Porphyrin Architectures Bearing Functionalized Xanthene Spacers

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Abstract: A modular synthetic strategy for the construction of cofacial porphyrin architectures bearing hydrogen-bond synthons on a xanthene platform is presented. The convergent approach is based on a xanthene aldehyde-ester building block that is easily obtainable on a multigram scale with minimal purification. Treatment of this xanthene derivative with a variety of aryl aldehydes and pyrrole under standard Lindsey conditions affords a family of *meso*-substituted porphyrins bearing a single functionalized xanthene spacer. Direct modification of the hydrogen-bond synthon after macrocyclization proceeds smoothly to furnish porphyrin systems with a variety of cofacial functionalities (e.g., carboxylic acid, ester, amide). Porphyrins bearing two *trans*-functionalized xanthene spacers are prepared by the MacDonald [2 + 2] condensation of the xanthene aldehyde-ester with readily available 5-aryl-substituted dipyrromethanes such as 5-mesityldipyrromethane to afford the pure α,α- and α,*β*-porphyrin atropisomers after chromatographic separation. The versatility of this synthetic method offers intriguing opportunities for the use of these and related templates for the study of proton-coupled activation of small molecules.

Porphyrins functionalized with hydrogen-bond synthons offer attractive building blocks for the efficient construction of supramolecular assemblies with appealing structural and electronic properties.[1] Of particular interest is the use of such systems toward unraveling the effect of hydrogen bonding on energy and electron-transfer reactions.[2−4] We have exploited this approach in the development of hydrogen-bond networks for the study of proton-coupled electron transfer (PCET) reactions.[2,5−13] In particular, our work has focused on porphyrins modified with an amidinium group;[9,11,13] these porphyrins associate with carboxylates to form stable, directional salt bridge complexes where the porphyrin macrocycle and hydrogen-bond functionality are juxtaposed in a *side-to-side* arrangement.

We sought to extend our PCET studies to the multielectron activation chemistry of oxygen and other small molecules.[2,5] To this end, we have developed methods for the facile assembly of symmetric cofacial bisporphyrins bearing dibenzofuran (DPD)[14,15] and xanthene (DPX)[16] spacers that exhibit variable pocket sizes with minimal lateral displacements. In these systems, the *face-to-face* arrangement of porphyrin subunits allows for the efficient delivery of the oxidizing or reducing equivalents necessary to effect the overall multielectron activation of small molecule substrates.

A complement to both these approaches is the construction of chemical architectures containing porphyrins *and* hydrogen-bond synthons in a face-to-face arrangement.[17−32] To achieve this goal, we recently introduced asymmetric cofacial platforms in which the rigid xanthene anchor is used to "hang" a hydrogen-bond functionality over the porphyrin macrocycle (HPX = hanging porphyrin xanthene).[33] Remarkably, the monomeric iron(III) hydroxide derivative of this "Hangman" porphyrin has the unprecedented ability to orient exogeneous water via hydrogen bonding, affording a minimalist model for the heme/water channel assemblies found in the oxygen-activating cytochrome P450 enzymes. In this report, we describe the design and synthetic details for preparing this novel HPX porphyrin and expand this approach to afford a modular and facile methodology for the synthesis

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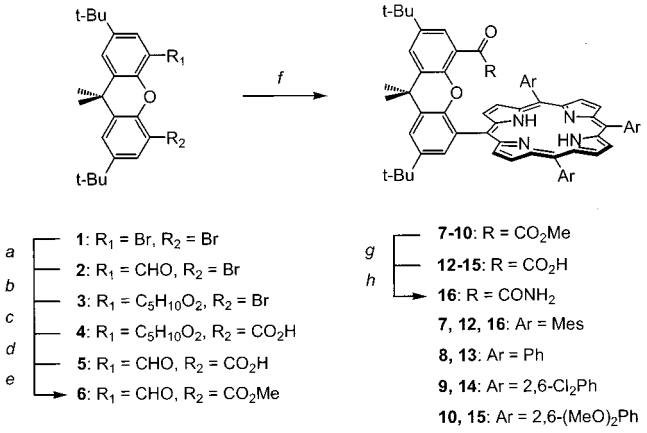
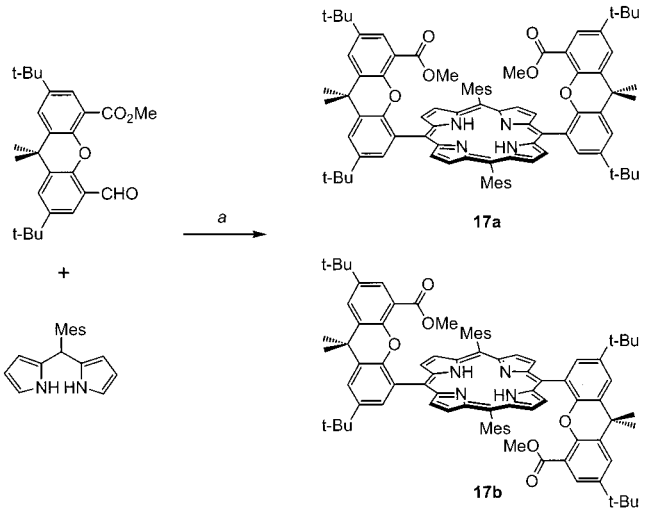
Scheme 1[a]



[a] (a) (1) Phenyllithium, cyclohexane/THF, (2) DMF, H_2O; (b) neopentyl glycol, benzenesulfonic acid, toluene, N_2, reflux; (c) (1) phenyllithium, cyclohexane/THF, (2) CO_2 gas; (d) trifluoroacetic acid, water; (e) methanol, H_2SO_4, reflux; (f) (1) pyrrole, arylaldehyde, $BF_3{\cdot}OEt_2$, chloroform/ethanol, (2) DDQ; (g) (1) $Zn(OAc)_2{\cdot}2H_2O$, chloroform/methanol, reflux, (2) NaOH, THF/H_2O, N_2, reflux, (3) HCl; (h) (1) $SOCl_2$, N_2, reflux, (2) NH_3 gas.

Scheme 2[a]



[a] (a) (1) $BF_3{\cdot}OEt_2$, chloroform/ethanol, (2) DDQ.

of porphyrins bearing xanthene spacers functionalized with hydrogen-bond synthons. The convenience and versatility of this synthetic method presents enticing possibilities for the use of these and related porphyrinic structures for the study of proton-coupled small molecule activation.

The synthetic strategy for the hanging porphyrin xanthene (HPX) complexes is outlined in Schemes 1 and 2. We employ a stepwise protection−deprotection route for the xanthene pillar; this modular approach provides a number of synthetically useful intermediates that are isolated and purified on a multigram scale.[37]

Selective monolithiation of Rebek's xanthene dibromide **1** with phenyllithium in the presence of dry DMF followed by hydrolysis of the intermediate imidate salt provides aldehyde **2** in 81% yield. Protection of the aldehyde group using neopentyl glycol with a catalytic amount of benzenesulfonic acid affords acetal **3** in 93% yield. Lithiation of the remaining bromide on **3** and subsequent quenching with CO_2 gas delivers acid **4** in 86% yield. Deprotection of the acetal of **4** with trifluoroacetic acid (TFA) proceeds smoothly to furnish aldehyde **5** in 89% yield. Reaction of **5** with H_2SO_4 in methanol supplies ester **6** in 93% yield. Compound **6** serves as a common synthon for construction of a variety of porphyrins containing hydrogen-bond functionalities anchored to xanthene spacers. In all cases, standard high-dilution Lindsey conditions are employed for macrocyclization,[34] as exemplified by the acid-catalyzed condensation of **6** with mesitylaldehyde and pyrrole to produce H_2(HPX-CO_2Me) **7** in 26% yield. As illustrated in Scheme 1, the Lindsey reaction proves to be quite versatile. Through simple substitutions of the aryl groups, this general pathway allows for the isolation of singly bridged, xanthene-functionalized ester porphyrins **8**−**10** with varying steric and electronic properties. Yields for cyclization range from 20 to 30%. Especially noteworthy are the mild reaction conditions used for porphyrin formation, in contrast to the harsh Alder-Longo methods employed by Rebek in the synthesis of related dixanthene cleft porphyrins.[23]

The HPX ester groups of **7**−**10** are easily converted to their corresponding acid derivatives in the following way. Zinc(II) derivatives of **7**−**10** are prepared in essentially quantitative yields upon reaction of the free base porphyrin with $Zn(OAc)_2{\cdot}2H_2O$; the trimesityl complex **11** has been isolated and fully characterized. Treatment of the zinc(II)-protected porphyrins with aqueous sodium hydroxide in THF under harsh conditions (reflux, 3 days) followed by zinc(II) removal with HCl affords the HPX acid derivatives **12**−**15** in excellent yields (>90%). In addition, the carboxylic acid group also provides access to other functional groups; as an example, the HPX amide derivative **16** is obtained in 90% yield by reaction of **12** with $SOCl_2$ (to generate the acid chloride) followed by quenching with NH_3 gas. It is noteworthy that taken together, mesityl HPX derivatives **7**, **12**, and **16** comprise a structurally homologous series of singly bridged xanthene "Hangman" porphyrins bearing hydrogen-bond functionalities.

The use of compound **6** is not limited to porphyrin architectures containing a single xanthene pillar. For example, the MacDonald [2 + 2] condensation of **6** with aryl dipyrromethanes such as 5-mesityldipyrromethane generates the corresponding *trans*-porphyrins bearing a pair of xanthene pillars in overall 16% yield.[23] Equimolar amounts of the α,α- and α,*β*-atropisomers (**17a** and **17b**, respectively) are secured from the reaction in pure form after column chromatography. As expected by literature precedence,[35] the α,α isomer has a lower R_f on silica gel. Unambiguous identification of the atropisomers of **17** is revealed by ^{1}H NMR spectroscopy. The C_s-symmetric α,α-atropisomer (**17a**) displays two distinct resonances at δ = 1.82 and 2.01 ppm for the *ortho* methyl groups on the flanking mesityl rings while the C_2-symmetric α,*β*-atropisomer (**17b**) exhibits a single resonance for these groups at δ = 1.90 ppm. The atropisomers are quite thermally stable; no interconversion between atropisomers is observed by ^{1}H NMR up to 100 °C. However, refluxing a solution of pure **17a** or **17b** in toluene for several hours leads to detectable amounts of the other atropisomer.

To summarize, we have presented a modular synthetic methodology for the construction of asymmetric, cofacial

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architectures composed of porphyrins and hydrogen-bond functionalities anchored to a xanthene spacer (HPX). These "Hangman" porphyrins complement our ongoing work with the amidinium porphyrins[9,11,13] bearing side-to-side hydrogen-bond synthons for PCET model studies and the face-to-face bisporphyrin structures for PCET small-molecule activation.[14−16] Notably, the key xanthene aldehyde-ester building block **6** is readily obtained on a gram scale with minimal purification and serves as a useful synthon for the preparation of a host of porphyrins bearing one or two functionalized xanthene spacers. The mild Lindsey conditions[34] employed for cyclization are tolerant of a wide range of substituent patterns and should allow for the synthesis of more elaborate structures. In addition, direct modification of the hydrogen-bond synthon after cyclization readily affords a systematic, homologous series of functional groups for study. Efforts toward the use of these and related species for PCET small-molecule activation studies are currently underway.

Experimental Section

Materials. Silica gel 60 (70−230 and 230−400 mesh, Merck) was used for column chromatography. Analytical thin-layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Solvents for synthesis were of reagent grade or better and were dried according to standard methods.[36] Chloroform (stabilized with ethanol) was distilled from K_2CO_3. Pyrrole was distilled from CaH_2 and stored under nitrogen in the dark at −20 °C. 4,5-Dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene **1** was prepared as described by Rebek and co-workers.[37] 5-Mesityldipyrromethane was obtained according to literature procedures.[38] All other reagents were used as received. High-resolution mass spectral analyses were carried out at the University of Illinois Mass Spectrometry Laboratory or the MIT Department of Chemistry Instrumentation Facility. All synthesized compounds were characterized using ^{1}H NMR spectroscopy, and all porphyrins gave satisfactory mass spectral and elemental analyses. The latter was performed at Quantitative Technologies, Inc. (NJ). These characterization data are given in the Supporting Information.

4-Formyl-5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2). Phenyllithium (1.2 mL, 1.8 M solution in cyclohexane) was added over a period of 10 min to a solution of xanthene dibromide **1** (1.00 g, 2.08 mmol) in dry THF (40 mL) cooled to −78 °C under an N_2 atmosphere. After stirring at −78 °C under nitrogen for 1 h, dry DMF (1 mL) was added and the mixture was warmed to room temperature and stirred for an additional hour. The reaction was quenched with water (30 mL) and the organic solvent was removed by rotary evaporation. The resulting white precipitate was filtered and washed with water. Purification by column chromatography (silica gel, 7:3 hexanes/dichloromethane) supplied **2** as a fluffy white powder (0.73 g, 81% yield).

4-(5,5′-Dimethyl-1,3-dioxane)-5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (3). A 100 mL round-bottom flask fitted with a Dean−Stark trap and reflux condenser was charged with a solution of aldehyde **2** (1.07 g, 2.50 mmol), neopentyl glycol (0.27 g, 2.62 mmol), and benzenesulfonic acid (5 mg) in toluene (50 mL) under an N_2 atmosphere. The reaction was refluxed under nitrogen for 2 h, cooled to room temperature, and washed with a saturated aq $NaHCO_3$ solution and then H_2O. After drying with Na_2SO_4 and evaporation to dryness, purification by column chromatography (silica gel, dichloromethane) gave bromide **3** as a white solid (1.2 g, 93% yield).

4-(5,5′-Dimethyl-1,3-dioxane)-5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (4). Phenyllithium (1.2 mL, 1.8 M solution in cyclohexane) was added over a period of 10 min to a solution of bromide **3** (1.03 g, 2.0 mmol) in THF (40 mL) cooled to −78 °C under an N_2 atmosphere. After stirring at −78 °C under nitrogen for 1 h, CO_2 gas was bubbled into the lithiate at a rapid rate until the yellow color of the solution had faded. The mixture was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with 2 N HCl (15 mL), and the organic solvent was removed by rotary evaporation. The resulting white precipitate was filtered and washed with water. Purification by column chromatography (silica gel, dichloromethane) delivered **4** as a white powder (0.83 g, 86% yield).

4-Formyl-5-hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (5). Acetal **4** (1.5 g, 3.12 mmol) was dissolved in trifluoroacetic acid (10 mL), and water (3 mL) was added. The solution was stirred at room temperature for 24 h and concentrated under vacuum to give an orange oil. Water (20 mL) was added, and the resulting precipitate was filtered. Purification by column chromatography (silica gel, dichloromethane) afforded **5** as a white compound (1.10 g, 89% yield).

4-Formyl-5-methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (6). A solution of acid **5** (1.0 g, 2.53 mmol) in methanol (50 mL) and H_2SO_4 (2 mL) was refluxed for 4 h. The solvent was removed in vacuo, water (20 mL) was added to the residue, and the resulting precipitate was filtered. The solid was redissolved in dichloromethane (50 mL), washed with 15% HCl and water, dried over Na_2SO_4, and taken to dryness by rotary evaporation. Purification by column chromatography (silica gel, dichloromethane) provided ester **6** as a white powder (0.96 g, 93% yield).

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-trimesitylporphyrin, H_2(HPX-CO_2Me) (7). A solution of aldehyde **6** (0.41 g, 1 mmol), mesitylaldehyde (2.22 g, 15 mmol), and pyrrole (1.11 mL, 16 mmol) in chloroform (1.6 L) was purged with nitrogen for 20 min after which a portion of BF_3·OEt_2 (0.67 mL, 5.28 mmol) was added via syringe. The solution was stirred at room temperature under nitrogen in the dark for 90 min and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.72 g, 12 mmol) was added to the reaction. After stirring for an additional hour under nitrogen, the solvent was removed by rotary evaporation. The dark residue was redissolved in dichloromethane (300 mL) and filtered. The filtrate was loaded directly onto a silica gel column packed with dichloromethane and eluted with dichloromethane until no more porphyrinic product was detected. Several subsequent recrystallizations from dichloromethane and methanol removed a significant portion of the symmetric tetramesitylporphyrin (H_2TMP) byproduct. Final purification by column chromatography (silica gel, 4:1 hexanes/dichloromethane to 2:1 hexanes/dichloromethane) afforded porphyrin **7** as a plum purple microcrystalline solid (270 mg, 26% yield based on bridge **6**).

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-triphenylporphyrin, H_2(HTPPX-CO_2Me) (8). A solution of aldehyde **6** (0.41 g, 1 mmol), benzaldehyde (1.60 g, 15 mmol), and pyrrole (1.11 mL, 16 mmol) in chloroform (1.6 L) was purged with nitrogen for 45 min after which a portion of BF_3·OEt_2 (0.67 mL, 5.28 mmol) was added via syringe. The solution was stirred at room temperature under nitrogen in the dark for 1 h, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.72 g, 12 mmol) was added to the reaction. After stirring for an additional hour under nitrogen, the solvent was removed by rotary evaporation. The dark residue was redissolved in dichloromethane (250 mL) containing 2% triethylamine and filtered. The filtrate was loaded directly onto a silica gel column packed with dichloromethane and eluted with dichloromethane until no more porphyrinic product was detected. Several subsequent recrystallizations from dichloromethane and methanol removed a significant portion of the symmetric tetraphenylporphyrin (H_2-TPP) byproduct. Final purification by column chromatography (silica gel, 2:1 hexanes/dichloromethane) gave porphyrin **8** as a royal purple microcrystalline solid (200 mg, 22% yield based on bridge **6**).

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tris(2,6-dichlorophenyl)porphyrin, H_2-(HTDCPPX-CO_2Me) (9). A solution of aldehyde **6** (0.41 g, 1

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mmol), 2,6-dichlorobenzaldehyde (2.63 g, 15 mmol), and pyrrole (1.11 mL, 16 mmol) in chloroform (1.6 L) was purged with nitrogen for 45 min after which a portion of $BF_3{\cdot}OEt_2$ (0.67 mL, 5.28 mmol) was added via syringe. The solution was stirred at room temperature under nitrogen in the dark for 90 min, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.72 g, 12 mmol) was added to the reaction. After stirring for an additional hour under nitrogen, the solvent was removed by rotary evaporation. The dark residue was redissolved in dichloromethane (500 mL) and filtered. The filtrate was loaded directly onto a silica gel column packed with dichloromethane and eluted with dichloromethane until no more porphyrinic product was detected. Purification by repeated column chromatography (silica gel, 1:1 hexanes/dichloromethane) furnished porphyrin **9** as a purple powder (210 mg, 20% yield based on bridge **6**).

5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tris(2,6-dimethoxyphenyl)porphyrin, H_2(HTDMPPX-CO_2Me) (10). A solution of aldehyde **6** (0.41 g, 1 mmol), 2,6-dimethoxybenzaldehyde (2.49 g, 15 mmol), and pyrrole (1.11 mL, 16 mmol) in chloroform (1.6 L) was purged with nitrogen for 1 h after which a portion of $BF_3{\cdot}OEt_2$ (0.67 mL, 5.28 mmol) was added via syringe. The solution was stirred at room temperature under nitrogen in the dark for 1 h, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4.08 g, 18 mmol) was added to the reaction. After stirring for an additional hour under nitrogen, the solvent was removed by rotary evaporation. The dark residue was redissolved in dichloromethane (250 mL) and filtered. The filtrate was loaded directly onto a silica gel column packed with dichloromethane and eluted with dichloromethane until no more porphyrinic product was detected. Purification by repeated column chromatography (silica gel, dichloromethane) delivered porphyrin **10** as a reddish purple powder (220 mg, 20% yield based on bridge **6**).

Zinc(II) 5-(4-(5-Methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-trimesitylporphyrin, Zn(HPX-CO_2Me) (11). A saturated methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (5 mL) and a solution of **7** (250 mg, 0.040 mmol) in 15 mL of chloroform were combined and refluxed for 20 min. The solvent was removed by rotary evaporation. The remaining solid was purified by flash column chromatography (silica gel, 3:1 dichloromethane) followed by recrystallization from dichloromethane/methanol to yield **11** as a ruby red solid in quantitative yield.

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-trimesitylporphyrin, H_2(HPX-CO_2H) (12). Zinc(II) complex **11** (100 mg, 0.09 mmol) was dissolved in THF (20 mL), and 20% aq NaOH (10 mL) was added. The resulting mixture was refluxed for 3 days under an N_2 atmosphere. The organic solvent was removed by rotary evaporation, and the precipitate was filtered and washed with water until the washings were at neutral pH. The solid was redissolved in dichloromethane (50 mL), washed with 10% HCl (2 × 25 mL) and water (5 × 25 mL), and dried over Na_2SO_4. Removal of the solvent and purification by column chromatography (silica gel, 2:1 hexanes/dichloromethane to dichloromethane) provided porphyrin **12** as a royal purple powder (83 mg, 90% yield).

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-triphenylporphyrin, H_2(HTPPX-CO_2H) (13). The zinc(II) complex of **8** (60 mg) was prepared as described for **11** and dissolved in THF (20 mL). A portion of 20% aq NaOH (10 mL) was added, and the resulting mixture was refluxed for 3 days under an N_2 atmosphere. The organic solvent was removed by rotary evaporation, and the precipitate was filtered and washed with water until the washings were at neutral pH. The solid was redissolved in dichloromethane (25 mL), washed with 6 M HCl (1 × 10 mL) and water (7 × 25 mL), and dried over Na_2SO_4. Removal of the solvent and purification by column chromatography (silica gel, 1:1 hexanes/dichloromethane to dichloromethane) gave porphyrin **13** as purple flakes (56 mg, 95% yield based on **8**).

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tris(2,6-dichlorophenyl)porphyrin, H_2(HTDCPPX-CO_2H) (14). The zinc(II) complex of **9** (50 mg) was prepared as described for **11** and dissolved in THF (16 mL). A portion of 20% aq NaOH (8 mL) was added, and the resulting mixture was refluxed for 3 days under an N_2 atmosphere. The organic solvent was removed by rotary evaporation, and the precipitate was filtered and washed with water until the washings were at neutral pH. The solid was redissolved in dichloromethane (20 mL), washed with 6 M HCl (1 × 7 mL) and water (7 × 25 mL), and dried over Na_2SO_4. Removal of the solvent and purification by column chromatography (silica gel, 1:1 hexanes/dichloromethane to dichloromethane) delivered porphyrin **14** as a purple powder (47 mg, 95% yield based on **9**).

5-(4-(5-Hydroxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-tri(2,6-dimethoxyphenyl)porphyrin, H_2(HTDMPPX-CO_2H) (15). The zinc(II) complex of **10** (145 mg) was prepared as described for **11** and dissolved in THF (45 mL). A portion of 20% aq NaOH (20 mL) was added, and the resulting mixture was refluxed for 3 days under an N_2 atmosphere. The organic solvent was removed by rotary evaporation, and the precipitate was filtered and washed with water until the washings were at neutral pH. The solid was redissolved in dichloromethane (100 mL), washed with 10% HCl (1 × 100 mL) and water (5 × 50 mL), and dried over Na_2SO_4. Removal of the solvent and purification by column chromatography (silica gel, 30:1 dichloromethane/methanol) provided porphyrin **15** as a purple powder (143 mg, quantitative yield based on **10**).

5-(4-(5-Aminocarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,15,20-trimesitylporphyrin, H_2(HPX-$CONH_2$) (16). Thionyl chloride (2 mL) was added to a solution of porphyrin **12** (103 mg, 0.1 mmol) in dry CH_2Cl_2 (20 mL), and the resulting solution was refluxed for 90 min under an N_2 atmosphere. The solvent and excess thionyl chloride were removed by rotary evaporation. The residue was further dried under high vacuum, redissolved in dry CH_2Cl_2 (35 mL), and NH_3 gas was bubbled through the solution at a rapid rate for 2 min. The reaction was washed with water (3 × 25 mL) and dried over Na_2SO_4. Purification by column chromatography (silica gel, 100:1 dichloromethane/methanol) followed by recrystallization from dichloromethane/methanol afforded porphyrin **16** as a purple solid (92 mg, 90% yield).

5,15-Bis(4-(5-methoxycarbonyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene))-10,20-dimesitylporphyrin, H_2(HPBX-CO_2Me) (17a and 17b). A solution of **6** (204 mg, 0.5 mmol) and 5-mesityldipyrromethane (132 mg, 0.5 mmol) in dichloromethane (100 mL) was purged with nitrogen for 30 min after which a portion of $BF_3{\cdot}OEt_2$ (13 μL) was added via syringe. The solution was stirred at room temperature under nitrogen in the dark for 90 min, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (227 mg, 1 mmol) was added to the reaction. After stirring for an additional 30 min under nitrogen, the reaction was loaded directly onto a silica gel column packed with dichloromethane and eluted with dichloromethane until no more porphyrinic product was detected. Purification by column chromatography (silica gel, 1:1 hexanes/dichloromethane) separated the α,α- and α,β-atropisomers (**17a** and **17b**, respectively) from the crude reaction mixture in 8% yield each.

Physical Measurements. ^{1}H NMR spectra were collected in $CDCl_3$ or d_8-toluene (Cambridge Isotope Laboratories) at the MIT Department of Chemistry Instrumentation Facility (DCIF) using either a Mercury 300 or an Inova 500 spectrometer at 25 °C. All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. Absorption spectra were obtained using either a Cary-17 spectrophotometer modified by On-Line Instruments (OLIS) to include computer control or a Spectral Instruments 440 Series spectrophotometer.

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Supporting Information Available: Characterization data for all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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