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

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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-dibenzo-porphyrins (DBPs) and syn-dinaphthoporphyrins (DNPs) were synthesized by [2 + 2] condensation of the corresponding dipyrrromethanes and subsequent oxidative aromatization. Butyrylcarbonyl 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 alkoxy carbonyl 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, tetranaphthoporphyrins, and tetraanthraporphyrins79 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 Pt31–35 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.

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 where 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
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. 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. Consequently, strongly allowed 1P transitions into B (Soret) and Q states, 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, 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, we set out to examine whether asymmetrically regular metalloporphyrins, are mutually exclusive. Transition probabilities in centrosymmetrical molecules, such as regular metalloporphyrins, are mutually exclusive. Consequently, strongly allowed 1P transitions into B (Soret) and Q states, 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, 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.

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 C2v symmetry group, unlike regular metalloporphyrins, which have D4h-type symmetry and thus possess a center of inversion.

The saturated precursor porphyrins for syn-DBPs and syn-DNPs may be obtained from dipyromethanes bearing C1 synthons at the 1- and 9-positions and appropriate unsubstituted counterparts (Scheme 1). Following the methods developed by Lindsey and co-workers, we chose to use bis(N,N-dimethylaminomethyl) and bis(propyliminomethyl) 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-dipyromethanes derived from unsubstituted pyrrole.

Generally, 1,9-bis(N,N-dimethylaminomethyl)-dipyromethanes such as 1 (Chart 2) are simpler to synthesize, and they lead to excellent results when condensations are carried out in alcohols. 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)dipyromethane 2 allowed us to achieve significant improvements in the yield. Dipyromethanes 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 tetrahydronaphthalen-fused (7) dipyromethane esters were synthesized in 70–90% yield from the respective pyroles and aldehydes (or dimethoxymethane) following the previously developed procedures (Scheme 2). In the case of sterically more hindered structures 5 and 7, longer times (up to 72 h) were required to complete the condensation.

Chart 1. Structures of the Target Porphyrins

Pd(II) complexes. Rational approaches to a number of related tetrapyroles have been explored previously. In particular, there is an example of a 5,15-meso-diaryl DBP, reported by Smith et al., that is very similar to one of our compounds (porphyrin 20) but was obtained via different route, i.e., from a sulfonloporphyrin precursor by the Diels–Alder reaction. The methodology explored in our synthesis is based on the oxidative aromatization method and its 4,7-dihydroisoxindole variant, developed by Cheprakov and co-workers. 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 alkoxy carbonyl 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.
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 tetrahydronaphthalene-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)$_8$ and then introduced into the TFA-mediated decarboxylation without isolation. De-esterification/decarboxylation was carried out immediately prior to the porphyrin synthesis, since $\alpha,\alpha'$-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-propylaminomethyl)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-propylaminomethyl)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 dipyrromethanes. The formation of the corresponding dehydroproporphyrinogens and depletion of the starting materials was monitored by MALDI-TOF analysis. Once the concentration of the dehydroproporphyrinogens 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 dehydroproporphyrinogens 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 dehydroproporphyrinogens into porphyrins. The dipyrromethanes in the meantime continued to undergo condensation to generate new dehydroproporphyrinogens 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...
exocyclic ring annealed with the macrocycle, whereas dehydrogenation of less-saturated rings generally occurs much more easily. 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. 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. Planar meso-unsubstituted71 and 5,15-diarylporphyrins72,73 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 tetraalkoxy carbonylporphyrins 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 tetrnapthophorphyrins. 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 or using the microwave-assisted method. 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 CH2Cl2/MeOH (1:50) afforded the Pt(II)−porphyrin complexes in 20−56% yield. In spite of the moderate yields, the benzoic acid method in our hands has proved to be general.

Reagents and conditions: (a) p-TsOH, NBu4Cl, CH2Cl2, r.t., 24 h (3), 48 h (4), 72 h (5). (b) p-TsOH, AcOH, 24 h (6), 48 h (7). (c) H2/Pd(OH)2/THF, r.t., 24−48 h. (d) (i) TFA/CH2Cl2 1:1, 20 °C, 1 h; (ii) NaHCO3.

Scheme 2. Synthesis of β-Substituted Dipyrrromethanes

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 or using the microwave-assisted method. 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 CH2Cl2/MeOH (1:50) afforded the Pt(II)−porphyrin complexes in 20−56% yield. In spite of the moderate yields, the benzoic acid method in our hands has proved to be general.
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 alkoxy carbonyl groups, all of the porphyrins were found to be well-soluble in a range of organic solvents (e.g., toluene, CH2Cl2, 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 N2) 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 phospho-
rescence quantum yields are about 2 times lower (Table 1). These trends are common for Pt and Pd porphyrins and

| complex | absorption λ_{max} (nm) | phosphorescence λ_{max} (nm) | Φ_{pl} 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                |
| Pt−21   | 417 570                | 706 0.15, 850               |
| Pt−20   | 427 581                | 702 0.16, 730               |
| Pt−22   | 435 605                | 774 0.04, 410               |

“The phosphorescence quantum yields (Φ) and lifetimes (τ) were measured at 22 °C in deoxygenated solutions. The fluorescence of rhodamine 6G in EtOH (Φ_R = 0.95) was used as a standard. 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-tetraphenyltetrabenzo-porphyrin (Ph_3TBP) in deoxygenated DMF is 0.085.

below we discuss only Pt complexes Pt−18 through Pt−22, while the properties of the Pd complexes can be inferred by analogy.

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.

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 tetrabenzo-porphyrins (PtTBP)s (D_{4h} symmetry). The Soret (or B) (S_0), 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) and those of PtTBP,25,32,35,71 The Q band of Pt−22 (λ_{max} = 593 nm) is bathochromically shifted, approaching the Q bands of PtTBP (∼605−615 nm),32,71 while its B band is also red-shifted, but broadened similar to the B bands of tetraphenophorphyrins. 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_e, e = a, b, c) that are formed by configuration interaction involving single-electron excitations between pairs of nearly degenerate HOMOs and LUMOs.π-Extension lifts the degeneracy of one of the HOMOs (a_y), leading to a spectral red shift as well to an increase in the oscillator strength of the Q band. Just as in fully symmetrical PtTBP, the orthogonal transition dipoles in Pt syn-DBPs and Pt syn-DNP are identical to each other. Consequently, the x and y bands are fully superimposed, giving rise to narrow spectral lines, similar to those of PtTBP. 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.

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 PtTBP. In syn-DNP Pt−22, on the other hand, the macrocycle diameter along the polarization axes is similar to that of PtTBP. 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 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 hypsochronically 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 (2J) because of the increase in the size of the π-system, 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 S_15-dialylporphyrins (see the X-ray structure in Figure 2 and the computed structures in
The phosphorescence quantum yields of PtTCHP (Δν0) 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 PrTCHP. In the case of Pt−22, measurements could not be conducted at wavelengths shorter than 860 nm because of the interfering linear excitation into the triplet state (S0 → T1) by the femtosecond pulses. (It should be kept in mind that in Pt porphyrins, because of the very strong spin–orbit coupling, spin-forbidden S0 → T1 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 PrTCHP (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 3).
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 nonfullerene symmetrical sbn-DBP and sym-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 1H NMR peak assignments are shown on p S20 in the Supporting Information. HRMS data are reported for the mass spectrometer software. The abbreviations used in the 1H NMR peak assignments are shown on p S20 in the Supporting Information. HRMS data are reported for the mass spectrometer software.

To a solution of 1,9-Bis(N,N-dimethylaminomethyl)-5-(4-methoxy carbonylphenyl)dipyrromethane (1). 4-Methoxy-carbonylbenzaldehyde (2.40 g, 15 mmol) and pyrrole (100 g, 1.5 mol) were mixed together and purged with Ar for 10 min. InCl3 (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 washed with the residue with hexane (3 × 30 mL). The remaining material was dissolved in hot MeOH (100−150 mL). 5-(4-Methoxy carbonylphenyl)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%). 1H NMR (DMSO-d6) δ (ppm): 2.07 (12H, s, −NCH2), 3.26 (4H, d, J = 2.51 Hz, −CH(NH3)(CH3)), 3.81 (3H, s, −OCH3), 3.57 (1H, s, −CH3), 5.33 (1H, d, J = 2.8 Hz, Pyr), 5.54 (1H, d, J = 2.8 Hz, Pyr), 5.72 (1H, d, J = 2.8 Hz, Pyr), 7.53 (1H, d, J = 2.8 Hz, Pyr), 7.23 (2H, d, J = 8.3 Hz, Ar), 7.85 (2H, d, J = 8.3 Hz, Ar). Yield: 0.82 g (62%).

To a solution of 1a (0.9468 g, 2.9 mmol) in CH2Cl2 (50 mL), N,N-dimethylethlenimine oxide (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 CH2Cl2 (350 mL), and K2CO3 (10% aq., 350 mL) was added. The organic layer was separated, washed with K2CO3 (10% aq., 3× 350 mL), dried over Na2SO4, and concentrated in vacuum. The title compound was precipitated from CH2Cl2 upon addition of hexanes, collected by filtration, and dried in vacuum. Pale-yellow crystalline powder (mp 111−113 °C). Yield: 0.8223 g (62%). 1H NMR (DMSO-d6) δ (ppm): 2.07 (12H, s, −NCH2), 3.26 (4H, d, J = 2.51 Hz, −CH(NH3)(CH3)), 3.81 (3H, s, −OCH3), 3.57 (1H, s, −CH3), 5.33 (1H, d, J = 2.8 Hz, Pyr), 5.54 (1H, d, J = 2.8 Hz, Pyr), 5.72 (1H, d, J = 2.8 Hz, Pyr), 7.53 (1H, d, J = 2.8 Hz, Pyr), 7.23 (2H, d, J = 8.3 Hz, Ar), 7.85 (2H, d, J = 8.3 Hz, Ar). Yield: 0.8223 g (62%).

1.9-Bis(N-Propylaminomethyl)-5-(3,5-dibutoxycarbonylphenyl)dipyrromethane (2). 3,5-Dibutoxy carbonylbenzaldehyde (3.06 g, 10 mmol) and pyrrole (66 g, 1.0 mol) were mixed together and purged with Ar for 10 min. InCl3 (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, CH2Cl2) 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 DMP (10 mL) was added POCl3 (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 CH2Cl2 (3 × 100 mL), and dried over Na2SO4. The solvent was removed in vacuum, and the residue was purified by column chromatography (silica gel, CH2Cl2/ethyl acetate = 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). 1H NMR (CDCl3) δ (ppm): 0.90 (6H, t, J = 7.4 Hz, −CH3), 0.95 (6H, t, J = 7.4 Hz, −CH3), 1.38−1.49 (4H, m, −CH2−CH2), 1.60−1.78 (8H, m, −CH2−CH2), 3.41 (4H, d, dd, J = 6.8, J = 6.9 Hz, −NCH3−), 4.30 (4H, t, J = 6.7 Hz, −OCH2−CH2), 5.99 (1H, s, broad, −CH), 5.96 (2H, d, J = 3.6 Hz, Pyr), 6.50 (2H, d, J = 3.6 Hz, Pyr), 7.72 (2H, s, −NH2), 8.08 (2H, d, J = 1.4 Hz, Ar), 8.55 (1H, t, J = 1.4 Hz, Ar). 13C NMR δ (ppm): 11.17, 13.7, 19.2, 24.2, 30.8, 44.1, 62.3, 65.2, 109.6, 114.8, 119.6, 129.4, 130.6, 131.2, 133.6, 135.6, 135.7, 142.2, 151.4, 165.7. MALDI-TOF (m/z): calcd for C63H91N2O16 1131.63623, found 1131.63613.

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benzoylcarbonyl-5,6-dimethoxy carbonyl-4,5,6,7-dihydro-2H-isoo-
dole² (1.3 g, 3.5 mmol) and dimethoxysilane (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 the reaction mixture was purged with Ar. An excess of Zn(OAc)²

(0.020 g, 0.029 mmol) was dissolved in CH₂Cl₂ (35 mL), and the solution

was stirred for 2 h, during which 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 chromato-
graphy (silica gel, CH₂Cl₂). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy)

was collected and evaporated to dryness to give crude Zn−18.

Zn−18 (0.020 g, 0.029 mmol) was dissolved in CH₂Cl₂ (35 mL), and the solution

was stirred with H₂O (5 mmol) for 2 h under Ar. The reaction mixture was passed through a Dean−Stark trap for 2 h under

Ar. The reaction mixture was then stirred under H₂ for 12 h. 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, CH₂Cl₂). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy)

was collected and evaporated to dryness to give crude Zn−18.

Zn−18 (0.020 g, 0.029 mmol) was dissolved in THF (50 mL), and the solution was purged with Ar for 10 min. Pearlman’s catalyst (0.02 g) was added, and the reaction mixture was cooled to room temperature under Ar for 24 h. The mixture was diluted with CH₂Cl₂ (100 mL), washed with NaHCO₃ (10% aq.), and brine (50 mL), and dried over Na₂SO₄. The solvent was removed in vacuum, and the resulting solid was subjected to column chromatography (silica gel, CH₂Cl₂). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy) was collected and evaporated to dryness to give crude Zn−18.

Zn−18 (0.020 g, 0.029 mmol) was dissolved in CH₂Cl₂ (35 mL), and the solution was purged with Ar for 10 min. Pearlman’s catalyst (0.020 g) was added, and the reaction mixture was purged with Ar for 24 h. The mixture was diluted with CH₂Cl₂ (100 mL), washed with NaHCO₃ (10% aq., 50 mL) and brine (50 mL), and dried over Na₂SO₄. The solvent was removed in vacuum, and the resulting solid was subjected to column chromatography (silica gel, CH₂Cl₂). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy) was collected and evaporated to dryness to give crude Zn−18.

Zn−18 (0.020 g, 0.029 mmol) was dissolved in CH₂Cl₂ (35 mL), and the solution was purged with Ar for 10 min. Pearlman’s catalyst (0.02 g) was added, and the reaction mixture was purged with Ar for 24 h. The mixture was diluted with CH₂Cl₂ (100 mL), washed with NaHCO₃ (10% aq., 50 mL) and brine (50 mL), and dried over Na₂SO₄. The solvent was removed in vacuum, and the resulting solid was subjected to column chromatography (silica gel, CH₂Cl₂). The fraction containing the target porphyrin (as monitored by UV−vis spectroscopy) was collected and evaporated to dryness to give crude Zn−18.
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 DDO (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 CH2Cl2 (100 mL), washed with Na2SO4 (2 × 50 mL) and water, and dried over Na2SO4. The solution was concentrated, and the product was purified by column chromatography (silica gel, CH2Cl2/EToAc (20:1)) to give porphyrin Zn–19 as a purple crystalline powder. Yield: 0.2 g (29% over two steps). UV–vis (THF) \( \lambda_{\text{max}} \) (nm): 430, 561, 597. MALDI-TOF (m/z): calcd for \( \text{C}_{95}\text{H}_{104}\text{N}_{4}\text{O}_{8}\text{Zn} \ 1124.37 \), found 1124.05 \([\text{M}]+\). 

1H NMR (CDCl3) \( \delta \) (ppm): 1.01 (24H, m), 1.53 (4H, m, \( J = 4.5 \) Hz, Pyr), 8.94 (1H, m, Ar), 9.07 (1H, d, \( J = 4.3 \) Hz, Pyr), 9.12 (1H, dd, \( J_{1} = J_{2} = 1.4 \) Hz, Ar), 9.17 (2H, d, \( J = 1.4 \) Hz, Ar), 9.59 (1H, dd, \( J_{1} = J_{2} = 1.5 \) Hz, Ar), 9.82 (2H, s, meso-H). 13C NMR (CDCl3) \( \delta \) (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, 126.1, 127.1, 128.6, 129.0, 129.7, 130.1, 130.2, 130.3, 131.5, 132.5, 132.7, 136.3, 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 \( \text{C}_{95}\text{H}_{104}\text{N}_{4}\text{O}_{8}\text{Zn} \ 1124.6 \), found 1124.01 \([\text{M}+\text{H}]+\). HRMS (ESI-TOF) \( m/z \): \([\text{M}+\text{H}]+\) calcd for \( \text{C}_{95}\text{H}_{104}\text{N}_{4}\text{O}_{8}\text{Zn} \ 1124.63399 \), found 1124.6333.

Zn–19 (0.300 g, 0.21 mmol) was dissolved in CH2Cl2 (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 Na2SO4. The solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH2Cl2/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 \( \text{C}_{95}\text{H}_{104}\text{N}_{4}\text{O}_{8}\text{Zn} \ 1432.61 \), found 1432.87 \([\text{M}]+\).

Zn–15 (0.300 g, 0.21 mmol) was dissolved in CH2Cl2 (200 mL), and the solvent was removed in vacuum, and the product was purified by column chromatography (silica gel, CH2Cl2/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 \( \text{C}_{95}\text{H}_{104}\text{N}_{4}\text{O}_{8}\text{Zn} \ 1432.61 \), found 1432.87 \([\text{M}]+\).
Mesyl and the vessel was sealed, after which the mixture was subjected to spectroscopy; samples were analyzed every 20 min. The reaction was complete after 40 min. Chromatography was performed using CHCl₃/THF gradient from 50:1 to 25:1. Pt→16 was synthesized as an orange crystalline solid (mp >300 °C). Yield: 0.060 g (100%). UV–vis (DMA) λmax (nm): 384, 500, 531. 1H NMR (CDCl₃) δ (ppm) (mixture of conformers): 0.88–1.00 (6H, m, −CH₂−CH₂−), 1.42–1.54 (4H, m, −CH₂−CH₂−), 1.71–1.87 (4H, m, −CH₂−), 2.99–3.52 (8H, m, −CH(CH₃)₂−), 3.71 (3H, s, −OCH₃), 3.76 (3H, s, −OCH₃), 3.79 (3H, s, −OH), 4.06–4.34 (4H, m, −CH₂−), 4.40–4.53 (4H, m, −OCH₂−), 8.78 (1H, d, J = 4.8 Hz, Pyr), 8.79 (1H, d, 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). The 13C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (m/z): calc for C₃H₅NO₄P₄ 1191.32, found 1191.37 [M⁺]: HRMS (ESI-TOF) m/z: [M + H⁺] calc for C₃H₅NO₄P₄ 1120.3305, found 1120.3304. Pt→5–(3,5-Dibutoxycarbonylphenyl)–syn-bis(4′,5′‐dimethoxycarbonylcyclohexeno)porphyrin (Pt→16). Method 2. Pt→16 was synthesized from 16 (0.015 g, 0.0162 mmol) and Pt(acac)₂ (0.041 g, 0.0161 mmol). The reaction was complete in 40 min. Chromatography was performed using CHCl₃/THF gradient (25:1) to give crude Pt→16 (0.0165 g), which was used in the amination step without further purification (see below).

Pt→5-Phenyl-15-(p-methoxybiphenylyl)-syn-dibenzo-orphyrin (Pt→18). Method 1. Pt→18 was synthesized from 18 (0.018 g, 0.026 mmol) and Pt(acac)₂ (0.041 g, 0.0161 mmol) in benzoic acid (1.5 g). The reaction was complete in 2 h. Chromatography was performed using CHCl₃. The target compound was isolated as a pink crystalline powder (mp >300 °C). Yield: 0.008 g (38%). UV–vis (DMA) λmax/λnm (log e): 401 (5.33), 519 (4.19), 556 (4.91). 1H NMR (CDCl₃) δ (ppm): 4.13 (3H, s, −OCH₃), 7.04 (2H, d, J = 8.3 Hz, −Bn), 7.58 (2H, dd, J₁ = 8.0, J₂ = 7.8 Hz, −Bn), 7.89–7.96 (4H, m, −Bn–Ph), 8.02–8.12 (3H, m, Ph), 8.26 (2H, d, J = 8.2 Hz, Ar), 8.46 (2H, d, J = 8.2 Hz, Ar), 8.82 (2H, d, J = 4.7 Hz, Pyr), 9.16 (2H, d, J = 4.7 Hz, −Bn), 9.25 (2H, d, J = 7.8 Hz, −Bn), 10.39 (3H, s, meso–H). 13C NMR (CDCl₃) δ (ppm): 52.5, 101.4, 114.5, 119.9, 122.1, 125.9, 127.7, 127.3, 128.6, 128.6, 129.7, 129.8, 130.4, 130.5, 132.5, 133.8, 136.3, 137.5, 139.2, 140.2, 141.5, 145.9, 167.3. MALDI-TOF (m/z): calc for C₅H₅NO₄P₄ 813.17, found 813.41 [M⁺]: HRMS (ESI-TOF) m/z: [M + H⁺] calc for C₅H₅NO₄P₄ 813.1702, found 813.16860.

Pt→5-15-Bis(3,5-dibutoxybiphenylyl)-syn-bis(4′,5′-dibutoxycarbonylcyclohexeno)porphyrin (Pt→15). Method 2. Pt→15 was synthesized from 15 (0.015 g, 0.016 mmol) and Pt(acac)₂ (0.021 g, 0.053 mmol) in benzoic acid (2.00 g, 16.4 mmol). The reaction was complete in 6 h. Chromatography was performed using CHCl₃/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) λmax/λnm (log e): 402 (5.34), 521 (4.16), 559 (4.92). 1H NMR (CDCl₃) δ (ppm): 0.87 (6H, t, J = 7.4 Hz, −Bn), 0.94 (6H, t, J = 7.4 Hz, −CH₃), 1.35–1.51 (8H, m, −CH₂–CH₃), 1.68–1.83 (8H, m, −CH₂–CH₂–), 4.41 (4H, t, J = 6.7 Hz, −OCH₂–), 4.45 (4H, t, J = 6.7 Hz, −OCH₂–), 6.96 (2H, d, J = 8.0 Hz, −Bn), 7.60 (2H, dd, J₁ = 7.3 Hz, −Bn), 7.96 (2H, dd, J₂ = 7.3 Hz, −Bn), 8.78 (2H, d, J = 3.5 Hz, Pyr), 9.03 (2H, d, J = 1.6 Hz, Ar), 9.07 (2H, d, J = 1.6 Hz, Ar), 9.12 (2H, d, J = 1.6 Hz, Ar), 9.24 (2H, d, J = 1.6 Hz, Ar), 9.31 (2H, d, J = 1.6 Hz, Ar), 9.44 (2H, d, J = 1.6 Hz, Ar), 10.50 (2H, s, meso–H). 13C NMR (CDCl₃) δ (ppm): 12.0, 13.8, 19.2, 19.3, 30.6, 30.8, 65.6, 65.8, 101.4, 114.5, 120.1, 120.5, 122.7, 127.4, 128.7, 129.8, 130.1, 130.3, 131.7, 132.1, 136.1, 137.1, 137.4, 137.7, 138.1, 139.1, 140.1, 141.7, 141.7.
9.82 (2H, m, broad), 10.46
8.47 (2H, m, broad), 8.66
recorded because of the low solubility. HRMS (ESI-TOF)
16 into DBPs M
above. Yield: 0.022 g (92%).

Pd–5,15-Bis(3,5-dibutoxyaryl)benzophenone (Pd–19). Method 2. Pd–19 was synthesized from 19 (0.01 g, 0.011 mmol) and Pt(acac)3 (0.024 g, 0.062 mmol) and purified as in method 1 above. Yield: 0.012 g (92%).

Pd–5,15-Bis(3,5-dibutoxyaryl)benzophenone (Pd–19) + Pd–5,15-Bis(3,5-dibutoxyaryl)benzophenone (Pd–20). Pd–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 CH2Cl2/THF = 50:1. Pd–20 was isolated as a bright-purple crystalline solid (mp 256–258 °C). Yield: 0.04 g (88%). UV–vis (DMA) λmax (nm): ε: 412 (5.43), 527 (4.29), 568 (5.01). 1H NMR (CDCl3) δ (ppm): 0.87 (6H, t, J = 7.4 Hz, –CH3), 0.95 (6H, t, J = 7.4 Hz, –CH3), 1.35–1.54 (8H, m, –CH2–), 1.68–1.84 (8H, m, –CH2–), 4.41 (4H, t, J = 6.8 Hz, –OCH2–), 4.46 (4H, t, J = 6.7 Hz, –OCH2–), 7.01 (2H, d, J = 8.1 Hz, –Br–), 7.62 (2H, dd, J1 = 7.6, J2 = 7.4 Hz, –Br–), 7.95 (2H, dd, J1 = J2 = 4.6 Hz, Pyr), 9.03 (2H, d, J = 1.6 Hz, Ar), 9.07 (2H, d, J = 1.6 Hz, Ar), 9.13–1.19 (3H, m, Pyr, Ar), 9.29 (2H, d, J = 7.8 Hz, –Br–), 8.76 (2H, d, J = 4.6 Hz, Pyr).

The reaction was complete in 2 h. Chromatography was performed using CH2Cl2. The target compound was isolated as a dark-green crystalline powder (mp > 300 °C). Yield: 0.0075 g (20%). UV–vis (DMA) λmax (nm) (log ε): 423 (5.02), 549 (4.16), 593 (4.93). 1H NMR (CDCl3) δ (ppm): 0.81 (6H, t, J = 7.3 Hz, –CH3), 0.95 (6H, t, J = 7.3 Hz, –CH3), 1.30–1.41 (4H, m, –CH2–), 1.59–1.67 (4H, m, –CH2–), 1.75–1.84 (4H, m, –CH2–), 4.29 (4H, t, J = 6.7 Hz, –OCH2–), 4.46 (4H, t, J = 6.7 Hz, –OCH2–), 7.53–7.83 (2H, broad), 7.60–7.67 (2H, broad), 7.69–7.76 (2H, broad), 7.76–8.73 (2H, broad), 8.36–8.40 (2H, broad), 8.67 (2H, broad), 9.02 (2H, d, J = 1.5 Hz, Ar), 9.11 (2H, m, broad), 9.15 (1H, dd, J1 = J2 = 1.6 Hz, Ar), 9.17 (2H, d, J = 1.5 Hz, Ar), 9.63 (1H, dd, J1 = J2 = 1.5 Hz, Ar), 9.72 (2H, broad), 10.46 (2H, s, broad, meso-H). The 13C NMR spectrum was not recorded because of the low solubility. HRMS (ESI-TOF) m/z: [M]+ calcd for C40H33NO10Pd 1066.3146, found 1066.3140.

Pd–5,15-Bis(3,5-dibutoxyaryl)benzophenone (Pd–21). Pd–21 was synthesized from 22 (0.032 g, 0.03 mmol) and Pt(acac)3 (0.05 g, 0.12 mmol) in benzoic acid (2 g).

The reaction was complete in 40 min. Chromatography was performed using CH2Cl2. Pd–22 was isolated as a dark-green crystalline powder (mp > 300 °C). Yield: 0.0036 g (82%). UV–vis (DMA) λmax (nm): 435, 561, 605. 1H NMR (CDCl3) δ (ppm): 0.81 (6H, t, J = 7.4 Hz, –CH3), 0.95 (6H, t, J = 7.4 Hz, –CH3), 1.28–1.41 (4H, m, –CH2–), 1.41–1.54 (4H, m, –CH2–), 1.64–1.74 (4H, m, –CH2–), 1.74–1.84 (4H, m, –CH2–), 4.40 (4H, t, J = 6.5 Hz, –OCH2–), 4.46 (4H, t, J = 6.6 Hz, –OCH2–), 7.42–7.59 (2H, broad), 8.70–7.97 (2H, broad), 7.70–7.78 (2H, broad), 7.80–8.78 (2H, broad), 8.38–8.47 (2H, broad), 8.66–8.74 (2H, broad), 9.00–9.05 (2H, broad), 9.10–9.20 (5H, broad, medium), 9.60–7.16 (2H, broad, medium), 9.73–9.82 (2H, broad, medium), 10.46–10.53 (2H, broad). The 13C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (m/z): calcd for C40H33NO10Pd 1166.3464, found 1166.3467.

Pd–5,15-Bis(3,5-dibutoxyaryl)benzophenone (Pd–21). Pd–21 was synthesized from Pd–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 CH2Cl2/THF = 5:1. Pd–21 was isolated as a pink crystalline powder (mp > 300 °C). Yield: 0.032 g (81%). UV–vis (DMA) λmax (nm): 405 (5.40), 542 (4.27), 562 (5.03). 1H NMR (DMSO-d6, 80 °C) δ (ppm): 0.99 (6H, t, J = 7.3 Hz, –CH3), 1.49–1.61 (4H, m, –CH2–), 1.79–1.90 (4H, m, –CH2–), 4.20 (6H, s, –OCH3), 4.31 (4H, s, –OCH3), 4.41 (4H, s, –OCH3), 7.91–8.03 (2H, broad), 8.09–8.27 (2H, broad), 8.65–8.99 (10H, broad). The 13C NMR spectrum was not recorded because of the low solubility. MALDI-TOF (m/z): calcd for C40H33NO10Pd 1161.2604, found 1161.2623.
**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.

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