0.221 g, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature under Ar for 1.5 h. NaOH (1.2 g, 30 mmol) was added to the mixture, and the stirring was continued for 45 min. The precipitates were removed by filtration, and pyrrole was removed by distillation in vacuum (~1 mmHg, 18−20 °C). The residue was purified by chromatography on a short silica gel column (10 cm, CH_2Cl_2) to give crude 5-(3,5-dibutoxycarbonylphenyl)-dipyrromethane (**2a**) (3.6 g).

To a solution of **2a** (3.6 g, 8.5 mmol) in dry DMF (10 mL) was added $POCl_3$ (2.74 g, 17.9 mmol) dropwise at 0 °C under Ar. The reaction mixture was stirred for 1 h at room temperature, poured into a saturated aqueous solution of sodium acetate (250 mL), extracted with CH_2Cl_2 (3 × 100 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 4:1) to give crude 1,9-diformyl-5-(3,5-dibutoxycarbonylphenyl)dipyrromethane (**2b**) (3.3 g).

n-Propylamine (15 mL, 183 mmol) was added to **2b** (3.3 g, 6.9 mmol), and the mixture was stirred for 1 h at room temperature. Excess *n*-propylamine was removed in vacuum to give the title compound **2** as a dark-orange solid (mp 112−114 °C). Yield: 3.86 g (69% over 3 steps). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (6H, t, $^3J = 7.4$ Hz, $-CH_3$), 0.95 (6H, t, $^3J = 7.4$ Hz, $-CH_3$), 1.38−1.49 (4H, m, $-CH_2-$), 1.60−1.78 (8H, m, $-CH_2-$), 3.41 (4H, dd, $^3J_1 = 6.8$, $^3J_2 = 6.9$ Hz, $-NCH_2-$), 4.30 (4H, t, $^3J = 6.7$ Hz, $-OCH_2-$), 5.59 (1H, s, broad, $-CH-$), 5.96 (2H, d, $^3J = 3.6$ Hz, Pyr), 6.50 (2H, d, $^3J = 3.6$ Hz, Pyr), 7.72 (2H, s, $-NH-$), 8.08 (2H, d, $^4J = 1.4$ Hz, Ar), 8.55 (1H, t, $^4J = 1.4$ Hz, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.7, 13.7, 19.2, 24.2, 30.6, 44.1, 62.3, 65.2, 109.6, 114.8, 114.9, 129.4, 130.4, 131.2, 133.6, 135.6, 135.7, 142.2, 151.4, 165.7. MALDI-TOF (*m*/*z*): calcd for $C_{33}H_{44}N_4O_4$ 560.34, found 561.24 $[M + H]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{45}N_4O_4$ 561.34349, found 561.34371.

***α*,*α*′-Bis(*tert*-butoxycarbonyl)-*meso*-(3,5-dibutoxycarbonylphenyl)methylenebis(1,1′-(5,6-dibutoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole)) (5).** *p*-Toluenesulfonic acid (0.090 g, 0.48 mmol) and *tert*-butylammonium chloride (0.135 g, 0.48 mmol) were added to a solution of 1-*tert*-butoxycarbonyl-5,6-dibutoxycarbonyl-4,5,6,7-dihydro-2*H*-isoindole[71] (2 g, 4.75 mmol) and 3,5-dibutoxycarbonylbenzaldehyde[70] (0.727 g, 2.4 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature under Ar for 72 h. Small amounts of *p*-toluenesulfonic acid (0.045 g, 0.24 mmol) and *tert*-butylammonium chloride (0.07 g, 0.25 mmol) were added to the reaction mixture after 24 h and then again after 48 h. The reaction progress was monitored by TLC until the spot corresponding to aldehyde disappeared. The mixture was diluted with CH_2Cl_2 (100 mL), washed with $NaHCO_3$ (10% aq., 50 mL) and brine (50 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was purified by column chromatography (silica gel, CH_2Cl_2/THF = 50:1) to give the title compound **5** as an orange oil. Yield 2.23 g (83%). ^{1}H NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 0.83−0.91 (12H, m, $-CH_3$), 0.95 (6H, t, $^3J = 7.3$ Hz, $-CH_3$), 1.22−1.50 (16H, m, $-CH_2-$), 1.50−1.53 (18H, m, *t*Bu), 1.48−1.60 (4H, m, $-CH_2-$), 1.68−1.78 (4H, m, $-CH_2-$), 2.24−2.47 (2H, m, $-CHH-$), 2.55−2.80 (2H, m, $-CHH-$), 2.99−3.27 (8H, m, $-CHH-$, $-CH-$), 3.92−4.10 (8H, m, $-OCH_2-$), 4.30 (4H, t, $^3J = 6.6$ Hz, $-OCH_2-$), 5.50−5.54 (1H, m, broad, $-CH-$), 7.88−7.95 (2H, m, Ar), 8.39−8.44 (1H, m, Ar), 8.52−8.50 (2H, m, $-NH-$). ^{13}C NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 13.62, 13.64, 13.71, 19.01, 19.04, 19.1, 19.2, 22.2, 22.3, 22.4, 22.5, 23.5, 23.6, 23.7, 23.8, 28.39, 28.42, 30.3, 30.47, 30.52, 30.54, 30.6, 40.56, 40.58, 40.7, 40.8, 40.90, 40.94, 40.96, 41.00, 41.1, 64.45, 64.49, 64.55, 64.60, 64.63, 65.3, 80.63, 80.65, 80.69, 116.9, 117.17, 117.23, 117.3, 118.76, 118.84, 118.9, 119.0, 125.3, 125.4, 125.5, 128.1, 128.3, 128.4, 128.5, 129.77, 129.8, 129.9, 131.85, 131.90, 133.2, 133.3, 139.5, 139.7, 139.8, 160.68, 160.70, 160.9, 165.25, 165.33, 172.6, 172.7, 172.76, 172.79, 173.01, 173.02. MALDI-TOF (*m*/*z*): calcd for $C_{63}H_{90}N_2O_{16}$ 1130.63, found 1153.42 $[M + Na]^+$, 1169.39 $[M + K]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{63}H_{91}N_2O_{16}$ 1131.63623, found 1131.63613.

***α*,*α*′-Bis(benzyloxycarbonyl)methylenebis(1,1′-(5,6-dimethoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole)) (6).** *p*-Toluenesulfonic acid (0.033 g, 0.175 mmol) was added to a solution of 1-

benzyloxycarbonyl-5,6-dimethoxycarbonyl-4,5,6,7-dihydro-2*H*-isoindole[71] (1.3 g, 3.5 mmol) and dimethoxymethane (0.133 g, 1.75 mmol) in acetic acid (25 mL), and the reaction mixture was stirred at room temperature under Ar for 24 h. The mixture was poured into cold water (80 mL), and the formed precipitate was collected by filtration and dried in vacuum. The resulting solid was dissolved in MeOH (20 mL) and precipitated upon addition of water (10−15 mL) at 0 °C. The precipitate was collected by centrifugation, washed with water (3 × 20 mL), and dried in vacuum to give the title compound as a white solid (mp 104−106 °C). Yield 1.23 g (93%). ^{1}H NMR (CDCl$_3$) δ (ppm) (mixture of conformers): 2.65−2.78 (2H, m, −CH*H*−), 2.90−3.03 (2H, m, −CH*H*−), 3.04−3.24 (6H, m, −CH*H*−, −C*H*−), 3.26−3.38 (2H, m, −C*H*−), 3.62−3.69 (12H, m, −OC*H*$_3$), 3.69−3.81 (2H, m, −C*H*$_2$−), 5.17−5.33 (4H, m, −C*H*$_2$Ph), 7.25−7.34 (10H, m, Ar), 9.30−9.48 (2H, m, −N*H*−). ^{13}C NMR (CDCl$_3$) δ (ppm) (mixture of conformers): 21.80, 21.87, 21.92, 21.98, 22.4, 22.5, 22.6, 23.7, 23.76, 23.83, 23.9, 24.0, 40.7, 40.8, 51.4, 51.95, 52.00, 65.7, 65.8, 116.42, 116.48, 116.54, 116.58, 126.2, 126.5, 126.6, 127.66, 127.68, 127.71, 127.90, 127.92, 128.0, 128.4, 128.5, 129.15, 129.24, 136.2, 161.4, 162.3, 173.33, 173.35, 173.36, 173.39, 173.45, 173.49, 173.52, 173.55. MALDI-TOF (*m*/*z*): calcd for $C_{41}H_{42}N_2O_{12}$ 754.27, found 752.96 [M − H]$^+$, 776.95 [M + Na]$^+$, 792.92 [M + K]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{41}H_{43}N_2O_{12}$ 755.28099, found 755.27822.

***meso*-(3,5-Dibutoxycarbonylphenyl)methylenebis(1,1′-(5,6-dibutoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole)) (10).** Dipyrromethane ester **5** (1.98 g, 1.75 mmol) was dissolved in CH$_2$Cl$_2$ (15 mL), and the solution was cooled to 0 °C on an ice bath. TFA (15 mL) was added dropwise to the solution under Ar. The ice bath was removed, and the reaction mixture was stirred at room temperature for 1.5 h. The mixture was diluted with CH$_2$Cl$_2$ (100 mL), washed with NaHCO$_3$ (10% aq., 50 mL) and brine (50 mL), and dried over Na$_2$SO$_4$. The solvent was removed in vacuum, and the residue was purified by column chromatography (silica gel, CH$_2$Cl$_2$/THF, gradient from 15:1 to 2:1) to give crude dipyrromethane 10 as a dark-brown oil (0.92 g). The thus-obtained crude dipyrromethane 10 was used immediately in the porphyrin synthesis (see below).

Methylenebis(1,1′-(5,6-dibutoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole)) (11). Dipyrromethane ester **6** (1.23 g, 1.63 mmol) was dissolved in THF (50 mL), and the solution was purged with Ar for 10 min. Pearlman's catalyst[83] (0.2 g) was added, and the reaction mixture was purged with Ar again for 10 min and then with H$_2$ for 15−20 min. The mixture was kept under vigorous stirring overnight under H$_2$ (1 atm). The mixture was purged with Ar and then passed through Celite to remove the catalyst. The resulting solution was concentrated in vacuum to give crude α,α'-bis(carboxy)-methylenebis(1,1′-(5,6-dibutoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole)) (**6a**) (0.936 g) as a slightly pink viscous oil. MALDI-TOF (*m*/*z*): calcd for $C_{27}H_{30}N_2O_{12}$ 574.18, found 596.90 [M + Na]$^+$, 612.88 [M + K]$^+$.

Crude **6a** (0.936 g, 1.63 mmol) was dissolved in THF (5 mL)/CH$_2$Cl$_2$ (20 mL), and the solution was cooled to 0 °C on an ice bath. TFA (10 mL) was added dropwise to the solution under Ar. The ice bath was removed, and the reaction mixture was stirred at room temperature for 1 h. The mixture was diluted with CH$_2$Cl$_2$ (100 mL), washed with NaHCO$_3$ (10% aq., 2 × 50 mL) and brine (50 mL), and dried over Na$_2$SO$_4$. The solvent was removed in vacuum, and the residue was purified on a short column (silica gel, 10 cm, CH$_2$Cl$_2$/THF, 25:1) to give crude dipyrromethane 11 (0.42 g) as a dark-brown oil. MALDI-TOF (*m*/*z*): calcd for $C_{25}H_{30}N_2O_8$ 486.20, found 487.01 [M + H]$^+$. The thus-obtained 11 was used immediately in the subsequent porphyrin synthesis.

Dipyrromethanes 3, 4, 7, 8, 9, and 12. Dipyrromethane 3[73] was prepared from 2-*tert*-butoxycarbonyl-4,7-dihydro-2*H*-isoindole (1.18 g, 5.4 mol) and benzaldehyde (0.285 g, 2.7 mmol) following the procedure described above for dipyrromethane **5**. Decarboxylation of 3 gave of crude dipyrromethane 8 (0.47 g).

Dipyrromethane 4 was prepared from 1-*tert*-butoxycarbonyl-4,7-dihydro-2*H*-isoindole (0.8672 g, 4 mmol) and 3,5-dibutoxycarbonylbenzaldehyde (0.606 g, 2 mmol) following the procedure described above for dipyrromethane **5**. Decarboxylation of 4 gave crude dipyrromethane 9 (0.46 g).

Dipyrromethane 7 was prepared from 1-benzyloxycarbonyl-4,9-dihydro-2*H*-benzo[*f*]isoindole (1.175 d, 3.88 mmol) and 3,5-dibutoxycarbonylbenzaldehyde (0.593 g, 1.94 mmol) following the procedure described above for dipyrromethane **6**. Hydrogenolysis followed by decarboxylation gave crude dipyrromethane 12 (0.35 g). MALDI-TOF (*m*/*z*): calcd for $C_{41}H_{42}N_2O_4$ 626.31, found 627.13 [M + H]$^+$.

To avoid degradation, dipyrromethanes 3, 4, 7, 8, 9, and 12 were immediately introduced into their respective subsequent syntheses without purification.

5-Phenyl-15-(*p*-methoxycarbonylphenyl)-*syn*-dibenzoporphyrin (18). 1 (0.5664 g, 1.44 mmol) and 8[73] (0.47 g, 1.44 mmol) were dissolved in methanol (145 mL), and the reaction mixture was purged with Ar. An excess of Zn(OAc)$_2$·2H$_2$O (3.1409 g, 14.4 mmol) was added, and the reaction mixture was refluxed for 2 h, during which time the solution color turned deep red. After 2 h, the reaction mixture was cooled to room temperature, and DDQ (0.9820 g, 4.3 mmol) was added. The mixture was allowed to react overnight. The methanol was evaporated under reduced pressure, and the product was purified by column chromatograpy (silica gel, CH$_2$Cl$_2$). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy) was collected and evaporated to dryness to give crude Zn−13.

Zn−13 (0.14 g, 0.2 mmol) was treated with DDQ (0.145 g, 0.64 mmol) in refluxing THF (200 mL) during 30 min. The reaction progress was monitored by UV−vis spectroscopy, whereby samples were analyzed every 10 min. The reaction was stopped when no more changes were detected in the spectra. The reaction mixture was concentrated in vacuum and subjected to column chromatography (silica gel, CH$_2$Cl$_2$). After solvent removal and drying in vacuum, Zn−**18** was isolated as a purple crystalline powder. Yield 0.13 g (13% over two steps). UV−vis (THF) λ_{max} (nm): 427, 561, 599. ^{1}H NMR (CDCl$_3$) δ (ppm): 4.11 (3H, s, OC*H*$_3$), 7.09 (2H, d, ^3J = 8.0 Hz, −Bn−), 7.59 (2H, dd, $^3J_1$ = $^3J_2$ = 7.5 Hz, −Bn−), 7.87−7.95 (4H, m, −Bn−, Ph), 8.01−8.09 (3H, m, Ph), 8.19 (2H, d, ^3J = 8.3 Hz, Ar), 8.40 (2H, d, ^3J = 8.3 Hz, Ar), 8.82 (2H, d, ^3J = 4.3 Hz, Pyr), 9.07 (2H, d, ^3J = 4.3 Hz, Pyr), 9.25 (2H, d, ^3J = 7.5 Hz, −Bn−), 10.20 (2H, s, *meso*-*H*). MALDI-TOF (*m*/*z*): calcd for $C_{42}H_{26}N_4O_2Zn$ 684.07, found 684.36 [M]$^+$.

Zn−**18** (0.020 g, 0.029 mmol) was dissolved in CH$_2$Cl$_2$ (35 mL), and the mixture was shaken with HCl (20% aq., 2 × 35 mL) in a separatory funnel. The organic layer was washed with water (30 mL) and dried over Na$_2$SO$_4$. The solvent was removed in vacuum, and the solid was subjected to column chromatography (silica gel, CH$_2$Cl$_2$). Target porphyrin **18** was isolated as a purple crystalline powder (mp >300 °C). Yield 0.018 g (100%). UV−vis (THF) λ_{max} (nm): 420, 527, 560, 585, 641. ^{1}H NMR (CDCl$_3$) δ (ppm): −2.00 to −1.91 (1H, m, broad), −1.71 to −1.58 (1H, m, broad), 4.14 (3H, s, −OC*H*$_3$), 7.33 (2H, d, ^3J = 8.1 Hz, Ph), 7.71 (2H, dd, $^3J_1$ = 7.9, $^3J_2$ = 7.3 Hz, −Bn−), 7.95 (2H, dd, $^3J_1$ = 7.4, $^3J_2$ = 7.3 Hz, −Bn−), 8.01−8.08 (3H, m, Ph), 8.17−8.23 (2H, m, −Bn−), 8.32−8.38 (2H, m, Ar), 8.46−8.51 (2H, m, Ar), 8.89−8.95 (2H, m, Pyr), 9.24−9.29 (2H, m, Pyr), 9.42−9.49 (2H, m, −Bn−), 10.47−10.53 (2H, m, *meso*-*H*). ^{13}C NMR (CDCl$_3$) δ (ppm): 52.5, 99.1, 114.7, 120.4, 120.9, 125.5, 127.6, 127.6, 128.3, 129.2, 129.3, 129.6, 129.9, 130.0, 132.8, 134.5, 137.5, 139.9, 140.3, 141.3, 144.6, 144.8, 144.9, 145.8, 167.4. MALDI-TOF (*m*/*z*): calcd for $C_{42}H_{28}N_4O_2$ 620.22, found 621.69 [M + H]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{42}H_{29}N_4O_2$ 621.22848, found 621.22687.

5,15-Bis(3,5-dibutoxycarbonylphenyl)-*syn*-dibenzoporphyrin (19). 2 (0.373 g, 0.67 mmol) and 9 (0.350 g, 0.67 mmol) were dissolved in benzene (65 mL), and the solution was purged with Ar. Zn(OAc)$_2$·2H$_2$O was added in excess (1.45 g, 6.7 mmol), and the mixture was heated under reflux with a Dean−Stark trap for 2 h under Ar. The reaction mixture was purged with air, and the refluxing was continued under air for 12 h. The reaction progress was monitored by UV−vis spectroscopy. The solvent was removed in vacuum, and the remaining material was subjected to column chromatography (silica gel, CH$_2$Cl$_2$/EtOAc = 20:1). The band containing the target porphyrin was collected, and the solvent was removed in vacuum to give crude Zn−14.

Zn−14 (0.205 g, 0.2 mmol) was dissolved in THF (50 mL), and DDQ (0.095 g, 0.42 mmol) was added. The reaction mixture was heated under reflux for 40 min, and the reaction progress was monitored by UV−vis spectroscopy. The solvent was removed under vacuum, and the residue was diluted with CH_2Cl_2 (100 mL), washed with Na_2SO_3 (2 × 50 mL) and water, and dried over Na_2SO_4. The solution was concentrated, and the product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 20:1) to give porphyrin Zn−**19** as a purple crystalline powder. Yield: 0.2 g (29% over two steps). UV−vis (THF) λ_{max} (nm): 430, 561, 597. MALDI-TOF (*m*/*z*): calcd for $C_{60}H_{56}N_4O_8Zn$ 1024.34, found 1024.35 [M$^+$].

Zn−**19** (0.200 g, 0.195 mmol) was dissolved in CH_2Cl_2 (150 mL). The solution was vigorously shaken with HCl aq. (20%, 2 × 100 mL) and then water (100 mL) and dried over Na_2SO_4. The solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 20:1) and further by reprecipitation from CH_2Cl_2 upon addition of MeOH/H_2O (~50:0.5 v/v). The precipitate was isolated by centrifugation, washed with MeOH, and dried in vacuum to give the title compound as a purple crystalline powder (mp 274−275 °C). Yield 0.17 g (91%). UV−vis (THF) λ_{max} (nm): 421, 529, 562, 584, 640. ^{1}H NMR ($CDCl_3$) δ (ppm): −2.04 to −1.52 (2H, m, broad), 0.89 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.96 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.36−1.54 (8H, m, −C*H*$_2$−), 1.70−1.85 (8H, m, −C*H*$_2$−), 4.42 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 4.48 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 7.23 (2H, d, ^3J = 8.1 Hz, −Bn−), 7.74 (2H, dd, $^3J_1$ = $^3J_2$ = 7.3 Hz, −Bn−), 8.07 (2H, dd, $^3J_1$ = $^3J_2$ = 7.3 Hz, −Bn−), 8.87 (2H, d, ^3J = 4.4 Hz, Pyr), 9.09−9.13 (4H, m, Ar), 9.15−9.18 (1H, m, Ar), 9.30 (2H, d, ^3J = 4.4 Hz, Pyr), 9.42−9.45 (1H, m, Ar), 9.48 (2H, d, ^3J = 7.9 Hz, −Bn−), 10.53 (2H, s, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.69, 13.74, 19.2, 19.3, 30.6, 30.8, 65.6, 65.8, 99.4, 112.2, 119.5, 121.1, 124.9, 127.7, 127.9, 130.0, 130.06, 130.14, 130.3, 131.6, 131.9, 137.1, 137.5, 138.4, 139.9, 140.3, 141.6, 142.3, 144.5, 144.9, 145.1, 165.8, 166.1. MALDI-TOF (*m*/*z*): calcd for $C_{60}H_{58}N_4O_8$ 962.43, found 963.11 [M + H]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{60}H_{59}N_4O_8$ 963.43269, found 963.43134.

5,15-Bis(3,5-dibutoxycarbonylphenyl)-*syn*-dinaphtho[2,3]-porphyrin (22). Zn−17 was prepared similarly to Zn−14 (see the synthesis of Zn−**19** above) from **2** (0.316 g, 0.56 mmol) and 12 (0.353 g, 0.56 mmol). The reaction was complete in 18 h. Zn−17 was purified by column chromatography (silica gel, CH_2Cl_2/THF = 70:1). MALDI-TOF (*m*/*z*): calcd for $C_{68}H_{64}N_4O_8Zn$ 1128.40, found 1128.52 [M]$^+$.

Zn−17 (0.09 g, 0.08 mmol) was dissolved in CH_2Cl_2 (30 mL), and DDQ (0.038 g, 0.168 mmol) was added. The reaction mixture was stirred for 10 min at room temperature and was monitored by UV−vis spectroscopy. The solvent was removed in vacuum, and the remaining material was dissolved in CH_2Cl_2 (100 mL), washed with Na_2SO_3 (2 × 50 mL) and water (50 mL), and dried over Na_2SO_4. The mixture was chromatographed (silica gel, CH_2Cl_2/THF = 70:1), and Zn−**22** was isolated as a green crystalline powder. Yield: 0.08 g (13% over two steps). UV−vis (THF) λ_{max} (nm): 452, 583, 623. MALDI-TOF (*m*/*z*): calcd for $C_{68}H_{60}N_4O_8Zn$ 1124.37, found 1124.05 [M]$^+$.

Zn−**22** (0.080 g, 0.071 mmol) was dissolved in CH_2Cl_2 (100 mL), and the solution was shaken with HCl aq. (10%, 4 × 100 mL) in a separatory funnel, washed with water (100 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH_2Cl_2/THF = 70:1). The title porphyrin **22** was precipitated from CH_2Cl_2/THF solution upon addition of MeOH (~1:100 v/v) and isolated as a green crystalline powder (mp 286−288 °C). Yield 0.068 g (90%). UV−vis (THF) λ_{max} (nm): 422, 454, 521, 560, 594, 661. ^{1}H NMR ($CDCl_3$) δ (ppm): −0.72 (1H, broad), −0.25 (1H, broad), 0.83 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.96 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.31−1.43 (4H, m, −C*H*$_2$−), 1.44−1.55 (4H, m, −C*H*$_2$−), 1.65−1.76 (4H, m, −C*H*$_2$−), 1.76−1.86 (4H, m, −C*H*$_2$−), 4.41 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 4.47 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 7.59 (2H, s), 7.67 (2H, dd, $^3J_1$ = 7.4, $^3J_2$ = 7.0 Hz), 7.76 (2H, dd, $^3J_1$ = 7.4, $^3J_2$ = 6.9 Hz), 7.88 (2H, d, ^3J = 8.1 Hz), 8.44 (2H, d, ^3J = 8.1 Hz), 8.66 (2H, d, ^3J = 4.3 Hz, Pyr), 9.05 (2H, d, ^3J = 1.4 Hz, Ar), 9.07 (2H, d, ^3J = 4.3 Hz, Pyr), 9.12 (1H, dd, $^3J_1$ = $^3J_2$ = 1.4 Hz, Ar), 9.17 (2H, d, ^3J = 1.4 Hz, Ar), 9.59 (1H, dd, $^3J_1$ = $^3J_2$ = 1.5 Hz, Ar), 9.82 (2H, s), 10.33 (2H, s, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 13.8, 19.2, 19.3, 30.6, 30.8, 65.6, 65.8, 98.3, 110.2, 119.7, 121.0, 125.3, 126.2, 127.1, 128.6, 129.0, 129.7, 130.1, 130.2, 130.3, 131.5, 132.5, 132.57, 132.63, 135.1, 137.7, 138.1, 138.2, 141.3, 141.5, 142.6, 144.0, 145.5, 146.5. MALDI-TOF (*m*/*z*): calcd for $C_{68}H_{62}N_4O_8$ 1062.46, found 1063.21 [M + H]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{68}H_{63}N_4O_8$ 1063.46399, found 1063.46533.

5,15-Bis(3,5-dibutoxycarbonylphenyl)-*syn*-bis(4′,5′-dibutoxycarbonylcyclohexeno)porphyrin (15). Zn−**15** was synthesized similarly to porphyrin Zn−14 (see the synthesis of Zn−**19** above) from **2** (0.554 g, 1 mmol) and 10 (0.92 g, 1 mmol). The reaction was complete in 16 h. The product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 20:1) to give the title compound Zn−**15** as a purple solid. Yield: 0.3 g (21%). MALDI-TOF (*m*/*z*): calcd for $C_{80}H_{96}N_4O_{16}Zn$ 1432.61, found 1432.87 [M]$^+$.

Zn−**15** (0.300 g, 0.21 mmol) was dissolved in CH_2Cl_2 (200 mL), and the solution was shaken with HCl aq. (20%, 2 × 100 mL) in a separatory funnel, washed with water (100 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc = 20:1) and further by reprecipitation from CH_2Cl_2 upon addition of MeOH. The precipitate was isolated by centrifugation, washed with MeOH, and dried in vacuum to give the title compound as a purple crystalline powder (mp 140−142 °C). Yield 0.27 g (94%). UV−vis (THF) λ_{max} (nm): 409, 504, 535, 575, 629. ^{1}H NMR ($CDCl_3$) δ (ppm) (mixture of conformers): −3.02 to −2.58 (2H, m, broad), 0.58−1.01 (24H, m, −C*H*$_3$), 1.04−1.19 and 1.33−1.86 (32H, m, −C*H*$_2$−), 2.97−3.27 (4H, m, −CH*H*−), 3.55−3.71 (4H, m, −CH*H*−), 3.83−4.02 (4H, m, −OC*H*$_2$−), 4.17−4.27 (4H, m, −OC*H*$_2$−), 4.40−4.49 (8H, m, −OC*H*$_2$−), 4.49−4.72 (4H, m, −C*H*−), 8.94 (2H, d, ^3J = 4.5 Hz, Pyr), 8.94−8.96 (1H, m, Ar), 8.97−9.00 (1H, m, Ar), 9.07−9.12 (2H, m, Ar), 9.13−9.16 (1H, m, Ar), 9.20−9.24 (1H, m, Ar), 9.38 (2H, d, ^3J = 4.5 Hz, Pyr), 10.23−10.24 (2H, m, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 13.3, 13.4, 13.67, 13.70, 13.74, 13.77, 13.77, 13.78, 18.75, 18.84, 19.14, 19.17, 19.21, 19.27, 19.31, 22.7, 24.0, 24.3, 28.1, 28.5, 29.7, 30.27, 30.34, 30.63, 30.65, 30.74, 40.7, 40.8, 41.8, 41.9, 64.6, 64.7, 64.9, 65.56, 65.66, 65.72, 101.6, 115.0, 115.1, 117.3, 129.1, 129.2, 130.03, 130.04, 130.06, 130.5, 130.6, 130.7, 131.1, 131.8, 136.6, 136.8, 137.0, 137.1, 138.59, 138.60, 140.0, 140.1, 141.8, 142.0, 142.3, 144.8, 144.9, 146.3, 165.5, 165.8, 166.0, 166.1, 172.5, 172.6, 173.1, 173.3. MALDI-TOF (*m*/*z*): calcd for $C_{80}H_{98}N_4O_{16}$ 1370.70, found 1371.14 [M + H]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{80}H_{99}N_4O_{16}$ 1371.70497, found 1371.70702.

5-(3,5-Dibutoxycarbonylphenyl)-*syn*-bis(4′,5′-dimethoxycarbonylcyclohexeno)porphyrin (16). Zn−**16** was synthesized similarly to porphyrin Zn−14 (see the synthesis of Zn−**19** above) from **2** (0.484 g, 0.86 mmol) and 11 (0.42 g, 0.86 mmol). The reaction was complete in 12 h. The product was purified by column chromatography (silica gel, CH_2Cl_2/THF, gradient from 50:1 to 25:1). Zn−**16** was isolated as a purple crystalline powder. Yield: 0.2 g (24%). MALDI-TOF (*m*/*z*): calcd for $C_{52}H_{52}N_4O_{12}Zn$ 988.29, found 987.93 [M]$^+$.

Zn−**16** (0.200 g, 0.2 mmol) was dissolved in CH_2Cl_2 (200 mL), and the solution was shaken with HCl aq. (20%, 2 × 100 mL) in a separatory funnel, washed with water (100 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH_2Cl_2/THF = 5:1) and further by reprecipitation from CH_2Cl_2/THF (1:1) upon addition of MeOH. The precipitate was isolated by centrifugation, washed with MeOH, and dried in vacuum to give the title compound as a brown crystalline powder (mp 287−288 °C). Yield 0.182 g (98%). UV−vis (DMA) λ_{max} (nm): 404, 499, 531, 568, 623. ^{1}H NMR ($CDCl_3$) δ (ppm) (mixture of conformers): −3.75 to −3.17 (2H, m, broad), 0.90−1.04 (6H, m, −C*H*$_3$), 1.42−1.53 (4H, m, −C*H*$_2$−), 1.74−1.85 (4H, m, −C*H*$_2$−), 3.62−3.99 (4H, m, −CH*H*−), 3.76 (3H, s, −OC*H*$_3$), 3.77 (3H, s, −OC*H*$_3$), 3.80 (3H, s, −OC*H*$_3$), 3.82 (3H, s, −OC*H*$_3$), 4.07−4.28 (4H, m, −CH*H*−), 4.39−4.49 (4H, m,

$-OCH_2-$), 4.50−4.65 (4H, m, $-CH-$), 8.89 (1H, d, ^{3}J = 4.5 Hz, Pyr), 8.90 (1H, d, ^{3}J = 4.5 Hz, Pyr), 9.06−9.12 (2H, m, Ar), 9.13−9.17 (1H, m, Ar), 9.33 (1H, d, ^{3}J = 4.5 Hz, Pyr), 9.34 (1H, d, ^{3}J = 4.5 Hz, Pyr), 9.64−9.79 (1H, m, *meso-H*), 10.05 (2H, s, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 13.7, 13.8, 19.25, 19.27, 23.7, 23.9, 24.0, 30.7, 30.8, 40.87, 40.90, 41.05, 41.07, 52.19, 52.23, 65.6, 95.59, 95.63, 101.1, 101.2, 117.82, 117.83, 129.8, 130.1, 130.5, 130.8, 136.6, 136.7, 138.39, 138.42, 142.56, 142.59, 166.1, 166.2, 173.36, 173.38, 173.44. MALDI-TOF (*m*/*z*): calcd for $C_{52}H_{54}N_4O_{12}$ 926.37, found 927.13 $[M + H]^+$, 965.07 $[M + K]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{52}H_{55}N_4O_{12}$ 927.38102, found 927.38357.

Insertion of Pt and Pd into Porphyrins. *Method 1 (Benzoic Acid Melt Method,[85] Used for Insertion of Pt).* A free-base porphyrin, platinum(II) acetylacetonate, and benzoic acid were mixed together and heated to 130−140 °C under Ar. The reaction progress was monitored by UV−vis spectroscopy; samples were analyzed every 15 min. The reaction was stopped after the Q_{00} band maximum of the free-base porphyrin disappeared. The mixture was dispersed in MeOH/H_2O (∼2:1, 50 mL), and the precipitate, which contained the target Pt porphyrin, was isolated by centrifugation. It was redispersed in MeOH/H_2O (∼2:1, 20 mL) and centrifuged again. This washing procedure was repeated three times, after which the final solid was dried in vacuum. The product was purified by column chromatography, and the fraction containing the target compound was collected. The solvent was removed in vacuum, and the target metalloporphyrin was reprecipitated from CH_2Cl_2 by addition of MeOH. The precipitate was collected by centrifugation and dried in vacuum.

Method 2 (Microwave-Assisted Method).[86] A free-base porphyrin was dissolved in dry benzonitrile (∼2−4 mL), and the solution was placed into a thick-walled microwave vial (Biotage, 5 mL). Platinum(II) acetylacetonate or palladium(II) acetate was added, and the vessel was sealed, after which the mixture was subjected to microwave irradiation at 250 °C (∼2 bar, 105−145 W) for 40 min under stirring. The reaction progress was monitored by UV−vis spectroscopy; samples were analyzed every 20 min. The reaction was stopped after the Q_{00} band maximum of the free-base porphyrin disappeared. After the mixture was cooled, benzonitrile was removed in vacuum, and the product was purified by column chromatography on silica gel. The fraction containing the target compound was collected, and the solvent was removed in vacuum. The target metalloporphyrin was reprecipitated from CH_2Cl_2 upon addition of MeOH, and the precipitate was collected by centrifugation and dried in vacuum.

*Pt−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-bis(4′,5′-dibutoxycarbonylcyclohexeno)porphyrin (Pt−**15**). Method 1.* Pt−**15** was synthesized from **15** (0.153 g, 0.108 mmol) and Pt(acac)$_2$ (0.170 g, 0.433 mmol) in benzoic acid (3 g). The reaction was complete in 6 h. Chromatography was performed using CH_2Cl_2/THF (50:1). The target compound was isolated as an orange solid (mp 157−160 °C). Yield: 0.07 g (42%). UV−vis (THF) λ_{max} (nm): 391, 503, 535. ^{1}H NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 0.59−1.01 (24H, m, $-CH_3$), 1.04−1.19 and 1.34−1.86 (32H, m, $-CH_2-$), 2.87−3.12 (4H, m, $-CHH-$), 3.48−3.63 (4H, m, $-CHH-$), 3.86−4.02 (4H, m, $-OCH_2-$), 4.17−4.59 (16H, m, $-OCH_2-$, $-CH-$), 8.79 (2H, d, ^{3}J = 4.9 Hz, Pyr), 8.90−8.94 (2H, m, Ar), 8.98−9.06 (2H, m, Ar), 9.12−9.16 (1H, m, Ar), 9.19−9.25 (3H, m, Ar, Pyr), 10.03−10.08 (2H, m, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 13.37, 13.44, 13.68, 13.70, 13.73, 13.76, 13.78, 18.76, 18.83, 19.15, 19.18, 19.20, 19.26, 19.31, 23.68, 23.71, 23.99, 28.82, 29.16, 29.69, 30.30, 30.36, 30.63, 30.65, 30.73, 40.36, 40.41, 41.86, 41.94, 64.6, 64.7, 64.9, 65.6, 65.7, 65.8, 104.0, 117.3, 177.4, 119.4, 129.8, 129.9, 130.3, 130.5, 130.6, 130.7, 131.2, 131.3, 136.6, 136.7, 137.0, 137.1, 137.2, 137.8, 138.3, 138.4, 138.6, 138.7, 139.1, 139.2, 139.4, 140.5, 141.70, 141.79, 141.83, 165.5, 165.7, 166.0, 166.1, 172.5, 172.6, 173.1, 173.2. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{80}H_{97}N_4O_{16}Pt$ 1565.65650, found 1565.65826.

Method 2. Pt−**15** was synthesized from **15** (0.065 g, 0.0475 mmol) and Pt(acac)$_2$ (0.056 g, 0.143 mmol). The reaction was complete in 40 min. Yield: 0.074 g (100%).

*Pd−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-bis(4′,5′-dibutoxycarbonylcyclohexeno)porphyrin (Pd−**15**). Method 2.* Pd−**15** was synthesized from **15** (0.017 g, 0.0124 mmol) and Pd(OAc)$_2$ (0.011 g, 0.05 mmol). The reaction was complete in 40 min. Chromatography was performed using CH_2Cl_2/THF (50:1) to give crude Pd−**15** (0.018 g), which was used in the subsequent aromatization reaction without further purification.

*Pt−5-(3,5-Dibutoxycarbonylphenyl)-syn-bis(4′,5′-dimethoxycarbonylcyclohexeno)porphyrin (Pt−**16**). Method 2.* Pt−**16** was synthesized from **16** (0.05 g, 0.054 mmol) and Pt(acac)$_2$ (0.085 g, 0.22 mmol). The reaction was complete in 40 min. Chromatography was performed using a CH_2Cl_2/THF gradient from 50:1 to 25:1. Pt−**16** was isolated as an orange crystalline solid (mp >300 °C). Yield: 0.060 g (100%). UV−vis (DMA) λ_{max} (nm): 384, 500, 531. ^{1}H NMR ($CDCl_3$) δ (ppm) (mixture of conformers): 0.88−1.00 (6H, m, $-CH_3$), 1.42−1.54 (4H, m, $-CH_2-$), 1.71−1.87 (4H, m, $-CH_2-$), 2.99−3.52 (8H, m, $-CHH-$), 3.71 (3H, s, $-OCH_3$), 3.75 (3H, s, $-OCH_3$), 3.76 (3H, s, $-OCH_3$), 3.79 (3H, s, $-OCH_3$), 4.06−4.34 (4H, m, $-CH-$), 4.40−4.53 (4H, m, $-OCH_2-$), 8.78 (1H, d, ^{3}J = 4.8 Hz, Pyr), 8.79 (1H, d, ^{3}J = 4.9 Hz, Pyr), 8.84−8.91 and 8.96−9.00 (2H, m, Ar), 9.07−9.11 (1H, m, Ar), 9.12−9.20 (3H, m, Ar, Pyr), 9.21−9.29 and 9.48−9.63 (2H, m, *meso-H*), 9.71 (1H, s, broad, *meso-H*). The ^{13}C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (*m*/*z*): calcd for $C_{52}H_{52}N_4O_{12}Pt$ 1119.32, found 1119.73 $[M]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{52}H_{53}N_4O_{12}Pt$ 1120.33057, found 1120.33205.

*Pd−5-(3,5-Dibutoxycarbonylphenyl)-syn-bis(4′,5′-dimethoxycarbonylcyclohexeno)porphyrin (Pd−**16**). Method 2.* Pd−**16** was synthesized from **16** (0.015 g, 0.0162 mmol) and Pd(OAc)$_2$ (0.0145 g, 0.065 mmol). The reaction was complete in 40 min. Chromatography was performed using CH_2Cl_2/THF (25:1) to give crude Pd−**16** (0.0165 g), which was used in the aromatization step without further purification (see below).

*Pt−5-Phenyl-15-(p-methoxycarbonylphenyl)-syn-dibenzoporphyrin (Pt−**18**). Method 1.* Pt−**18** was synthesized from **18** (0.015 g, 0.026 mmol) and Pt(acac)$_2$ (0.041 g, 0.1 mmol) in benzoic acid (1.5 g). The reaction was complete in 2 h. Chromatography was performed using CH_2Cl_2. The target compound was isolated as a pink crystalline powder (mp >300 °C). Yield: 0.008 g (38%). UV−vis (DMA) λ_{max}/nm (log ε): 401 (5.33), 519 (4.19), 556 (4.91). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.13 (3H, s, $-OCH_3$), 7.04 (2H, d, ^{3}J = 8.3 Hz, −Bn−), 7.58 (2H, dd, $^{3}J_1$ = 8.0, $^{3}J_2$ = 7.8 Hz, −Bn−), 7.89−7.96 (4H, m, −Bn−, Ph), 8.02−8.12 (3H, m, Ph), 8.26 (2H, d, ^{3}J = 8.2 Hz, Ar), 8.46 (2H, d, ^{3}J = 8.2 Hz, Ar), 8.82 (2H, d, ^{3}J = 4.7 Hz, Pyr), 9.16 (2H, d, ^{3}J = 4.7 Hz, Pyr), 9.25 (2H, d, ^{3}J = 7.8 Hz, −Bn−), 10.39 (2H, s, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm): 52.5, 101.4, 114.5, 119.9, 122.1, 125.9, 127.2, 127.3, 128.2, 128.6, 129.37, 129.43, 129.8, 130.4, 130.5, 132.5, 133.8, 136.3, 137.5, 139.2, 139.4, 140.2, 141.5, 145.9, 167.3. MALDI-TOF (*m*/*z*): calcd for $C_{42}H_{26}N_4O_2Pt$ 813.17, found 813.41 $[M]^+$. HRMS (ESI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{42}H_{26}N_4O_2Pt$ 813.17012, found 813.16860.

*Pt−5,15-Bis(3,5-Dibutoxycarbonylphenyl)-syn-dibenzoporphyrin (Pt−**19**). Method 1.* Pt−**19** was synthesized from **19** (0.12 g, 0.132 mmol) and Pt(acac)$_2$ (0.21 g, 0.53 mmol) in benzoic acid (2.00 g, 16.4 mmol). The reaction was complete in 6 h. Chromatography was performed using CH_2Cl_2/THF = 50:1. The target compound was isolated as a dark-red crystalline powder (mp >300 °C). Yield: 0.08 g (56%). UV−vis (DMA) λ_{max}/nm (log ε): 402 (5.34), 521 (4.16), 559 (4.92). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.87 (6H, t, ^{3}J = 7.4 Hz, $-CH_3$), 0.94 (6H, t, ^{3}J = 7.4 Hz, $-CH_3$), 1.35−1.51 (8H, m, $-CH_2-$), 1.68−1.83 (8H, m, $-CH_2-$), 4.41 (4H, t, ^{3}J = 6.7 Hz, $-OCH_2-$), 4.45 (4H, t, ^{3}J = 6.7 Hz, $-OCH_2-$), 6.96 (2H, d, ^{3}J = 8.0 Hz, −Bn−), 7.60 (2H, dd, $^{3}J_1$ = $^{3}J_2$ = 7.5 Hz, −Bn−), 7.96 (2H, dd, $^{3}J_1$ = $^{3}J_2$ = 7.2 Hz, −Bn−), 8.78 (2H, d, ^{3}J = 3.5 Hz, Pyr), 9.03 (2H, d, ^{3}J = 1.6 Hz, Ar), 9.07 (2H, d, ^{3}J = 1.6 Hz, Ar), 9.15 (1H, dd, $^{3}J_1$ = $^{3}J_2$ = 1.6 Hz, Ar), 9.22 (2H, d, ^{3}J = 3.6 Hz, Pyr), 9.31 (2H, d, ^{3}J = 7.5 Hz, −Bn−), 9.44 (1H, dd, $^{3}J_1$ = $^{3}J_2$ = 1.6 Hz, Ar), 10.50 (2H, s, *meso-H*). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 13.8, 19.2, 19.3, 30.6, 30.8, 65.6, 65.8, 101.4, 114.5, 120.1, 120.5, 125.2, 127.4, 127.5, 128.7, 129.8, 130.1, 130.3, 131.7, 132.1, 136.1, 137.1, 137.1, 137.4, 137.7, 138.1, 139.1, 140.1, 141.7, 142.4, 165.8, 166.1. MALDI-TOF (*m*/*z*): calcd for $C_{60}H_{56}N_4O_8Pt$ 1155.37, found 1155.01 [M]$^+$. HRMS (ESI-TOF) *m*/*z*: [M]$^+$ calcd for $C_{60}H_{56}N_4O_8Pt$ 1155.37445, found 1155.37554.

Method 2. Pt−**19** was synthesized from **19** (0.02 g, 0.021 mmol) and Pt(acac)$_2$ (0.024 g, 0.062 mmol) and purified as in method 1 above. Yield: 0.022 g (92%).

*Pd−5,15-Bis(3,5-Dibutoxycarbonylphenyl)-syn-dibenzoporphyrin (Pd−**19**). Method 2.* Pd−**19** was synthesized from **19** (0.01 g, 0.01 mmol) and Pd(OAc)$_2$ (0.0093 g, 0.042 mmol). Chromatography was performed using CH$_2$Cl$_2$/THF = 50:1. Pd−**19** was isolated as a dark-purple crystalline solid (mp 296−297 °C). Yield: 0.011 g (100%). UV−vis (DMA) λ_{max} (nm): 417, 534, 570. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.88 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.95 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.35−1.54 (8H, m, −C*H*$_2$−), 1.68−1.84 (8H, m, −C*H*$_2$−), 4.41 (4H, t, ^3J = 6.8 Hz, −OC*H*$_2$−), 4.46 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 7.01 (2H, d, ^3J = 8.1 Hz, −Bn−), 7.62 (2H, dd, $^3J_1$ = 7.8, $^3J_2$ = 7.4 Hz, −Bn−), 7.95 (2H, dd, $^3J_1$ = $^3J_2$ = 7.4 Hz, −Bn−), 8.76 (2H, d, ^3J = 4.6 Hz, Pyr), 9.03 (2H, d, ^3J = 1.6 Hz, Ar), 9.07 (2H, d, ^3J = 1.6 Hz, Ar), 9.13−9.19 (3H, m, Pyr, Ar), 9.29 (2H, d, ^3J = 7.8 Hz, −Bn−), 9.44 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 10.42 (2H, s, *meso-H*). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.69, 13.74, 19.2, 19.3, 30.6, 30.8, 65.6, 65.8, 101.2, 114.6, 120.0, 120.3, 125.1, 127.3, 127.4, 129.4, 129.8, 130.2, 130.6, 131.7, 132.0, 136.9, 137.5, 137.7, 137.8, 138.6, 138.7, 139.4, 140.8, 142.1, 142.8, 165.8, 166.1. MALDI-TOF (*m*/*z*): calcd for $C_{60}H_{56}N_4O_8Pd$ 1066.31, found 1065.90 [M]$^+$. HRMS (ESI-TOF) *m*/*z*: [M]$^+$ calcd for $C_{60}H_{56}N_4O_8Pd$ 1066.31478, found 1066.31410.

*Pt−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-dinaphtho[2,3]-porphyrin (Pt−**22**). Method 1.* Pt−**22** was synthesized from **22** (0.032 g, 0.03 mmol) and Pt(acac)$_2$ (0.05 g, 0.12 mmol) in benzoic acid (2 g). The reaction was complete in 2 h. Chromatography was performed using CH$_2$Cl$_2$. The target compound was isolated as a dark-green crystalline powder (mp >300 °C). Yield: 0.0075 g (20%). UV−vis (DMA) λ_{max}/nm (log ε): 423 (5.02), 549 (4.16), 593 (4.93). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.81 (6H, t, ^3J = 7.3 Hz, −C*H*$_3$), 0.95 (6H, t, ^3J = 7.3 Hz, −C*H*$_3$), 1.30−1.41 (4H, m, −C*H*$_2$−), 1.41−1.53 (4H, m, −C*H*$_2$−), 1.65−1.74 (4H, m, −C*H*$_2$−), 1.75−1.84 (4H, m, −C*H*$_2$−), 4.40 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 4.46 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 7.35−7.43 (2H, m, broad), 7.60−7.67 (2H, m, broad), 7.69−7.76 (2H, m, broad), 7.76−7.83 (2H, m, broad), 8.36−8.40 (2H, m, broad), 8.67 (2H, m, broad), 9.02 (2H, d, ^3J = 1.5 Hz, Ar), 9.11 (2H, m, broad), 9.15 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 9.17 (2H, d, ^3J = 1.5 Hz, Ar), 9.63 (1H, dd, $^3J_1$ = $^3J_2$ = 1.5 Hz, Ar), 9.72 (2H, s, broad), 10.46 (2H, s, broad, *meso-H*). The ^{13}C NMR spectrum was not recorded because of the low solubility. HRMS (ESI-TOF) *m*/*z*: [M]$^+$ calcd for $C_{68}H_{60}N_4O_8Pt$ 1256.40747, found 1256.40717.

*Pd−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-dinaphtho[2,3]-porphyrin (Pd−**22**). Method 2.* Pd−**22** was synthesized from **22** (0.004 g, 0.0038 mmol) and Pd(OAc)$_2$ (0.0034 g, 0.015 mmol). The reaction was completed in 40 min. Chromatography was performed using CH$_2$Cl$_2$. Pd−**22** was isolated as a dark-green crystalline powder (mp >300 °C). Yield: 0.0036 g (82%). UV−vis (DMA) λ_{max} (nm): 435, 561, 605. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.81 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.95 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.28−1.41 (4H, m, −C*H*$_2$−), 1.41−1.54 (4H, m, −C*H*$_2$−), 1.64−1.74 (4H, m, −C*H*$_2$−), 1.74−1.84 (4H, m, −C*H*$_2$−), 4.40 (4H, t, ^3J = 6.5 Hz, −OC*H*$_2$−), 4.46 (4H, t, ^3J = 6.6 Hz, −OC*H*$_2$−), 7.42−7.49 (2H, m, broad), 7.60−7.69 (2H, m, broad), 7.70−7.78 (2H, m, broad), 7.80−7.87 (2H, m, broad), 8.38−8.47 (2H, m, broad), 8.66−8.74 (2H, m, broad), 9.00−9.05 (2H, m, broad), 9.10−9.20 (5H, m, broad), 9.60−9.66 (1H, m, broad), 9.73−9.82 (2H, m, broad), 10.46−10.53 (2H, m, broad). The ^{13}C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (*m*/*z*): calcd for $C_{68}H_{60}N_4O_8Pd$ 1166.34, found 1165.88 [M]$^+$. HRMS (ESI-TOF) *m*/*z*: [M]$^+$ calcd for $C_{68}H_{60}N_4O_8Pd$ 1166.34628, found 1166.34671.

Aromatization of Dicyclohexenoporphyrins M−15 and M−16 into DBPs M−20 and M−21 (M = Pd, Pt). The porphyrin was dissolved in toluene (~50 mL), and DDQ was added. The reaction mixture was refluxed, and the reaction progress was monitored by UV−vis spectroscopy. The reaction was stopped when no further changes could be observed in the spectra. The reaction mixture was diluted with CH$_2$Cl$_2$ (100 mL), washed with Na$_2$SO$_3$ (10% aqueous solution, 2 × 50 mL) and water (50 mL), and dried over Na$_2$SO$_4$. The solvents were removed in vacuum, and the product was purified by column chromatography on silica gel. The fraction containing the target compound was collected, and the solvent was removed in vacuum. The target metalloporphyrin was reprecipitated from CH$_2$Cl$_2$ upon addition of MeOH, and the precipitate was collected by centrifugation and dried in vacuum.

*Pt−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-bis(4′,5′-dibutoxycarbonylbenzo)porphyrin (Pt−**20**).* Pt−**20** was synthesized from Pt−**15** (0.05 g, 0.033 mmol) using DDQ (0.03 g, 0.132 mmol). The reaction was complete in 10 h. Chromatography was performed using CH$_2$Cl$_2$/THF = 50:1. Pt−**20** was isolated as a bright-purple crystalline solid (mp 256−258 °C). Yield: 0.04 g (88%). UV−vis (DMA) λ_{max}/nm (log ε): 412 (5.43), 527 (4.29), 568 (5.01). ^{1}H NMR (CDCl$_3$) δ (ppm): 0.87 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.95 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.05 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.10 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.34−1.62 (16H, m, −C*H*$_2$−), 1.69−1.92 (16H, m, −C*H*$_2$−), 4.35 (4H, t, ^3J = 7.1 Hz, −OC*H*$_2$−), 4.42 (4H, t, ^3J = 6.8 Hz, −OC*H*$_2$−), 4.46 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 4.54 (4H, t, ^3J = 6.8 Hz, −OC*H*$_2$−), 7.55 (2H, s, −Bn−), 8.85 (2H, d, ^3J = 4.9 Hz, Pyr), 9.03 (2H, d, ^3J = 1.6 Hz, Ar), 9.07 (2H, d, ^3J = 1.6 Hz, Ar), 9.17 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 9.31 (2H, d, ^3J = 4.9 Hz, Pyr), 9.46 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 9.61 (2H, s, −Bn−), 10.63 (2H, s, *meso-H*). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.66, 13.73, 13.79, 13.83, 19.16, 19.17, 19.26, 19.32, 30.63, 30.68, 30.73, 65.65, 65.68, 65.8, 66.1, 103.3, 116.0, 120.8, 121.4, 126.9, 129.4, 130.1, 130.4, 130.6, 131.4, 132.2, 132.3, 132.7, 135.4, 136.7, 137.1, 137.5, 137.6, 139.1, 140.3, 140.9, 141.1, 141.2, 165.2, 165.9, 166.7, 168.8. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{80}H_{89}N_4O_{16}Pt$ 1557.59389, found 1557.5965.

*Pd−5,15-Bis(3,5-dibutoxycarbonylphenyl)-syn-bis(4′,5′-dibutoxycarbonylbenzo)porphyrin (Pd−**20**).* Pd-**20** was prepared from Pd−**15** (0.018 g, 0.012 mmol) using DDQ (0.011 g, 0.049 mmol). The reaction was complete in 8 h. Chromatography was performed using CH$_2$Cl$_2$/THF = 50:1. Pd−**20** was isolated as a dark-purple crystalline solid (mp 243−245 °C). Yield: 0.0165 g (92% over two steps based on **15**). UV−vis (DMA) λ_{max} (nm): 427, 541, 581. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.88 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 0.95 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.05 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.10 (6H, t, ^3J = 7.4 Hz, −C*H*$_3$), 1.35−1.62 (16H, m, −C*H*$_2$−), 1.70−1.92 (16H, m, −C*H*$_2$−), 4.36 (4H, t, ^3J = 7.1 Hz, −OC*H*$_2$−), 4.42 (4H, t, ^3J = 6.8 Hz, −OC*H*$_2$−), 4.47 (4H, t, ^3J = 6.7 Hz, −OC*H*$_2$−), 4.54 (4H, t, ^3J = 6.8 Hz, −OC*H*$_2$−), 7.61 (2H, s, −Bn−), 8.86 (2H, d, ^3J = 4.8 Hz, Pyr), 9.04 (2H, d, ^3J = 1.5 Hz, Ar), 9.08 (2H, d, ^3J = 1.5 Hz, Ar), 9.17 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 9.32 (2H, d, ^3J = 4.8 Hz, Pyr), 9.46 (1H, dd, $^3J_1$ = $^3J_2$ = 1.6 Hz, Ar), 9.66 (2H, s, −Bn−), 10.67 (2H, s, *meso-H*). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.67, 13.74, 13.80, 13.84, 19.16, 19.18, 19.27, 19.32, 30.63, 30.69, 30.74, 65.65, 65.66, 65.8, 66.2, 102.7, 115.7, 120.7, 121.0, 126.9, 129.3, 130.0, 130.5, 130.9, 131.7, 132.09, 132.12, 132.4, 136.0, 136.7, 137.2, 137.3, 137.8, 137.9, 140.3, 141.50, 141.52, 165.2, 166.0, 166.8, 168.8. MALDI-TOF (*m*/*z*): calcd for $C_{80}H_{88}N_4O_{16}Pd$ 1466.52, found 1465.90 [M]$^+$. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{80}H_{89}N_4O_{16}Pd$ 1467.53279, found 1467.53562.

*Pt-5-(3,5-Dibutoxycarbonylphenyl)-syn-bis(4′,5′-dimethoxycarbonylbenzo)porphyrin (Pt−**21**).* Pt−**21** was synthesized from Pt−**16** (0.04 g, 0.036 mmol) using DDQ (0.032 g, 0.143 mmol). The reaction was complete in 12 h. Chromatography was performed using CH$_2$Cl$_2$/THF = 5:1. Pt−**21** was isolated as a pink crystalline powder (mp >300 °C). Yield: 0.032 g (81%). UV−vis (DMA) λ_{max} (nm): 405 (5.40), 522 (4.27), 562 (5.03). ^{1}H NMR (DMSO-*d*$_6$, 80 °C) δ (ppm): 0.99 (6H, t, ^3J = 7.3 Hz, −C*H*$_3$), 1.49−1.61 (4H, m, −C*H*$_2$−), 1.79−1.90 (4H, m, −C*H*$_2$−), 4.20 (6H, s, −OC*H*$_3$), 4.21 (6H, s, −OC*H*$_3$), 4.51 (4H, t, ^3J = 6.5 Hz, −OC*H*$_2$−), 7.91−8.03 (2H, m, broad), 8.09−8.27 (2H, m, broad), 8.65−8.99 (10H, m, broad). The ^{13}C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (*m*/*z*): calcd for $C_{52}H_{44}N_4O_{12}Pt$ 1111.26, found 1111.72 [M]$^+$. HRMS (ESI-TOF) *m*/*z*: [M]$^+$ calcd for $C_{52}H_{44}N_4O_{12}Pt$ 1111.26014, found 1111.26239.

*Pd−5-(3,5-Dibutoxycarbonylphenyl)-syn-bis(4′,5′-dimethoxycarbonylbenzo)porphyrin (Pd−**21**).* Pd−**21** was synthesized from Pd−**16** (0.0165 g, 0.016 mmol) using DDQ (0.0145 g, 0.064 mmol). The target porphyrin was purified by column chromatography (silica gel, CH_2Cl_2/THF = 5:1) and then by reprecipitation from THF upon addition of MeOH. Pd−**21** was isolated as a dark-purple crystalline powder (mp >300 °C). Yield: 0.013 g (79% over two steps based on **16**). UV−vis (DMA) λ_{max} (nm): 421, 534, 574. ^{1}H NMR (DMSO-d_6, 80 °C) δ (ppm): 1.00 (6H, t, ^3J = 7.3 Hz, $-CH_3$), 1.50−1.61 (4H, m, $-CH_2-$), 1.80−1.89 (4H, m, $-CH_2-$), 4.12−4.22 (12H, m, $-OCH_3$), 4.50 (4H, t, ^3J = 6.5 Hz, $-OCH_2-$), 7.62−7.72 (2H, m, broad), 7.73−7.86 (2H, m, broad), 8.00−8.26 (3H, m, broad), 8.29−8.50 (4H, m, broad), 8.50−8.59 (2H, m, broad), 8.85−8.92 (1H, m, broad). MALDI-TOF (m/z): calcd for $C_{52}H_{44}N_4O_{12}Pd$ 1022.20, found 1021.71 $[M]^+$. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{52}H_{44}N_4O_{12}Pd$ 1022.20031, found 1022.20218.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details; NMR, MALDI-TOF, and optical data; and X-ray crystallographic data for compound Pt−**19** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support from the Penn Medicine Neuroscience Center and the National Institutes of Health (Grant R01-GM103591) is gratefully acknowledged. The authors are grateful to Dr. Patrick Carroll (Department of Chemistry, University of Pennsylvania) for the X-ray structure determination and Dr. Leland Maine (Department of Biochemistry and Biophysics, University of Pennsylvania) for assistance with HRMS measurements.

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