# Synthesis of "Porphyrin-Linker-Thiol" Molecules with Diverse Linkers for Studies of Molecular-Based Information Storage

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The attachment of redox-active molecules such as porphyrins to an electroactive surface provides an attractive approach for electrically addressable molecular-based information storage. Porphyrins are readily attached to a gold surface via thiol linkers. The rate of electron transfer between the electroactive surface and the porphyrin is one of the key factors that dictates suitability for molecular-based memory storage. This rate depends on the type and length of the linker connecting the thiol unit to the porphyrin. We have developed different routes for the preparation of thiol-derivatized porphyrins with eight different linkers. Two sets of linkers explore the effects of linker length and conjugation, with one set comprising phenylethyne units and one set comprising alkyl units. One electron-deficient linker has four fluorine atoms attached directly to a thiophenyl unit. To facilitate the synthesis of the porphyrins, convenient routes have been developed to a wide range of aldehydes possessing a protected *S*-acetylthio group. An efficient synthesis of 1-(*S*-acetylthio)-4-iodobenzene also has been developed. A set of porphyrins, each bearing one *S*-acetyl-derivatized linker at one meso position and mesityl moieties at the three remaining meso positions, has been synthesized. Altogether seven new aldehydes, eight free base porphyrins and eight zinc porphyrins have been prepared. The zinc porphyrins bearing the different linkers all form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetyl protecting group. The SAM of each porphyrin is electrochemically robust and exhibits two reversible oxidation waves.

## Introduction

We recently reported an approach for molecular-based memory storage that employs a monolayer of redox-active molecules attached to an electroactive surface.[1] Information is stored in the distinct oxidation states of the redox-active molecules. Multiple bits of information can be stored through the use of molecules or molecular arrays that afford a set of distinct oxidation states. Writing and reading information in the molecules is accomplished electrically at room temperature under real-world conditions. This molecular-based approach differs from the use of semiconductor technology or disk drives for information storage and is anticipated to provide a much higher storage density.

This molecular-based information storage approach has an absolute requirement for reversible electrochemical writing and reading processes. While information can in principle be stored either in cationic or anionic states, we have chosen to work with molecules that afford reversible interconversion among neutral and cationic states due to the greater stability of cations versus anions under ambient conditions. Among the molecules considered for information storage, porphyrinic molecules stand out for the following reasons. (1) Porphyrins provide three accessible oxidation states, the neutral state, monocation, and dication. Porphyrins form stable radical cations and dications and undergo reversible electrochemistry.[2] (2) The electrochemical potential of a porphyrin can be tuned over a large range (>0.5 V) by choice of central metal[3] and peripheral substituents.[4] (3) The use of arrays comprising multiple porphyrins (and other redox-active moieties) with distinct oxidation potentials affords the possibility of storing a large number of bits in a single memory cell. (4) The methodology for synthesizing porphyrin monomers[5] and multiporphyrin arrays,[6] while far from mature, has been developed sufficiently for explora-

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tion of the basic concepts in this approach toward molecular information storage. No other class of molecules appears to offer such a rich set of possibilities for information storage applications.

A host of scientific issues has emerged from consideration of this basic concept of electrically addressable molecular-based information storage. How is the rate of writing and reading information affected by the nature of the linker that attaches the redox-active molecule to the surface? What molecular features (e.g., linker length and composition, nature of the redox-active unit, 3-dimensional architecture) affect the retention of charge necessary for information storage? What is the maximum number of bits that can be stored in a molecular array? Do different oxidation states in a given molecule exhibit different charge retention properties?

To begin addressing the above-noted fundamental scientific questions, we have synthesized several families of porphyrinic molecules and examined the electrochemical behavior of the molecules self-assembled on gold via the thiol unit. While there is a sizable literature concerning self-assembled monolayers (SAMs) of thiol-derivatized porphyrins on gold electrodes,[7−22] families of such porphyrins suitable for systematic studies have heretofore not been available. Our studies of the thiol-derivatized porphyrins are reported herein and in the four accompanying papers. This first paper describes thiol-derivatized porphyrins containing diverse linkers designed to explore how the linker affects the rates of writing and reading as well as duration of information storage (i.e., retention). The second paper describes a set of weakly coupled thiol-derivatized ferrocene-porphyrin arrays for studies of multibit information storage with different types of redox-active units.[23] The third paper describes weakly coupled multiporphyrin arrays for multibit information storage.[24] The fourth and fifth papers describe tightly coupled multiporphyrin arrays[25] and lanthanide porphyrinic triple-decker sandwich complexes,[26] respectively, also for multibit information storage.

The studies reported in this first paper build from the methods we have previously described for the synthesis of thiol-derivatized porphyrin monomers for studies of molecular-based information storage.[27] In this previous work, porphyrins bearing one thiol group were designed for vertical organization on a gold surface, while porphyrins bearing two or four thiol groups were designed for horizontal arrangement on a gold surface. The redox potentials were tuned through variation in the meso substituents and/or the central metal. The different meso substituents can also give rise to altered packing patterns of the molecules in a self-assembled monolayer (SAM). Thiol protecting groups were examined for compatibility with the reactions for porphyrin formation, metal insertion, Pd-mediated coupling to form multiporphyrin arrays, and in situ deprotection on a gold surface. The *S*-acetylthio protecting group gave the best overall results (including in situ cleavage on gold) and has been used in almost all of our subsequent work.

The synthetic methodology described above is used herein to prepare a set of porphyrins, each bearing one thioacetate group and three mesityl groups. These molecules are designed for vertical organization on a gold surface. The prototypical example, synthesized in our previous work,[27] incorporates a thiol-derivatized *p*-phenylene unit (linker A, Chart 1). This molecule binds to a gold electrode and exhibits facile electronic communication with the gold surface.[1] The *p*,*p*′-diphenylethyne unit (linker B) increases the distance of the porphyrin from the gold surface, potentially slowing writing/reading rates, though linkers of this type are known to provide efficient hole transport.[28] A similar structure with one additional methylene unit (linker C) provides a test of whether a conjugated connection (e.g., a direct thiophenyl attachment) is essential. An electron-deficient *p*-phenylene linker is provided by linker D. The effects of a progressive increase in the alkyl character of the linker can be examined by comparison of linkers A, E, F, G, and H. Finally, an ethynylphenyl linker (I) is employed to achieve direct conjugation to the porphyrin.[29] A systematic investigation of these porphyrins as memory storage entities will be reported elsewhere.

## Results and Discussion

A large number of porphyrin monomers bearing free thiols or *S*-acetyl-derivatized thiols have been prepared.[7,9,12,14,22,27,30−36] The traditional method of synthesis

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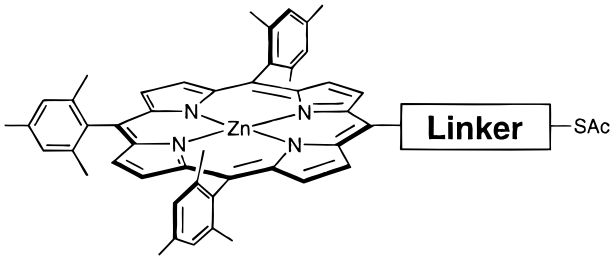
**Chart 1**





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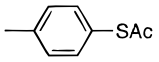
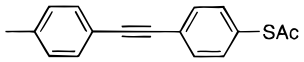
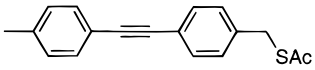
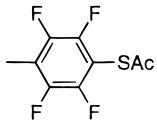
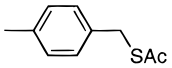
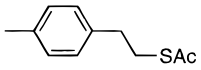
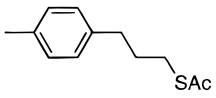
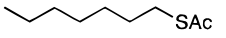
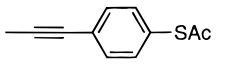
| A |  | ref. 27 |
| B |  | Zn-19 |
| C |  | Zn-20 |
| D |  | Zn-21 |
| E |  | Zn-22 |
| F |  | Zn-23 |
| G |  | Zn-24 |
| H |  | Zn-25 |
| I |  | Zn-26 |

involves the derivatization of a substituted porphyrin with a thiol reagent or protected thiol unit. The emergence of mild conditions for preparing porphyrins has made possible those strategies where sensitive or elaborate substituents are incorporated in the aldehyde precursor to the porphyrin.[5,37,38] This latter approach has been explored using *S*-acetyl-protected thio-derivatized benzaldehydes, which are converted to the respective porphyrin with the protecting group intact.[22,27,30,36] The advantages of introducing the *S*-acetylthio moiety at the aldehyde stage are as follows. (1) Synthetic manipulation of the porphyrins is minimized. (2) The polarity imparted by the *S*-acetylthio moiety facilitates separation of the desired porphyrin from a mixed aldehyde condensation. (3) Purification of the mixture formed upon thiol introduction is often more straightforward at the aldehyde rather than the porphyrin stage. For those molecules where the linker is constructed using a Pd-mediated coupling reaction (e.g., diphenylethyne), the reaction conditions for use with aldehydes (high concentration, inclusion of CuI) afford superior results compared with those with porphyrins.[39] Thus, we have opted to introduce the *S*-acetyl-protected thiol unit at the aldehyde stage throughout this work.

**Synthesis of Aldehydes.** The synthesis of aldehydes possessing a thioacetate group required several different approaches. Five of the aldehydes possess an alkanethiol unit, and three contain an aryl thiol unit. The former are usually obtained by straightforward reaction of an alkyl halide and a thiol reagent (thioacetate, thiourea), while the latter (S-protected or free thiol form) are often obtained with more difficulty. The few known methods for preparing aryl thiols, from aryl sulfides or aryl halides, generally require harsh conditions. Thus, we searched for other approaches for incorporating the *S*-acetyl group in arenes. The *S*-acetyl group is compatible with a variety of reaction conditions, including those in porphyrin formation and Pd-mediated iodoethyne couplings,[27] but is labile in the presence of some bases (e.g., triethylamine, alumina) if attached to an arene.

The structure of the aldehyde bearing linker B suggested an obvious method of synthesis via Pd-coupling of 4-iodobenzaldehyde with 1-(*S*-acetylthio)-4-ethynylbenzene (**3**) (Scheme 1). The synthesis of compound **3** requires 1-(*S*-acetylthio)-4-iodobenzene (**1**). We found that the reported procedures[40,41] for preparing **1** required tedious purification. In searching for a more efficient pathway to this key molecule, the selective transformation of 1-fluoro-4-iodobenzene into 1-(*S*-acetylthio)-4-iodobenzene using conditions developed by Tiecco and coworkers[42] was attempted. However, we obtained an inseparable mixture of products, regardless of the temperature and the amount of MeSNa used. Sita and coworkers converted pipsyl chloride (4-iodobenzenesulfonyl chloride) to 1-iodo-4-mercaptobenzene.[43] We adopted this attractive route but with the use of the nonaqueous conditions for reduction of sulfonyl chlorides recently reported by Uchiro and Kobayashi,[44] thereby obtaining a much higher yield. Thus, pipsyl chloride was successfully reduced to 1-iodo-4-mercaptobenzene which upon treatment in situ with acetyl chloride gave the desired

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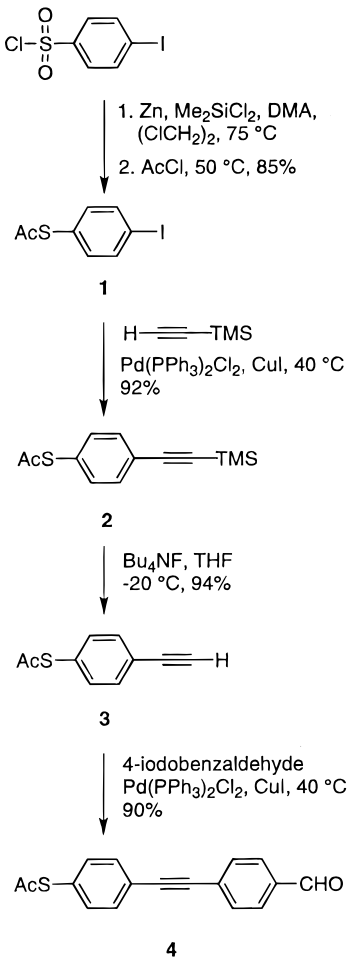
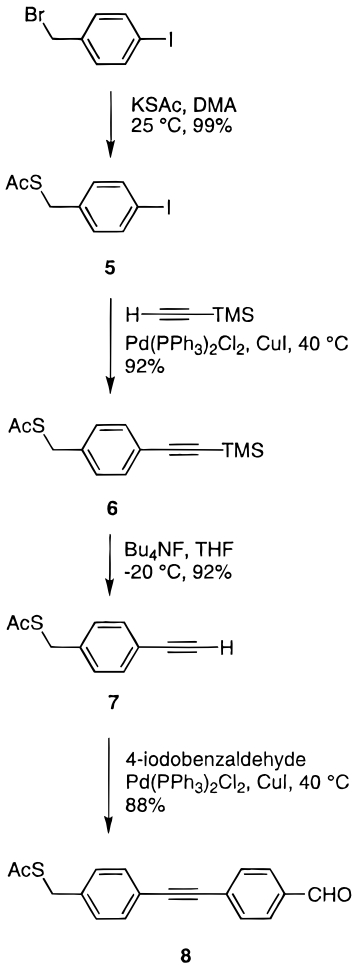
**Scheme 1**



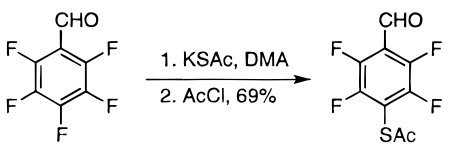

**Scheme 2**




1-(*S*-acetylthio)-4-iodobenzene (**1**, 85%) after straightforward chromatographic purification. The zinc chloride formed in the first step is a likely catalyst of the acylation in the second step. The iodobenzene **1** obtained in this manner was successfully converted into the ethyne derivative **3** using established procedures.[40,41] The Pd-mediated coupling of **3** and 4-iodobenzaldehyde smoothly afforded aldehyde **4** in 90% yield. As noted by Sita and co-workers,[41] it is essential to use a hindered amine such as *N*,*N*-diisopropylethylamine (DIEA) instead of triethylamine to obtain satisfactory yields in all Pd-coupling reactions involving the *S*-acetylthiophenyl group.

The synthesis of aldehyde **8** proceeded along a similar strategy (Scheme 2). Treatment of 1-(bromomethyl)-4-iodobenzene with thioacetate under very mild conditions[45] gave **5**, which upon Pd-coupling with trimethylsilylacetylene afforded the building block bearing two protecting groups (**6**). Deprotection of the TMS group in **6** gave **7**, which upon Pd-mediated coupling with 4-iodobenzaldehyde furnished aldehyde **8**. Each reaction in this sequence afforded high yields.

The next target aldehyde was 4-(*S*-acetylthio)-2,3,5,6-tetrafluorobenzaldehyde (**9**) (eq 1). The fluorine atom in




(eq 1)

**9**

the para position of pentafluorobenzenes is known to be very reactive toward nucleophilic substitution. Indeed, pentafluorophenyl-substituted porphyrins were recently reported to undergo fluoro-substitution by alkanethiols.[34,35] Thus, treatment of pentafluorobenzaldehyde with thioacetate (using conditions resembling those used in the reaction of potassium thioacetate with benzyl halides) resulted in disappearance of the substrate, and the only product was a very polar substance which bound at the origin upon TLC analysis (silica, $CH_2Cl_2$). We surmised that the latter might be the anion of 2,3,5,6-tetrafluoro-4-mercaptobenzaldehyde (formed by thioester cleavage following nucleophilic substitution), and upon treatment with acetyl chloride the desired aldehyde **9** was obtained in 69% yield after chromatography.

The synthesis of aldehyde **10** was accomplished using the strategy previously reported for 3-(*S*-acetylthiomethyl)benzaldehyde.[27] Reduction of the commercially available 4-(bromomethyl)benzonitrile with DIBALH gave the corresponding 4-(bromomethyl)benzaldehyde.[33,46,47] Substitution of the bromide with potassium thioacetate gave the desired *S*-acetyl-protected thiobenzaldehyde **10** in good yield (eq 2).

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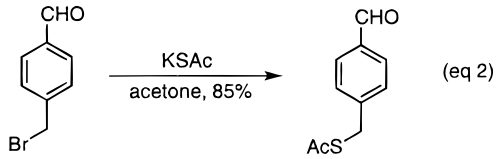
(46) Bookser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 4208−4218.

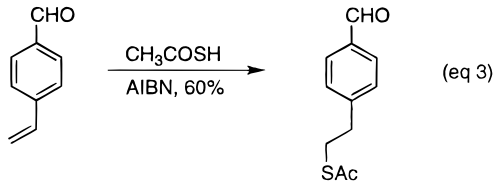
(47) The reduction was performed according to the procedure for the synthesis of 3-(bromomethyl)benzaldehyde. See: Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 6755−6790.




(eq 2)

**10**

Aldehyde **11** was synthesized by radical addition[48] of thioacetic acid to 4-vinylbenzaldehyde[49] (eq 3).

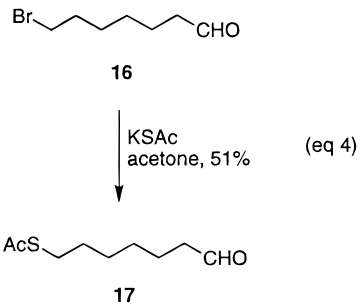



(eq 3)

**11**

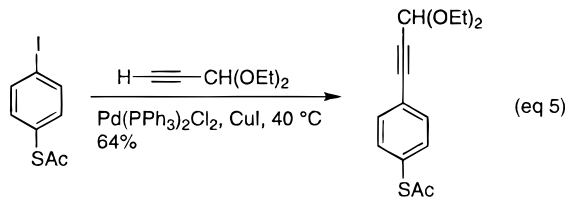
The homologous propyl aldehyde **15** was synthesized starting from 4-bromobenzaldehyde (Scheme 3). Protection of the carbonyl group as the cyclic acetal **12**[50] and conversion to the corresponding Grignard reagent followed by addition of allyl bromide furnished intermediate **13**. Radical addition of thioacetic acid afforded acetal **14**, which was easily hydrolyzed to the respective aldehyde **15** (overall yield 18% from 4-bromobenzaldehyde).

The aliphatic aldehyde **17** was accessed via the same procedure used for aldehyde **10**. Aldehyde **16** was prepared by reduction of 7-bromoheptanitrile with 1 equiv of DIBALH (~50% yield) or by oxidation of 7-bromo-1-heptanol with PCC (82% yield).[51] Treatment of crude aldehyde **16** with potassium thioacetate afforded aldehyde **17** as a yellow oil in 51% yield (eq 4).




(eq 4)

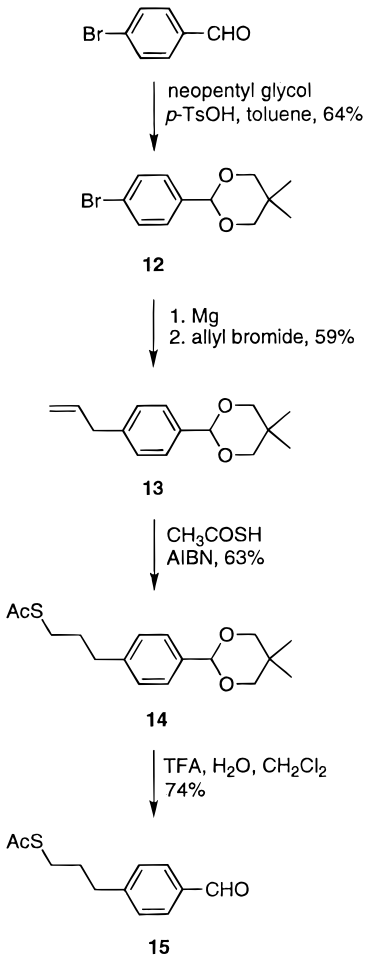
One approach for the synthesis of porphyrin **26** involves the preparation of 3-[4-(*S*-acetylthio)phenyl]propynal followed by mixed-aldehyde condensation, rather than attempting the Pd-mediated coupling of an iodo or ethynyl porphyrin. Due to the instability of propynal, we performed a Pd-coupling of commercially available propiolaldehyde diethylacetal with 1-(*S*-acetylthio)-4-iodobenzene (**1**) (eq 5). The desired acetal **18** was obtained in 64% yield.




(eq 5)

**1** **18**

**Scheme 3**




It is noteworthy that in each strategy employed, the *S*-acetyl protecting group and the sulfur atom were incorporated in one step, or the thiol unit was protected in situ with an acetyl group. In so doing, the handling of free thiols was avoided while working with a wide range of thiol-derivatized compounds.

**Synthesis of Porphyrins.** The investigation of porphyrins oriented in a vertical manner on an electroactive surface can be achieved by the synthesis of porphyrins bearing a *p*-thioaryl or *ω*-thioalkyl unit at one meso position. Such $A_3B$-porphyrins were prepared by a mixed-aldehyde condensation in a two-step, one-flask synthesis procedure. The conditions for condensation of pyrrole and mesitaldehyde require $BF_3$−ethanol cocatalysis, with optimal reaction occurring in the presence of increased $BF_3$−etherate concentration (but not ethanol) as the concentrations of pyrrole and aldehyde are increased.[52] Nonsterically hindered aldehydes also undergo condensation with pyrrole in the presence of $BF_3$−ethanol cocatalysis.[5] A mixed-aldehyde condensation of mesitalde-

(48) Lub, J.; Broer, D. J.; van den Broek, N. *Liebigs Ann. Recueil* **1997**, 2281−2288.

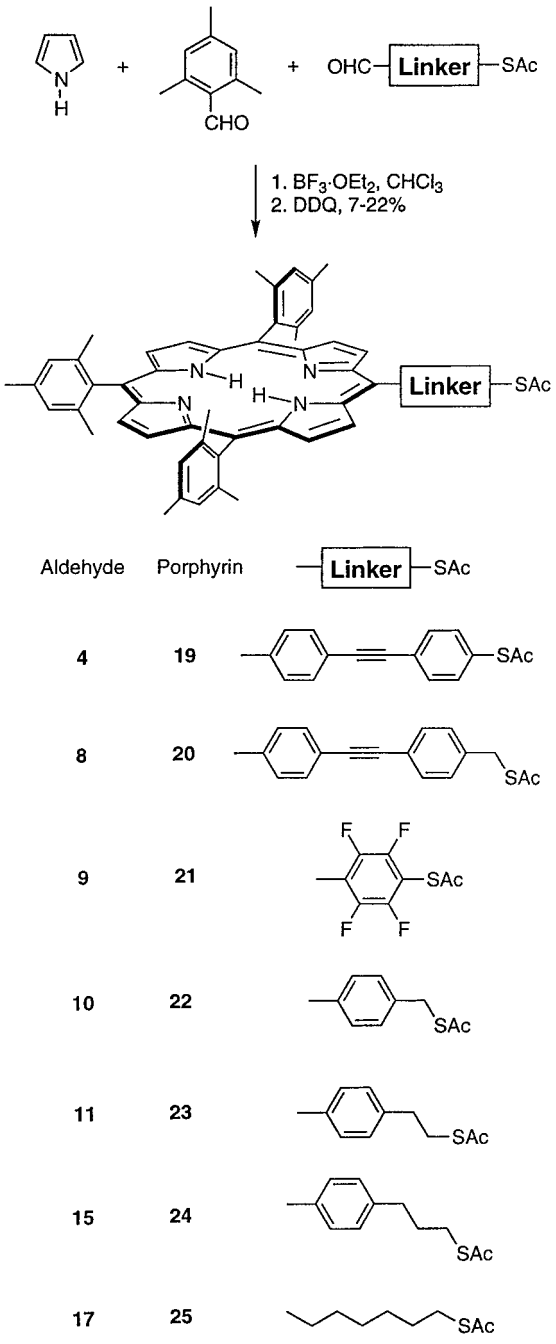
(49) Vinyl benzaldehyde was synthesized by the procedure of Ren, J.; Sakakibara, K.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1897−1902 with the following changes: The addition of DMF was performed at a 38 mmol scale at 0 °C. Purification by column chromatography (silica, $Et_2O$/hexanes, 1:3) afforded 4-vinylbenzaldehyde in 60% yield.

(50) Hewlins, M. J. E.; Jackson, A. H.; Long, A.; Oliveira-Campos, A.; Shannon, P. V. R. *J. Chem. Res., Miniprint* **1986**, *8*, 2645−2696.

(51) Enders, D.; Bartzen, D. *Liebigs Ann. Chem.* **1991**, 569−574.

(52) Wagner, R. W.; Li, F.; Du, H.; Lindsey, J. S. *Org. Proc. Res. Dev.* **1999**, *3*, 28−37.

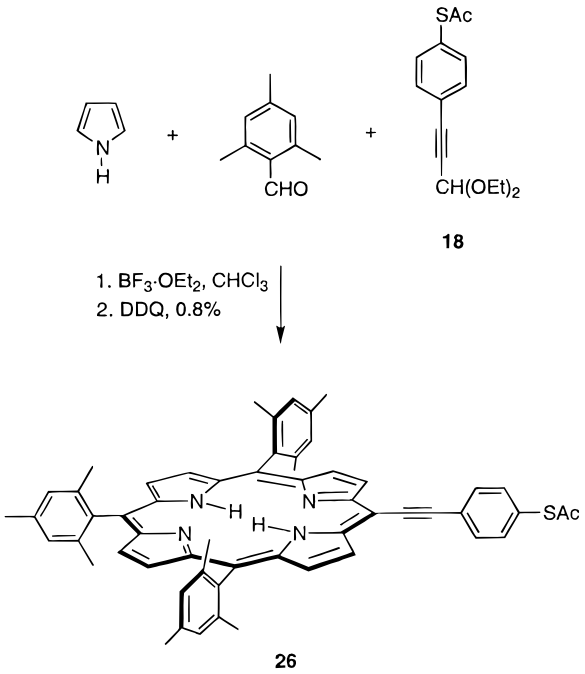
**Scheme 4**




hyde, a thiol-protected aldehyde, and pyrrole afforded a mixture of porphyrins, from which the desired thiol-protected $A_3B$-porphyrin was obtained by chromatography. The polarity imparted by the thioacetate group facilitated separation of the mixture of free base porphyrins.

In this manner, aldehydes **4**, **8**−**11**, **15**, and **17** were converted to the thiol-protected $A_3B$-porphyrins **19**−**25**, respectively, in yields of 7−22% (Scheme 4). It is noteworthy that purification of most of the porphyrins was achieved by silica pad filtration followed by one column chromatography (or centrifugal preparative TLC) operation. This same approach was applied to acetal **18**, but the yield of the desired $A_3B$ porphyrin was only 0.8% (Scheme 5). We attribute the low yield in part to the competitive Michael reaction of pyrrole and the activated alkyne. Ethynyl aldehydes are well-known to present

**Scheme 5**




difficulties in conversion to the porphyrin.[5] The corresponding zinc chelates **Zn-19**−**Zn-26** were obtained by reaction of the free base porphyrins **19**−**26** with $Zn(OAc)_2{\cdot}2H_2O$ (Chart 1). In each case, zinc insertion occurred without altering the thiol protecting group.

**Electrochemical Studies.** The electrochemical behavior of the Zn-porphyrins was investigated for samples both in solution and self-assembled on gold. The solution electrochemistry of each of the porphyrins is similar to that previously reported for other aryl-substituted Zn-porphyrins.[2] In particular, each porphyrin exhibits two reversible oxidation waves. The $E_{1/2}$ values for all the porphyrins in solution are similar to one another ($E_{1/2}(1)$ ~0.58 V; $E_{1/2}(2)$ ~0.86 V; versus $Ag/Ag^+$; $E_{1/2}(FeCp_2/FeCp_2^+) = 0.19$ V), with the exception of **Zn-21** and **Zn-26**. The $E_{1/2}$ values for **Zn-21** are shifted ~0.1 V more positive due to fluorination of one of the porphyrin aryl groups. The $E_{1/2}$ values for **Zn-26** are shifted ~0.1 V more negative due to the presence of the conjugating meso-alkynyl group. The porphyrins bearing the different linkers all form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetyl protecting group. The SAM of each of the porphyrins is electrochemically robust and exhibits two reversible oxidation waves. Representative fast-scan (100 V/s) cyclic voltammograms of the **Zn-20** SAM and **Zn-23** SAM are shown in Figure 1. The voltammograms of the other Zn-porphyrins are similar (not shown). As can be seen, the two oxidation waves of the Zn-porphyrin SAMs are well resolved, as is the case for the Zn-porphyrins in solution (not shown). However, the two $E_{1/2}$ values of the **Zn-20** and **Zn-23** SAM are each shifted ~0.10−0.15 V more positive than those observed in solution. This same behavior is observed for the SAMs of the other Zn-porphyrins. The positive shifts in redox potentials observed upon formation of the porphyrin SAMs are consistent with the results of previous experiments on other electroactive species (e.g., thiol-derivatized ferrocenes) on gold.[53] Knowledge of such shifts in potential is essential for the rational

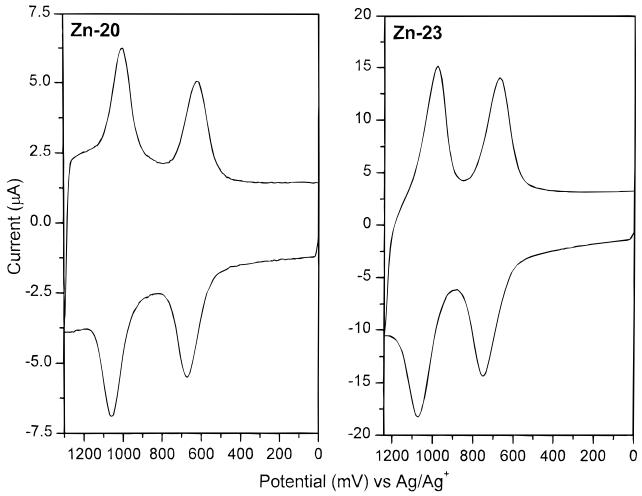



**Figure 1.** Fast-scan (100 V/s) voltammetry of the **Zn-20** SAM (left panel) and the **Zn-23** SAM (right panel).

design of molecular architectures for multibit information storage.[23−26]

## Conclusions

The introduction of an *S*-acetyl-protected thiol unit in an aldehyde enables the corresponding porphyrin to be prepared without handling free porphyrin thiols. The combination of a few simple strategies provided access to a broad range of thiol-derivatized aldehydes. A set of porphyrins has been prepared for vertical organization via one linker on an electroactive surface. The *S*-acetyl protecting group cleaves in situ when the porphyrin contacts a gold surface. The porphyrins form SAMs that exhibit robust, reversible electrochemistry. Collectively, the studies indicated that all of the linker architectures examined are potential candidates for molecular information storage elements. This synthetic work now makes possible a systematic examination of the effects of diverse linker architectures on information storage properties, including writing rate, reading rate, and information retention. The results from such studies on linkers will be incorporated with studies on multibit architectures described in the companion papers[23−26] in an effort to design more sophisticated molecular information storage systems.

## Experimental Section

**General Methods.** All chemicals obtained commercially were used as received unless otherwise noted. Reagent-grade solvents ($CH_2Cl_2$, $CHCl_3$, hexanes, diethyl ether, acetone) and HPLC-grade solvents (acetonitrile, toluene) were used as received from Fisher. THF was distilled from sodium. Pyrrole and triethylamine were each distilled from $CaH_2$. All reported NMR spectra were collected in $CDCl_3$ ($^1$H NMR at 300 MHz; $^{13}$C NMR at 75 MHz) unless noted otherwise. UV−vis absorption and fluorescence spectra were recorded in $CH_2Cl_2$ or toluene as described previously.[54] Melting points are uncorrected. Flash chromatography was performed on flash silica (Baker, 200−400 mesh) or alumina (Fisher, 80−200 mesh). Centrifugal preparative thin-layer chromatography was performed using a Harrison Research Chromatotron (Palo Alto, CA). Mass spectra were obtained via laser desorption (LD-MS) in the absence of an added matrix,[55] fast atom bombardment (FAB-MS, 10 ppm elemental compositional accuracy for the porphyrins), or electron-impact mass spectrometry (EI-MS). ACS-grade chloroform (containing 0.75% ethanol) was used in all porphyrin-forming reactions. Porphyrin metalation was monitored by fluorescence emission and excitation spectroscopy. 4-Iodobenzaldehyde and 1-bromomethyl-4-iodobenzene were obtained from Karl Industries, Ltd.

**1-(*S*-Acetylthio)-4-iodobenzene (1).** Following a general procedure,[44] to a stirred suspension of zinc powder (3.80 g, 58.0 mmol) and dichlorodimethylsilane (7.00 mL, 58.0 mmol) in 1,2-dichloroethane (126 mL) was added a solution of 4-iodobenzenesulfonyl chloride (5.00 g, 16.5 mmol) and *N*,*N*-dimethylacetamide (4.60 mL, 50.0 mmol) in dichloroethane (126 mL). The mixture was stirred at 75 °C for 2 h until the zinc powder was no longer visible. The reaction mixture was cooled to 50 °C, and acetyl chloride (1.53 mL, 21.5 mmol) was added. After 15 min, the mixture was poured into water. The aqueous layer was extracted with $CH_2Cl_2$, and the combined organic layers were dried ($Na_2SO_4$), filtered, and evaporated. The colorless oil thus obtained was chromatographed (silica, $CH_2Cl_2$/hexanes, 1:4) affording a colorless oil (3.93 g, 85%) that solidified at −20 °C: mp 56−57 °C (lit.[43] mp 54−55 °C); $^1$H NMR $\delta$ 2.42 (s, 3H), 7.12, 7.73 (AA′BB′, 2 × 2H); $^{13}$C NMR $\delta$ 31.0, 96.7, 128.4, 136.7, 139.0, 193.9. Anal. Calcd for $C_8H_7IOS$: C, 34.55; H, 2.54; I, 45.63; S, 11.53. Found: C, 34.69; H, 2.59; I, 45.52; S, 11.59.

**1-[4-(*S*-Acetylthio)phenyl]-2-(4-formylphenyl)acetylene (4).** Samples of 4-iodobenzaldehyde (660 mg, 2.80 mmol), **3**[40,41] (500 mg, 2.80 mmol), CuI (29 mg, 15 $\mu$mol), and $Pd(PPh_3)_2Cl_2$ (13 mg, 18 $\mu$mol) were placed in a Schlenk flask. The flask was evacuated for 3 min then backflushed with argon for 3 min. The process of evacuation and flushing was repeated three times. The argon flow rate was increased, the threaded stopcock was removed, and deaerated THF (5.0 mL) and DIEA (5.0 mL) were added in succession by gastight syringe. The threaded stopcock was replaced, the argon flow rate was reduced, and the flask was immersed in an oil bath thermostated at 40 °C. The reaction was stopped after 40 h. The mixture was then filtered and evaporated. The resulting orange-brown solid was chromatographed (silica, $CH_2Cl_2$/hexanes, 2:3, then 1:1, then 3:2) to afford yellowish-white crystals, which upon recrystallization (ethyl acetate/heptane) afforded white crystals (707 mg, 90%): mp 128−129 °C (lit.[36] mp 122−123 °C); $^1$H NMR $\delta$ 2.65 (s, 3H), 7.63, 7.79 (AA′BB′, 2 × 2H), 7.87, 8.07 (AA′BB′, 2 × 2H), 10.22 (s, 1H); $^{13}$C NMR $\delta$ 31.2, 91.0, 93.5, 124.5, 129.9, 130.0, 130.5, 133.1, 133.2, 135.2, 136.5, 192.3, 194.1; FAB-MS obsd 280.0551, calcd exact mass 280.0558. Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.31; S, 11.44. Found: C, 72.66; H, 4.39; S, 11.52.

**1-(*S*-Acetylthiomethyl)-4-iodobenzene (5).** Following a general procedure,[45] potassium thioacetate (2.20 g, 19.3 mmol) was added to a solution of 1-(bromomethyl)-4-iodobenzene (4.80 g, 16.2 mmol) in anhydrous *N*,*N*-dimethylacetamide (15 mL). The mixture was stirred overnight at room temperature, poured into water, and extracted with $CH_2Cl_2$. The combined organic extracts were washed with water, dried ($Na_2SO_4$), and evaporated. The resulting brown oil was distilled (90 °C, 0.005 mmHg) to give a pale-yellow oil that solidified after a few days (4.68 g, 99%): mp 40−41 °C; $^1$H NMR $\delta$ 2.37 (s, 3H), 4.07 (s, 2H), 7.07, 7.64 (AA′BB′, 2 × 2H); $^{13}$C NMR $\delta$ 31.1, 33.6, 93.5, 131.6, 138.2, 138.4, 195.5; FAB-MS obsd 291.9425, calcd exact mass 291.9419. Anal. Calcd for $C_9H_9IOS$: C, 37.00; H, 3.11; I, 43.44; S, 10.98. Found: C, 37.39; H, 3.13; I, 43.04; S, 11.26.

**1-[4-(*S*-Acetylthiomethyl)phenyl)]-2-(trimethylsilyl)-acetylene (6).** Following the procedure for **4**, samples of **5** (2.92 g, 10.0 mmol), CuI (105 mg, 553 $\mu$mol), and $Pd(PPh_3)_2Cl_2$ (46 mg, 66 $\mu$mol) were degassed, and then deaerated THF (10.0 mL), DIEA (10.0 mL) and trimethylsilylacetylene (2.00 mL, 14.0 mmol) were added, and the reaction was carried out

(53) Creager, S. E.; Rowe, G. K. *J. Electroanal. Chem.* **1994**, *370*, 203-211.
(54) Li, F.; Gentemann, S.; Kalsbeck, W. A.; Seth, J.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Mater. Chem.* **1997**, *7*, 1245−1262.
(55) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99.

at 40 °C for 40 h. The mixture was then filtered and evaporated. The resulting orange-brown solid was chromatographed (silica, $CH_2Cl_2$/hexanes, 1:4, then 3:7) to afford a slightly yellow oil that solidified upon standing at room temperature (2.40 g, 92%): mp 41−42 °C; $^1$H NMR $\delta$ 0.23 (s, 9H), 2.32 (s, 3H), 4.07 (s, 2H), 7.21, 7.36 (AA′BB′, 2 × 2H); $^{13}$C NMR $\delta$ 0.7, 31.0, 33.9, 95.1, 105.5, 122.8, 129.4, 132.8, 138.9, 195.4; FAB-MS obsd 262.0839, calcd exact mass 262.0848. Anal. Calcd for $C_{14}H_{18}SiOS$: C, 64.07; H, 6.91; S, 12.22. Found: C, 64.02; H, 6.99; S, 12.23.

**1-[4-(*S*-Acetylthiomethyl)phenyl]acetylene (7).** To a solution of **6** (2.52 g, 9.60 mmol) in THF (30 mL) were added acetic acid (0.2 mL) and acetic anhydride (0.2 mL). The mixture was cooled to −20 °C, and a solution of $Bu_4NF$ (2.40 g, 9.60 mmol) in THF (20 mL) was added dropwise during 5 min. The reaction mixture was kept at −20 °C for another 10 min and then poured on a silica pad and eluted with $CH_2Cl_2$/hexanes (1:1). The solvents were removed, and the residue was dissolved in $CH_2Cl_2$, dried ($Na_2SO_4$), and evaporated, affording a yellowish oil (1.69 g, 92%): $^1$H NMR $\delta$ 2.13 (s, 3H), 2.88 (s, 1H), 3.88 (s, 2H), 7.02, 7.20 (AA′BB′, 2 × 2H); $^{13}$C NMR $\delta$ 30.8, 33.6, 83.8, 121.5, 129.3, 132.8, 139.0, 195.3; EI-MS obsd 190.0458, calcd exact mass 190.0452 ($C_{11}H_{10}OS$).

**1-[4-(*S*-Acetylthiomethyl)phenyl]-2-(4-formylphenyl)-acetylene (8).** Following the procedure for **4**, samples of 4-iodobenzaldehyde (1.18 g, 5.00 mmol), **7** (950 mg, 5.00 mmol), CuI (52 mg, 270 $\mu$mol), and $Pd(PPh_3)_2Cl_2$ (23 mg, 33 $\mu$mol) were reacted in the presence of THF (5.0 mL) and DIEA (5.0 mL) at 40 °C for 40 h. The mixture was then filtered and evaporated. The resulting orange-brown solid was chromatographed (silica, $CH_2Cl_2$/hexanes, 2:3, 1:1, then 3:2) to afford yellowish-white crystals. Recrystallization (ethyl acetate/heptane) gave white crystals (1.30 g, 88%): mp 128−129 °C; $^1$H NMR $\delta$ 2.49 (s, 3H), 4.07 (s, 2H), 7.25, 7.43 (AA′BB′, 2 × 2H), 7.59, 7.79 (AA′BB′, 2 × 2H), 9.95 (s, 1H); $^{13}$C NMR $\delta$ 30.9, 33.9, 89.5, 93.9, 122.1, 129.8, 130.1, 130.2, 132.7, 132.7, 136.1, 139.5, 192.0, 195.4; FAB-MS obsd 294.0717, calcd exact mass 294.0715. Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.18; H, 4.82; S, 10.88.

**4-(*S*-Acetylthio)-2,3,5,6-tetrafluorobenzaldehyde (9).** Potassium thioacetate (1.28 g, 11.2 mmol) was added to a solution of pentafluorobenzaldehyde (1.24 mL, 10.2 mmol) in anhydrous *N*,*N*-dimethylacetamide (20 mL). After an exotherm subsided, the mixture was stirred at room temperature for 30 min. Acetyl chloride (1.60 mL, 22.4 mmol) was added, and the mixture was stirred for another 30 min, then poured into water and extracted thoroughly with diethyl ether. The combined organic extracts were dried ($Na_2SO_4$) and evaporated to obtain an orange oil, which was chromatographed (silica, $CH_2Cl_2$/hexanes, 2:3) affording a pale-yellow solid. Recrystallization from heptane gave white crystals (1.77 g, 69%): mp 86−87 °C; $^1$H NMR $\delta$ 2.53 (s, 3H), 10.30 (s, 1H); $^{13}$C NMR $\delta$ 30.9, 115.5, 117.2, 145.3, 148.7, 182.9, 187.9; FAB-MS obsd 252.9936, calcd exact mass 252.9946. Anal. Calcd for $C_9H_4F_4O_2S$: C, 42.86; H, 1.60; S, 12.72. Found: C, 43.00; H, 1.71; S, 12.67.

**4-(*S*-Acetylthiomethyl)benzaldehyde (10).** To a solution of 4-(bromomethyl)benzaldehyde[43,46,47] (0.43 g, 2.2 mmol) in acetone (10 mL) was added potassium thioacetate (280 mg, 2.5 mmol) under stirring at room temperature, and then the mixture was refluxed. A precipitate formed after a few minutes. The reaction was monitored by TLC and cooled to room temperature when no starting material was detectable (3.5 h). Water (25 mL) was added, the mixture was extracted with ethyl acetate, and column chromatography (silica, $Et_2O$/hexanes, 1:1) gave a brown oil (359 mg, 85%): IR (neat) $\tilde{\nu}$ 3052, 2923, 2830, 2737, 1694, 1606, 1576; $^1$H NMR $\delta$ 2.36 (s, 3H), 4.15 (s, 2H), 7.45, 7.81 (AA′BB′, 2 × 2H), 9.97 (s, 1H); $^{13}$C NMR (APT) $\delta$ 30.1 (−), 32.9 (+), 129.3 (−), 129.9 (−), 135.2 (+), 144.7 (+), 191.5 (−), 194.3 (+); GC−MS (EI) obsd 194. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19; S, 16.51. Found: C, 61.97; H, 5.20; S, 16.60.

**4-[2-(*S*-Acetylthio)ethyl]benzaldehyde (11).** Following a general procedure,[48] 4-vinylbenzaldehyde[49] (1.15 g, 8.70 mmol) and thioacetic acid (2.20 mL, 30.8 mmol) were dissolved in toluene (20 mL), and the solution was purged with argon for 15 min. Then AIBN (20 mg) was added, and the mixture was heated to 90 °C. After 2 h, more AIBN (160 mg) was added. This was repeated after an additional 1 h. After 2 h, AIBN (100 mg) was added again and the mixture was heated for an additional 1 h. Then aqueous $NaHCO_3$ (10%, 50 mL) was added, and the phases were separated. The aqueous phase was washed with diethyl ether, and the combined organic phases were dried ($Na_2SO_4$). Purification by column chromatography (silica, $Et_2O$/hexanes, 1:3) gave an orange oil, which solidified and darkened upon standing at −20 °C to give a black solid (983 mg, 54%), which was pure enough for the next reaction. A small sample was recrystallized from refluxing heptane to afford colorless plates: mp 35 °C; IR (neat) $\tilde{\nu}$ 3029, 2929, 2828, 2737, 1699, 1606, 1578; $^1$H NMR $\delta$ 2.34 (s, 3H), 2.96 (t, $J$ = 8.1 Hz, 2H), 3.15 (t, $J$ = 8.1 Hz, 2H), 7.40, 7.83 (AA′BB′, 2 × 2H), 9.99 (s, 1H); $^{13}$C NMR (APT) $\delta$ 30.5 (+), 31.3 (−), 36.5 (+), 129.0 (−), 129.7 (−), 134.7 (+), 146.8 (+), 191.5 (−), 194.9 (+); GC−MS (EI) obsd 208. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.40. Found: C, 63.63; H, 5.90; S, 15.62.

**2-(4-Bromophenyl)-5,5-dimethyl-1,3-dioxane (12).** The following describes an improved procedure at three times larger scale and in much shorter time compared with the literature.[50] 4-Bromobenzaldehyde (3.00 g, 16.2 mmol), neopentyl glycol (1.86 g, 17.9 mmol), and *p*-toluenesulfonic acid (50 mg, 0.3 mmol) were dissolved in toluene (30 mL), and the solution was refluxed for 3 h. Then the solution was cooled to room temperature, washed with aqueous $NaHCO_3$ (10%) and water, and dried ($Na_2SO_4$). The solvent was evaporated, and the oily residue was crystallized from hexanes, affording colorless needles (2.81 g, 64%): $^{13}$C NMR (APT) $\delta$ 21.7 (−), 22.9 (−), 30.1 (+), 77.5 (+), 100.8 (−), 122.7 (+), 127.8 (−), 131.3 (−), 137.5 (+). Analytical data were consistent with the literature.[50]

**2-(4-Allylphenyl)-5,5-dimethyl-1,3-dioxane (13).** A solution of **12** (2.05 g, 7.60 mmol) in THF (15 mL) was added dropwise to magnesium powder (0.22 g, 9.1 mmol) under argon. After the addition was completed, the mixture was refluxed for 45 min. Then the mixture was cooled to room temperature, and a solution of allyl bromide (720 $\mu$L, 8.30 mmol) in THF (10 mL) was added slowly. The mixture was stirred for 4.5 h, quenched with saturated aqueous $NH_4Cl$ (25 mL), and extracted with diethyl ether. The combined organic phases were washed with aqueous $NaHCO_3$ (5%), brine, and dried ($Na_2SO_4$). The solvent was removed, and the residue was treated with hexanes and filtered. The filtrate was purified by column chromatography (silica, $Et_2O$/hexanes, 1:4), affording a light yellow oil (1.04 g, 59%): IR (neat) $\tilde{\nu}$ 3077, 2955, 2904, 2846, 1639, 1619, 1517; $^1$H NMR $\delta$ 0.79 (s, 3H), 1.29 (s, 3H), 3.38 (d, $J$ = 6.6 Hz, 2H), 3.64 (d, $J$ = 11.0 Hz, 2H), 3.76 (d, $J$ = 11.0 Hz, 2H), 5.00−5.10 (m, 2H), 5.37 (s, 1H), 5.86−6.01 (m, 1H), 7.19, 7.43 (AA′BB′, 2 × 2H); $^{13}$C NMR (APT) $\delta$ 21.7 (−), 22.9 (−), 30.0 (+), 39.8 (+), 77.5 (+), 101.5 (−), 115.6 (+), 126.1 (−), 128.4 (−), 136.3 (+), 137.2 (−), 140.5 (+); GC−MS (EI) obsd 232. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.52; H, 8.77.

**2-[4-[3-(*S*-Acetylthio)propyl]phenyl]-5,5-dimethyl-1,3-dioxane (14).** Following a general procedure,[48] **13** (845 mg, 3.60 mmol) and thioacetic acid (910 $\mu$L, 12.7 mmol) were dissolved in toluene (20 mL), and the solution was purged with argon for 15 min. Then AIBN (200 mg) was added, and the mixture was heated to 90 °C. Over a period of 23 h, more AIBN (1.10 g) was added in several portions. Then aqueous $NaHCO_3$ (10%, 50 mL) was added, and the phases were separated. The aqueous phase was extracted with diethyl ether, and the combined organic phases were dried ($Na_2SO_4$). Purification by column chromatography (silica, $Et_2O$/hexanes, 1:4) gave an orange oil, which solidified upon standing at −20 °C and was recrystallized from pentane to give colorless needles (708 mg, 63%): mp 44 °C; IR (neat) $\tilde{\nu}$ 2951, 2850, 1692, 1620, 1518; $^1$H NMR $\delta$ 0.79 (s, 3H), 1.29 (s, 3H), 1.78−1.94 (m, 2H), 2.33 (s, 3H), 2.68 (t, $J$ = 7.3 Hz, 2H), 2.86 (t, $J$ = 7.3 Hz, 2H), 3.64 (d, $J$ = 11.0 Hz, 2H), 3.76 (d, $J$ = 11.0 Hz, 2H), 5.37 (s, 1H), 7.18, 7.42 (AA′BB′, 2 × 2H); $^{13}$C NMR (APT) $\delta$ 21.6 (−), 22.8 (−), 28.1 (+), 29.9 (+), 30.4 (−), 30.8 (+), 34.3 (+), 77.3 (+), 101.4 (−), 126.0 (−), 128.1 (−), 136.1 (+), 141.5 (+), 195.3 (+); GC−

MS (EI) obsd 308. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84; S, 10.40. Found: C, 66.19; H, 7.89; S, 10.54.

**4-[3-(*S*-Acetylthio)propyl]benzaldehyde (15).** Compound **14** (525 mg, 1.70 mmol) was dissolved in $CH_2Cl_2$ (10 mL). TFA (2.0 mL) was added together with a drop of water. The solution was stirred for 15 h at room temperature. Then aqueous $NaHCO_3$ (5%, 35 mL) was added, and the phases were separated. The organic phase was washed with aqueous $NaHCO_3$ (5%) and brine and dried ($Na_2SO_4$). The solvents were removed, and the oily residue was purified by column chromatography (silica, $Et_2O$/hexanes, 1:2), affording a yellow oil (279 mg, 74%): IR (neat) $\tilde{\nu}$ 3037, 2928, 2849, 2731, 1693, 1605; $^1$H NMR $\delta$ 1.88−1.99 (m, 2H), 2.35 (s, 3H), 2.78 (t, $J$ = 7.3 Hz, 2H), 2.89 (t, $J$ = 7.3 Hz, 2H), 7.35, 7.81 (AA′BB′, 2 × 2H), 9.98 (s, 1H); $^{13}$C NMR (APT) $\delta$ 28.1 (+), 30.4 (+), 34.7 (+), 128.8 (−), 129.7 (−), 134.4 (+), 148.3 (+), 191.6 (−), 195.2 (+); GC−MS (EI) obsd 222; FAB-MS obsd 222.0709, calcd exact mass 222.0715 ($C_{12}H_{14}O_2S$).

**7-(*S*-Acetylthio)heptanal (17).** To a solution of crude 7-bromoheptanal[51] (3.32 g, 17.2 mmol) in acetone (50 mL) was added potassium thioacetate (2.36 g, 21 mmol) under stirring at room temperature. Then the mixture was refluxed, yielding a precipitate after a few minutes. The reaction was monitored by TLC and cooled to room temperature when no starting material was detectable (4 h). Water (50 mL) was added, the mixture was extracted with diethyl ether until the organic phase was colorless, and the combined organic phases were dried ($Na_2SO_4$) and evaporated. Distillation at 98 °C with a water suction pump afforded a yellow oil (1.66 g, 51%; 42% from 7-bromoheptanol): IR (neat) $\tilde{\nu}$ 2938, 2857, 2721, 1725, 1694; $^1$H NMR $\delta$ 1.28−1.43 (m, 4H), 1.53−1.69 (m, 4H), 2.33 (s, 3H), 2.43 (dt, $J$ = 7.3 Hz, $J$ = 1.5 Hz, 2H), 2.86 (t, $J$ = 7.3 Hz, 2H), 9.77 (t, $J$ = 1.5 Hz, 1H); $^{13}$C NMR (APT) $\delta$ 21.6 (+), 28.1 (+), 28.3(+), 28.6 (+), 29.0 (+), 30.3 (−), 43.3 (+), 195.4 (+), 202.0 (−); GC−MS (EI) obsd 188; FAB-MS obsd 188.0862, calcd 188.0871 ($C_9H_{16}O_2S$).

**1-[4-(*S*-Acetylthio)phenyl]-2-(diethoxymethyl)acetylene (18).** Following the procedure for **4**, samples of **1** (500 mg, 1.80 mmol), CuI (19.0 mg, 100 $\mu$mol), and $Pd(PPh_3)_2Cl_2$ (8.4 mg, 12 $\mu$mol) were deoxygenated, and then deaerated THF (5.0 mL), DIEA (5.0 mL), and propiolaldehyde diethyl acetal (258 $\mu$L, 1.80 mmol) were added and the reaction was carried out at 40 °C for 40 h. The mixture was evaporated, and the resulting orange-brown solid was chromatographed (silica, $CH_2Cl_2$/hexanes, 1:1, then 7:3) to afford a pale yellow oil (319 mg, 64%): $^1$H NMR $\delta$ 1.27 (t, $J$ = 6.6 Hz, 6H), 2.40 (s, 3H), 3.5−4.0 (m, 4H), 5.49 (s, 1H), 7.36, 7.50 (AA′BB′, 2 × 2H); $^{13}$C NMR $\delta$ 15.8, 30.9, 61.7, 85.0, 86.8, 92.4, 123.7, 129.5, 133.1, 134.8, 193.7; FAB-MS obsd 278.0970, calcd exact mass 278.0977. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52; S, 11.52. Found: C, 64.45; H, 6.53; S, 11.34.

**5-[4-[2-[4-(*S*-Acetylthio)phenyl]ethynyl]phenyl]-10,15,-20-trimesitylporphyrin (19).** Following a general procedure for mixed-aldehyde condensations[38] with mesitaldehyde,[52] aldehyde **4** (204 mg, 0.730 mmol) was added to $CHCl_3$ (40 mL, containing 0.75% ethanol), followed by mesitaldehyde (0.32 mL, 2.2 mmol), pyrrole (200 $\mu$L, 2.92 mmol), and $BF_3$·$OEt_2$ (90 $\mu$L, 0.71 mmol). The reaction mixture was stirred at room temperature for 1.5 h. Then DDQ (500 mg, 2.20 mmol) in THF (10 mL) was added. The resulting mixture was stirred at room temperature for 1 h and then passed over a short silica column ($CH_2Cl_2$/hexanes, 1:1) affording porphyrins free from dark pigments and quinone species. The mixture of porphyrins was purified by preparative centrifugal chromatography (silica, $CH_2Cl_2$/hexanes, 5:7). The title porphyrin eluted as the second purple band (78 mg, 12%): $^1$H NMR $\delta$ −2.40 (s, 2H), 1.99 (s, 18H), 2.57 (s, 3H), 2.73 (s, 9H), 7.40 (s, 6H), 7.58, 7.61 (AA′BB′, 2 × 2H), 8.04, 8.34 (AA′BB′, 2 × 2H), 8.78 (s, 4H), 8.8−9.0 (m, 4H); LD-MS obsd 917.2; FAB-MS obsd 914.4059, calcd exact mass 914.4018 ($C_{63}H_{54}N_4OS$); $\lambda_{abs}$ ($CH_2Cl_2$) 420, 515, 550, 592, 646 nm.

**5-[4-[2-[4-(*S*-Acetylthiomethyl)phenyl]ethynyl]phenyl]-10,15,20-trimesitylporphyrin (20).** Following the general procedure for **19**, aldehyde **8** (214 mg, 0.730 mmol), mesitaldehyde (0.32 mL, 2.2 mmol), pyrrole (200 $\mu$L, 2.92 mmol), and $BF_3$·$OEt_2$ (90 $\mu$L, 0.71 mmol) were stirred in $CHCl_3$ (40 mL) for 1.5 h. The resulting mixture was treated with DDQ (500 mg, 2.20 mmol) in THF (10 mL) for 1 h. Filtration over a silica pad ($CH_2Cl_2$) followed by preparative centrifugal chromatography (silica, $CH_2Cl_2$/hexanes, 5:7) gave the title porphyrin as the second purple band (96 mg, 14%): $^1$H NMR $\delta$ −2.53 (s, 2H), 1.85 (s, 18H), 2.35 (s, 3H), 2.59 (s, 9H), 4.13 (s, 2H), 7.26 (s, 6H), 7.31, 7.59 (AA′BB′, 2 × 2H), 7.90, 8.19 (AA′BB′, 2 × 2H), 8.65 (s, 4H), 8.7−8.9 (m, 4H); LD-MS obsd 932.1; FAB-MS obsd 928.4193, calcd exact mass 928.4175 ($C_{64}H_{56}N_4OS$); $\lambda_{abs}$ ($CH_2Cl_2$) 420, 515, 548, 592, 648 nm.

**5-[4-(*S*-Acetylthio)-2,3,5,6-tetrafluorophenyl]-10,15,20-trimesitylporphyrin (21).** Following the general procedure for **19**, aldehyde **9** (184 mg, 0.730 mmol), mesitaldehyde (0.32 mL, 2.2 mmol), pyrrole (200 $\mu$L, 2.92 mmol), and $BF_3$·$OEt_2$ (90 $\mu$L, 0.71 mmol) were stirred in $CHCl_3$ (40 mL) for 1.5 h. The resulting mixture was treated with DDQ (500 mg, 2.20 mmol) in THF (10 mL) for 1 h. Filtration over a silica pad ($CH_2Cl_2$) followed by preparative centrifugal chromatography (silica, $CH_2Cl_2$/hexanes, 1:4) gave the title porphyrin as the second purple band (46 mg, 7.1%): $^1$H NMR (THF-$d_8$) $\delta$ −2.51 (s, 2H), 1.83 (s, 18H), 2.61 (s, 9H), 2.67 (s, 3H), 7.29 (s, 6H), 8.8−9.0 (m, 8H); LD-MS obsd 887.2; FAB-MS obsd 886.3364, calcd exact mass 886.3328 ($C_{55}H_{46}F_4N_4OS$); $\lambda_{abs}$ ($CH_2Cl_2$) 418, 513, 546, 588, 644 nm.

**5-[4-(*S*-Acetylthiomethyl)phenyl]-10,15,20-trimesitylporphyrin (22).** Following the general procedure for **19**, aldehyde **10** (148 mg, 0.76 mmol), mesitaldehyde (337 $\mu$L, 2.3 mmol), pyrrole (211 $\mu$L, 3.0 mmol), and $BF_3$·$OEt_2$ (94 $\mu$L, 0.74 mmol) were stirred in $CHCl_3$ (125 mL) for 3 h. The resulting mixture was treated with DDQ (519 mg, 2.3 mmol) for 1 h. The mixture was then filtered through a pad of silica ($CH_2Cl_2$) followed by column chromatography (silica, $CH_2Cl_2$/hexanes, 1:3−1:1). The title compound eluted as the second purple band (118 mg, 19%): IR (neat) $\tilde{\nu}$ 3318, 2921, 2861, 1695, 1608, 1561; $^1$H NMR $\delta$ −2.58 (s, 2H), 1.84 (s, 12H), 1.85 (s, 6H), 2.50 (s, 3H), 2.63 (s, 9H), 4.46 (s, 2H), 7.27 (s, 6H), 7.65, 8.12 (AA′BB′, 2 × 2H), 8.63 (brs, 4H), 8.67 (d, $J$ = 5.1 Hz, 2H), 8.77 (d, $J$ = 5.1 Hz, 2H); LD-MS obsd 829.0; FAB-MS obsd 828.3892, calcd exact mass 828.3862 ($C_{56}H_{52}N_4OS$); $\lambda_{abs}$ (toluene) 420, 515, 548, 592, 649 nm.

**5-[4-[2-(*S*-Acetylthio)ethyl]phenyl]-10,15,20-trimesitylporphyrin (23).** Following the general procedure for **19**, aldehyde **11** (98 mg, 0.47 mmol), mesitaldehyde (208 $\mu$L, 1.4 mmol), pyrrole (131 $\mu$L, 1.9 mmol), and $BF_3$·$OEt_2$ (52 $\mu$L, 0.4 mmol) were stirred in $CHCl_3$ (100 mL) for 3 h. The resulting mixture was treated with DDQ (320 mg, 1.4 mmol) for 1.5 h. The mixture was then filtered through a pad of silica ($CH_2Cl_2$) followed by column chromatography (silica, $CH_2Cl_2$/hexanes, 1:1−3:2). The title compound comprised the second purple band (69 mg, 17%): IR (neat) $\tilde{\nu}$ 3319, 2920, 2861, 1694, 1608, 1561; $^1$H NMR $\delta$ −2.57 (s, 2H), 1.85 (s, 18H), 2.45 (s, 3H), 2.62 (s, 9H), 3.21 (t, $J$ = 8.1 Hz, 2H), 3.37−3.52 (m, 2H), 7.27 (s, 6H), 7.58, 8.13 (AA′BB′, 2 × 2H), 8.62 (s, 4H), 8.67 (d, $J$ = 5.1 Hz, 2H), 8.77 (d, $J$ = 4.4 Hz, 2H); LD-MS 845.3; FAB-MS obsd 842.4025, calcd exact mass 842.4018 ($C_{57}H_{54}N_4OS$); $\lambda_{abs}$ (toluene) 420, 515, 548, 593, 650 nm.

**5-[4-[3-(*S*-Acetylthio)propyl]phenyl]-10,15,20-trimesitylporphyrin (24).** Following the general procedure for **19**, aldehyde **15** (108 mg, 0.49 mmol), mesitaldehyde (215 $\mu$L, 1.5 mmol), pyrrole (135 $\mu$L, 1.9 mmol), and $BF_3$·$OEt_2$ (54 $\mu$L, 0.4 mmol) were stirred in $CHCl_3$ (100 mL) for 3.5 h. The resulting mixture was treated with DDQ (331 mg, 1.5 mmol) for 1 h. The mixture was then filtered through a pad of silica ($CH_2Cl_2$) followed by column chromatography (silica, $CH_2Cl_2$/hexanes 3:2−2:1). The title compound comprised the second purple band, which was triturated with methanol to give a purple solid (41 mg, 10%): IR (neat) $\tilde{\nu}$ 3322, 3102, 2920, 2852, 1693, 1612, 1559; $^1$H NMR $\delta$ −2.56 (s, 2H), 1.85 (s, 18H), 2.14−2.25 (m, 2H), 2.41 (s, 3H), 2.61 (s, 9H), 3.02 (t, $J$ = 7.3 Hz, 2H), 3.37 (t, $J$ = 7.3 Hz, 2H), 7.27 (s, 6H), 7.53, 8.11 (AA′BB′, 2 × 2H), 8.63 (s, 4H), 8.67 (d, $J$ = 4.4 Hz, 2H), 8.79 (d, $J$ = 4.4 Hz, 2H); LD-MS obsd 858.4; FAB-MS obsd 856.4216, calcd exact mass 856.4175 ($C_{58}H_{56}N_4OS$); $\lambda_{abs}$ (toluene) 420, 515, 548, 593, 649 nm.

**5-[6-(*S*-Acetylthio)hexyl]-10,15,20-trimesitylporphyrin (25).** Following the general procedure for **19**, aldehyde **17** (111 mg, 0.59 mmol), mesitaldehyde (261 $\mu$L, 1.8 mmol), pyrrole (164 $\mu$L, 2.4 mmol), and $BF_3{\cdot}OEt_2$ (65 $\mu$L, 0.5 mmol) were stirred in $CHCl_3$ (100 mL) for 3 h. The resulting mixture was treated with DDQ (401 mg, 1.8 mmol) for 1.5 h. The mixture was then filtered through a pad of silica ($CH_2Cl_2$) followed by two column chromatography procedures (silica, $CH_2Cl_2$/hexanes, 1:1−3:2). The title compound eluted as the second purple band and was purified by a further column (silica, $CH_2Cl_2$/hexanes, 2:1) to afford a purple solid (105 mg, 22%): IR (neat) $\tilde{\nu}$ 3317, 3107, 2922, 2856, 1691, 1609, 1562; $^1$H NMR $\delta$ −2.51 (s, 2H), 1.52−1.67 (m, 4H), 1.74−1.89 (m, 2H), 1.85 (s, 18H), 2.30 (s, 3H), 2.45−2.58 (m, 2H), 2.60 (s, 3H), 2.63 (s, 6H), 2.88 (t, $J$ = 6.6 Hz, 2H), 4.98 (t, $J$ = 8.1 Hz, 2H), 7.25 (s, 2H), 7.28 (s, 4H), 8.55−8.62 (m, 4H), 8.75 (d, $J$ = 3.7 Hz, 2H), 8.40 (d, $J$ = 3.7 Hz, 2H); LD-MS obsd 825.2; FAB-MS obsd 822.4355, calcd exact mass 822.4331 ($C_{55}H_{58}N_4OS$); $\lambda_{abs}$ (toluene) 419, 516, 549, 594, 652 nm.

**5-{2-[4-(*S*-Acetylthio)phenyl]ethynyl}-10,15,20-trimesitylporphyrin (26).** Following the general procedure for **19**, acetal **18** (100 mg, 0.36 mmol), mesitaldehyde (0.16 mL, 1.1 mmol), pyrrole (100 $\mu$L, 1.46 mmol) and $BF_3{\cdot}OEt_2$ (45 $\mu$L, 0.35 mmol) were stirred in $CHCl_3$ (20 mL) for 1.5 h. The resulting mixture was treated with DDQ (250 mg, 1.10 mmol) in THF (5 mL) for 1 h. Filtration over a silica pad ($CH_2Cl_2$) followed by two preparative centrifugal chromatography procedures (silica, $CH_2Cl_2$/hexanes, 1:3, then 1:1) gave the title porphyrin as the second purple band (2.5 mg, 0.83%): $^1$H NMR $\delta$ −2.14 (s, 2H), 1.85 (s, 18H), 2.50 (s, 3H), 2.63 (s, 9H), 7.25 (s, 6H), 7.60, 8.03 (AA′BB′, 2 × 2H), 8.54 (s, 4H), 8.73 (m, 2H), 9.63 (m, 2H); LD-MS obsd 841.6; FAB-MS obsd 838.3737, calcd exact mass 838.3705 ($C_{57}H_{50}N_4OS$); $\lambda_{abs}$ ($CH_2Cl_2$) 436, 534, 576, 611, 668 nm.

**General Procedure for Zinc Insertion.** The porphyrin was dissolved in $CHCl_3$ or $CH_2Cl_2$, and a solution of $Zn(OAc)_2{\cdot}2H_2O$ in methanol was added. The reaction mixture was stirred at room temperature. After metalation was complete (TLC, fluorescence excitation spectroscopy), the reaction mixture was washed with water, dried ($Na_2SO_4$), filtered and concentrated to a purple solid. Purification was achieved by column chromatography on silica.

**Zn(II)-5-[4-[2-[4-(*S*-Acetylthio)phenyl]ethynyl]phenyl]-10,15,20-trimesitylporphyrin (Zn-19).** A solution of porphyrin **19** (37 mg, 0.040 mmol) in $CH_2Cl_2$ (15 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (880 mg, 4.00 mmol) in methanol (15 mL), and the mixture was stirred for 16 h. Column chromatography (silica, $CH_2Cl_2$/hexanes, 1:1) afforded 35.6 mg (92%): $^1$H NMR $\delta$ 1.85 (s, 18H), 2.48 (s, 3H), 2.64 (s, 9H), 7.27 (s, 6H), 7.48, 7.72 (AA′BB′, 2 × 2H), 7.92, 8.23 (AA′BB′, 2 × 2H), 8.70 (s, 4H), 8.70−8.90 (m, 4H); LD-MS obsd 979.8; FAB-MS obsd 976.3177, calcd exact mass 976.3153 ($C_{63}H_{52}N_4OSZn$); $\lambda_{abs}$ ($CH_2Cl_2$) 422, 550 nm.

**Zn(II)- 5-[4-[2-[4-(*S*-Acetylthiomethyl)phenyl]ethynyl]-phenyl]-10,15,20-trimesitylporphyrin (Zn-20).** A solution of porphyrin **20** (37 mg, 0.040 mmol) in $CH_2Cl_2$ (15 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (880 mg, 4.00 mmol) in methanol (15 mL), and the mixture was stirred for 16 h. Column chromatography (silica, $CH_2Cl_2$/hexanes, 1:1) afforded 37.7 mg (95%): $^1$H NMR (THF-$d_8$) $\delta$ 1.86 (s, 18H), 2.34 (s, 3H), 2.60 (s, 9H), 4.18 (s, 2H), 7.29 (s, 6H), 7.38, 7.58 (AA′BB′, 2 × 2H), 7.88, 8.19 (AA′BB′, 2 × 2H), 8.63 (s, 4H), 8.6−8.8 (m, 4H); LD-MS obsd 992.4; FAB-MS obsd 990.3280, calcd exact mass 990.3310 ($C_{64}H_{56}N_4OS$); $\lambda_{abs}$ ($CH_2Cl_2$) 422, 550 nm.

**Zn(II)-5-[4-(*S*-Acetylthio)-2,3,5,6-tetrafluorophenyl]-10,15,20-trimesitylporphyrin (Zn-21).** A solution of porphyrin **21** (35 mg, 0.040 mmol) in $CH_2Cl_2$ (15 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (880 mg, 4.00 mmol) in methanol (15 mL), and the mixture was stirred for 16 h. Column chromatography (silica, $CH_2Cl_2$/hexanes, 1:4) afforded 31.4 mg (83%): $^1$H NMR (THF-$d_8$) $\delta$ 1.87 (s, 18H), 2.66 (s, 9H), 2.71 (s, 3H), 7.30 (s, 6H), 8.7−9.0 (m, 8H); LD-MS obsd 953.5; FAB-MS obsd 948.2480, calcd exact mass 948.2463 ($C_{55}H_{44}F_4N_4OSZn$); $\lambda_{abs}$ ($CH_2Cl_2$) 421, 548 nm.

**Zn(II)-5-[4-(*S*-Acetylthiomethyl)phenyl]-10,15,20-trimesitylporphyrin (Zn-22).** A solution of porphyrin **22** (54.8 mg, 66.1 $\mu$mol) in $CHCl_3$ (20 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (435 mg, 2.00 mmol) in methanol (5 mL), and the mixture was stirred for 6 h. Excess $Zn(OAc)_2{\cdot}2H_2O$ (290 mg, 1.3 mmol) was then added, and stirring was continued for 23 h. The organic phase was washed with aqueous $NaHCO_3$ (5%). Column chromatography (silica, $CH_2Cl_2$/hexanes, 1:1) afforded a purple solid in quantitative yield: IR (neat) $\tilde{\nu}$ 2922, 2853, 1663; $^1$H NMR $\delta$ 1.84 (s, 18H), 2.49 (s, 3H), 2.63 (s, 9H), 4.46 (s, 2H), 7.27 (s, 6H), 7.63, 8.14 (AA′BB′, 2 × 2H), 8.70 (brs, 4H), 8.74 (d, $J$ = 4.4 Hz, 1H), 8.75 (d, $J$ = 4.4 Hz, 1H), 8.84(5) (d, $J$ = 4.4 Hz, 1H), 8.85(0) (d, $J$ = 4.4 Hz, 1H); LD-MS obsd 891.3; FAB-MS obsd 890.3035, calcd exact mass 890.2997 ($C_{56}H_{50}N_4OSZn$); $\lambda_{abs}$ (toluene) 423, 550 nm; $\lambda_{em}$ (toluene) 593, 644 nm.

**Zn(II)-5-[4-[2-(*S*-Acetylthio)ethyl]phenyl]-10,15,20-trimesitylporphyrin (Zn-23).** A solution of porphyrin **23** (48 mg, 57 $\mu$mol) in $CHCl_3$ (20 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (1.25 g, 5.70 mmol) in methanol (5 mL), and the mixture was stirred for 17 h. The organic phase was washed with aqueous $NaHCO_3$ (5%). Column chromatography (silica, $CH_2Cl_2$/hexanes, 3:1) afforded a purple solid in quantitative yield: IR (neat) $\tilde{\nu}$ 3096, 2910, 2849, 1646; $^1$H NMR $\delta$ 1.84 (s, 12H), 1.85 (s, 6H), 2.44 (s, 3H), 2.63 (s, 9H), 3.20 (t, $J$ = 7.3 Hz, 2H), 3.38−3.46 (m, 2H), 7.27 (s, 6H), 7.57, 8.14 (AA′BB′, 2 × 2H), 8.70 (s, 4H), 8.75 (d, $J$ = 4.4 Hz, 2H), 8.86 (d, $J$ = 4.4 Hz, 2H); LD-MS obsd 906.4; FAB-MS obsd 904.3121, calcd exact mass 904.3153 ($C_{57}H_{52}N_4OSZn$); $\lambda_{abs}$ (toluene) 423, 550 nm; $\lambda_{em}$ (toluene) 593, 644 nm.

**Zn(II)-5-[4-[3-(*S*-Acetylthio)propyl]phenyl]-10,15,20-trimesitylporphyrin (Zn-24).** A solution of porphyrin **24** (37.7 mg, 44 $\mu$mol) in $CHCl_3$ (20 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (965 mg, 4.40 mmol) in methanol (5 mL), and the mixture was stirred for 5 h. The organic phase was washed with aqueous $NaHCO_3$ (5%) and dried ($Na_2SO_4$). Column chromatography (silica, $CH_2Cl_2$/hexanes, 4:1) afforded a purple solid in quantitative yield: IR (neat) $\tilde{\nu}$ 3107, 2919, 2849, 1650; $^1$H NMR $\delta$ 1.84 (s, 12H), 1.85 (s, 6H), 2.13−2.26 (m, 2H), 2.40 (s, 3H), 2.63 (s, 9H), 3.03 (t, $J$ = 7.3 Hz, 2H), 3.11 (t, $J$ = 7.3 Hz, 2H), 7.27 (s, 6H), 7.53, 8.13 (AA′BB′, 2 × 2H), 8.69 (s, 4H), 8.74 (d, $J$ = 5.1 Hz, 2H), 8.86 (d, $J$ = 5.1 Hz, 2H); LD-MS obsd 921.8; FAB-MS obsd 918.3343, calcd exact mass 918.3310 ($C_{58}H_{54}N_4OSZn$); $\lambda_{abs}$ (toluene) 423, 550 nm; $\lambda_{em}$ (toluene) 593, 644 nm.

**Zn(II)-5-[6-(*S*-Acetylthio)hexyl]-10,15,20-trimesitylporphyrin (Zn-25).** A solution of porphyrin **25** (93 mg, 110 $\mu$mol) in $CHCl_3$ (25 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (2.50 g, 11.4 mmol) in methanol (7 mL), and the mixture was stirred for 18 h. The organic phase was washed with aqueous $NaHCO_3$ (5%) and dried ($Na_2SO_4$). Column chromatography (silica, $CH_2Cl_2$/hexanes, 2:1) afforded a purple solid (85 mg, 85% yield): IR (neat) $\tilde{\nu}$ 3107, 2920, 2849, 1690, 1658, 1608; $^1$H NMR $\delta$ 1.55−1.67 (m, 4H), 1.78−1.89 (m, 2H), 1.83 (s, 18H), 2.20 (s, 3H), 2.5−2.7 (m, 11H), 2.83 (t, $J$ = 6.6 Hz, 2H), 5.02 (t, $J$ = 8.1 Hz, 2H), 7.25 (s, 2H), 7.28 (s, 4H), 8.64 (d, $J$ = 5.1 Hz, 2H), 8.66 (d, $J$ = 5.1 Hz, 2H), 8.81 (d, $J$ = 4.4 Hz, 2H), 9.49 (d, $J$ = 4.4 Hz, 2H); LD-MS obsd 887.7; FAB-MS obsd 884.3490, calcd exact mass 884.3466 ($C_{55}H_{56}N_4OSZn$); $\lambda_{abs}$ (toluene) 423, 552 nm; $\lambda_{em}$ (toluene) 593, 646 nm.

**Zn(II)-5-[2-[4-(*S*-Acetylthio)phenyl]ethynyl]-10,15,20-trimesitylporphyrin (Zn-26).** A solution of porphyrin **26** (2.5 mg, 2.9 $\mu$mol) in $CH_2Cl_2$ (5 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (64 mg, 29 $\mu$mol) in methanol (5 mL), and the mixture was stirred for 16 h. Column chromatography (silica, $CH_2Cl_2$/hexanes, 1:1) afforded 2.4 mg (92%): $^1$H NMR $\delta$ 1.85 (s, 18H), 2.50 (s, 3H), 2.62 (s, 9H), 7.29 (s, 6H), 7.60, 8.04 (AA′BB′, 2 × 2H), 8.64 (m, 4H), 8.82 (m, 2H), 9.73 (m, 2H); LD-MS obsd 906.1; FAB-MS obsd 900.2825, calcd exact mass 900.2840 ($C_{57}H_{48}N_4OSZn$); $\lambda_{abs}$ ($CH_2Cl_2$) 440, 566, 611 nm.

**Electrochemistry.** The solution electrochemical studies of the Zn-porphyrins were performed using techniques and instrumentation previously described.[28] 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.

The SAM electrochemical studies of the Zn-porphyrins were performed on 75-micron wide gold band electrodes formed via E-beam evaporation (to a thickness of 100 nm) onto piranha-solution-etched glass slides that had a 1 nm thick underlayer of chromium. The electrochemical cell was constructed by forming a 3-mm diameter poly(dimethylsiloxane) (PDMS) well (∼3 mm deep) over the gold band. The Zn-porphyrins were dissolved in absolute ethanol, and the solution (∼1 mM) was added to the well and allowed to stand. Deposition times of 30 min were found to give the same quality cyclic voltammograms as those obtained with much longer deposition times (12 h). After soaking, the solvent was removed and the PDMS well was rinsed with absolute ethanol followed by a final rise with $CH_2Cl_2$. A small amount of $CH_2Cl_2$ containing 1 M TBAH was then added to the PDMS well. Silver and platinum wires were inserted into the well to serve as the reference and counter electrodes, respectively. The cyclic voltammograms were recorded with an Ensman Instruments 400 potentiostat at a rate of 100 V/s.

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**Supporting Information Available:** LD-MS and $^1H$ NMR spectra for all porphyrins; $^1H$ NMR and $^{13}C$ NMR spectra for compounds **7**, **15** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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