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Synthesis of 5,15-Diaryltetrabenzoporphyrins

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Abstract

A general method of synthesis of 5,15-diaryltetrabenzoporphyrins (Ar₂TBPs) has been developed, based on 2 + 2 condensation of dipyrromethanes followed by oxidative aromatization. Two pathways to Ar₂TBPs were investigated: the tetrahydroisindole pathway and the dihydroisindole pathway. In the tetrahydroisindole pathway, precursor 5,15-diaryltetracyclohexenoporphyrins (5,15-Ar₂TCHPs) were assembled from cyclohexeno-fused *meso*-unsubstituted dipyrromethanes and aromatic aldehydes or, alternatively, by way of the classical MacDonald synthesis. In the first case, scrambling was observed. Aromatization by tetracyclone was more effective than aromatization by DDQ but failed in the cases of porphyrins with electron-withdrawing substituents in the *meso*-aryl rings. The dihydroisindole pathway was found to be much superior to the tetrahydroisindole pathway, and it was developed into a general preparative method, consisting of (1) the synthesis of 4,7-dihydroisindole and its transformation into *meso*-unsubstituted dipyrromethanes, (2) the synthesis of 5,15-diaryloctahydrodipyrromethanes (5,15-Ar₂OHTBPs), and (3) their subsequent aromatization by DDQ. Ar₂TBP free bases exhibit optical absorption spectra similar to those of *meso*-unsubstituted tetrabenzoporphyrins and fluoresce with high quantum yields. Pd complex of Ph₂TBP was found to be highly phosphorescent at room temperature.

Introduction

π -Extended porphyrins form a class of porphyrinoids in which pyrrole rings are fused with external aromatic fragments via the β -carbon atoms. The best known representatives of this class are symmetrically π -extended porphyrins, such as tetrabenzoporphyrins and tetranaphthoporphyrins, whose optical and other properties attract interest in materials research,¹ biomedical imaging and sensing,² up-conversion of noncoherent NIR light,³ and photodynamic and boron neutron-capture therapy.⁴

Until recently, synthetic approaches to tetrabenzo- and tetranaphthoporphyrins were limited by the so-called “template condensation” method and variants thereof,⁵ which require severe reaction conditions and prohibit introduction of many useful functionalities into the macrocycle. In the search for more practical approaches, efforts were mainly directed toward tetraarylated tetrabenzo- and tetranaphthoporphyrins (Ar₄TBPs and Ar₄TNPs), whose modification can be conveniently accomplished via the *meso*-aryl rings. The method employing oxidative aromatization⁶ has emerged as a straightforward and Ar₄TNPs.⁸ and practical approach to Ar₄TBPs.⁷ The synthesis in this route proceeds via the well-established Lindsey chemistry,⁹ allowing for a variety of functional groups to be placed at the macrocycle

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Supporting Information Available: Additional procedures, details of photophysical experiments, and characterization data for the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

periphery. This strategy was later extended on the synthesis of *meso*-unsubstituted tetrabenzoporphyrins (TBP) and tetranaphthoporphyrins (TNP).¹⁰

Recently, a useful extension of the oxidative aromatization method was developed, which is based on a convenient precursor, 4,7-dihydroisoindole.¹¹ Using this method, we synthesized and for the first time unambiguously characterized *meso*-5,15-diphenyltetrabenzoporphyrin,¹² the simplest representative of the class of 5,15-diaryltetrabenzoporphyrins (Ar_2TBP , Chart 1).¹³ It appeared that the optical absorption spectrum of free base 5,15- Ph_2TBP ($\text{H}_2\text{Ph}_2\text{TBP}$) strongly resembled the spectra of *meso*-unsubstituted H_2TBP s,^{10,14} suggesting that $\text{H}_2\text{Ar}_2\text{TBP}$ s also possess undistorted planar geometries¹⁵ and highly emissive excited states.^{2a,14,16} The combination of the red absorption, strong emissivity, and ease of functionalization suggests that Ar_2TBP s can be utilized in a wide variety of applications, including biomedical imaging, optical sensing, and PDT.

CHART 1.
5,15-Diaryltetrabenzoporphyrin (Ar_2TBP)

In addition to forming a distinct group among π -extended porphyrins, Ar₂TBPs belong to a much wider family of *meso*-5,15-diarylporphyrins (Ar₂Ps). Ar₂Ps have been known since 1968,¹⁷ and over the years, they have become one of the most widely used building blocks for construction of porphyrin-based macrostructures. The latter include, but are not limited to, porphyrin dimers,¹⁸ linear¹⁹ and branched²⁰ arrays, models of the photosynthetic antenna and reaction center,²¹ supramolecular assemblies,²² strapped porphyrins, including biomimetic models,²³ porphyrin-based catenanes and rotaxanes,²⁴ dyads and triads in combination with other electro- and/or optically active fragments,²⁵ and scaffolds for chiral organopalladium complexes.²⁶ Ar₂Ps have also been studied as agents for PDT,²⁷ recognition motifs for aminoacids and other small molecules,²⁸ cores for dendrimers,²⁹ and ligands for DNA intercalation.³⁰

Given such an overwhelming array of applications, it appeared interesting and relevant to complement the Ar₂P family by their π -extended relatives, which on one hand bear the key structural features of Ar₂P but on the other hand possess distinctly different optical properties. In this paper, we report a detailed account on the synthesis of Ar₂TBPs with variously substituted *meso*-aryl groups, suitable for further functionalization.

Results and Discussion

I. Synthesis of Ar₂TBPs via Tetrahydroisoindole Route. Assembly of Precursor Porphyrins (Ar₂TCHPs)

Initially, we examined the approach to Ar₂TBPs via aromatization of 5,15-diarylhexadecahydrotetrabenzoporphyrins or, simpler, 5,15-diaryltetracyclohexenoporphyrins (Ar₂TCHPs), using the methodology developed earlier for Ar₄TBPs and TBPs.^{7,8} Ar₂TCHPs can be assembled using either of the two orthogonal pathways, **A** and **B/B'**, depicted in Scheme 1.

Route **A** is based on the acid-catalyzed condensation of *meso*-unsubstituted dipyrromethanes with aromatic aldehydes.^{17,31} This route has been used in the past for preparation of various types of 5,15-diaryloctaalkylporphyrins.^{21,31b,32} The alternative route has two major variants: **B**, the classical MacDonald's method,³³ in which the substituent-free methine groups in the target porphyrin originate from the formyl groups in 1,9-diformyldipyrromethanes, and **B'**, the method of Baldwin et al.,³⁴ which makes use of the condensation of 1,9-unsubstituted 5-aryldipyrromethanes with orthoformate. A variant of the latter reaction, employing *N,O*-acetal of formaldehyde (EtOCH₂NBn₂), has been used to synthesize Ar₂TCHPs,³⁵ but the practical value of this method was undermined by a significant degree of scrambling.

Our goal was to establish the simplest, most versatile approach to Ar₂TCHPs and, at the same time, allow alternative protection-deprotection schemes in the syntheses of intermediate pyrrole derivatives, permitting different types of sensitive peripheral functionalities.³⁶ Potentially, approach **A** could lead to scrambling since formation of the methylene bridges between pyrrole residues is reversible under acidic conditions.³⁷ Nevertheless, this route appeared more simple and straightforward, as it required only one dipyrromethane derivative.

In route **A**, *meso*-unsubstituted dipyrromethane **3** was synthesized in high yield using a published procedure³⁸ from readily available tetrahydroisoindole ester **1a**³⁹ and introduced into the condensation with aromatic aldehydes to afford Ar₂TCHPs **4a-e** in good overall yields (Scheme 2).

MALDI-TOF MS analysis revealed that in the majority of cases scrambling was insignificant, and only small amounts of "defective" porphyrins (i.e., monoaryl- or *meso*-unsubstituted) could be detected in reaction mixtures. However, in the case of strongly electrophilic

pentafluorobenzaldehyde, extensive scrambling occurred, yielding a mixture of porphyrins with one, two, or no *meso*-aryl groups. As a result, porphyrin **4e** could not be isolated in the pure form.

The classical MacDonald's synthesis (pathway **B** in Scheme 1) requires two dipyrromethane derivatives: dialdehyde and diacid. The common precursors of both components are *tert*-butyl esters of 5-aryldipyrromethane-1,9-dicarboxylic acids **5a-c**, which were synthesized as shown in Scheme 3.

The yields of esters **5a-c** could be improved significantly in the presence of anhydrous tetrabutylammonium chloride. Condensation of pyrrole-2-carboxylates with aldehydes usually results in yields not exceeding 60-70%, which is likely to be caused by side reactions, promoted by strong acids in the presence of the liberated water. Addition of anhydrous Bu₄NCl, a highly hygroscopic compound, raised the yields of dipyrromethanes **5a-c** nearly up to quantitative, suggesting the salt effected water scavenging.⁴⁰ Notably, in the original MacDonald synthesis, water was sometimes removed by azeotropic distillation.⁴¹

Diesters **5a-c** were further converted into 1,9-unsubstituted dipyrromethanes **6a-c** or, alternatively, *ipso*-formylated to give 1,9-diformyldipyrromethanes **7a-c** for the following porphyrin synthesis. Since the synthesis of **6a-c** and the Lindsey reaction⁹ required practically the same conditions, **6a-c** could be used without isolation and purification. The acid-catalyzed ester cleavage/decarboxylation of **5a-c** was followed by the immediate addition of diformyldipyrromethanes **7a-c** and oxidation by DDQ to afford target porphyrins **4a-c** in good yields.

MALDI MS analysis of the crude reaction mixtures containing **4a-c** did not reveal any traces of scrambling. Notably, condensation of diformyldipyrromethane with dipyrromethane gives porphodimethene,⁴² but not porphyrinogen—the key intermediate in the type **A** condensations (Scheme 1). Porphodimethenes are expected to be much more stable toward the acid-catalyzed cleavage. Unlike porphyrinogens, whose fission is initiated by protonation of their α -carbons, porphodimethenes contain more basic nitrogen atoms in the azafulvene rings (Scheme 4).⁴³ Besides, even if the *ipso*-protonation was to occur, it would result in an unfavorable σ -complex, destabilized by the pyrrolenine nitrogen on the conjugation path.

For comparison, we have implemented the standard Mac-Donald's protocol, for which dipyrromethanes **6** and **7** had to be isolated and purified. Overall, this method appeared to be less efficient, as it was more labor intensive and fraught with losses due to the poor stability of 1,9-unsubstituted dipyrromethanes.

Aromatization of Ar₂TCHPs Using DDQ—Conversion of tetracyclohexenoporphyrins into tetrabenzoporphyrins requires removal of 16 hydrogens by way of oxidative aromatization.⁶ For this reaction, Ar₄TCHPs need to be first transformed into their metal complexes,^{7a} whereas *meso*-unsubstituted TCHPs can be converted into TBPs with or without metalation.¹⁰

Our attempts to synthesize Ar₂TBPs by oxidizing metalated Ar₂TCHPs surprisingly turned out unsuccessful. First of all, the metalation itself appeared to be difficult because of the very poor solubility of **4a-c** free bases (H₂Ar₂TCHP). For example, prolonged refluxing of H₂Ar₂TCHPs with Zn or Cu salts in common solvents (CHCl₃, CHCl₃/MeOH, MeCN, or DMF) gave only traces of the corresponding metal complexes, while the attempts to insert Pd in either DMF or PhCN simply led to decomposition of the starting porphyrins. Using porphyrin dications (H₄Ar₂TCHP²⁺), which are much more soluble than free bases, improved the metalation yields. In a typical procedure, a mixture containing the dication chloride (or

trifluoroacetate) and, for example, Cu or Zn acetate was brought to reflux in $\text{CHCl}_3/\text{MeOH}$ and treated with triethylamine (Et_3N). The free base, formed instantaneously upon the addition of Et_3N , was metalated prior to aggregation and precipitation. To insert Pd, a similar procedure in benzonitrile was adopted. Metalated Ar_2TCHPs (MAR_2TCHP : M-4, M = Zn, Ni, Cu, Pd) appeared to be much more soluble than the corresponding free bases, especially in CHCl_3 and CH_2Cl_2 .

The second, more serious, problem was encountered during the aromatization step. The protocol developed for the synthesis of MAR_4TBPs ,⁷ that is, treatment of MAR_2TCHPs with DDQ in boiling solvents, failed to give MAR_2TBPs . Analysis of the reaction mixtures revealed that aromatization of MAR_2TCHPs occurred very slowly and never came to completion. MAR_2TCHPs remained largely unaffected even when DDQ was activated by Lewis acids (e.g., $\text{Sc}(\text{OTf})_3$). Initially, we speculated that *meso*-unsubstituted porphyrins undergo oxidative oligomerization,⁴⁴ which could account for the disappearance of both DDQ and the starting metalloporphyrins. However, MALDI MS spectra showed no presence of dimers or trimers. Lower reactivity of MAR_2TCHPs compared to that of either MAR_4TCHPs or MTCHPs remains to be understood.

We further attempted to carry out aromatization of Ar_2TCHPs without premetalation^{6a}—a strategy employed successfully in the synthesis of *meso*-unsubstituted TBPs.¹⁰ Refluxing free bases **4** in toluene with DDQ indeed effected some oxidation, although complete conversions could not be achieved. Therefore, in terms of reactivity, $\text{H}_2\text{Ar}_2\text{TCHPs}$ occupy an intermediate position between $\text{H}_2\text{Ar}_4\text{TCHPs}$, which are altogether inactive in aromatization,^{7a} and *meso*-unsubstituted H_2TCHPs , which can be fully aromatized by DDQ.¹⁰ Such trend in the reactivity could be a consequence of different basicities of the respective free bases;⁴⁵ that is, more basic $\text{H}_2\text{Ar}_4\text{TCHPs}$ form dications easier than H_2TCHPs , and dications are inactive in aromatization. Another possible reason for lower reactivity of $\text{H}_2\text{Ar}_2\text{TCHPs}$ is their poor solubility.

The yields of aromatization were greatly improved by using molten naphthalene as a solvent. We have found that molten naphthalene provides an excellent solubilizing medium for poorly soluble porphyrins. However, in this particular reaction, the role of naphthalene could not be fully explained by its solubilizing capacity. No other high-boiling solvent, such as di- or trichlorobenzenes, benzonitrile, nitrobenzene, or durene, was as effective as naphthalene, but at the same time, aromatization in mixtures containing small amounts of naphthalene was in some cases as effective as that in neat naphthalene.

The reaction of $\text{H}_2\text{Ar}_2\text{TCHPs}$ **4a-d** with DDQ in molten naphthalene at 180–190 °C resulted in the full conversion after about 10 h. Unfortunately, MALDI MS analysis revealed the presence of chlorinated Ar_2TBPs as satellite products, and similar results were obtained when PhCN was used as a solvent for aromatization of Pd complexes (**Pd-4**). Preparative separation of Ar_2TBPs from chlorinated Ar_2TBPs is not feasible since introduction of the chlorine atom (s) into a large porphyrin molecule produces only negligible effect on its chromatographic mobility.

In summary, all attempts to use DDQ for aromatization of Ar_2TCHPs failed to produce pure Ar_2TBPs . The reactions were either incomplete or suffered from inseparable byproduct.

Aromatization of Ar_2TCHPs Using Tetracyclone—Recently, we have found that 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) provides an effective alternative to DDQ in aromatization of porphyrins.⁴⁶ Tetracyclone is not a single electron-transfer agent, and therefore, it is incapable of inducing oxidative oligomerization. On the other hand, it does not contain chlorine atoms. Heating of porphyrins **4a-d** with tetracyclone in the absence of solvent at 180–230° (Scheme 5) led to their complete aromatization into Ar_2TBPs . MALDI MS analysis

revealed only two products in the reaction mixtures (i.e., Ar₂TBPs **8a-d**) and the Diels-Alder adducts of the intermediate porphyrins and tetracyclone, which were aromatized by way of CO extrusion.⁴⁷ The byproduct did not form in large quantities, and Ar₂TBPs could be purified by chromatography.

Porphyrins **8a** (Ar = Ph) and **8c** (Ar = 4-BrC₆H₄) were obtained in moderate yields; however, yields of **8b** and **8d** were quite low. Even prolonged heating of the corresponding precursors with tetracyclone resulted in very low conversions. The reason for such dramatic difference in reactivity of Ar₂TCHPs with different substituents in the *meso*-aryl rings remains unclear.

In conclusion, because of the problems arising at the stage of aromatization, tetrahydroisondole approach as a whole was not regarded as general, although in certain cases, it was a relatively straightforward and cost-effective way to Ar₂TBPs.

II. Synthesis of Ar₂TBPs via Dihydroisondole Route

Recently, we have demonstrated that problems associated with oxidative aromatization in the synthesis of tetrabenzoporphyrins can be effectively overcome by employing 4,7-dihydroisondoles.¹¹ The latter compounds lead to precursor porphyrins with fewer hydrogen atoms in the pendant rings, facilitating aromatization. Earlier, we have shown that reduction in the number of hydrogens greatly improved the efficiency of aromatization in a similar synthesis of Ar₄TNPs.⁸

4,7-Dihydroisondoles are studied very scarcely, although the first representative of this class was synthesized over 60 years ago.⁴⁸ An early attempt to approach π -extended porphyrins via dihydroisondole—the closest relative of thermodynamically unstable 2*H*-isondole—was performed by Fuhrhop et al. in 1985⁴⁹ but was unsuccessful. 4,7-Dihydroisondole was prepared using the classical Paal-Knorr chemistry (Scheme 6A) under conditions which probably harmed the electron-rich pyrrole ring. The apparent instability of 4,7-dihydroisondole led researchers to conclude that it was not a useful intermediate in the porphyrin chemistry. It turned out that changing the conditions made it possible to isolate 4,7-dihydroisondole, which proved to be an extremely practical synthon on the way to tetrabenzoporphyrins.

4,7-Dihydroisondole is accessible in three major steps from readily available tosylacetylene (Scheme 6B).¹¹ A modified variant of the Barton-Zard reaction⁵⁰ (Scheme 6B) allows synthesis of 2-alkoxycarbonyl derivatives of 4,7-dihydroisondole, which are perfectly stable and, in fact, do not differ much in their chemical behavior from well-known and much studied β -disubstituted 2-alkoxycarbonylpyrroles. Removal of the alkoxycarbonyl group can be accomplished either under acidic (trifluoroacetic acid in CH₂Cl₂) or basic (reflux with KOH in ethylene glycol) conditions. In either case, the double bond remains intact.

Similarity in the behavior of 4,7-dihydroisondole and tetrahydroisondole enabled us to directly apply methods developed for the tetrahydroisondole pathway to the syntheses originating in 4,7-dihydroisondole. Both routes shown in Scheme 1 (**A** and **B**) were realized in this pathway, leading to precursor 5,15-diaryloctahydrodibenzoporphyrins (Ar₂OHTBPs).

Route **B** (Scheme 7) almost entirely matched its tetrahydroisondole analogue (see Scheme 3).

Similar to the synthesis depicted in Scheme 3, addition of Bu₄NCl improved the yield of dipyrromethane **10a**. In this case, water scavenging was especially beneficial, as in the absence of Bu₄NCl, tarring occurred, and **10a** could be isolated only in a modest yield. Apparently, in

the presence of water, the double bond of the cyclohexadiene ring interferes with acid-catalyzed condensations.

The formylation reaction, leading to dipyrromethane **12a**, gave a somewhat lower yield than the similar reaction in the synthesis of Ar₂TCHPs (Scheme 3). This also could be caused by side reactions, affecting the isolated double bonds in the presence of the strong electrophilic reagent.

In general, route **A** (Scheme 1) when applied to the dihydroisindole pathway appeared to be more reliable than route **B**, and therefore, it was developed into a general preparative protocol (Scheme 8).

meso-Unsubstituted dipyrromethane **15** was obtained in a good yield from 2-ethoxycarbonyl-4,7-dihydroisindole **9a**. Remarkably, the double bond tolerated harsh conditions of the ester cleavage and decarboxylation. Dipyrromethane **15** was introduced into the condensation with aromatic aldehydes under Lindsey conditions to yield the respective Ar₂OHTBPs **13a-e**. These porphyrins were identified in the reaction mixtures by MALDI MS analysis, although they were not isolated and/or characterized. The MALDI spectra revealed only an insignificant degree of scrambling, that is, porphyrins with different numbers of aryl groups. The aromatization was effected directly by changing the solvent to higher-boiling toluene, followed by a short heating with an extra portion of DDQ. Like in the synthesis of Ar₄TNPs,⁸ no metalation was required for aromatization.

Interestingly, in spite of the overall facile reaction, electron-withdrawing groups in *meso*-aryls, especially the nitro group, decreased the rate of aromatization. Porphyrins **13a** and **13d** were oxidized almost instantaneously upon bringing their solutions with DDQ to reflux, porphyrin **13c** had to be refluxed for 30 min, but 4-nitrophenyl-substituted porphyrin **13b** could not be completely aromatized even after prolonged heating. For quantitative aromatization, **13b** had to be treated with DDQ in benzonitrile. It is possible that this effect is associated with solubility rather than with electronic factors. In general, contrary to the tetrahydroisindole pathway, aromatization of the precursors was smooth and no traces of chlorination byproduct were observed.

Overall, the dihydroisindole pathway is by far the method of choice for the synthesis of Ar₂TBPs, permitting introduction of various functionalities and giving pure target compounds in good yields.

III. Optical Properties of Ar₂TBPs

In this section, we only briefly outline the optical properties of Ar₂TBPs, leaving the detailed discussion for a separate account.

The optical absorption and fluorescence spectra of porphyrin **8a** are shown in Figure 1A. The optical absorption spectra of free base **8a** (A) are strikingly similar to those of *meso*-unsubstituted H₂TBPs,¹⁴ showing a well-resolved vibronic structure in the Q-band region and a significant (750 cm⁻¹) splitting of the B (Soret) band. This feature is typically attributed to a strong mixing of the Q and B states and to an increase in the oscillator strengths of the Q-bands in TBPs compared to regular nonextended porphyrins.^{14a,51} The fluorescence of **8a** exhibits a sharp band ($\lambda_{\text{max}} = 670$ nm), characterized by a very small Stokes shift (only 2 nm) and a very high for porphyrins quantum yield ($\phi_{\text{fl}} = 0.38$), pointing toward rigid planar structure, similar to that of *meso*-unsubstituted H₂TBP.¹⁵

The Pd complex of **8a**, prepared by refluxing the free base with PdCl₂ in benzonitrile, exhibits spectral properties (Figure 1B) close to those of *meso*-unsubstituted PdTBPs.^{2a,10,16b,52} An

unusual feature of **Pd-8a** is the slight splitting of the Q-band ($\lambda_{\text{max}} = 615 \text{ nm}$) and a shoulder of the main band in the phosphorescence spectrum ($\lambda_{\text{max}} = 796 \text{ nm}$). The latter property is unique for **Pd-8a** and probably for other PdAr_2TBP s since *meso*-unsubstituted PdTBP s and Pd *meso*-tetraaryl-TBP>s exhibit quite symmetrical phosphorescent bands, accompanied by small vibrational satellites. The phosphorescence lifetime of **Pd-8a**, measured in Ar-purged dimethylacetamide solution, was found to be $490 \mu\text{s}$, and on air, the phosphorescence was completely quenched. The phosphorescence quantum yield in the absence of oxygen was 0.19, which is quite high compared to the other Pd tetrabenzoporphyrins.^{7,10} These characteristics suggest suitability of PdAr_2TBP s for oxygen sensing and imaging² as well as for PDT.⁴

Conjugated porphyrin-based molecules are currently under intensive scrutiny as nonlinear optical materials.^{19a,53} Tetrabenzoporphyrins in particular have been investigated as potential two-photon probes for biomedical imaging.^{2g} We have determined that, upon irradiation with 110 fs pulses from a Ti:sapphire laser (76 MHz rep. rate), solutions of **8a** exhibit strong fluorescence, whose intensity was proportional to the square of the excitation flux, confirming that the two-photon absorption was the main process underlying the emission from the singlet excited state (Figure 2).

The two-photon absorption cross-section (σ_2) of **8a**, determined by the relative fluorescence method versus Rhodamine B in methanol ($\sigma_2 = 210 \text{ GM}$,⁵⁴ $\lambda_{\text{ex}} = 840 \text{ nm}$, $\phi_{\text{fl}} = 0.555$), was found to be 28 GM ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$), which is several times higher than the values reported for regular nonextended porphyrins.⁵⁶ This value is consistent with other measurements performed on tetrabenzoporphyrins,⁵⁷ confirming that π -extension has a profound effect on nonlinear absorption of tetrapyrroles.

In conclusion, Ar_2TBP s possess an array of useful optical properties. They combine strong emissivity of the planar TBP system and enhanced two-photon absorption cross-sections with the possibility of derivatization via functional substituents in the *meso*-aryl rings. These characteristics suggest a wide array of utilities, including biomedical imaging, sensing, and nonlinear optical applications. The developed method of synthesis provides a general route to Ar_2TBP s with various substituents, facilitating engagement of these molecules into applied research.

Experimental Part

For general description of methods, see Supporting Information. Tetrahydroisindole esters **1a** and **1b**³⁹ and dihydroisindole **9b**¹¹ were synthesized as described previously.

Bis(3-ethoxycarbonyl-4,5,6,7-tetrahydro-2H-isindolyl)methane (**2**)

A mixture of 2-ethoxycarbonyl-4,5,6,7-tetrahydro-2H-isindole **1a** (1.93 g, 10 mmol), dimethoxymethane (0.38 g, 5 mmol), and *p*-toluenesulfonic acid (0.095 g, 0.5 mmol) was dissolved in acetic acid (50 mL). The mixture was stirred at room temperature for 24 h and poured into cold water (200 mL). The precipitate formed, and it was collected by filtration, dried in vacuum over P_2O_5 , and recrystallized from ethanol: yield 1.79 g (90%), white powder, mp 210–211 °C; ^1H NMR (CDCl_3 - d_6 -DMSO) δ 10.86 (br s, 2H), 4.15 (q, $J = 7.11 \text{ Hz}$, 4H), 3.60 (s, 2H), 2.62 (m, 4H), 2.38 (m, 4H), 1.60 (m, 8H), 1.23 (t, $J = 7.11 \text{ Hz}$, 6H); ^{13}C NMR (CDCl_3 - d_6 -DMSO) δ 161.2, 129.7, 127.5, 117.3, 115.7, 58.7, 22.9, 22.8, 22.8, 21.2, 20.9, 14.2. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_4$ (398.49): C, 69.32; H, 7.59; N, 7.03. Found: C, 69.40; H, 7.50; N, 7.31.

Bis(4,5,6,7-tetrahydro-2*H*-isoindolyl)methane (**3**) and Bis(4,7-dihydro-2*H*-isoindolyl)methane (**15**)

A mixture of the corresponding dipyrromethane **2** or **14** (3 mmol), KOH (18 mmol, 1.00 g) and ethylene glycol (30 mL) was refluxed under argon for 1 h. The mixture was cooled to room temperature, diluted with CH₂Cl₂ (50 mL), and washed with water (5 × 100 mL) and saturated brine (20 mL). The mixture was concentrated by evaporation in vacuum, passed through a short silica gel column (5 cm, eluent: CH₂Cl₂), and evaporated in vacuum to dryness. The obtained dipyrromethane was either immediately used in the porphyrin synthesis without further purification or stored at -18 °C.

Ar₂TCHPs (**4a-d**) via Route A (Scheme 2)

Dipyrromethane **3** (1 mmol, 0.25 g) and aromatic aldehyde (1 mmol) were dissolved in CH₂Cl₂ (60 mL) and freshly distilled over CaH₂. The mixture was stirred for 10 min under Ar, and trifluoroacetic acid (TFA) (0.135 mmol, 0.015 g) was added and the mixture stirred for 6 h. A solution of DDQ (1.5 mmol, 0.34 g) in toluene (20 mL) was added, and the mixture was stirred for an additional 2 h, evaporated in vacuum, and chromatographed on silica gel (eluent: CH₂Cl₂/Et₃N, 100:1 v/v). Fractions containing the desired porphyrins (selected by UV-vis spectroscopy) were combined, evaporated in vacuum to dryness, treated with TFA (0.02 mL), dried in vacuum, and precipitated from CH₂Cl₂ solution as free bases upon addition of diethyl ether.

4a—Yield 0.16 g (48%), dark red crystalline powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) λ_{max} (log ε) 426 (5.62), 566 (4.28), 610 (3.93); ¹H NMR (CDCl₃/TFA) δ 10.12 (s, 2H), 8.22 (m, 4H), 7.88 (m, 6H), 3.78 (m, 8H), 2.66 (m, 8H), 2.31 (m, 8H), 1.73 (m, 8H), -2.14 (br s, 4H); ¹³C NMR (CDCl₃/TFA) δ 142.6, 140.6, 139.1, 138.5, 138.2, 134.9, 130.0, 128.7, 119.3, 96.7, 25.2, 23.6, 22.9, 22.1; ESI HRMS *m/z* 679.3823; calcd for C₄₈H₄₇N₄ (MH⁺) 679.3801.

4b—Yield 0.049 g (13%), dark red crystalline powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) λ_{max} (log ε) 432 (5.47), 568 (4.28), 614 (3.91); ¹H NMR (CDCl₃/TFA) δ 10.18 (s, 2H), 8.77 (m, 4H), 8.49 (m, 4H), 3.79 (m, 8H), 2.63 (m, 8H), 2.33 (m, 8H), 1.76 (m, 8H), -1.94 (br s, 4H); ¹³C NMR (CDCl₃/TFA) δ 148.9, 143.6, 141.4, 139.8, 137.7, 135.8, 123.7, 116.5, 97.7, 25.7, 23.6, 22.8, 21.9; MALDI-TOF MS *m/z* 768.96; calcd for C₄₈H₄₅N₆O₄ (MH⁺) 769.35.

4c—Yield 0.11 g (27%), dark red crystalline powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) λ_{max} (log ε) 428 (5.61), 562 (4.26), 612 (3.83); ¹H NMR (CDCl₃/TFA) δ 10.14 (s, 2H), 8.12 (m, 4H), 8.05 (m, 4H), 3.78 (m, 8H), 2.70 (m, 8H), 2.33 (m, 8H), 1.77 (m, 8H), -2.24 (br s, 4H); ¹³C NMR (CDCl₃/TFA) δ 142.3, 140.9, 139.3, 138.1, 137.0, 136.3, 132.1, 125.3, 117.7, 97.0, 25.5, 23.6, 22.9, 22.0; MALDI-TOF MS *m/z* 836.77; calcd for C₄₈H₄₅Br₂N₄ (MH⁺) 837.20.

4d—Yield 0.24 g (60%), dark red crystalline powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) λ_{max} (log ε) 428 (5.59), 568 (4.23), 612 (3.82); ¹H NMR (CDCl₃/TFA) δ 10.18 (s, 2H), 8.58 (m, 2H), 8.35 (m, 2H), 4.15 (s, 3H), 3.79 (m, 8H), 2.65 (m, 8H), 2.32 (m, 8H), 1.74 (m, 8H), -2.37 (br s, 4H); ¹³C NMR (CDCl₃-TFA) δ 167.1, 142.0, 141.7, 140.9, 139.6, 138.3, 135.0, 131.3, 129.8, 118.0, 97.2, 52.8, 25.4, 23.5, 22.8, 21.9; ESI HRMS *m/z* 795.3878; calcd for C₅₂H₅₁N₄O₄ (MH⁺) 795.3905; MALDI-TOF MS *m/z* 795.33; calcd for C₅₂H₅₁N₄O₄ (MH⁺) 795.39.

Arylbis(3-*tert*-butoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindolyl)-methanes (**5a-c**)

p-Toluenesulfonic acid (0.25 mmol, 0.048 g) and *n*-tetrabutylammonium chloride (0.1 mmol, 0.028 g) were added to a solution of 2-*tert*-butoxycarbonyl-4,5,6,7-tetrahydro-2*H*-isoindole

1b (5 mmol, 1.105 g) and the corresponding aldehyde (2.5 mmol) in CHCl_3 (50 mL). The reaction mixture was stirred at room temperature under argon for 12 h, washed by NaHCO_3 (10% aqueous solution, 20 mL) and saturated brine (20 mL), and dried over Na_2SO_4 . The solution was evaporated to dryness, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 5:1). The fractions containing the target dipyrromethane were identified by TLC (silica gel plates, eluent: petroleum ether/ethyl acetate, 5:1). Upon heating to 150 °C the spots with R_f 0.85-0.9 turned red. These fractions were combined and evaporated to dryness.

5a—Yield 1.26 g (95%), orange amorphous solid; ^1H NMR (CDCl_3) δ 8.27 (br s, 2H), 7.36-7.26 (m, 3H), 7.12 (m, 2H), 5.39 (s, 1H), 2.78 (m, 4H), 2.17 (m, 4H), 1.69 (m, 8H), 1.54 (s, 18H); ^{13}C NMR (CDCl_3) δ 161.2, 138.8, 129.9, 129.0, 128.2, 127.4, 119.4, 117.8, 80.1, 41.4, 28.5, 23.3, 23.2, 23.1, 21.2. Anal. Calcd for $\text{C}_{33}\text{H}_{42}\text{N}_2\text{O}_4$ (530.70): C, 74.69; H, 7.98; N, 5.28. Found: C, 74.93; H, 8.16; N, 4.94.

5b—Yield 1.22 g (85%), yellow amorphous solid; ^1H NMR (CDCl_3) δ 8.52 (br s, 2H), 8.09 (m, 2H), 7.22 (m, 2H), 5.47 (s, 1H), 2.74 (m, 4H), 2.13 (m, 4H), 1.65 (m, 8H), 1.50 (s, 18H); ^{13}C NMR (CDCl_3) δ 161.2, 147.1, 146.7, 129.2, 128.3, 128.1, 124.1, 119.9, 118.7, 80.6, 40.9, 28.5, 23.3, 23.1, 21.4. Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{N}_3\text{O}_6$ (575.70): C, 68.85; H, 7.18; N, 7.30. Found: C, 68.41; H, 7.47; N, 7.02.

5c—Yield 1.44 g (95%), orange amorphous solid; ^1H NMR (CDCl_3) δ 8.30 (s, 2H), 7.41 (m, 2H), 6.95 (m, 2H), 5.32 (s, 1H), 2.74 (m, 4H), 2.13 (m, 4H), 1.66 (m, 8H), 1.51 (s, 18H); ^{13}C NMR (CDCl_3) δ 161.2, 138.0, 132.1, 130.0, 129.2, 128.2, 121.3, 119.5, 118.1, 80.2, 40.5, 28.5, 23.3, 23.1, 23.1, 21.3. Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{BrN}_2\text{O}_4$ (609.59): C, 65.02; H, 6.78; Br, 13.11; N, 4.60. Found: C, 65.42; H, 6.77; N, 4.21.

Arylbis(3-formyl-4,5,6,7-tetrahydro-2H-isoindolyl)methanes (7a-c)

Dipyrromethanes **5a-c** (2 mmol) were dissolved in TFA (20 mL) under argon. The solution was stirred for 5 min and cooled to 0 °C on an ice bath. Trimethoxymethane (20 mmol, 2.1 g) was added dropwise to the mixture. The mixture was stirred for 15 min at room temperature, diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous NaHCO_3 (2×20 mL) and saturated brine (20 mL), and dried over Na_2SO_4 . The resulting solution was evaporated to dryness, and the remaining solid was chromatographed on silica gel (eluent: $\text{CH}_2\text{Cl}_2/\text{MeOH}$). Compounds **7a-c** could not be recrystallized due to their rather poor solubility, and therefore, they did not give satisfactory elemental analyses.

7a—Yield 0.46 g (60%), gray powder, mp >300 °C; ^1H NMR (CDCl_3) δ 9.85 (br s, 2H), 9.35 (s, 2H), 7.30 (m, 3H), 7.11 (m, 2H), 5.50 (s, 1H), 2.83 (m, 4H), 2.30 (m, 4H), 1.77 (m, 8H); ^{13}C NMR (CDCl_3) δ 176.2, 138.1, 129.0, 128.6, 128.2, 127.5, 127.5, 120.9, 40.4, 23.1, 22.7, 21.0, 20.9.

7b—Yield 0.69 g (80%), gray powder, mp >300 °C; ^1H NMR (CDCl_3 - d_6 -DMSO) δ 11.31 (s, 2H), 9.38 (s, 2H), 8.02 (m, 2H), 7.16 (m, 2H), 5.50 (s, 1H), 2.74 (m, 4H), 2.41 (m, 4H), 1.70 (m, 8H); ^{13}C NMR (d_6 -DMSO) δ 176.8, 147.3, 146.4, 133.7, 129.4, 127.7, 123.6, 120.3, 30.3, 22.8, 22.3, 20.5.

7c—Yield 0.56 g (60%), gray powder, mp >300 °C; ^1H NMR (d_6 -DMSO) δ 11.39 (br s, 2H), 9.43 (s, 2H), 7.51 (m, 2H), 6.99 (m, 2H), 5.56 (s, 1H), 2.75 (m, 4H), 2.40-2.18 (m, 4H), 1.64 (m, 8H); satisfactory ^{13}C NMR spectrum could not be obtained because of the very low solubility.

Ar₂TCHPs (4a-d) via Route B (Scheme 3)

Aryldipyrromethanes **5a-c** (1 mmol) were dissolved in TFA (20 mL) under argon. The solution was stirred for 5 min, diluted with CH₂Cl₂ (50 mL), and added to a solution of the respective diformyldipyrromethane **7a-c** in CH₂Cl₂ (45 mL). The resulting mixture was stirred at room temperature for 4 h, treated with DDQ (1.5 mmol, 0.34 g), and stirred for an additional 2 h. The workup and the isolation of the target compounds were performed as in route A. Yields: **4a** 0.07 g (20%), **4b** 0.10 g (26%), **4c** 0.07 g (17%).

Metal Complexes of Porphyrins 4a-c

Porphyrins **4a-c** (0.1 mmol) were dissolved in TFA (0.2 mL), and the solution was evaporated to dryness. The remaining solid was dissolved in CH₂Cl₂ (50 mL), and a solution of Cu or Zn acetate in MeOH (5 mL) was added. The mixture was stirred for 5 min, and Et₃N (0.05 mL) was added in one portion by a pipet. The mixture was stirred for an additional 5 min, transferred to a separatory funnel, washed with water (20 mL) and brine (20 mL), and dried over Na₂SO₄. The solution was concentrated in vacuum to about 10 mL, and the resulting metal complex was precipitated by ether. The crystalline solid was filtered off, washed with ether, and dried. The purity of the metal complex was assessed by MALDI MS analysis and UV-vis spectroscopy.

Aromatization of Porphyrins 4a and 4c by 2,3,4,5-Tetraphenylcyclopentadienone (Tetracyclone) (Scheme 5)

A mixture of the porphyrin (**4a** or **4c**) (0.1 mmol) and tetracyclone (2.6 mmol, 1 g) was placed into a high-pressure glass tube, which was purged with Ar and closed with a PTFE screw cap. The mixture was heated to at 230 °C and kept under stirring for 3 h. After cooling to the room temperature, the mixture was dissolved in CH₂Cl₂ and chromatographed on silica gel (eluent: CH₂Cl₂). Further purification of porphyrins **8a** and **8c** was achieved by recrystallization from CH₂Cl₂/ether. Yields: **8a** 0.036 g (55%), **8c** 0.037 g (45%). See the analytical data for porphyrins **8a** and **8c** below.

2-Ethoxycarbonyl-4,7-dihydro-2H-isoindole (9a)

9a was obtained by the method used previously for the synthesis of *tert*-butyl ester **9b**:¹¹ yield 73%, white powder, mp 87-88 °C; ¹H NMR (CDCl₃) δ 8.97 (br s, 1H), 6.70 (m, 1H), 5.87 (m, 2H), 4.30 (q, *J* = 7.12 Hz, 2H), 3.43 (m, 2H), 3.22 (m, 2H), 1.35 (t, *J* = 7.12 Hz, 3H); ¹³C NMR (CDCl₃) δ 161.6, 124.9, 124.4, 123.8, 118.9, 117.5, 59.8, 24.0, 22.3, 14.5. Anal. Calcd for C₁₁H₁₃NO₂ (191.23): C, 69.09; H, 6.85; N, 7.32. Found: C, 68.77; H, 7.00; N, 7.03.

Bis(3-ethoxycarbonyl-4,7-dihydro-2H-isoindolyl)methane (14)

Compound **14** was obtained from **9a** by the same procedure as used in the synthesis of dipyrromethane **2**: yield 1.81 g (92%), white powder, mp 269-270 °C; ¹H NMR (CDCl₃-d₆-DMSO) δ 11.21 (br s, 2H), 5.76 (m, 4H), 4.18 (q, *J* = 7.08 Hz, 4H), 3.71 (s, 2H), 3.25 (m, 4H, overlapped with solvent), 3.00 (m, 4H), 1.26 (t, *J* = 7.08 Hz, 4H); ¹³C NMR (CDCl₃-d₆-DMSO) δ 160.7, 129.3, 124.0, 123.9, 123.1, 115.3, 114.2, 58.6, 23.8, 21.6, 21.4, 14.2. Anal. Calcd for C₂₃H₂₆N₂O₄ (394.46): C, 70.03; H, 6.64; N, 7.10. Found: C, 69.88; H, 6.34; N, 6.85.

Ar₂TBPs 8a-d via Dihydroisoindole Pathway (Scheme 8)

Freshly prepared dipyrromethane **15** (1 mmol, 0.25 g) was dissolved in CH₂Cl₂ (60 mL), distilled over CaH₂, and the aromatic aldehyde (1 mmol) was added to this solution. The mixture was stirred under Ar at room temperature for 10 min and treated with TFA (0.135 mmol, 0.015 g). The reaction mixture was stirred at room temperature for 4 h, treated with DDQ (1.5 mmol, 0.34 g) in toluene (20 mL), and stirred for an additional 2 h. The solution

was evaporated to dryness, and the residue was dissolved in either toluene (30 mL, **8a,c,d**) or in benzonitrile (30 mL, **8b**). DDQ (2 mmol, 0.45 g) was added, and the mixture was refluxed for 5–30 min under Ar. The reaction was monitored by UV-vis spectroscopy. The solvent was removed in vacuum, and the residue was purified by chromatography on silica gel (eluent: CH₂Cl₂). Emerald green fractions were collected, combined, and evaporated to dryness. The residue was treated with TFA (0.01 mL) and dried in vacuum. The porphyrins were additionally purified by reprecipitation from CH₂Cl₂ solutions by ether. Porphyrins **8a–e** were isolated as free bases.

8a—Yield 0.073 g (22%), the material was characterized in ref ¹¹.

8b—Yield 0.056 g (15%), green powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) $\lambda_{\max}$ (log ϵ) (CH₂Cl₂) as free base 394 (4.92), 420 (5.70), 436 (5.62), 570 (4.64), 612 (4.99), 666 (4.75); ¹H NMR (CDCl₃/TFA) δ 11.01 (s, 2H), 9.36 (d, J = 7.96 Hz, 4H), 8.32 (m, 4H), 8.24 (m, 4H), 8.20 (m, 4H), 7.94 (m, 4H), 7.69 (d, J = 8.34 Hz, 4H), -0.35 (br s, 4H); ¹³C NMR (CDCl₃/TFA) δ 139.9, 139.0, 137.3, 136.0, 133.4, 132.9, 131.9, 130.8, 130.6, 125.9, 125.2, 123.6, 114.9, 92.4; LDI-TOF MS m/z 752.17; calcd for C₄₈H₂₈N₆O₄ (M⁺) 752.22. Anal. Calcd for C₄₈H₂₈N₆O₄·0.33Et₂O: C, 76.21; H, 4.06; N, 10.81. Found: C, 76.07; H, 4.20; N, 10.73.

8c—Yield 0.041 g (10%), green powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) $\lambda_{\max}$ (log ϵ) as dication 454 (5.67), 616 (4.30), 672 (4.84), as free base 394 (4.78), 422 (5.64), 436 (5.71), 570 (4.35), 610 (4.88), 666 (4.59); ¹H NMR (CH₂Cl₂/TFA) δ 11.00 (s, 2H), 9.36 (d, J = 7.96 Hz, 4H), 8.36 (m, 4H), 8.22 (m, 8H), 7.93 (m, 4H), 7.70 (d, J = 8.21 Hz, 4H), 0.02 (br s, 4H); ¹³C NMR (CDCl₃/TFA) δ 139.9, 139.0, 137.4, 136.0, 133.3, 132.9, 131.9, 130.6, 130.4, 125.8, 125.2, 123.5, 114.9, 92.4; ESI HRMS m/z 819.0765; calcd for C₄₈H₂₉N₄Br₂ (MH⁺) 819.0759.

8d—Yield 0.105 g (27%), green powder, mp >300 °C; UV/vis (CH₂Cl₂/TFA) $\lambda_{\max}$ (log ϵ) as dication salt 454 (5.64), 618 (4.40), 672 (4.92), (CH₂Cl₂) as free base 394 (4.90), 422 (5.59), 436 (5.62), 570 (4.52), 610 (4.93), 666 (4.72); ¹H NMR (CH₂Cl₂/TFA) δ 11.04 (s, 2H), 9.37 (d, J = 7.96 Hz, 4H), 8.73 (m, 4H), 8.60 (m, 4H), 8.22 (m, 4H), 7.88 (m, 4H), 7.60 (d, J = 8.21 Hz, 4H), 4.25 (s, 6H), -0.24 (br s, 4H); ¹³C NMR (CH₂Cl₂/TFA) δ 168.1, 142.7, 139.4, 139.2, 134.8, 133.0, 131.9, 131.8, 131.2, 130.8, 130.7, 125.2, 123.7, 115.0, 92.7, 53.4; LDI-TOF MS m/z 778.11; calcd for C₅₂H₃₄N₄O₄ (M⁺) 778.26. Anal. Calcd for C₅₂H₃₄N₄O₄·0.5Et₂O: C, 79.49; H, 4.82; N, 6.87. Found: C, 79.30; H, 4.72; N, 6.74.

8e—Yield 0.14 g (32%), green crystals, mp > 300 °C; UV/vis (CH₂Cl₂/TFA) $\lambda_{\max}$ (log ϵ) (CH₂Cl₂) as free base 394 (4.85), 420 (5.51), 438 (5.55), 570 (4.44), 612 (4.86), 666 (4.70); ¹H NMR as dication (CH₂Cl₂/TFA) δ 10.97 (s, 2H), 9.32 (d, J = 7.83 Hz, 4H), 8.33 (d, J = 1.01 Hz, 4H), 8.15 (dd, J_{app} = 7.33 Hz, 4H), 8.13 (d, 2H, overlapped), 7.80 (dd, J_{app} 7.83 Hz, 4H), 7.60 (d, J = 8.08 Hz, 4H), 1.55 (s, 36H), 0.49 (br s, 4H); ¹H NMR as free base (CH₂Cl₂) δ 11.13 (s, 2H), 9.70 (d, J = 6.94 Hz, 4H), 8.19 (m, 4H), 8.12 (m + d overlapped, 6H), 7.77 (m, 4H), 7.51 (m, 4H), 1.57 (s, 36H), -1.33 (br s, 2H); ¹³C NMR (CH₂Cl₂) δ 151.7, 141.8, 139.0, 138.9, 137.2, 127.2, 127.0, 126.7, 125.3, 122.0, 120.8, 117.8, 92.8, 35.4, 31.7; ESI HRMS m/z 887.5054; calcd for C₆₄H₆₃N₄ (MH⁺) 887.5053.

Pd-8a

Porphyrin **8a** (11 mg, 0.017 mmol) was dissolved in PhCN (5 mL) and heated to about 100 °C. PdCl₂ (10 mg, 0.056 mmol) was added, and the mixture was refluxed under Ar. The reaction was stopped when the absorption bands of the free base porphyrin disappeared. Complete conversion required refluxing for about 2 h. The solvent was evaporated in vacuum. The remaining emerald green solid was dissolved in a small volume of CH₂Cl₂ (~3 mL) and chromatographed a silica gel column (Ø2 × 20 cm, eluent: CH₂Cl₂). The emerald green band

was collected, and evaporation of the solvent gave **Pd-8a** as a dark green powder: yield 11 mg (86%); ^1H NMR ($\text{DMF-}d_7$, 100 °C) δ 11.11 (s, 2H), 9.75 (s, 4H), 8.64 (aa'bb', $J_1 = 6.83$ Hz, $J_2 = 1.46$ Hz, 4H), 8.30 (t, $J = 6.8$ Hz, 4H), 8.06 (overlapped with solvent), 7.60 (m, 4H), 7.23 (d, $J = 7.71$ Hz, 4H); MALDI-TOF (m/z) calcd for $\text{C}_{48}\text{H}_{28}\text{N}_4\text{O}_{12}\text{Pd}$ 767.2, found 770.9 [$\text{M} + \text{H}^+$].

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FIGURE 1.

Absorption and emission (insets) spectra of **8a** (A) in toluene and of **Pd-8a** (B) in Ar-purged dimethylacetamide at 23 °C. A (inset): fluorescence, $\lambda_{\text{ex}} = 571$ nm, $\phi_{\text{fluor}} = 0.38$. B (inset): phosphorescence, $\lambda_{\text{ex}} = 610$ nm, $\phi_{\text{phos}} = 0.19$.

FIGURE 2.

Fluorescence of **8a** induced by two-photon absorption at 840 nm (110 fs, 76 MHz rep. rate) and its dependence on the incident laser power (inset). The data points (integrated fluorescence intensity (I) versus excitation power (P)) were fitted to a quadratic function $I(P) = aP^2$ (solid line).

SCHEME 1.
Approaches to Ar_2TCHPs

SCHEME 2. Synthesis of Ar₂TCHPs 4a-e Following Route A (Scheme 1)

SCHEME 3.

Synthesis of Ar₂TCHPs 4a-c from 5-Aryldipyrromethanes Following Route B from Scheme 1

SCHEME 4.

Protonation of Porphodimethenes Occurs Predominantly at Their Pyrroline Nitrogens
(*ipso*-Protonation, Required for Scrambling, is Improbable)

SCHEME 5.
Aromatization of Ar₂TCHPs 4a-d by Tetracyclone

SCHEME 6.
Approaches to 4,7-Dihydroisoindole

SCHEME 7.
Synthesis of 5,15-Diphenyloctahydro-tetrabenzoporphyrin

SCHEME 8.

Synthesis of Ar₂TBPs via Dihydroisoinidole Pathway (Route A from Scheme 1)