

Synthesis of Porphyrins Bearing Hydrocarbon Tethers and Facile Covalent Attachment to Si(100)

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The use of redox-active molecules as the active storage elements in memory chips requires the ability to attach the molecules to an electroactive surface in a reliable and robust manner. To explore the use of porphyrins tethered to silicon via carbosilane linkages, 17 porphyrins have been synthesized. Fourteen porphyrins bear a tether at a single meso site, and three porphyrins bear functional groups at two β sites for possible two-point attachment. Two high-temperature processing methods (400 °C under inert atmosphere) have been developed for rapid (minutes), facile covalent attachment to Si platforms. The high-temperature processing conditions afford attachment either by direct deposition of a dilute solution (1 μ M–1 mM) of the porphyrin sample onto the Si substrate or sublimation of a neat sample onto the Si substrate. The availability of this diverse collection of porphyrins enables an in-depth examination of the effects of the tether (length, composition, terminal functional group, number of tethers) and steric bulk of nonlinking substituents on the information-storage properties of the porphyrin monolayers obtained upon attachment to silicon. Attachment proceeds readily with a wide variety of hydrocarbon tethers, including 2-(trimethylsilyl)ethynyl, vinyl, allyl, or 3-butenyl directly appended to the porphyrin and iodo, bromomethyl, 2-(trimethylsilyl)ethynyl, ethynyl, vinyl, or allyl appended to the 4-position of a *meso*-phenyl ring. No attachment occurs with substituents such as phenyl, *p*-tolyl, mesityl, or ethyl. Collectively, the studies show that the high-temperature attachment procedure (1) has broad scope encompassing diverse functional groups, (2) tolerates a variety of arene substituents, and (3) does not afford indiscriminate attachment. The high-temperature processing conditions are ideally suited for use in fabrication of hybrid molecular/semiconductor circuitry.

Introduction

The field of molecular electronics has been driven in part by the prospect that devices that rely on the bulk properties of semiconductors will fail to retain the required characteristics to function when feature sizes reach nanoscale dimensions. As a consequence, there has been much interest in developing molecule-based electronic materials for use in both memory architectures and circuit elements.¹ Toward this goal, we have been engaged in a program aimed at constructing devices that use the properties of molecules to store information.^{2–6} In our approach, a collection of redox-active porphyrinic molecules attached to an electroactive surface serves as

the active storage medium, and information is stored in the discrete redox states of the molecules. The focus of our work has been developing a hybrid architecture, where the molecular material is attached to a semiconductor platform. The implementation of hybrid molecular/semiconductor architectures as a transition technology leverages the vast infrastructure of the semiconductor industry with the advantages afforded by molecule-based active media.

The success of such a hybrid architecture requires (1) a straightforward means of attaching porphyrins to an

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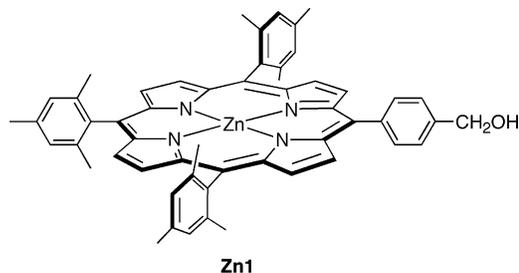
(6) Roth, K. M.; Yasseri, A. A.; Liu, Z.; Dabke, R. B.; Malinovskii, V.; Schweikart, K.-H.; Yu, L.; Tiznado, H.; Zaera, F.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. *J. Am. Chem. Soc.* **2003**, *125*, 505–517.

electroactive surface, particularly large-wafer silicon, and (2) a robust linkage that can withstand large numbers of redox cycles. A number of methods have been developed for covalent attachment of organic molecules to silicon surfaces.⁷ For example, the reaction of Si (hydrogen-passivated or chlorine-modified) with an alcohol affords the self-assembled film containing RO–Si linkages. However, the reaction requires use of neat liquids or a very high concentration of the molecules to be attached.^{8–11} Porphyrins generally have low solubility in organic solutions, with concentrations of ~50 mM being a typical upper limit. The method we previously developed for attaching porphyrins to Si platforms (either hydrogen-passivated or iodine-modified) involved depositing a drop of solution containing the porphyrin compound in a high-boiling solvent (e.g., benzonitrile, bp 191 °C) onto a photolithographically patterned micrometer-size Si electrode, followed by heating at ~170 °C for several hours, during which time additional solvent was added to the sample area.⁶ This method afforded attachment of porphyrins⁶ (and ferrocenes^{3,6}) to Si(100) via tethers that are terminated with OH, SAc, and SeAc groups, yielding RO–Si, RS–Si, and RSe–Si linkages (the acetyl protecting group is cleaved upon attachment) where R represents the tether and accompanying redox-active unit.¹² This procedure produced high quality monolayers useful for academic studies but was unsuited for reproducible fabrication of memory chips on large Si wafers. In addition, in the past few years it has become apparent that more stable monolayers are generally obtained with carbosilane linkages (RC–Si) than alkoxysilane linkages (RO–Si). Achieving a stable linkage of the redox-active unit to the Si surface is essential because as many as 10¹⁵ cycles may be encountered over an operational lifetime in a memory chip.¹³

A number of methods have been developed for derivatizing silicon surfaces via carbosilane linkages.⁷ The methods include pyrolysis of diacyl peroxides,^{14,15} reaction of Grignard reagents (with halogenated silicon surfaces),¹⁶ and electrografting of aryldiazonium salts,¹⁷ alkyl halides,¹⁸ or Grignard reagents.¹⁹ Alkenes have been

employed for attachment to Si via thermal,^{15,20,21} free radical,¹⁵ photochemical (UV),^{22–24} and Lewis acid mediated reactions.^{25,26} Alkynes have been less studied but generally appear to react via the same methods as for alkenes, including thermal,²⁷ free radical,¹⁵ photochemical,²⁸ Lewis acid mediated,^{26,28} and electrografting processes.²⁸ Of these, the thermal methods (typically ~100 °C) with alkenes or alkynes appeared to be most applicable for attaching porphyrinic compounds to large-scale Si wafers. However, the requirement for use of very high concentrations of reactants appeared to exclude such an application.

The success of our thermal attachment method with alcohol tethers (both for porphyrins and other types of molecules)⁶ combined with the fact that porphyrins are known to be stable at very high temperatures (400 °C under inert atmosphere conditions)⁴ where other types of organic molecules decompose prompted us to explore very-high-temperature processing strategies. We developed two high-temperature processing conditions that enable attachment to Si(100) of porphyrins containing a wide variety of functional groups. The conditions entail direct deposition of the sample onto the Si substrate or sublimation onto the Si substrate. The porphyrins examined initially were those that bear functional groups known to attach to silicon, such as the benzyl alcohol porphyrin **Zn1**.⁶ We subsequently found that a number of hydrocarbon tethers also afford attachment. The latter finding prompted the synthesis of a systematic set of porphyrins bearing a wide variety of hydrocarbon tethers.

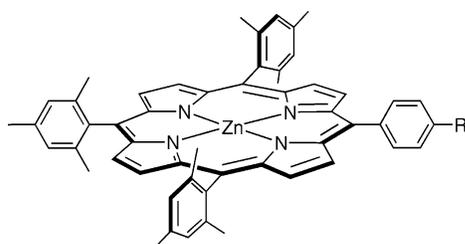


In this paper, we first describe the synthesis of the porphyrins bearing hydrocarbon tethers. We then describe the two high-temperature processing methods for

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CHART 1



- Zn2:** R = -I
Zn3: R = -CH₂Br
Zn4: R = $\text{---}\equiv\text{---TMS}$
Zn5: R = $\text{---}\equiv\text{---H}$
Zn6: R = -CH=CH₂
Zn7: R = -CH₂CH=CH₂

attachment to silicon substrates. Taken together, this work greatly expands the scope of porphyrins that can be attached to silicon and enables attachment under conditions suitable for reproducible fabrication.

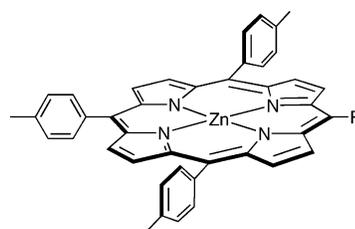
Results and Discussion

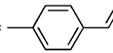
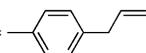
1. Molecular Design. The porphyrins examined herein are designed to probe (1) the effects of the tether (length, composition, terminal functional group) on the ease of attachment and quality of the resulting monolayers on silicon, (2) the ability to attach to silicon via two linkages, and (3) the effects of the size and pattern of nonlinking substituents on the charge-storage properties of the resulting monolayers on silicon. The motivation for these studies stems from the fact that the electron-transfer rates vary depending on the nature of the tether^{2,5} and on the surface density⁶ of the attached redox-active molecules. Most of the porphyrins are zinc chelates, bear a tether at one meso site, and incorporate inert groups at the three nonlinking meso sites. Within this class, one set of molecules varies the nature of the surface attachment group (iodo, bromomethyl, ethyne, vinyl, allyl; **Zn2**–**Zn7**; Chart 1) with mesityl groups at the three nonlinking meso sites. A second set of molecules varies the steric bulk of the nonlinking meso substituents (*p*-tolyl vs mesityl) and the length of the tether (4-vinylphenyl vs 4-allylphenyl) [**Zn6** and **Zn7**, Chart 1; **Zn10** and **Zn11**, Chart 2]. A third set incorporates alkene-terminated tethers of different length (vinyl, allyl, 3-butenyl, 4-vinylphenyl, 4-allylphenyl) with nonlinking *p*-tolyl groups [**Zn10**–**Zn14**, Chart 2]. A fourth set of molecules employs a fixed tether (4-allylphenyl) and varies the size of the two flanking meso substituents (*p*-tolyl, methyl) and the distal meso substituent (*p*-tolyl, mesityl, 2,4,6-triethylphenyl) [**Zn14**–**Zn19**, Chart 3]. Two additional zinc porphyrins bear two halo or two vinyl groups at porphyrin β positions. The final porphyrin is a free base, core-modified monothia-porphyrin with two bromo groups at the β -thiophene positions. Porphyrins **Zn2**,²⁹ **Zn3**,³⁰

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CHART 2



- Zn8:** R = -I
Zn9: R = $\text{---}\equiv\text{---TMS}$
Zn10: R = -CH=CH₂
Zn11: R = -CH₂CH=CH₂
Zn12: R = -CH₂CH₂CH=CH₂
Zn13: R = 
Zn14: R = 

Zn4,³¹ and **Zn5**³² have been prepared previously. A report on the charge-storage properties of the various porphyrin molecules is beyond the scope of this paper and will be described elsewhere.

2. Synthesis of Porphyrins Bearing Meso-Linked Tethers. A. Statistical Approach. Two A₃B-porphyrins were prepared [A = mesityl; B = 4-vinylphenyl (**Zn6**) or 4-allylphenyl (**Zn7**)] for attachment to Si(100). Porphyrins bearing three *meso*-mesityl groups are not available via rational synthesis but can be prepared via statistical mixed-aldehyde condensations. The synthesis of **Zn6** is shown in Scheme 1. 4-Iodobenzaldehyde was protected as the dimethyl acetal (**20**) in 96% yield. Kumada cross-coupling³³ of **20** and vinylmagnesium bromide afforded acetal **21** in 64% yield. Removal of the acetal protecting group of **21** was not attempted given the high reactivity of the styryl moiety under either acidic or basic conditions. A mixed-aldehyde condensation³⁴ was carried out at elevated concentration³⁵ using BF₃·O(Et)₂–EtOH co-catalysis³⁶ with acetal **21**, mesitaldehyde, and pyrrole. Oxidation with DDQ afforded a mixture of porphyrins. The porphyrin mixture was treated with zinc acetate to give the corresponding zinc porphyrins. Porphyrins that have substituents of similar polarity but different degrees of facial encumbrance are more readily separated as the zinc chelates than as the free base forms.³¹ Chromatography afforded **Zn6** in 14% yield.

Allyl-porphyrin **Zn7** was prepared as shown in Scheme 2. Acetal **22**³⁷ was treated with a biphasic solution³⁸ of

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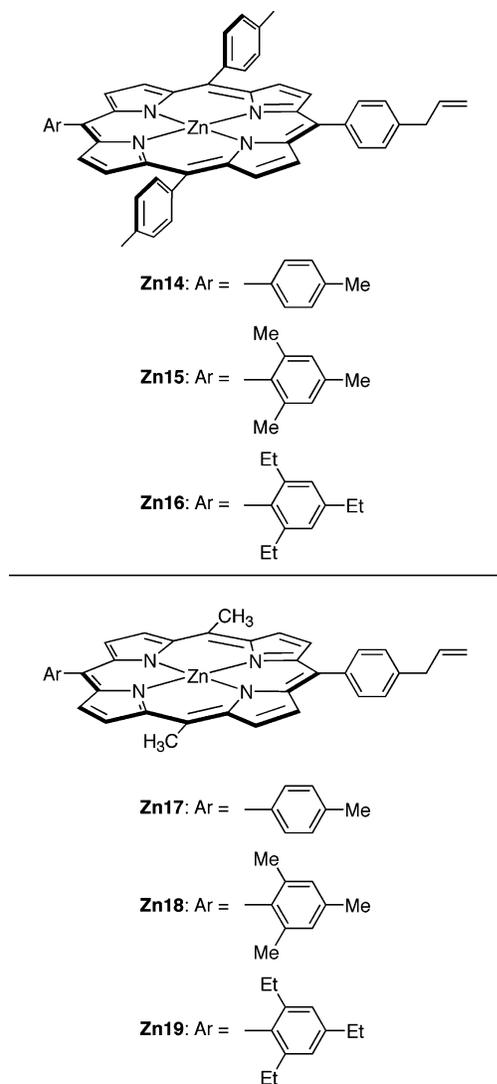
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CHART 3

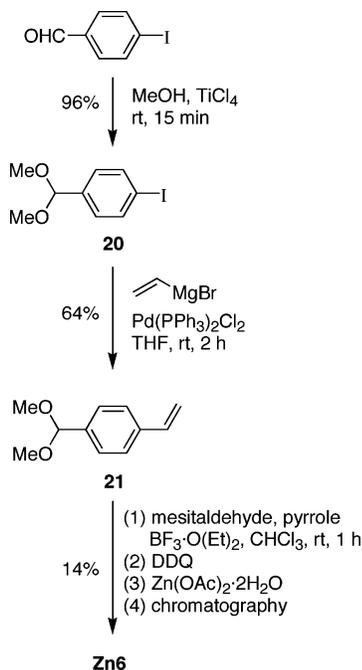


aqueous TFA and CH_2Cl_2 to afford 4-allylbenzaldehyde (**23**) in 81% yield. A mixed-aldehyde condensation³⁴ of **23** with mesitaldehyde and pyrrole was carried out using $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ -EtOH cocatalysis³⁶ followed by DDQ oxidation. Zinc insertion and chromatographic workup afforded **Zn7** in 12% yield.

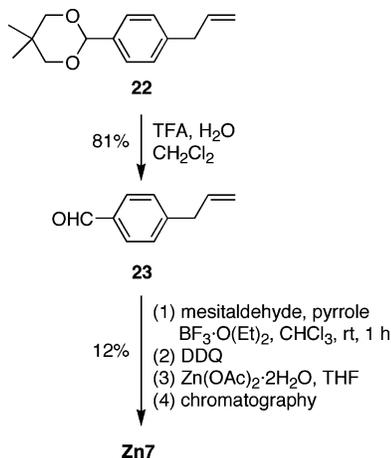
B. Rational Approach. To achieve a scalable synthesis, we have investigated meso substituents that are compatible with a rational synthesis of porphyrins. The rational synthesis relies on the condensation of a dipyrromethane and a dipyrromethane-dicarbonyl.³⁹ The synthesis of the dipyrromethanes and 1,9-diacylidipyrromethanes is described below.

Synthesis of Dipyrromethanes. The synthesis of dipyrromethanes can be achieved via the one-flask reaction of an aldehyde with excess pyrrole.^{40–42} The synthetic method has generally employed TFA as the acid catalyst

SCHEME 1



SCHEME 2



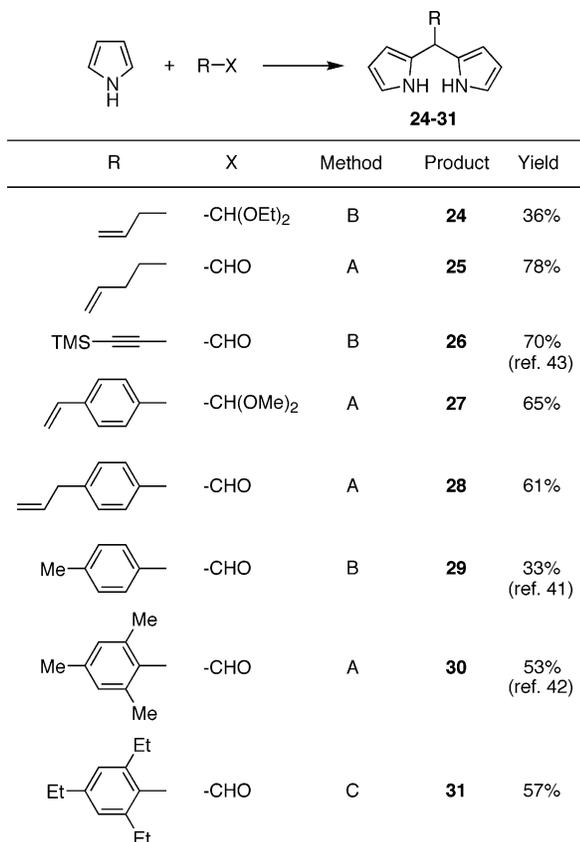
and workup via chromatography and Kugelrohr distillation,⁴¹ but recently we found that milder acids could be employed in conjunction with a more simple purification procedure via direct crystallization.⁴² These procedures were employed to prepare dipyrromethanes **24–31** (Scheme 3). In method A,⁴² an aldehyde (**21**, **23**, mesitaldehyde, or 4-pentenal) was condensed with pyrrole (100 equiv) under InCl_3 (0.1 equiv) catalysis at room temperature for 1.5 h, followed by quenching of the reaction with powdered NaOH, filtration to remove neutralized catalyst, removal of pyrrole, and recrystallization (or column chromatography). In this manner, the new dipyrromethanes **25**, **27**, **28** and the known dipyrromethane **30**⁴² were prepared in good yields. Application of method A to 3-butenal diethyl acetal was unsuccessful. Therefore, the latter was condensed with excess pyrrole (40 equiv) under TFA (0.1 equiv) catalysis at room temperature for 10 min (method B).⁴¹ Analysis of the crude reaction mixture by GC showed a much higher percentage of *N*-confused dipyrromethane (~25%) than is typically observed (~5%) under these conditions.

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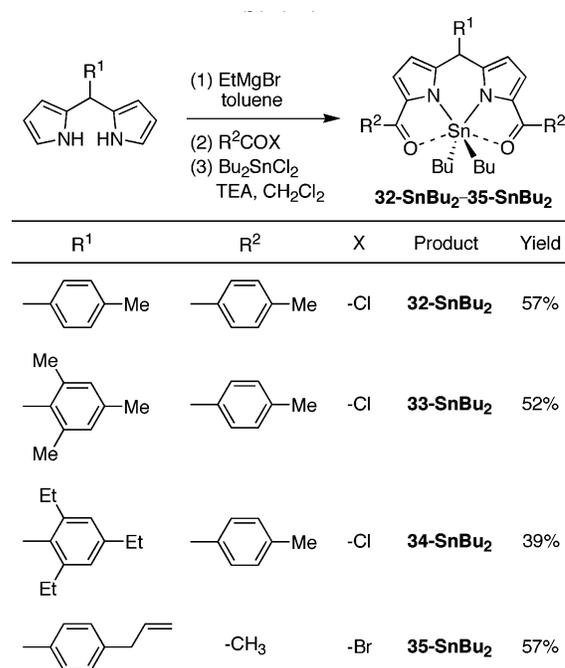
SCHEME 3^a

^a Method A = InCl₃ (0.1 equiv), pyrrole (100 equiv) rt, 1.5 h; method B = TFA (0.1 equiv), pyrrole (40 equiv) rt, 10 min; method C = MgBr₂ (0.5 equiv), pyrrole (100 equiv) rt, 1 h.

Nevertheless, the two regioisomers were readily separated by column chromatography, affording **24** as a viscous oil in 36% yield. The known dipyrromethanes **26**⁴³ and **29**⁴¹ were also prepared following method B. The condensation of 2,4,6-triethylbenzaldehyde⁴⁴ with excess pyrrole (100 equiv) under MgBr₂ (0.5 equiv) catalysis at room temperature for 1 h (method C)⁴² afforded **31** as a viscous oil in 57% yield after column chromatography. All attempts to prepare 5-vinyldipyrromethane (to serve as a precursor to porphyrin **Zn10**) from acrolein or acrolein diethyl acetal via method A or B were unsuccessful.

Synthesis of 1,9-Diacetyldipyrromethanes. The synthesis of several 1,9-diacetyldipyrromethanes is shown in Scheme 4. Treatment of a dipyrromethane with EtMgBr in toluene followed by reaction with an acid chloride typically affords a mixture of the 1-acyldipyrromethane and 1,9-diacetyldipyrromethane.³⁹ Acyldipyrromethanes typically afford amorphous powders upon attempted crystallization and streak extensively on column chromatography. To facilitate isolation of the 1,9-diacetyldipyrromethane, the crude acylation mixture is treated with dibutyltin dichloride. The diacyldipyrromethane–tin complex, which forms selectively, typically is nonpolar and crystallizes readily.⁴⁵

SCHEME 4



In this manner, each dipyrromethane (**28**–**31**) was separately treated with EtMgBr in toluene followed by reaction with the appropriate acid halide (*p*-toluoyl chloride or acetyl bromide). Subsequent reaction with dibutyltin dichloride gave the corresponding tin complex, which was readily isolated by passage through a silica pad followed by precipitation from MeOH. The diacyldipyrromethane–tin complexes **32-SnBu₂**–**35-SnBu₂** were isolated in yields of 39–57%.

Synthesis of Porphyrins. The meso-substituted porphyrins **Zn9** and **Zn11**–**Zn19** were prepared by reaction of a dipyrromethane and a dipyrromethane-dicarbonyl (Scheme 5). The dipyrromethane-dicarbonyls were prepared by reduction with NaBH₄ of the corresponding 1,9-diacetyldipyrromethane–tin complex⁴⁵ or of the unsubstituted 1,9-diacetyldipyrromethane.³⁹ The complete reduction of the tin(IV) complexes requires a slightly longer reaction time (~2 h) versus that of the uncomplexed diacyldipyrromethane (40 min). The dipyrromethane + dipyrromethane-dicarbonyl condensation was performed at room temperature with catalysis by TFA (30 mM) in CH₃CN³⁹ or Yb(OTf)₃ (3.2 mM) in CH₂Cl₂.⁴⁶ Subsequent oxidation with DDQ and zinc metalation afforded the target porphyrin.

The use of mild Lewis acids in CH₂Cl₂ generally affords slightly higher yields and a more facile workup than use of TFA in CH₃CN. However, attempts to prepare **Zn9** (entry 1) using either InCl₃ or Yb(OTf)₃ gave lower yields (3–11%) than with TFA (13%). The yields of porphyrins **Zn16** and **Zn19** were somewhat low (~10%), which is attributed to the bulky 2,4,6-triethylphenyl moiety. Also, porphyrins bearing *meso*-methyl groups (entries 8–10) gave lower yields than the analogous porphyrins bearing *meso-p*-tolyl groups (entries 5–7). In each case, the porphyrin-forming reaction was rapid (<30 min). Analy-

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SCHEME 5^a

| Entry | Components | R ¹ | R ² | R ³ | Conditions | Product | Yield |
|-------|--|----------------|------------------|----------------|------------|-------------|-------|
| 1 | 32 + 26 | | | | A | Zn9 | 13% |
| 2 | 32-SnBu₂ + 24 | | | | B | Zn11 | 44% |
| 3 | 32-SnBu₂ + 25 | | | | B | Zn12 | 42% |
| 4 | 32 + 27 | | | | A | Zn13 | 26% |
| 5 | 32-SnBu₂ + 28 | | | | B | Zn14 | 23% |
| 6 | 33-SnBu₂ + 28 | | | | B | Zn15 | 21% |
| 7 | 34-SnBu₂ + 28 | | | | B | Zn16 | 10% |
| | | R ³ | R ² | R ¹ | | | |
| 8 | 35-SnBu₂ + 29 | | -CH ₃ | | B | Zn17 | 15% |
| 9 | 35-SnBu₂ + 30 | | -CH ₃ | | B | Zn18 | 19% |
| 10 | 35-SnBu₂ + 31 | | -CH ₃ | | B | Zn19 | 9% |

^a Method A = TFA, MeCN, rt; method B = Yb(OTf)₃, CH₂Cl₂, rt.

sis by laser desorption mass spectrometry (LDMS)⁴⁷ of the crude reaction mixtures after bulk oxidation showed no evidence of the presence of any other porphyrin species.

One porphyrin that was not available via this route was the vinyl-porphyrin **Zn10**, owing to the lack of access to 5-vinyldipyrromethane (vide supra). The synthesis of **Zn10** was achieved following the route outlined in Scheme 6. Diacyldipyrromethane **32**⁴⁸ was reduced with NaBH₄ and the resulting **32-diol** was condensed with dipyrromethane (**36**)^{41,49} in CH₂Cl₂ containing Yb(OTf)₃ at room temperature. Subsequent oxidation with DDQ afforded free base porphyrin **37** in 33% yield. Porphyrin

37 was iodinated at the meso position using I₂ and (CF₃-CO₂)₂IC₆H₅ in CHCl₃/pyridine⁵⁰ to furnish free base porphyrin **8** in 82% yield. Zinc insertion afforded **Zn8** in 75% yield. Porphyrin **Zn8** was then subjected to a Stille cross-coupling reaction⁵¹ with (vinyl)tributyltin and Pd(PPh₃)₄ to afford vinylporphyrin **Zn10** in 77% yield.

3. Synthesis of Porphyrins Bearing β-linked Tethers. Porphyrin **Zn8** was of great interest for surface attachment because the meso-iodo substituent would potentially afford a C–Si bond from the porphyrin meso carbon, thereby affording a porphyrin monolayer with direct attachment to the surface. However, **Zn8** displayed poor surface attachment and redox behavior, presumably due to steric hindrance of the flanking hydrogen atoms

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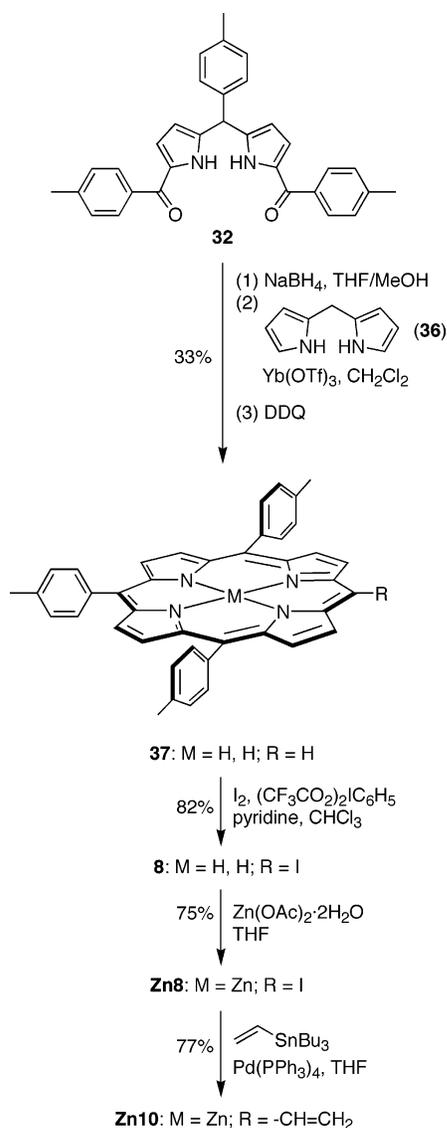
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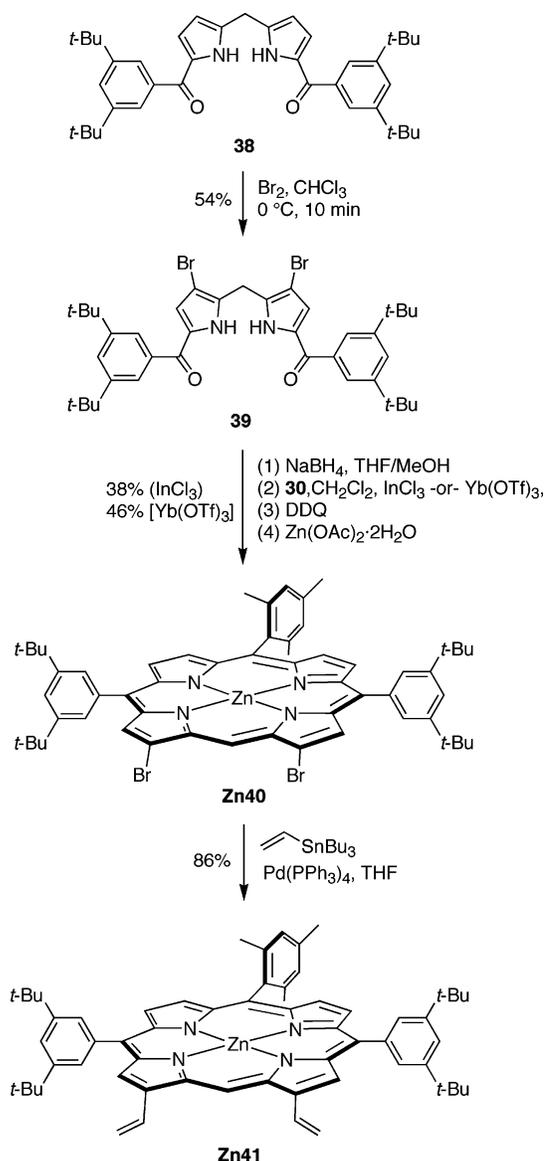
SCHEME 6



at the 3- and 7-positions of the porphyrin. A next-best design entailed placement of halo substituents at the flanking β -positions of the porphyrin, which again should afford a monolayer with direct C–Si bonds from the porphyrin to the surface.

The synthesis of a porphyrin (**Zn40**) bearing two β -bromo substituents is shown in Scheme 7. The three nonlinking meso substituents include two 3,5-di-*tert*-butyl phenyl groups and one mesityl group to aid in the solubility of the dibromo-porphyrin. Treatment of diacyldipyrromethane **38**⁵² with 2 equiv of Br₂ in CHCl₃ at 0 °C for 10 min afforded **39** in 54% yield. The acyl substituents at the 1- and 9-positions direct the electrophilic substitution to the 3- and 7-positions of the dipyrromethane backbone.⁵³ Reduction of **39** with NaBH₄ afforded the corresponding dipyrromethane-dicarbonyl, which was immediately condensed with dipyrromethane **30** in CH₂Cl₂ containing either InCl₃ or Yb(OTf)₃ to yield

SCHEME 7



the free base porphyrin. Zinc insertion afforded porphyrin **Zn40** in 38% yield (using InCl₃) or 46% yield [using Yb(OTf)₃]. We also attempted to brominate porphyrin **Zn40** with NBS to give a 3,5,7-tribrominated porphyrin, which could potentially bind to a Si(100) surface at three sites of the porphyrin backbone (not shown). However, ¹H NMR analysis of the resulting product showed a mixture of several polybrominated porphyrin species that proved inseparable (TLC showed one spot under a variety of conditions). The reaction of **Zn40** with tributyl(vinyl)tin and Pd(PPh₃)₄ in THF afford the corresponding 3,7-divinylporphyrin (**Zn41**) in 86% yield. This porphyrin bears two sites for attachment to Si(100) and may provide increased stability as a result of the double tether.

We also prepared a porphyrin bearing bromine atoms attached to two adjacent β -positions. For this design, we settled on a core-modified mono-thia (N₃S) porphyrin because of the greater ease of synthesis as compared to the analogous N₄-porphyrin. The synthesis of the N₃S-porphyrin followed a “3 + 1” approach.⁵⁴ 2,5-Dimethylthiophene was exhaustively brominated with Br₂ (7 equiv) in CH₂Cl₂ to afford the tetrabromothiophene

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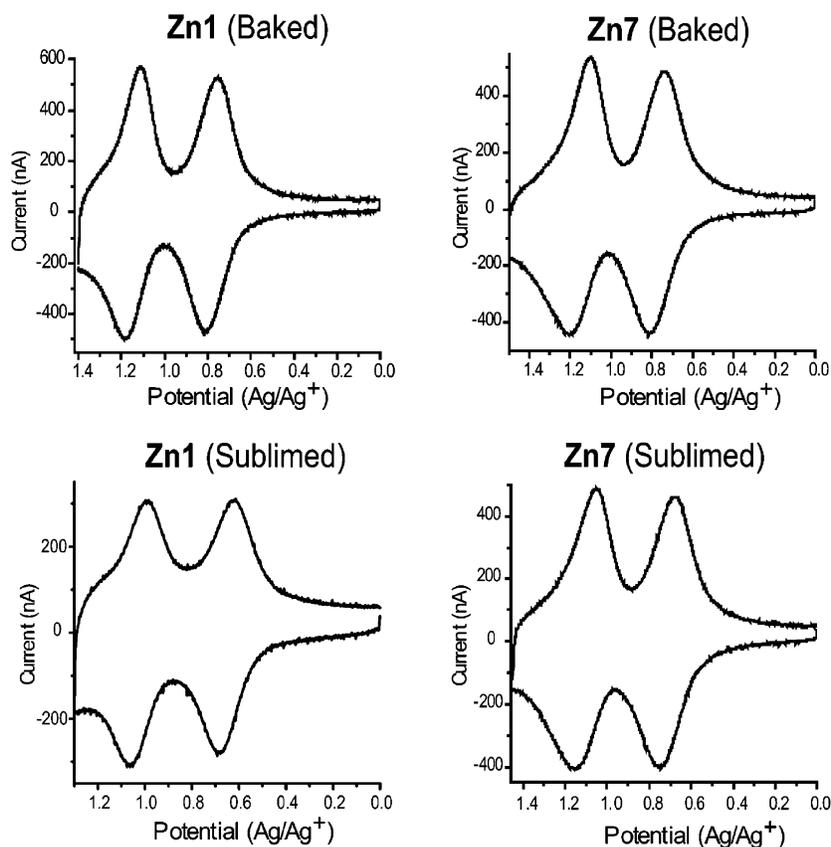


FIGURE 1. Fast-scan cyclic voltammograms (100 V s^{-1}) of monolayers of **Zn1** and **Zn7** on *p*-type Si(100) microelectrodes. The solvent/electrolyte overlayer is composed of propylene carbonate containing $1.0 \text{ M Bu}_4\text{NPF}_6$.

these molecules were attached by subliming at $400 \text{ }^\circ\text{C}$ for 20 min. The “best” attachment conditions for indirect deposition were determined via a systematic study that probed the effects of varying the sublimation temperature and baking time. At temperatures below $300 \text{ }^\circ\text{C}$, relatively little attachment was achieved via the sublimation method. At $400 \text{ }^\circ\text{C}$, the surface coverage monotonically increased as the sublimation time was increased. No further coverage was observed for times longer than 20 min. It is noteworthy that although sublimation of porphyrinic compounds is a well-known process for purification and for generation of thin films,⁵⁶ the sublimation process developed herein employs porphyrins bearing a reactive tether and enables fabrication of surface-attached monolayers of the porphyrins.

Scope of Application. With the baking and sublimation methods in hand for attachment of porphyrins to Si, porphyrins **Zn1**–**Zn19**, **Zn40**, **Zn41**, and **45** were examined for attachment using the same deposition conditions (baking temperature $400 \text{ }^\circ\text{C}$; baking time 2 min; deposition solution porphyrin concentration 1 mM). The functional groups that afforded attachment include 2-(trimethylsilyl)ethynyl, vinyl, allyl, and 3-butenyl directly appended to the porphyrin; and iodo, bromomethyl, 2-(trimethylsilyl)ethynyl, ethynyl, vinyl, and allyl appended to the 4-position of a *meso*-phenyl ring. The

surface coverage varied somewhat as a function of porphyrin and/or linker type; however, the surface coverages were typically in the range 4×10^{-11} to $8 \times 10^{-11} \text{ mol cm}^{-2}$. Attachment was not achieved for the sterically congested porphyrins *meso*-iodo, **Zn8**; β -dibromo, **Zn40**; and vicinal β -dibromo, **45**. In general, the surface coverages and characteristic features of the voltammograms obtained via the sublimation method (sublimation temperature $400 \text{ }^\circ\text{C}$; sublimation time 20 min) are quite similar to those obtained via the baking method, indicating covalent attachment and robust electrochemical behavior.⁶ The relatively narrow voltammetric waves and the absence of visible surface oxidation at high potentials suggest that the porphyrins are packed relatively uniformly and fully cover the surface. As controls, the zinc chelates of various porphyrins that lack functional groups were examined, including 2,3,7,8,12,13,17,18-octaethylporphyrin, *meso*-tetraphenylporphyrin, *meso*-tetra-*p*-tolylporphyrin, and *meso*-tetramesitylporphyrin. No attachment was observed for any of these porphyrins, as was evident from the observation that the baked film was completely removed by washing (in addition, no voltammetric peaks were observed). Collectively, these results indicate that the high-temperature attachment procedure (1) has broad scope encompassing diverse functional groups, (2) tolerates a variety of arene substituents, and (3) does not afford indiscriminate attachment. Finally, the **Zn7** monolayer was used in an initial series of tests to evaluate the robustness to electrochemical cycling of the carbosilane tethered porphyrins. This test was con-

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ducted as described previously⁴ and showed that the voltammetric characteristics of the monolayer were unchanged after $\sim 10^{10}$ redox cycles.

Conclusions

We have prepared a set of porphyrins bearing carbon tethers for attachment to Si(100). Collectively, the studies reported herein indicate that porphyrins bearing a variety of functional groups can be covalently attached to Si via high-temperature processing. The baking and sublimation methods are complementary and together afford a nearly universal strategy for attaching porphyrins. The baking method employs the porphyrin in a dilute solution (1 μM –1 mM), whereas the sublimation method employs the porphyrin as a neat solid. We note that the success of both approaches apparently does not depend on melting the porphyrins. Indeed, the melting points of the porphyrins ranged from 230 °C (**Zn19**) to 435 °C (**Zn14**), yet good quality monolayers were obtained regardless of melting point value. The baking approach is essentially “dry” inasmuch as only a small amount of solvent is used in the attachment process; the sublimation approach is totally “dry” in that no solvents are required in the process. This latter process is particularly appealing from a semiconductor processing perspective, wherein uniform attachment of molecules to very large (30 cm) Si wafers might be anticipated in the manufacture of future generation hybrid molecular/semiconductor devices.

Experimental Section

Electrochemical Studies and Attachment Procedure.

The porphyrins were attached to Si microelectrodes (100 μm \times 100 μm) that were prepared photolithographically from device-grade wafers (B-doped Si(100); $\rho = 0.005$ –0.1 Ω cm). The procedure for preparing these microelectrodes has been described in detail.⁶ The electrochemical procedures, techniques, and instrumentation were also the same as described previously.⁶ The surface coverage of the molecules was determined by integrating the peaks in the voltammogram. The temperature of the Si platform was measured by attaching a thermocouple directly to the platform.

The basic procedures for attachment via the baking and sublimation methods are as described in Results and Discussion. Additional details of these procedures are described below.

For the baking procedure, porphyrin concentrations in the range 1 μM to 3 mM were investigated. The solvents included

benzonitrile, THF, and CH_2Cl_2 . The choice of solvent was primarily dictated by solubility of the porphyrin rather than any specific characteristics of the solvent. However, monolayers prepared using benzonitrile or THF exhibited superior voltammetric characteristics relative to those prepared using CH_2Cl_2 , likely as a result of the fact that the halogenated solvent can react with the surface at high temperature.

Prior to introduction of the porphyrin and baking, the Si microelectrode was placed in a vial. The vial was sealed with a Teflon cap and purged with Ar for 15 min. A syringe containing the porphyrin solution was inserted through the Teflon cap, and a drop of the solution was placed onto the microelectrode. The solvent was then allowed to dry under the continued Ar purge. The purge was stopped, the vial was transferred to the hot plate at the preset temperature, and the electrode was baked for a specified time. The temperatures investigated ranged from 200 to 450 °C; the times ranged from 2 to 30 min. The vial was then removed from the hot plate, and the Ar purge was reinitiated. After the vial had reached room temperature, solvent was syringed into the vial to wash the electrode and remove nonattached porphyrin. In some cases, the microelectrode was removed from the vial and washed in air. No difference was observed in the voltammetric characteristics of the monolayers for electrodes washed under inert versus ambient conditions.

For the sublimation procedure, the vessel containing the solid porphyrin was placed into the vial, the microelectrode was placed on top of the vessel, and the vial was sealed. The vial was then purged gently (to prevent displacing the microelectrode from the vessel) for 15 min. The purge was stopped, and the vial was transferred to the hot plate at the preset temperature for a specific time. Times in the range 2–20 min were investigated. The vial was then removed from the hot plate and allowed to cool to room temperature. The microelectrode was then removed and washed to remove nonattached porphyrin.

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Supporting Information Available: Complete Experimental Section describing the synthesis of all new compounds, summary of melting point data for the porphyrins, and characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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