Synthesis of Thiol-Derivatized Ferrocene−Porphyrins for Studies of Multibit Information Storage

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One approach toward storage of multiple bits of information at the molecular level requires the construction of molecular architectures comprised of multiple redox-active units. Four new ferrocene−porphyrins have been synthesized to investigate questions concerning (1) the scope of redox-active molecules that can be employed in molecular information-storage schemes and (2) writing/reading rates as well as retention of charge in redox-active units located at different sites in a molecular architecture. Three of the ferrocene−porphyrins have linkers of different lengths between the ferrocene and porphyrin. The fourth ferrocene−porphyrin has two ferrocenes positioned at the lateral sites on the porphyrin. The latter architecture is designed to provide a shorter distance between the electroactive surface and the ferrocene while maintaining an upright orientation of the porphyrin. Each ferrocene−porphyrin affords three cationic oxidation states (ferrocene monocation, porphyrin monocation, porphyrin dication) in addition to the neutral state, thereby affording the capability of storing two bits of information. Each ferrocene−porphyrin bears an *S*-acetyl or *S*-(*N*-ethyl)carbamoyl-protected thiol moiety, thereby avoiding handling of free thiols. Each ferrocene−porphyrin forms a self-assembled monolayer (SAM) on gold via in situ cleavage of the thiol protecting group. The SAM of each array is electrochemically robust and exhibits three well-resolved, reversible oxidation waves.

Introduction

We have shown that a self-assembled monolayer (SAM) of porphyrins attached to an electroactive surface can be used for molecular-based information storage. The porphyrins are addressed electrically, and information is stored in the distinct oxidation states provided by the porphyrins.[1] In principle, multiple bits of information can be stored in a given memory storage location (i.e., a memory cell) by accessing a series of distinct oxidation states of a molecular assembly. Gold, the electroactive surface predominantly employed, presents an electrochemical window that extends to ∼+1.2 V (versus Ag/Ag^+). A number of writing and reading schemes require a potential difference of $\Delta E = 150$ mV in order to distinguish distinct oxidation states. Thus, to store multiple bits it is essential to have redox-active molecules that span the full potential provided by the gold electrode. For purposes of stability, we have selected redox-active molecules that are reversibly cycled between neutral and cationic states rather than anionic states, given the greater stability of cations under ambient conditions.

In the preceding paper, we described the synthesis of thiol-derivatized porphyrins for attachment to electroactive surfaces.[2] Porphyrins have two stable and easily accessible cationic oxidation states (monocation, dication).[3] In porphyrins the electrochemical potentials can be tuned by attachment of appropriate substituents[4] or by variation in the central metal,[5] thereby achieving oxidation potentials in the range of +0.5 to +1.2 V. The challenges of extending the electrochemical window and storing multiple bits in a single memory location have raised a series of questions. (1) What is the scope of redox-active molecules that can be utilized for molecular-based information storage? (2) Is there a difference between co-depositing a collection of different types of molecules having distinct oxidation potentials in a memory storage location, versus employing a homogeneous population of molecules where each molecule is comprised of multiple redox-active units? The former approach is more easily implemented while the latter avoids potential problems such as differential partitioning onto the surface and/or compartmentalization of attached molecules that may occur with a heterogeneous population of molecules. (3) In the design of arrays comprised of multiple redox-active units, how is the rate of electron transfer (and therefore the rate of writing and reading) and the retention of charge affected by molecular architecture? Though some information has been obtained concerning the effects of linker length and composition on rate of

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(1) Roth, K.; Dontha, N.; Dabke, R.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. *J. Vac. Sci. Technol. B* **2000**, *18*, 2359−2364.
(2) Gryko, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7345−7355.
(3) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 53−126.
(4) Yang, S. I.; Seth, J.; Strachan, J. P.; Gentemann, S.; Kim, D.; Holten, D.; Lindsey, J. S.; Bocian, D. F. *J. Porphyrins Phthalocyanines* **1999**, *3*, 117−147.
(5) Fuhrhop, J.-H.; Mauzerall, D. *J. Am. Chem. Soc.* **1969**, *91*, 4174−4181.

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electron transfer of redox-active molecules incorporated in SAMs, very little is known concerning the factors that control information retention.

One of the most widely studied redox-active molecules in SAMs is ferrocene,[6] due to the central role played by ferrocene in nonaqueous electrochemical studies. Ferrocene and its derivatives present a number of attractive electrochemical features. Ferrocenes exhibit relatively stable radical cations. The electrochemical potential can be tuned by attachment of appropriate substituents, affording oxidation potentials in the range of −0.2 to >+0.5 V.[7] One key distinction between a ferrocene and a porphyrin, however, is that ferrocene only has two easily accessible oxidation states (neutral, monocation), while porphyrins have three accessible and stable oxidation states (neutral, monocation, dication). The distinct electrochemical windows that are readily accessible with ferrocenes and porphyrins prompted us to explore the combination of porphyrins and ferrocenes in order to span the electrochemical window provided on a gold surface.

Thiol-derivatized ferrocene−porphyrins are attractive as prototypical molecular arrays comprised of multiple redox-active units for studies of multibit information storage. A large number of ferrocene−porphyrins have been prepared to date.[8−16] The type of linker between the two electroactive units in these structures ranges from nonconjugated (ether,[8,9] ester,[10] amide[11,12]) to conjugated (direct linkage,[13] imine,[14] phenyl,[15] alkene[16]). Two ferrocene−porphyrins that bear a thiol unit attached to the end of a long flexible hydrocarbon chain have been prepared for attachment to a gold electrode.[8,12] For our studies, we required a set of molecules with a high level of architectural rigidity and appropriate positioning of ferrocene, porphyrin, linkers, and thiol unit.

In this paper, we describe a set of four thiol-derivatized ferrocene−porphyrins. To achieve a high degree of 3-dimensional order, the *p*-phenylene linker has been used for attachment of the porphyrin to the thiol group. Three of the ferrocene−porphyrins are designed such that the ferrocene and porphyrin are separated by linkers of different length. Each ferrocene−porphyrin is designed for vertical orientation upon binding of the thiol group on a gold surface, thereby disposing the ferrocene far from the gold surface (**Zn-1**, **Zn-2**, and **Zn-3**). A fourth ferrocene−porphyrin explores a different architecture, where the ferrocenes are attached to the lateral positions of the porphyrin (**Zn-4**). In this case, the through-bond distance from thiol to ferrocene remains essentially the same as with the ferrocene−porphyrin having the same spacer but in an upright position (**Zn-2**) while the through-space distance to the gold surface is much shorter. This set of ferrocene−porphyrins should provide valuable guidance concerning the design of molecular devices for the storage of multiple bits of information. All of the thiol-derivatized molecules are prepared with *S*-acetyl or *S*-(*N*-ethylcarbamoyl) protected thiol groups, which undergo in situ cleavage on a gold electrode and thereby obviate handling of free thiols.[17,18]

Results and Discussion

Synthesis. We first sought to prepare ferrocene−porphyrins for studying the effects of linkers of various length interposed between the porphyrin and the ferrocene. Three such ferrocene−porphyrins are shown in Chart 1. The different linkers in the ferrocene−porphyrins can be constructed using precursor ferrocenyl aldehydes that contain the corresponding linkers. Thus, the syntheses of **Zn-1**−**Zn-3** require ferrocene carboxaldehyde (**5**), 4-ferrocenylbenzaldehyde (**6**), and a diphenylethyne-linked ferrocene aldehyde **7**. This approach minimizes manipulations of the porphyrin. Ferrocenecarboxaldehyde (**5**) is available commercially, and several syntheses of 4-ferrocenylbenzaldehyde **6** have been described.[19] We prepared **6** by reduction of ethyl 4-ferrocenylbenzoate[20] with $LiAlH_4$ followed by PCC oxidation of the resulting alcohol (see the Supporting Information).

(6) (a) Chidsey, C. E. D. *Science* **1991**, *251*, 919−922. (b) Tender, L.; Carter, M. T.; Murray, R. W. *Anal. Chem*. **1994**, *66*, 3173−3178. (c) Weber, K.; Creager, S. E. *Anal. Chem*. **1994**, *66*, 3164−3172. (d) Abbott, N. L.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1493−1497. (e) Everett, W. R.; Welch, T. L.; Reed, L.; Fritsch-Faules, I. *Anal. Chem*. **1995**, *67*, 292−298. (f) Campbell, D. J.; Herr, B. R.; Hulteen, J. C.; Van Duyne, R. P.; Mirkin, C. A. *J. Am. Chem. Soc*. **1996**, *118*, 10211−10219. (g) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc*. **1997**, *119*, 10563−10564. (h) Creager, S.; Yu, C. J.; Bamdad, C.; O'Connor, S.; Maclean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc*. **1999**, *121*, 1059−1064. (i) Kondo, T.; Horiuchi, S.; Yagi, I.; Ye, S.; Uosaki, K. *J. Am. Chem. Soc*. **1999**, *121*, 391−398. (j) Ye, S.; Haba, T.; Sato, Y.; Shimazu, K.; Uosaki, K. *Phys. Chem. Chem. Phys*. **1999**, *1*, 3653−3659.

(7) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1979; Vol. 13, pp 3−27.

(8) (a) Uosaki, K.; Kondo, T.; Zhang, X.-Q.; Yanagida, M. *J. Am. Chem. Soc*. **1997**, *119*, 8367−8368. (b) Yanagida, M.; Kanai, T.; Zhang, X.-Q.; Kondo, T.; Uosaki, K. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2555−2559. (c) Kondo, T.; Kanai, T.; Iso-o, K.; Uosaki K. *Z. Phys. Chem*. **1999**, *212*, 23−30.

(9) Thornton, N. B.; Wojtowicz, H.; Netzel, T.; Dixon, D. W. *J. Phys. Chem. B*. **1998**, *102*, 2101−2110.

(10) (a) Beer, P. D.; Kurek, S. S. *J. Organomet. Chem*. **1987**, *336*, C17−C21. (b) Beer, P. D.; Kurek, S. S. *J. Organomet. Chem*. **1989**, *366*, C6−C8. (c) Wagner, R. W.; Brown, P. A.; Johnson, T. E.; Lindsey, J. S. *J. Chem. Soc., Chem. Commun*. **1991**, 1463−1466. (d) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 6755−6790.

(11) (a) Hisatome, M.; Takano, S.; Yamakawa, K. *Tetrahedron Lett*. **1985**, *26*, 2347−2350. (b) Beer, P. D.; Drew, M. G. B.; Hesek, D.; Jagessar, R. *J. Chem. Soc., Chem. Commun*. **1995**, 1187−1189. (c) Beer, P. D.; Drew, M. G. B.; Jagessar, R. *J. Chem. Soc., Dalton Trans*. **1997**, 881−886. (d) Fujitsuka, M.; Ito, O.; Imahori, H.; Yamada, K.; Yamada, H.; Sakata, Y. *Chem. Lett*. **1999**, 721−722.

(12) Imahori, H.; Yamada, H.; Ozawa, S.; Ushida, K.; Sakata, Y. *Chem. Commun*. **1999**, 1165−1166.

(13) (a) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem*. **1977**, *16*, 3079−3089. (b) Maiya, G. B.; Barbe, J.-M.; Kadish, K. M. *Inorg. Chem*. **1989**, *28*, 2524−2527. (c) Loim, N. M.; Abramova, N. V.; Sokolov, V. I. *Mendeleev Commun*. **1996**, *2*, 46−47. (d) Loim, N. M.; Abramova, N. V.; Khaliullin, R. Z.; Sokolov, V. I. *Russ. Chem. Bull*. **1997**, *46*, 1193−1194. (e) Loim, N. M.; Abramova, N. V.; Khaliullin, R. Z.; Lukashov, Y. S.; Vorontsov, E. V.; Sokolov, V. I. *Russ. Chem. Bull*. **1998**, *47*, 1016−1020. (f) Boyd, P. D. W.; Burrell, A. K.; Campbell, W. M.; Cocks, P. A.; Gordon, K. C.; Jameson, G. B.; Officer, D. L.; Zhao, Z. *Chem. Commun*. **1999**, 637−638. (g) Nadtochenko, V. A.; Denisov, N. N.; Gak, V. Y.; Abramova, N. V.; Loim, N. M. *Russ. Chem. Bull*. **1999**, *48*, 1900−1903.

(14) Vaijayanthimala, G.; D'Souza, F.; Krishnan, V. *J. Coord. Chem*. **1990**, *21(Part A)*, 333−342.

(15) Schmidt, E. S.; Calderwood, T. S.; Bruice, T. C. *Inorg. Chem*. **1986**, *25*, 3718−3720.

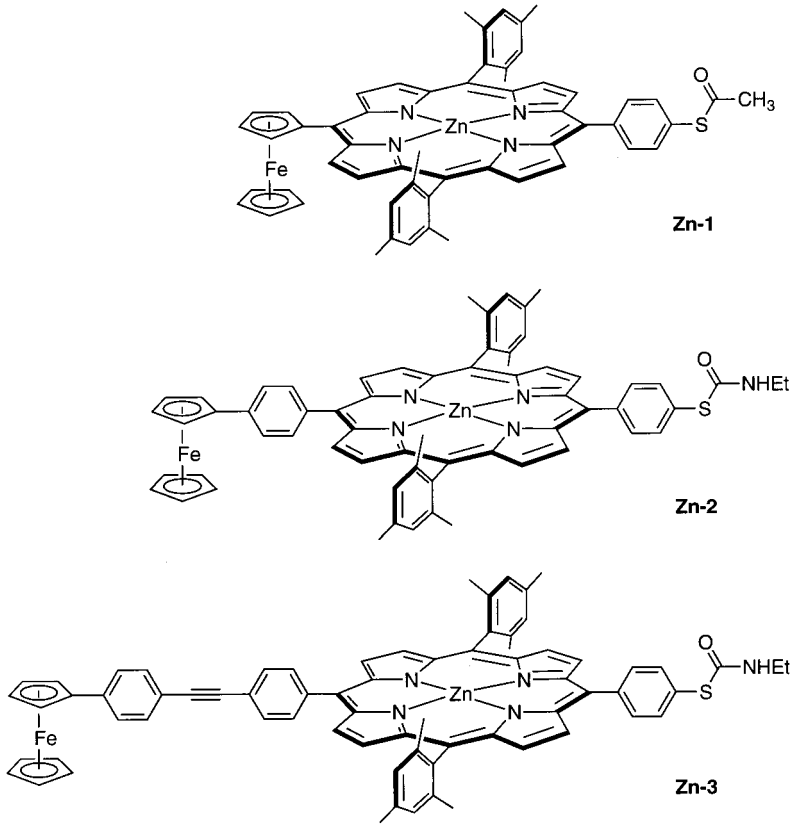
(16) (a) Giasson, R.; Lee, E. J.; Zhao, X.; Wrighton, M. S. *J. Phys. Chem*. **1993**, *97*, 2596−2601. (b) Burrell, A. K.; Campbell, W.; Officer, D. L. *Tetrahedron Lett*. **1997**, *38*, 1249−1252. (c) Burrell, A. K.; Campbell, W. M.; Officer, D. L.; Scott, S. M.; Gordon, K. C.; McDonald, M. R. *J. Chem. Soc., Dalton Trans*. **1999**, 3349−3354.

(17) Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc*. **1995**, *117*, 9529−9534.

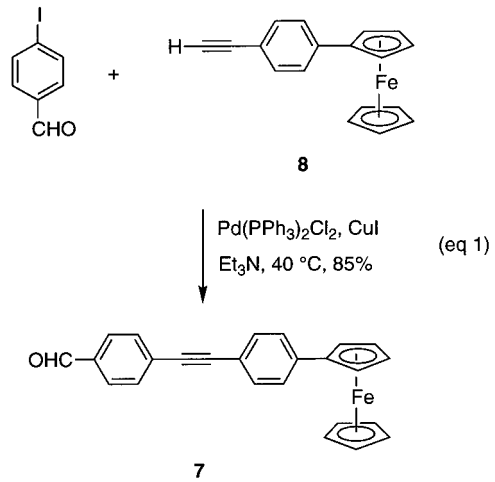
(18) Gryko, D. T.; Clausen, C.; Lindsey, J. S. *J. Org. Chem*. **1999**, *64*, 8635−8647.

(19) (a) Egger, H.; Schoegl, K. *Monatsh. Chem*. **1964**, *95*, 1750−1758. (b) Shih, S.-C.; Sung, H.-T.; Li, F.-C. CA **1965**, 63: 13314b. (c) Moiseev, S. K.; Meleshonkova, N. N.; Sazonova, V. A. *Koord. Khim*. **1988**, *14*, 328−331. (d) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G. *J. Organomet. Chem* **1994**, *464*, 225−232. (e) Imrie, C.; Loubser, C.; Engelbrecht, P.; McCleland, C. W. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2513−2523.

Chart 1



The diphenylethyne-linked ferrocene carboxaldehyde **7** was synthesized via Pd-coupling of ethynylphenylferrocene **8**[21] with 4-iodobenzaldehyde in 85% yield (eq 1).



Each of the target porphyrins bears three different meso substituents (AB_2C type). One route to AB_2C-porphyrins involves a mixed condensation of one dipyrromethane and two aldehydes, forming three porphyrin products. The porphyrins are then separated chromatographically. This overall synthetic route has been augmented recently by the development of improved conditions for the condensation. Sterically hindered dipyrromethanes (e.g., 5-mesityldipyrromethane) give the expected three porphyrin products with no observable scrambling upon reaction with 17.8 mM TFA in CH_2Cl_2 at room temperature, while sterically unhindered dipyrromethanes (e.g., 5-phenyldipyrromethane) give rise to only a low level of scrambling upon reaction with BF_3-etherate and NH_4Cl in CH_3CN at 0 °C.[22] (Scrambling refers to acidolysis and recombination processes that lead to a mixture of porphyrins in a rational porphyrin synthesis.[22]) While not elegant, this statistical route is expedient if the porphyrins can be readily separated. The difficulty of this separation depends on the difference in polarity imparted by the substituents on the two aldehyde compounds. In the course of this study, we found that the *N*-ethylcarbamoyl or the acetyl group attached to the thiophenol moiety (aldehyde **9** or **10**) provides moderate polarity, thereby facilitating separation of the porphyrin mixtures.

The condensation of 4-ferrocenylbenzaldehyde (**6**), 4-[*S*-(*N*-ethylcarbamoyl)thio]benzaldehyde (**9**),[18] and 5-mesityldipyrromethane (**11**)[23] was performed in the presence of 17.8 mM TFA in CH_2Cl_2 at room temperature (Scheme 1). The oxidation conditions were modified in two ways due to the presence of the easily oxidized ferrocene unit. (1) The acidic reaction mixture was neutralized with DIEA prior to oxidation, given that acids are known to increase the oxidation potential of quinones,[24] and (2) the

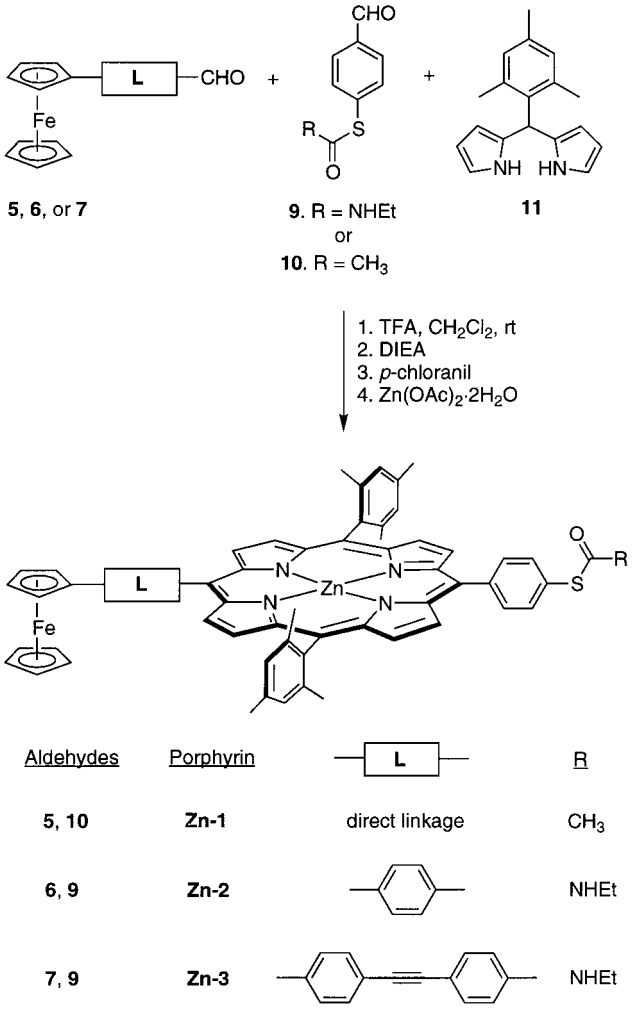
(20) (a) Nesmeyanov, A. N. *Proc. Royal Soc. London, Ser. A* **1958**, *246*, 495−503. (b) Akiyama, T.; Kitamura, T.; Kato, T.; Watanabe, H.; Serizawa, T.; Sugimori, A. *Bull. Chem. Soc. Jpn*. **1977**, *50*, 1137−1141. (c) Shimizu, I.; Umezawa, H.; Kanno, T.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn*. **1983**, *56*, 2023−2028.

(21) Ambroise, A.; Wagner, R. W.; Rao, P. D.; Riggs, J. A.; Hascoat, P.; Diers, J. R.; Seth, J.; Bocian, D. F.; Holten, D.; Lindsey, J. S. Manuscript in preparation.

(22) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem*. **1999**, *64*, 2864−2872.

(23) (a) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440. (b) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem*. **1999**, *64*, 1391−1396.

Scheme 1

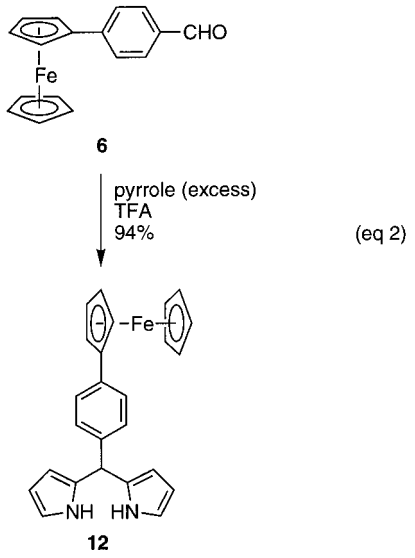


weaker oxidant *p*-chloranil was used instead of DDQ. Chromatographic workup yielded the desired free base porphyrin (**2**) accompanied by a small amount of impurities. This material was treated with zinc acetate and upon final purification porphyrin **Zn-2** was obtained in 19% yield.

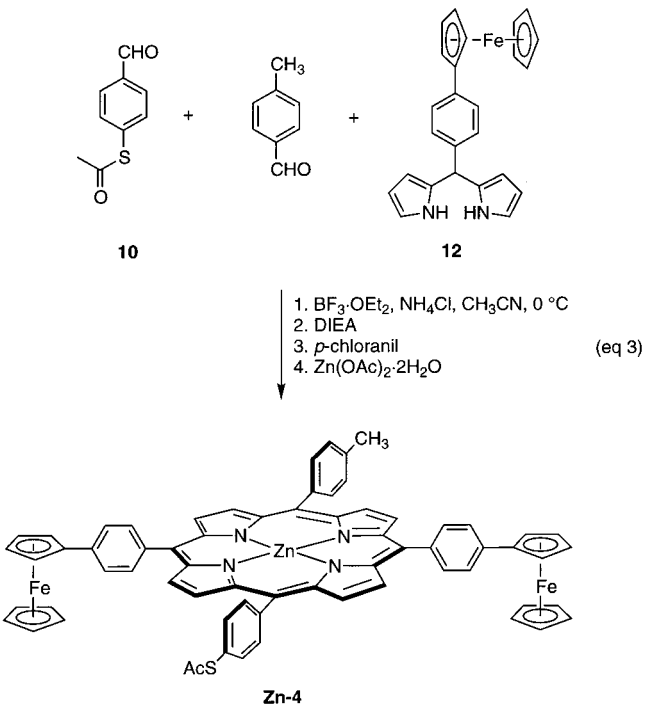
The reaction of ferrocenecarboxaldehyde (**5**), 5-mesityldipyrromethane (**11**), and 4-(*S*-acetylthio)benzaldehyde (**10**)[18] was performed identically, affording **Zn-1** in 37% overall yield, a much higher yield compared with that of porphyrin **Zn-2**. Analysis by TLC and LD-MS showed significant skewing from the statistical 1:2:1 ratio of the three expected porphyrins.

The same mixed-condensation approach was employed with aldehydes **7** and **9**, affording free base porphyrin **3** in 10% yield. Subsequent metalation afforded **Zn-3** in 70% yield (Scheme 1). Thus a significant decrease in yield of the ferrocenyl Zn porphyrin occurred with increasing length of the linker in the ferrocene−aldehyde, from **5** (37%) through **6** (19%) to **7** (7%). As expected, analysis by TLC or LD-MS of the crude reaction mixtures showed no sign of scrambling in any of these reactions.

To synthesize the porphyrin bearing two lateral ferrocenes (**Zn-4**) we needed the corresponding dipyrromethane **12**. Treatment of 4-ferrocenylbenzaldehyde **6** with excess pyrrole at room temperature using a standard one-flask procedure[23] afforded **12** in high yield (eq 2). The reaction of ferrocenyldipyrromethane **12**, 4-(*S*-



acetylthio)benzaldehyde (**10**), and 4-methylbenzaldehyde was carried out in the presence of BF_3−etherate and NH_4Cl in CH_3CN at 0 °C followed by neutralization with DIEA and oxidation with *p*-chloranil (eq 3). The three expected porphyrins and a small amount of scrambling giving other porphyrins were observed. After purification, the desired free base porphyrin **4** was isolated, contaminated with some undefined species. Conversion to the zinc chelate enabled purification of **Zn-4** by column chromatography (3.1% yield overall). (The same reaction using DDQ alone instead of DIEA and *p*-chloranil gave 0.33% yield.) In summary, we have successfully prepared four thiol-derivatized ferrocenyl Zn porphyrins, with reasonable yields except for **Zn-4**.



Electrochemical Studies. The electrochemical behavior of the ferrocenyl Zn porphyrins was investigated for samples both in solution and self-assembled on gold.

(24) Fukuzumi, S.; Ishikawa, K.; Hironaka, K.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 751−760.

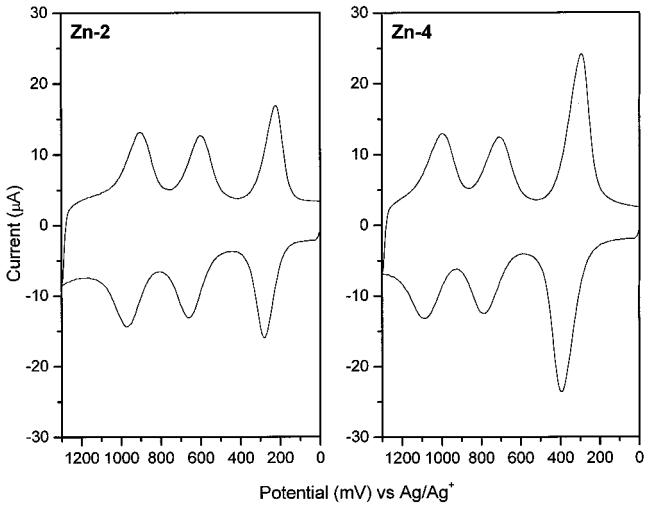


Figure 1. Fast-scan (100 V/s) voltammetry of the **Zn-2** SAM (left panel) and the **Zn-4** SAM (right panel).

The solution electrochemistry of the ferrocenyl Zn porphyrins is characterized by three resolved oxidation waves (not shown). These waves correspond to the oxidation of the ferrocene constituent(s) and the two oxidations of the Zn porphyrin. In the case of **Zn-4**, the wave due to ferrocene corresponds to the overlapping waves of the two identical ferrocene constituents. For **Zn-2**, **Zn-4**, and **Zn-3**, the oxidation potentials for the ferrocene constituent(s) and the porphyrin are essentially identical to those of the isolated components (Zn porphyrin, $E_{1/2}(1) \sim 0.6$ V; $E_{1/2}(2) \sim 0.9$ V; ferrocene, $E_{1/2} = \sim 0.20$ V versus Ag/Ag^+; $E_{1/2}$ ($FeCp_2/FeCp_2^+$) = 0.19 V). This result indicates that the ferrocene constituent(s) and the Zn porphyrins are electrically isolated from one another. In the case of **Zn-1**, the potentials for all three oxidations are shifted negatively by ~0.1 V. This shift is attributed to conjugative interactions that occur because the ferrocene is directly bound to the porphyrin.

The ferrocenyl Zn-porphyrins bearing the different linkers all form self-assembled monolayers (SAMs) on gold via in situ cleavage of the thioacetyl protecting group. The SAMs of all the ferrocenyl Zn porphyrins are electrochemically robust and exhibit three reversible oxidation waves. This is illustrated in Figure 1 which shows representative fast-scan (100 V/s) cyclic voltammograms of the SAMs of two ferrocenyl Zn porphyrins (**Zn-2** and **Zn-4**). The $E_{1/2}$ values for the ferrocenes and the Zn porphyrins in the SAMs are each shifted by ~0.15 V more positive than those observed in solution. This trend parallels that previously reported for SAMs of both ferrocenes[25] and porphyrins.[2] The observation that the voltammograms of the **Zn-2** and **Zn-4** SAMs are generally similar indicates that positioning the ferrocene substituents either on top of (**Zn-2**) or at the sides of (**Zn-4**) the porphyrin is a viable design for constructing multibit information storage elements. However, the former design offers the advantage of a smaller molecular area and therefore, a higher packing density.

Conclusions

Ferrocene has been the benchmark for a wide variety of electrochemical studies of self-assembled monolayers on electroactive surfaces. Most prior studies have employed ferrocene alkanethiols. The facile in situ deprotection of the *S*-acetyl and *S*-(*N*-ethylcarbamoyl) protecting groups on gold surfaces has motivated the synthesis of the corresponding thiol-protected ferrocene−porphyrins. Conditions giving no or minimal scrambling in aldehyde-dipyrromethane condensations facilitated the synthesis of the AB_2C-type ferrocene−porphyrin-thiol structures. A small set of ferrocene-aldehydes enabled the preparation of the corresponding ferrocene−porphyrins. Each ferrocene−porphyrin is designed for vertical organization on an electroactive surface yet possesses a distinct location of the ferrocene in the molecular architecture. Each of the ferrocene−porphyrins forms a SAM that exhibits robust, reversible electrochemistry. The electrochemical studies indicated that all of the architectures examined are potential candidates for multibit molecular information storage elements. Of particular interest are the writing/reading rates and the information retention of the various architectures. The comparison of ferrocene−porphyrin arrays of different architectural composition will provide a valuable assessment of the prospects for use of arrays comprised of multiple redox-active units for multibit information storage.

Experimental Section

General Methods. Sources of reagents, solvents, and chromatographic media are described in the preceding paper.[2] All reported NMR spectra were collected in $CDCl_3$ (^1H NMR at 300 MHz; ^{13}C NMR at 75 MHz). UV−vis absorption and fluorescence spectra were recorded in CH_2Cl_2 or toluene as described previously.[26] Porphyrin metalation was monitored by fluorescence emission and excitation spectroscopy. Melting points are uncorrected. Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix,[27] fast atom bombardment (FAB-MS, 10 ppm elemental compositional accuracy for the porphyrins), or electron-impact mass spectrometry (EI-MS). The synthesis of **6** is described in the Supporting Information.

1-(4-Ferrocenylphenyl)-2-(4-formylphenyl)acetylene (7). Following a general procedure,[28] samples of **8** (500 mg, 1.75 mmol), 4-iodobenzaldehyde (406 mg, 1.75 mmol), CuI (18 mg, 94 μmol) and $Pd(PPh_3)_2Cl_2$ (8 mg, 11 μmol) were reacted in the presence of THF (5 mL) and DIEA (5.0 mL) at 40 °C for 40 h on a Schlenk line. The mixture was then evaporated and the resulting orange solid was chromatographed (silica, CH_2Cl_2/hexanes, 1:1). The second orange band comprised the title compound (579 mg, 85%): mp 219−220 °C; ^1H NMR δ 4.10 (s, 5H), 4.42 (s, 2H), 4.73 (s, 2H), 7.52 (s, 4H), 7.72, 7.92 (AA′BB′, 2 × 2H), 10.07 (s, 1H); ^{13}C NMR δ 67.3, 70.3, 70.5, 84.6, 89.4, 94.8, 120.2, 126.6, 130.4, 130.6, 132.6, 132.7, 135.9, 141.6, 192.2; EI-MS obsd 390.0696 (M^+), calcd exact mass 390.0707. Anal. Calcd for $C_{25}H_{18}FeO$: C, 76.94; H, 4.65. Found: C, 76.75; H, 4.68.

Zn(II)-5-[4-(*S*-Acetylthio)phenyl]-15-ferrocenyl-10,20-dimesitylporphyrin (Zn-1). Following a general procedure,[22] samples of 5-mesityldipyrromethane (264 mg, 1.0 mmol), ferrocenecarboxaldehyde (107 mg, 0.50 mmol) and **10** (90 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (100 mL, undistilled) and then TFA (0.137 mL, 1.78 mmol) was added slowly over 30 s. The mixture was stirred at room temperature for 30 min, and then DIEA (0.31 mL, 1.8 mmol) was added followed by a solution of *p*-chloranil (370 mg, 1.5 mmol) in THF (20 mL) and the mixture was stirred at room temperature for a further 6

(25) Creager, S. E.; Rowe, G. K. *J. Electroanal. Chem.* **1994**, *370*, 203−211.
(26) (a) Li, F.; Gentemann, S.; Kalsbeck, W. A.; Seth, J.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Mater. Chem.* **1997**, *7*, 1245−1262. (b) Li, J.; Ambroise, A.; Yang, S.-Y.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927−8940.
(27) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99.
(28) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−628.

h. The reaction mixture was evaporated to one-third of its initial volume and then filtered through a silica pad (CH_2Cl_2/hexanes, 1:1). The filtrate was chromatographed (silica, CH_2Cl_2/hexanes, 3:7; then 1:1). The second green band contained the title porphyrin (188 mg, ~95% pure). LD-MS obsd 945.6, 961.8 [$M^+ + 15$], 905.4 [$M^+ - CH_3CO$], impurities 762.7 and 1096.8; FAB-MS obsd 880.2839, calcd exact mass 880.2898 ($C_{56}H_{46}N_4OSZnFe$); λ_{abs} (CH_2Cl_2) 422, 510, 602 nm. A solution of crude free base porphyrin (100 mg) in CH_2Cl_2 (30 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (498 mg, 2.27 mmol) in methanol (15 mL) and the mixture was stirred for 16 h. After metalation was complete (TLC), the reaction mixture was washed with water and dried (Na_2SO_4), filtered, concentrated, and chromatographed (silica, CH_2Cl_2/hexanes, 6:4) to give the pure title compound (91 mg, 37% overall yield): ^{1}H NMR δ 1.87 (s, 12H), 2.57 (s, 3H), 2.67 (s, 6H), 4.24 (s, 5H), 4.79 (s, 2H), 5.52 (s, 2H), 7.31 (s, 6H), 7.77, 8.28 (AA′BB′, 2 × 2H), 8.7−8.9 (m, 6H), 10.17 (m, 2H); LD-MS obsd 945.6, 961.8 [$M^+ + 15$], 905.4 [$M^+ - CH_3CO$]; FAB-MS obsd 942.2073, calcd exact mass 942.2033 ($C_{56}H_{46}N_4OSZnFe$); λ_{abs} (CH_2Cl_2) 423, 563, 616 nm.

Zn(II)-5-[4-[*S*-(*N*-Ethylcarbamoyl)thio]phenyl]-15-(4-ferrocenylphenyl)-10,20-dimesitylporphyrin (Zn-2). Following a general procedure,[22] samples of 5-mesityldipyrromethane (264 mg, 1.0 mmol), **6** (145 mg, 0.50 mmol) and **9** (105 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (100 mL, undistilled) and then TFA (0.137 mL, 1.78 mmol) was added slowly over 30 s. The mixture was stirred at room temperature for 30 min, and then DIEA (0.30 mL, 1.8 mmol) was added followed by a solution of *p*-chloranil (370 mg, 1.5 mmol) in THF (20 mL) and the mixture was stirred at room temperature for a further 6 h. The reaction mixture was concentrated and chromatographed (silica, CH_2Cl_2/hexanes, 1:1). The dark purple solid was subsequently chromatographed (silica, CH_2Cl_2/hexanes, 7:3; then CH_2Cl_2). The second purple band ($R_f = 0.54$) contained the title porphyrin together with some blue impurities. A subsequent column chromatography procedure did not improve the product purity (101 mg, ~95% pure). LD-MS obsd 988.6, 917.4 [$M^+ - CH_3CH_2NHCO$], impurity 850.0; FAB-MS obsd 985.3434, calcd exact mass 985.3477 ($C_{63}H_{55}N_5OSFe$); λ_{abs} (CH_2Cl_2) 419, 517, 553, 593, 648 nm; λ_{abs} 653, 720 nm. A solution of crude free base porphyrin (17 mg) in CH_2Cl_2 (15 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (380 mg, 1.73 mmol) in methanol (10 mL), and the mixture was stirred at room temperature under argon. TLC analysis (silica, CH_2Cl_2) after 6 h showed no starting material (expected $R_f = 0.58$) and the presence of two new components ($R_f = 0.51$, $R_f = 0.91$). The reaction was stopped by adding 100 mL of saturated aqueous $NaHCO_3$ and 20 mL of CH_2Cl_2. The aqueous solution was extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were dried (Na_2SO_4) and concentrated, and the residue was chromatographed (silica, CH_2Cl_2). The red band was collected and evaporated, affording the pure title compound (16 mg, 19% overall yield): ^{1}H NMR 1.30 (t, $J = 7.0$ Hz, 3H), 1.84 (s, 12H), 2.64 (s, 6H), 3.4−3.6 (m, 2H), 4.24 (s, 5H), 4.47 (s, 2H), 4.91 (s, 2H), 5.60 (s, 1H), 7.29 (s, 4H), 7.84, 8.15 (AA′BB′, 2 × 2H), 7.92, 8.28 (AA′BB′, 2 × 2H), 8.7−9.1 (m, 8H); LD-MS obsd 1051.2, 979.0 [$M^+ - CH_3CH_2NHCO$]; FAB-MS obsd 1047.2625, calcd exact mass 1047.2612 ($C_{63}H_{53}N_5OSZnFe$); λ_{abs} (CH_2Cl_2) 424, 552, 593 nm; λ_{abs} 610, 650 nm.

5-[4-[*S*-(*N*-Ethylcarbamoyl)thio]phenyl]-15-[4-[2-(4-ferrocenylphenyl)ethynyl]phenyl]-10,20-dimesitylporphyrin (3). Samples of 5-mesityldipyrromethane (264 mg, 1.0 mmol), **7** (195 mg, 0.50 mmol) and **9** (105 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (100 mL) and then TFA (0.137 mL, 1.78 mmol) was added slowly over 30 s. The reaction mixture was stirred at room temperature for 30 min, and then DIEA (0.3 mL, 1.8 mmol) was added followed by a solution of *p*-chloranil (370 mg, 1.5 mmol) in THF (20 mL) and the mixture was stirred at room temperature for a further 6 h. The reaction mixture was evaporated to one-third of its initial volume and filtered through a silica pad (CH_2Cl_2/hexanes, 1:1). Fractions containing the second purple band were collected and chromatographed (silica, CH_2Cl_2/hexanes, 1:1; then CH_2Cl_2) to afford a slightly impure product. A second column (silica, CH_2Cl_2) afforded the pure title porphyrin (56 mg, 10%): ^{1}H NMR δ −2.55 (s, 2H); 1.31 (t, $J = 7.2$ Hz, 3H), 1.90 (s, 12H), 2.68 (s, 6H), 3.51 (m, 2H), 4.12 (s, 5H), 4.40 (s, 2H), 4.73 (s, 2H), 5.61 (brt, $J = 6$ Hz, 1H), 7.34 (s, 6H), 7.56, 7.64 (AA′BB′, 2 × 2H), 7.9−8.4 (m, 8H), 8.7−9.0 (m, 8H); LD-MS obsd 1089.0, 1018.0 [$M^+ - CH_3CH_2NHCO$]; FAB-MS obsd 1085.3766, calcd exact mass 1085.3790 ($C_{71}H_{59}N_5OSFe$); λ_{abs} (CH_2Cl_2) 422, 516, 551, 590, 647 nm.

Zn(II)-5-[4-[*S*-(*N*-Ethylcarbamoyl)thio]phenyl]-15-[4-[2-(4-ferrocenylphenyl)ethynyl]phenyl]-10,20-dimesitylporphyrin (Zn-3). A solution of porphyrin **3** (43 mg, 40 μmol) in CH_2Cl_2 (20 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (430 mg, 1.95 mmol) in methanol (15 mL) and the mixture was stirred for 16 h. After metalation was complete, the reaction mixture was washed with water, dried (Na_2SO_4), filtered, concentrated, and chromatographed (silica, CH_2Cl_2) affording a purple solid (32 mg, 70%): ^{1}H NMR δ 1.30 (t, $J = 7.2$ Hz, 3H), 1.87 (s, 12H), 2.67 (s, 6H), 3.4−3.6 (m, 2H), 4.10 (s, 5H), 4.39 (s, 2H), 4.73 (s, 2H), 5.57 (brs, 1H), 7.32 (s, 6H), 7.54, 7.62 (AA′BB′, 2 × 2H), 7.9−8.4 (m, 8H), 8.7−9.0 (m, 8H); LD-MS obsd 1154.0, 1082.7 [$M^+ - CH_3CH_2NHCO$]; FAB-MS obsd 1147.2724, calcd exact mass 1147.2925 ($C_{71}H_{59}N_5OSFe$); λ_{abs} (CH_2Cl_2) 423, 549 nm.

5-(4-Ferrocenylphenyl)dipyrromethane (12). Following a general procedure,[23] pyrrole (3.00 mL, 43.2 mmol) and **6** (0.50 g, 1.7 mmol) were added to a 25 mL flask and degassed with a stream of argon. Then TFA (13.0 μL) was added and the mixture was stirred under argon at room temperature for 10 min and then quenched with 0.1 M NaOH. Ethyl acetate was then added, and the phases were separated. The organic phase was washed with water, dried (Na_2SO_4), and concentrated to afford an orange oil. The oil was chromatographed using centrifugal preparative TLC (silica, CH_2Cl_2/hexanes, 1:1) to afford a yellow oil (660 mg, 94%): ^{1}H NMR δ 4.19 (s, 5H), 4.45 (s, 2H), 4.75 (s, 2H), 5.45 (s, 1H), 6.05 (s, 2H), 6.30 (m, 2H), 6.71 (m, 2H), 7.22, 7.53 (AA′BB′, $J = 8.5$ Hz, 2 × 2H), 7.94 (brs, 2H); ^{13}C NMR δ 61.3, 67.4, 69.8, 70.5, 86.0, 108.1, 109.1, 118.2, 127.1, 129.3, 133.5, 138.6, 140.6; EI-MS obsd 406.1144, calcd exact mass 406.1132 ($C_{25}H_{22}N_2Fe$).

Zn(II)-5-[4-(*S*-acetylthio)phenyl]-10,20-bis(4-ferrocenylphenyl)-15-[4-methylphenyl]porphyrin (Zn-4). Following a general procedure,[22] acetonitrile (50 mL) was degassed with a stream of Ar for 10 min. Freshly ground NH_4Cl (268 mg, 5.00 mmol) was added, and the flask was placed in an ice-bath and cooled under Ar. Samples of **12** (203 mg, 0.50 mmol), 4-methylbenzaldehyde (30 μL, 0.25 mmol) and **10** (45 mg, 0.25 mmol) were added, followed by BF_3−etherate (7.0 μL, 0.055 mmol), and the mixture was stirred at 0 °C under Ar. After 6 h, DIEA (10 μL, 0.055 mmol) was added followed by a solution of *p*-chloranil (185 mg, 0.75 mmol) in THF (30 mL). The ice bath was removed and the mixture was stirred overnight at room temperature. Removal of the solvent gave a black solid which was chromatographed (silica, CH_2Cl_2/hexanes, 1:1). The first band was collected and chromatographed further (silica, CH_2Cl_2/hexanes 7:3, then CH_2Cl_2). The second purple band from the second column contained the title porphyrin (29 mg). LD-MS obsd 1075.1; FAB-MS obsd 1070.2435, calcd exact mass 1070.2404 ($C_{67}H_{50}N_4Fe_2OS$). The crude free base porphyrin in CH_2Cl_2 was treated with methanolic $Zn(OAc)_2 \cdot 2H_2O$ (595 mg, 2.7 mmol) and the mixture was stirred overnight at room temperature. The reaction mixture was washed with water, dried, concentrated, and chromatographed (silica, CH_2Cl_2/hexanes), affording the pure title compound (8.8 mg, 3.1% overall yield): ^{1}H NMR δ 2.60 (s, 3H), 2.72 (s, 3H), 4.26 (s, 5H), 4.49 (s, 2H), 4.94 (s, 2H), 7.5−8.4 (m, 4 × AA′BB′, 16H), 8.95−9.10 (m, 8H); LD-MS obsd 1138.7, 1153.9 [$M^+ + 15$], 1095.5 [$M^+ - CH_3CO$], 966.0; FAB-MS obsd 1132.1526, calcd exact mass 1132.1529 ($C_{67}H_{48}N_4Fe_2OS$); λ_{abs} (CH_2Cl_2) 421, 551 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.[2] 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 ^1H NMR spectra of all porphyrins; ^1H NMR and ^{13}C NMR spectra for **12**. Experimental procedure for the synthesis of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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