

Diverse Redox-Active Molecules Bearing O-, S-, or Se-Terminated Tethers for Attachment to Silicon in Studies of Molecular Information Storage

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A molecular approach to information storage employs redox-active molecules tethered to an electroactive surface. Attachment of the molecules to electroactive surfaces requires control over the nature of the tether (linker and surface attachment group). We have synthesized a collection of redox-active molecules bearing different linkers and surface anchor groups in free or protected form (hydroxy, mercapto, *S*-acetylthio, and *Se*-acetylseleno) for attachment to surfaces such as silicon, germanium, and gold. The molecules exhibit a number of cationic oxidation states, including one (ferrocene), two [zinc(II)porphyrin], three [cobalt(II)porphyrin], or four (lanthanide triple-decker sandwich compound). Electrochemical studies of monolayers of a variety of the redox-active molecules attached to Si(100) electrodes indicate that molecules exhibit a regular mode of attachment (via a Si-X bond, X = O, S, or Se), relatively homogeneous surface organization, and robust reversible electrochemical behavior. The acetyl protecting group undergoes cleavage during the surface deposition process, enabling attachment to silicon via thio or seleno groups without handling free thiols or selenols.

Introduction

The attachment of electroactive molecules to diverse surfaces including metals (e.g., Au), semiconductors (e.g., Si, SnO₂, TiO₂), and insulators (e.g., SiO₂) is essential for studies in the field of molecular electronics. Achieving successful device properties requires strategies that afford (1) uniform surface coverage, (2) a regular mode of attachment, and (3) homogeneous organization of the electroactive molecules. A large number of electroactive molecules bearing thiol tethers have been prepared and examined in self-assembled monolayers (SAMs) on Au given the facile formation of Au-S bonds.¹ Much less work has been done to attach electroactive molecules to silicon, though a number of approaches have been described for derivatizing Si surfaces with small molecules.² Attachment of molecules to oxide surfaces has been investigated for purposes that are quite distinct from molecular electronics. For example, SiO₂ has been derivatized using

approaches similar to those employed for derivatizing chromatographic media; however, the use of siloxane chemistry often affords polymeric multilayers that tend to be insulative.³ Other oxides such as ZrO₂ have been derivatized with molecules bearing phosphonic acid tethers.⁴

We have been engaged in a program aimed at constructing devices that use the properties of molecules to store information. Our approach employs a collection of redox-active molecules in a self-assembled monolayer (SAM) attached to an electroactive surface.⁵ The generic

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design of the molecules includes a redox-active unit, a linker, and a surface attachment group. Information is stored in the distinct redox states of the molecules. As such, the charge-storage molecules constitute molecular capacitors. The surface attachment group serves a mechanical role in tethering the molecule to the surface and an electronic role in providing communication between the surface and the redox-active unit. The duration of charge storage (i.e., charge-retention time) depends on the nature of the redox-active unit and the length and composition of the linker.

We have prepared a large number (100+) of redox-active molecules that bear thiol-derivatized tethers. The redox-active molecules include ferrocenes and a wide variety of porphyrinic macrocycles in diverse molecular architectures; the architectures include porphyrin monomers,^{6,7} ferrocene-porphyrins,⁸ multiporphyrin arrays,^{9,10} triple-decker sandwich compounds composed of lanthanide metals coordinated by porphyrin and phthalocyanine ligands,^{11,12} and dyads¹³ of such triple deckers. The thiol-derivatized molecules have been examined in SAMs on Au. The major objectives of the studies on Au were to carry out fundamental studies of the effects of molecular architecture and linker composition/length on charge-retention properties and rates of electron transfer.^{14–16} For practical applications, we recently examined a much more limited selection of compounds on Si(100).^{17,18} The molecules examined were 4-(hydroxymethyl)phenylferrocene (**1-OH**) and 5-[4-(hydroxymethyl)phenyl]-10,15,20-trimesitylporphyrin zinc(II) (**2-OH**). For surface dilution effects, the inert adsorbate biphenylmethanol (**3-OH**) was employed. In each case, the benzyl alcohol tether afforded an alkyl siloxane connection upon attachment to the silicon surface. We also have prepared a ferrocenylmethylphosphonic acid, which was attached to a thin layer of SiO₂ on a silicon substrate.¹⁹

In this paper, we describe the synthesis of a much more diverse collection of candidate charge-storage molecules that incorporate a terminal functional group suitable for attachment to silicon. We also report the electrochemical properties of a representative selection of the molecules attached to silicon. One set of ferrocenes, porphyrins, and biphenylmethyl derivatives has alcohol, thiol, or selenol termini (in free or protected form) for comparative studies of the effect of the attachment atom on electron-transfer rates. The motivation for this study originated in part from a report by Ratner, who predicted the conductivity of a tether depends on the surface attachment atom, increasing along the series O, S, and Se.²⁰ A group of porphyrin-alcohol/thiols was designed to have minimal facial encumbrance, thereby offering no steric barrier to lateral electron-transfer interactions in SAMs. Two triple deckers have been prepared that incorporate alcohol tethers of different length. The synthetic work described herein spanned a period of years, during which the synthetic methods for preparing porphyrins have evolved. Accordingly, both traditional statistical methods and more recent rational methods have been employed for the synthesis of porphyrins.

This paper is the first in a series. The second paper in this series describes methodology for preparing diverse porphyrinic molecules bearing phenylphosphonic acid tethers for attachment to oxides (e.g., SiO₂, TiO₂).²¹ The third paper in the series describes methodology for preparing porphyrins bearing benzylphosphonic acid tethers or tripodal tethers composed of benzylphosphonic acid legs.²² The tripodal tethers are employed to enforce a vertical orientation of porphyrins at a defined distance from the surface. The fourth paper in the series describes tripodal tethers bearing a protected benzylthiol group on each leg of the tripod and a redox-active molecule at the vertex of the tripod.²³ The redox-active molecules include a ferrocene, a porphyrin, a phthalocyanine, a ferrocene-porphyrin, and two examples of triple decker sandwich compounds. Taken together, this work provides the foundation for the synthesis of diverse redox-active molecules suitable for attachment to a range of surfaces for studies of information storage.

Results and Discussion

A. Ferrocenes and Porphyrins Bearing Alcohol, Thiol, or Selenoacetate Groups.

We sought to prepare ferrocenes, porphyrins, and inert analogues bearing benzyl linkers with different heteroatom (O, S, or Se) termini for attachment to silicon or gold. The structures of the target compounds are shown in Chart 1. Several of these compounds (**1-OH**,¹⁸ **2-OH**,¹⁸ **2-SAc**,⁷ **3-SAc**,²⁴ **3-SH**²⁵) are known, and **3-Cl** and **3-OH** are commercially available. The general strategy for preparing the alcohols

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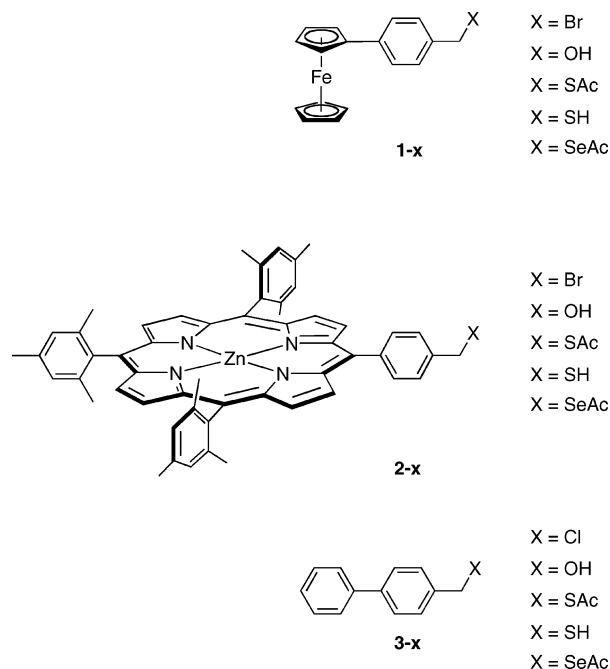
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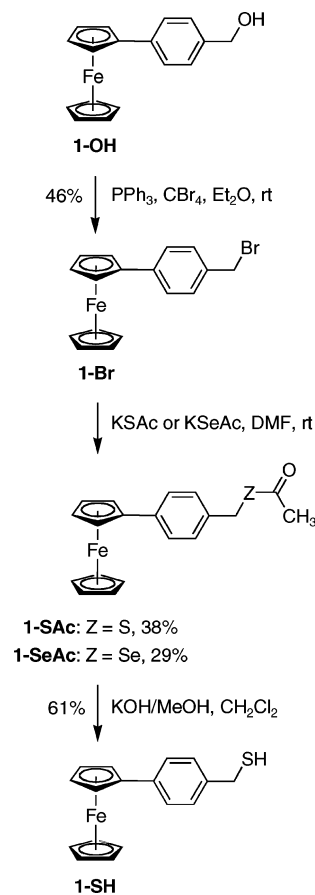
CHART 1



is to synthesize the corresponding ester followed by reduction to the alcohol. The general strategy for the remaining compounds begins with a halomethyl derivative, available commercially or by direct synthesis. Treatment of the halomethyl compound with KSAc or KSeAc affords the thio or selenyl ester, which can be hydrolyzed to give the free thiol or selenol if desired. The *S*-acetylthio derivatives of diverse molecules are known to undergo deprotection on exposure to Au, thereby enabling in situ surface attachment via the Au-S linkage without handling free thiols.^{6,26} We prepared several compounds bearing free thiols for studies of surface coverage densities. The selenols are more air-sensitive than thiols and readily form the corresponding diselenides.²⁷ Tour has prepared various protected selenols and studied their deprotection chemistry.²⁸ Given the sensitivity of free selenols, we decided to maintain the selenyl derivatives in the *Se*-acetylseleno form for attempted in situ deprotection or, if needed, chemical deprotection immediately prior to use.

We have previously prepared a hydroxymethyl-substituted ferrocene (**1-OH**) by reduction of the corresponding ester.¹⁸ Treatment of **1-OH** with PPh₃ and CBr₄ in dry diethyl ether at room temperature afforded **1-Br** in 46% yield (Scheme 1). This compound was unstable on silica and was used immediately in the next step. Reaction of

SCHEME 1



1-Br with KSAc in DMF²⁹ at room temperature for 1 h afforded the corresponding *S*-acetylthio-derivatized ferrocene (**1-SAc**) in 38% yield. In a similar way, KSeAc³⁰ reacted with **1-Br** generated in situ, affording **1-SeAc** in 29% yield. Treatment of **1-SAc** in CH₂Cl₂ with methanolic KOH at room temperature afforded the ferrocene-thiol **1-SH** in 61% yield.

The A₃B-type porphyrin **2-Br**, which bears three mesityl groups, is not available via rational synthetic methods. Synthesis of **2-Br** was realized by a mixed-aldehyde condensation³¹ at elevated concentration³² of pyrrole, mesitaldehyde, and α -bromo-*p*-tolualdehyde^{7,33} with BF₃·O(Et)₂-ethanol cocatalysis³⁴ (achieved by reaction in CHCl₃ containing ethanol as stabilizer). The resulting mixture of porphyrins was treated with Zn(OAc)₂·2H₂O to give the zinc porphyrins. A mixture of porphyrins where the porphyrins possess different degrees of facial encumbrance is more readily separated upon forming the zinc chelates because the facial encumbrance modulates the affinity of the apical zinc site for adsorption media.³¹

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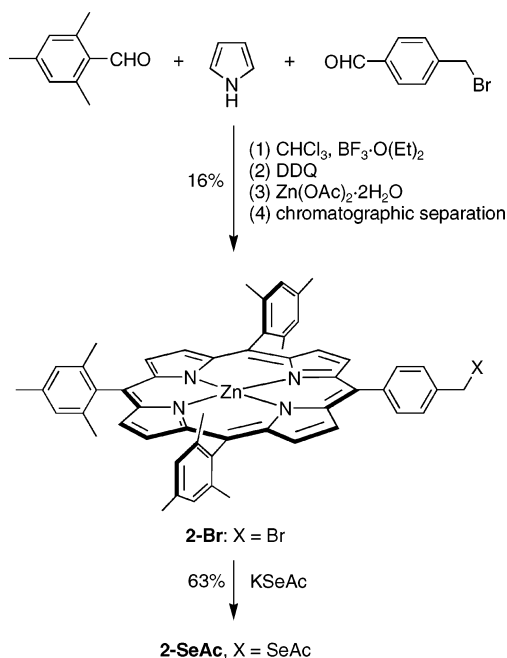
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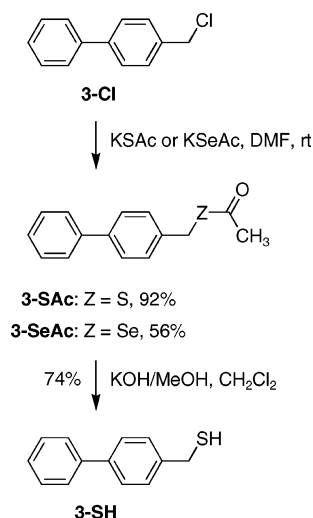
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SCHEME 2



SCHEME 3

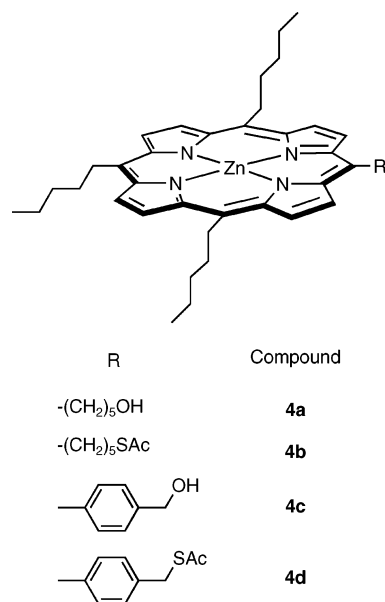


The required porphyrin **2-Br** was separated by chromatography (silica, hexanes/ CH_2Cl_2) in 16% yield (Scheme 2). Compound **2-Br** was treated with KSeAc to give **2-SeAc** in 63% yield. Treatment of the known porphyrin **2-SAc** with methanolic KOH in CH_2Cl_2 gave the porphyrin-thiol **2-SH** in 78% yield.

To obtain the biphenylmethyl derivatives, 4-phenylbenzyl chloride was treated with KSac in DMF to obtain **3-SAc** in 92% yield, which upon hydrolysis with KOH in methanol gave **3-SH** in 74% yield. Compound **3-SAc** has been described in a patent,²⁴ and the hydrolysis product **3-SH** has been prepared as a reaction intermediate.²⁵ Similar reaction with KSeAc in DMF gave **3-SeAc** in 56% yield (Scheme 3).

B. Sterically Unencumbered Porphyrins Bearing Alcohol or S-Acetylthio Groups. Our prior studies of information storage have employed porphyrins bearing mesityl groups at the nonlinking meso positions. Mesityl groups suppress cofacial interactions between neighbor-

CHART 2



ing porphyrins. Porphyrins bearing pentyl groups at the meso positions have very little steric hindrance, yet such porphyrins exhibit high solubility in organic solvents.³⁵ Four target molecules that incorporate pentyl groups at the three nonlinking meso positions are shown in Chart 2. The linker is either a benzyl unit or a pentyl unit, while the surface attachment groups include an alcohol (for attachment to silicon) or a protected thiol (for attachment to gold or silicon).

The synthesis of A_3B -porphyrins **4a–c** was achieved by mixed-aldehyde condensation of pyrrole, hexanal, and a given aldehyde followed by oxidation with DDQ and chromatographic purification. The aldehydes employed to introduce the tether were **5**,³⁶ **6** (prepared from 6-bromohexanal³⁷ and used immediately owing to instability), and methyl 4-formylbenzoate (**7**). The polarity difference between the pentyl and ester/*S*-acetylthioester groups enabled facile separation, affording the free base porphyrins in ~9%, 7%, and 16% yields, respectively. Subsequent metalation gave the zinc chelates **8**, **4b**, and **9** in 64%, 63%, and 73% yields, respectively. Finally, reduction of porphyrins **8** and **9** using excess LiAlH_4 afforded the target porphyrin alcohols **4a** and **4c** in 87% and 92% yields, respectively (Scheme 4).

A rational synthetic route was employed for the synthesis of porphyrin **4d**. Dipyrromethane **10**³⁸ and dipyrromethane-dicarbonyl **11-diol** (derived by reduction of **11**³⁹) were condensed under new acid catalysis conditions [$\text{Yb}(\text{OTf})_3$ in CH_2Cl_2 at room temperature]⁴⁰ followed by oxidation with DDQ, affording porphyrin **12** in 8.8% yield. TLC and laser-desorption mass spectrometry in the

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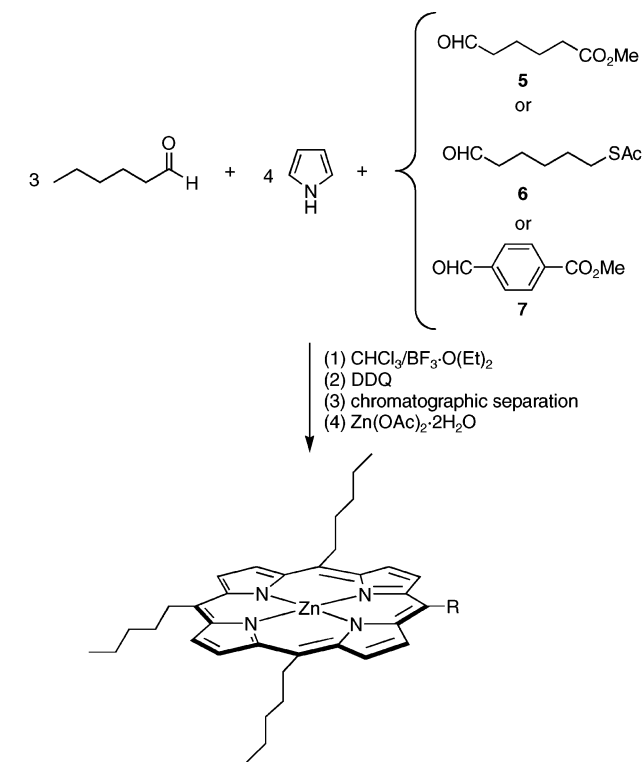
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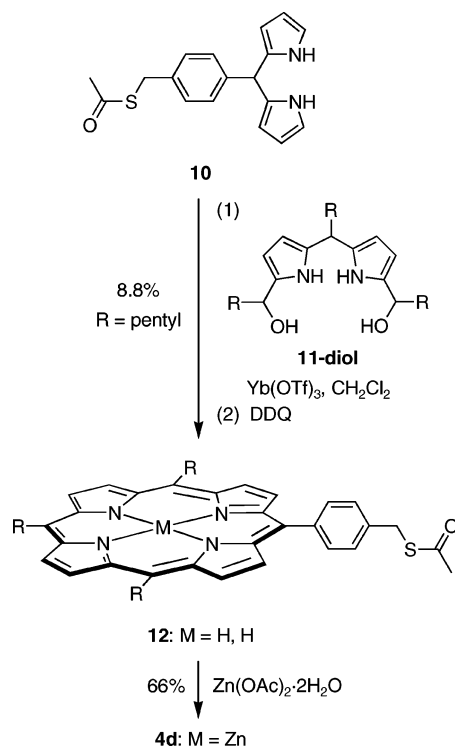
SCHEME 4



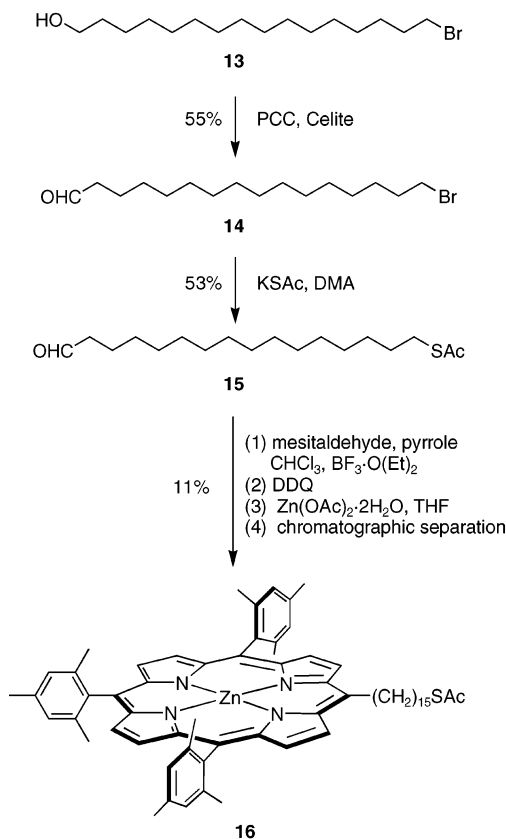
absence of a matrix (LDMS)⁴¹ showed the presence of trace levels of *meso*-tetrapentylporphyrin, indicating the occurrence of a low level of acidolysis leading to the formation of undesired porphyrins (i.e., scrambling). A low level of scrambling is characteristic of pentyl-substituted dipyrromethane-dicarbonyls such as **11-diol**.⁴⁰ The target free base porphyrin **12** was readily purified. Metalation afforded the zinc chelate **4d** in 66% yield (Scheme 5).

C. Porphyrins Bearing Diverse Linkers and Surface Attachment Groups. An A₃B-porphyrin bearing a long alkyl tether was prepared to examine the effects of a long, nonaryl spacer on the charge-retention properties. The long-chain aldehyde was prepared using the strategy reported for 7-(*S*-acetylthio)heptanal⁷ (Scheme 6). Oxidation of 16-bromo-hexadecanol (**13**) with PCC on Celite⁴² gave 16-bromohexadecanal (**14**, 55% yield), which upon substitution with KSAc gave the desired *S*-acetylthio-protected aldehyde **15** in 53% yield. A mixed-aldehyde condensation of pyrrole, mesitaldehyde, and **15** at elevated concentration³² with BF3·O(Et)2-ethanol coa-

SCHEME 5



SCHEME 6

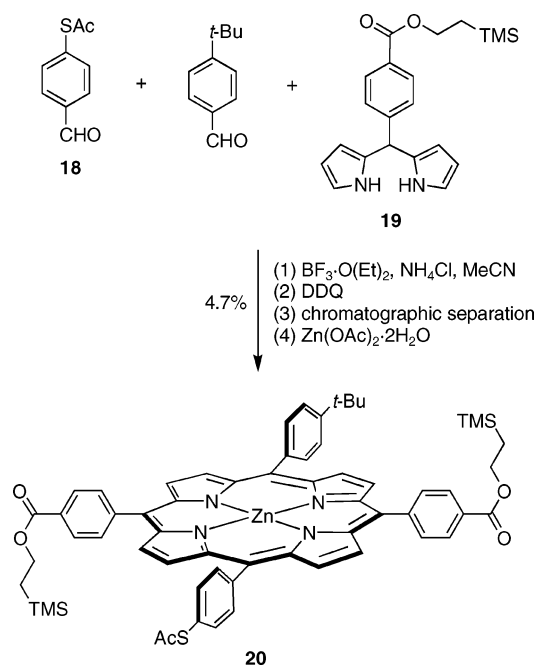


talysis³⁴ followed by oxidation with DDQ afforded a readily separable mixture of porphyrins. The free base porphyrin was isolated (13% yield) and metalated to give zinc porphyrin **16** in 11% overall yield.

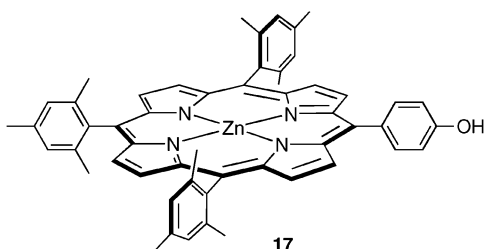
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SCHEME 7



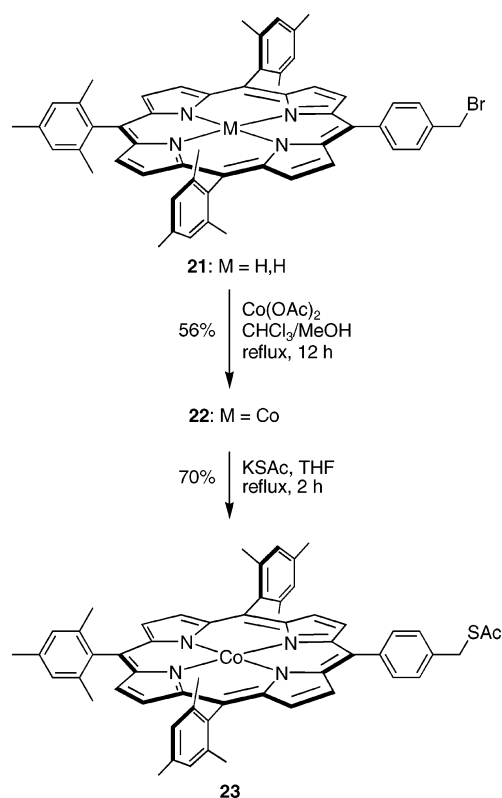
We also prepared an A₃B-type porphyrin bearing a phenol group to investigate the effects of attachment to a silicon surface without the intervening methylene group as in **2-OH**. Zinc porphyrin **17** was prepared in 50% yield by metalation of 5-(4-hydroxyphenyl)-10,15,20-trimesitylporphyrin.⁴³



To investigate the effects of lateral interactions among porphyrins in a SAM, we prepared a porphyrin bearing two carboxy groups in the flanking “wing” positions. The mixed condensation of 4-*tert*-butylbenzaldehyde, aldehyde **18**,⁶ and dipyrromethane **19**⁴⁴ was carried out using the minimal-scrambling conditions⁴⁵ that were identified from studies of dipyrromethane + aldehyde reactions for use with unhindered aldehydes. The free base porphyrin bearing two protected carboxy groups in a *trans* position and one *S*-acetylthio tether was obtained in 5.1% yield (Scheme 7). Subsequent metalation gave the target zinc porphyrin **20** in 93% yield.

D. Molecules with Increased Number of Oxidation States. 1. Cobalt Porphyrins. We have explored the use of cobalt(II) porphyrins to serve as molecules that provide three cationic oxidation states: the mono- and

SCHEME 8



dication porphyrin radicals and a metal-centered Co(II)/Co(III) oxidation. Treatment of porphyrin **21**²² with Co(OAc)₂ afforded cobalt porphyrin **22** in 56% yield. Treatment of the latter with KSac in THF furnished the *S*-acetylthio-derivatized cobalt porphyrin **23** in 70% yield (Scheme 8).

2. Triple-Decker Sandwich Compounds Bearing Alcohol Groups. Triple-decker sandwich coordination compounds (composed of two lanthanides and three porphyrinic ligands)⁴⁶ provide a straightforward means for storage of multiple bits of information.^{11–13} To attach triple deckers to silicon, we sought to prepare triple deckers bearing alcohol tethers of different length. The synthesis of triple deckers of composition (Pc)Eu(Pc)Eu(Por) (where Pc and Por indicate phthalocyaninato and porphyrinato ligands, respectively) begins with the reaction of a porphyrin and Eu(acac)₃·*n*H₂O in refluxing 1,2,4-trichlorobenzene (1,2,4-TCB).^{47,48} The resulting europium-porphyrin half-sandwich complex⁴⁹ is then treated with a (Pc)Eu(Pc) double decker under continued reflux. This method is superior to the statistical route wherein the porphyrin, phthalocyanine, and europium salt are reacted simultaneously, affording a mixture of several types of triple deckers.

The first triple-decker alcohol was prepared by reaction of porphyrin ester **24**⁵⁰ and Eu(acac)₃·*n*H₂O in refluxing

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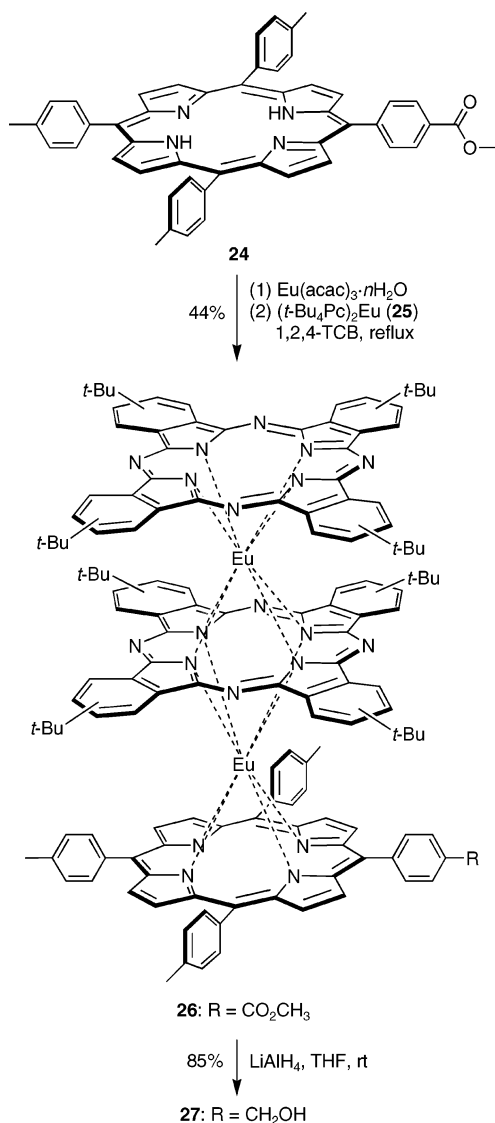
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1,2,4-TCB ($\sim 230^\circ\text{C}$). After the half-sandwich complex was formed, double decker $(t\text{-Bu}_4\text{Pc})_2\text{Eu}$ (**25**)⁴⁸ was added with continued reflux for 17 h. Chromatographic workup including use of preparative size exclusion chromatography (SEC)⁵¹ afforded triple-decker ester **26** in 44% yield. Reduction of **26** with LiAlH_4 in dry THF at room temperature gave the desired triple-decker alcohol **27** in 85% yield (Scheme 9). It is noteworthy that the similar reaction of the analogous porphyrin-alcohol (obtained by reduction of **24**) and double decker **25** did not give triple decker **27**.

The synthesis of the second triple-decker alcohol was initiated by mixed-aldehyde condensation of pyrrole, *p*-tolualdehyde, and ethyne-protected aldehyde **28**¹¹ under new cocatalysis conditions [$\text{BF}_3 \cdot \text{O}(\text{Et})_2 - \text{NaCl}$ in $\text{CH}_2\text{-Cl}_2$ at room temperature]⁵² followed by oxidation with

DDQ. The desired porphyrin **29** was readily separated owing to the polarity of the hydroxyl-substituted protecting group. Treatment of **29** with $\text{Eu}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ in refluxing 1,2,4-TCB followed by double decker $(t\text{-Bu}_4\text{Pc})_2\text{Eu}$ (**25**) under continued reflux afforded the deprotected ethynyl-triple decker **30** in 65% yield. The latter was coupled with 4-iodobenzyl alcohol under standard Sonogashira Pd-coupling conditions⁵³ to give the desired triple-decker alcohol (**31**) in 58% yield following workup using preparative SEC (Scheme 10).

E. Electrochemical Studies of Monolayers on Si(100). The redox-active molecules bearing an alcohol, *S*-acetylthio, or *Se*-acetylseleno group were attached to Si surfaces for electrochemical measurements. The molecules bearing an alcohol were attached to iodine-modified surfaces, whereas the *S*-acetylthio- or *Se*-acetylseleno-derivatized compounds were attached to hydrogen-passivated surfaces.¹⁸ With the latter compounds, cleavage of the acetyl protecting group occurred during the deposition process, thereby enabling attachment without handling the free thiols or selenols. The details of the procedure for attaching the molecules to Si surfaces can be found in ref 18. The basic procedure involves placing a drop of solution containing the molecules on the surface and heating to dryness, followed by continued heating of the dry deposit.

The electrochemical behavior was investigated for a variety of the complexes tethered to Si(100) via an O, S, or Se atom. Below, we describe the general characteristics of the electrochemical behavior of the monolayers by using several representative examples rather than presenting a comprehensive analysis of all of the complexes studied. These examples illustrate the salient features of the electrochemical behavior of the larger body of complexes that have been examined.

The fast-scan (100 V s^{-1}) cyclic voltammograms of monolayers of **1-SH**, **2-SH**, **23**, and **31** are shown in Figure 1. The voltammetric signatures of these complexes exhibit increasing complexity, with the number of redox waves monotonically increasing from one to four. As we have previously discussed, access to multiple oxidation states provides a possible basis for multibit information storage.^{5,7-13}

The voltammetric characteristics observed for the monolayers of **1-SH** and **2-SH** on Si(100) (Figure 1A and 1B, respectively) are very similar to those we have previously reported for monolayers of **1-OH** and **2-OH**.¹⁸ The ferrocene exhibits one redox wave ($E_{1/2} \sim 0.5 \text{ V}$), and the porphyrin exhibits two waves ($E_{1/2}(1) \sim 0.79 \text{ V}$; $E_{1/2}(2) \sim 1.15 \text{ V}$). The voltammetric characteristics observed for monolayers formed from the protected thiols **1-SAc** and **2-SAc** are similar to those observed for monolayers of the unprotected thiols. These data indicate that the *S*-acetylthio protecting group cleaves upon interaction with the hydrogen-passivated silicon surface, resulting in formation of an Si-S linkage. The cleavage of the *S*-acetylthio protecting group that occurs upon interaction of **1-SAc** and **2-SAc** with the hydrogen-passivated silicon surface parallels the behavior observed upon exposure to a gold surface.^{5,8,14,15} Along these lines, the voltam-

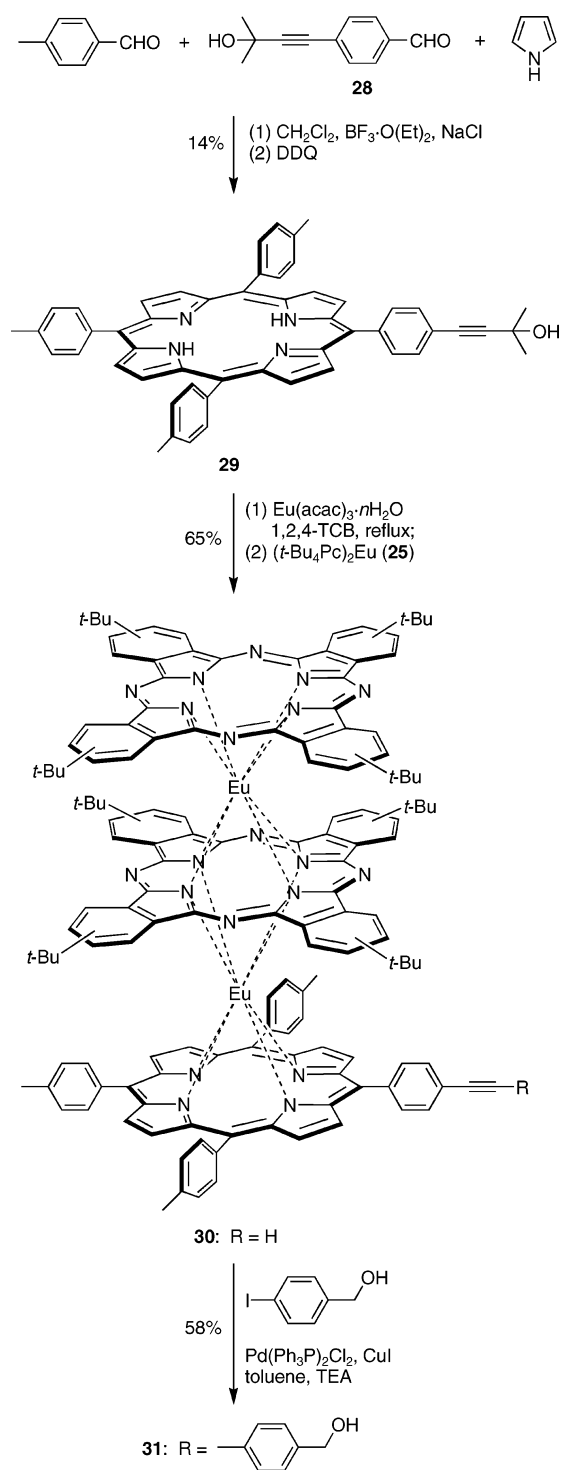
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SCHEME 10



metric characteristics observed for monolayers formed from **1-SeAc** and **2-SeAc** (not shown), either on silicon or gold surfaces, are very similar to those observed for the thiol analogues. The electrochemical results indicate that the *Se*-acetylseleno protecting group undergoes cleavage on gold and on hydrogen-passivated silicon, as observed for the *S*-acetylthio protecting group. The cleavage process enables in situ attachment without necessitating preparation and handling of the corresponding free selenols. Collectively, these studies indicate that attachment of redox-active species to silicon surfaces

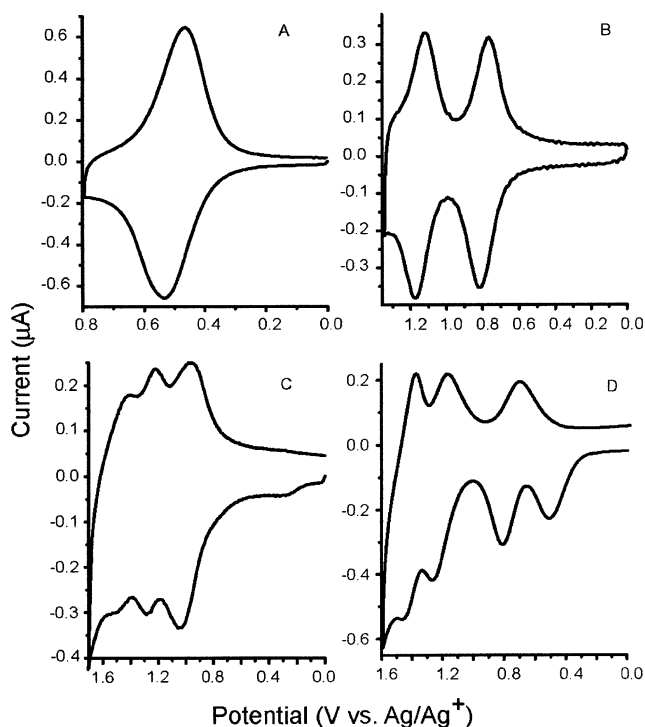


FIGURE 1. Fast-scan (100 V s^{-1}) cyclic voltammograms of monolayers of (A) **1-SH**, (B) **2-SH**, (C) **23**, and (D) **31** on *p*-type Si(100) microelectrodes in propylene carbonate containing $1.0 \text{ M Bu}_4\text{NPF}_6$.

via an S- or Se-atom tether elicits robust monolayers that are comparable in general electrochemical characteristics to those obtained via an O-atom tether. At present, we are investigating the detailed features of the electron-transfer and charge-retention characteristics of the S- and Se-attached ferrocene and porphyrin monolayers.

The fast-scan (100 V s^{-1}) cyclic voltammogram of the monolayer of the thiol-derivatized cobalt porphyrin **23** on Si(100) (Figure 1C) exhibits three redox waves ($E_{1/2}(1) \sim 1.02 \text{ V}$; $E_{1/2}(2) \sim 1.25 \text{ V}$; $E_{1/2}(3) \sim 1.52 \text{ V}$), generally consistent with the expectation that the metal center as well as the porphyrin are redox active. The lowest potential wave would be expected to be associated with the metal center, whereas the two higher potential waves would correspond to the first and second oxidations of the porphyrin. The fact that the potential of the $\text{Co}^{2+}/\text{Co}^{3+}$ couple (nominally $E_{1/2}(1) \sim 1.02 \text{ V}$) is quite close in potential to the first porphyrin wave (nominally $E_{1/2}(2) \sim 1.25 \text{ V}$) is generally consistent with a structure in which the metal center is four-coordinate (no axial ligands). In particular, axial ligation of cobalt porphyrins typically shifts the $\text{Co}^{2+}/\text{Co}^{3+}$ couple to less positive potentials, resulting in the $\text{Co}^{2+}/\text{Co}^{3+}$ potential being much less positive than the first porphyrin oxidation potential.⁵⁴ For example, solution electrochemical studies of **23** in the coordinating solvent THF indicate that the potential of the $\text{Co}^{2+}/\text{Co}^{3+}$ couple is $\sim 0.7 \text{ V}$ lower than that of the first porphyrin potential. A four-coordinate cobalt ion in the monolayer of **23** is consistent with an architecture in which the porphyrins are well packed. In support of this

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argument, voltammetric data recorded for a monolayer of **23** using THF as the solvent yielded essentially the same potential for the $\text{Co}^{2+}/\text{Co}^{3+}$ couple as for the noncoordinating solvent CH_2Cl_2 . Accordingly, the packing in the monolayer is sufficiently tight that the metal center is inaccessible to the THF molecules.

The fast-scan (100 V s^{-1}) cyclic voltammogram of the monolayer of triple-decker alcohol **31** on Si(100) (Figure 1D) exhibits redox characteristics that are qualitatively similar to the thiol-derivatized analogue on Au(111).^{11–14} However, there are certain differences in the voltammetry on the gold versus silicon surfaces. In particular, monolayers on Au(111) exhibit four distinct oxidation and reduction waves in the 0.0–1.6 V range. For the monolayers on Si(100), four oxidation waves are also observed [$E_{\text{ox}}(1) \sim 0.51 \text{ V}$; $E_{\text{ox}}(2) \sim 0.82 \text{ V}$; $E_{\text{ox}}(3) \sim 1.28 \text{ V}$; $E_{1/2}(4) \sim 1.47 \text{ V}$]; however, only three reduction waves are observed [$E_{\text{red}}(2) \sim 0.70 \text{ V}$; $E_{\text{red}}(3) \sim 1.17 \text{ V}$; $E_{\text{red}}(4) \sim 1.37 \text{ V}$]. The reduction wave that is the partner of the lowest potential oxidation wave is completely absent. Scans to more negative potentials (-0.5 V) and/or scans at much slower rates (100 mV s^{-1}) failed to detect this wave. Regardless, the monolayer is completely reduced to the neutral state as evidenced by the observation that repeated scans always yield the lowest potential oxidation wave. One possible explanation for the absence of the lowest potential reduction wave is that the potential for this process is lower in energy than the Fermi level of the *p*-type Si(100), which lies at $\sim 0.25 \text{ eV}$ (as determined by X-ray photoelectron spectroscopy). At potentials greater than the Fermi energy, the Fermi level is pulled completely into the valence band and the semiconductor is “metal-like,” with excess carriers available for facile redox processes with the attached molecules. On the other hand, at potentials lower than the Fermi energy, the Fermi level is above the valence band and the number of carriers available for redox processes is greatly diminished. This could result in what appears to be highly irreversible electrochemical behavior (i.e., absence of the first reduction wave).

Conclusions

The synthetic pathways outlined herein provide access to a diverse collection of redox-active compounds bearing tethers for attachment to an electroactive surface. The surface attachment groups, which were chosen for comparative studies of information storage on silicon platforms, include hydroxy, mercapto, *S*-acetylthio, and *Se*-acetylseleno groups. The acetyl-protecting unit cleaves in situ during the process of attachment to silicon. The redox-active molecules include ferrocene, zinc porphyrin, cobalt porphyrin, and triple-decker lanthanide sandwich coordination compounds. This set of compounds affords 1–4 cationic oxidation states, respectively. The porphyrins have been tailored in terms of facial encumbrance and linker length. The results obtained from examining a selection of compounds in SAMs on silicon indicate that molecules of this design are suitable candidates for the active elements in molecular-based information storage devices.

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Supporting Information Available: Complete experimental procedures; ^1H NMR and LDMS (or MALDI-MS) spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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