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Tetraaryltetraanthra[2,3]porphyrins: Synthesis, Structure, and Optical Properties

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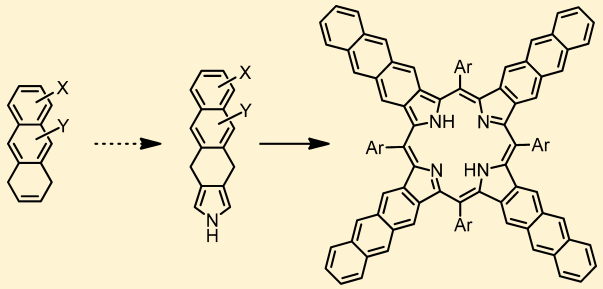
Supporting Information

ABSTRACT: A synthetic route to symmetrical tetraaryltetraanthra[2,3]porphyrins (Ar_4TAPs) was developed. Ar_4TAPs bearing various substituents in *meso*-phenyls and anthracene residues were prepared from the corresponding pyrrolic precursors. The synthesized porphyrins possess high solubility and exhibit remarkably strong absorption bands in the near-infrared region (790−950 nm). The scope of the method, selection of the peripheral substituents, choice of the metal, and their influence on the optical properties are discussed together with the first X-ray crystallographic data for anthraporphyrin.



INTRODUCTION

The fusion of aromatic rings to porphyrin cores received much attention because such modification was expected to have a strong influence on electronic properties of core motifs, particularly reducing HOMO−LUMO gap and shifting the absorption and emission into near-IR. Because of these properties, such porphyrins are attractive for numerous applications, such as NIR photodetectors,[1] photovoltaics,[2] semiconductors,[3] and two-photon absorbing materials.[4] A variety of π-extended porphyrins have been synthesized by fusing benzene,[5] naphthalene,[6] pyrene,[7] azulene,[8] anthracene,[9] corannulene,[10] and other aromatic moieties across the *meso*- and β-positions of porphyrins. Among the π-extended porphyrins, the linear fusion of aromatic rings results in particularly strong red-shift and intensification of Q-band.[11] So far, the best known and most useful representatives of this class are tetrabenzoporphyrins (TBPs, Figure 1) and tetranaphtho-[2,3]porphyrins (TNPs).[12] The effect is manifested only when all four aromatic residues, which can be different (e.g., mixed benzo-naphthoporphyrins reported by Niedermair and co-workers[13]), are linearly annelated to β-positions of porphyrin macrocycle (discussion of annelation modes[12a]). Moreover, linearly annelated extended porphyrins exhibit another important and very interesting trend revealed in their tetra-*meso*-aryl derivatives: the steric repulsion of aryl rings and annelated residues results in a strong distortion of the system. In the domain of regular porphyrins, the distortion inevitably leads to dramatic deterioration of emissive properties. Linearly annelated extended porphyrins, however, were shown to retain a useful level of emissivity upon distortion of the system.[14] Moreover, the distortion at the same time dramatically improves the solubility and processability of such porphyrins, making such huge polyaromatic compounds conveniently handled and modified in contrast to practically insoluble planar annelated porphyrins. Symmetric tetraaryl derivatives are additionally the easiest for synthesis. Such a unique combination of useful properties makes tetraaryl derivatives of linearly annelated extended porphyrins and their metal complexes promising models for materials research,[15] research on biomedical imaging and sensing,[16] triplet−triplet annihilation photon upconversion,[17] and photodynamic and boron neutron-capture therapy.[18] Recently, a far less well-studied representative of this class, tetraanthra[2,3]porphyrins (TAP, Figure 1), was also shown to possess valuable optical properties with respect to upconversion of noncoherent NIR light (800 nm) into visible light (550 nm)[19] and fabrication of organic light emitting diodes.[20]

Comparison of absorption spectra of TBP, TNP, and TAP (Figure 2) demonstrates the trend of changing the optical properties in this series. Annelation of each extra layer of benzo-rings to the porphyrin core has a strong and cumulative effect on the energies of S_1 state of the molecule, similar to what is observed for linear polybenzenoid hydrocarbons (acenes).[21] It is seen from the pronounced red shift of the Q-bands by about 100 nm for each additional ring. On the

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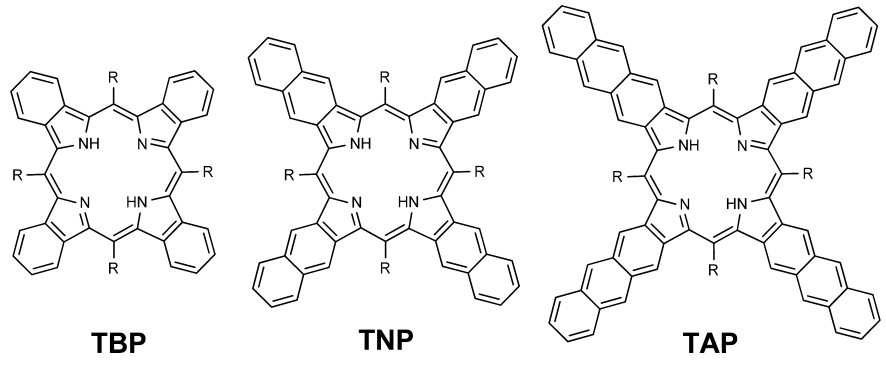


Figure 1. Linearly annelated π-extended porphyrins.

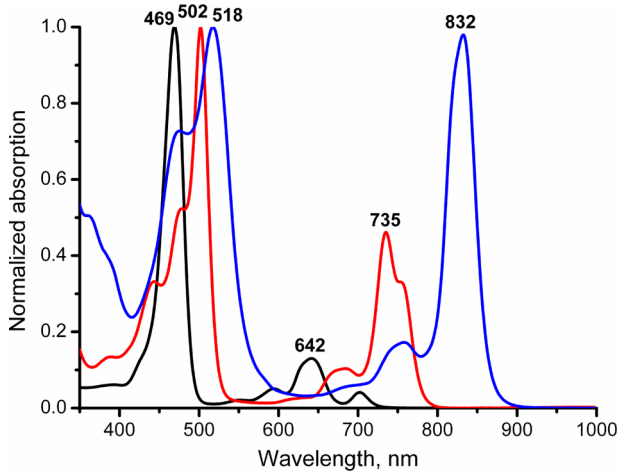


Figure 2. UV–vis absorption spectra of free base Ar_4TBP (black), Ar_4TNP (red), and Ar_4TAP (blue). Ar = 4-MeO_2C–C_6H_4.

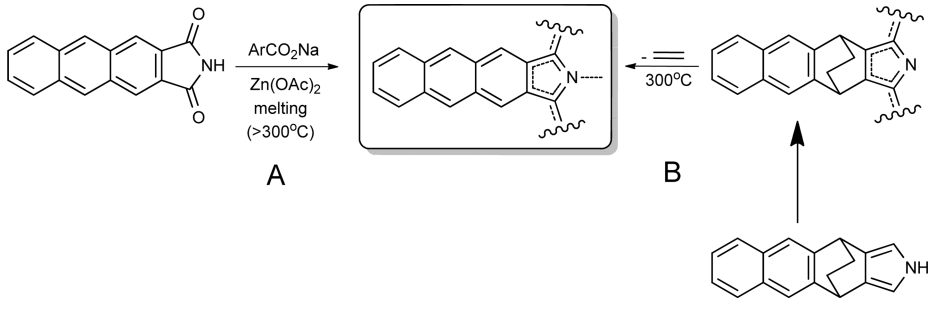
other hand, the effect on S_2 state energies is much less pronounced: the Soret band is shifted only by 20–30 nm. As a result, a "spectral window" between Soret and Q-bands increases from TBP through TNP to TAP, despite bandwidth broadening due to increased molecular size. Moreover, the relative intensity of the Q-band also increases and in the case of TAPs becomes as strong as the Soret band (extinction coefficients $\sim 10^5$ cm mol L^{-1}). These spectral features make TAP a unique representative of π-extended porphyrins. Although some of the reported molecular systems, designed by annelation or fusion of aromatic fragments to the porphyrin core, reach absorptions at as far as 1500 nm,[22] none of them exhibit narrow and symmetrical bands along with a broad "spectral window" in the visible region. These characteristics are crucial if such photonic application as photon up-conversion is targeted.[23]

Despite promising properties, tetraanthraporphyrins have until this time been little studied. As was theoretically predicted, π-extension results in the case of TAPs in the destabilization of the third LUMOs and the first HOMOs that makes it unstable against oxidation and reduction.[24] The first representative of the TAP family was prepared by Kobayashi and co-workers,[25] using the Luk'yanets–Kopranenkov high-temperature template condensation method,[26] which resembles the classical procedures of phthalocyanine chemistry. Melting of anthracene-2,3-dicarboxyimide with sodium biphenylacetate in the presence of zinc acetate (Scheme 1, route A) resulted in the formation of zinc complex of triarylsubstituted TAP (aryl = *p*-phenylphenyl). The synthesis of both *meso*-unsubstituted and *meso*-aryl-substituted TAPs was very recently reported by Ono and co-workers using a common approach to extended porphyrins relying on thermal retro-Diels–Alder extrusion of ethylene from bicyclo[2.2.2]octadiene-annelated porphyrins (Scheme 1, route B).[27] Thus obtained materials were reported to be poorly soluble and unstable toward photooxidation.

An obvious drawback of reported syntheses of TAPs is a need for harsh conditions of condensation or aromatization steps, which are poorly compatible with the emerging huge and fragile TAP system. This results in low yields and poor quality of the obtained materials and limits opportunities of introducing functionality to improve solubility and stability or to modulate optical properties.

As an advanced method delivering tetraanthraporphyrins, the dihydroisoindole method based on an oxidative aromatization of the closest partially hydrogenated porphyrin precursor can be applied. It warrants that the conditions of aromatization of the annelated system are as soft as possible and occur spontaneously along with the aromatization of the porphyrinogen intermediates. The method was earlier optimized for the

Scheme 1. Reported Approaches toward the Synthesis of TAP



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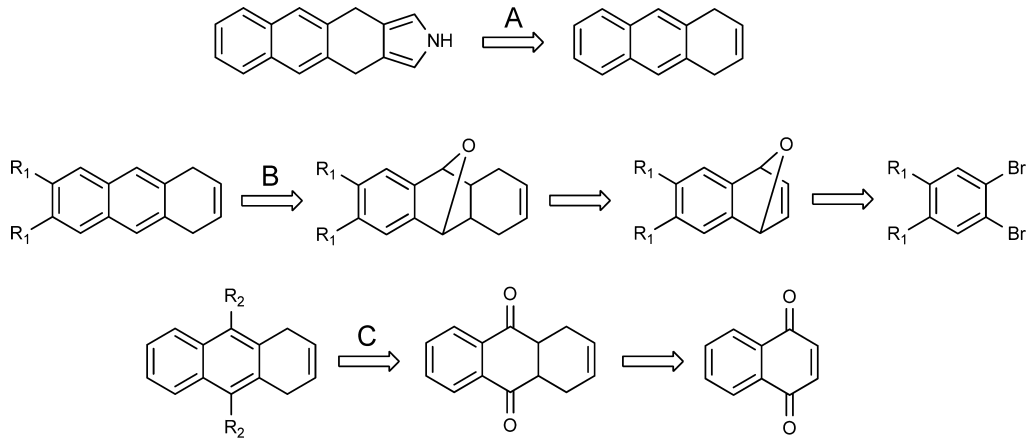
Scheme 2. Retrosynthetical Analysis of TAP Precursors



synthesis of various derivatives of tetrabenzo- and tetranaphthoporphyrin.[28] A key feature of the approach is the use of a common line of synthons, dihydroisoindole derivatives, which (i) can be prepared from readily available starting materials by well-established methods, (ii) upon condensation with aldehydes form porphyrins that are then easily oxidized by DDQ or chloranil to corresponding annelated porphyrins using the same Lindsey' protocol as broadly applied to regular porphyrins,[29] only with an extra amount of aromatizing agent added. However, in the application of this methodology to the TAP system notorious for its high sensitivity toward oxidation, severe if not fatal complications could have been expected. To our delight, however, we have succeeded in preparing TAP derivatives from the corresponding naphtho-annelated dihydroisoindole precursor,[19,30] which was then successfully reproduced by Schanze et al.[31] Herein, we report a detailed account of this methodology, describing the synthesis of Ar_4TAP with both substituted and unsubstituted anthracene subsystem. In addition, we present basic optical properties of new TAPs and report the first X-ray crystallographic structure of a free base of tetraanthraporphyrin.

RESULTS AND DISCUSSION

Synthesis. The known attempts to synthesize TAPs, as well as our first experiments, made us to suspect that such a huge extension of porphyrin system would render the materials extremely prone to aggregation via strong $\pi-\pi$ stacking interactions between molecules, to result in a miserable solubility and difficulties in isolation, purification, and characterization. Therefore, we initially planned, besides attempting the synthesis of the core TAP system, to introduce solubilizing bulky substituents not only at the *meso*-phenyls, but also into the annelated anthracene residues, similar to what was earlier done with tetrabenzo- and tetranaphthoporphyrins.[6e] Introduction of substituents to anthracene rings may also provide the means for additional shifting of the absorption and the emission bands further into NIR. Medium-size alkoxy groups (e.g., *n*-butyloxy) are an obvious first choice for such modification, as the introduction of a pair of such into each anthracene residue would be expected to render adequate solubility in common organic solvents, besides offering red-shifting auxochromic effect due to strong electron donation.

The oxidative aromatization approach regards the corresponding dihydronaphthoisoindoles as the most suitable synthons for the synthesis of TAP.[32] These pyrrolic precursors can be accessed from 1,4-dihydroanthracenes by analogy with previously developed syntheses of dihydroisoindole and dihydrobenzoisoindoles. In the case of TAPs with unsubstituted anthracene rings, the corresponding precursor is 1,4-dihydroanthracene (Scheme 2, route A), which is readily accessible by the reported procedures.[33] For the synthesis of TAPs with substituted anthracene rings, two pathways can be regarded. The precursors of the corresponding dihydronaphthoisoindoles bearing substituents in the outermost rings can be obtained through a sequential construction of polycyclic system using Diels–Alder reactions starting from the readily available adduct of benzyne and furan (Scheme 2, route B). The precursors bearing substituents in the inner ring of anthracene system are accessible from Diels–Alder adducts of 1,4-naphthoquinone (Scheme 2, route C). Both routes present broad opportunities for varying substituents and utilizing conventional well-established procedures, capable of upscaling.

The synthesis of TAPs **5a–d** bearing no substituents on the anthracene rings is shown in Scheme 3.

The synthesis started from 1,4-dihydroanthracene **1**, which was prepared by a three-step procedure described by Dehaen et al.[33] Compound **1** was then transformed into allylic sulfone **2** using the procedure reported in the synthesis of TBP and TNP derivatives.[28] The latter was subjected to the Barton–Zard reaction with ethyl isocyanacetate, delivering naphthoisoindolecarboxylate **3**. Obtained naphthoisoindolecarboxylate **3** was cleanly transformed into 4,11-dihydro-2*H*-naphtho-[2,3-*f*]-isoindole **4**, which was introduced into Lindsey's porphyrin synthesis.[34] MALDI spectra of the samples of the reaction mixtures obtained after quenching with DDQ showed appreciable amounts of partially dehydrogenated intermediate porphyrins, with one, two, or three anthracene residues. Without separation of the individual components, the mixture was further treated with additional portion of DDQ at room temperature for 30 min to achieve complete aromatization of the fused rings. After chromatographic purification, the target TAPs **5a–c** were obtained in good yields.

This scheme was applied also for the synthesis of TAPs bearing alkoxy-substituents in the outermost rings (Scheme 4). The corresponding benzyne dienophile was generated from 4,5-dibromo-1,2-di-*n*-butoxybenzene **8**, which was obtained by bromination of *o*-dibutoxybenzene **7**, produced by alkylation of catechol. The adduct of Diels–Alder reaction between dibutoxybenzyne and furan **9** was further introduced into second Diels–Alder reaction with butadiene. Because of the

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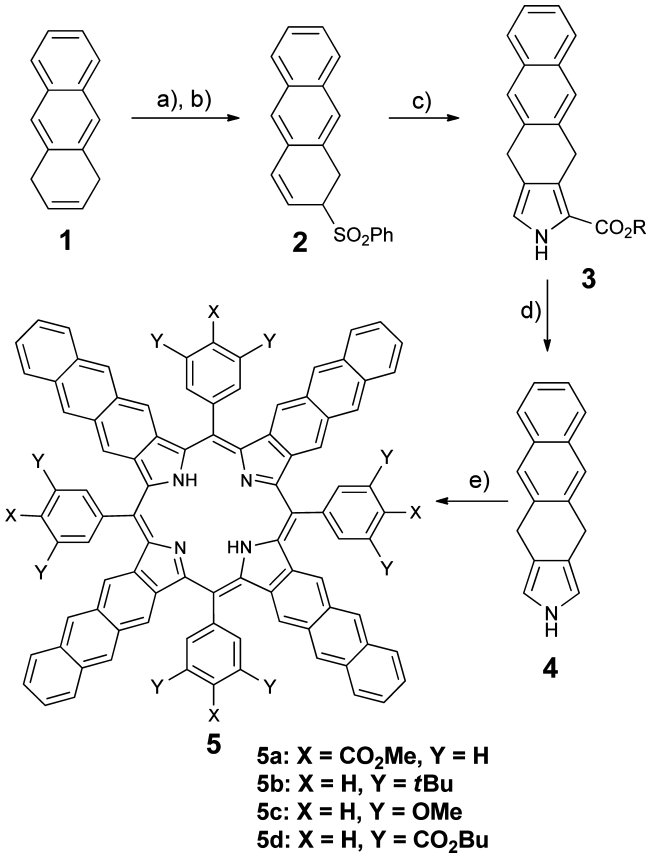
Scheme 3. Synthesis of Anthra-Unsubstituted Porphyrins 5[a]



[a]Reagents and conditions: (a) (i) $PhSCl$, CH_2Cl_2, rt, 1 h; (ii) oxone, $MeOH-H_2O$ (2:1), rt, 7 days (78%); (b) DBU, CH_2Cl_2, rt, 1 h (90%); (c) $CNCH_2CO_2Et$, *t*BuOK, THF (80−90%), rt, 4 h; (d) KOH, $(CH_2OH)_2$, reflux, 30 min (70−85%); (e) (i) $Y_2XC_6H_4CHO$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, rt, 2 h; (ii) DDQ, rt, 30−60 min (15−40%).

rather low reactivity of this dienophile, the cycloaddition requires prolonged heating above 100 °C, which is a rather dangerous procedure requiring special equipment for work under elevated pressure, if neat butadiene is used. Therefore, we used butadiene generated in situ by thermal sulfur dioxide extrusion from 3-sulfolene, in which case no buildup of butadiene pressure could be expected as the liberated diene is consumed in the cycloaddition, and therefore the equilibrium of the reversible extrusion reaction acts as an internal "safety valve". The reaction was performed in the presence of $NaHCO_3$ in pyridine, used as a scavenger of liberated SO_2 to prevent uncontrolled increase of pressure. It allowed us to use a high-pressure thick-wall glass tube instead of an autoclave even for syntheses on a tens-of-grams scale. The obtained adduct **10** is smoothly transformed into 1,4-dihydroanthracene **11** by mild acid-catalyzed dehydration. Further transformation (steps f, g, h, and i in the Scheme 4) of the synthesis leading to corresponding pyrrole **15** follows the previously established approach. Lindsey's condensation followed by subsequent additional treatment with DDQ successfully delivered the corresponding porphyrin **16**.

The synthesis of porphyrins **24**, bearing butoxy-groups in the middle ring (Scheme 5), was performed according to route C shown in Scheme 2. The preparation of corresponding butoxy-substituted 1,4-dihydroanthracenes makes use of the Diels−Alder adduct of 1,4-naphthoquinone **17** with butadiene. Surprisingly, the exact procedure for laboratory-scale synthesis of **18** has not been so far published in the literature, although the adduct **18** is mentioned in the original paper by Diels and Alder but without any experimental details.[35] In this case, 3-sulfolene as 1,3-butadiene synthetic equivalent cannot be used, because the liberated SO_2 can be expected to reduce the quinone moiety. In our work, we succeeded to prepare the adduct **18** by two different methods: (i) long (45 days) exposure of naphthoquinone in neat liquid butadiene taken in huge excess at room temperature in a thick-wall glass tube and (ii) fast catalyzed cycloaddition[36] at low temperature in the presence of 1 equiv of Lewis acid ($SnCl_4$). The first method was found to provide high yields, although it took a very long reaction time. The second method allows for almost immediate reaction, but the yield of target product is substantially lower probably due to competitive cationic polymerization of butadiene. Adduct **18** upon treatment with bases irreversibly forms deprotonated hydroquinone, which was used for alkylation reaction without isolation to give diether **19**. The attempt to perform the acid-catalyzed rearrangement of diketone **18** into the respective enol form (hydroquinone) was abandoned because of extensive formation of dark byproducts. The substituted 1,4-dihydroanthracene **19** was next used in a series of transformations analogous to those shown in Schemes 3 and 4 to obtain corresponding dihydronaphthoisoindole **23**, which was then used for the preparation of anthraporphyrin **24**. The latter was obtained in lower yield as compared to porphyrins **5a−d**, which is probably due to the steric hindrance effect on the macrocyclization process.

The products **5a−d**, **16**, and **24** were additionally purified by recrystallization and characterized by NMR and mass spectroscopy (see the Supporting Information). To our utmost surprise, instead of the envisaged problems with aggregation and poor solubility of these huge compounds supposedly prone to π-stacking, we observed rather good solubility (as compared to previously studied tetranaphtho[2,3]porphyrins) of obtained products in common organic solvents (chlorohydrocarbons, aromatics, THF) even in the case of porphyrins **5a−d** having no solubilizing substituents on the anthracene rings. The observed solubility was comparable or even higher than that of the corresponding TBP and TNP ancestors. Moreover, unlike in the case of TBP and TNP, ^1H NMR spectra of **5a−d** can be obtained for their free base forms without the need of running the spectra at elevated temperatures, adding coordinating solvents or conversion into protonated forms or metal complexes. Free base forms of nonplanar tetraaryl derivatives of extended porphyrins are known to exhibit complex fluxional behavior due to simultaneous occurrence of several dynamic processes such as tautomerization and macrocycle inversion,[37] additionally complicated by aggregation. In the case of tetraaryl TBP and TNP, this fluxionality causes a severe broadening of NMR spectra, particularly in the region of resonances of annelated rings, the signals of which are usually not resolved. Therefore, the spectra were registered for diprotonated forms of higher symmetry and lesser tendency toward aggregation. In the case of TAP, the spectra of free base forms are quite adequately resolved, although the broadening and coalescence of some lines are still observed, and the spectra are improved upon protonation (Figure 3, porphyrin **5b**). Running spectra for diprotonated forms is a common trick used to improve the resolution of the spectra of tetraannelated porphyrins. Usually it is performed by just adding a drop of TFA to samples.

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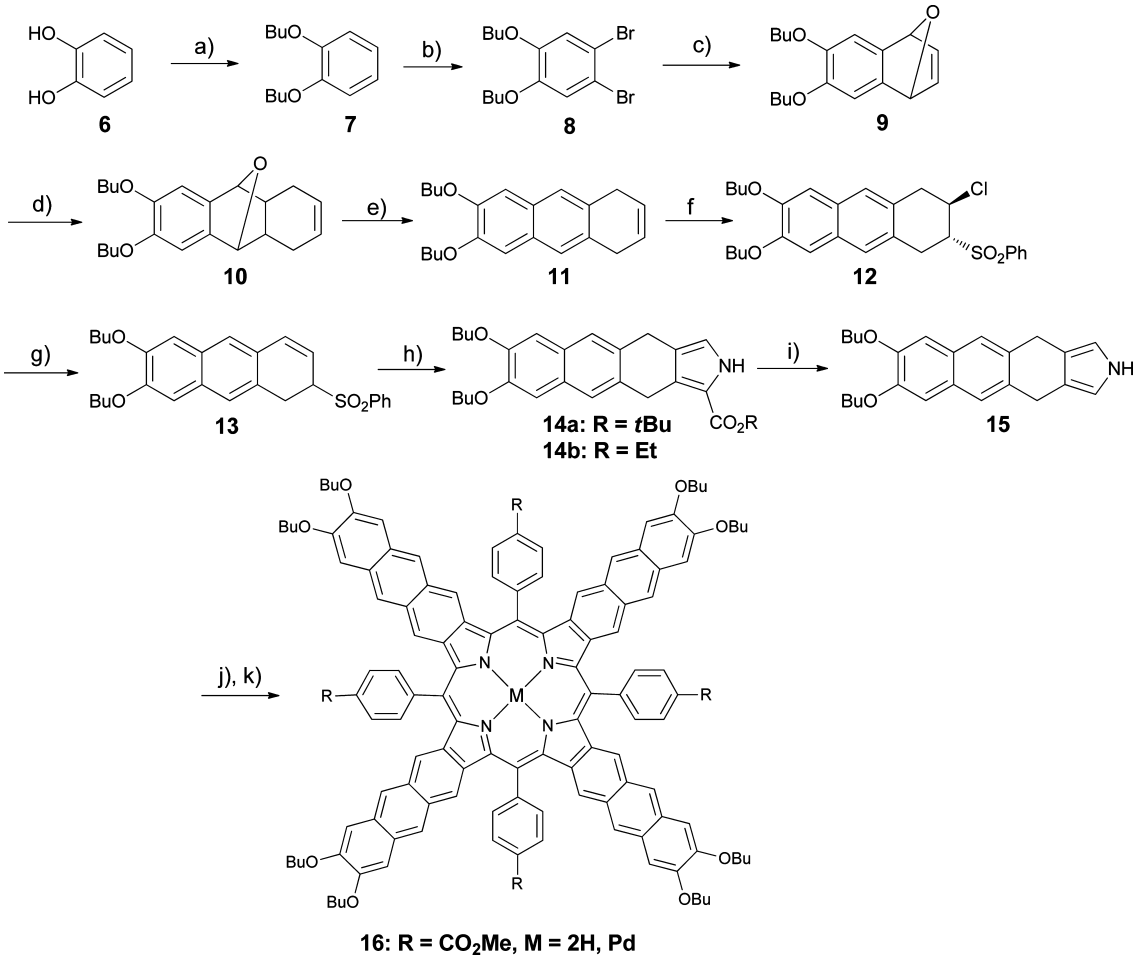
Scheme 4. Synthesis of Octabutoxyporphyrin 16[a]



[a]Reagent and conditions: (a) *n*-BuI, K_2CO_3, acetone, reflux, 2 days (92%); (b) Br_2, CH_2Cl_2, rt, 3 h (90%); (c) furan, *n*-BuLi, THF, −50 °C, 1 h (91%); (d) sulfolene, $NaHCO_3$, Py, 120 °C (58%); (e) HCl, EtOH, reflux, 24 h (61%); (f) (i) PhSCl, CH_2Cl_2, rt, 1 h; (ii) oxone, MeOH−H_2O (2:1), rt, 7 days (78%); (g) DBU, CH_2Cl_2, rt, 1 h (90%); (h) $CNCH_2CO_2R$, *t*BuOK, THF, rt, 4 h, R = *t*Bu (80%), R = Et (85%); (i) for R = *t*Bu, TFA, Ar, rt, 30 min (60%); for R = Et, KOH, $(CH_2OH)_2$, reflux, 30 min (85%); (j) (i) *p*-$MeOOCC_6H_4CHO$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, rt, 2 h; (ii) DDQ, rt, 1 h (18% for two steps); (k) $PdCl_2$, PhCN, reflux, 30 min (88%).

However, in the case of TAP, severe broadening took place if the sample would contain even traces of free acid, probably because the extended aromatic system can undergo reversible protonation at carbon atoms, which adds yet another process to the already complex fluxional behavior of these molecules. In fact, we earlier noted the same behavior already for some tetranaphthoporphyrins. However, if the dication salt is isolated in crystalline form and redissolved in NMR solvents, well-resolved spectra of dicationic forms are observed. This trick generally worked well for recording ^1H NMR spectra. With ^{13}C NMR, the approach is less efficient. An increase of sample concentrations, necessary to warrant reasonable acquisition times, resulted in broadening of spectral lines, particularly in the aromatic portion of spectra, taking place because of either spontaneous deprotonation or aggregation (cf., Supporting Information).

The solubility of substituted porphyrins **16** and especially **24** is particularly high, justifying the efforts for their synthesis. The other gratifying and intriguing feature probably at least partly associated with good solubility of obtained TAPs is an unprecedented ease of metalation. Particularly, Pd insertion, which usually requires prolonged reflux in high boiling solvents like benzonitrile, was found to proceed smoothly at room temperature. Upon stirring TAPs with $Pd(OAc)_2$ in dioxane for 24−48 h at rt, high conversion (70−80%) of free base into metalloporphyrin was observed, although quantitative transformation takes place only upon heating.

Structural Aspects. A good solubility of the obtained TAPs enabled us to obtain crystals suitable for X-ray diffraction analysis and determination of structure for porphyrin **5d** free base as shown in Figure 4. This structure completes the series of structures of linearly annelated extended porphyrins obtained by us[6e,14,28] and others.[6c,37]

The geometry of porphyrin **5d** like all known geometries of tetraaryl derivatives of tetraannelated porphyrins is distorted to take a very characteristic "saddle" shape. The degree and main mode of distortion obtained by applying Shelnutt's normal-coordinate structural decomposition[38] show that total out-of-plane distortion D_{oop} is equal to 2.81 Å, in which saddle distortion B_{2u} is a main component (2.73 Å), with a very slight contribution of the ruffling mode evident from a slight tilt of bonds between β-carbons of pyrrolic residues relative to mean plane of the porphyrin core (cf., Figure 5C). By comparing all known structures of tetraaryl derivatives of tetraannelated

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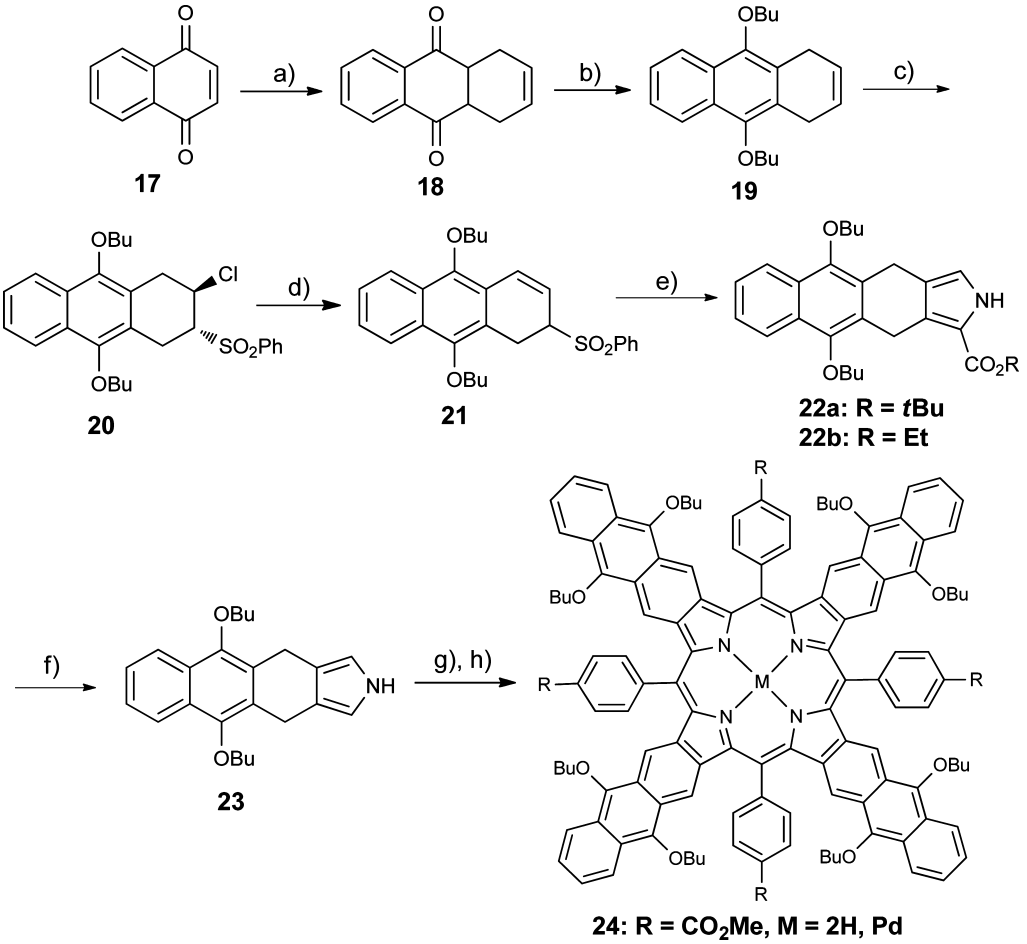
Scheme 5. Synthesis of Butoxy-Substituted Anthtaporphyrins 24[a]



[a]Reagents and conditions: (a) 1,3-butadiene (neat), rt, 45 days (98%) or 1,3-butadiene, $SnCl_4$, CH_2Cl_2, −50 °C, 1.5 h (45%); (b) *n*-BuI, K_2CO_3, acetone, reflux, 2 days (84%); (c) (i) PhSCl, CH_2Cl_2, rt, 1 h; (ii) oxone, MeOH−H_2O (2:1), rt, 7 days (82%); (d) DBU, CH_2Cl_2, rt, 1 h (95%); (e) $CNCH_2CO_2R$, *t*BuOK, THF (72% (R = *t*Bu), 83% (R = Et)); (f) for R = *t*Bu, TFA, Ar, rt, 30 min (56%); for R = Et, KOH, $(CH_2OH)_2$, reflux, 30 min (90%); (g) (i) 4-$MeO_2CC_6H_4CHO$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, rt, 2 h; (ii) DDQ, rt, 1 h (12% for two steps); (h) $PdCl_2$, PhCN, reflux, 30 min (80%).

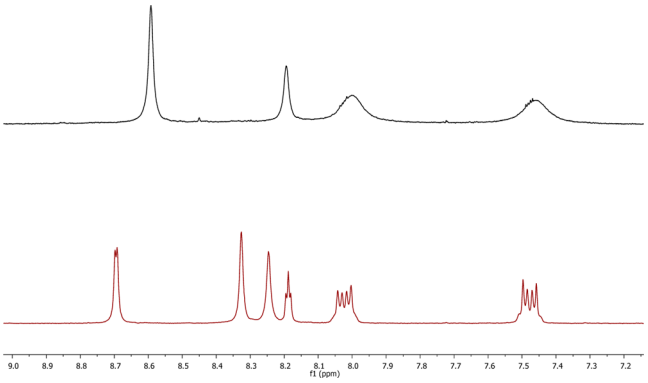


Figure 3. ^{1}H NMR spectra comparison of free base (black line) and dication (red line) of **5b**.

porphyrins, we see that both the degree and the mode of distortion are practically conserved along the series with total out-of-plane distortion D_{oop} staying within very close range of 2.7−3.0 Å and dominated by saddle B_{2u} mode. Noteworthy, such a practically invariant geometry was recorded both for free porphyrins and their metal complexes, and not only for π-extended molecules (TBP, TNP, TAP) but also for tetracyclohexeno derivatives with partially flexible saturated annelated rings (for distortion analysis, see red 14). No intermediate forms with noticeably weaker or stronger saddle-type of distortion have been observed, although if the steric repulsion would be the main factor determining the distortion, a wider range of distortion degrees could be expected to meet the particular internal interaction profile of each of such molecules. Indeed, a broad variation of distortion degrees has been revealed for a large body of saddle distorted dodecasubstituted porphyrins,[39] interpreted by Rosa et al.[40] as a consequence of softness of the porphyrin core toward deformation, thus making each particular porphyrin molecule seek its own balance of steric repulsion, distortion, and stabilization due to improved conjugation with *meso*-aryls. Certainly, in the known annelated porphyrins, steric repulsion can be regarded to be mainly localized in the interaction of the *meso*-aryl ring with the CH-site of the first annelated ring, which are likely to be roughly the same in all published structures, and so far no annelated porphyrins bearing substituents at this site, or *ortho*-substituted meso-aryls have appeared. There is, however, an important and intriguing exclusion explicitly showing that steric repulsion cannot be the main factor defining the geometry of saddling distortion. Krautler and co-workers described a planar structure for tetraaryl derivatives of tetraannelated porphyrin with annelated naphthoquinone

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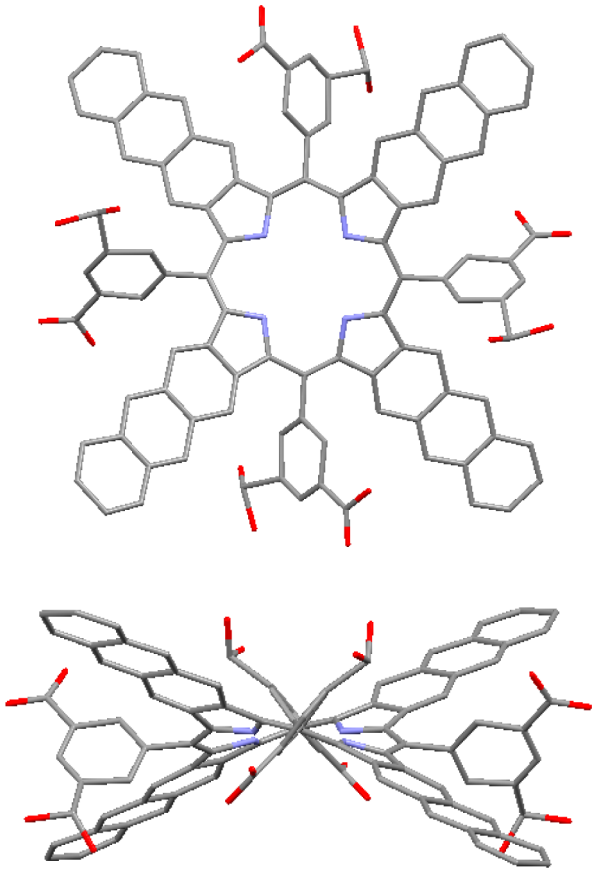

Figure 4. X-ray structure of **5d**: top and side views. Alkyl chains of alkoxycarbonyl groups are omitted for clarity.

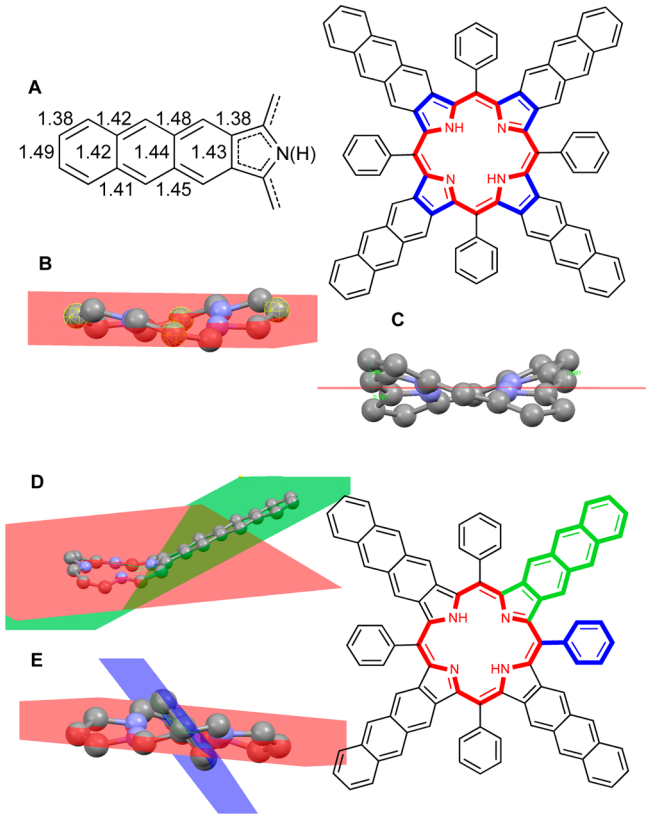

Figure 5. Main structural features of tetraarylTAP as seen from the X-ray structure of **5b**. (A) Bond alternation in anthracene residues; (B) effective planarity of the macrocyclic core (marked red); (C) the same, but including pyrrolic rings (blue); (D) the angle between the macrocyclic core mean plane and the annelated residue (green); and (E) the angle between the macrocyclic core mean plane and *meso*-aryl (blue).

residues,[41] thus being structurally very close (in what concerns the spatial arrangement and thus the steric interaction of *meso*-aryls and annelated fragments) to the tetraaryl TNP series. Thus, the observed trends ("a bewildering variation"[40a] of distortion degrees reported for dodecasubstituted porphyrins vs practically invariant distortion degree and core geometry of the tetraannelated tetraarylporphyrins) suggest that the configuration of the porphyrin core in the latter is defined not only by variable balance of steric repulsion between *meso*-aryls and annelated rings and stabilizing factors such as the conjugation with *meso*-aryl rings. Rather, the repulsion very likely acts as a weak push, which brings the geometry out of equilibrium, and a new equilibrium is sought and attained. This new equilibrium, saddle-shaped with out-of-plane B_{2u} distortion of about 2.7 Å, is likely to be an interesting compromise between the destabilization of aromatic macrocyclic core and stabilization due to increased conjugation with *meso*-aryl groups.

When discussing the structures of tetraryl derivatives of tetraannelated porphyrins, both we and others referred to their characteristic structure as "heavily saddle-distorted", and the side view of the new representative of the series (Figure 4) seems to justify such an epithet. However, a closer scrutiny of the structures shows that such a way of describing the character of geometry is an exaggeration, hiding really important features of such geometry. Indeed, if the mean plane of the porphyrin core is drawn in these structures (shown in Figure 5B,C for TAP, but similar pictures drawn for all other known structures of such porphyrins are virtually indistinguishable from the one shown), it becomes evident that the inner macrocyclic ring (the inner 18*e*-contour) remains practically planar with the largest deviation from the plane measured for α-pyrrolic atoms being a meager 0.3 Å (Figure 5B). Importantly, all four nitrogen atoms and all four *meso*-carbons lie in a plane with negligible deviations from it. Thus, from the point of view of macrocyclic aromaticity, the core of saddle-shaped porphyrins can be regarded as effectively planar, not much different from the geometry of the core in regular porphyrins; thus, it is not surprising that the position of Soret bands in a very long list of tetraarylporphyrins from TPP to TAP stay within a narrow range of less than 40 nm. The only part of the core that substantially deviates from the plane includes β-pyrrolic atoms and the connecting bond to which the annelated rings are attached. However, even these atoms deviate only by 0.7−1.0 Å (the largest values are in TBP, while in TNP and TAP the deviations are smaller), which is less than the van der Waals radii of these atoms. It should be noted that the main contribution to the overall stabilization of porphyrin molecules is believed, at least in the frames of model advocated by Aihara and coauthors,[42] to be due to aromatic stabilization of 6-electron circuits of pyrrolic/pyrrolenic fragments, which is not likely to be dependent on the deviation of these fragments from the plane. The annelated rings form acute angles with the mean plane (Figure 5D) of only 23−26°, being within a very short range in all of the known structures, and in TAP the angle is among the smallest. Thus, the saddled geometry of the annelated porphyrins including TAP benefits from the conservation of aromatic stabilization in both almost planar

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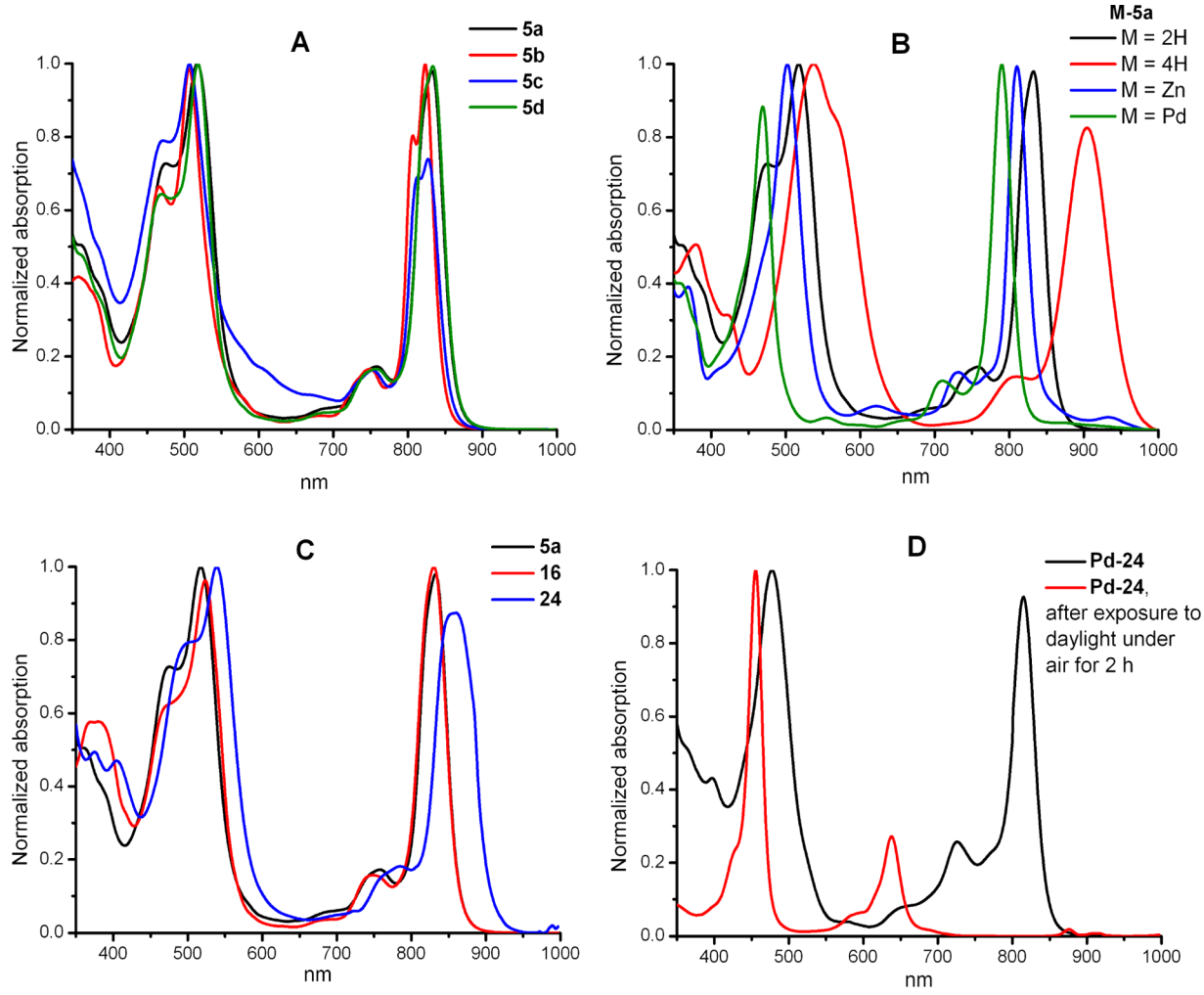

Figure 6. Comparison of the UV−vis absorption spectra for free base porphyrins **5a−d** (A), free base, dication, and metalated porphyrin **5a** (B), free base porphyrins **5a**, **16**, and **24** (C), and **Pd-24** and the product of its photooxidation (D).

inner macrocyclic core and annelated pyrrolic/pyrrolenic fragments.

In TAP and all other known structures of β-annelated tetraarylporphyrin, the *meso*-aryls are tilted relative to the macrocyclic mean plane with angles of ca. 55° (Figure 5E). These angles are substantially smaller than the tilt angles of *meso*-aryls known for planar tetraarylporphyrins,[43] in which the degree of conjugation between the aryls and the core is largely disrupted. Therefore, the structure of the saddled porphyrins implies a substantially better conjugation of *meso*-aryls to the core. Such a small tilt angle is accounted for by the checkerboard pattern of deviation of annelated rings to the opposite directions from the plane, which enables the aryl to rotate deeper inward at the side where the annelated ring bends out (Figure 4 side view and Figure 5E) until a close van der Waals contact of *ortho*-carbon of *meso*-aryl and the first atom of the annelated ring is reached. Interestingly, the conjugation of *meso*-aryl rings with the core defined by the tilt angle was earlier shown by Rosa et al.,[4044] to counterbalance the distortion in both dodecasubstituted porphyrins, and protonated forms of regular porphyrins in a synergic fashion to generate a continuum of variable saddled geometries.

Thus, the saddled geometry of an important class of porphyrins (tetraaryl derivatives of tetraannelated porphyrins) is characterized by (a) practically planar macrocyclic core, and (b) the arrangement of annelated residues and *meso*-aryls enforcing the highest possible degree of conjugation of the latter with the core. The conservation of geometric parameters along the series tentatively identifies this as a discrete structural type in the porphyrin chemistry, and high-level theoretical treatment and more of resolved structures are required to enforce or refute this hypothesis.

TetraarylTAP thus can be considered as regular members of large class of saddle-shaped tetraannelated porphyrins. Anthracene residues annelated to the core interact very tightly with it. The strong interaction is well manifested by bond alternation in the residues. In fact, the alternation of bonds is a well-known feature of linear polybenzenoid hydrocarbons (acenes), being the result of the impossibility to localize favorable aromatic sextets in such an arrangement of benzene rings. Therefore, the acenes behave as integral conjugated systems, the aromaticity of which is rapidly declining with the addition of each new benzene ring, which in its turn leads to destabilization of the frontier energy levels and huge red-shifting of the absorption bands. In TAP molecule, the degree of bond alternation (Figure 5A) is unprecedented, with some of the bonds reaching 1.48−1.49 Å, which is close to the regular single C−C bond length. Bond alternation in TAP is thus more manifested than that in either TBP or TNP analogues, but this is not only in free anthracene, but also for higher acenes at least

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up to pentacene.[45] This observation shows that porphyrin core annelated to anthracene residues very strongly interacts with the latter, which results in a large extent of bond localization in the rings belonging to these residues. This mode of annelation creates a sort of huge heteroacene.

UV−Vis Spectra. Electronic absorption properties of anthraporphyrins prepared are presented in Figure 6. All TAPs showed a rather broad Soret band with a shoulder at the hypsochromic side. Because of extension of π-system and acene-type destabilization of one of the orbitals of the Gouteman's model (b_1 (a_{1u}) HOMO) leading to the lift of pseudodegeneracy (this effect was computationally predicted for lower members of the family[46]), TAPs exhibit strongly red-shifted and hyperchromic Q-bands. The maximum of absorption is about 830 nm for **5a−d**. The molar extinction coefficients of both Soret and Q-bands reach 10^5 scale. As is seen from Figure 6A, the nature of aryl substituent has only a weak effect on absorption properties. In contrast, protonation and metal insertion were found to have a profound effect. The comparison of absorption spectra of **5a** in free base and protonated forms, as well as for Zn and Pd-complexes, is shown in Figure 6B. Very strong red-shift by about 90 nm upon protonation and blue-shift by 20−40 nm upon metal insertion are observed. Surprisingly, the introduction of electron donor substituents into anthra rings was found to have an effect on the absorption properties only in the case of porphyrin **24**, bearing butoxy-groups in the middle rings. Its Soret and Q-bands are shifted into red by 20 and 30 nm, respectively. In contrast, the absorption of porphyrin **16**, bearing butoxy-groups in the outmost rings, is almost identical to that of parent porphyrin **5a** (Figure 6C).

In the course of synthetic procedures and purification of obtained products **5a−d**, **16**, and **24**, special attention was paid to protection of the products from the light as the instability toward photooxidation was noted in previous works.[25] However, in the course of experiments, no reasonable decomposition or impurities formation derived from photodegradation was observed upon protecting the working solutions of porphyrins with foil. In contrast, diluted solutions of TAPs were found to be sensitive to photooxidation. Air-exposed solutions with a concentration in a range of 10^{-4}−10^{-5} M undergo complete photooxidation under ambient light in 10−15 min, while the same solutions are stable in the dark. Deoxygenated solutions are not sensitive to the light. Absorption spectra of the oxidized solutions show the disappearance of the intensive near-IR absorption accompanied by the appearance of new Q-bands in the visible. The effect is much stronger pronounced for corresponding metallo-complexes, especially with palladium, then for free base porphyrins. As an example, a transformation of absorption spectra of oxygenated solution of **Pd-24** upon exposition to light is shown in Figure 6C. Such transformation of absorption spectra is likely to be accounted for by addition of singlet dioxygen formed upon sensibilization of its triplet form by excited state of the porphyrin, know to be quite efficient.[47] From Figure 6C it becomes clear that the spectra of the oxidized solution closely resemble the spectra of tetrabenzoporphyrin system both by position and by relative intensities of B- and Q-bands. Therefore, we can tentatively suppose that the photooxidation probably leads to the addition of singlet oxygen across the diene system of inner rings similarly to what happens with anthracene and higher acenes in the cycloaddition reactions (Figure 7, the addition of from 1 to 4 oxygen molecules can be

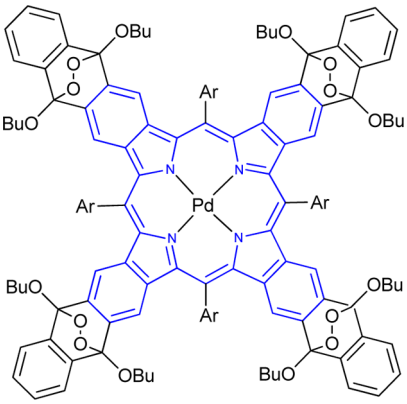

Figure 7. Probable structure of the product of TAP system photooxidative bleaching.

hypothesized to result in the loss of TAP long-wavelength intense bands). Such self-sensitized photoreaction with oxygen forming macrocycle with four endoperoxide bridges was previously described by Freyer et al. for tetraanthraporphyrazinato palladium.[48] The ease of addition is likely to correlate with the destabilization of anthracene residues as was discussed above. Currently, we are working on the isolation and characterization of such adducts, which are of considerable interest as potentially reversible photoactivated singlet oxygen reservoirs.

■ CONCLUSIONS

In summary, we have developed a reliable and effective method for the preparation of tetraanthraporphyrins bearing functional substituents in *meso*-positions of the core or on the anthracene rings. A series of new TAPs were synthesized, and the structure of a representative molecule was identified by single crystal X-ray diffraction. The analysis of the structure of representative tetraarylTAP molecule shows that it has the same structure as all other known tetraaryl derivatives of tetraannelated porphyrins, which are characterized by saddle-type out-of-plane distortion of porphyrin system. The degree of distortion quantitatively characterized by normal-coordinate structure decomposition along with such basic geometric parameters as the deviation of atoms belonging to the macrocyclic system from the mean plane of the macrocycle, the dihedral angles between this plane and annelated rings and *meso*-aryl rings, show that saddle distortion, a robust arrangement of constituents of such systems, is reproduced with a substantial degree of accuracy in practically all of the representatives of the series including TAP. This type of distortion allows for practically full conservation of planarity of the internal macrocyclic 18-electron aromatic core and higher extent of conjugation between the core and *meso*-aryls than that occurring in planar porphyrins of the common TPP type. On the other hand, the linear fusion of anthracene residues and porphyrin core enables a very strong interaction between these aromatic moieties to elicit the behavior known for linearly fused acenes. This interaction leads to strong destabilization of frontier orbitals manifested in huge red shift of absorption bands. The new porphyrins were shown to be soluble in common organic solvents showing only marginal tendency for aggregation, and to exhibit strong absorption in the near-IR, which makes them promising materials for various applications in biological and materials fields.

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EXPERIMENTAL SECTION

o-Dibutoxybenzene (7). A mixture of catechol (27.5 g, 0.25 mol), *n*-butyliodide (138 g, 0.75 mol), anhydrous K_2CO_3 (75.9 g, 0.55 mol), and acetone (200 mL) was refluxed for 48 h. The resulting mixture was filtered, concentrated by evaporation, and the residue was distilled in vacuum: yield 51 g (92%), colorless oil, bp 155−161 °C at 16 mm/Hg (lit.[49] 149−157 °C at 149−157 mm/Hg).

1,2-Dibromo-4,5-di-*n*-butoxybenzene (8). The title compound was prepared following a modified literature procedure.[50] To a solution of *o*-dibutoxybenzene (20 g, 90 mmol) and I_2 (0.5 g, 2 mmol) in CH_2Cl_2, distilled over CaH_2, was added 11.6 mL of Br_2 (36 g, 225 mmol) dropwise over a period of 30 min. The solution was stirred at rt for 3 h, then evaporated in vacuum. Residual dark-brown oil was diluted with 150 mL of ethanol and kept in a fridge at −20 °C for 12 h. Formed crystals were filtered and dried in vacuum. **8**: 30.8 g (90%), colorless easily melting (∼20 °C) crystals; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 3.8 Hz, 2H), 3.95 (t, J = 6.5 Hz, 4H), 1.79 (dt, J = 14.5, 6.7 Hz, 4H), 1.59−1.38 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 118.1, 114.8, 77.7, 77.2, 76.6, 69.4, 31.2, 19.3, 13.9. Anal. Calcd for $C_{14}H_{20}Br_2O_2$: C, 44.24; H, 5.30. Found: C, 43.87; H, 5.48.

6,7-Di-*n*-butoxy-1,4-epoxy-1,4-dihydronaphthalene (9). The title compound was prepared following a modified literature method.[51] 1,2-Dibromo-4,5-di-*n*-butoxybenzene **8** (28.5 g, 75 mmol) and 27.3 mL of freshly distilled furan (25.5 g, 375 mmol) were dissolved in THF (75 mL), freshly distilled from $LiAlH_4$. The solution was cooled to −50 °C under Ar, and 46.8 mL (75 mmol) of 1.6 M *n*-BuLi solution in hexane was added dropwise over a period of 30 min. After the addition was complete, the mixture was stirred for 1 h at −30 °C. Next, 5 mL of water was added, and the reaction mixture was allowed to warm to room temperature. The solvent was evaporated in vacuum, residual oil was dissolved in CH_2Cl_2 (100 mL), washed with water, dried with Na_2SO_4, and evaporated in vacuum. Resulting product was used in the next step without additional purification. **9**: 20.6 g (91%), pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 0.8 Hz, 2H), 6.95 (s, 2H), 5.65 (s, 2H), 4.01−3.90 (m, 4H), 1.79−1.70 (m, 4H), 1.54−1.42 (m, 4H), 0.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.4, 142.0, 110.0, 82.7, 77.7, 77.2, 76.6, 70.0, 31.7, 31.5, 19.3, 14.0. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.57.

1,4,4*a*,9,9*a*,10-Hexahydro-6,7-di-*n*-butoxy-9,10-epoxyanthracene (10). The title compound was prepared following a modified literature method.[20] A mixture of 6,7-di-*n*-butoxy-1,4-epoxy-1,4-dihydronaphthalene **9** (15.1 g, 50 mmol), 3-sulfolene (1.5 g, 13 mmol), $NaHCO_3$ (2.5 g, 30 mmol), and pyridine (30 mL) was placed into a high-pressure glass tube and heated at 120−125 °C for 18 h. During this time, 5.0 g of 3-sulfolene was added to the reaction mixture in five portions. The resulting mixture was filtered and evaporated in vacuum. The residue was purified on a silica gel column (eluent: CH_2Cl_2). After evaporation of the solvent, the product was crystallized from methanol. **10**: 10.1 g (59%), beige crystals, mp 31−33 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 2H), 5.91−5.79 (m, 2H), 4.84 (s, 2H), 3.97−3.80 (m, 4H), 2.38 (dd, J = 7.7, 5.8 Hz, 2H), 2.03−1.61 (m, 8H), 1.42 (dq, J = 14.4, 7.3 Hz, 4H), 0.89 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 138.5, 129.2, 106.8, 85.2, 77.5, 77.0, 76.5, 69.7, 42.9, 31.5, 27.5, 19.2, 13.9. Anal. Calcd for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83. Found: C, 76.87; H, 8.98.

6,7-Di-*n*-butoxy-1,4-dihydroanthracene (11). The title compound was prepared following a modified literature method.[33] 1,4,4*a*,9,9*a*,10-Hexahydro-6,7-di-*n*-butoxy-9,10-epoxyanthracene **10** (8.55 g, 25 mmol) was dissolved in ethanol (100 mL), then concentrated HCl solution (10 mL) was added, and the resulting mixture was refluxed in Ar for 24 h. The reaction mixture was allowed to cool to room temperature, and the resulting precipitate was filtered and recrystallized from methanol. **11**: 4.9 g (61%), colorless crystals, mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.03 (s, 2H), 6.01 (t, J = 1.4 Hz, 2H), 4.10 (t, J = 6.6 Hz, 4H), 3.52 (d, J = 0.8 Hz, 4H), 1.89 (dt, J = 14.5, 6.7 Hz, 4H), 1.55 (dq, J = 14.4, 7.3 Hz, 4H), 1.01 (t, J = 7.4 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 149.1, 131.1, 128.0, 125.2, 124.7, 107.2, 77.5, 77.0, 76.5, 68.5, 31.2, 29.9, 19.3, 13.9. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.17; H, 8.91.

1,4,4*a*,9*a*-Tetrahydroanthraquinone-9,10 (18). *Method 1.* Naphthoquinone (20 g, 126 mmol) was added at 0 °C to 1,3-butadiene (50 mL), and the mixture was stirred for 45 days at room temperature in a high-pressure glass tube in the dark. The excess amount of butadiene was evaporated, and the residue was recrystallized from methanol. **18**: 26.3 g (98%), white powder, mp 102 °C (lit.[35] 102 °C).

Method 2. Synthesis was performed following a modified literature procedure.[36] A solution of naphthoquinone (20 g, 126 mmol) in dry CH_2Cl_2 (500 mL) was cooled to 0 °C, and 1,3-butadiene (40 mL) was added. The mixture was cooled to −60 °C, and 43 mL of $SnCl_4$ (95.7 g, 367 mmol) was added dropwise over 30 min, keeping the temperature between −60 and −50 °C. The resulting solution was stirred at −50 °C for 1 h, then warmed to room temperature, and 200 mL of water was added. Organic phase was separated, washed with water, dried with Na_2SO_4, and evaporated in vacuum. Solid residue was recrystallized from ethanol. **18**: 12 g (45%), white powder, mp 102 °C (lit.[35] 102 °C).

1,4-Dihydro-9,19-di-*n*-butoxyanthracene (19). Synthesis generally followed the procedure described for the synthesis of *o*-dibutoxybenzene (7). Crude product was purified by recrystallization from methanol. **19**: 84%, colorless crystals, mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 6.4, 3.3 Hz, 2H), 7.35 (dd, J = 6.4, 3.2 Hz, 2H), 5.93 (s, 2H), 3.86 (t, J = 6.6 Hz, 4H), 3.47 (s, 4H), 1.96−1.73 (m, 4H), 1.55 (dq, J = 14.4, 7.1 Hz, 4H), 0.96 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 127.4, 125.1, 124.3, 122.1, 77.5, 77.0, 76.5, 73.5, 32.7, 24.6, 19.5, 14.1. Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.25; H, 8.88.

6,7-Di-*n*-butoxy-2-chloro-3-phenylsulfonyl-1,2,3,4-tetrahydroanthracene (12) and 9,10-Di-*n*-butoxy-2-chloro-3-phenylsulfonyl-1,2,3,4-tetrahydroanthracene (20). Synthesis was performed following a previously published general procedure for the preparation of α-chlorosulfones.[52] Thiophenol (2 mL, 2.2 g, 20 mmol) was added dropwise to a suspension of *N*-chlorosuccinimide (2.14 g, 16 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 1 h, then filtered from the white precipitate of succinimide. The orange filtrate was added dropwise to a stirred solution of corresponding dihydroanthracene (20 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was stirred at room temperature for 2 h and evaporated in vacuum. The residue was dissolved in methanol (60 mL), and a suspension of oxone (12.3 g, 20 mmol) in water (30 mL) was added under vigorous stirring. The mixture was stirred at room temperature for 7 days, diluted with water (100 mL), and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and evaporated to dryness. Solid residue was recrystallized from MeOH. **12**: 7.8 g (78%), beige crystals, mp 135−136 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01−7.91 (m, 2H), 7.76−7.53 (m, 3H), 7.43 (s, 2H), 7.04 (d, J = 4.5 Hz, 2H), 4.89 (q, J = 4.4 Hz, 1H), 4.09 (t, J = 6.6 Hz, 4H), 3.81−3.65 (m, 1H), 3.53−3.09 (m, 4H), 1.96−1.79 (m, 4H), 1.65−1.45 (m, 4H), 1.01 (dd, J = 7.7, 6.9 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 149.6, 137.9, 134.3, 129.5, 129.3, 129.0, 128.7, 128.6, 125.6, 124.9, 107.5, 77.7, 77.2, 76.6, 68.7, 67.9, 53.3, 37.9, 31.2, 26.9, 19.4, 14.0. Anal. Calcd for $C_{28}H_{33}ClO_4S$: C, 67.12; H, 6.64. Found: C, 66.80; H, 6.89. **20**: 8.2 g (82%), biege crystals, mp 99−101 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.10−8.01 (m, 2H), 8.00−7.93 (m, 2H), 7.78−7.57 (m, 3H), 7.54−7.45 (m, 2H), 5.00 (q, J = 4.3 Hz, 1H), 3.99−3.84 (m, 4H), 3.75 (tt, J = 9.2, 4.6 Hz, 1H), 3.59−3.33 (m, 3H), 3.18 (dd, J = 16.5, 7.3 Hz, 1H), 1.97−1.75 (m, 4H), 1.70−1.43 (m, 4H), 1.10−0.96 (m, 6H); ^{13}C NMR (63 MHz, CD_2Cl_2) δ 149.3, 148.6, 138.1, 134.7, 129.9, 129.7, 129.2, 128.4, 126.2, 125.7, 123.2, 122.7, 122.6, 75.2, 75.0, 66.9, 54.7, 54.28, 53.8, 53.4, 53.0, 52.8, 32.9, 32.9, 31.9, 21.5, 19.8, 19.8, 14.2. Anal. Calcd for $C_{28}H_{33}ClO_4S$: C, 67.12; H, 6.64. Found: C, 66.87; H, 6.86.

2-Benzenesulfonyl-6,7-dibutoxy-1,2-dihydro-anthracene (13) and 2-Benzenesulfonyl-9,10-dibutoxy-1,2-dihydro-anthracene (21). Synthesis was performed following a modified literature procedure.[52] To a solution of corresponding α-chlorosulfone

(15 mmol) in CH_2Cl_2 (30 mL) was added 1,8-diazabicycloundec-7-ene (2.2 mL, 2.3 g, 15 mmol) dropwise over a period of 10 min at 0 °C. The mixture was stirred for 1 h at room temperature, washed with water, dried with Na_2SO_4, and evaporated in vacuum. Solid residue was recrystallized from MeOH. **13**: 6.3 g, 90%, colorless crystals, mp 116−118 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.64 (dd, J = 5.3, 3.3 Hz, 2H), 7.29−7.06 (m, 4H), 6.99 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 6.64 (d, J = 9.7 Hz, 1H), 5.94 (dd, J = 9.6, 5.0 Hz, 1H), 4.13−3.86 (m, 5H), 3.54−3.16 (m, 2H), 1.90−1.69 (m, 4H), 1.58−1.35 (m, 4H), 0.94 (td, J = 7.4, 3.0 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 150.0, 149.4, 136.4, 134.4, 133.5, 129.7, 129.4, 128.3, 128.2, 127.2, 125.0, 124.5, 118.4, 108.0, 107.5, 77.7, 77.2, 76.6, 68.7, 61.7, 31.3, 28.6, 19.4, 14.1. Anal. Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94. Found: C, 72.61; H, 7.22. **21**: 6.6 g, 95%, colorless crystals, mp 86−87 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.96 (ddt, J = 11.6, 7.0, 3.5 Hz, 2H), 7.81−7.73 (m, 2H), 7.52−7.39 (m, 2H), 7.33−7.09 (m, 3H), 6.15 (dd, J = 9.9, 5.2 Hz, 1H), 4.18−4.07 (m, 1H), 4.01−3.80 (m, 4H), 3.70 (qt, J = 9.3, 6.6 Hz, 2H), 3.22 (dd, J = 17.4, 7.9 Hz, 1H), 1.99−1.78 (m, 4H), 1.72−1.50 (m, 4H), 1.06 (td, J = 7.3, 4.4 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 147.8, 147.8, 136.6, 133.4, 129.4, 129.3, 128.5, 128.2, 128.0, 126.4, 125.8, 122.6, 122.2, 121.2, 120.3, 119.1, 77.6, 77.0, 76.5, 75.8, 73.9, 60.7, 32.5, 32.4, 22.4, 19.5, 19.4, 14.1, 14.0. Anal. Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94. Found: C, 72.33; H, 7.34.

7,8-Dibutoxy-4,11-dihydro-2*H*-naphtho[2,3-*f*]isoindole-1-carboxylates (14a,b) and 5,10-Dibutoxy-4,11-dihydro-2*H*-naphtho[2,3-*f*]isoindole-1-carboxylates (22a,b). Barton−Zard syntheses of pyrroles **14** and **22** were performed following a previously published general procedure.[28] A solution of corresponding isocyanoacetate (10 mmol) in THF (10 mL) was dropwise over a period of 10 min to a stirred suspension of potassium *tert*-butoxide (1.12 g, 10 mmol) at 0 °C. The resulting mixture was stirred for 30 min, and then a solution of corresponding allyl sulfone (10 mmol) in THF (20 mL) was added dropwise over a period of 30 min. The reaction mixture was stirred at room temperature for 4 h, then evaporated in vacuum, dissolved in CH_2Cl_2 (50 mL), washed with water, dried with Na_2SO_4, and evaporated in vacuum. Solid residue was recrystallized from methanol. **14a**: 3.7 g (80%), colorless crystals, mp 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 7.63 (s, 1H), 7.57 (s, 1H), 7.10 (s, 1H), 7.08 (s, 1H), 6.82 (d, J = 2.40 Hz, 1H), 4.31 (s, 4H), 4.13 (t, 4H), 4.03 (s, 4H), 1.91 (m, 4H), 1.66 (s, 9H), 1.58 (m, 4H), 1.04 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 149.2, 132.2, 128.1, 128.0, 125.6, 125.2, 121.2, 117.1, 107.2, 80.6, 68.5, 31.2, 29.7, 28.6, 27.5, 19.3, 14.0. Anal. Calcd for $C_{29}H_{37}NO_4$: C, 75.13; H, 8.04; N, 3.02. Found: C, 74.88; H, 8.34; N, 2.70. **14b**: 3.7 g (85%), yellowish crystals, 126−128 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 9.01 (br s, 1H), 7.59 (d, J = 15.9 Hz, 2H), 7.08 (d, J = 2.9 Hz, 2H), 6.86 (d, J = 2.7 Hz, 1H), 4.43−4.22 (m, 4H), 4.19−3.96 (m, 6H), 1.95−1.77 (m, 4H), 1.65−1.47 (m, 4H), 1.42 (t, J = 7.1 Hz, 3H), 1.03 (dd, J = 9.7, 5.0 Hz, 6H); ^{13}C NMR (63 MHz, CD_2Cl_2) δ 161.6, 149.6, 132.7, 132.6, 128.4, 128.4, 127.2, 125.8, 125.5, 121.7, 118.1, 117.8, 107.5, 107.4, 68.9, 60.3, 54.7, 54.2, 53.8, 53.4, 52.9, 31.7, 28.8, 27.7, 19.7, 14.8, 14.1. Anal. Calcd for $C_{27}H_{33}NO_4$: C, 74.45; H, 7.64; N, 3.22. Found: C, 74.10; H, 8.02; N, 2.85. **22a**: 3.34 g (72%), colorless crystals, mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (br s, 1H), 8.12 (m, 2H), 7.49 (m, 2H), 6.89 (d, J = 2.78 Hz, 1H), 4.37 (s, 4H), 4.10 (s, 4H), 4.03 (m, 4H), 2.01 (m, 4H), 1.72 (s, 9H), 1.68 (m, 4H), 1.10 (t, 3H), 1.09 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 148.7, 148.4, 127.5, 127.4, 126.4, 126.2, 125.2, 124.8, 122.22, 122.16, 120.17, 119.0, 117.7, 80.7, 73.8, 32.74, 32.69, 28.7, 23.0, 21.7, 19.5, 14.1. Anal. Calcd for $C_{29}H_{37}NO_4$: C, 75.13; H, 8.04; N, 3.02. Found: C, 74.97; H, 8.22; N, 2.59. **22b**: 3.61 g (83%), yellowish crystals, 138−140 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 9.05 (br s, 1H), 8.20−8.05 (m, 2H), 7.59−7.42 (m, 2H), 6.95 (d, J = 2.9 Hz, 1H), 4.47−4.33 (m, 4H), 4.17−3.91 (m, 6H), 2.10−1.90 (m, 4H), 1.84−1.62 (m, 4H), 1.48 (t, J = 7.1 Hz, 3H), 1.11 (td, J = 7.3, 2.8 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 181.7, 161.8, 148.7, 148.4, 127.5, 127.4, 126.2, 126.1, 125.8, 125.28, 122.2, 122.2, 120.4, 118.2, 117.7, 77.6, 77.0, 76.5, 73.8, 73.8, 60.1, 32.7, 32.7, 22.9, 21.7, 19.6, 19.5, 14.6, 14.2, 14.1. Anal. Calcd for $C_{27}H_{33}NO_4$: C, 74.45; H, 7.64; N, 3.22. Found: C, 74.18; H, 7.24; N, 2.96.

7,8-Dibutoxy-4,11-dihydro-2*H*-naphtho[2,3-*f*]isoindole (15) and 5,10-Dibutoxy-4,11-dihydro-2*H*-naphtho[2,3-*f*]isoindole (23). *Method 1*. *tert*-Butyl esters **14a** or **22a** (1 mmol) were dissolved in TFA (10 mL), and the solution was stirred for 30 min under Ar at room temperature. After the addition of CH_2Cl_2 (20 mL), the mixture was washed with water, then with 10% solution of Na_2CO_3, dried with Na_2SO_4, and evaporated in vacuum. The residue was passed through a layer of silica using CH_2Cl_2 as eluent. The solvent was evaporated to give a product. **15**: 0.218 g (60%), gray powder, mp 74−76 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.56 (s, 1H), 7.56 (s, 2H), 7.08 (s, 2H), 6.67 (d, J = 2.5 Hz, 2H), 4.09 (t, J = 6.6 Hz, 4H), 3.99 (s, 4H), 1.95−1.77 (m, 4H), 1.66−1.45 (m, 4H), 1.11−0.94 (m, 6H); ^{13}C NMR (63 MHz, CD_2Cl_2) δ 149.7, 134.6, 128.4, 125.5, 119.9, 112.9, 107.8, 69.1, 54.9, 54.4, 54.0, 53.6, 53.1, 31.9, 28.6, 19.9, 14.3. Anal. Calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.12; H, 8.30; N, 3.59. **23**: 203 g (56%), gray powder, mp 89−90 °C; ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.23−7.92 (m, 3H), 7.57−7.32 (m, 2H), 6.70 (d, J = 2.5 Hz, 2H), 4.06 (s, 4H), 3.97 (t, J = 6.6 Hz, 4H), 1.97 (ddd, J = 14.6, 9.5, 6.5 Hz, 4H), 1.67 (tdd, J = 14.5, 8.5, 6.3 Hz, 4H), 1.08 (dd, J = 9.2, 5.5 Hz, 6H); ^{13}C NMR (63 MHz, CD_2Cl_2) δ 148.6, 128.3, 127.8, 125.5, 122.5, 118.8, 113.1, 74.1, 54.7, 54.2, 53.8, 53.4, 52.9, 33.0, 22.3, 19.9, 14.3. Anal. Calcd for $C_{24}H_{29}NO_2$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.03; H, 8.35; N, 3.40.

Method 2. A mixture of ethyl ester **14b** or **22b** (1 mmol) and potassium hydroxide (0.56 g, 10 mmol) in ethylene glycol (10 mL) was heated at reflux under an atmosphere of Ar for 30 min. The mixture was cooled to room temperature, and CH_2Cl_2 (100 mL) was added. The solution was washed with water and brine, dried with Na_2SO_4, and the solvent was evaporated in vacuum. The residue was passed through a layer of silica using CH_2Cl_2 as eluent, and the resulting solution was evaporated to give a product. **15**, 0.31 g (85%); **23**, 0.326 g (90%).

Tetraanthroporphyrins 5a−d, 16, 24. Naphthoisoindole **4**, **15**, or **23** (1 mmol) and the corresponding aldehyde (1 mmol) were dissolved in freshly distilled CH_2Cl_2 (100 mL), and the mixture was kept under continuous stirring in the dark under Ar for 10 min. $BF_3{\cdot}Et_2O$ (8.5 μL, 0.014 g, 0.1 mmol) was added in one portion, and the mixture was left to react at rt under Ar for 2 h. A solution of DDQ (0.17 g, 0.75 mmol) in THF (10 mL) was added, and the mixture was allowed to stir for another 1 h. The resulting green solution was washed with 10% solution of Na_2SO_3 (100 mL), dried with Na_2SO_4, and evaporated in vacuum. The residue was dissolved in THF (20 mL), DDQ (0.17 g, 0.75 mmol) was added, and the mixture was stirred in the dark under Ar for 30 min then evaporated in vacuum. The resulting material was washed again with the solution of Na_2SO_3, dried with Na_2SO_4, and evaporated to dryness. The residue was purified on a silica gel column twice (eluent: CH_2Cl_2, then CH_2Cl_2−THF, 10:1). Each time, a purple band eluting with CH_2Cl_2−THF was collected, and the solvent was removed in a vacuum. All manipulations were performed either in the dark or in vessels covered by aluminum foil. The remaining green solid was purified by recrystallization from CH_2Cl_2−diethyl ether mixture (4:1). The crystals that formed after 1−2 days were centrifuged, washed by ether, and dried in a vacuum.

Palladium complexes were obtained by heating of a mixture of porphyrin, excess $Pd(OAc)_2$ (2 equiv), and Et_3N (1−2 drops) in benzonitrile at 160 °C for 0.5−3 h (control by UV−vis spectroscopy), with subsequent filtration through a layer of silica (eluent CH_2Cl_2) and evaporation of filtrate.

5a: 0.145 g (40%), green powder, analytical data are in correspondence to those described previously.[20]

5b: 0.062 g (15%), green powder. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.69 (d, J = 1.5 Hz, 8H), 8.33 (s, 8H), 8.25 (s, 8H), 8.19 (t, J = 1.7 Hz, 4H), 8.02 (dd, J = 6.6, 3.2 Hz, 8H), 7.48 (dd, J = 6.7, 3.1 Hz, 8H), 1.52 (s, 72H). UV/vis for free base (toluene) λ_{max} (log ε) 467 (4.82), 507 (5.0), 749 (4.23), 807 (4.91), 823 (5.0); diprotonated form (toluene, CF_3COOH) 535 (4.74), 575 (4.74), 797 (4.19), 884 (4.68). HRMS (ESI): m/z found 1663.9368, calcd for $[M^+]$ $C_{124}H_{118}N_4$ 1663.9390.

5c: 0.073 g (20%), green powder. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.54 (s, 8H), 8.42 (s, 8H), 8.06 (dt, J = 11.1, 5.5 Hz, 8H), 7.88 (d, J = 2.1 Hz, 8H), 7.52 (dd, J = 6.7, 3.0 Hz, 8H), 7.25 (t, J = 2.1 Hz, 4H),

4.02 (s, 24H), 1.85 (d, J = 68.3 Hz, 4H). UV/vis for free base (CH_2Cl_2) λ_{max} (log ε) 472 (4.82), 507 (4.92), 753 (4.14), 813 (4.76), 827 (4.79); diprotonated form (CH_2Cl_2, CF_3COOH) 534 (4.78), 647 (4.28), 788 (4.1), 881 (4.7). HRMS (ESI): m/z found 1455.5211, calcd for $[M^+]$ $C_{100}H_{70}N_4O_8$ 1455.5227.

5d: 0.098 g (19%), green powder. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 9.54−9.46 (m, 4H), 9.45−9.36 (m, 8H), 8.45−8.20 (m, 8H), 8.11−7.94 (m, 8H), 7.93−7.56 (m, 8H), 7.55−7.42 (m, 8H), 4.41 (t, J = 6.7 Hz, 16H), 1.77 (dt, J = 14.4, 6.7 Hz, 16H), 1.40 (dd, J = 15.0, 7.5 Hz, 16H), 0.85 (t, J = 7.4 Hz, 24H). UV/vis for free base (toluene) λ_{max} (log ε) 468 (5.08), 518 (5.27), 757 (4.49), 833 (5.26); diprotonated form (toluene, CF_3COOH) 537 (5.15), 821 (4.41), 911 (5.08). HRMS (ESI): m/z found 2015.8512, calcd for $[M^+]$ $C_{132}H_{118}N_4O_{16}$ 2015.8576.

16: 0.091 g (18%), green powder. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.65 (dd, J = 24.3, 8.0 Hz, 16H), 8.49−7.34 (m, 16H), 7.20 (s, 8H), 4.24 (s, 12H), 4.17 (t, J = 6.5 Hz, 16H), 2.00−1.80 (m, 16H), 1.67−1.47 (m, 24H), 1.05 (t, J = 7.4 Hz, 24H). UV/vis for free base (toluene) λ_{max} (log ε) 471 (4.98), 523 (5.17), 748 (4.39), 830 (5.2); diprotonated form (toluene, CF_3COOH) 535 (4.74), 575 (4.74), 797 (4.19), 884 (4.68). HRMS (ESI): m/z found 2023.9203, calcd for $[M^+]$ $C_{132}H_{126}N_4O_{16}$ 2023.9202.

Pd-16: 88%, brown solid. ^{1}H NMR (500 MHz, d_8-toluene, 223 K) δ 9.53−7.66 (m, 24H), 3.76−2.79 (m, 28H), 1.85−1.11 (m, 26H), 1.04−0.58 (m, 26H). UV/vis (toluene) λ_{max} (log ε) 469 (4.88), 710 (4.23), 789 (4.93). HRMS (ESI): m/z found 2127.8067, calcd for $[M^+]$ $C_{132}H_{124}N_4O_{16}Pd$ 2127.8081.

24: 0.06 g (12%), green powder. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.85−7.35 (m, 40H), 4.20 (s, 12H), 3.87 (m, 4H), 1.84 (m, 16H), 1.62 (m, 16H), 1.11 (m, 24H). UV/vis for free base (toluene) λ_{max} (log ε) 501 (5.0), 539 (5.11), 785 (4.36), 859 (5.04); diprotonated form (toluene, CF_3COOH) 446 (4.83), 560 (5.1), 850 (4.42), 953 (4.93). HRMS (ESI): m/z found 2024.9242, calcd for $[MH^+]$ $C_{132}H_{127}N_4O_{16}$ 2024.9281.

Pd-24: 80%, brown solid. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.82−8.56 (m, 16H), 8.42−7.96 (m, 18H), 7.59−7.35 (m, 10H), 4.25−4.12 (m, 12H), 3.96−3.76 (m, 16H), 3.74−3.62 (m, 6H), 1.88−1.75 (m, 12H), 1.70−1.52 (m, 24H), 1.15−1.02 (m, 24H). UV/vis (toluene) λ_{max} (log ε) 477 (4.69), 643 (3.69), 726 (4.18), 815 (4.65). HRMS (ESI): m/z found 2127.8047, calcd for $[M^+]$ $C_{132}H_{124}N_4O_{16}Pd$ 2127.8081.

■ ASSOCIATED CONTENT

Supporting Information

Details of X-ray structure determination and copies of the NMR spectra of newly synthesized compounds. 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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