Investigation of Tightly Coupled Porphyrin Arrays Comprised of Identical Monomers for Multibit Information Storage

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Our prior designs for molecular-based information storage devices have employed multiple redox-active units organized in weakly coupled, covalently linked arrays. To explore a simpler design, we report here the synthesis of porphyrin arrays where porphyrins with identical oxidation potentials are directly linked to one another instead of joined via a molecular linker. Oxidative coupling with $AgPF_6$ of zinc(II)-5,15-bis(4-*tert*-butylphenyl)-10-phenylporphyrin, obtained by a rational synthesis, afforded the expected dimer joined by a meso-meso linkage and an unexpected trimer joined by meso-meso linkages. For attachment to an electroactive surface we synthesized a meso-linked porphyrin dimer with a thiol-linker in one of the meso positions. The *S*-acetyl protecting group was used to avoid handling free thiol groups. Coupling of zinc(II)-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin ("upper half") and zinc(II)-5-[4-(*S*-acetylthio)phenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin ("lower half") afforded three different meso-linked dimers with the desired dimer as the main product. Electrochemical examination of the meso-linked dimer in solution shows that the first two oxidation potentials of the array differ by ∼0.15 V and straddle the value exhibited by the monomeric constituents. The third and fourth oxidation potentials of the array are also split although to a lesser extent (∼0.08 V) than the first and second. For the meso-linked trimer, the first three oxidation waves are also split; however, these waves are severely overlapped. The electrochemical behavior of the dimers and trimer is indicative of strong electronic interactions among the porphyrins. The thiol-derivatized meso-linked dimers form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetylthio protecting group. The porphyrin SAM exhibits four well-resolved oxidation waves. Regardless, the meso−meso linkage is relatively unstable upon formation of the π-cation radical(s). This characteristic indicates that the structural motif is of limited utility for molecular information storage elements.

Introduction

As part of a program in molecular electronics, we are searching for compounds that are suitable for molecular-based information storage. Our prior approaches to multibit molecular-based information storage employed weakly coupled arrays of redox-active units such as porphyrins[1] and ferrocenes,[2] with each redox-active unit having a distinct and different oxidation potential. With porphyrins, the electrochemical potentials can be tuned through placement of electron-withdrawing or electron-releasing groups around the macrocycle perimeter[3] or by the use of different central metals.[4] This approach to multibit information storage requires the synthesis of a family of distinct monomeric porphyrin molecules for incorporation into the arrays. Upon incorporation into the arrays, the porphyrins retain their distinctive oxidation potentials.

To simplify the construction of the arrays for molecular-based information storage, we decided to synthesize porphyrin arrays where the porphyrins are directly linked to one another instead of joined via a molecular linker. Osuka and co-workers have pioneered the synthesis of such meso-linked porphyrins.[5−9] We expected that the juxtaposition of the porphyrins in the arrays would result in strong ("tight") coupling between the two constituents. Tight coupling should result in a splitting of the redox potentials corresponding to individual one-electron events in the array. In this manner, identical porphyrins can be used in the construction of the multiporphyrin array while still maintaining the ability to access multiple oxidation states. One of the major issues is how many porphyrin units can be assembled in a tightly coupled manner and still obtain significantly distinct oxidation states.

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Storing and retrieving information in redox-active molecules requires a means of electrical communication from the macroscopic world to the molecular assemblies. One means of electrical communication involves the attachment of redox-active molecules via a thiol linker to an electroactive surface such as gold.[10] To overcome the problem of handling free thiol groups, we decided to use protected thiol groups, especially after the report of Tour et al. that an *S*-(acetylthio)-substituted phenylethynyl oligomer underwent deprotection in situ upon exposure to a gold surface.[11] Recently, we have synthesized a number of porphyrin monomers bearing one, two, or four protected thiol units and have investigated the utility of a variety of different thiol protecting groups.[12]

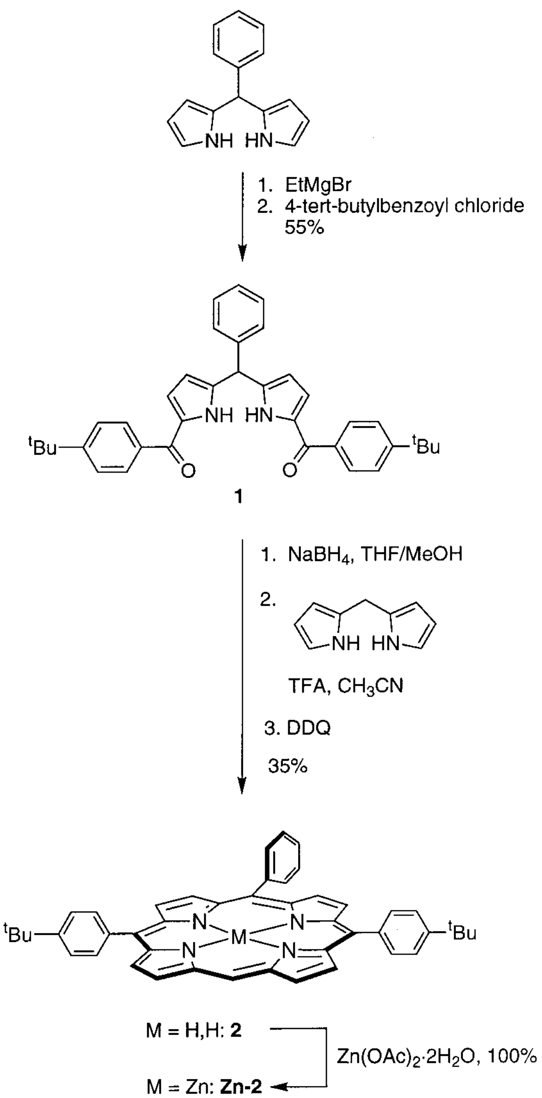
In this paper, we report the synthesis of four different porphyrin dimers and one trimer joined by meso,meso linkages. The electrochemical properties of the dimers and trimers have been investigated in solution. Two dimers bearing *S*-acetyl protected thiol groups were also prepared, and the electrochemical properties of these molecules attached to gold surfaces were investigated.

Results and Discussion

Our first target molecule was a meso-linked porphyrin dimer consisting of two identical porphyrin monomers. The rationale for the preparation of this molecule was to determine whether the juxtaposition of porphyrins affords sufficiently strong coupling between the two constituents such that the oxidation potentials would be split by an easily resolvable amount. Splittings of the potentials by ~0.15 V satisfy this criterion.

The preparation of the monomer relies on a new rational synthesis of meso-substituted porphyrins.[13] Treatment of 5-phenyldipyrromethane[14,15] with ethylmagnesium bromide followed by acylation with 4-*tert*-butylbenzoyl chloride led to the diacylated dipyrromethane **1** (Scheme 1). Reduction with excess $NaBH_4$ in THF/methanol afforded the corresponding dicarbinol, which was condensed with dipyrromethane[15] under TFA catalysis in acetonitrile at room temperature (nonscrambling conditions)[13] followed by oxidation with DDQ. The desired porphyrin **2** was obtained in 35% yield. This synthesis route afforded the desired porphyrin with one free meso position without acidolytic scrambling. Porphyrin **2** is almost insoluble in common solvents. Metalation with $Zn(OAc)_2{\cdot}2H_2O$ in refluxing $CHCl_3$ afforded **Zn-2** in quantitative yield, which also has low solubility.

Scheme 1



For the meso,meso coupling of **Zn-2**, we used the method reported by Osuka et al.,[5-7] which employed the oxidant $AgPF_6$ in a mixture of $CHCl_3$ and acetonitrile. Due to the low solubility of **Zn-2**, the reaction was run under reflux instead of room temperature. Using 0.5 molar equiv of $AgPF_6$ as reported by Osuka et al.[5] led to only a small amount of dimer (~10%, checked by analytical SEC). After addition of another 0.5 molar equiv of $AgPF_6$, quantitative conversion occurred within 15 h. Because slight demetalation occurred under the coupling conditions, the crude mixture was again treated with $Zn(OAc)_2{\cdot}2H_2O$. We obtained two different oligomers, the expected dimer **Zn-3** in 89% yield and, surprisingly, also the trimer **Zn-4** in 9% yield (Scheme 2). Both are brown-purple solids and exhibit good solubility in common solvents. The structure proposed for **Zn-4** is consistent with the molecule ion peak observed by mass spectrometry and the substitution pattern indicated by ^1H NMR spectroscopy. The ^1H NMR spectrum of **Zn-4** is almost identical with that of **Zn-3** with the addition of a peak due to the *tert*-butyl groups and the presence of the AA′BB′ pattern from the protons of the *meso*-aryl groups of the central porphyrin. Such a spectrum arises from a symmetrical molecule, and the suggested structure is the only possibility for **Zn-4**.

After preparation of **Zn-3**, the meso-linked porphyrin dimer bearing a thiol linker for attachment to a gold surface was synthesized. Thiol-derivatized trimeric arrays were not pursued owing to their nonoptimal redox characteristics (vide infra). To improve the solubility of the monomers we chose 3,5-di-*tert*-butylphenyl groups as substituents for the nonlinking meso positions. The synthesis of a "lower" porphyrin bearing an *S*-acetyl-protected thiol group in a route similar to that of

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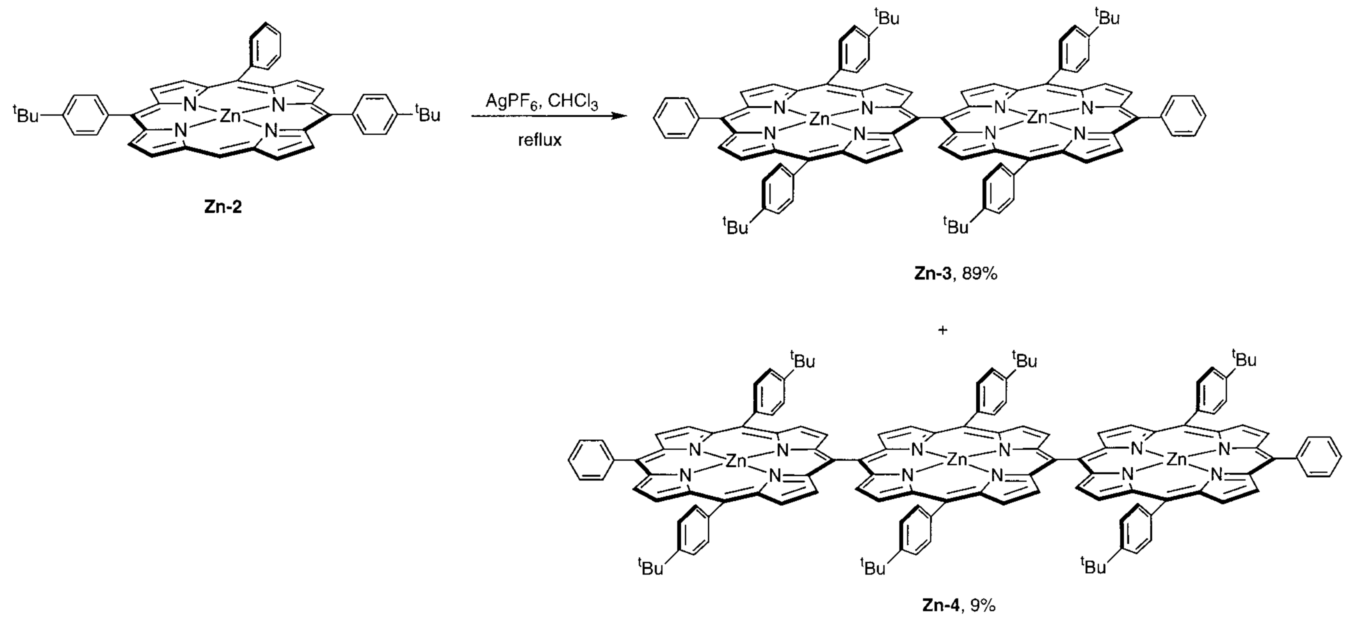
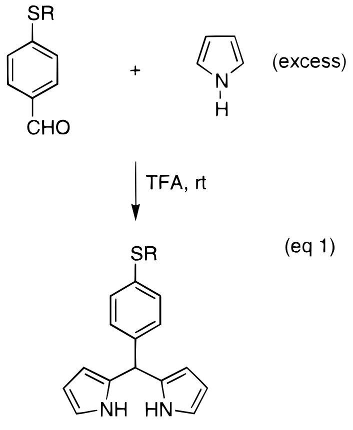
Scheme 2



Zn-2

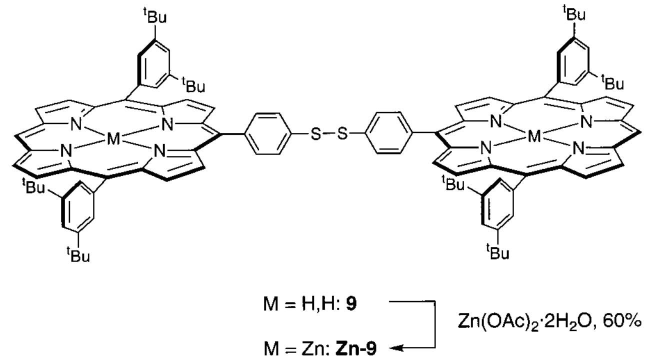
Zn-3, 89%

Zn-4, 9%



5, R = Me (65%)
6, R = Ac (62%)

monomer **Zn-2** requires an *S*-(acetylthio)-derivatized dipyrromethane. Such a dipyrromethane can be obtained via at least two conceivable pathways. Our first attempt involved reaction of commercially available 4-(methylthio)benzaldehyde with pyrrole to give the corresponding dipyrromethane **5** (eq 1). However, subsequent treatment with sodium *tert*-thiobutoxide,[16] followed by quenching of the anion with acetyl chloride, did not afford the desired product **6**. We then reacted 4-(*S*-acetylthio)-benzaldehyde[12] with pyrrole, affording dipyrromethane **6** in 62% yield (eq 1). To prepare the other half of the "lower" porphyrin, dipyrromethane[15] was diacylated with 3,5-di-*tert*-butylbenzoyl chloride giving **7** as a white powder after crystallization (Scheme 3). Reduction of **7** to the corresponding dicarbinol and condensation with **6** yielded porphyrin **8** in 10% yield, accompanied by disulfide **9** in 3% yield. Metalation of **8** with Zn(OAc)$_2$·2H$_2$O gave **Zn-8** as a purple solid in 90% yield. Disulfide **9** was metalated likewise, affording **Zn-9** in 60% yield as an orange-purple solid (eq 2).



(eq 2)

The synthesis of the "upper" porphyrin **Zn-10** proceeded similarly but in much better yield. Reduction of the diacylated dipyrromethane **7** with NaBH$_4$ and condensation of the resulting dicarbinol with 5-(3,5-di-*tert*-butylphenyl)dipyrromethane[17] gave porphyrin **10** in 21% yield (Scheme 4). Metalation with Zn(OAc)$_2$·2H$_2$O led to **Zn-10** in quantitative yield. **Zn-10**, like all of the other porphyrin monomers (**8**, **Zn-8**, and **10**) and disulfides (**9** and **Zn-9**) bearing 3,5-di-*tert*-butylphenyl groups in the meso positions, exhibits good solubility in common organic solvents.

Coupling of **Zn-8** and **Zn-10** with AgPF$_6$ in refluxing CHCl$_3$ afforded the expected three dimers in almost quantitative yield. Traces of higher oligomers were also present. After re-metalation with Zn(OAc)$_2$·2H$_2$O, we obtained porphyrin dimers **Zn-11**, **Zn-12**, and **Zn-13** in 30, 44, and 23% yield, respectively (Scheme 5). All of these porphyrin dimers are purple solids with good solubility in common organic solvents. Under these reaction conditions the *S*-acetylthio group remained intact.

Electrochemical Studies. The electrochemical behavior of the dimers **Zn-3**, **Zn-12**, and **Zn-13** and the

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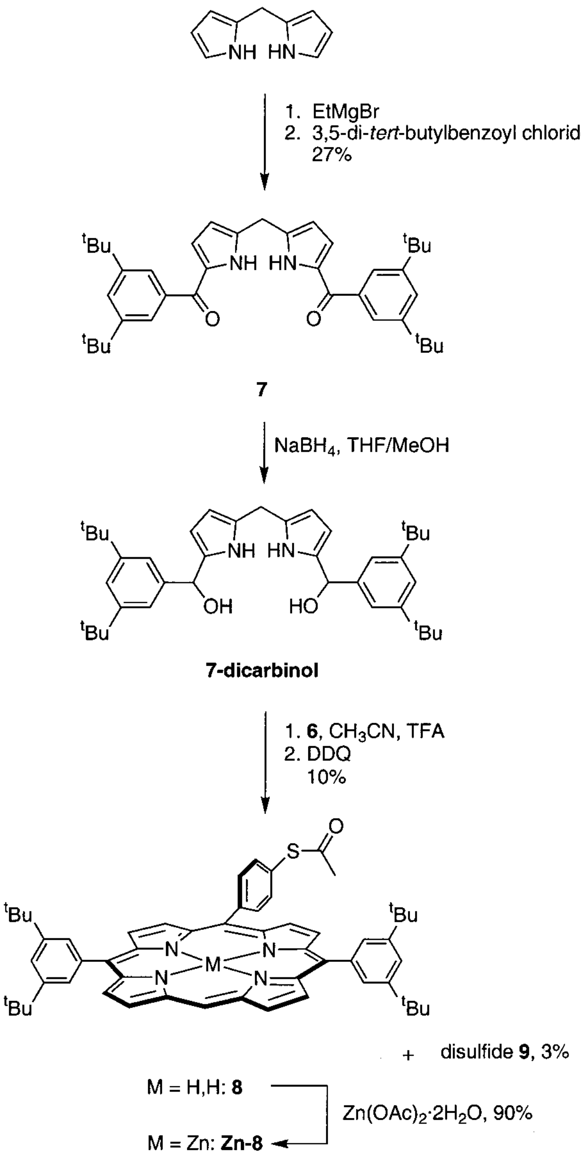
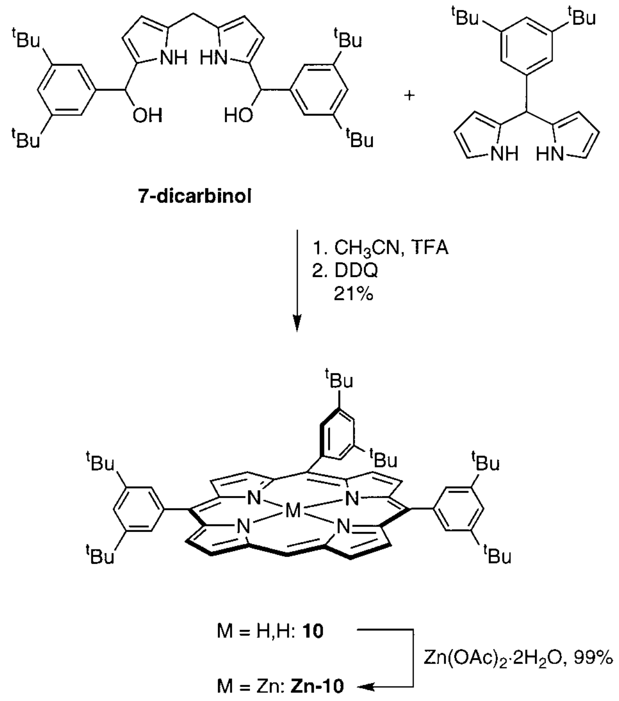
Scheme 3



Scheme 4



trimer **Zn-4** was investigated in solution. All three dimers exhibit four reversible oxidation waves at ~0.50, 0.65, 0.95, and 1.03 V (versus Ag/Ag$^+$; $E_{1/2}$ (FeCp$_2$/FeCp$_2^+$) = 0.19 V). The first and second oxidation waves straddle the $E_{1/2}$ value for the first oxidation of a monomeric porphyrin with similar substituents ($E_{1/2}$ ~0.6 V).[18] The third and fourth oxidation waves of the array are both at slightly higher potentials than the second oxidation of similar monomeric porphyrins ($E_{1/2}$ ~0.9 V). For the trimer **Zn-4**, the first three oxidation waves are also split and occur in the 0.45−0.7 V range. However, these waves are severely overlapped and their exact potentials cannot be accurately determined. The splittings observed in the oxidation potentials of both the dimeric and trimeric arrays are indicative of strong electronic interactions among the porphyrins.

The electrochemical behavior of the dimers **Zn-12** and **Zn-13** was also investigated for the arrays attached to gold. Thiolated trimeric arrays were not prepared due to the fact that the overlapping redox waves render these arrays poor candidates for memory storage elements. Both **Zn-12** and **Zn-13** form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetylthio protecting group. The SAMs of the dimers are electrochemically robust and exhibit four well-resolved oxidation waves. These waves occur at ~0.35, 0.55, 0.95, and 1.2 V. A representative fast-scan (100 V/s) cyclic voltammogram of the **Zn-12** SAM is shown in Figure 1. One unexpected redox characteristic of the meso-linked dimers is that the first two oxidation waves occur at a slightly lower potential than those observed in solution.[1,2,10] This behavior is contrary to that observed for all of the other porphyrins examined (in which the oxidation potentials of the SAMs are shifted positively compared with those in solution). In addition, the third oxidation wave of the SAMs occurs at approximately the same potential as that observed in solution, whereas the fourth wave is shifted positively. We have no explanation for the inconsistent shifts of the oxidation potentials for the SAMs of the meso-linked arrays. One other point worthy of comment concerns the stability of the meso-linked dimers under repeated cycles of oxidation/reduction. After several cycles, a new feature appears in the voltammogram near 0.6 V. This same feature is observed in solution when the sample is bulk oxidized. Spectroscopic studies of the oxidation product suggest that this species is a porphyrin monomer. This monomer is apparently generated via cleavage of the meso,meso linkage when the π-cation radical is formed.

Conclusion

Various meso-linked porphyrin dimers and a trimer have been synthesized. Electrochemical studies of the dimers and trimer are consistent with strong coupling between the porphyrins in the array. In the case of the dimers, all four oxidation potentials exhibit sufficient splitting to permit resolution of individual states that could serve to store two bits of information. In the case

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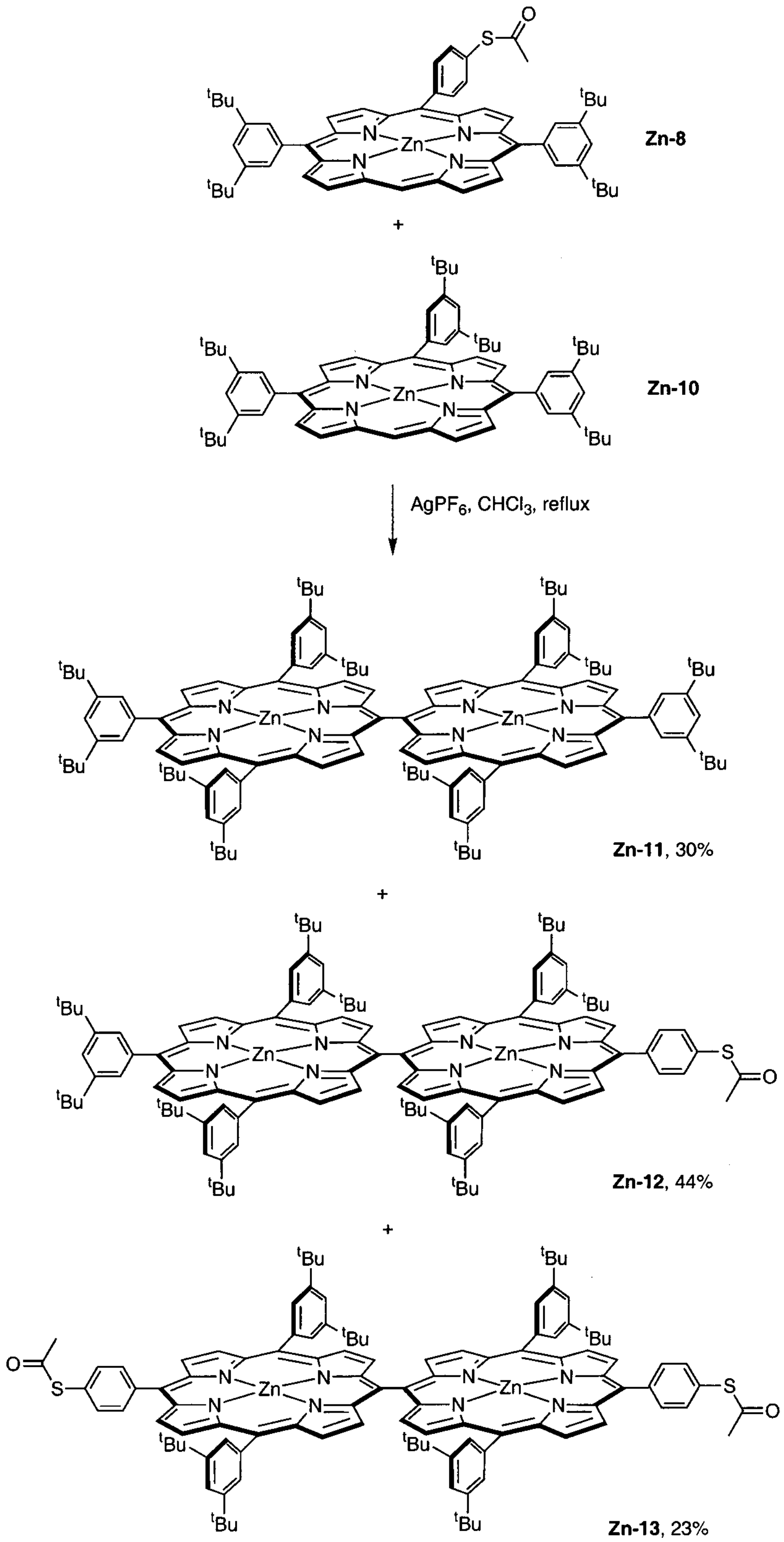
Scheme 5



of the trimer, the splittings are not well enough resolved to be useful in this application. Thiol-derivatized analogues of the dimers form SAMs on gold via cleavage of the *S*-acetylthio protecting groups. The porphyrin SAM exhibits four well-resolved oxidation waves. Regardless, the meso−meso linkage appears to be relatively unstable upon formation of the π-cation radical(s). Given the critical importance of stability toward repeated cycles of oxidation and reduction, the instability of the meso−meso linkage suggests that this structural motif is of limited utility for molecular information storage elements.

Experimental Section

General Methods. Sources of reagents, solvents, and chromatographic media are described in the first paper of this series.[10] All reported NMR spectra were collected in CDCl$_3$ (^{1}H

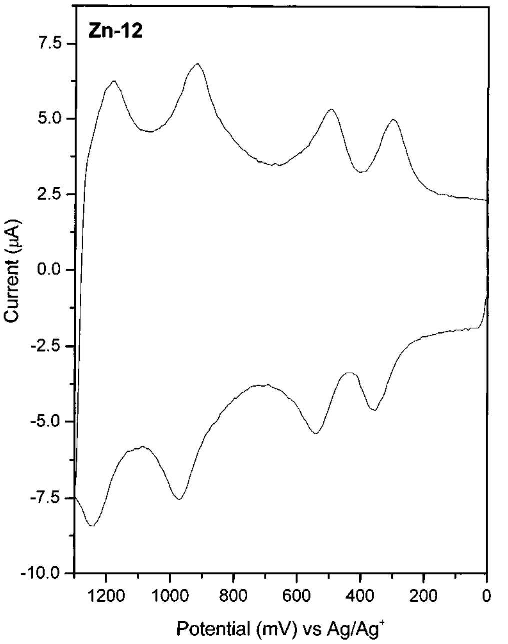


Figure 1. Fast-scan (100 V/s) voltammetry of **Zn-12**.

NMR at 300 MHz; ^{13}C NMR at 75 MHz). UV−vis absorption and fluorescence spectra were recorded in toluene as described previously.[19] Porphyrin metalation was performed and monitored by fluorescence spectroscopy as described in the preceding paper in this series.[1] Melting points are uncorrected. Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix,[20] fast atom bombardment (FAB-MS, 10 ppm elemental compositional accuracy for the porphyrins), or electron-impact mass spectrometry (EI-MS). Preparative-scale size-exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1 with toluene as eluent. Analytical scale SEC was performed with a 1000 Å column (5 μL, styrene-divinylbenzene copolymer) with THF as eluent (0.8 mL/min).[21]

1,9-Bis(4-*tert*-butylbenzoyl)-5-phenyldipyrromethane (1). Following a general procedure,[13,22] to a solution of 5-phenyldipyrromethane[14,15] (2.22 g, 10 mmol) in toluene (200 mL) stirred under argon and cooled in a water bath was slowly added a solution of ethylmagnesium bromide (1 M solution in THF, 50 mL, 50 mmol). The resulting brown-orange mixture was stirred for 30 min at room temperature. Then a solution of 4-*tert*-butylbenzoyl chloride (4.9 mL, 25 mmol) in toluene (25 mL) was added dropwise. The solution became darker and was stirred for 1 h after the addition was completed. Then the reaction was quenched with saturated aqueous NH_4Cl (100 mL). Ethyl acetate (100 mL) was added, and the phases were separated. The organic phase was washed with water, 2 M aqueous NaOH, water, and brine and then dried (Na_2SO_4). The solvent was removed, and the residue was filtered through a pad of silica (CH_2Cl_2/ethyl acetate, 10:1). The solvent was again removed, and the brown residue was purified by column chromatography (first column: alumina, hexanes−CH_2Cl_2/hexanes/CH_2Cl_2; CH_2Cl_2/methanol; second column: silica, Et_2O/hexanes, 1:2; third column: silica CH_2Cl_2/ethyl acetate, 5:1), affording a brown solid (2.96 g, 55%): mp 133 °C; IR (neat) $\tilde{\nu}$ 3438, 3251, 2963, 2903, 2868, 1611, 1556, 1479; ^{1}H NMR δ 1.34 (s, 18H), 5.67 (s, 1H), 6.00 (dd, $J = 3.7$ Hz, $J = 2.9$ Hz, 2H), 6.64 (dd, $J = 3.7$ Hz, $J = 2.2$ Hz, 2H), 7.30−7.51 (m, 5H), 7.42, 7.73 (AA′BB′, 2 × 4H), 11.04 (brs, 2H); ^{13}C NMR (APT): δ 31.1 (−), 34.9 (+), 44.9 (−), 111.0 (−), 120.6 (−), 124.9 (−), 127.3 (−), 128.8 (−), 129.2 (−), 129.5 (−), 131.0 (+), 135.6 (+), 140.5 (+), 140.8 (+), 155.0 (+), 184.3 (+); EI-MS obsd 542. Anal. Calcd for $C_{37}H_{38}N_2O_2$: C, 81.88; H, 7.06; N, 5.16. Found: C, 81.79; H, 7.22; N, 5.21.

5,15-Bis(4-*tert*-butylphenyl)-10-phenylporphyrin (2). Following a general procedure,[13,22] to a solution of **1** (500 mg, 921 μmol) in THF/methanol (27 mL, 2:1) was added $NaBH_4$ (1.74 g, 46 mmol) in several portions. The mixture was stirred for 2.5 h, quenched with water (40 mL), and extracted with CH_2Cl_2. The organic phase was dried (K_2CO_3), and the solvent was removed. The yellow residue and dipyrromethane[15] (135 mg, 923 μmol) were then dissolved in acetonitrile (370 mL) and stirred at room temperature. Then TFA (852 μL, 11.1 mmol) was added, and the solution turned dark immediately. After 20 min, DDQ (630 mg, 2.8 mmol) was added because the yield did not increase any further (checked by oxidizing an aliquot with DDQ and quantifying with UV/vis spectroscopy). After being stirred for 1.5 h, the mixture was filtered through a pad of alumina and eluted with CH_2Cl_2. A second column (silica, CH_2Cl_2/hexanes, 1:1, then CH_2Cl_2) afforded a purple solid (211 mg, 35%): IR (neat) $\tilde{\nu}$ 3312, 3030, 2957, 2864, 1596, 1560, 1500; ^{1}H NMR δ −2.99 (s, 2H), 1.62 (s, 18H), 7.70−7.82 (m, 3H), 7.78, 8.18 (AA′BB′, 2 × 4H), 8.14−8.24 (m, 2H), 8.85 (d, $J = 5.1$ Hz, 2H), 8.95 (d, $J = 5.1$ Hz, 2H), 9.06 (d, $J = 4.4$ Hz, 2H), 9.33 (d, $J = 4.4$ Hz, 2H), 10.20 (s, 1H); LD-MS obsd 649.9; FAB-MS obsd 650.3416, calcd exact mass 650.3409 ($C_{46}H_{42}N_4$); λ_{abs} 415, 509, 543, 586, 641 nm.

Zinc(II)-5,15-bis(4-*tert*-butylphenyl)-10-phenylporphyrin (Zn-2). A suspension of **2** (112 mg, 172 μmol) in $CHCl_3$ (50 mL) was treated with a solution of $Zn(OAc)_2$•$2H_2O$ (3.78 g, 172 mmol) in methanol (10 mL) and the mixture was refluxed for 2 h. The standard workup[1] afforded a bright purple solid (123 mg, 100%): IR (neat) $\tilde{\nu}$ 3081, 3022, 2956, 1498; ^{1}H NMR δ 1.63 (s, 18H), 7.71−7.83 (m, 3H), 7.78, 8.17 (AA′BB′, 2 × 4H), 8.20−8.25 (m, 2H), 8.96 (d, $J = 5.1$ Hz, 2H), 9.04 (d, $J = 5.1$ Hz, 2H), 9.14 (d, $J = 4.4$ Hz, 2H), 9.40 (d, $J = 4.4$ Hz, 2H), 10.25 (s, 1H); LD-MS obsd 714.1; FAB-MS obsd 712.2565, calcd exact mass 712.2544 ($C_{46}H_{40}N_4Zn$); λ_{abs} 419, 544, 582 nm; λ_{em} 592, 639 nm.

Porphyrin Trimer Zn-4 and Dimer Zn-3. To a suspension of **Zn-2** (31.1 mg, 43.5 μmol) in $CHCl_3$ (20 mL) was added a solution of $AgPF_6$ (5.5 mg, 21.8 μmol) in acetonitrile (3 mL). The mixture was refluxed for 8 h. Then more $AgPF_6$ (5.5 mg, 22 μmol) was added because the reaction stopped (monitored by analytical SEC). After being refluxed for an additional 15 h, the reaction was quenched with water (30 mL). The organic phase was washed with water and dried (Na_2SO_4). The solvent was removed, the resulting brown-purple solid was dissolved in $CHCl_3$ (30 mL) and treated with a solution of $Zn(OAc)_2$•$2H_2O$ (290 mg, 1.3 mmol) in methanol (7 mL), and the mixture was stirred for 3 h. Then the reaction was quenched with water, and the organic phase was washed with 5% aqueous $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed, and the residue was dissolved in a minimum amount of toluene. Purification by preparative SEC with toluene afforded the meso-linked trimer as a brown solid (2.8 mg, 9%) and the meso-linked dimer as a brown-purple solid (27.6 mg, 89%). Data for **Zn-4**: IR (neat) $\tilde{\nu}$ 2959, 2922, 2854, 1542, 1458; ^{1}H NMR δ 1.54 (s, 18H), 1.56 (s, 36H), 7.59, 8.15 (AA′BB′, 2 × 4H), 7.70, 8.18 (AA′BB′, 2 × 8H), 7.78−7.85 (m, 6H), 8.15−8.22 (m, 4H), 8.23 (d, $J = 4.4$ Hz, 4H), 8.30−8.36 (m, 4H), 8.76 (d, $J = 4.4$ Hz, 4H), 8.77 (d, $J = 4.4$ Hz, 4H), 9.03 (d, $J = 4.4$ Hz, 4H), 9.07 (d, $J = 4.4$ Hz, 4H); LD-MS obsd 2056.8; FAB-MS obsd 2062.68, calcd exact mass 2062.70 ($C_{132}H_{112}N_{12}Zn_3$); λ_{abs} 419, 477, 567 nm; λ_{em} 641, 664 nm. Data for **Zn-3**: IR (neat) $\tilde{\nu}$ 2958, 2868, 1558, 1488; ^{1}H NMR δ 1.52 (s, 36H), 7.67, 8.15 (AA′BB′, 2 × 8H), 7.74−7.86 (m, 6H), 8.18−8.20 (m, 4H), 8.31 (d, $J = 3.7$ Hz, 4H), 8.71 (d, $J = 4.4$ Hz, 4H), 9.01 (d, $J = 4.4$ Hz, 4H), 9.04 (d, $J = 4.4$ Hz, 4H); LD-MS obsd 1423.7; FAB-MS obsd 1422.48, calcd exact mass 1422.49 ($C_{92}H_{78}N_8Zn_2$); λ_{abs} 421, 459, 561 nm; λ_{em} 634, 659 nm.

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5-(4-Methylthiophenyl)dipyrromethane (5). Following a general procedure,[14,15] pyrrole (50.0 mL, 720 mmol) and 4-(methylthio)benzaldehyde (3.83 mL, 28.8 mmol) were added to a 250 mL flask and degassed with a stream of argon. Then TFA (0.22 mL, 2.9 mmol) was added, and the mixture was stirred under argon at room temperature for 5 min and then quenched with 0.1 M NaOH. Ethyl acetate was then added, and the organic phase was washed with water and dried (Na_2SO_4). Then the solvent was removed under vacuum to afford an orange oil. Bulb-to-bulb distillation (200 °C, 0.01 mmHg) gave a yellow oil. The oil was dissolved in ethanol, and addition of a small amount of water resulted in white crystals (5.00 g, 64.7%): mp 94−95 °C; ^{1}H NMR δ 2.51 (s, 3H), 5.43 (s, 1H), 5.95 (s, 2H), 6.21 (m, 2H), 6.69 (m, 2H), 7.17, 7.25 (AA′BB′, 2×2H), 7.87 (brs, 2H); ^{13}C NMR δ 16.6, 44.1, 108.0, 109.2, 118.1, 127.6, 129.6, 133.1, 137.7, 139.8; EI-MS obsd 268.1033, calcd exact mass 268.1034. Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.60; H, 6.01; N, 10.44; S, 11.95. Found: C, 71.60; H, 5.99; N, 10.31; S, 11.81.

5-[4-(*S*-Acetylthio)phenyl]dipyrromethane (6). Following a general procedure,[14,15] pyrrole (34.0 mL, 489 mmol) and 4-(*S*-acetylthio)benzaldehyde[12] (3.50 g, 19.4 mmol) were added to a 100 mL flask and degassed with a stream of argon. Then TFA (0.15 mL, 1.9 mmol) was added, and the mixture was stirred under argon at room temperature for 5 min and then quenched with *N*,*N*-diisopropylethylamine (0.330 mL, 1.94 mmol). All volatile materials were evaporated under high-vacuum. The crude mixture was filtered through a pad of silica to afford a yellow oil, which was dissolved in ethanol and allowed to stand at −20 °C for 3 days. Yellowish crystals were isolated by filtration. The filtrate was concentrated, a small amount of water was added, and the mixture was allowed to stand at −20 °C for a few days, affording a second crop of crystals giving 3.56 g altogether (62%): mp 100−101 °C; ^{1}H NMR δ 2.44 (s, 3H), 5.40 (s, 1H), 5.90 (s, 2H), 6.18 (m, 2H), 6.62 (m, 2H), 7.20, 7.34 (AA′BB′, 2×2H), 7.97 (brs, 2H); ^{13}C NMR δ 31.0, 44.3, 108.2, 108.9, 118.3, 126.8, 130.1, 132.8, 135.3, 144.7, 195.7; EI-MS obsd 296.0996, calcd exact mass 296.0983. Anal. Calcd for $C_{17}H_{16}N_2OS$: C, 68.89; H, 5.44; N, 9.45; S, 10.82. Found: C, 68.69; H, 5.56; N, 9.39; S, 10.91.

1,9-Bis(3,5-di-*tert*-butylbenzoyl)dipyrromethane (7). To a solution of dipyrromethane[15] (421 mg, 2.9 mmol) in toluene (60 mL) stirred under argon and cooled in a water bath was slowly added a solution of ethylmagnesium bromide (1 M solution in THF, 14.4 mL, 14.4 mmol). The resulting brown-orange mixture was stirred for 30 min at ambient temperature. [In a separate reaction, 3,5-di-*tert*-butylbenzoic acid was refluxed in thionyl chloride in the presence of 1 vol % DMF, affording a colorless liquid (bp 167 °C; water suction pump) in 89% yield.] A solution of 3,5-di-*tert*-butylbenzoyl chloride (1.82 g, 7.2 mmol) in toluene (8 mL) was added dropwise to the dipyrromethane-containing mixture. The solution became darker and was stirred for 2 h after the addition was completed. Then the reaction was quenched with saturated aqueous NH_4Cl (30 mL). Ethyl acetate was added, and the organic phase was washed with water, 2 M aqueous NaOH, water, and brine and then dried (Na_2SO_4). The solvent was removed, and the residue was filtered through a pad of silica (CH_2Cl_2/ethyl acetate gradient, 6:1−5:3). The solvent was again removed, and the residue was dissolved in a small amount of ethyl acetate. Hexanes was added until turbidity occurred. The mixture was cooled overnight at −20 °C and filtered, affording a white powder (442 mg, 27%): mp 220 °C; IR (neat) $\tilde{\nu}$ 3263, 2963, 1607, 1582, 1485; ^{1}H NMR δ 1.32 (s, 36H), 4.27 (s, 2H), 6.17−6.13 (m, 2H), 6.71−6.77 (m, 2H), 7.57 (s, 2H), 7.72 (s, 4H), 11.47 (brs, 2H); ^{13}C NMR (APT): δ 26.8 (+), 31.3 (−), 34.9 (+), 110.0 (−), 121.1 (−), 123.6 (−), 125.6 (−), 131.2 (+), 137.5 (+), 138.0 (+), 150.5 (+), 185.6 (−). Anal. Calcd for $C_{39}H_{50}N_2O_2$: C, 80.93; H, 8.71; N, 4.84; Found: C, 80.69; H, 8.72; N, 4.85.

5-[4-(*S*-Acetylthio)phenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (8). To a solution of **7** (397 mg, 686 μmol) in THF/methanol (21 mL, 2:1) under argon was added $NaBH_4$ (1.30 g, 34 mmol) in several portions. The mixture was stirred for 2.5 h, quenched with water (40 mL), and extracted with CH_2Cl_2. The organic phase was dried (K_2CO_3) and the solvent was removed. The resulting yellow foam and **6** (204 mg, 686 μmol) were dissolved in acetonitrile (275 mL), and stirred at room temperature. Then TFA (640 μL, 8.3 mmol) was added, and the solution immediately turned dark blue. After 25 min DDQ (467 mg, 2.1 mmol) was added because the yield did not increase any further (checked by oxidizing an aliquot with DDQ and quantifying with UV/vis spectroscopy). After 1.5 h, the mixture was filtered through a pad of alumina (CH_2Cl_2). The solvent was removed and the residue was purified by column chromatography on silica (first column: CH_2Cl_2/hexanes, 1:4−1:1; second column: CH_2Cl_2/hexanes, 1:2). Two brown-purple solids were obtained, yielding the disulfide **9** (14 mg, 3%) and **8** (57 mg, 10%). Data for **9**: IR (neat) $\tilde{\nu}$ 3316, 2961, 2924, 2854, 1592, 1466; ^{1}H NMR δ −2.94 (s, 4H), 1.52 (s, 72H), 7.79 (t, J = 1.5 Hz, 4H), 8.10, 8.30 (AA′BB′, 2×4H), 8.10 (d, J = 1.5 Hz, 8H), 8.94 (d, J = 5.1 Hz, 4H), 8.96 (d, J = 5.1 Hz, 4H), 9.07 (d, J = 5.1 Hz, 4H), 9.34 (d, J = 4.4 Hz, 4H), 10.22 (s, 2H); LD-MS obsd 1589.4; FAB-MS obsd 1586.87, calcd exact mass 1586.86 ($C_{108}H_{114}N_8S_2$); λ_{abs} 417, 511, 544, 586, 642 nm. Data for **8**: IR (neat) $\tilde{\nu}$ 3307, 2958, 2861, 1708, 1590, 1467; ^{1}H NMR δ −2.95 (s, 2H), 1.55 (s, 36H), 2.60 (s, 3H), 7.81, 8.28 (AA′BB′, 2×2H), 7.82 (t, J = 1.5 Hz, 2H), 8.12 (d, J = 1.5 Hz, 4H), 8.88 (d, J = 5.1 Hz, 2H), 8.97 (d, J = 5.1 Hz, 2H), 9.08 (d, J = 5.1 Hz, 2H), 9.35 (d, J = 4.4 Hz, 2H), 10.2 (s, 1H); LD-MS obsd 837.2; FAB-MS obsd 836.4503, calcd exact mass 836.4488 ($C_{56}H_{60}N_4OS$); λ_{abs} 416, 510, 544, 585, 641 nm.

Zinc(II)-5-[4-(*S*-Acetylthio)phenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (Zn-8). A solution of **8** (56 mg, 67 μmol) in $CHCl_3$ (20 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (734 mg, 3.3 mmol) in methanol (5 mL) and the mixture was stirred for 6.5 h. Purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:1) afforded a purple solid (54 mg, 90%): IR (neat) $\tilde{\nu}$ 3066, 2956, 1703, 1675, 1590, 1469; ^{1}H NMR δ 1.55 (s, 36H), 2.59 (s, 3H), 7.79, 8.28 (AA′BB′, 2×2H), 7.82 (t, J = 2.2 Hz, 2H), 8.12 (d, J = 2.2 Hz, 4H), 8.99 (d, J = 4.4 Hz, 2H), 9.06 (d, J = 4.4 Hz, 2H), 9.17 (d, J = 4.4 Hz, 2H), 9.43 (d, J = 4.4 Hz, 2H), 10.29 (s, 1H); LD-MS obsd 900.1; FAB-MS obsd 898.3617, calcd exact mass 898.3623 ($C_{56}H_{58}N_4OSZn$); λ_{abs} 420, 545, 583 nm; λ_{em} 591, 640 nm.

Zinc(II) Disulfide Zn-9. A solution of **9** (14 mg, 8.8 μmol) in $CHCl_3$ (5 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (193 mg, 879 μmol) in methanol (2 mL), and the mixture was stirred for 7 h. Then additional $Zn(OAc)_2 \cdot 2H_2O$ (194 mg, 879 μmol) was added, and stirring was continued for 15.5 h. Purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:2) afforded an orange-purple solid (9.0 mg, 60%): IR (neat) $\tilde{\nu}$ 3067, 2959, 2923, 2862, 1592, 1468; ^{1}H NMR δ 1.51 (s, 72H), 7.78 (s, 4H), 8.10, 8.30 (AA′BB′, 2×4H), 8.10 (s, 8H), 9.05 (s, 8H), 9.16 (d, J = 4.4 Hz, 4H), 9.42 (d, J = 4.4 Hz, 4H), 10.28 (s, 2H); LD-MS obsd 1716.6; FAB-MS obsd 1710.71, calcd exact mass 1710.69 ($C_{108}H_{110}N_8S_2Zn_2$); λ_{abs} 421, 545, 585 nm; λ_{em} 594, 641 nm.

5,10,15-Tris(3,5-di-*tert*-butylphenyl)porphyrin (10). Following a general procedure,[13,22] a solution of **7** (578 mg, 1.0 mmol) in THF/methanol (30 mL, 2:1) under argon was treated with $NaBH_4$ (1.89 g, 50 mmol) in several portions. The mixture was stirred for 2 h, then quenched with water and extracted with CH_2Cl_2. The organic phase was dried (K_2CO_3) and the solvent was removed. The resulting orange oil and 5-(3,5-di-*tert*-butylphenyl)dipyrromethane[17] (334 mg, 1.0 mmol) were dissolved in acetonitrile (400 mL) and stirred at room temperature. Then TFA (930 μL, 12.1 mmol) was added, and the solution immediately turned dark blue. After 25 min DDQ (680 mg, 3.0 mmol) was added because the yield did not increase any further (checked by oxidizing an aliquot with DDQ and quantifying with UV/vis spectroscopy). After 75 min, the solution was filtered through a pad of alumina and eluted with CH_2Cl_2. Further purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:4−1:2) afforded a purple solid (183 mg, 21%): IR (neat) $\tilde{\nu}$ 3305, 3064, 2958, 1588, 1468; ^{1}H NMR δ −2.91 (s, 2H), 1.51 (s, 18H), 1.55 (s, 36H), 7.79 (t, J = 1.5 Hz, 1H), 7.81 (t, J = 2.2 Hz, 2H), 8.0−8.2 (m, 6H), 8.92 (d, J = 5.1 Hz, 2H), 8.96 (d, J = 5.1 Hz, 2H), 9.07 (d, J = 4.4 Hz, 2H), 9.34 (d, J = 5.1 Hz, 2H), 10.20 (s, 1H); LD-MS obsd 875.7;

FAB-MS obsd 874.5935, calcd exact mass 874.5913 ($C_{62}H_{74}N_4$); λ_{abs} 416, 510, 544, 585, 641 nm.

Zinc(II)-5,10,15-Tris(3,5-di-*tert*-butylphenyl)porphyrin (Zn-10). A solution of **10** (177 mg, 202 μmol) in $CHCl_3$ (40 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (2.22 g, 10.1 mmol) in methanol (10 mL), and the mixture was stirred for 21 h. Purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:2) afforded a red-purple solid (187 mg, 99%): IR (neat) $\tilde{\nu}$ 3060, 2960, 2872, 1591, 1470; ^{1}H NMR δ 1.52 (s, 18H), 1.54 (s, 36H), 7.78 (t, $J = 1.5$ Hz, 1H), 7.81 (t, $J = 1.5$ Hz, 2H), 8.0−8.2 (m, 6H), 9.03 (d, $J = 4.4$ Hz, 2H), 9.06 (d, $J = 4.4$ Hz, 2H), 9.15 (d, $J = 4.4$ Hz, 2H), 9.41 (d, $J = 5.1$ Hz, 2H), 10.27 (s, 1H); LD-MS obsd 937.6; FAB-MS obsd 936.5057, calcd exact mass 936.5048 ($C_{62}H_{72}N_4Zn$); λ_{abs} 419, 545 nm; λ_{em} 591, 639 nm.

Porphyrin Dimers Zn-11, Zn-12 and Zn-13. To a solution of **Zn-8** (15.9 mg, 17.7 μmol) and **Zn-10** (16.6 mg, 17.7 μmol) in $CHCl_3$ (20 mL) was added a solution of $AgPF_6$ (8.9 mg, 35 μmol) in acetonitrile (3 mL). The mixture was refluxed for 7 h. Then more $AgPF_6$ (15 mg, 59 μmol) was added because the reaction stopped (monitored by analytical SEC). After the mixture was refluxed for an additional 22 h, 22 mg (87 μmol) of $AgPF_6$ was added because the reaction stopped again. Refluxing was continued for a further 19 h, and then the reaction was quenched with water. The phases were separated, and the organic phase was washed with water and dried (Na_2SO_4). The solvent was removed, and the dark purple solid was dissolved in $CHCl_3$ (30 mL). A solution of $Zn(OAc)_2 \cdot 2H_2O$ (390 mg, 1.8 mmol) in methanol (7 mL) was added, and the mixture was stirred for 3 h in the dark. Then the reaction was quenched with water (50 mL), and the organic phase was washed with 5% aqueous $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed, and the residue was dissolved in a minimum amount of toluene. Purification by preparative SEC (toluene) followed by column chromatography (silica, CH_2Cl_2/hexanes, 1:2−2:3) afforded **Zn-11** (9.9 mg, 30%) as an orange solid, **Zn-12** (14.3 mg, 44%) as a red-purple solid, and **Zn-13** (7.3 mg, 23%) as a brown-purple solid. Data for **Zn-11**: IR (neat) $\tilde{\nu}$ 3060, 2956, 2861, 1592, 1465; ^{1}H NMR δ 1.43 (s, 72H), 1.57 (s, 36H), 7.68 (t, $J = 2.2$ Hz, 4H), 7.83 (t, $J = 1.4$ Hz, 2H), 8.08 (d, $J = 2.2$ Hz, 8H), 8.15 (d, $J = 4.4$ Hz, 4H), 8.30 (d, $J = 1.4$ Hz, 4H), 8.71 (d, $J = 4.4$ Hz, 4H), 9.04 (d, $J = 4.4$ Hz, 4H), 9.08 (d, $J = 5.1$ Hz, 4H); LD-MS obsd 1877.1; FAB-MS obsd 1870.87, calcd exact mass 1870.99 ($C_{124}H_{142}N_8Zn_2$); λ_{abs} 421, 460, 561 nm; λ_{em} 625, 660 nm. Data for **Zn-12**: IR (neat): $\tilde{\nu}$ 3069, 2955, 1700, 1588, 1465; ^{1}H NMR δ 1.43 (s, 36H), 1.44 (s, 36H), 1.57 (s, 18H), 7.66−7.72 (m, 4H), 7.82 (t, $J = 2.2$ Hz, 1H), 7.85, 8.37 (AA′BB′, 2 × 2H), 8.09 (d, $J = 1.5$ Hz, 8H), 8.12 (d, $J = 5.1$ Hz, 2H), 8.17 (d, $J = 2.2$ Hz, 2H), 8.17 (d, $J = 4.4$ Hz, 2H), 8.71 (d, $J = 5.1$ Hz, 2H), 8.72 (d, $J = 5.1$ Hz, 2H), 9.02−9.07 (m, 6H), 9.08 (d, $J = 4.4$ Hz, 2H); LD-MS obsd 1423.7; FAB-MS obsd 1832.85, calcd exact mass 1832.85 ($C_{118}H_{128}N_{16}OSZn_2$); λ_{abs} 420, 460, 561 nm; λ_{em} 626, 660 nm. Data for **Zn-13**: IR (neat): $\tilde{\nu}$ 2919, 1702, 1561, 1461; ^{1}H NMR δ 1.44 (s, 72H), 7.70 (t, $J = 1.5$ Hz, 4H), 7.85, 8.37 (AA′BB′, 2 × 4H), 8.09 (d, $J = 1.5$ Hz, 8H), 8.14 (d, $J = 4.4$ Hz, 4H), 8.72 (d, $J = 5.1$ Hz, 4H), 9.03 (d, $J = 5.1$ Hz, 4H), 9.05 (d, $J = 5.1$ Hz, 4H); LD-MS obsd 1801.1; FAB-MS obsd 1794.62, calcd exact mass 1794.71 ($C_{112}H_{114}N_8O_2S_2Zn_2$); λ_{abs} 421, 461, 561 nm; λ_{em} 626, 659 nm.

Electrochemistry. Both the solution and SAM electrochemical studies were conducted using the same instrumentation, techniques, and preparation strategies as described in Paper 1 of this series.[10] The solvent was CH_2Cl_2; tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M) (Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) served as supporting electrolyte. The potentials reported are vs Ag/Ag^+; $E_{1/2}(FeCp_2/FeCp_2^+) = 0.19$ V.

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Supporting Information Available: LD-MS and ^{1}H NMR spectra for all porphyrins and arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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