Supporting Information

Meso-Substituted [34]Octaphyrin(1.1.1.0.1.1.1.0) and Corrole Formation in Reactions of a Dipyrromethanedicarbinol with 2,2'-Bipyrrole

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Table of Contents

	<u>Page</u>
Experimental section	
General experimental methods	S2
Synthesis of 2,2'-(1'-pyrrolinyl)pyrrole 2	S2
Analytical-scale reactions of 2 leading to 2,2'-bipyrrole 3	S2
GC/MS monitoring of reactions of 2 leading to 2,2'-bipyrrole 3	S3
Calculations for the spectrophotometric determination of the yield of octaphyrin and corrole	S3-S4
Survey of catalysis conditions	S4-S5
Reaction time course experiments	S5
Examination of oxidation conditions for reactions leading to HPO	S5
Stability of the [34]octaphyrin(1.1.1.0.1.1.1.0) species	S5
GC data from the refinement of the synthesis of 2,2'-bipyrrole 3	S6-S8
Plots of the yield of HPO 4a as a function of acid concentration	S9-S12
Plots of the yield of HPO 4a or HpFPO 4c as a function of time	S13-S14
Plots of the yield of HPO 4a as a function of oxidant quantity	S15
TLC analysis of octaphyrins 4a,b	S15-S16
UV-vis spectra of octaphyrins 4a-c	S16
LD-MS spectra of octaphyrins	
4a	S17
4b	S18
4c	S19
¹ H NMR spectra of octaphyrins	
4a	S20-S23
4b	S24
4c	S25

Experimental Section

General Experimental Methods. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and absorption spectra were collected routinely. Melting points are uncorrected. Column chromatography was performed on silica (Merck, 230-400 mesh, 60 Å). CH_2Cl_2 used in reactions of **1-OH** with **3** was distilled from potassium carbonate and stored over 4-Å Linde molecular sieves. CH_2Cl_2 used in spectrophotometric determination of yield of octaphyrin/corrole was passed through a pad of basic alumina prior to use. THF used in the reduction of diacyl dipyrromethanes was stored over 4-Å Linde molecular sieves. Monoglyme, diglyme, and triglyme were stored over 4-Å Linde molecular sieves. Pyrrole was distilled from calcium hydride and stored at $-15\text{ }^\circ\text{C}$ until use. The sodium dithionite is technical grade, 85%. All other chemicals are reagent grade and were used as obtained. Diacyl dipyrromethanes **1a**,¹ **1b**,² and **1c**,² and their precursors [5-phenyldipyrromethane,³ and 5-(pentafluorophenyl)-dipyrromethane³] were prepared as described in the literature.

2,2'-(1'-pyrrolinyl)pyrrole (2). Following a published procedure,⁴ POCl_3 (4.2 mL, 45 mmol) was added slowly over a period of 1 h to pyrrole (15.6 mL, 225 mmol) under argon and cooled in an ice bath. To that solution, 2-pyrrolidinone (3.9 mL, 51 mmol) was added slowly over a period of 2 h with the reaction under argon and cooled in an ice bath. After the addition was complete, the viscous, amber solution was allowed to warm to room temperature. CHCl_3 (25 mL) was added, and the solution was transferred to a flask containing water (100 mL) and sodium acetate (40 g) cooled in an ice bath. The pH of the turbid, orange solution was adjusted to ~ 10 with aq KOH (~ 20 mL, 10 M). The organic layer was separated and saved. The aqueous layer was extracted three times with CHCl_3 (~ 25 mL). The organic extracts were combined with the saved organic layer, and extracted five times with aq HCl (50 mL, 0.5 M). The pH of each aq extract was adjusted to ~ 10 with aq KOH (10 M) to produce a yellow/orange precipitate. The aq extracts with the precipitate were combined and extracted four times with CHCl_3 (100 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated to dryness to afford a light orange waxy solid. Crude **2** was purified by sublimation at $80\text{ }^\circ\text{C}$ (100 mTorr) to afford 4.7 g of a white powder. Crystallization from ethanol affording **2** as white crystals (4.1 g, 68%). mp $162\text{--}163\text{ }^\circ\text{C}$ (lit mp $162\text{--}163\text{ }^\circ\text{C}$).⁴ Anal. Calcd for $\text{C}_8\text{H}_{10}\text{N}_2$: C, 71.60; H 7.51; N, 20.88. Found: C, 71.53; H, 7.58; N, 20.99. Analytical data are consistent with literature values.⁵

Analytical-Scale Reactions of (2) Leading to 2,2'-bipyrrole (3). To a 25-mL flask equipped with a condenser was added 2,2'-(1'-pyrrolinyl)pyrrole (85.8 mg, 0.640 mmol) and solvent (10 mL). Argon was directed through a needle so as to continuously bubble through the solution. The solution was warmed to a few degrees below the boiling point of the solvent, and the desired quantity of 10% palladium on carbon was added. Timing of the reaction began with the addition of palladium. The reactions were monitored at 5 min, 15 min, 30 min, 1 h and so on until judged to be complete by GC/MS analysis.

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GC/MS Monitoring of Reactions of (2) Leading to 2,2'-bipyrrole (3). An aliquot of the reaction mixture (~0.25 mL) was passed through a Pasteur filter pipet into a microcentrifuge tube. The solution (~0.5 μ L) was immediately analyzed by GC/MS. The GC conditions were as follows: HP-5 column; 30 m x 0.32 mm x 0.25 μ m [temperature gradient: temperature 1, 150 $^{\circ}$ C (5 min); temperature 2, 250 $^{\circ}$ C (0 min); rate 20 $^{\circ}$ C/min, total runtime 10 min].

Calculations for the Spectrophotometric Determination of the Yield of Octaphyrin and Corrole. The yield of octaphyrin was determined by comparing the absorbance at ~661 nm with the theoretical absorbance calculated from the following equation:

$$A_{theoretical} = (133,000 \text{ cm}^{-1}\text{M}^{-1})(1.0 \text{ cm})(0.00125 \text{ M})\left(\frac{200 \mu\text{L}}{500 \mu\text{L}}\right)\left(\frac{50 \mu\text{L}}{3050 \mu\text{L}}\right)(1.30) = 1.42$$

Where 133,000 $\text{cm}^{-1}\text{M}^{-1}$ is the molar extinction coefficient for HPO and **4b**, (161,000 $\text{cm}^{-1}\text{M}^{-1}$ was used for **4c**), 1.0 cm is the pathlength of the cuvette, 0.00125 M is the theoretical concentration of octaphyrin given the initial concentration of dipyrromethanedicarbinol (2.5 mM), (200 μ L/500 μ L) and (50 μ L/3050 μ L) account for the dilution of the octaphyrin upon oxidation of an aliquot in the DDQ solution and passage through the silica pipet respectively, and 1.30 is an empirically derived correction factor for the volume of CH_2Cl_2 eluent that is retained on the silica pipet.⁶ An example is provided in Figure S1.

The yield of corrole was determined similarly, with the exception that a baseline correction for the absorbance at 414 nm due to the octaphyrin had to be first applied. The absorbance at 661 nm was multiplied by the ratio of the absorbance at 414 to 661 nm in a sample of pure HPO (0.78). The result was then subtracted from the absorbance at 414 nm to provide the corrected absorbance due to corrole alone. The corrected absorbance at 414 nm was then compared to the theoretical absorbance calculated from the following equation:

$$A_{theoretical} = (110,000 \text{ cm}^{-1}\text{M}^{-1})(1.0 \text{ cm})(0.0025 \text{ M})\left(\frac{200 \mu\text{L}}{500 \mu\text{L}}\right)\left(\frac{50 \mu\text{L}}{3050 \mu\text{L}}\right)(1.30) = 2.34$$

Where 110,000 $\text{cm}^{-1}\text{M}^{-1}$ is the reported molar extinction coefficient for TPC,⁷ 1.0 cm is the pathlength of the cuvette, 0.0025 M is the theoretical concentration of corrole given the initial concentration of dipyrromethane-dicarbinol (2.5 mM), (200 μ L/500 μ L) and (50 μ L/3050 μ L) account for the dilution of the corrole upon oxidation of an aliquot in the DDQ solution and passage through the silica pipet respectively, and 1.30 is an empirically derived correction factor for the volume of CH_2Cl_2 eluent that is retained on the silica pipet.⁶ An example is provided in Figure S1.

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Figure S1. UV-vis spectra of crude reaction mixtures illustrating the calculation of spectral yields for samples containing, (A) HPO only, and (B) HPO and TPC.

Survey of Catalysis Conditions. Immediately prior to the condensation reactions, **1a** (215 mg, 0.500 mmol) was reduced to the corresponding dipyrromethanedicarbinol **1a-OH** with NaBH₄ (1.3 g, 36 mmol) in THF/methanol (40 mL, 3:1) following a literature procedure.² After drying under vacuum for 30 min, the dicarbinol was dissolved in the desired solvent and transferred to a 100-mL volumetric flask. A solution of **3** (66.0 mg, 0.500 mmol) was prepared in the desired solvent in a second 100-mL volumetric flask. The contents of the two volumetric flasks were mixed in an amber bottle equipped with a solvent pump, thereby providing a stock solution of **1a-OH** and **3** (2.5 mM each). Reactions were performed at room temperature in tightly capped 20-mL vials that were stirred with a micro stir bar. Solid acids were weighed into all reaction vials prior to beginning the reaction sequence for the day, and each reaction was started by the addition of 5-10 mL of the reactant solution from the solvent pump. Reactions involving TFA were initiated by the addition of TFA to reaction vials already containing 5 mL of the reactant

stock solution. The reactions were monitored spectrophotometrically for yield of TPC at 15 min and 1 h as described above. TLC was performed on the crude, oxidized mixture [silica, CH₂Cl₂/ethyl acetate (25:1)] after washing with the aq dithionite solution.

Reaction Time Course Experiments. Reaction monitoring as a function of time was performed as described above for the survey of catalysis conditions with the exception of using an 8-mL reaction volume. Each reaction was initiated by the addition of the appropriate acid at room temperature. The reactions were monitored for yield of octaphyrin and corrole as described above at 1 min, 4 min, 8 min, 15 min, 30 min, 1 h, 2 h, 4 h, and 8 h. TLC was performed on the crude, oxidized mixtures [silica, CH₂Cl₂/ethyl acetate (25:1)] after washing with the aq dithionite solution.

Examination of Oxidation Conditions for Reactions Leading to HPO.

(i) **DDQ.** Aliquots (200 μ L) of the reaction of **1a-OH** with **3** (2.5 mM each) catalyzed by Yb(OTf)₃ (10 mM) at room temperature for 45 min were transferred to microcentrifuge tubes containing DDQ (0.5 to 40 equiv. relative to **1a-OH**) in toluene (300 μ L). The mixtures were vortex mixed and monitored for yield of HPO (UV-vis). TLC was performed on the crude, oxidized mixtures [silica, CH₂Cl₂/ethyl acetate (25:1)] after washing with the aq dithionite solution.

(ii) ***p*-Chloranil.** Aliquots (10 mL) of the reaction of **1a-OH** with **3** (2.5 mM each) catalyzed by Yb(OTf)₃ (10 mM) at room temperature for 50 min and treated with triethylamine (5 equiv. relative to acid) were transferred to 25-mL flasks containing *p*-chloranil (2.5 to 50 equiv. relative to **1a-OH**). Each flask was equipped with a condenser and the mixtures were heated to reflux open to the air. The oxidation reactions were monitored for yield of HPO from 30 min to 2 h [UV-vis, with the exception that an aliquot of the reaction mixture (200 μ L) was transferred to a microcentrifuge tube containing toluene (300 μ L) rather than DDQ solution]. TLC was performed on the crude, oxidized mixtures [silica, CH₂Cl₂/ethyl acetate (25:1)] after washing with the aq dithionite solution.

Determination of the Stability of the [34]Octaphyrin(1.1.1.0.1.1.1.0) Species. Solutions of **4a-c** were prepared in CH₂Cl₂ in the dark. The concentration of each solution was adjusted to provide an absorbance of ~1.0. UV-vis spectra were recorded in the dark, and again from 5 min to 24 h after the room lights were turned on.

GC Data from the Refinement of the Synthesis of 2,2'-Bipyrrole (3).

Figure S2 provides chromatograms showing the conversion of **2** to **3** as a function of time for dehydrogenation reactions performed at reflux in monoglyme, diglyme, or triglyme with palladium on carbon ranging from 0.0625 to 0.50 equiv relative to **2**. The best balance of palladium quantity, solvent volatility, and reaction time was provided by reflux in diglyme with palladium on carbon (0.125 equiv) for ~1.5 h.

Figure S2. GC/MS monitoring of dehydrogenation reactions of **2** leading to 2,2'-bipyrrole. (A) monoglyme (bp 85 °C), palladium (0.50 equiv), (B) diglyme (bp 162 °C), palladium (0.50 equiv), (C) triglyme (bp 216 °C), palladium (0.50 equiv), (D) diglyme, palladium (0.25 equiv), (E) diglyme, palladium (0.125 equiv), (F) diglyme, palladium (0.0625 equiv).

C Triglyme (bp 216 °C), Pd (0.50 equiv relative to 2)

D Diglyme (bp 162 °C), Pd (0.25 equiv relative to 2)

Figure S2. continued

E Diglyme (bp 162 °C), Pd (0.125 equiv relative to 2)

F Diglyme (bp 162 °C), Pd (0.0625 equiv relative to 2)

Figure S2. continued

Plots of Yield of HPO (4a) as a Function of Acid Concentration.

Figures S3-S6 provide plots of the spectral yield of HPO as a function of acid concentration in CH₂Cl₂, acetonitrile, toluene, or THF. TPC was generally not detected in these reactions, with the exception of some conditions involving TFA catalysis in THF.

Figure S3. Yield of HPO as a function of acid concentration for reactions of dipyrromethane-dicarbinol **1a-OH** and 2,2'-bipyrrole (2.5 mM each) in CH₂Cl₂ at rt. Reactions were monitored at 15 min (●) and 1 h (□) by removing an aliquot of the reaction mixture, oxidizing with DDQ, washing with aq dithionite, filtering through a silica pad, and analyzing spectrophotometrically for yield of HPO. (A) Dy(OTf)₃, (B) Yb(OTf)₃, (C) Sc(OTf)₃, (D) InCl₃, and (E) TFA.

Figure S4. Yield of HPO as a function of acid concentration for reactions of dipyrromethane-dicarbinol **1a-OH** and 2,2'-bipyrrole (2.5 mM each) in acetonitrile at room temperature. Reactions were monitored at 15 min (●) and 1 h (□) by removing an aliquot of the reaction mixture, oxidizing with DDQ, washing with aq dithionite, filtering through a silica pad, and analyzing spectrophotometrically for yield of HPO. (A) $\text{Dy}(\text{OTf})_3$, (B) $\text{Yb}(\text{OTf})_3$, (C) $\text{Sc}(\text{OTf})_3$, (D) InCl_3 , and (E) TFA.

Figure S5. Yield of HPO as a function of acid concentration for reactions of dipyrromethane-dicarbinol **1a-OH** and 2,2'-bipyrrrole (2.5 mM each) in toluene at room temperature. Reactions were monitored at 15 min (●), 1 h (□) and 4 h (▲) by removing an aliquot of the reaction mixture, oxidizing with DDQ, washing with aq dithionite, filtering through a silica pad, and analyzing spectrophotometrically for yield of HPO. (A) Dy(OTf)₃, (B) Yb(OTf)₃, (C) Sc(OTf)₃, (D) InCl₃, and (E) TFA.

Figure S6. Yield of HPO as a function of acid concentration for reactions of dipyrromethane-dicarbonyl **1a-OH** and 2,2'-bipyrrrole (2.5 mM each) in THF at room temperature. Reactions were monitored at 15 min (●), 1 h (□) and 4 h (▲) by removing an aliquot of the reaction mixture, oxidizing with DDQ, washing with aq dithionite, filtering through a silica pad, and analyzing spectrophotometrically for yield of HPO. (A) Dy(OTf)₃, (B) Yb(OTf)₃, (C) Sc(OTf)₃, (D) InCl₃, (E) TFA, and (F) TFA, yield of TPC.

Plots of the Yield of HPO (4a) or HpFPO (4c) as a Function of Time.

The yield of octaphyrins **4a,c** as a function of condensation time are summarized in Figures S7-S8.

Figure S7. Percent yield of HPO as a function of condensation time for reactions of dipyrromethanedicarbinol **1a-OH** and 2,2'-bipyrrole (2.5 mM each) at rt. Reactions were monitored by removing an aliquot of the reaction mixture, oxidizing with DDQ, washing with aq dithionite, filtering through a silica pad, and analyzing spectrophotometrically for yield of HPO. Note the log scale for time. The reaction condition in Panel F provided both HPO and TPC.

Figure S8. Percent yield of HpFPO as a function of condensation time for reactions of dipyrromethanedicarbinol **1c-OH** and 2,2'-bipyrrole (2.5 mM each) at room temperature. Reactions were monitored by removing an aliquot of the reaction mixture, oxidizing with DDQ, filtering through a silica pad, and analyzing spectrophotometrically for yield of HpFPO. Note the log scale for time.

Plots of the Yield of HPO (4a) as a Function of Oxidant Quantity.

The yield of HPO as a function of oxidant quantity is summarized in Figure S9.

Figure S9. Percent yield of HPO as a function of oxidant quantity for reactions of dipyrromethanedicarbinol **1a-OH** and 2,2'-bipyrrrole (2.5 mM each) mediated by Yb(OTf)₃ (10 mM) in CH₂Cl₂ at room temperature. Aliquots were removed from the reaction mixture and treated with varying quantities of oxidant. The oxidized mixtures were washed with aq dithionite, filtered through a silica pad, and analyzed spectrophotometrically for yield of HPO. (A) DDQ, and (B) *p*-chloranil. Note: the stoichiometric quantity of oxidant required for HPO synthesis is 2.5 equiv relative to **1a-OH**.

TLC Analysis of Octaphyrins (4a,b).

Octaphyrins **4a,b** were more strongly retained on silica (R_f ~0.45) than HpFPO (R_f 0.90) [(CH₂Cl₂/ethyl acetate (25:1)]. On some occasions, **4a,b** would elute as two to three closely spaced, but distinct spots. This behavior was observed intermittently, and it did not appear to be due to insufficient drying of the sample spot prior to development. The individual spots could be scrapped from a TLC plate and extracted from the silica. The UV-vis spectra were identical, but

subsequent TLC analysis still revealed separate spots. The samples did not interconvert upon standing in solution at room temperature for up to 8 h. Solutions made from purified solid **4a,b** would in some instances show a blue-green spot of variable intensity at the origin of the TLC plate. Allowing the solution to stand led to gradual but incomplete disappearance of the blue-green baseline material in favor of the green spot at the usual location. Washing with aq basic dithionite for 1 h led to nearly complete conversion of the blue-green species to the characteristic green spot of the octaphyrin. The origin of this behavior is not known.

UV-vis Spectra of Octaphyrins (**4a-c**).

Comment 1 no matrix
Comment 2 PEG1000 calibration, no matrix

Bruker Daltonics flexAnalysis

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Comment 1 no matrix
Comment 2 PEG1000 calibration, no matrix

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Contains 4 μL PhSH (100 mM in CDCl_3)
 298 K
 CDCl_3

Contains 32 μL PhSH (100 mM in CDCl_3)
298 K
 CDCl_3