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meso-Tetraaryl Cofacial Bisporphyrins Delivered by Suzuki Cross-Coupling

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Abstract: The Suzuki cross-coupling methodology provides a facile synthetic approach for the modular preparation of *meso*-tetraaryl cofacial bisporphyrins anchored by xanthene and dibenzofuran. This synthetic method furnishes cofacial bisporphyrin templates with enhanced steric and electronic protection from μ-oxo formation and oxidative degradation. The ability of these platforms to support multielectron oxidation chemistry mediated by proton-coupled electron transfer (PCET) is demonstrated by their reactivity for the catalytic disproportionation of hydrogen peroxide to oxygen and water.

Porphyrins presented in a face-to-face manner are a prominent structural motif for developing multielectron catalytic cycles.[1,2] Most successful in this regard are the Pacman systems consisting of two etio-type porphyrins linked by a single rigid bridge; these platforms have been utilized extensively in the catalytic reduction of small-molecule substrates (e.g. O_2, H_2, N_2).[3−17] The exceptional activity of Pacman complexes is based on the cofacial presentation of macrocyclic subunits with minimal lateral perturbations, allowing two proximate metal centers to act cooperatively in promoting the multielectron transformation of substrate.

The ability to tune the spatial orientation between catenated porphyrins is central to controlling their multielectron reactivity. For example, we have explored the limits of pocket size and flexibility within the Pacman motif by creating new systems with two etio-type porphyrins anchored by a xanthene (DPX) or dibenzofuran (DPD) scaffold.[18−20] In particular, the DPD framework provided the first direct observation of the Pacman effect for a single cofacial bisporphyrin platform. A comparative structural study of its biszinc(II) and bisiron(III) μ-oxo complexes shows that the cofacial DPD cleft can open and close its binding pocket by a vertical distance of over 4 Å in the presence of the appropriate exogeneous ligands.[19] In addition, subsequent reactivity studies reveal that biscobalt(II) complexes of both DPX and DPD are efficient electrocatalysts for the selective four-electron, four-proton reduction of oxygen to water despite their ca. 4 Å difference in metal−metal distances, demonstrating that effective multielectron reduction chemistry can be mediated within Pacman platforms that undergo large changes in vertical pocket sizes.[21]

Encouraged by these results, we sought to expand the reactivity of the DPX and DPD constructs to pursue multielectron oxidation reactions mediated by proton-coupled electron transfer (PCET).[22−25] However, the etioporphyrin-type substitution patterns of the parent DPX and DPD systems are generally unstable to oxidizing conditions owing to their unprotected *meso* positions. Additionally, the sterically modest alkyl functionalities of DPX and DPD lead to the facile formation of μ-oxo complexes, which represent a thermodynamic sink for oxidative catalysis. To circumvent these problems, we targeted cofacial bisporphyrins that would avoid the formation of bridging oxo species and display enhanced stability to oxidizing media. In this paper, we present the synthesis of such Pacman porphyrins and their application as oxidation catalysts. A modular and general synthetic method for the facile preparation of *meso*-tetraaryl cofacial bisporphyrins affixed to a xanthene (DTMPX = di-trimesitylporphyrin xanthene) or dibenzo-

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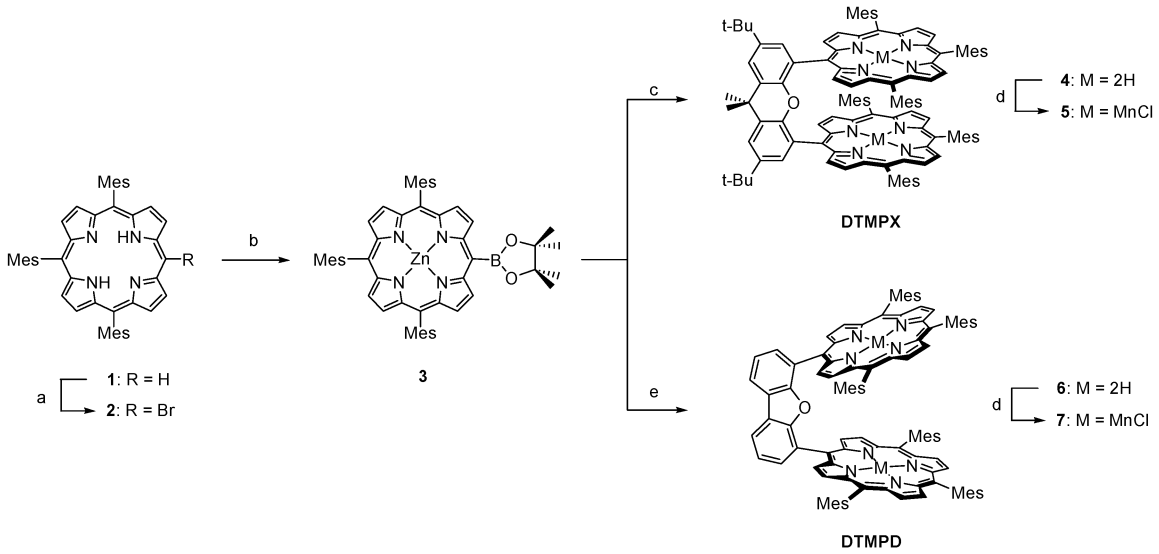
SCHEME 1[a]



[a] Reagents and conditions: (a) *N*-bromosuccinimide (NBS), chloroform; (b) (1) $Zn(OAc)_2 \cdot 2H_2O$, chloroform/methanol; (2) pinacol borane, $Pd(PPh_3)_2Cl_2$, Et_3N, 1,2-dichloroethane, 90 °C; (c) (1) 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene, $Pd(PPh_3)_4$, $Ba(OH)_2 \cdot 8H_2O$, 1,2-dimethoxyethane/water, 95 °C; (2) 6 N HCl; (d) (1) $Mn(OAc)_2 \cdot 4H_2O$, DMF; (2) aq NaCl, HCl; (e) (1) 4,6-dibromodibenzofuran, $Pd(PPh_3)_4$, K_3PO_4, DMF, 100 °C; (2) 6 N HCl.

furan (DTMPD = di-trimesitylporphyrin dibenzofuran) scaffold using Suzuki cross-coupling methods has been developed. We demonstrate the suitability of these platforms for multielectron oxidation reactions by using the bismanganese(III) derivatives of mesityl-derived DTMPX and DTMPD to catalyze oxygen evolution via the catalase-like disproportionation of hydrogen peroxide. Our results establish that appropriate ancillary modification of the porphyrin subunits can enhance oxidative stability and reactivity, and provide a synthetic underpinning for the design of additional Pacman systems for application in PCET-mediated oxidation catalysis.

Metal-catalyzed cross-coupling reactions have emerged as powerful tools in porphyrin synthesis.[26−40] As outlined in Scheme 1, these methods work well for obtaining *meso*-tetraaryl cofacial bisporphyrins anchored by xanthene and dibenzofuran spacers. The H_4(DTMPX) (**4**) and H_4(DTMPD) (**6**) derivatives are exemplary of the synthetic strategy. The mesityl substituents provide steric bulk as well as oxidative stability for high-valent transition-metal species.[41,42] It is noteworthy that the modular cross-coupling approach employed in Scheme 1 allows for control of the *meso* substitution pattern. The methods of Scheme 1 can easily be adapted to permit facile modification of the *meso* group trans to the bridge. To this end, the strategy provides an alternative to the statistical methods that have been previously used to prepare related DPA and DPB systems featuring *meso*-tetraaryl substitution patterns.[43,44]

meso-Triarylporphyrin, 5,10,15-trimesitylporphyrin (**1**)[45] (Scheme 1), is the key synthon of the cross-coupling approach, delivering *meso*-boronate zinc(II) porphyrin **3** in three steps. Regioselective *meso*-bromination of **1** with *N*-bromosuccinimide in chloroform at room temperature affords bromoporphyrin **2** in 90% yield. Zinc insertion with $Zn(OAc)_2 \cdot 2H_2O$ in a chloroform/methanol solvent mixture quantitatively affords zinc(II) haloporphyrin, which is smoothly converted to boronate **3** in excellent yield (96%) with use of the pinacol borane under Masuda conditions.[32,34,46]

The resulting boronate porphyrin **3** serves as a versatile transmetalating agent for the preparation of pillared cofacial bisporphyrins (Scheme 1). For example, reactions of **3** with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-

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TABLE 1. Turnover Numbers (TON) for Oxygen Release from H_2O_2 Dismutation

catalyst	TON
Mn_2Cl_2(DTMPX) (**5**)	579 ± 30
Mn_2Cl_2(DTMPD) (**7**)	54 ± 5
Mn_2Cl_2(DPX) (**8**)	37 ± 4
Mn_2Cl_2(DPD) (**9**)	27 ± 3
MnCl(TMP)	58 ± 5

xanthene or 4,6-dibromodibenzofuran under standard Suzuki conditions[32,34,47−49] furnish the Pacman porphyrins H_4(DTMPX) (**4**) and H_4(DTMPD) (**6**) in modest to good yields (21% and 77%, respectively). Suzuki cross-coupling reactions with hindered substrates can often be difficult, resulting in modest yields.[47−49] The lower yield obtained for the xanthene derivative as opposed to that of its dibenzofuran counterpart is likely due to steric constraints imposed on the double transmetalation reactions of the former.

With the preparation of *meso*-tetraaryl Pacman porphyrins in hand, we sought to establish their suitability for catalyzing multielectron oxidation reactions. We were interested in the biological oxygen evolution process related to water oxidation: the catalase-like disproportionation of hydrogen peroxide to oxygen and water.[50] The homobimetallic bischloromanganese(III) complexes Mn_2Cl_2(DTMPX) (**5**) and Mn_2Cl_2(DTMPD) (**7**) were prepared in excellent yields (81% and 89%, respectively) by reaction of the corresponding free-base porphyrins with $Mn(OAc)_2 \cdot 4H_2O$ followed by treatment with NaCl and HCl. Compounds **5** and **7** gave satisfactory high-resolution mass spectral analyses. For comparative purposes, we also examined the analogous etio-type bisporphyrins Mn_2Cl_2(DPX) (**8**) and Mn_2Cl_2(DPD) (**9**) along with the tetraarylporphyrin monomer MnCl(TMP).

The manganese complexes were screened for their H_2O_2 disproportionation reactivity. Oxygen evolution was monitored volumetrically and detected by using a standard pyrogallol assay.[51] The comparative catalytic activities in turnover numbers (TON) for binuclear complexes **5** and **7** along with Mn_2Cl_2(DPX) (**8**), Mn_2Cl_2(DPD) (**9**), and the monomer MnCl(TMP) are summarized in Table 1. Complex **5**, containing the xanthene bridge with *meso*-tetraarylporphyrin subunits, is the most active (579 ± 30 TON), catalyzing the oxygen evolution process by 10-fold over all the other compounds examined. Notably, the analogous platforms with an etio-type substitution pattern (DPX **8**, 37 ± 4 TON) and/or a dibenzofuran bridge (DPD **9**, 27 ± 3 TON; DTMPD **7**, 54 ± 5 TON) show no enhanced reactivity over that obtained for the monomer MnCl(TMP) (58 ± 5 TON) control catalyst.

In conclusion, we have developed a general approach for preparing Pacman porphyrins to catalyze the multielectron oxidation of small-molecule substrates via PCET. This method affords cofacial bisporphyrin templates with enhanced steric and electronic protection from μ-oxo formation and oxidative degradation. Modular Suzuki cross-coupling methods have been exploited to prepare *meso*-tetraaryl Pacman porphyrins anchored by either xanthene or dibenzofuran. We anticipate that this synthetic method can be extended to the synthesis of other cofacial homo- and heteroporphyrin architectures by coupling the appropriate *meso*-triaryl boronate porphyrin precursor with the desired pillar. The facile synthesis of the mesityl derivatives DTMPX and DTMPD attests to the efficacy of this approach. In addition, we have demonstrated the suitability of the *meso*-tetraaryl Pacman porphyrins for catalyzing multielectron transformations under oxidizing conditions. Manganese derivatives of DTMPX and DTMPD have been employed to effect catalytic oxygen evolution from the disproportionation of hydrogen peroxide. Comparative reactivity studies with the parent etioporphyrin-type DPX and DPD frameworks reveal that both the choice of pillar and ancillary porphyrin substitution are critical for achieving cooperative bimetallic reactivity. With the modular Suzuki cross-coupling method for Pacman synthesis at our disposal, we are poised to synthetically tailor the electronic and steric properties of the ancillary porphyrin subunits at will. Current studies are aimed at expanding the opportunities for these and related architectures in catalytic multielectron oxidation chemistry.

Experimental Section

Materials. Silica gel 60 (70−230 and 230−400 mesh) was used for column chromatography. Analytical thin-layer chromatography was performed with use of silica gel (precoated sheets, 0.2 mm thick). Solvents for synthesis were of reagent grade or better, and were dried according to standard methods.[52] The compounds 5,10,15-trimesitylporphyrin (**1**),[45] 4,6-dibromodibenzofuran,[53] Mn(TMP)Cl,[54,55] 4,5-bis[(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl-5-porphyrinyl)-9,9-dimethylxanthene],[18] and 4,6-bis[(5-(2,8,13,17-tetraethyl-3,7,12,18-tetra-methylporphyrinyl)]dibenzofuran][19] were prepared according to literature procedures. All other reagents were used as received. ^{1}H NMR spectra were collected in $CDCl_3$ at the MIT Department of Chemistry Instrumentation Facility (DCIF), using either a 300 MHz or a 500 MHz spectrometer at 25 °C. High-resolution mass spectral analyses were carried out at the University of Illinois Mass Spectrometry Laboratory or the MIT DCIF. Elemental analyses were carried out at Quantitative Technologies, Inc. (Whitehouse, NJ) and Michigan State University.

5-Bromo-10,15,20-trimesitylporphyrin (2). *N*-Bromosuccinimide (164 mg, 0.920 mmol) was added in one portion to a solution of **1** (612 mg, 0.920 mmol) in chloroform (450 mL) and the reaction was stirred at room temperature under air for 20 min. The solvent was removed and the residue was purified by column chromatography (silica gel, 1:1 hexanes/dichloromethane) to yield the product as a reddish-brown solid (616 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 9.60 (d, J = 4.7 Hz, 2H), 8.74 (d, J = 4.7 Hz, 2H), 8.61 (s, 4H), 7.29 (s, 6H), 2.64 (s, 6H), 2.62 (s, 3H), 1.86 (s, 6H), 1.85 (s, 12H), −2.54 (s, 2H). HRESIMS (MH^+) calcd for $C_{47}H_{44}BrN_4$ m/z 743.2744, found 743.2753.

Zinc(II) 5,10,15-trimesityl-20-(4′,4′,5′,5′-tetramethyl-[1′,3′,2′]dioxaborolan-2′-yl)porphyrin (3). To a solution of **2** (600 mg, 0.807 mmol) in dicholoromethane (200 mL) was added

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a solution of $Zn(OAc)_2 \cdot 2H_2O$ (354 mg, 1.61 mmol) in methanol (10 mL). The reaction mixture was stirred at room temperature under air overnight. Purification by column chromatography (silica gel, 1:1 hexanes/dichloromethane) furnished the zinc-metalated porphyrin of **2** as a bright red solid in quantitative yield. Under nitrogen, triethylamine (1.4 mL, 10 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (16.2 mg, 0.023 mmol), and pinacolborane (0.94 mL, 6.47 mmol) were added to a solution of the zinc-metalated porphyrin of **2** (622 mg, 0.771 mmol) in anhydrous 1,2-dichloroethane (90 mL). The resulting mixture was stirred at 90 °C for 45 min under nitrogen. The reaction was cooled to room temperature, quenched with 30% aq KCl (30 mL), and washed with water (100 mL) and the solvent was removed by rotary evaporation. The residue was then purified by column chromatography (silica gel, 1:1 hexanes/dicholoromethane) to deliver **3** as a ruby red powder (635 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 9.82 (d, J = 4.5 Hz, 2H), 8.90 (d, J = 4.5 Hz, 2H), 8.73 (d, J = 4.5 Hz, 2H), 8.69 (d, J = 4.5 Hz, 2H), 7.28 (s, 6H), 2.65 (s, 6H), 2.63 (s, 3H), 1.86 (s, 18H), 1.82 (s, 12H). HRESIMS (MH^+) calcd for $C_{53}H_{54}BN_4O_2Zn$ m/z 853.3626, found 853.3608.

4,5-Bis[5-(10,15,20-trimesitylporphyrinyl)]-2,7-di-*tert*-butyl-9,9-dimethylxanthene, H_4(DTMPX) (4). A Schlenk tube was charged with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (46 mg, 0.0958 mmol), **3** (245 mg, 0.287 mmol), $Ba(OH)_2 \cdot 8H_2O$ (90.6 mg, 0.287 mmol), and $Pd(PPh_3)_4$ (55 mg, 0.0479 mmol) under a nitrogen atmosphere. 1,2-Dimethoxyethane (31 mL) and deionized water (3.1 mL) were added and the resulting solution was heated at 95 °C for 22 h under nitrogen. The solvent was removed and the residue was redissolved in dichloromethane (50 mL) and stirred with 6 N HCl (25 mL) for 30 min. The organic layer was separated and washed with 20% aq Na_2CO_3 (40 mL) followed by water (2 × 60 mL). The solvent was evaporated and the residue was purified by column chromatography (silica gel, 2:1 hexanes/dichloromethane) to afford the product **4** as a purple powder (33 mg, 21% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.36 (d, J = 4.8 Hz, 4H), 8.33 (d, J = 4.4 Hz, 4H), 8.15 (d, J = 4.4 Hz, 4H), 7.92 (d, J = 2.5 Hz, 2H), 7.65 (d, J = 4.8 Hz, 4H), 7.24 (s 2H), 7.09 (s, 2H), 7.00 (s, 4H), 6.87 (d, J = 2.5 Hz, 2H), 6.38 (s, 4H), 2.56 (s, 6H), 2.45 (s, 12H), 2.34 (s, 6H), 1.93 (s, 6H), 1.57 (s, 12H), 1.40 (s, 6H), 1.23 (s, 18H), −0.31 (s, 12H), −3.30 (s, 4H). HRESIMS (MH^+) calcd for $C_{117}H_{115}N_8O$ m/z 1647.9188, found 1647.9171.

4,6-Bis[5-(10,15,20-trimesitylporphyrinyl)]dibenzofuran, H_4(DTMPD) (6). A mixture of 4,6-dibromodibenzofuran (50.8 mg, 0.156 mmol), **3** (400 mg, 0.468 mmol), potassium phosphate (397 mg, 1.87 mmol), $Pd(PPh_3)_4$ (54 mg, 0.0467 mmol), and anhydrous DMF (71 mL) was heated at 100 °C for 20 h under a nitrogen atmosphere. The solvent was removed and the residue was redissolved in dichloromethane (90 mL) and stirred with 6 N HCl (40 mL) for 30 min. The organic layer was separated and washed with 20% aq Na_2CO_3 (40 mL) followed by water (2 × 60 mL). The solvent was evaporated and the residue was purified by column chromatography (silica gel, 2:1 hexanes/dichloromethane) to deliver the product **6** as a plum purple solid (180 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.62 (dd, J = 7.7, 1.1 Hz, 2H), 8.46 (d, J = 4.9 Hz, 4H), 8.35 (d, J = 4.7 Hz, 4H), 8.26 (d, J = 4.7 Hz, 4H), 8.16 (d, J = 4.7 Hz, 4H), 8.04 (dd, J = 7.5, 1.1 Hz, 2H), 7.79 (t, J = 7.5 Hz, 2H), 7.16 (s, 2H), 7.13 (s, 2H), 7.10 (s, 4H), 6.76 (s, 4H), 2.55 (s, 6H), 2.53 (s, 12H), 1.71 (s, 6H), 1.59 (s, 12H), 1.45 (s, 6H), 0.73 (s, 12H), −3.07 (s, 4H). HRESIMS (MH^+) calcd for $C_{106}H_{93}N_8O$ m/z 1493.7467, found 1493.7462.

Manganese Cofacial Porphyrins. The procedure for preparing these compounds was similar, differing primarily in the porphyrin starting material and scale of the reaction. For example, $Mn(OAc)_2 \cdot 4H_2O$ (16 mg, 0.0653 mmol) was added to a refluxing solution of **4** (20 mg, 0.012 mmol) in DMF (9 mL) and the reaction was refluxed in air for 30 min. Two more portions of $Mn(OAc)_2 \cdot 4H_2O$ (16 mg each) were added at intervals of 30 min and heating was continued for 30 min after the last addition of metal salt. The reaction was cooled to room temperature and poured into ice-cold brine (12 mL). The green precipitate was collected by filtration and washed with deionized water (120 mL). The solid was then redissolved in methanol (12 mL) and the solution was poured into ice-cold 6 N HCl (12 mL). The brownish precipitate was redissolved in dichloromethane (20 mL), the organic phase was washed with water (2 × 50 mL), and the solvent was removed. The residue was purified by column chromatography (silica gel, dichloromethane to 10% methanol/dichloromethane), redissolved in dichloromethane (10 mL), and stirred with 4 N HCl (2 mL) for 30 min. The organic layer was separated, washed with water (3 × 40 mL), and dried over Na_2SO_4, and the solvent was removed by rotary evaporation to give **5** as a green powder (18 mg, 81% yield). HRFABMS ([M − Cl]$^+$) calcd for $C_{117}H_{110}ClMn_2N_8O$ m/z 1787.7252, found 1787.7252. The detailed experimental procedures for **7**−**9** are provided in the Supporting Information.

Hydrogen Peroxide Disproportionation Reactions. Standard conditions were employed for catalase reactivity studies.[56] Dismutation reactions were performed at room temperature in a 5-mL conical reaction vial with a side port, equipped with a magnetic spinvane stirbar and a capillary gas delivery tube linked to a graduated buret filled with water. The reaction vial was charged with 0.5 μmol of the bis-manganese porphyrin dimer (or 1 μmol of the Mn(TMP)Cl), 25 μmol of 1,5-dicyclohexylimidazole, 4 μmol of benzyldimethyltetradecylammonium chloride, 2 mL of dichloromethane, and 1 mL of phosphate buffer, pH 7. The solution was stirred to ensure gas pressure equilibration. An aliquot of 30% H_2O_2 (0.11 mL) was added to the reaction mixture via syringe through the side port. The oxygen evolution was measured with a buret. The identity of the oxygen gas was confirmed independently by using the alkaline pyrogallol test.[51]

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Supporting Information Available: Synthesis and characterization data of compounds **7**−**9** and ^{1}H NMR spectra for compounds **2**−**4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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