J. Org. Chem. **2000,** *65,* 7363−7370

Synthesis of Thiol-Derivatized Porphyrin Dimers and Trimers for Studies of Architectural Effects on Multibit Information Storage

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Received March 30, 2000

We present the rational design and synthesis of multiporphyrin arrays containing thiol-derivatized linkers for the purpose of multibit molecular information storage. Porphyrin dimers and trimers were synthesized by the Pd-mediated coupling of iodo-substituted and ethynyl-substituted porphyrin building blocks in 5−51% yields. Each porphyrin dimer bears one *S*-acetylthio group. The architecture of the trimers incorporates a trans-substituted porphyrin (central) bearing two *S*-acetylthio groups and two diphenylethyne-linked porphyrins (wings) in a trans geometry. The central porphyrin and the wing porphyrins bear distinct substituents and central metals, thereby affording different oxidation potentials. The *S*-acetylthio groups provide a means for attachment of the arrays to an electroactive surface. The dimers are designed for vertical orientation on an electroactive surface while the trimers are designed for horizontal orientation of the central porphyrin. Altogether seven different arrays were synthesized. Each array forms a self-assembled monolayer (SAM) on gold via in situ cleavage of the *S*-acetyl protecting group. The SAM of each array is electrochemically robust and exhibits multiple, reversible oxidation waves. In general, however, the trimeric arrays appear to form more highly ordered monolayers that exhibit sharper, better-defined redox features.

Introduction

The development of molecular-based information storage systems is one of the central problems in the nascent field of molecular electronics. The creation of molecular-scale memory devices is expected to lead to substantially higher densities of information storage than is now possible using conventional semiconductor technology. Our approach toward this problem involves the storage of information in the distinct oxidation states of redox-active molecules. One of our major objectives is to investigate approaches for the storage of multiple bits in molecular architectures. Among redox-active units suitable for such architectures, metalloporphyrins are exceptionally attractive due to their ability to form stable radical cations and dications.[1] The oxidation potentials of metalloporphyrins can be tuned either by variation of peripheral substituents[2] or by variation of the centrally coordinated metal.[3]

In the preceding papers, we described the synthesis of thiol-derivatized porphyrin monomers[4] and thiol-derivatized ferrocene−porphyrins.[5] Monomeric porphyrins can be cycled between three states (neutral, monocation, dication), while attachment of a ferrocene to the porphyrin provides access to a fourth state (ferrocene monocation). An issue that has emerged for multibit information storage concerns whether redox-active moieties at sites in a molecular array distant from the surface exhibit the same information storage properties as redox-active units close to the surface. This question can be addressed to some extent with the ferrocene−porphyrins, though the ferrocene differs considerably from the porphyrin in structure and composition. We sought to investigate multiporphyrin arrays of similar and dissimilar porphyrins, and in so doing take advantage of the synthetic chemistry that has been developed for preparing multiporphyrin arrays.

The synthesis of multiporphyrin arrays is an area of active interest.[6−16] We have previously developed modu-

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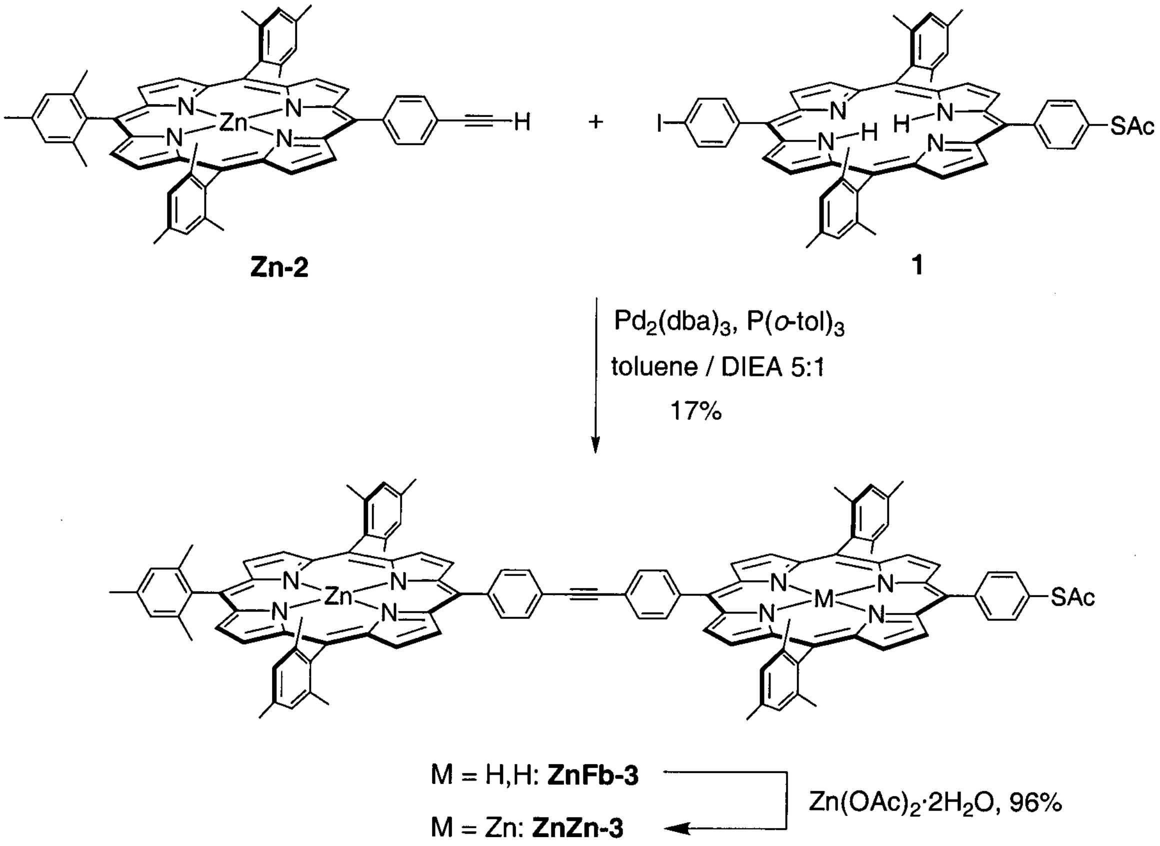
10.1021/jo000488m CCC: $19.00

Scheme 1



lar routes to multiporphyrin arrays that function as molecular wires, optoelectronic gates, light-harvesting arrays, and integrated antenna-reaction center complexes.[16] Studies of various members of these multiporphyrin arrays have revealed that rapid hole-hopping occurs in the oxidized complexes.[17] The rapid hole-hopping indicates the suitability of these structures for electrically addressing distant sites in multiporphyrin architectures. However, these multiporphyrin arrays were examined in solution and did not include provisions for attachment to electroactive surfaces. The exploitation of this fundamental synthetic methodology for studies of molecular-based information storage requires provisions for inclusion of thiol-derivatized linkers. We have developed methodology for incorporating one, two, or four thiol units in porphyrins, enabling vertical or horizontal positioning of the porphyrins in a self-assembled monolayer (SAM) on a gold surface.[18]

We have combined the thiol and multiporphyrin array chemistry to gain access to two different architectures of thiol-derivatized multiporphyrin arrays. Porphyrin dimers designed for vertical orientation ("vertical dimers") are comprised of a "lower" porphyrin with an *S*-(acetylthio)phenyl unit linked at the para phenyl position and an "upper" porphyrin joined to the first via a diphenylethyne linker. Porphyrin trimers are comprised of a central porphyrin that rests horizontally on the gold surface and two "wing" porphyrins lacking thiols but attached to the central porphyrin. As the central porphyrin we chose a trans-oriented S-protected *m*-(thiomethyl)phenyl porphyrin for attachment to the gold surface. (The methylene unit was incorporated to enable binding of the sulfur atom to a surface without steric hindrance.) The remaining two meso positions were used for the linkage of the two wing porphyrin units.

In this paper, we describe the synthesis and electrochemical properties of the vertical dimers and winged trimers. The arrays were constructed with a variety of central metal ions and peripheral substituent groups in order to access multiple oxidation states. The electrochemical properties of the arrays were investigated in solution and upon attachment to gold. Two fundamental questions can be addressed through study of these molecules. (1) Can the porphyrins not connected directly to gold be addressed electrochemically by communication through the central porphyrin and intervening linker? (2) Are there substantive differences in a design with the low-potential porphyrin attached to the surface and the high potential porphyrins in upper or lateral positions of the arrays or vice versa? Gaining information about these issues is essential for the rational design of more elaborate molecular architectures for information storage.

Results and Discussion

The ability to tune the electrochemical potentials of all porphyrins in the dimers and trimers is essential for

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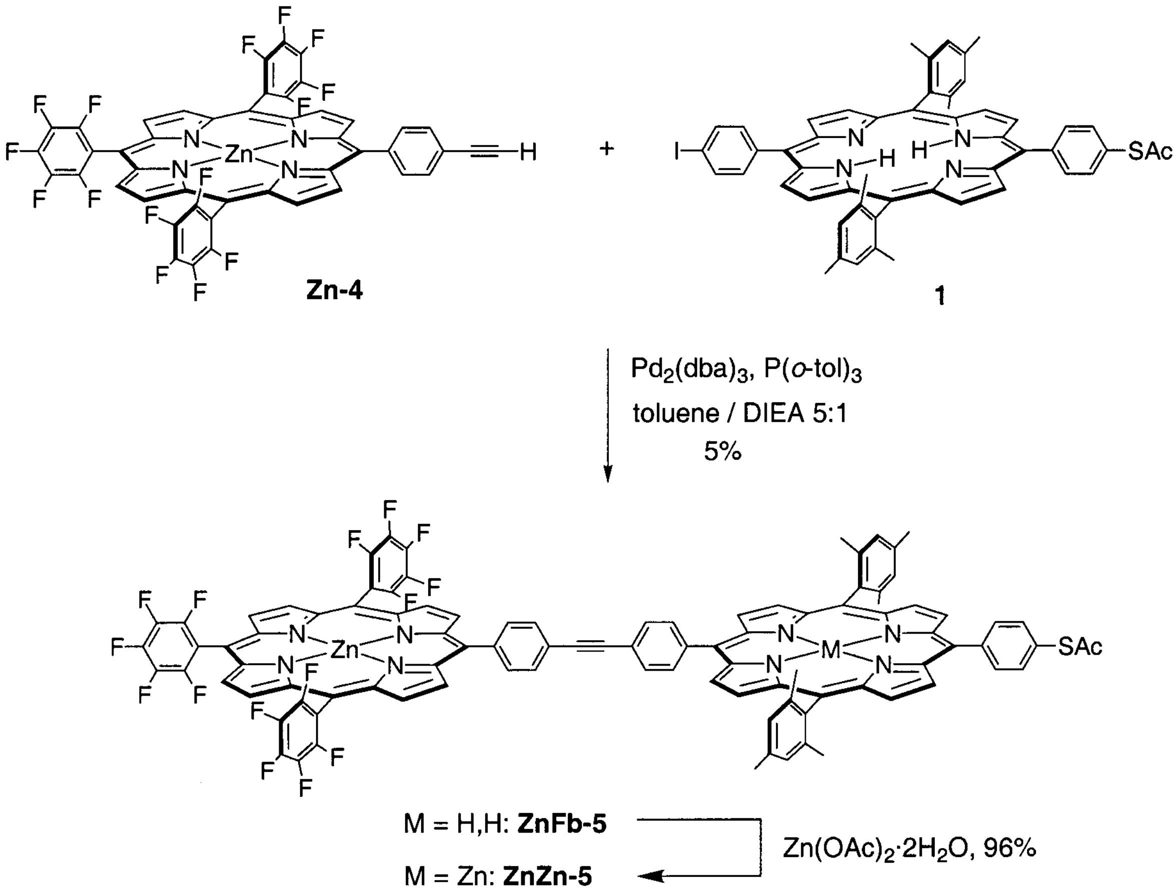
Scheme 2



achieving the maximum number of distinct oxidation states and hence the greatest amount of information storage. In the case of the dimers, the potential can be altered by incorporation of different substituents in the meso positions of both porphyrins and by variation of the metals comprising the metalloporphyrins. In the case of the trimers, the oxidation potential of the central porphyrin can only be easily altered by varying the chelated metal, as two meso positions are used for attachment of the porphyrin wings and the other two bear the thiol units. The potentials of the wing porphyrins can be altered either by variation of the metals or by incorporation of different substituents in the three nonlinking meso positions. This provides a good deal of control over the oxidation potentials. The thiol unit in the porphyrins has been protected with an *S*-acetyl protecting group. The *S*-acetylthio-derivatized porphyrins undergo deprotection in situ upon exposure to the gold surface[18] (which is consistent with the pioneering report by Tour et al. dealing with substituted phenylethynyl oligomers).[19]

Synthesis of Porphyrin Dimers. Our strategy for synthesizing dimers for attachment to a gold surface involved a porphyrin bearing one protected 4-mercaptophenyl group at the 5-position and one 4-iodophenyl unit at the 15-position of the porphyrin. The coupling of this thiol-protected trans-porphyrin with 1 equiv of a porphyrin bearing a 4-ethynylphenyl group would give the desired dimer. Free base porphyrin **1** was obtained from the mixed condensation of 4-iodobenzaldehyde, 4-(*S*-acetylthio)benzaldehyde, and 5-mesityldipyrromethane under nonscrambling conditions[20] in a yield of 5%.[18] Although metalation of porphyrin **1** with zinc acetate was straightforward, free base porphyrin **1** was used in the subsequent Pd-coupling reaction because of the very poor solubility of the zinc complex. The required 4-ethynylporphyrin **Zn-2** was obtained according to published procedures.[21]

To synthesize the desired arrays, we used the Pd-catalyzed coupling of an aryl iodide with an arylethyne. The conditions for the special case of porphyrin coupling[21] have recently been refined[22] and involve use of $Pd_2(dba)_3$ and tri-*o*-tolylphosphine in toluene/triethylamine (5:1) at 35 °C (in the absence of copper salts as cocatalysts). Our attempts to couple two monomeric porphyrins (e.g., **1** and **Zn-2**) using this method failed to give the desired product. We attributed this failure to the instability of the thioacetate group in the presence of triethylamine (TEA). The stability of the (*S*-acetylthio)aryl group in the presence of the more sterically hindered base *N*,*N*-diisopropylethylamine (DIEA) was identified by Sita and co-workers.[23] Coupling of porphyrins **Zn-2** and **1** in the presence of DIEA instead of TEA gave dimeric porphyrin **ZnFb-3** in 17% yield (Scheme 1). Reaction at longer time or higher temperature did not improve the yield.

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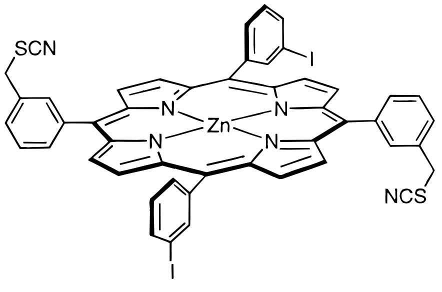
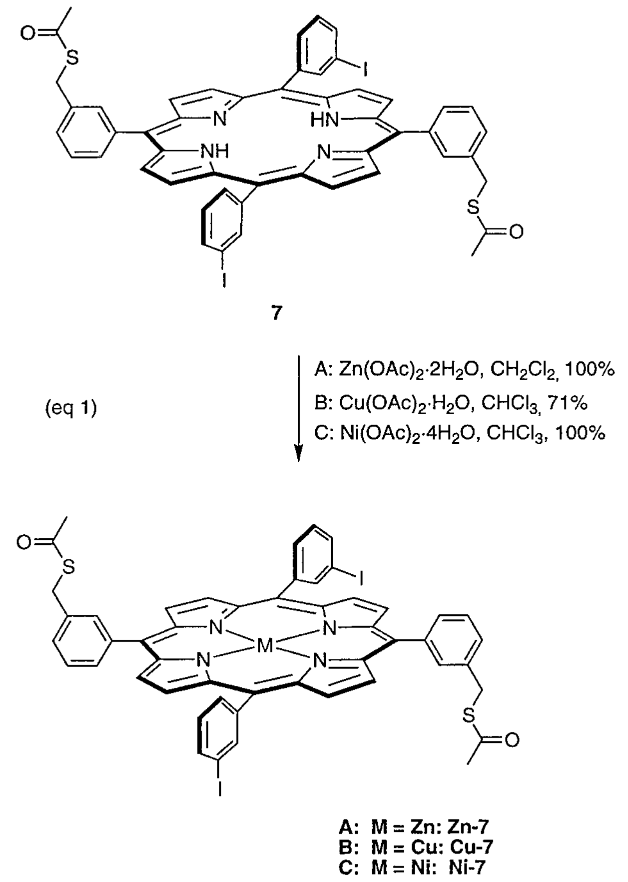
A second dimer was prepared through use of a monoethynyl porphyrin bearing three pentafluorophenyl groups (**Zn-4**).[24] Coupling of **Zn-4** and **1** with the use of DIEA in the Pd-coupling reaction gave the desired dimer **ZnFb-5** in 5% yield (Scheme 2). One explanation of the poor yields with *S*-acetyl protected thiophenol moieties is the presence of acetyl transfer reactions from the *S*-acetylthio substituted porphyrin, liberating the free thiol and capping the ethynyl moiety as the acetylethyne. We have obtained evidence for this type of side reaction.[25] Porphyrin dimers **ZnFb-3** and **ZnFb-5** were converted to the corresponding metal chelates **ZnZn-3** and **ZnZn-5** in nearly quantitative yield.

Synthesis of Porphyrin Trimers. Our strategy for synthesizing trimers for attachment to gold surfaces involved a central porphyrin unit bearing two protected 3-mercaptomethylphenyl groups and two 3-iodophenyl groups in a trans orientation. The coupling of this key porphyrin building block with 2 equiv of a porphyrin bearing an ethynylphenyl group would give the desired trimer. Our first approach toward protected thiol porphyrins for use in the Pd-coupling reaction[22] began with **Zn-6**, available by metalation of free base porphyrin **6**[18] with $Zn(OAc)_2 \cdot 2H_2O$. The thiocyanato group was chosen as the "protected" thiol unit due to its high chemical stability. A Pd-coupling reaction of **Zn-6** and **Zn-2** under standard conditions ($Pd_2(dba)_3$/P(*o*-tol)$_3$/TEA/35 °C)[22] failed in either THF or toluene. The mechanism of this failure has not been unequivocally established, but one possibility involves complexation of the Pd by the nitrogen atoms of the thiocyanates, forming an insoluble complex. Such complexes have been observed before.[26] To overcome this problem we returned to the use of the *S*-acetyl group for protecting the thiol groups in the central porphyrin.



Zn-6

The oxidation potential of the central porphyrin was tuned by use of different metals. Metalation of the trans-porphyrin bearing two *S*-acetyl protecting groups (**7**)[18] with $Zn(OAc)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$ or $Ni(OAc)_2 \cdot 4H_2O$ in $CHCl_3$ gave the corresponding metalloporphyrin **Zn-7**, **Cu-7** or **Ni-7** (eq 1). The oxidation potentials of the porphyrins on the wings were additionally tuned through use of different meso substituents. To shift the oxidation potential compared to trimesityl-substituted porphyrins, we used porphyrins bearing 2,6-difluorophenyl groups.[2] A mixed condensation of pyrrole, 2,6-difluorobenzaldehyde and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde[27] in CH_2Cl_2 gave porphyrin **8** together with other porphyrins (Scheme 3). Metalation of **8** with $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-8** which was deprotected with K_2CO_3 in THF at room temperature to yield the free ethynyl porphyrin **Zn-9**.



In the Pd-coupling reactions leading to the winged trimers, THF was used as the solvent (in conjunction with the base TEA) to achieve improved solubility of the diiodoporphyrins **Zn-7**, **Cu-7**, and **Ni-7**, which are only slightly soluble in toluene. Even in THF the solubility of **Cu-7** was so low that only a suspension could be obtained. The reactions were performed at 35 °C under argon. Slightly higher temperatures (40 °C) led to an increase in the amount of higher molecular material and lower yields of the desired trimer. The addition of more $Pd_2(dba)_3$ started the reaction again, but too much $Pd_2(dba)_3$ also resulted in an increase of higher molecular weight material at the expense of the trimer. (The formation of higher molecular weight material is a significant side reaction in Pd-coupling reactions with porphyrins.[22]) The reactions were monitored by analytical SEC and stopped when no increase in yield was observed and the amount of monomers and dimer present was less than 25%. In this manner, the trimers **ZnZnZn-10**, **ZnCuZn-10**, and **ZnNiZn-10** were obtained in yields from 26 to 51% (Scheme 4). The sluggish formation of **ZnCuZn-10** and **ZnNiZn-10** was accelerated by the addition of extra Pd catalyst. The sluggish nature of these reactions may be attributed to the poor solubility of the components. The coupling of **Cu-2** and **Mg-2**[28] afforded the trimer **MgCuMg-10** in 21% yield. The trimer **MgCuMg-10**

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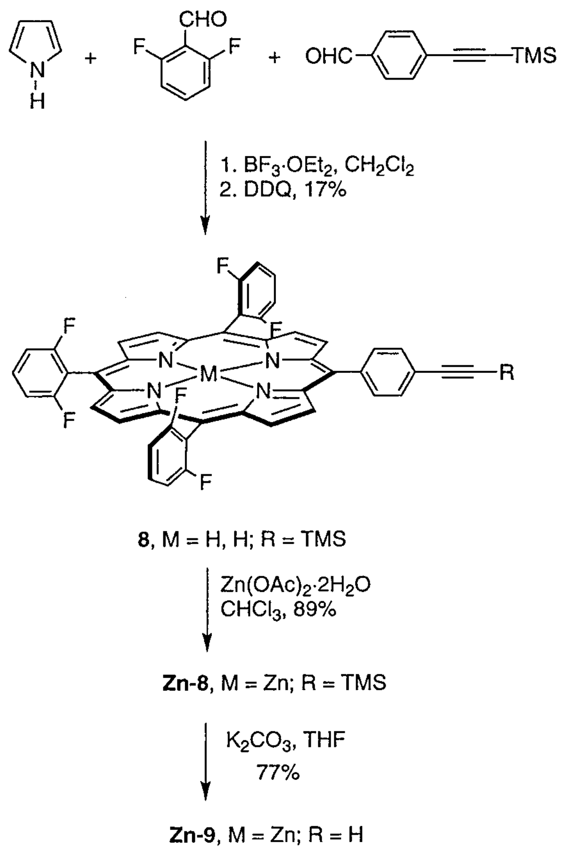
Scheme 3



must be handled with care; basic conditions can cause cleavage of the *S*-acetyl unit while traces of acid lead to demetalation of magnesium. Insertion of magnesium(II) is not possible in the presence of *S*-acetylthio groups. Finally, the trimer **ZnZnZn-11** was prepared in 38% yield by coupling **Zn-7** with **Zn-9** (Scheme 5). It is noteworthy that in no cases during chromatography of the trimers have we observed any indication of atropisomers (which could potentially arise from the up/down orientation of the *m*-aryl substituents appended to the meso positions of the central porphyrin).

Electrochemical Studies. The electrochemical behavior of the dimers and trimers was investigated for samples both in solution and self-assembled on gold. The solution electrochemistry of each of the arrays (not shown) is similar to that previously reported for other aryl-substituted porphyrins.[2] In the case of **ZnZn-3** and **ZnZnZn-10**, two reversible oxidation waves are observed with $E_{1/2}(1)$ ~0.58 V and $E_{1/2}(2)$ ~0.86 V (versus Ag/Ag$^+$; $E_{1/2}$ FeCp$_2$/FeCp$_2^+$ = 0.19 V). These two waves are due to the first and second oxidations of each porphyrin in the array. The waves due to the individual porphyrins cannot be resolved because the redox potentials of the different Zn-porphyrins are intrinsically quite similar to one another and the electronic interactions among the porphyrins in the array are relatively weak.[17] In the case of **ZnZn-5** and **ZnZnZn-11**, both oxidation waves of the fluorinated porphyrin(s) in the array are shifted positively relative to those of the nonfluorinated constituent. The magnitude of these shifts are ~0.5 V for **ZnZn-5** and ~0.25 V for **ZnZnZn-11**, consistent with previous studies of fluorinated porphyrins.[2] The fluorination-induced shift in potentials result in the first oxidation wave of the fluorinated porphyrin severely overlapping the second oxidation wave of the nonfluorinated porphyrin. This same behavior is observed for **ZnCuZn-10**, **ZnNiZn-10**, and **MgCuMg-10**. For these trimers, the first oxidation wave of the central Cu or Ni-porphyrins occurs in the ranges 0.7−0.9 V, which severely overlaps the second oxidation wave of the Zn or Mg-porphyrin in the wings.

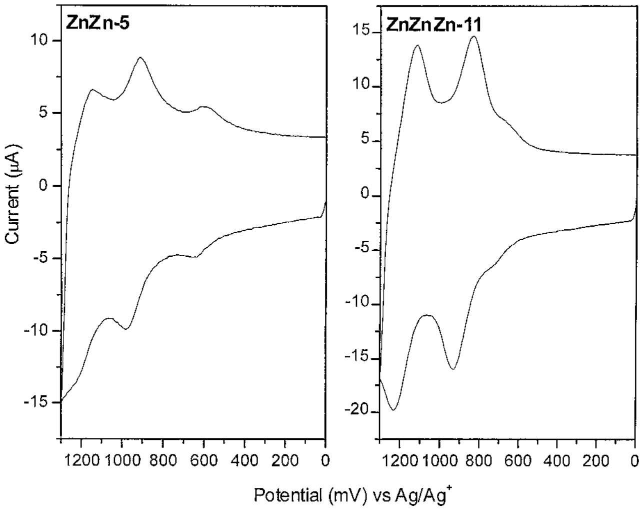


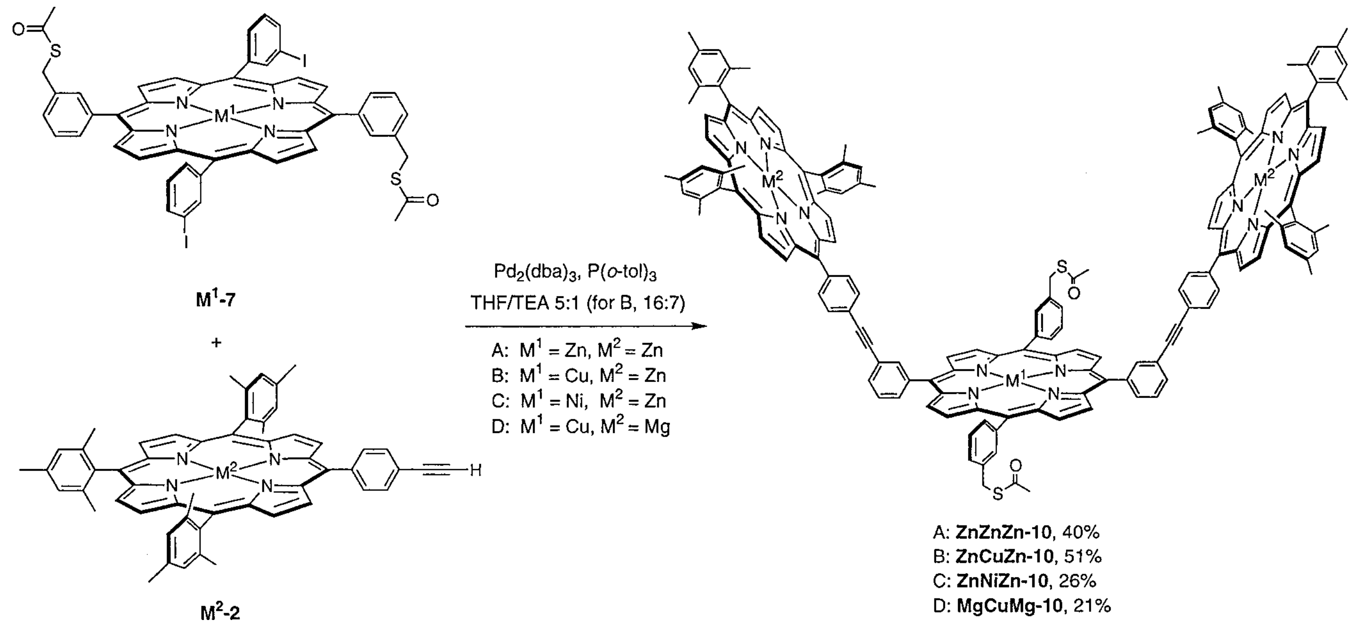
Figure 1. Fast-scan (100 V/s) voltammetry of the **ZnZn-5** SAM (left panel) and the **ZnZnZn-11** SAM (right panel).

The porphyrin dimers and trimers all form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetyl protecting groups. The electrochemical behavior of the SAMs is in general similar to that observed in solution. Representative fast-scan (100 V/s) cyclic voltammograms of the **ZnZn-5** and **ZnZnZn-11** SAMs are shown in Figure 1. Inspection of the data for **ZnZn-5** (and **ZnZn-3** (not shown)) reveals that the quality of the voltammogram is decidedly inferior to that of **ZnZnZn-11** (or any of other trimers (not shown)) or any of the monomeric porphyrins investigated in Papers 1 and 2 of this series.[4,5] The redox waves for **ZnZn-5** are relatively weak and broad. This behavior is indicative of an inhomogeneous environment, suggesting a relatively poorly formed monolayer. In contrast, the voltammogram for **ZnZnZn-11** exhibits much stronger and better-defined waves. For the trimer, the first oxidation wave of the central porphyrin ($E_{1/2}(1)$ ~0.6 V) can be distinguished from the first wave of the fluorinated porphyrins in the wings ($E_{1/2}(1)$ ~0.9 V), albeit the waves are overlapped (as is the case in solution). These data suggest that the trimers form more highly ordered monolayers than do the dimers. The rationale for this result is not clear given that the trimers are much bulkier molecules. Finally, as is the case for the other porphyrin SAMs, the oxidation potentials for the SAMs of the dimers and trimers are shifted positively (0.1−0.15 V) versus their solution values. For both types of arrays, the shift for the porphyrin closest to the surface appears to be larger than that of the upper or wing porphyrins. Knowledge of such shifts in potential is essential for designing architectures for multibit information storage.

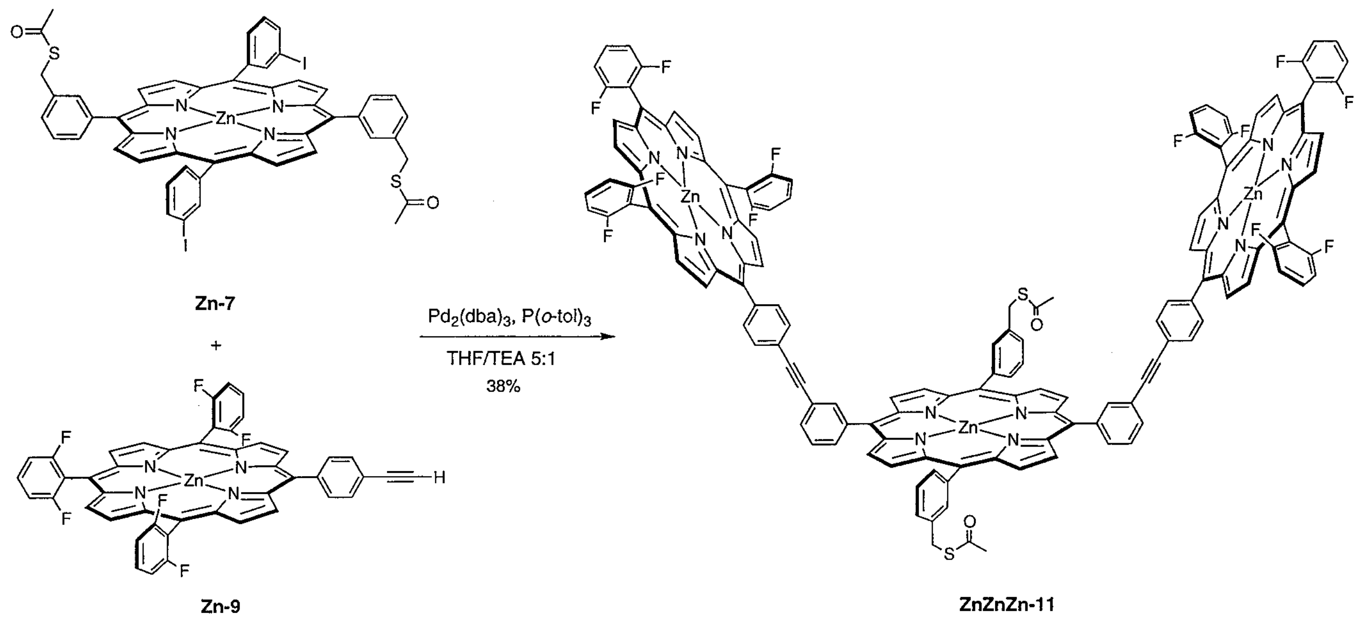
Conclusions

Porphyrin building blocks bearing *S*-acetylthio groups have been incorporated via Pd-coupling reactions in multiporphyrin arrays suitable for attachment to an electroactive surface. Porphyrin dimers bearing one thiol group have been designed for vertical orientation on a

Scheme 4



Scheme 5



surface. Porphyrin trimers have been designed wherein the central porphyrin bears two thiol groups for horizontal orientation on a surface. A clear understanding of the low yields obtained in dimer formation is not yet in hand, but it is clear that aliphatic thioacetate groups give superior results compared with aromatic thioacetate groups. Although the SAMs of both types of arrays exhibit robust electrochemical behavior, the trimeric architectures form higher quality monolayer structures. Tuning of the electrochemical potentials has been achieved by use of various meso substituents and central metals. Although the specific choice of metals and peripheral substituents is not optimal for obtaining well-resolved specifically addressable redox waves, these molecules in principle present a possible architectural motif for the storage of up to two bits of information.

Experimental Section

General Methods. Sources of reagents, solvents, and chromatographic media are described in the first paper of this series.[4] All reported ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ unless noted otherwise. UV−vis absorption and fluorescence spectra were recorded in toluene (unless noted otherwise) as described previously.[28] Porphyrin metalation was monitored by fluorescence emission and excitation spectroscopy. Preparative scale size exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1 with toluene as eluent. Analytical scale SEC was performed using a 1000 Å column (5 μL, styrene-divinylbenzene copolymer) with THF as eluent (0.8 mL/min).[29] Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix,[30] fast atom bombardment (FAB-MS, 10 ppm elemental compositional accuracy for the porphyrins), or electron-impact mass spectrometry (EI-MS).

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General Procedure for Pd-Coupling Reactions.[22] The porphyrins, $Pd_2(dba)_3$, and P(*o*-tol)$_3$ were placed in a Schlenk flask, which was then evacuated and purged with argon three times. Then the solvents were added, and the mixture was purged with argon for 30 min. The Schlenk flask was placed in a preheated oil bath (35 °C). The mixture was then stirred at this temperature under argon in the dark. When the reaction was finished (checked by analytical SEC), the flask was cooled to room temperature and the solvents were removed under reduced pressure. To remove Pd species, the mixture was filtered through a short silica column. The products were then separated on a gravity-flow SEC column with toluene as eluent.

General Procedure for Metal Insertion. A solution of porphyrin in $CHCl_3$ or CH_2Cl_2 was treated with a solution/suspension of the metal acetate in methanol and the mixture was stirred in the dark. After the metalation was complete (checked by fluorescence excitation spectroscopy), H_2O was added. The phases were separated, and the organic layer was washed with 5% aqueous $NaHCO_3$ and dried (Na_2SO_4). The solvents were removed under reduced pressure. Purification was done by column chromatography over flash silica gel.

ZnFb-3. Iodoporphyrin **1**[18] (20.0 mg, 22.0 μmol), ethynylporphyrin **Zn-2**[21] (18.4 mg, 22.0 μmol), $Pd_2(dba)_3$ (3.0 mg, 3.2 μmol), and P(*o*-tol)$_3$ (8.1 mg, 27 μmol) were dissolved in a mixture of toluene (7.4 mL) and DIEA (1.5 mL). After 6 h the reaction was finished. The reaction mixture was concentrated to dryness, redissolved in CH_2Cl_2 (20 mL), and poured on top of a flash silica column. All porphyrin species were eluted with CH_2Cl_2. The mixture of porphyrins was then chromatographed on a preparative SEC column. Two subsequent SEC columns afforded a dimer fraction which was chromatographed on silica ($CHCl_3$) to afford a purple solid (6.0 mg, 17%): ^1H NMR δ −2.54 (s, 2H), 1.85 (brs, 30H), 2.62 (s, 3H), 2.66 (brs, 15H), 7.25−7.35 (m, 10H), 7.8−8.4 (m, 12H), 8.7−9.0 (m, 16H); LD-MS obsd 1600.5; FAB-MS obsd 1596.61, calcd exact mass 1596.61 ($C_{107}H_{88}N_8OSZn$); λ_{abs} (CH_2Cl_2) 424, 516, 551, 591, 647 nm.

ZnZn-3. A solution of **ZnFb-3** (6.0 mg, 3.7 μmol) in $CHCl_3$ (10 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (81.0 mg, 370 μmol) in methanol (10 mL), and the mixture was stirred overnight at room temperature. After metalation was complete, the reaction mixture was washed with water (not aqueous $NaHCO_3$ in order to avoid the risk of hydrolyzing the *S*-acetyl unit), dried, and purified by chromatography (silica, $CHCl_3$) to afford a purple solid (6.0 mg, 96%): ^1H NMR δ 1.86 (brs, 30H), 2.61 (s, 3H), 2.65 (brs, 15H), 7.27−7.32 (m, 10H), 7.7−8.4 (m, 12H), 8.7−9.1 (m, 16H); LD-MS obsd 1664.2; FAB-MS obsd 1658.52, calcd exact mass 1658.52 ($C_{107}H_{86}N_8OSZn_2$); λ_{abs} (CH_2Cl_2) 426, 550 nm.

ZnFb-5. Iodoporphyrin **1**[18] (20.0 mg, 22.0 μmol), ethynylporphyrin **Zn-4**[24] (21.6 mg, 22.0 μmol), $Pd_2(dba)_3$ (3.0 mg, 3.2 μmol), and P(*o*-tol)$_3$ (8.1 mg, 27 μmol) were dissolved in a mixture of toluene (7.4 mL) and DIEA (1.5 mL). The reaction was stopped after 6 h. The mixture was concentrated to dryness, redissolved in CH_2Cl_2 (20 mL) and poured on top of a flash silica column. All porphyrin species were eluted with CH_2Cl_2. The mixture of porphyrins was then chromatographed on a preparative SEC column. Two subsequent SEC columns afforded pure dimer fraction which was further purified by centrifugal preparative thin-layer chromatography (silica, CH_2Cl_2/hexanes, 2:3) to afford a purple solid (2.0 mg, 5.2%): ^1H NMR δ − 2.65 (s, 2H), 1.87 (brs, 12H), 2.58 (s, 3H), 2.65 (s, 6H), 7.31 (s, 4H), 7.7−8.4 (m, 12H), 8.7−9.2 (m, 16H); LD-MS obsd 1737.8; FAB-MS obsd 1740.42, calcd exact mass 1740.33 ($C_{98}H_{53}F_{15}N_8OSZn$); λ_{abs} (CH_2Cl_2) 422, 515, 548, 588 nm.

ZnZn-5. A solution of **ZnFb-5** (2.0 mg, 1.1 μmol) in $CHCl_3$ (10 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (24.0 mg, 110 μmol) in methanol (10 mL) and the mixture was stirred overnight at room temperature. The reaction mixture was washed with water (not aqueous $NaHCO_3$ in order to avoid the risk of hydrolyzing the *S*-acetyl unit), dried, and purified by chromatography (silica, THF/hexanes) to afford a purple solid (2.0 mg, 96%): ^1H NMR (THF-d_8) δ 1.87 (brs, 12H), 2.62 (m, 9H), 7.31 (m, 4H), 7.7−8.4 (m, 12H), 8.6−9.1 (m, 16H); LD-MS obsd 1815.1; FAB-MS obsd 1802.30, calcd exact mass 1802.24 ($C_{98}H_{53}N_8OSZn_2$); λ_{abs} (CH_2Cl_2) 429, 554 nm.

Zn(II)-5,15-Bis(3-iodophenyl)-10,20-bis[3-(thiocyanatomethyl)phenyl]porphyrin (Zn-6). A solution of 5,15-bis(3-iodophenyl)-10,20-bis[3-(thiocyanatomethyl)phenyl]porphyrin[18] (90.0 mg, 89.2 μmol) in CH_2Cl_2 (90 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (200 mg, 0.9 mmol) in methanol (10 mL) were combined and stirred for 3 h at room temperature. The title compound was obtained without chromatography in quantitative yield as a purple solid: IR (neat) $\tilde{\nu}$ 2922, 2154, 1583; ^1H NMR δ 4.45 (s, 4H), 7.45−7.53 (m, 2H), 7.77−7.85 (m, 4H), 8.10−8.27 (m, 8H), 8.58 (brs, 2H), 8.97 (s, 8H); LD-MS obsd 1071.3; FAB-MS obsd 1069.9185, calcd exact mass 1069.9198 ($C_{48}H_{28}I_2N_6S_2Zn$); λ_{abs} 425, 551, 590 nm; λ_{em} 598, 647 nm.

Zn(II)-5,15-Bis[3-(*S*-acetylthiomethyl)phenyl]-10,20-bis(3-iodophenyl)porphyrin (Zn-7). A solution of **7**[18] (80.0 mg, 76.7 μmol) in CH_2Cl_2 (70 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (180 mg, 0.8 mmol) in methanol (10 mL) were combined and stirred for 4 h at room temperature. The title compound was obtained without chromatography in quantitative yield as a purple solid: IR (neat) $\tilde{\nu}$ 3052, 2921, 2852, 1690, 1583; ^1H NMR δ 2.37 (s, 6H), 4.38 (s, 4H), 7.45−7.54 (m, 2H), 7.65−7.75 (m, 4H), 8.06−8.25 (m, 8H), 8.59 (brs, 2H), 8.90−9.02 (m, 8H); LD-MS obsd 1105.4; FAB-MS obsd 1103.9500, calcd exact mass 1103.9504 ($C_{50}H_{34}I_2N_4O_2S_2Zn$); λ_{abs} 425, 551, 590 nm; λ_{em} 601, 646 nm.

Cu(II)-5,15-Bis[3-(*S*-acetylthiomethyl)phenyl]-10,20-bis(3-iodophenyl)porphyrin (Cu-7). A solution of **7**[18] (23.6 mg, 22.6 μmol) in $CHCl_3$ (40 mL) and a solution of $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol) in methanol (15 mL) were combined and stirred for 2 h. Column chromatography (CH_2Cl_2/hexanes 1:1) afforded an orange solid (25 mg, quantitative): IR (neat) $\tilde{\nu}$ 2918, 2846, 1686, 1584, 1510; LD-MS obsd 1103.0; FAB-MS obsd 1102.9495, calcd exact mass 1102.9509 ($C_{50}H_{34}CuI_2N_4O_2S_2$); λ_{abs} 419, 541 nm; λ_{em} 602, 653 nm.

Ni(II)-5,15-Bis[3-(*S*-acetylthiomethyl)phenyl]-10,20-bis(3-iodophenyl)porphyrin (Ni-7). A solution of **7**[18] (18.2 mg, 17.5 μmol) in $CHCl_3$ (20 mL) and a solution of $Ni(OAc)_2 \cdot 4H_2O$ (100 mg, 402 μmol) in methanol (5 mL) were combined and stirred for 4 days at reflux. The title compound was obtained without chromatography in quantitative yield as a brown-purple solid: IR (neat) $\tilde{\nu}$ 3056, 2921, 2849, 1691, 1584, 1555, 1508; ^1H NMR δ 2.38 (s, 6H), 4.35 (s, 4H), 7.36−7.45 (m, 2H), 7.57−7.67 (m, 4H), 7.86−7.91 (m, 2H), 7.94 (brs, 2H), 7.97−8.01 (m, 2H), 8.03−8.08 (m, 2H), 8.38−8.41 (m, 2H), 8.72 (d, J = 4.4 Hz, 4H), 8.75 (d, J = 4.4 Hz, 4H); LD-MS obsd 1099.8; FAB-MS obsd 1097.9591, calcd exact mass 1097.9566 ($C_{50}H_{34}I_2N_4NiO_2S_2$); λ_{abs} 417, 528, nm; λ_{em} 597, 646 nm.

5,10,15-Tris(2,6-difluorophenyl)-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (8). 2,6-Difluorobenzaldehyde (509 mg, 3.6 mmol), 4-[2-(trimethylsilyl)ethynyl]benzaldehyde[27] (200 mg, 1.0 mmol), and pyrrole (330 μL, 4.8 mmol) were dissolved in CH_2Cl_2 (200 mL). The solution was stirred at room temperature in the dark, and $BF_3 \cdot O(Et)_2$ (150 μL, 1.9 mmol) was added. After 3 h DDQ was added, and the mixture was stirred for an additional 1 h. Then the solvent was removed, and the resulting black solid was purified by three column chromatography procedures on silica (column 1: CH_2Cl_2/hexanes 1:2; column 2: CH_2Cl_2/hexanes 3:7; column 3: CH_2Cl_2/hexanes 1:2). The title porphyrin comprised the second purple band, affording a brown-purple solid (135 mg, 17%): IR (neat) $\tilde{\nu}$ 3315, 2153, 1578, 1508; ^1H NMR δ −2.77 (s, 2H), 0.38 (s, 9H), 7.33−7.43 (m, 6H), 7.73−7.84 (m, 3H), 7.88, 8.17 (AA′BB′, 2 × 2H), 8.82−8.90 (m, 8H); LD-MS obsd 817.9; FAB-MS obsd 818.2300, calcd exact mass 818.2300 ($C_{49}H_{32}F_6N_4Si$); λ_{abs} 419, 511, 544, 589, 644 nm.

Zn(II)-5,10,15-Tris(2,6-difluorophenyl)-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Zn-8). A solution of **8** (110.0 mg, 134.3 μmol) in $CHCl_3$ (80 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (300 mg, 1.4 mmol) in methanol (10 mL) were combined and stirred for 5 h at room temperature. Then additional $Zn(OAc)_2 \cdot 2H_2O$ (110 mg, 0.50 mmol) was added because there was still free base porphyrin left. Stirring was continued for 9 h then more $Zn(OAc)_2 \cdot 2H_2O$ (630 mg, 2.9 mmol) was added, and after an additional 4 h the reaction was worked up. Purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:1) afforded a red-purple solid (106 mg, 89%): IR (neat) $\tilde{\nu}$ 2955, 2155, 1578, 1496; ^1H NMR (THF-d_8) δ 0.36 (s, 9H), 7.40−7.51 (m, 6H), 7.81−7.94 (m, 5H), 8.18−8.24 (m, 2H), 8.82−8.89 (m, 8H); LD-MS obsd 879.3; FAB-MS obsd 880.1470, calcd exact mass 880.1435 ($C_{49}H_{30}F_6N_4SiZn$); λ_{abs} 423, 548 nm.; λ_{em} 592, 642 nm.

Zn(II)-5-(4-Ethynylphenyl)-10,15,20-tris(2,6-difluorophenyl)porphyrin (Zn-9). To a solution of **Zn-9** (82 mg, 93 μmol) in THF (9 mL) was added a suspension of K_2CO_3 (30.0 mg, 217 μmol) in methanol (3 mL). The mixture was stirred for 1 h at room temperature, then CH_2Cl_2 (20 mL) was added. The mixture was washed with 5% aqueous $NaHCO_3$ (20 mL) and dried (Na_2SO_4). Purification by column chromatography (silica, CH_2Cl_2/hexanes, 1:2) afforded a red-purple solid (58 mg, 77%): IR (neat) $\tilde{\nu}$ 3107, 2924, 2849, 2108, 1581; ^1H NMR δ 3.32 (s, 1H), 7.34−7.44 (m, 6H), 7.74−7.93 (m, 5H), 8.17−8.23 (m, 2H), 8.91−8.99 (m, 8H); LD-MS obsd 808.2; FAB-MS obsd 808.1050, calcd exact mass 808.1040 ($C_{46}H_{22}F_6N_4Zn$); λ_{abs} 423, 548 nm.; λ_{em} 592, 642 nm.

ZnZnZn-10. Zn-7 (10 mg, 9.0 μmol), **Zn-2**[21] (15.0 mg, 18.1 μmol), $Pd_2(dba)_3$ (2.5 mg, 2.7 μmol), and P(*o*-tol)$_3$ (6.6 mg, 22 μmol) were dissolved in a mixture of THF (6.0 mL) and TEA (1.2 mL). After 24 h the reaction was finished. The mixture was filtered over silica (CH_2Cl_2/hexanes, 2:3). Chromatography using an SEC column followed by a silica column (CH_2Cl_2/hexanes, 5:1) afforded a purple solid (9.0 mg, 40%): IR (neat) $\tilde{\nu}$ 2923, 2857, 1688, 1597, 1498; ^1H NMR (THF-d_8) δ 1.80−1.87 (m, 36H), 2.36−2.40 (m, 6H), 2.56−2.62 (m, 18H), 4.47 (s, 4H), 7.23−7.30 (m, 12H), 7.68−7.79 (m, 4H), 7.85−8.00 (m, 6H), 8.08−8.34 (m, 12H), 8.57 (brs, 2H), 8.59−8.62 (m, 8H), 8.63 (d, J = 4.4 Hz, 2H), 8.64 (d, J = 4.4 Hz, 2H), 8.77 (d, J = 4.4 Hz, 2H), 8.78 (d, J = 4.4 Hz, 2H), 8.95 (d, J = 5.1 Hz, 4H), 8.98 (d, J = 5.1 Hz, 4H); LD-MS obsd 2509.4; FAB-MS obsd 2500.72, calcd exact mass 2500.73 ($C_{160}H_{124}N_{12}O_2S_2Zn_3$); λ_{abs} 424, 552, 593 nm; λ_{em} 601, 651 nm.

ZnNiZn-10. Ni-7 (10 mg, 9.1 μmol), **Zn-2**[21] (15.1 mg, 18.2 μmol), $Pd_2(dba)_3$ (2.5 mg, 2.7 μmol), and P(*o*-tol)$_3$ (6.7 mg, 22 μmol) were dissolved in a mixture of THF (6.0 mL) and TEA (1.2 mL). After 20.5 h an additional amount of $Pd_2(dba)_3$ (3.2 mg, 3.5 μmol) was added because the reaction had stopped. Stirring was continued for an additional 20 h. The mixture was filtered over silica (CH_2Cl_2/hexanes, 3:1). Final purification by SEC afforded a purple solid (5.9 mg, 26%): IR (neat) $\tilde{\nu}$ 2921, 2857, 1700, 1595, 1508; ^1H NMR (THF-d_8) δ 1.83 (s, 36H), 2.35 (s, 6H), 2.59 (s, 18H), 4.41 (s, 4H), 7.27 (s, 12H), 7.64−7.74 (m, 4H), 7.80−7.87 (m, 2H), 7.91−7.98 (m, 6H), 8.04−8.13 (m, 6H), 8.18−8.23 (m, 4H), 8.39 (brs, 2H), 8.60 (s, 8H), 8.63 (d, J = 4.4 Hz, 4H), 8.77 (d, J = 4.4 Hz, 4H), 8.84 (d, J = 4.4 Hz, 4H), 8.87 (d, J = 5.1 Hz, 4H); LD-MS obsd 2502.7; FAB-MS obsd 2499.63, calcd exact mass 2499.73 ($C_{160}H_{124}NiN_{12}O_2S_2Zn_2$); λ_{abs} 424, 551, 593 nm; λ_{em} 600, 646 nm.

ZnCuZn-10. Cu-7 (9.9 mg, 9.0 μmol), **Zn-2**[21] (14.2 mg, 17.1 μmol), $Pd_2(dba)_3$ (2.5 mg, 2.7 μmol), and P(*o*-tol)$_3$ (6.6 mg, 22 μmol) were suspended in a mixture of THF (8.1 mL) and TEA (3.6 mL). Even after sonication, the complete dissolution of porphyrins **Cu-7** and **Zn-2** was not obtained. After the mixture was stirred at 40 °C for 18.5 h, an additional amount of $Pd_2(dba)_3$ (1.3 mg, 1.4 μmol) was added because the reaction had stopped. Stirring was continued for an additional 9 h. The mixture was filtered over silica (CH_2Cl_2/hexanes, 4:1). Final purification by SEC afforded a purple solid (11.4 mg, 51%): IR (neat) $\tilde{\nu}$ 2919, 2857, 1696, 1595; LD-MS obsd 2508.5; FAB-MS obsd 2504.82, calcd exact mass 2504.73 ($C_{160}H_{124}CuN_{12}O_2S_2Zn_2$); λ_{abs} 424, 549 nm; λ_{em} 596, 646 nm.

MgCuMg-10. Cu-7 (10 mg, 9.2 μmol), **Mg-2**[28] (14.6 mg, 18.5 μmol), $Pd_2(dba)_3$ (2.6 mg, 2.8 μmol), and P(*o*-tol)$_3$ (6.8 mg, 22.3 μmol) were suspended in a mixture of THF (10.0 mL) and TEA (2.0 mL). Even after sonication **Cu-7** was not completely dissolved. After 6 h an additional amount of $Pd_2(dba)_3$ (1.0 mg, 1.1 μmol) was added because the reaction had stopped (probably because of insufficient solubility). Stirring was continued for an additional 18 h. The mixture was filtered over alumina with CH_2Cl_2 (1% MeOH). Final purification by SEC afforded a purple solid (4.8 mg, 21%): IR (neat) $\tilde{\nu}$ 2922, 2858, 1700, 1593; LD-MS obsd 2425.9; FAB-MS obsd 2422.75, calcd exact mass 2422.85 ($C_{160}H_{124}CuMg_2N_{12}O_2S_2$); λ_{abs} 430, 543, 566, 606 nm; λ_{em} 612, 665 nm.

ZnZnZn-11. Zn-7 (10.0 mg, 9.0 μmol), **Zn-9** (14.6 mg, 18.0 μmol), $Pd_2(dba)_3$ (2.5 mg, 2.7 μmol) and P(*o*-tol)$_3$ (6.7 mg, 22 μmol) were dissolved in a mixture of THF (6.0 mL) and TEA (1.2 mL). After 39 h the reaction was finished. The mixture was filtered over silica (CH_2Cl_2/hexanes, 2:3). An SEC column followed by a silica column (CH_2Cl_2/hexanes 1:1 to neat CH_2Cl_2) afforded a purple solid (8.5 mg, 38%): IR (neat) $\tilde{\nu}$ 2923, 2849, 1694, 1584, 1496; ^1H NMR (THF-d_8) δ 2.36−2.39 (m, 6H), 4.47 (s, 4H), 7.40−7.49 (m, 12H), 7.68−8.34 (m, 28H), 8.57 (brs, 2H), 8.82−8.87 (m, 12H), 8.90 (d, J = 4.4 Hz, 2H), 8.91 (d, J = 4.4 Hz, 2H), 8.95 (d, J = 4.4 Hz, 4H), 8.99 (d, J = 5.1 Hz, 4H); LD-MS obsd 2470.8; FAB-MS obsd 2470.41, calcd exact mass 2470.33 ($C_{142}H_{76}F_{12}N_{12}O_2S_2Zn_3$); λ_{abs} 423, 550 nm; λ_{em} 597, 644 nm.

Electrochemistry. The solution and SAM electrochemical studies were conducted using the same instrumentation, techniques, and preparation strategies as described in Paper 1 of this series.[4] 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.

Acknowledgment. This work was supported by the DARPA Moletronics Program, administered through the ONR (N00014-99-1-0357). Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the NSF.

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

JO000488M