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

Christian Clausen,† Daniel T. Gryko,† Amir A. Yasseri,‡ James R. Diers,‡ David F. Bodan,*† Werner G. Kuhr,*‡ and Jonathan S. Lindsey*†

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, and Department of Chemistry, University of California, Riverside, California 92521-0403

jlindsey@ncsu.edu

Received March 30, 2000

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-butyphenyl)-10-phenylporphyrin, obtained by a rational synthesis, afforded the expected dimer linked by a meso-meso linkage and an unexpected trimer linked 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-protecting group was used to allow handling free thiol groups. Coupling of zinc(II)-5,10,15,16-(3,5-di-tert-butyphenyl)porphyrin ("upper half") and zinc(II)-5-[4-(S-acetylthio)phenyl]-10,20-bis(3,5-di-tert-butyphenyl)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 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 porphyrins1 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 perimeter3 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.

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. 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. 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.

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. Splitting of the potentials by \( \sim 0.15 \) V satisfy this criterion.

The preparation of the monomer relies on a new rational synthesis of meso-substituted porphyrins. Treatment of 5-phenylpyrromethane with ethylmagnesium bromide followed by acylation with 4-tert-butylbenzoyl chloride led to the diacylated dipyrromethane (Scheme 1). Reduction with excess NaBH\(_4\) in THF/methanol afforded the corresponding dicarbinol, which was condensed with dipyrromethane under TFA catalysis in acetonitrile at room temperature (nonscrambling conditions) followed by oxidation with DDQ. The desired porphyrin \( \text{Zn-2} \) was obtained in 35% yield. This synthesis route afforded the desired porphyrin with one free meso position without acidolytic scrambling. Porphyrin \( \text{Zn-2} \) is almost insoluble in common solvents. Metallation with Zn(OAc)\(_2\)-2H\(_2\)O in refluxing CHCl\(_3\) afforded \( \text{Zn-2} \) in quantitative yield, which also has low solubility.

For the meso,meso coupling of \( \text{Zn-2} \), we used the method reported by Osaka et al., which employed the oxidant AgPF\(_6\) in a mixture of CHCl\(_3\) and acetonitrile. Due to the low solubility of \( \text{Zn-2} \), the reaction was run under reflux instead of room temperature. Using 0.5 molar equiv of AgPF\(_6\) as reported by Osaka et al., led to only a small amount of dimer (\( \sim 10\% \)), 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)\(_2\)-2H\(_2\)O. We obtained two different oligomers, the expected dimer \( \text{Zn-3} \) in 89% yield and, surprisingly, also the trimer \( \text{Zn-4} \) in 9% yield (Scheme 2). Both are brown-purple solids and exhibit good solubility in common solvents. The structure proposed for \( \text{Zn-4} \) is consistent with the molecular ion peak observed by mass spectrometry and the substitution pattern indicated by \(^1\)H NMR spectroscopy. The \(^1\)H NMR spectrum of \( \text{Zn-4} \) is almost identical with that of \( \text{Zn-3} \) with the addition of a peak due to the tert-butyl groups and the presence of the AAB'B' 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 \( \text{Zn-4} \).

After preparation of \( \text{Zn-3} \), 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

---

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, followed by quenching of the anion with acetyl chloride, did not afford the desired product 6. We then reacted 4-(S-acetylthio)benzaldehyde with pyrrole, affording dipyrromethane 6 in 62% yield (eq 1). To prepare the other half of the "lower" porphyrin, dipyrromethane 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).

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 gave porphyrin 10 in 21% yield (Scheme 4). Metalation with Zn(OAc)\(_2\)·2H\(_2\)O led to Zn-10 in quantitative yield. 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
trimer Zn-4 was investigated in solution. All three dimers exhibit four reversible oxidation waves at \( \sim 0.50, 0.65, 0.95, \) and 1.03 V (versus Ag/Ag\(^+\); \( E_{1/2} (\text{FeCp}_2/\text{FeCp}_2^{\text{+}}) = 0.19 \) V). The first and second oxidation waves straddle the \( E_{1/2} \) value for the first oxidation of a monomeric porphyrin with similar substituents (\( E_{1/2} \sim 0.6 \) 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 (\( E_{1/2} \sim 0.9 \) 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-acetyltio 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 \( \pi \)-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

---

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. All reported NMR spectra were collected in CDCl₃ (1H
NMR at 300 MHz; $^{13}$C NMR at 75 MHz). UV−vis absorption and fluorescence spectra were recorded in toluene as described previously. Porphyrin metalation was performed and monitored by fluorescence spectroscopy as described in the preceding paper in this series. Melting points are uncorrected. Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix, 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 as eluent. Analytical scale SEC was performed with a 1000 Å column (5 μL/min).21

1,9-Bis(4-tert-butylbenzoyl)-5-phenylpyrromethane (1). Following a general procedure,12,22 to a solution of 5-phenyldipyrromethane14,15 (2.22 g, 10 mmol) in toluene (25 mL) was added dropwise. The solution became dark immediately. The solvent was again removed, and the brown residue was purified by column chromatography (first column: alumina, second column: silica, Et 2O/hexanes, 1:2; third column: silica CH 2Cl2/ethyl acetate, 5:1), affording a brown solid (2.96 g, 55%): $\text{C}_{28}H_{28}N_4; \lambda_{\text{abs}} 415, 509, 543, 586, 641 \text{ nm}$. 

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 workup23 afforded a bright purple solid (123 mg, 100%): IR (neat) ν 3081, 2922, 2854, 1650; $\text{C}_{28}H_{30}N_4Zn; \lambda_{\text{em}} 649.9; \text{FAB-MS obsd} 650.3416, \text{calcd exact mass} 650.3409$ (C 37H 38N 2O 2); $\lambda_{\text{abs}} 415, 549, 582, 584 \text{ nm}$. 

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, and the remaining brown-purple solid was dissolved in CHCl 3 (30 mL) and treated with a solution of Zn(OAc) 2·2H 2O (290 mg, 1.33 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 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 (2.7 mg, 8%). Data for Zn-4: IR (neat) ν 2959, 2922, 2854, 1542, 1458; $\text{C}_{28}H_{30}N_4Zn; \lambda_{\text{abs}} 415, 549, 582 \text{ nm}$. 

Figure 1. Fast-scan (100 V/s) voltammetry of Zn-12.
5-(4-Methylthiophenyl)dipyrromethane (5). Following a general procedure,14,15 pyrrole (50.0 mL, 720 mmol) and 4-(methylthiophenyl)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 (Na2SO4). Then the mixture was filtered, affording a white powder (442 mg, 27%): mp 220 °C; IR (neat) 3100, 2960, 1703, 1607, 1582, 1485; 1H NMR (DMSO-d6) δ 1.16 (s, 3H), 2.55 (s, 3H), 7.81 (d, J = 8.9 Hz, 2H), 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 (C10H11N3S2); λmax 417, 511, 544, 586, 642 nm. Data for 8. IR (neat) ν 3307, 2958, 2861, 1708, 1590, 1467; 1H NMR δ −2.95 (s, 2H), 1.55 (s, 3H), 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), 10.12 (s, 1H); LD-MS obsd 837.8; FAB-MS obsd 836.45, calcd exact mass 836.4488 (Cu2H20N5O5S). λmax 416, 510, 544, 585, 641 nm.

Zinc(Ii)-5-[4-(4-Acetylthio)phenyl]-10,20-bis(3,5-di-t-butylbenzylo)dipyrromethane (Zn-8). A solution of 8 (56 mg, 67 µmol) in CHCl3 (20 mL) was treated with a solution of Zn(OC2H5)2H2O (734 mg, 3.3 mmol) in methanol (5 mL) and the mixture was stirred for 6.5 h. Purification by column chromatography (silica, CH3Cl2/hexanes, 1:1) afforded a purple solid (54 mg, 90%): IR (neat) ν 3066, 2956, 1703, 1675, 1590, 1469; 1H NMR δ 4.45 (s, 2H), 5.15 (s, 2H), 5.18 (s, 2H), 5.28 (s, 2H), 5.62 (m, 2H), 7.20, 7.34 (AA′BB′, 2 × 2H), 7.97 (2H, 2H), 13.45, 14.7, 195.7; EI-MS obsd 296.096; calcd exact mass 296.0983. Anal. Calcld for C36H34N2O2S: C, 71.60; H, 5.99; N, 10.31; S, 11.81.

1,9-Bis[3,5-di-t-tert-butylbenzoyl]dipyrromethane (7). To a solution of dipyrromethane14 (421 mg, 2.9 mmol) in toluene (60 mL) stirred under argon and cooled in an ice bath was slowly added a solution of Zn(OC2H5)2H2O (193 mg, 0.79 mmol) in methanol (2 mL), and the mixture was stirred for 7 h. Then the mixture was filtered through a pad of alumina (CH2Cl2). The organic phase was dried (K2CO3) and the solvent was removed. The resulting orange oil and 5-(3,5-di-t-tert-butylbenzoyl)dipyrromethane (57 mg, 10%). Data for 9. IR (neat) ν 2960, 1703, 1607, 1582, 1485; 1H NMR δ 1.51 (s, 3H), 1.53 (s, 3H), 1.55 (s, 3H), 1.57 (s, 3H), 2.59 (s, 3H), 7.45 (m, 2H), 7.55 (m, 2H), 8.20 (d, J = 8.9 Hz, 4H), 8.94 (d, J = 5.1 Hz, 2H), 8.96 (d, J = 4.4 Hz, 2H), 4.16 (J = 12.2 Hz, 2H), 10.29 (s, 1H); LD-MS obsd 990.1; FAB-MS obsd 988.3617, calcd exact mass 988.3623 (C56H58N4S2O8Zn); λmax 420, 545, 583, 588 nm; λem 594, 619, 641 nm.

Zinc(Ii) Disulfide Zn-9. A solution of 9 (14 mg, 8.8 µmol) in CHCl3 (5 mL) was treated with a solution of Zn(OC2H5)2H2O (193 mg, 0.79 mmol) in methanol (2 mL), and the mixture was stirred for 7 h. Then the mixture was filtered through a pad of alumina (CH2Cl2). The organic phase was dried (K2CO3) and the solvent was removed. The resulting orange oil and 5-(3,5-di-t-tert-butylbenzylo)dipyrromethane (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 CHCl3. Further purification by column chromatography (silica, CH3Cl2/hexanes, 1:1) afforded a purple solid (185 mg, 21%): IR (neat) ν 3305, 3064, 2958, 1588, 1468; 1H NMR δ −2.91 (s, 2H), 1.51 (s, 18H), 1.55 (s, 3H), 7.79 (t, J = 1.5 Hz, 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, calcld exact mass 874.5913 (C₆₂H₇₄N₄); λ<sub>abs</sub> 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 CHCl₃ (40 mL) was treated with a solution of Zn(OAc)<sub>2</sub>-2H₂O (2.22 g, 10.1 mmol) in methanol (10 mL), and the mixture was stirred for 21 h. Purification by column chromatography (silica, CH₃Cl/ hexanes, 1:1) afforded a red-purple solid (187 mg, 99%): IR (neat): ν 3060, 2960, 2872, 1591, 1470; ¹H NMR δ 1.54 (s, 36H); 7.68 (t, J = 1.4 Hz, 2H), 8.09 (d, J = 4.4 Hz, 2H), 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, calcld exact mass 1870.99 (C₁₃₁H₁₂₈N₈O₄S₂Zn₂); λ<sub>abs</sub> 421, 460, 561 nm; λ<sub>em</sub> 625, 660 nm. Data for Zn-12: IR (neat): ν 3069, 2955, 1700, 1588, 1465; ¹H 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, calcld exact mass 1832.85 (C₁₃₃H₁₃₀N₈O₄S₂Zn₂); λ<sub>abs</sub> 420, 460, 561 nm; λ<sub>em</sub> 626, 660 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 CHCl₃ (20 mL) was added a solution of AgPF<sub>6</sub> (8.9 mg, 35 μmol) in acetonitrile (3 mL). The mixture was refluxed for 7 h. Then more AgPF<sub>6</sub> (15 mg, 59 μmol) was added because the reaction stopped again. Refluxing was continued for a further 1 h, and then the mixture was quenched with water. The phases were separated, and the organic phase was washed with water and dried (Na₂SO₄). The solvent was removed, and the dark-purple solid was dissolved in CHCl₃ (30 mL). A solution zinc(II) porphyrin (Zn-11): To a solution of Zn-10 (177 mg, 177 μmol) in CHCl₃ (40 mL) was added a solution of AgPF<sub>6</sub> (8.9 mg, 35 μmol) in acetonitrile (3 mL). The mixture was refluxed for 7 h. Then more AgPF<sub>6</sub> (15 mg, 59 μmol) was added because the reaction stopped again. Refluxing was continued for a further 1 h, and then the mixture was quenched with water. The phases were separated, and the organic phase was washed with water and dried (Na₂SO₄). The solvent was removed, and the dark-purple solid was dissolved in CHCl₃ (30 mL). A solution of Zn(OAc)<sub>2</sub>-2H₂O (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 NaHCO₃ and dried (Na₂SO₄). 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, CH₃Cl/ hexanes, 1:2–3) 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) ν 3060, 2956, 2861, 1592, 1465; ¹H 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, calcld exact mass 1870.99 (C₁₃₁H₁₂₈N₈O₄S₂Zn₂); λ<sub>abs</sub> 421, 460, 561 nm; λ<sub>em</sub> 625, 660 nm. Data for Zn-12: IR (neat): ν 3069, 2955, 1700, 1588, 1465; ¹H 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, calcld exact mass 1832.85 (C₁₃₃H₁₃₀N₈O₄S₂Zn₂); λ<sub>abs</sub> 420, 460, 561 nm; λ<sub>em</sub> 626, 660 nm.

Electrochemistry. Both the solution and SAM electron spectroscopy, and preparation strategies as described in Paper 1 of this series.¹⁰ The solvent was CH₂Cl₂: 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<sub>1/2</sub>(FeCp₂/FeCp₂<sup>+</sup>) = 0.19 V.

Acknowledgment. This work was supported by the DARPA Mollectronics 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 and ¹H NMR spectra for all porphyrins and arrays. This material is available free of charge via the Internet at http://pubs.acs.org.