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A Facile and Reliable Method for the Synthesis of Tetrabenzoporphyrin from 4,7-Dihydroisoindole

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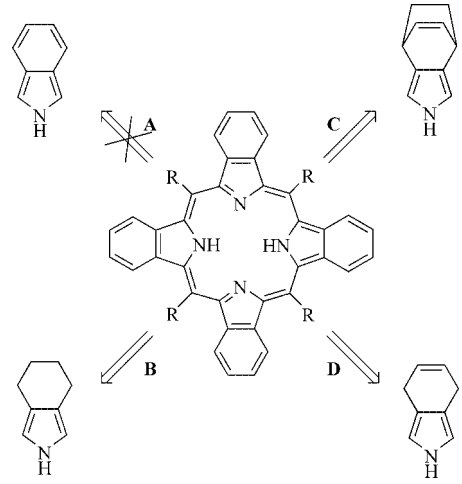
A new route to tetrabenzoporphyrins from the closest possible precursor of the unstable isoindole was developed. A key feature of this route is a dramatic facilitation of the aromatization of annelated rings, which is the most serious bottleneck in previous syntheses of tetrabenzoporphyrins. The capabilities of the new method are illustrated by the synthesis of *meso*-tetraaryltetrabenzoporphyrins, as well as the first unambiguous synthesis and characterization of 5,15-diphenyltetrabenzoporphyrin.

Introduction

Of all the so-called π-extended porphyrins,[1] tetrabenzoporphyrins (TBP) are probably the most interesting and the closest relatives of phthalocyanines. Owing to a rare combination of photophysical,[2] optoelectronic,[3] and physicochemical properties,[4] benzoporphyrins show promise in various applications, for example photodynamic or neutron capture therapy sensitizers, sensors, and electronic devices, etc.[5] This potential, however, has been so far largely unexplored because of a lack of effective and versatile approaches to these compounds. For the TBP system, the straightforward application of standard methods of porphyrin chemistry – the condensation of an appropriate pyrrole with aldehydes – is not possible, as in this case the progenitor pyrrole, *2H*-isoindole, is an unstable transient molecule (Scheme 1, path **A**). Therefore, until recently, the only available approach was through mimicking the phthalocyanine synthesis by a high-temperature templated condensation of phthalimide or similar compounds with various CH-acids,[6] which, as a rule, gives complex mixtures of porphyrins requiring HPLC for separation,[7] and is practically not applicable to anything except the unsubstituted TBP itself and some simple derivatives.

Alternatively, the TBP system can be assembled by the common methods of porphyrin synthesis; however, the use of the unstable isoindole should be avoided and a stable precursor of this transient compound, with aromatization being delayed until after the assembly of the porphyrin macrocycle, could be used. Indeed, recently two such approaches were simultaneously elaborated. One of these approaches used tetrahydroisoindole (Scheme 1, path **B**), and the final aromatization was performed by oxidative dehydrogenation with DDQ.[8] The other approach used bicyclooctadiene-fused pyrrole (Scheme 1, path **C**), and the aromatization was accomplished by a thermal retro-Diels–Alder reaction.[9] Both of these approaches enabled fast expansion of the scope and preparative value of TBP syntheses. However, as soon became evident, both methods still suffered from a common serious drawback, which was the harsh conditions required for the aromatization step (either prolonged heating of metallated hexadecahydroTBP precursors with DDQ leading to partial overoxidation in the tetrahydroisoindole method, or heating over 200 °C to effect ethylene extrusion). Thus, the scope of these approaches was limited, which resulted in losses of valuable target porphyrins at the final stage of a long synthesis. Yet, another elegant approach that should be mentioned uses pyrrole annelated to a sulfolene moiety, thus opening the possibility to



Scheme 1. General routes to tetrabenzoporphyrins.

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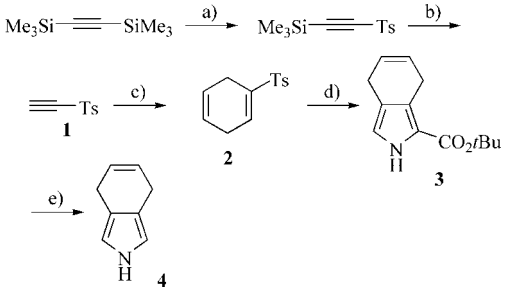
use cycloaddition with appropriate dienophiles either prior or after the porphyrin macrocycle assembly leading to partially hydrogenated benzoporphyrin precursors.[10] This approach, however, so far has not been developed into a general method of tetrabenzoporphyrin synthesis owing to incidental problems, associated with a poor solubility of intermediates, which can be overcome only through the use of large solubilizing substituents.[11]

In order to remove this bottleneck, the aromatization should be dramatically facilitated.[12] This could be achieved by taking as close a precursor to isoindole as possible, as compared to both pyrrolic compounds used in the published methods. The choice is not wide, as only a single candidate for this role – 4,7-dihydroisoindole – could be considered (Scheme 1, path **D**), which is surprisingly a so-far-unknown simple pyrrole derivative.[13] Herein we report such a precursor, and show that its use allows the synthesis of TBP to be realized with unprecedented ease thus superseding all extant approaches to this system.[14]

Results and Discussion

The synthesis of 4,7-dihydroisoindole (Scheme 2) is straightforward and employs tosylacetylene **1**, readily obtained by the published procedure[15] from commercial bis-(trimethylsilyl)acetylene (BTMSA). Tosylacetylene is regarded as a powerful dienophile.[16] Analysis of the published data shows that tosylacetylene is largely employed in very facile reactions with highly reactive, electron-rich cyclic dienes, such as *N*-acylpyrroles,[15a,17] furan,[18] and cyclopentadienes[19] with only a few examples published on the cycloaddition to less reactive acyclic dienes with the use of rather drastic reaction conditions.[20] We could not achieve the cycloaddition of tosylacetylene to 1,3-butadiene when trying to perform the reaction in various solvents by heating in a thick-walled vessel. However, a smooth and practically quantitative reaction did take place when a solution of **1** was treated with a large excess of butadiene and left at room temperature for 2 d in a thick-walled tube.

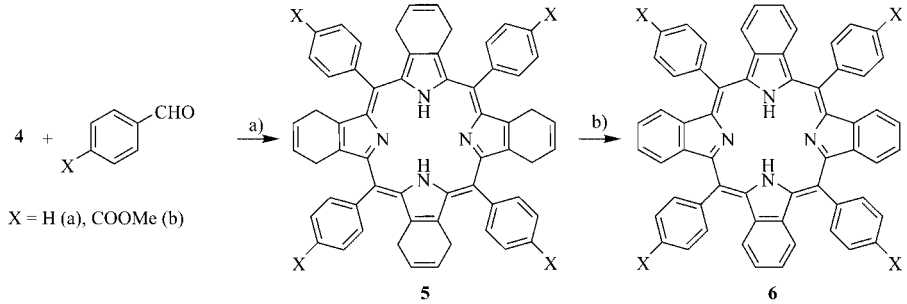


Scheme 2. a) TsCl, $AlCl_3$, CH_2Cl_2, 12 h, 80%; b) NaF, MeOH/H_2O, 0.5 h, 90%; c) 1,3-butadiene (excess), room temp., 48 h, 95%; d) $CNCH_2COOtBu$, *t*BuOK, THF, 4 h, 80%; e) TFA, 15 min, 55% or KOH, $HOCH_2CH_2OH$, reflux, 30 min, 85%.

Adduct **2** was used for the preparation of 4,7-dihydroisoindole **4** by using standard Barton–Zard chemistry.[21] All steps are high-yielding and reproducible on a multigram scale. Dihydroisoindole **4** is quite stable and survives during storage in a refrigerator, though it does rapidly darken at room temperature similarly to other electron-rich β-substituted pyrroles. Therefore, representative NMR spectra could not be obtained. Surprisingly, though it could be expected that under acidic or basic conditions the unwanted migration of double bond would happen, this does not take place at any of the stages even though at almost each stage of this synthesis either strong bases (*t*BuOK in THF, KOH in boiling ethyleneglycol) or acids (TFA, TsOH, BF_3) are involved. A likely reason for such stability is that the pyrrolic residue is more acidic (as NH-acid) as well as more nucleophilic than the respective reaction centers involved in the anticipated double bond migration; thus, the pyrrolic ring may serve to protect the double bond from the initiation of both carbocationic and carbanionic shifts.

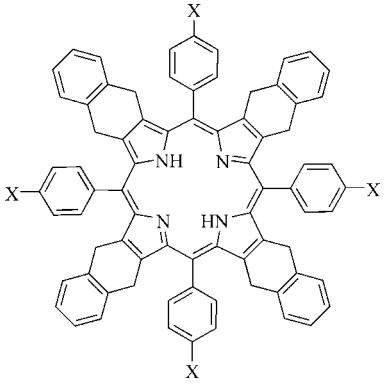
Tetrahydroisoindole **4** was further successfully used for the preparation of *meso*-tetraaryloctahydrotetrabenzoporphyrins **5** by using the standard Lindsey protocol[22] (Scheme 3). These porphyrins were formed in good yields comparable to those obtained with the same benzaldehydes and 4,5,6,7-tetrahydroisoindole, without the shift of the double bond or aromatization of the cyclohexadiene rings. Compounds **5** were isolated as pure diprotonated dication salts[23] and unambiguously characterized by ^1H and ^{13}C NMR spectroscopy; these compounds possess a highly symmetrical structure. Otherwise, the properties of these porphyrins, including the electronic absorption spectra, are very close to those of hexadecahydrotetrabenzoporphyrins described earlier.[8c]

To a certain degree, the method now being described mimics the dialine version of the synthesis of TNPs, devel-



Scheme 3. a) $BF_3{\cdot}Et_2O$, CH_2Cl_2, room temp., 2 h, then DDQ, room temp., 1 h, **5a** (25%), **5b** (40%); b) DDQ, toluene, reflux, 5 min, 95%.

oped earlier in our laboratory, with 4,7-dihydroisoindole serving the role of key synthon in place of benzo[*f*]-4,7-dihydroisoindole.[24] The synthesis of TNP should lead, after macrocyclization by the Lindsey procedure, to octahydrotetranaphthalo[2,3]porphyrins (Scheme 4), which are structurally similar to porphyrins **5**, possessing exactly the same degree and pattern of unsaturation in the inner rings and the same porphyrinic core (both belong to the same *meso*-tetraarylocta-β-alkyl strained nonplanar porphyrin class[25]).



Scheme 4. *meso*-Tetraaryloctahydrotetranaphthaloporphyrins are isostructural (with respect to inner core without peripheral benzene rings) to porphyrins **5**.

However, octahydrotetranaphthalo[2,3]porphyrins are readily aromatized in situ to fully aromatic systems during DDQ oxidation of the respective porphyrinogen, and could not be isolated in spite of many efforts to quench DDQ as fast as possible. MALDI spectra of the samples of the reaction mixtures that were obtained by early quenching never showed any appreciable amounts of these porphyrins, though partially dehydrogenated forms with one, two, or three naphthalene residues could be observed and even isolated.

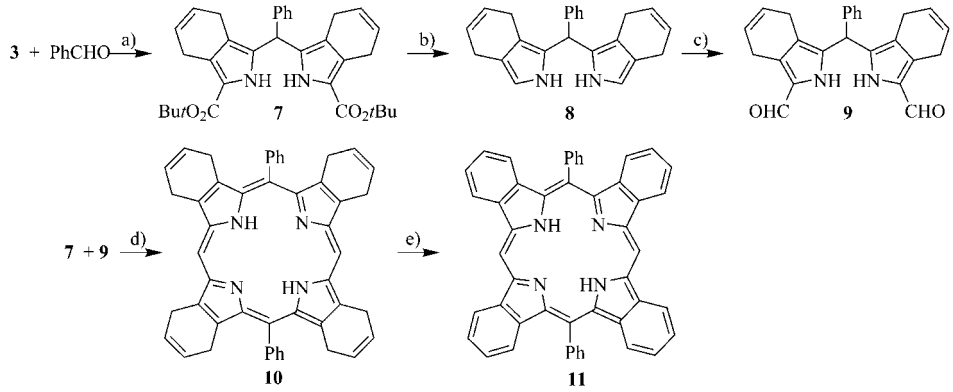
Bearing this apparent analogy in mind, the observed stability of porphyrins **5** towards dehydrogenation is not easily understandable, particularly if we take into account that the driving force for aromatization is generally lower for larger polycyclic systems as a result of the localization of aromaticity in subsystems. However, this phenomenon gives us a chance to exploit this new porphyrinic synthon possessing double bonds in the fixed symmetrical positions ready for further transformations towards new π-extended porphyrins. The examples of such chemistry will be reported separately.

Further aromatization of porphyrins **5** is nevertheless straightforward. This can be achieved even at room temperature, on keeping porphyrins **5** with DDQ for several days in the dark. Alternatively, a quantitative aromatization to tetraaryltetrabenzoporphyrins **6** takes place on heating the solution in toluene or another appropriate solvent with DDQ for a few minutes; the aromatization takes place almost instantaneously as the temperature is raised over 100 °C. In all cases the aromatization is clean and quantitative. The MALDI spectra of the crude reaction mixtures show no significant byproducts. This is in sharp contrast to what is observed in the former method of synthesis based on tetrahydroisoindole,[8b–8d] in which the dehydrogenation by DDQ was applied only after prior metallation by selected metal salts (Cu, Ni, Pd)[12] and required prolonged reflux temperatures in polar solvents. Modest yields of TBP products are often obtained[26] owing to both multiple side reactions and the need for metallation–aromatization–demetallation sequence in place of the direct aromatization as in the protocol described here. Additionally, owing to cleanness of aromatization in the current protocol, target tetrabenzoporphyrins **6** are readily isolated from the reaction mixtures by crystallization without the need for chromatography either as free bases or diprotonated dication salts.

Thus, tetraaryltetrabenzoporphyrins are made available by the reported method in only three major preparative steps (cycloaddition, Barton–Zard condensation, Lindsey's porphyrin synthesis) from readily available tosylacetylene. The aromatization in this protocol is ready and quantitative and is no longer a bottleneck in the synthesis, as in the earlier procedures.

It should be noted that when this article was in preparation, a paper appeared describing the synthesis of mono-, di-, and tribenzoporphyrins (but not tetrabenzoporphyrins) by intermediate porphyrins containing cyclohexadiene-annelated rings, the same fragment as in porphyrin **5**.[27] These intermediates were accessed from common tetraphenylporphyrin by electrophilic bromination, followed by Suzuki cross-coupling and olefin metathesis performed under high dilution conditions. The ease of aromatization of cyclohexadiene rings by DDQ in toluene has been noted.

To further illustrate the potential of a new synthon, we explored the [2+2] McDonald condensation as an easy route to very interesting 5,15-diaryltetrabenzoporphyrins (Scheme 5). Dipyrromethane-α,α′-dicarboxylates **7** can be formed by the condensation of **3** with benzaldehyde. We established that this condensation in our case gives poor yields under published conditions[28] as a result of incomplete conversion and tarring. Apparently, such behavior may be explained by side reactions at the double bonds, effected by the action of acid in the presence of liberated water. Indeed, the addition of a highly hygroscopic salt, namely, anhydrous tetrabutylammonium chloride, resulted in full suppression of tarring and desired dipyrromethane **7** was formed in near-to-quantitative yield. The action of salt, which binds the liberated water, is probably similar to the well-known salt effect in the formation of porphyrinogens, described by Lindsey et al.,[29] though, as far as we know, this effect was never employed in dipyrromethane chemistry. Besides, unlike the salt effect of Lindsey, which is delivered by a lot of various salts, in our reaction simple salts such as NaCl or Na_2SO_4 were helpless, as only the use of anhydrous Bu_4NCl led to success. The obtained dipyrromethane was utilized in the [2+2] condensation, with all stages being selective and free of side reactions arising from expectable double bond migration to give expected 5,15-di-



Scheme 5. a) TsOH (cat), nBu$_4$NCl, $CHCl_3$, room temp., 24 h, 90%; b) TFA, CH_2Cl_2, room temp., 30 min (not isolated); c) $CH(OMe)_3$, TFA, room temp., 30 min, 50% (based on **7**); d) TFA, CH_2Cl_2, room temp., 21 h, then DDQ, 4 h, 15%; e) DDQ, toluene, reflux, 5 min, >95%.

aryloctahydrotetrabenzoporphyrin **10**, which is cleanly aromatized to 5,15-diaryltetrabenzoporphyrin **11**.

It should be noted that 5,15-diphenylTBP has already appeared in the literature, but, as far as we know, has never been unambiguously characterized. All previous attempts were based on the high temperature templated condensation reactions, either in trace amounts by tedious HPLC separation of multiple side products of the reaction of benzylidenephthalimidine with Zn acetate at 360 °C,[7b,30] or by fusion of 3-oxoisoindoleninyl-3′-oxoisoindolinylidene-1,1′-methylidine with zinc acetate and sodium phenylacetate at 350 °C.[31] The templated fusion methods, however, owing to extreme harshness of reaction conditions fail to deliver pure tetrabenzoporphyrins and lead instead to complex mixtures of analogues with a varied degree of substitution and scrambling of substituents; well-resolved spectra cannot be obtained for such products. In the reported cases, according to the published descriptions the products were either inseparable mixtures of 5,10- and 5,15-diphenylTBP, or compounds of unidentifiable nature giving wrong and poorly resolved NMR and UV/Vis spectra. Therefore, this work is the first to report the unambiguously characterized 5,15-diphenyltetrabenzoporphyrin system. Well-resolved NMR spectra (^{1}H, ^{13}C) can be obtained for the dication salt of this porphyrin (e.g. Figure 1). As in the spectra of the free base, the signals are dynamically broadened, which is typical behavior for porphyrins with annelated rings, for example tetraaryltetrabenzoporphyrins. A very large difference in chemical shifts between the α protons of the benzo rings (695 Hz) is effected by superposition of ring currents of the porphyrin core plus the benzo rings (deshielding of H_4 protons in the *meso* unsubstituted bay of the TBP system) and the ring current of the *meso* phenyl groups, which are roughly perpendicular to the effective plane of the macrocycle is such molecules (shielding of H_1 protons in the *meso* substituted bay).

The electronic absorption spectrum of porphyrin **11** as a free base is rather unusual (Figure 2). Unlike tetraaryltetrabenzoporphyrins, this porphyrin shows very narrow Soret bands, as well as splitting of the Soret and Q-bands, with all these special features disappearing upon protonation. These

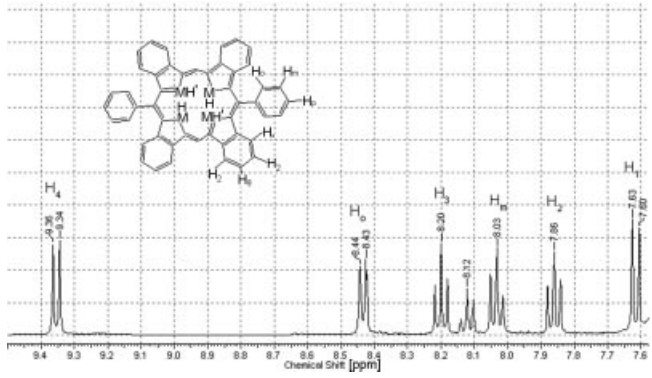


Figure 1. Aromatic portion (*meso* protons at 11.01 ppm excluded) of the ^{1}H NMR (400 MHz, $CDCl_3$) of 5,15-diphenyltetrabenzoporphyrin **11** as a dication salt.

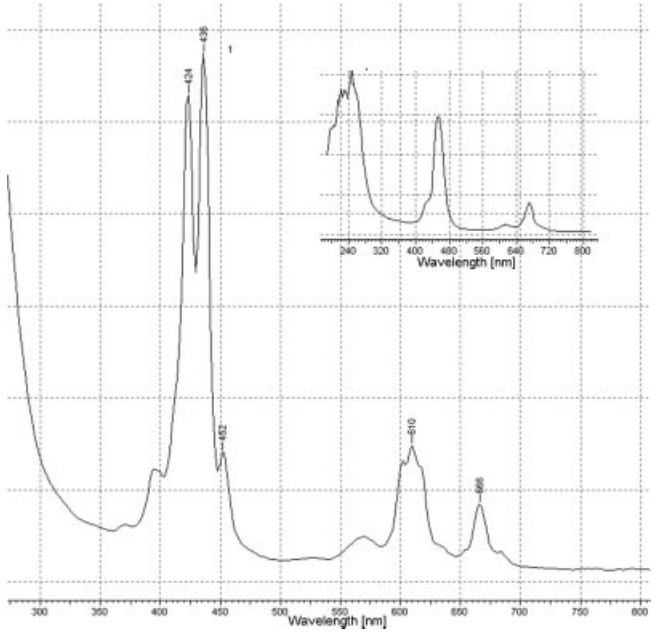


Figure 2. The electronic absorption spectrum of 5,15-diphenyltetrabenzoporphyrin **11** as a free base in CH_2Cl_2 (spectrum of dication is shown in the insert).

features almost exactly follow the overall appearance and pattern of bands in the spectra of *meso* unsubstituted tetrabenzoporphyrins.[32] Thus, it is very likely that the structure of 5,15-diphenyltetrabenzoporphyrin is closer to *meso* unsubstituted TBPs than to tetraaryl TBPs. The former are flat with a saddle shaped dication, and the latter are saddle-shaped in both the free base and the dication states. We may therefore at this stage tentatively conclude that the 5,15-diphenylporphyrin system is very likely a flat system. A detailed study of this important structural phenomenon will be reported in a forthcoming paper.

Conclusions

Tetraaryltetrabenzoporphyrins are made available in only three major preparative steps starting from readily available tosylacetylene in excellent yields and purity. In all the cases studied so far, the assembly of porphyrin macrocycle is selective and does not involve double bond shifts or spontaneous aromatization of annelated rings. Therefore, this protocol bears a dual advantage: (1) it is the most straightforward approach to tetrabenzoporphyrins and starts from the nearest relative of unstable isoindole and (2) it makes octahydrotetrabenzoporphyrins, bearing double bonds in fixed symmetrical positions, available, and these compounds are useful as new reaction centers for the preparation of novel functionalized porphyrins with annelated rings. The proposed method supersedes all extant methods for the synthesis of tetrabenzoporphyrin in terms of preparative value and the mild reaction conditions of the final aromatization step, which allows the ready synthesis of previously inaccessibly structures, as exemplified here by the synthesis and unambiguous characterization of 5,15-diphenyltetrabenzoporphyrin.

Experimental Section

General Procedures: All commercial reagents (Acros, Aldrich) were used as received, or purified before use by standard procedures. Ethynyl *p*-tolyl sulfone (**1**) was obtained according to the published procedure.[15a] THF was distilled from $LiAlH_4$ before use; dichloromethane and chloroform were washed by standard procedures and distilled from CaH_2 before use. NMR spectra were recorded with a Bruker Avance-400 spectrometer. MALDI-TOF and LDI-TOF mass spectra were obtained by using a Bruker Daltonics Alphaflex II spectrometer with cinnamic acid as matrix. UV/Vis spectra were recorded with a Hewlett–Packard 8452A instrument.

1-Tosyl-1,4-cyclohexadiene (2): Ethynyl *p*-tolyl sulfone (5.0 g, 27.7 mmol) was added to 1,3-butadiene (20 mL), and the mixture was stirred for 48 h at room temp. in a heavy-walled pressure tube. The excess amount of butadiene was evaporated, and the residue was purified by flash chromatography on a silica column (hexane/EtOAc). The product was recrystallized from petroleum ether to give a white crystalline powder (6.2 g, 95%). M.p. 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS): δ = 7.75 (m, 2 H), 7.33 (m, 2 H), 7.01 (m, 1 H), 5.72–5.60 (m, 2 H), 2.98–2.90 (m, 2 H), 2.85–2.77 (m, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 144.24, 137.83, 143.59, 129.76, 128.15, 122.82, 122.28, 27.02, 23.77, 21.56 ppm. $C_{13}H_{14}O_2S$ (234.31): calcd. C 66.64, H 6.02; found C 66.16, H 5.88.

2-*tert*-Butoxycarbonyl-4,7-dihydro-2*H*-isoindole (3): A solution of *tert*-butyl isocyanacetate (3.28 g, 23.3 mmol) in THF (10 mL) was added dropwise to a stirred suspension of *t*BuOK (2.61 g, 23.3 mmol) in THF (20 mL) at 0 °C under an atmosphere of argon. A solution of 1-tosyl-1,4-cyclohexadiene (5.2 g, 22.2 mmol) in THF (20 mL) was added dropwise, and the resulting mixture was stirred at room temp. After 4 h, the volume of the mixture was reduced by rotary evaporation and CH_2Cl_2 (100 mL) was added. The resulting solution was washed with water and brine and dried with Na_2SO_4. The solvents were removed in vacuo, and the residue was purified on silica column (CH_2Cl_2). The product was recrystallized from hexane to give white crystals (3.89 g, 80%). M.p. 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS): δ = 9.59 (br. s, 1 H, position of this signal is concentration dependent and may vary in a range 9.1–9.6 ppm), 6.72 (d, J = 2.40 Hz, 1 H), 5.94 (AB, J = 10.4 Hz, 1 H), 5.90 (AB, J = 10.4 Hz, 1 H), 3.46 (m, 2 H), 3.25 (m, 2 H), 1.61 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 161.57, 124.55, 124.02, 123.90, 118.79, 118.68, 118.19, 80.47, 28.56, 24.30, 22.47 ppm. $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.21, H 7.81, N 6.39; found C 71.11, H 8.04, N 6.20.

4,7-Dihydro-2*H*-isoindole (4): *Method A:* 2-*tert*-Butoxycarbonyl-4,7-dihydroisoindole (**3**; 1.5 g, 6.84 mmol) was dissolved in TFA (20 mL), and the solution was left for 30 min under an atmosphere of Ar in the dark at room temp. After the addition of CH_2Cl_2 (20 mL), the mixture was poured into cold water. The organic layer was collected, washed with water, then with 10% solution of Na_2CO_3, water, and dried with Na_2SO_4. The solvent was removed in vacuo, and the residue was passed through a layer of silica using CH_2Cl_2 as eluent. The solvent was evaporated to give the product as a yellow oil (0.45 mg, 55%). *Method B:* A mixture of 2-*tert*-butoxycarbonyl-4,7-dihydroisoindole (2.0 g, 9.13 mmol) and potassium hydroxide (45.6 mmol, 2.55 g) in ethylene glycol (30 mL) was heated at reflux under an atmosphere of Ar for 30 min. The mixture was cooled to 0 °C 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 vacuo. The residue was passed through a layer of silica using CH_2Cl_2 as eluent, and the resulting solution was evaporated to give the product as a yellow oil (0.92 mg, 85%). The compound was used in further transformations either immediately, or after storage in the refrigerator at –18 °C. It rapidly darkens if kept open in air at room temp.

5,10,15,20-Tetraaryloctahydrotetrabenzoporphyrins (5a,b): 4,7-Dihydroisoindole (2.5 mmol, 0.30 g) was dissolved in CH_2Cl_2 (250 mL) and an aromatic aldehyde (2.5 mmol) was added. The mixture was stirred under an atmosphere of Ar for 10 min in the dark at room temp. $BF_3{\cdot}Et_2O$ (0.5 mmol, 0.071 g) was added in one portion, and the mixture was stirred at room temp. for an additional 2 h. DDQ (2.8 mmol, 0.63 g) was added, and the mixture was stirred for an hour. The resulting solution was washed with 10% aqueous Na_2SO_3 and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified on a silica column (CH_2Cl_2, then CH_2Cl_2/AcOH, 50:1; green band collected), and then by recrystallization from CH_2Cl_2/MeOH. Zn complex was obtained by reaction of porphyrins **5** with $Zn(OAc)_2$ in CH_2Cl_2/MeOH, controlled by UV/Vis spectroscopy. **5a**: green crystals (0.13 g, 25%). M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS, as dication salt): δ = 8.41 (m, 8 H), 7.88 (m, 12 H), 5.48 (s, 8 H), 3.20 (m, 8 H), 2.69 (m, 8 H), 1.50 (br. s., 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 143.41, 138.45, 136.38, 132.23, 130.03, 128.72, 123.02, 118.62, 25.63 ppm. UV/Vis

(CH_2Cl_2): λ (logε) = 438 (5.23), 532 (4.03), 568 (3.66), 576 (3.67), 614 (3.31) nm. UV/Vis (CH_2Cl_2/TFA, as dication): λ (logε) = 460 (5.28), 610 (3.89), 670 (4.17) nm. UV/Vis (CH_2Cl_2, as Zn complex): λ (logε) = 436, 574, 624 (sh) nm. MALDI-TOF: calcd. for $C_{60}H_{47}N_4$ $[M + H]^+$ 823.38; found 823.39. MALDI-TOF (as Zn complex): calcd. for $C_{60}H_{44}N_4Zn$ 884.28; found 884.38. **5b**: green crystals (0.264 g, 40%). M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS, as dication salt): δ = 8.57 (m, 16 H), 5.50 (m, 8 H), 4.15 (s, 12 H), 1.56 (br.s.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 166.78, 143.01, 141.73, 136.29, 132.63, 131.51, 129.88, 122.77, 118.13, 52.72, 25.85 ppm. UV/Vis (CH_2Cl_2): λ (logε) = 446 (5.29), 540 (4.14), 574 (3.84), 616 (3.80), 682 (3.41) nm. UV/Vis (CH_2Cl_2/TFA, as dication): λ (logε) = 468 (5.34), 614 (4.05), 672 (4.27) nm. UV/Vis (CH_2Cl_2, as Zn complex): λ (logε) = 448, 578, 625 (sh) nm. MALDI-TOF: calcd. for $C_{68}H_{55}N_4O_8$ $[M + H]^+$ 1055.40; found 1055.46. MALDI-TOF (As Zn complex): calcd. for $C_{68}H_{52}N_4O_8Zn$ 1116.31; found 1116.40.

5,10,15,20-Tetraaryltetrabenzoporphyrins (6a,b): Porphyrin **5a** (50 mg) was dissolved in toluene (10 mL). To this solution was added DDQ (69 mg, 5 equiv.), and the solution was heated at reflux. The reaction was controlled by removing samples and measuring the electronic absorption spectra. After 5 min of heating at reflux, the conversion was complete as evidenced by the full disappearance of the Q-bands of the starting porphyrin. After cooling, the mixture was washed by Na_2SO_3 solution, water, brine, dried with Na_2SO_4, and the solvents were evaporated to dryness. The residue was recrystallized from CH_2Cl_2/MeOH to afford green crystals of tetraphenyltetrabenzoporphyrin **6a** (47 mg, 96%), identical to the material obtained by the tetrahydroisoindole method.[8c] Aromatization of porphyrin **5b** took place analogously to afford tetrakis(*p*-methoxycarbonylphenyl)tetrabenzoporphyrin **6b** in 98% yield, identical to the material obtained by the tetrahydroisoindole method.[8c]

3,3′-Bis(*tert*-butoxycarbonyl)-1,1′-phenylmethylenebis-4,7-dihydro-2*H*-isoindole (7): A mixture of 2-*tert*-butoxycarbonyl-4,7-dihydroisoindole (1.095 g, 5 mmol), benzaldehyde (0.265 g, 2.5 mmol), *p*-toluenesulfonic acid (0.094 g, 0.5 mmol), and tetrabutylammonium chloride (0.1 g, 0.35 mmol) in chloroform (50 mL) that was degassed by purging with argon for 20 min was stirred at room temp. under an atmosphere of argon for 24 h. The reaction mixture was washed with 10% aqueous $NaHCO_3$, brine, and dried with Na_2SO_4. The solution was evaporated in vacuo, and the residue was purified on a silica column (hexane/EtOAc, 4:1). The solvents were evaporated to give the product as a yellow semisolid froth. Yield: 1.18 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°, TMS): δ = 8.43 (br. s, 2 H), 7.38–7.27 (m, 3 H), 7.17–7.12 (m, 2 H), 5.91–5.84 (m, 2 H), 5.80–5.73 (m, 2 H), 5.46 (s, 1 H), 3.42 (m, 4 H), 2.83 (m, 4 H), 1.56 (s, 18 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 161.15, 138.42, 129.56, 129.19, 128.31, 127.62, 125.00, 124.44, 123.38, 117.92, 116.58, 80.41, 41.46, 28.51, 24.43, 21.97 ppm. $C_{33}H_{38}N_2O_4$ (526.67): calcd. C 75.26, H 7.27, N 5.32; found C 74.98, H 7.40, N 5.02.

3,3′-Diformyl-1,1′-phenylmethylenebis-4,7-dihydro-2*H*-isoindole (9): Dipyrromethane **7** (1.052 g, 2 mmol) was dissolved in trifluoroacetic (20 mL) acid under an atmosphere of argon, and the solution was cooled to 0–5 °C. After 30 min, trimethylorthoformate (2.12 g, 20 mmol) was added. The mixture was stirred for an additional 30 min at room temp. and then poured into cold water. The product was extracted with CH_2Cl_2, then washed with 10% aqueous $NaHCO_3$ and brine, and dried with Na_2SO_4. The solution was evaporated in vacuo, and the remaining material was purified on a silica column (CH_2Cl_2/MeOH). The solvents were evaporated to give the product as a grey powder. Yield: 0.382 g (50%). M.p. >200 °C (dec.). ^{1}H NMR (400 MHz, $[D_8]$DMSO, 25°, TMS): δ = 11.58 (s, 2 H), 9.50 (s, 2 H), 7.40–7.25 (m, 3 H), 7.14–7.08 (m, 2 H), 5.85 (br. d, J = 10.23 Hz, 2 H), 5.80 (br. d, J = 10.23 Hz, 2 H), 5.70 (s, 1 H), 3.44 (m, 4 H), 2.83 (m, 4 H) ppm. ^{13}C NMR not obtained because of very poor solubility. $C_{25}H_{22}N_2O_2$ (382.45): calcd. C 78.51, H 5.80, N 7.32; found C 78.45, H 6.02, N 7.04.

5,15-Diphenyloctahydrotetrabenzoporphyrin (10): Dipyrromethane **7** (1.05 g, 2 mmol) was stirred in trifluoroacetic acid (5 mL) for 30 min at room temp. under an atmosphere of argon. The mixture was diluted with CH_2Cl_2 (60 mL), and a solution of diformyldipyrromethane (**9**; 0.76 g, 2 mmol) in CH_2Cl_2 (90 mL) was added. The reaction mixture was stirred for 21 h at room temp. under an atmosphere of argon. DDQ (0.68 g, 3 mmol) was added, and the mixture was stirred for an additional 4 h. The resulting solution was washed with 10% aqueous Na_2SO_3 and brine and then dried with Na_2SO_4. The solvent was evaporated in vacuo, and the residue was purified on a silica column (CH_2Cl_2, then CH_2Cl_2/THF) and by crystallization from CH_2Cl_2/Et_2O to afford dark-purple powder (0.10 g; 15%). M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA): δ = 10.26 (c, 2 H), 8.33–8.22 (m, 4 H), 8.03–7.88 (m, 6 H), 6.22 (br. d, J = 10.10 Hz, 4 H), 5.97 (br. d, J = 9.98 Hz, 4 H), 4.58 (m, 8 H), 3.35 (m, 8 H), 3.71 (m, 8 H), –2.04 (br. s, 4 H) ppm. UV/Vis (as free base, CH_2Cl_2): λ (logε) = 406 (5.04), 504 (3.91), 538 (3.41), 572 (3.47), 624 (2.58) nm. UV/Vis (as dication, CH_2Cl_2/TFA): λ (logε) = 422(5.49), 526 (3.28), 562 (4.15), 607 (sh, 3.54) nm. MALDI-TOF: calcd. for $C_{48}H_{39}N_4$ $[M+ H]^+$ 671.32; found 671.28.

5,15-Diphenyltetrabenzoporphyrin (11): Porphyrin **10** (35 mg) was dissolved in toluene (10 mL). To this solution was added DDQ (60 mg, 5 equiv.), and the solution was heated at reflux for 5 min (monitored by UV/Vis spectra). After cooling, the mixture was washed with a Na_2SO_3 solution, water, and brine, dried with Na_2SO_4, and the solvents were evaporated to dryness. The residue was eluted through a short silica column (CH_2Cl_2) collecting the first green band. After evaporation of the solvent, a green crystalline powder was obtained (33 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$/TFA): δ = 11.01 (s, 2 H), 9.35 (d, J = 7.96 Hz, 4 H), 8.43 (m, 4 H), 8.20 (ddd, J_1 = J_2 = 7.52 Hz, J_3 = 0.65 Hz, 4 H), 8.12 (m, 2 H), 8.03 (m, 4 H), 7.86 (ddd, J_1 = J_2 = 7.76 Hz, J_3 = 0.78 Hz, 4 H), 7.62 (d, J = 8.35 Hz, 4 H), –0.25 (br. s., 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°, TMS): δ = 140.20, 138.78, 138.60, 134.49, 132.94, 132.29, 130.82, 130.39, 130.28, 129.94, 125.43, 123.37, 116.32, 92.24 ppm. UV/Vis (CH_2Cl_2, as free base): λ (logε) = 396 (3.78), 422 (5.64), 436 (5.71), 450 (3.47), 570 (3.35), 610 (3.88), 666 (3.59) nm. UV/Vis (CH_2Cl_2/TFA, as dication): λ (logε) = 454 (5.67), 616 (3.30), 672 (3.84) nm. LDI-TOF: calcd. for $C_{48}H_{30}N_4$ 662.25; found 662.29.

Supporting Information (see footnote on the first page of this article): The selected spectra of the newly obtained compounds.

Acknowledgments

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[13] Although a poor choice, isomeric 6,7-dihydroisoindole should also be considered as the conjugated and very electron-rich double bond in this compound can be an alternative reaction center in the electrophilic reactions; thus, many side reactions are anticipated.

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[26] For example, for direct comparison with the results of this study, in tetrahydroisoindole method[8c] Ni complex of porphyrin **6a** is obtained by aromatization of the respective Ni complex of hexadecahydro TBP in 25–30% yield, and Ni cannot be withdrawn from this complex to afford free base **6a** by any means. Alternatively, for the respective Cu complexes aromatization gives 60% yield of Cu-**6a**, which can be demetallated to give free base **6a** in 80% yield, which overall amounts to as low as 48% yield of free base **6a**.
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