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Straightforward Syntheses That Avoid Scrambling of *meso*-Substituted [28]Hexaphyrins

Rémi Plamont,^[a] Teodor Silviu Balaban,^[a] and Gabriel Canard^{*[b]}

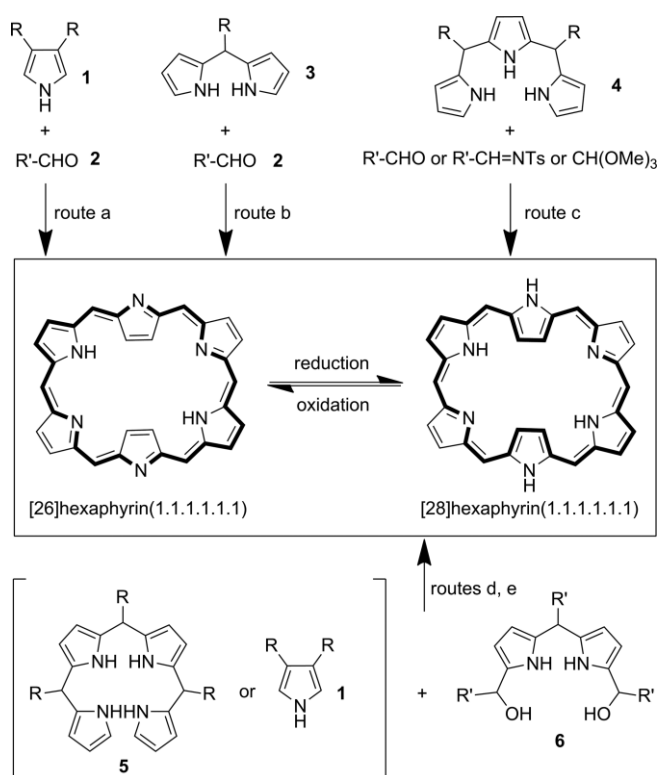
Abstract: A two-step synthesis of *meso*-substituted [28]hexaphyrins in an aqueous medium was developed and optimized, and scrambling processes are avoided despite the use of a high acid concentration. The efficiency of this procedure relies on

the nature of the starting material, and it can be extended to the straightforward preparation of unprecedented AB₂C₂D-[28]hexaphyrins bearing up to four different kinds of *meso*-appended aryl group.

Introduction

Expanded porphyrins and their core-modified analogues have been the subject of growing interest because of their versatile chemical, optical, and electrochemical properties as well as their unique coordination chemistry.^[1] Among the numerous described expanded porphyrinoid structures, hexaphyrin-(1.1.1.1.1.1) derivatives (Scheme 1), which can be viewed as the first expanded porphyrin homologues (alternating pyrrole units and bridging carbon atoms), were the subject of particularly intense research activity because of their fascinating physicochemical properties. For example, their cavities are suitable for the concomitant coordination of two identical or different metal centers.^[2] Moreover, although most of the [26]hexaphyrins are planar macrocycles that exhibit Hückel aromaticity,^[1g,3] their reduced forms, [28]hexaphyrins (Scheme 1), and their metal complexes may have twisted Möbius structures in solution.^[1g,4] Consequently, the oxidation state of a hexaphyrin has a crucial impact on its light-absorption and emission properties.^[5]

The main synthetic procedures that provide access to *meso*-substituted hexaphyrins are summarized in Scheme 1. The first stable derivative bearing six *meso*-pentafluorophenyl groups was prepared through a simple and straightforward synthesis from commercially available pyrrole (**1**, R = H) and pentafluorobenzaldehyde (Scheme 1, route a).^[6] This strategy can be used to introduce various kinds of *meso* substituents together with various β groups if these are born by the starting pyrrole unit **1** (R \neq H).^[7] Nevertheless, this one-pot procedure produces complex mixtures of expanded porphyrins, which are difficult to separate and purify. This problem can be overcome through ring-size-selective syntheses of hexaphyrins from oligopyrroles.



Scheme 1. Synthetic preparations of *meso*-substituted hexaphyrins.

For example, the acidic condensation of *meso*-substituted dipyrromethanes **3** with aldehydes **2** followed by oxidation can produce A₃B₃-hexaphyrin derivatives bearing up to two different kinds of *meso* groups (Scheme 1, route b).^[8] The first example of a *meso*-substituted hexaphyrin bearing six phenyl groups was prepared through the condensation of a tripyrrane **4** with benzaldehyde in an acidic medium (Scheme 1, route c).^[9] This approach was later used to synthesize simple to very sophisticated hexaphyrin derivatives such as A₂B₄-type compounds bearing an internal strap or dyes incorporating boron-dipyrromethene (Bodipy) units.^[3a,10] Less-symmetric compounds were prepared through the acidic condensation of tetrapyrroles **5**

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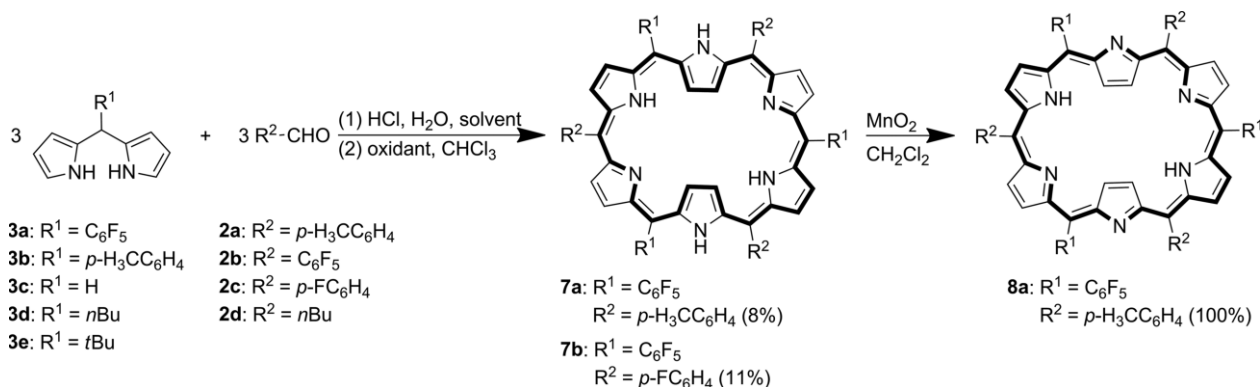
with dipyrromethane dicarbinols **6** (Scheme 1, route d). This elegant strategy allows access to derivatives bearing up to six different *meso* groups and was used to prepare unsymmetrical compounds bearing a free *meso* position or hexaphyrin dimers.^[11] Reactive compounds **6** were also condensed with β -substituted pyrrole units **1** to prepare partially β -substituted hexaphyrins (Scheme 1, route e).^[12]

The use of cyclic or linear oligopyrroles often suffers from a major drawback called "scrambling". These compounds are usually condensed or prepared in an acidic medium, which can also cause their acidolysis into fragments that then recombine into other different oligopyrroles.^[13] For example, this scrambling process was evident during the condensation of a tripyrrole **4** with an aldehyde or an *N*-sulfonyl-substituted aldimine forming the unexpected *N*-fused pentaphyrins, heptaphyrins, or octaphyrins.^[8c,10f] The acidolysis of oligopyrroles can be avoided through the use of sterically hindered or strongly electron-withdrawing *meso*-aryl substituents,^[14] and, in a spectacular breakthrough, Koszarna and Gryko showed in 2006 that it can also be suppressed if the solvent is an alcohol/water mixture, despite the use of very high concentrations of aqueous HCl.^[15] This efficient preparation of *trans*-A₂B corroles was later extended to the synthesis of porphyrins bearing up to three different kinds of *meso* substituents.^[16] We report herein how this strategy can be extended to the straightforward prepara-

tion of simple or complex *meso*-substituted [28]hexaphyrins bearing up to four different kinds of *meso* groups.

Results and Discussion

The optimized preparation of a *trans*-A₂B₂ porphyrin starting from a dipyrromethane (DPM) **3** and an aldehyde **2** in an aqueous medium was chosen as the starting point for the development of a new synthetic route to *meso*-substituted expanded porphyrin derivatives (Scheme 2). Equal amounts of DPM and aldehyde were dissolved in 4 mM concentrations in an ethanol/water (4:1) mixture in the presence of an HCl concentration of 38 mM. The porphyrinogen was then oxidized by *p*-chloranil in boiling chloroform for 1 h. Under these conditions with DPM **3a**, aldehyde **2a**, and *p*-chloranil (2 equiv.; Table 1, Entry 1), no expanded porphyrin was observed in the final mixture. The concentration of the starting materials was then increased to 100 mM, because this value was optimal for the production of A₄B₄-octaphyrins from DPM (Table 1, Entry 2).^[8e] The chromatographic purification of the oxidized reaction mixture revealed that only one supplementary colored compound was eluted after the *trans*-A₂B₂ porphyrin. A combination of ¹H NMR spectroscopy, UV/Vis spectroscopy, and mass spectrometry analyses proved that this compound was the [28]hexaphyrin **7a**



Scheme 2. Syntheses of *meso*-substituted [28]hexaphyrins **7a** and **7b** as well as [26]hexaphyrin **8a**.

Table 1. Optimization of the synthesis of [28]hexaphyrin **7a**.

Entry	[3a] [mmol/L]	Solvent	<i>t</i> [h]	Oxidation step ^[a]	UV yield [%]
1	4	EtOH	16	(a)	0
2	100	EtOH	16	(a)	14 (2) ^[b]
3	10	EtOH	16	(a)	1
4 ^[c]	33.3	EtOH	16	(a)	20 (8) ^[b]
5	50	EtOH	16	(a)	17
6	75	EtOH	16	(a)	16
7	33	MeOH	16	(a)	7
8	33	<i>i</i> PrOH	16	(a)	8
9	33	THF	16	(a)	0
10	33	EtOH	2	(a)	1
11	33	EtOH	6	(a)	3
12	33	EtOH	48	(a)	12
13	33	EtOH	16	(b)	0
14	33	EtOH	16	(c)	0

[a] Oxidation step: (a) *p*-chloranil (2 equiv.) in CHCl₃ under reflux (1 h), (b) *p*-chloranil (3 equiv.) in CHCl₃ under reflux (1 h), (c) air in CHCl₃ under reflux (1 h).

[b] Isolated yield. [c] Optimal conditions.

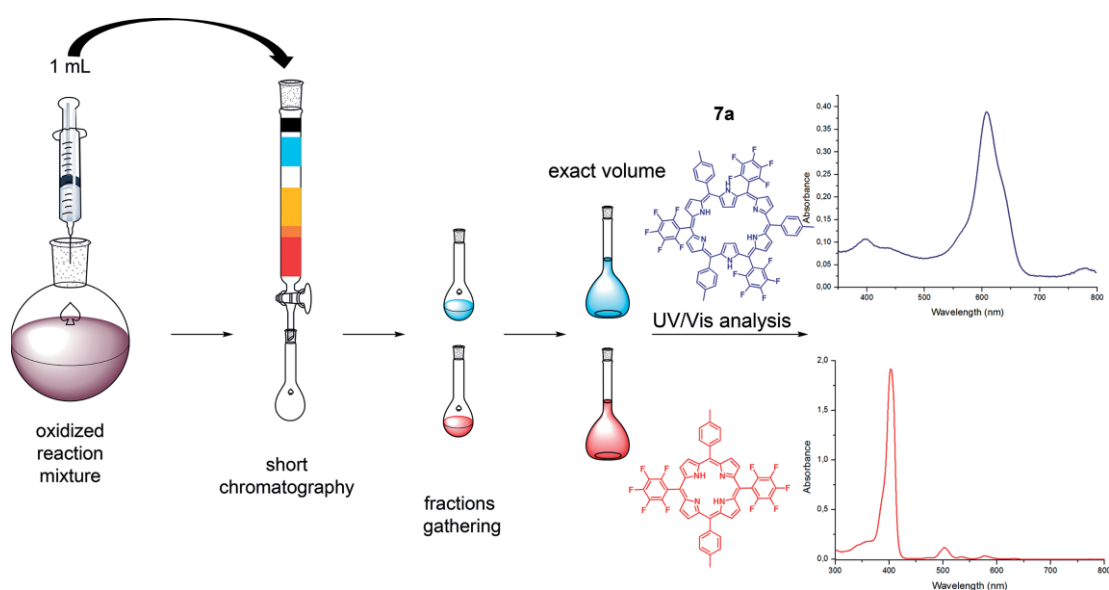
(Scheme 2) and not the expected A_4B_4 -octaphyrin. This result was quite surprising, because previous syntheses of [26]hexaphyrins starting from DPM **3a** and aldehydes required *ortho*-substituted benzaldehyde derivatives.^[8b] Moreover, despite the highly acidic conditions, no scrambling occurred, as demonstrated by the single isotope cluster in the corresponding HR mass spectrum (see the Supporting Information). Consequently, we attempted to improve the first isolated synthetic yield (2 %) of **7a** by varying the different reactions parameters such as the concentration of the reactants and the time of the acidic condensation (Table 1).

The first small sample of **7a** was used to record its UV/Vis spectrum and to measure the molar absorptivity at the Soret-like band maximum ($\lambda_{\text{max}} = 610$ nm). For each subsequent experiment, the solvent volume was kept constant (25 mL) during the acidic condensation and the oxidation steps. On the contrary, the concentrations of the reactants, the nature of the organic solvent, and the amount and the nature of the oxidant were varied. After the oxidation step, multiple colored species in the reaction mixture were detected by TLC or UV/Vis spectroscopy. Consequently, a 1 mL aliquot was collected from this mixture and passed through a short silica gel chromatography column with dichloromethane as the solvent (see Scheme 3). The first red fractions containing the *trans*- A_2B_2 porphyrin and traces of *p*-chloranil were removed before the elution of **7a** (Scheme 3). All the following blue fractions containing **7a** were gathered in a volumetric flask filled with dichloromethane. The UV/Vis spectrum of the resulting solution was then recorded and used to determine the corresponding UV yield. Considering the different preceding steps (extraction, washing, purification, etc.), a probable overestimation of the UV yields cannot be excluded and could be partly responsible for the discrepancies between the UV and isolated yields. As these uncertainties cannot be the principal source of the trends affecting the UV yield, we kept this short and quick procedure for the optimization of the synthetic preparation of **7a**.

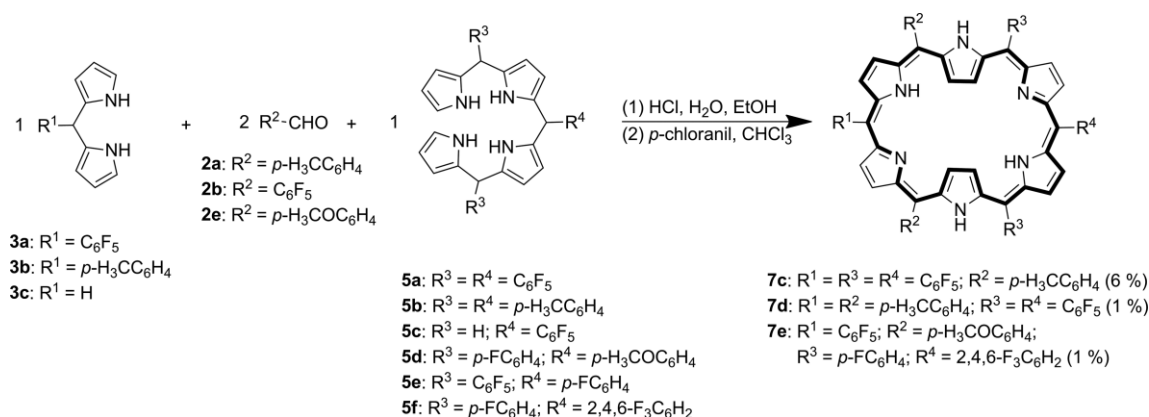
The highest UV yield was reached when a DPM concentration of 33.3 mM was used, as observed previously for the synthesis of [26]hexaphyrins (20 %; Table 1, Entry 4).^[8b] The replacement of ethanol by other organic solvents as well as the modification of the acidic condensation time did not increase the yield of **7a** (Table 1, Entries 7–12). Interestingly, no expanded porphyrin was detected when a higher quantity of *p*-chloranil (3 equiv.) was introduced during the oxidation step or when air was the oxidizing agent (Table 1, Entries 13 and 14). Consequently, *meso*-substituted [28]hexaphyrins or [26]hexaphyrins are probably unstable under strong oxidative conditions, which have to be avoided when considering their interconversion. This transformation was effective when **7a** was dissolved in a suspension of MnO_2 in dichloromethane to afford quantitatively its oxidized form [26]hexaphyrin **8a** (Scheme 2).

The optimized conditions were used on a preparative scale to produce [28]hexaphyrins **7a** and **7b** with yields of 8 and 11 %, respectively. The nature of the starting compounds is crucial. For example, only 2 % of **7a** was formed when DPM **3a** and aldehyde **2a** were replaced by **3b** and **2b**, respectively (Scheme 2). Although the *meso*-pentafluorophenyl group stabilizes dipyrromethane **3a** slightly towards acidolysis,^[14] no scrambling occurred during the utilization of **3b**, as illustrated by the concomitant formation of only the corresponding *trans*- A_2B_2 porphyrin. Moreover, a single and pure hexaphyrin (**7a**) was formed, as proved by its HR mass spectrum. The difference between the two yields could be due to a different preorganization of the intermediate oligopyrranes towards the cyclization. In the same way, we were not successful in preparing *meso*-free or *meso*-alkyl derivatives by condensation of DPMs **3c–3e** with aldehyde **2b** or of DPM **3a** with aldehyde **2d** (Scheme 2).

The lack of scrambling observed under the optimized conditions prompted us to introduce bilanes **5** into the reaction mixture (Scheme 4). Triarylbilanes (**5a–5f**) were then prepared under the conditions reported by the Gryko group and purified by silica chromatography (see the Experimental Section).^[15] As



Scheme 3. Schematic representation of the procedure used to measure the UV yields of **7a** during the optimization of the synthetic parameters.



Scheme 4. Synthesis of *meso*-substituted [28]hexaphyrins from tetrapyrroles.

Table 2. Selected UV/Vis maxima of [28]hexaphyrins in dichloromethane (for numbering scheme, see Scheme 4).

Compound	R ¹	R ²	R ³	R ⁴	λ _{max} [nm]
7a	C ₆ F ₅	<i>p</i> -MeC ₆ H ₄	C ₆ F ₅	<i>p</i> -MeC ₆ H ₄	610
7b	C ₆ F ₅	<i>p</i> -FC ₆ H ₄	C ₆ F ₅	<i>p</i> -FC ₆ H ₄	605
7c	C ₆ F ₅	<i>p</i> -MeC ₆ H ₄	C ₆ F ₅	C ₆ F ₅	605
7d	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	C ₆ F ₅	C ₆ F ₅	602
7e	C ₆ F ₅	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -FC ₆ H ₄	2,4,6-F ₃ C ₆ H ₂	615
7f ^[a]	C ₆ F ₅	C ₆ F ₅	C ₆ F ₅	C ₆ F ₅	561

[a] From ref.^[6]

suming that bilanes are formed in situ through the condensation of two DPM molecules with an aldehyde during the first step of the [28]hexaphyrins synthesis, we studied the condensation of bilanes with aldehyde and DPM in a 1:2:1 ratio and with a three times lower DPM concentration of 11.1 mM (Scheme 4). Compound **7c** was then produced with a mixture of different porphyrins and isolated in an encouraging yield of 6 % through the condensation of **3a**, **2a**, and **5a** (Scheme 4). The yield of this synthesis is again dependent on the nature of the starting materials and decreases with the electron-withdrawing strength of the substituents. Several combinations were tested (**3a/2a/5b**, **3a/2a/5d**, **3c/2b/5c**, and **3b/2e/5e**) and failed to give any expanded porphyrins. However, when the procedure was applied to the two sets **3b/2a/5a** and **3a/2e/5f**, the purification of the final reaction mixture afforded the new compounds **7d** and **7e** in yields of 1 %. Compound **7d** is the *cis* isomer of **7a** in which three successive *meso* carbon atoms bear identical substituents. Although the synthetic yield of **7e** is low (1 %), this result demonstrates how this simple procedure can lead to sophisticated compounds bearing up to four different kinds of *meso*-aryl groups. However, we noticed that [28]hexaphyrins display moderate stabilities emphasized by electron-donating substituents. After 1 year, the solid compounds **7a–7e** had converted slowly into mixtures of colored compounds containing their [26] isomers, even though they were stored at –20 °C under argon.

The complete ¹H NMR spectroscopic characterization of [28]hexaphyrins is difficult because of the equilibria between the different interconverting twisted Möbius isomers.^[4b] The complexity of this task is increased here by the presence of different tautomeric forms resulting from the substitution pat-

tern. Consequently, the complete assignment of the ¹H NMR signals of **7a–7e** and **8a** is far beyond the scope of the present work, which focuses on their synthetic preparation. We chose to report the ¹H NMR data recorded in deuterated tetrahydrofuran (THF) in the Experimental Section, because this solvent gave the best-resolved spectra at room temperature (see the Supporting Information). On the other hand, the UV/Vis spectra of [28]hexaphyrins **7a–7e** give the first insights into the relationship between the nature of the *meso*-aryl groups and the physicochemical properties of these derivatives (see the Supporting Information). The Soret-like band maxima of **7a–7e** are reported in Table 2 and are compared with that of **7f**, which bears six *meso*-pentafluorophenyl groups.^[6] Peripheral electron-donating groups produce a redshift of the absorption maximum. For example, when the three 5,15,25 *meso* groups of **7f** are replaced by *p*-fluorophenyl groups in **7b** and by *p*-tolyl groups in **7a**, the Soret-like band is redshifted by 44 and 49 nm, respectively. A larger redshift is observed for **7e** bearing several electron-donating groups. Although the bulkiness of the *meso* substituents cannot be excluded as the source of these shifts, the light-absorption properties of [28]hexaphyrins are also controlled by their symmetry, as illustrated by the different absorption maxima of the two isomeric compounds **7a** and **7d** (λ = 610 and 602 nm respectively).

Conclusions

We have described herein a new strategy to produce *meso*-substituted [28]hexaphyrins in a mixture of ethanol and water as the solvent with high concentrations of HCl. The yields are

modest, but these syntheses afford single expanded porphyrins without any scrambling that can be separated readily from the other porphyrin products. Starting from bilanes, this new procedure can afford unprecedented [28]hexaphyrins bearing up to four different kinds of *meso* substituents and, thereby, extends the variety of these compounds and enables the study of their physicochemical properties.

Experimental Section

General: Pure pyrrole was freshly purified by passage through a short chromatography column filled with neutral alumina. All other reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed with Geduran silica gel 40–63 μm from VWR. The reactions were monitored by thin-layer chromatography (Merck 60 F254). ^1H NMR spectra were recorded at 500 MHz with a Bruker Avance DPX-500 spectrometer, at 400 MHz with a Bruker Avance DPX-400 spectrometer, at 300 MHz with a Bruker Avance DPX-300 instrument, or at 200 MHz with a Bruker Avance DPX-200 instrument. ^1H NMR chemical shifts are given in ppm relative to the residual solvent peaks of CDCl_3 ($\delta = 7.26$ ppm) or $[\text{D}_8]\text{THF}$ ($\delta = 1.72$ and 3.58 ppm). UV/Vis spectra were recorded with a Shimadzu UV-2401 (PC) instrument or with a Varian Cary 1E spectrophotometer. HRMS-ESI data were recorded with a QStar Elite (Applied Biosystems SCIEX) spectrometer equipped with an ion source at atmospheric pressure [atmospheric pressure ionization (API)]. Dipyrrromethanes **3a–3f**^[17] and bilanes **5a** and **5b**^[15,16] were prepared according to literature procedures.

General Procedure for the Investigation of the Reaction Conditions To Form A_3B_3 -[28]hexaphyrins: 5-(Pentafluorophenyl)dipyrrromethane (**3a**; 1 equiv.) and *p*-tolualdehyde (**2a**; 1 equiv.) were dissolved in an organic solvent (20 mL), and an aqueous solution of HCl (37 % 0.1 mL) in water (5 mL) was added. The reaction mixture was stirred for a certain time and then extracted with CHCl_3 (150 mL). The organic phase was washed three times with water (100 mL), washed once with a saturated aqueous solution of NaHCO_3 (100 mL), dried with MgSO_4 , and filtered before the oxidation step with *p*-chloranil or air. The resulting mixture was heated to reflux for 1 h and then cooled to room temperature. A 1 mL aliquot of the resulting mixture was then subjected to a very short silica gel chromatography column in a Pasteur pipette with CH_2Cl_2 as the solvent. The first eluting fractions containing porphyrin derivatives together with unreacted oxidant were removed. The second-eluting blue fraction was collected entirely in a 25 mL volumetric flask, which was filled with CH_2Cl_2 . The UV/Vis spectra of these solutions were recorded and used to determine the corresponding amount of [28]hexaphyrin **7a** in the crude mixture.

5,15,25-Tris(pentafluorophenyl)-10,20,30-tris(4-methylphenyl)-hexaphyrin[28] (7a): A solution of 5-(pentafluorophenyl)dipyrrromethane (**3a**; 0.26 g, 0.83 mmol, 1 equiv.) and *p*-tolualdehyde (**2a**; 98 μL , 0.83 mmol, 1 equiv.) in ethanol (20 mL) was stirred, and an aqueous solution of HCl (37 % 0.1 mL) in water (5 mL) was added. The reaction mixture was stirred for 16 h and then extracted with CHCl_3 (150 mL). The organic phase was washed three times with water (100 mL) and once with a saturated aqueous solution of NaHCO_3 (100 mL), dried with MgSO_4 , and filtered, and *p*-chloranil (410 mg, 1.67 mmol, 2 equiv.) was added. The resulting mixture was heated to reflux for 1 h, cooled to room temperature, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (CH_2Cl_2) to afford pure **7a** as a dark blue powder

(27 mg, 22 μmol , 8 %). ^1H NMR (400 MHz, $[\text{D}_8]\text{THF}$, 25 $^\circ\text{C}$): $\delta = 9.22$ (br. s, NH_{outer}), 8.03 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, Ar-H), 7.92 (m, 6 H, $\beta\text{-H}_{\text{outer}}$), 7.68 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $\beta\text{-H}_{\text{outer}}$), 7.54 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, Ar-H), 7.49 (d, $^3J_{\text{H,H}} = 7.7$ Hz, 4 H, Ar-H), 7.26 (d, $^3J_{\text{H,H}} = 7.9$ Hz, 4 H, Ar-H), 4.72 (s, 2 H, NH_{inner}), 2.58 (s, 3 H, CH_3), 2.44 (s, 6 H, CH_3), 2.38 (br. s, 4 H, $\beta\text{-H}_{\text{inner}}$) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon_{\text{max}}$) = 397 (4.59), 441 (4.47), 610 (5.19), 640 (4.93), 778 (4.16), 869 (3.99), 925 (3.92), 1051 (3.83) nm. HRMS-ESI: calcd. for $\text{C}_{69}\text{H}_{38}\text{F}_{15}\text{N}_6$ [$\text{M} + \text{H}$]⁺ 1235.2913; found 1235.2919.

5,15,25-Tris(pentafluorophenyl)-10,20,30-tris(4-fluorophenyl)-hexaphyrin[28] (7b): A solution of 5-(pentafluorophenyl)dipyrrromethane (**3a**; 0.26 g, 0.83 mmol, 1 equiv.) and *p*-fluorobenzaldehyde (**2c**; 89 μL , 0.83 mmol, 1 equiv.) in ethanol (20 mL) was stirred, and a solution of HCl (37 % 0.1 mL) in water (5 mL) was added. The reaction mixture was stirred for 16 h and then extracted with CHCl_3 (150 mL). The organic phase was washed three times with water (100 mL) and once with a saturated aqueous solution of NaHCO_3 (100 mL), dried with MgSO_4 , and filtered, and *p*-chloranil (410 mg, 1.67 mmol, 2 equiv.) was added. The resulting mixture was heated to reflux for 1 h, cooled to room temperature, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (CH_2Cl_2) to afford pure **7b** as a dark blue powder (38 mg, 30 μmol , 11 %). ^1H NMR (400 MHz, $[\text{D}_8]\text{THF}$, 25 $^\circ\text{C}$): $\delta = 8.16$ (m, 2 H, Ar-H), 7.97 (m, 2 H, $\beta\text{-H}_{\text{outer}}$), 7.92 (m, 4 H, $\beta\text{-H}_{\text{outer}}$), 7.74 (m, 2 H, $\beta\text{-H}_{\text{outer}}$), 7.64 (m, 4 H, Ar-H), 7.49 (m, 2 H, Ar-H), 7.22 (m, 4 H, Ar-H), 4.75 (br. s, 1 H, NH_{inner}), 4.10 (br. s, 1 H, NH_{inner}), 2.18 (s, 2 H, $\beta\text{-H}_{\text{inner}}$), 1.93 (s, 2 H, $\beta\text{-H}_{\text{inner}}$) ppm. UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon_{\text{max}}$) = 398 (4.69), 605 (5.17), 776 (4.16), 864 (4.03), 918 (3.97), 1041 (3.81) nm. HRMS-ESI: calcd. for $\text{C}_{66}\text{H}_{29}\text{F}_{18}\text{N}_6$ [$\text{M} + \text{H}$]⁺ 1247.2161; found 1247.2161.

5,10,15-Tris(pentafluorophenyl)tetrapyrane (5a): Pentafluorobenzaldehyde (0.62 mL, 5 mmol) and pyrrole (694 μL , 10 mmol) were dissolved in a mixture of MeOH (200 mL) and water (200 mL). Subsequently, HCl (36 %, 4.25 mL) was added, and the reaction mixture was stirred at room temperature for 3 h. The resulting precipitate was collected by filtration and washed with an MeOH/ H_2O mixture (1:1; 100 mL) and with water (100 mL). The resulting paste was purified by silica gel chromatography (*n*-hexane/ethyl acetate/ CH_2Cl_2 , 7:1:2) to yield the pure bilane **5a** as a mixture of stereoisomers (0.46 g, 0.57 mmol, 34 %). ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): $\delta = 8.10$ (s, 2 H, NH), 7.99 (s, 2 H, NH), 6.73 (m, 2 H, H- α), 6.15 (m, 2 H, $\beta\text{-H}$), 5.99 (m, 2 H, H- β), 5.73–7.99 (m, 7 H, H- β /H-*meso*) ppm. HRMS-ESI: calcd. for $\text{C}_{37}\text{H}_{18}\text{F}_{15}\text{N}_4$ [$\text{M} + \text{H}$]⁺ 803.1286; found 803.1285. These analytical data are in accordance with the literature values.^[15,16]

5,10,15-Tris(*p*-methylphenyl)tetrapyrane (5b): *p*-Tolualdehyde (0.59 mL, 5 mmol) and pyrrole (694 μL , 10 mmol) were dissolved in a mixture of MeOH (200 mL) and water (200 mL). Subsequently, HCl (36 %; 4.25 mL) was added, and the reaction mixture was stirred at room temperature for 3 h. The resulting precipitate was collected by filtration, washed with an MeOH/ H_2O mixture (1:1; 100 mL) and with water (100 mL). The resulting paste was purified by silica gel chromatography (*n*-hexane/ethyl acetate/ CH_2Cl_2 , 7:1:2) to yield the pure bilane **5b** as a mixture of stereoisomers (0.55 g, 0.96 mmol, 57 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.86$ (s, 2 H, NH), 7.66 (s, 2 H, NH), 7.00–7.10 (m, 12 H, Ar-H), 6.66 (m, 2 H, H- α), 6.12 (m, 2 H, $\beta\text{-H}$), 5.86 (m, 2 H, $\beta\text{-H}$), 5.65–5.76 (m, 4 H, $\beta\text{-H}$), 5.32 (m, 2 H, H-*meso*), 5.21 (m, 1 H, H-*meso*), 2.33 (s, 9 H, CH_3) ppm. HRMS-ESI: calcd. for $\text{C}_{40}\text{H}_{40}\text{N}_4$ [$\text{M} + \text{H}$]⁺ 575.3169; found 575.3168.

10-(Pentafluorophenyl)tetrapyrane (5c): Dipyrrromethane (**3c**; 585 mg, 4 mmol) and pentafluorobenzaldehyde (**2b**; 247 μL , 2 mmol) were dissolved in MeOH (200 mL). Subsequently, a solution

of HCl (36 %, 10 mL) in water (200 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was collected by filtration and washed with a mixture of MeOH/H₂O (1:1; 200 mL) and then with water (100 mL). Subsequent silica gel chromatography (*n*-hexane/ethyl acetate/CH₂Cl₂, 7:1:2) afforded the pure bilane **5c** as a mixture of stereoisomers (380 mg, 0.81 mmol, 40 %). ¹H NMR (300 MHz, CDCl₃): δ = 7.80–7.88 (m, 4 H, NH), 6.66 (m, 2H, H-α), 6.14 (m, 2 H, H-β), 5.96 (m, 2 H, H-β), 5.91 (m, 2 H, H-β), 5.86 (m, 4 H, H-β), 5.73 (s, 1 H, H_{meso}), 3.91 (s, 4 H, H_{meso}) ppm. HRMS-ESI: calcd. for C₂₅H₂₀F₅N₄ [M + H]⁺ 471.1603; found 471.1603.

10-(4-Methoxyphenyl)-5,15-bis(4-fluorophenyl)tetrapyrane (5d): 5-(4-Fluorophenyl)dipyrromethane (**3f**; 480 mg, 2 mmol) and 4-methoxybenzaldehyde (**2e**; 121 μL, 1 mmol) were dissolved in MeOH (100 mL). Subsequently, a solution of HCl (36 %; 5 mL) in water (100 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was collected by filtration and washed with an MeOH/H₂O mixture (1:1; 100 mL) and then with water (100 mL). Subsequent silica gel chromatography (*n*-hexane/ethyl acetate/CH₂Cl₂, 7:1:2) afforded the pure bilane **5d** as a mixture of stereoisomers (205 mg, 0.34 mmol, 34 %). ¹H NMR (300 MHz, CDCl₃): δ = 7.91 (s, 2 H, NH), 7.69 (s, 2 H, NH), 7.12–7.05 (m, 6 H, Ar-H), 6.97 (m, 4 H, Ar-H), 6.82 (d, ³J_{H,H} = 8.64 Hz, 2 H, Ar-H), 6.69 (m, 2 H, H-α), 6.12 (m, 2 H, H-β), 5.82 (m, 2 H, H-β), 5.69 (m, 4 H, H-β), 5.34 (m, 2 H, H_{meso}), 5.24 (s, 1 H, H_{meso}), 3.79 (s, 3 H, OCH₃) ppm. HRMS-ESI: calcd. for C₃₈H₃₃F₂N₄O [M + H]⁺ 599.2617; found 599.2618.

10-(4-Fluorophenyl)-5,15-bis(pentafluorophenyl)tetrapyrane (5e): 5-(Pentafluorophenyl)dipyrromethane (**3a**; 624 mg, 2 mmol) and 4-fluorobenzaldehyde (**2c**; 107 μL, 1 mmol) were dissolved in MeOH (100 mL). Subsequently, a solution of HCl (36 %; 5 mL) in water (100 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was collected by filtration and washed with an MeOH/H₂O mixture (1:1; 100 mL) and then with water (100 mL). Subsequent silica gel chromatography (*n*-hexane/ethyl acetate/CH₂Cl₂, 7:1:2) afforded the pure bilane **5e** as a mixture of stereoisomers (400 mg, 0.55 mmol, 55 %). ¹H NMR (300 MHz, CDCl₃): δ = 8.13 (s, 2 H, NH), 7.85 (s, 2 H, NH), 7.10 (m, 2 H, Ar-H), 6.98 (m, 2 H, Ar-H), 6.72 (m, 2 H, H-α), 6.14 (m, 2 H, H-β), 5.96 (m, 2 H, H-β), 5.88 (m, 2 H, H-β), 5.81 (m, 2 H, H-β), 5.70 (m, 2 H, H_{meso}), 5.30 (s, 1 H, H_{meso}) ppm. HRMS-ESI: calcd. for C₃₇H₂₂F₁₁N₄ [M + H]⁺ 731.1663; found 731.1662.

10-(2,4,6-Trifluorophenyl)-5,15-bis(4-fluorophenyl)tetrapyrane (5f): 5-(4-Fluorophenyl)dipyrromethane (**3f**; 480 mg, 2 mmol) and 2,4,6-trifluorobenzaldehyde (160 mg, 1 mmol) were dissolved in MeOH (100 mL). Subsequently, a solution of HCl (36 %, 5 mL) in water (100 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The resulting precipitate was collected by filtration and washed with an MeOH/H₂O mixture (1:1, 100 mL) and then with water (100 mL). Subsequent silica gel chromatography (*n*-hexane/ethyl acetate/CH₂Cl₂, 7:1:2) afforded the pure bilane **5f** as a mixture of stereoisomers (306 mg, 49 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.88 (s, 2 H, NH), 7.69 (s, 2 H, NH), 7.12 (m, 4 H, Ar-H), 6.97 (m, 4 H, Ar-H), 6.70 (m, 2 H, H-α), 6.65 (m, 2 H, Ar-H), 6.14 (m, 2 H, β-H), 5.80 (m, 4 H, β-H), 5.68 (m, 3 H, β-H, H_{meso}), 5.34 (s, 2 H, H_{meso}) ppm. HRMS-ESI: calcd. for C₃₇H₂₈F₅N₄O [M + H]⁺ 623.2229; found 623.2231.

5,10,15,25-Tetrakis(pentafluorophenyl)-20,30-bis(4-methylphenyl)hexaphyrin[28] (7c): To a solution of 5-(pentafluorophenyl)dipyrromethane (**3a**; 87 mg, 0.28 mmol, 1 equiv.), bilane **5a** (225 mg, 0.28 mmol, 1 equiv.), and *p*-tolualdehyde (**2a**; 66 μL, 0.56 mmol, 2 equiv.) in EtOH (20 mL) was added a solution of HCl

(36 %; 0.1 mL) in water (5 mL). This mixture was stirred at room temperature for 16 h and then extracted with CHCl₃ (150 mL). The organic phase was washed three times with water (100 mL) and once with a saturated aqueous solution of NaHCO₃ (100 mL). The organic layer was dried with MgSO₄, and *p*-chloranil (410 mg, 1.67 mmol, 2 equiv.) was added. The resulting mixture was heated to reflux for 1 h, cooled to room temperature, and concentrated under reduced pressure. The reaction mixture was purified by silica gel chromatography (CH₂Cl₂) to afford **7c** as a dark blue powder (22 mg, 17 μmol, 6 %). ¹H NMR (300 MHz, [D₈]THF, 25 °C): δ = 9.41 (br. s, 2 H, NH_{outer}), 7.82 (d, ³J_{H,H} = 4.7 Hz, 1 H, β-H_{outer}), 7.78 (d, ³J_{H,H} = 4.7 Hz, 2 H, β-H_{outer}), 7.70 (m, 4 H, β-H_{outer}), 7.61 (d, ³J_{H,H} = 4.6 Hz, 2 H, β-H_{outer}), 7.43 (d, ³J_{H,H} = 7.8 Hz, 4 H, Ar-H), 7.24 (d, ³J_{H,H} = 7.8 Hz, 4 H, Ar-H), 5.02 (s, 1 H, NH_{inner}), 4.74 (s, 1 H, NH_{inner}), 2.37 (s, 4 H, β-H_{inner}), 1.28 (s, 6 H, CH₃) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ε_{max}) = 398 (4.78), 421 (4.81), 605 (5.01), 776 (4.18), 882 (4.14), 1082 (3.60) nm. HRMS-ESI: calcd. for C₆₈H₃₁F₂₀N₆ [M + H]⁺ 1311.2285; found 1311.2277.

5,10,15-Tris(pentafluorophenyl)-20,25,30-tris(4-methylphenyl)hexaphyrin[28] (7d): To a solution of 5-(4-methylphenyl)dipyrromethane (**3b**; 66 mg, 0.28 mmol, 1 equiv.), bilane **5a** (225 mg, 0.28 mmol, 1 equiv.), and *p*-tolualdehyde (**2a**; 66 μL, 0.56 mmol, 2 equiv.) in EtOH (20 mL) was added a solution of HCl (36 %; 0.1 mL) in water (5 mL). This mixture was stirred at room temperature for 16 h and then extracted with CHCl₃ (150 mL). The organic phase was washed three times with water (100 mL) and once with a saturated aqueous solution of NaHCO₃ (100 mL). The organic layer was dried with MgSO₄, and *p*-chloranil (410 mg, 1.67 mmol, 2 equiv.) was added. The resulting mixture was heated to reflux for 1 h, cooled to room temperature, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (CH₂Cl₂) to afford **7d** as a dark blue powder (3.5 mg, 2.8 μmol, 1 %). ¹H NMR (500 MHz, [D₈]THF): δ = 7.76 (d, ³J_{H,H} = 4.9 Hz, 2 H, β-H_{outer}), 7.68 (m, 4 H, β-H_{outer}), 7.59 (d, ³J_{H,H} = 4.2 Hz, 2 H, β-H_{outer}), 7.46 (d, ³J_{H,H} = 7.1 Hz, 2 H, Ar-H), 7.43 (d, ³J_{H,H} = 7.9 Hz, 4 H, Ar-H), 7.32 (d, ³J_{H,H} = 7.2 Hz, 2 H, Ar-H), 7.24 (d, ³J_{H,H} = 7.1 Hz, 4 H, Ar-H), 4.67 (s, 2 H, NH_{inner}), 4.08 (s, 1 H, NH_{inner}), 3.10 (s, 2 H, β-H_{inner}), 2.90 (s, 2 H, β-H_{inner}), 1.28 (s, 9 H, CH₃) ppm. UV/Vis (CH₂Cl₂): λ_{max} (relative intensity) = 392 (0.30), 437 (0.26), 602 (1.00), 772 (0.12) nm. HRMS-ESI: calcd. for C₆₉H₃₈F₁₅N₆ [M + H]⁺ 1235.2913; found 1235.2913.

5-(Pentafluorophenyl)-10,30-bis(4-methoxyphenyl)-15,25-bis(4-fluorophenyl)-30-(2,4,6-trifluorophenyl)hexaphyrin[28] (7e): To a solution of 5-(pentafluorophenyl)dipyrromethane (**3a**; 87 mg, 0.28 mmol, 1 equiv.), bilane **5f** (174 mg, 0.28 mmol, 1 equiv.), and *p*-methoxybenzaldehyde (**2e**; 68 μL, 0.56 mmol, 2 equiv.) in EtOH (20 mL) was added a solution of HCl (36 %; 0.1 mL) in water (5 mL). This mixture was stirred at room temperature for 16 h and then extracted with CHCl₃ (150 mL). The organic phase was washed three times with water (100 mL) and once with a saturated aqueous solution of NaHCO₃ (100 mL). The organic layer was dried with MgSO₄, and *p*-chloranil (410 mg, 1.67 mmol, 2 equiv.) was added. The resulting mixture was heated to reflux for 1 h, cooled to room temperature, and concentrated under reduced pressure. The reaction mixture was purified by silica gel chromatography (CH₂Cl₂) to afford **7e** as a dark blue powder (3.2 mg, 2.8 μmol, 1 %). ¹H NMR (400 MHz, [D₈]THF): δ = 7.69 (m, 2 H, Ar-H), 7.61 (m, 4 H, 2 H, β-H, Ar-H), 7.47 (m, 4 H, β-H), 7.36 (d, ³J_{H,H} = 8.3 Hz, 4 H, Ar-H), 7.22 (m, 2 H, Ar-H), 7.12 (m, 4 H, Ar-H), 6.92 (d, ³J_{H,H} = 8.4 Hz, 4 H, Ar-H), 5.10 (br. s, 1 H, NH_{inner}), 4.80 (br. s, 1 H, NH_{inner}), 3.77 (s, 6 H, OCH₃), 2.90 (s, 2 H, β-H_{inner}), 2.86 (s, 2 H, β-H_{inner}) ppm. UV/Vis (CH₂Cl₂): λ_{max} (relative intensity) = 402 (0.587), 428 (0.55), 615 (1.00), 778 (0.18) nm. HRMS-ESI: calcd. for C₆₈H₄₁F₁₀N₆O₂ [M + H]⁺ 1163.3126; found 1163.3123.

5,15,25-Tris(pentafluorophenyl)-10,20,30-tris(4-methylphenyl)-hexaphyrin[26] (8a): MnO₂ (1 mg, 12 μmol, 1 equiv.) was added to a solution of hexaphyrin[28] **7a** (15 mg, 12 μmol, 1 equiv.) in CH₂Cl₂ (20 mL). The progress of the reaction was monitored by UV/Vis absorption spectroscopy. After 90 min, the reaction mixture was purified by silica gel chromatography (CH₂Cl₂) to afford the pure [26]hexaphyrin **8a** (15 mg, 12 μmol, 100 %). ¹H NMR (400 MHz, [D₈]THF, 25 °C): δ = 9.43 (d, ³J_{H,H} = 4.7 Hz, 2 H, β-H_{outer}), 9.21 (d, ³J_{H,H} = 4.8 Hz, 2 H, β-H_{outer}), 9.07 (d, ³J_{H,H} = 4.7 Hz, 2 H, β-H_{outer}), 9.05 (d, ³J_{H,H} = 4.7 Hz, 2 H, β-H_{outer}), 8.52 (d, ³J_{H,H} = 7.6 Hz, 4 H, Ar-H), 8.27 (d, ³J_{H,H} = 7.7 Hz, 2 H, Ar-H), 7.73 (d, ³J_{H,H} = 7.7 Hz, 2 H, Ar-H), 7.69 (d, ³J_{H,H} = 7.7 Hz, 4 H, Ar-H), 2.74 (s, 3 H, CH₃), 2.70 (s, 6 H, CH₃), -1.53 (s, 2 H, β-H_{inner}), -1.60 (s, 2 H, β-H_{inner}) ppm. UV/Vis (CH₂Cl₂): λ_{max} (log ε_{max}) = 434 (4.47), 577 (4.94), 734 (3.98), 804 (3.95), 912 (3.70), 1049 (3.82) nm. HRMS-ESI: calcd. for C₆₉H₃₆F₁₅N₆ [M + H]⁺ 1233.2756; found 1233.2764.

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