

Porphyrins Bearing Mono or Tripodal Benzylphosphonic Acid Tethers for Attachment to Oxide Surfaces

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The ability to attach redox-active molecules to oxide surfaces in controlled architectures (distance, orientation, packing density) is essential for the design of a variety of molecular-based information storage devices. We describe the synthesis of a series of redox-active molecules wherein each molecule bears a benzylphosphonic acid tether. The redox-active molecules include zinc porphyrins, a cobalt porphyrin, and a ferrocene-zinc porphyrin. An analogous tripodal tether has been prepared that is based on a tris[4-(dihydroxyphosphorylmethyl)phenyl]-derivatized methane. A zinc porphyrin is linked to the methane vertex by a 1,4-phenylene unit. The tripodal systems are designed to improve monolayer stability and ensure vertical orientation of the redox-active porphyrin on the electroactive surface. For comparison purposes, a zinc porphyrin bearing a hexylphosphonic acid tether also has been prepared. The synthetic approaches for introduction of the phosphonic acid group include derivatization of a bromoalkyl porphyrin or use of a dimethyl or diethyl phosphonate substituted precursor in a porphyrin-forming reaction. The latter approach makes use of dipyrromethane building blocks bearing mono or tripodal dialkyl phosphonate groups. The zinc porphyrin-tripodal compound bearing benzylphosphonic acid legs tethered to a SiO₂ surface (grown on doped Si) was electrically well-behaved and exhibited characteristic porphyrin oxidation/reduction waves. Collectively, a variety of porphyrinic molecules can now be prepared with tethers of different length, composition, and structure (mono or tripodal) for studies of molecular-based information storage on oxide surfaces.

Introduction

In the preceding paper we described the synthesis of a variety of porphyrinic species bearing phenylphosphonic acid tethers for attachment to oxide surfaces.¹ Our chief application of such molecules is for studies of molecular-based information storage.² Upon attachment to an electroactive oxide surface, the porphyrinic species can be charged at a given electrochemical potential. The writing process for information storage entails the bulk oxidation of the molecules at the surface, and the reading process entails the bulk reduction to the neutral state.

One of the considerable attractions of molecular information storage is the ability to tune the properties of the charge-storage molecules through molecular design. In studies of thiol-derivatized porphyrins, we found that the

period during which the oxidized molecules remained charged (i.e., the charge-retention time) depends quite sensitively on the length of the tether (linker and surface attachment group). For example, as the number of methylene groups in the tether phenyl-(CH₂)_{*n*}-S- increased along the series 0, 1, 2, and 3, the charge-retention time increased from 116, 167, 656, to 885 s.² The rate of electron-transfer (reading process) also slowed with increase of linker length.³ Moreover, the quality (uniformity, integrity) of the self-assembled monolayers (SAMs) increased in going from the phenylthio tether (*n* = 0) to the phenylalkylthio tethers (*n* = 1–3). These results prompted us to undertake the synthesis of porphyrins bearing tethers longer than the phenylphosphonic acid tethers described in the previous paper.

The tethers of interest include benzylphosphonic acid, hexylphosphonic acid, and tripodal phosphonic acids. The benzyl and hexyl linkers are longer than a phenyl unit, and the tripodal tether is expected to anchor the redox-active molecule in a 3-point contact and thereby enforce a vertical orientation of the charge-storage molecule. The

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key design issues for tripods are (1) the nature of the atom or molecular unit to which the three legs of the tripod are attached, (2) the composition and length of the tripod legs, and (3) the nature of the three terminal groups for surface attachment. Diverse tripodal tethers have been prepared for attaching molecules to surfaces. Tripods containing a C atom,^{4–16} a Si atom,^{17,18} or an adamantane^{13,19–22} unit at the central core of the tripod have been prepared. The tripod legs include methyl,^{9,21} ethyl,⁸ propyl,^{4,6,7,9,10} alkyl ether,⁵ phenyl,^{13,19,20} benzyl,^{11,12,14,16} biphenyl,¹⁵ diphenylethyne,^{17,22} oligophenyl,¹⁸ and oligoethynylphenyl²² structures. The terminal groups include thiol,^{4,6,7,9,11,12,14,16,21} S-acetylthio,^{10,12,14,17,22} thiocyanate,⁹ alcohol,^{9,21} ester,^{5,13,19–21} carboxylic acid,^{5,8,13,20} allyl,¹⁸ diethyl phosphonate,¹⁵ or phosphonic acid¹⁵ groups. Some of the tripods bear redox-active groups including ferrocene,^{8,9} viologen,¹⁵ fullerene,^{5,12,14} ruthenium-tris(bpy),^{13,19} or oligothiophene^{12,14,16} units. Dendrimeric tripods bearing more than three sites of attachment also have been prepared.^{4,5,8,18,23}

A tripod built around a tetraarylmethane structure containing three terminal phosphonic acid groups appeared most attractive for our purposes owing to the rigid, compact, and tetrahedral architecture. The tripods of this type that have been prepared incorporate methylthiol^{11,12,14,16} or ester^{13,19} termini attached to phenyl legs or dialkyl phosphonate termini attached to biphenyl legs.¹⁵ The synthesis of the thiol-terminated tetraarylmethane tripod proceeded through the valuable intermediate 1,1,1-tris(4-bromomethylphenyl)(4-bromophenyl)methane.¹⁴ We felt that the route for preparing this intermediate could be adapted to incorporate porphyrins and phosphonic acid groups.

In this paper we describe the synthesis of a selection of porphyrins bearing benzylphosphonic acid, hexylphosphonic acid, and tripodal phosphonic acid groups. We then describe the electrochemical characteristics of a porphyrin-tripodal phosphonic acid compound tethered to a SiO₂ dielectric layer on a Si platform. Taken together, this work provides the basis for the design and synthesis of porphyrin-linker–phosphonic acid constructs for studies of molecular information storage.

Results and Discussion

1. Synthesis. Zinc Porphyrins Bearing Single Tethers. (a) Benzylphosphonic Acid Tethers. The preparation of a porphyrin bearing one phosphonic acid group requires the availability of a suitable phosphonate aldehyde. Compound **3** was prepared in three steps from commercially available α -bromo-*p*-toluic acid following a literature procedure without characterization data (Scheme 1).²⁴ An Arbuzov reaction of α -bromo-*p*-toluic acid and triethyl phosphite afforded compound **1** in 77% yield. Reduction of **1** with borane-THF furnished benzyl alcohol **2**, which upon oxidation with PCC gave aldehyde **3** in 77% yield (two steps). A mixed-aldehyde condensation²⁵ of **3**, mesitaldehyde, and pyrrole at high concentration²⁶ using BF₃·O(Et)₂/ethanol cocatalysis (achieved by reaction in CHCl₃ containing 0.75% ethanol)²⁷ gave a mixture of porphyrins, from which the desired A₃B-porphyrin **4** was obtained in 9.4% yield. The mixed-aldehyde condensation procedure is a statistical process and was employed because rational routes are not yet available for the synthesis of A₃B-porphyrins where A = mesityl. Metalation of **4** with Zn(OAc)₂·2H₂O afforded **Zn4** in 94% yield. Treatment of **Zn4** to the same conditions employed in the previous paper¹ to cleave di-*tert*-butyl groups [TMS-Br (15 equiv) and TEA (20 equiv) in refluxing CHCl₃] caused cleavage of the ethyl protecting groups to afford porphyrin-benzylphosphonic acid **Zn5** in 78% yield.

An alternate route to porphyrin **4** is shown in Scheme 2. A mixed-aldehyde condensation of α -bromo-*p*-tolualdehyde (**6**),²⁸ mesitaldehyde, and pyrrole afforded the desired A₃B-porphyrin **7** bearing one bromomethylphenyl group in 16% yield. This valuable porphyrin building block, as with other bromomethylporphyrins,²⁹ can be functionalized with a wide variety of nucleophiles. For example, treatment of **7** with triethyl phosphite in an Arbuzov reaction or sodium diethyl phosphite in THF gave porphyrin **4** in 80% or 73% yield, respectively. All three routes afford porphyrin **4** in a straightforward manner and differ mainly in the order of introduction of

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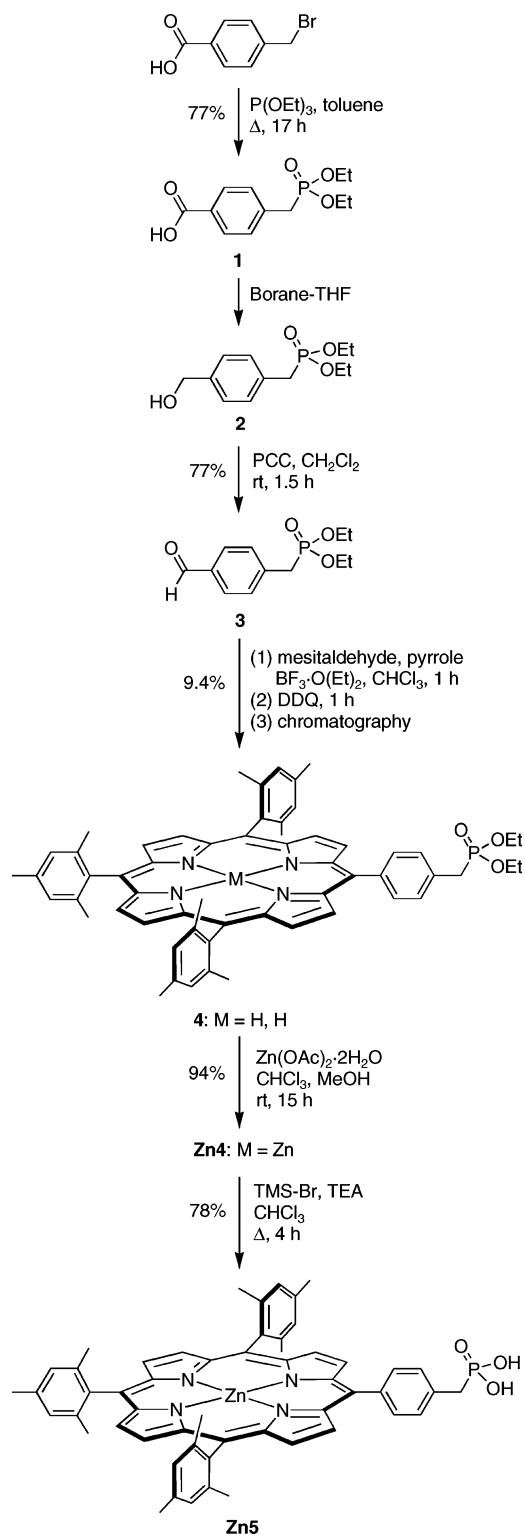
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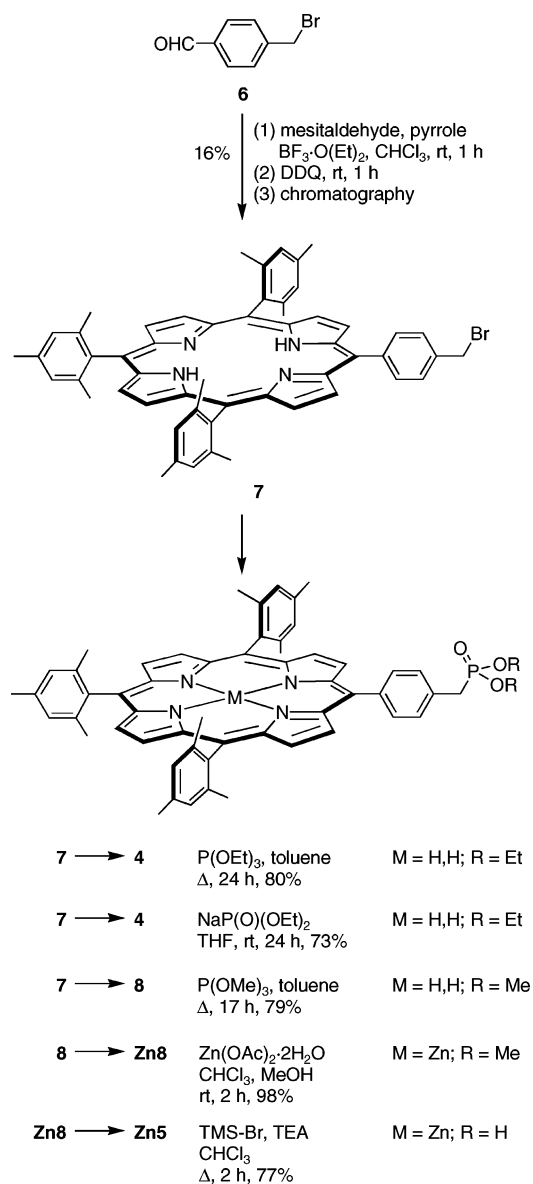
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SCHEME 1



the diethoxyphosphoryl group. Porphyrin **7** could also be treated with trimethyl phosphite in an Arbuzov reaction affording porphyrin **8** in 79% yield. Zinc insertion afforded porphyrin **Zn8** in 98% yield. The methyl groups were cleaved under the same conditions employed for **Zn4**, affording porphyrin **Zn5** in 77% yield. On the basis of this single comparison, the methyl and ethyl protecting groups seem comparable in affording the corresponding porphyrin-phosphonic acid.

SCHEME 2



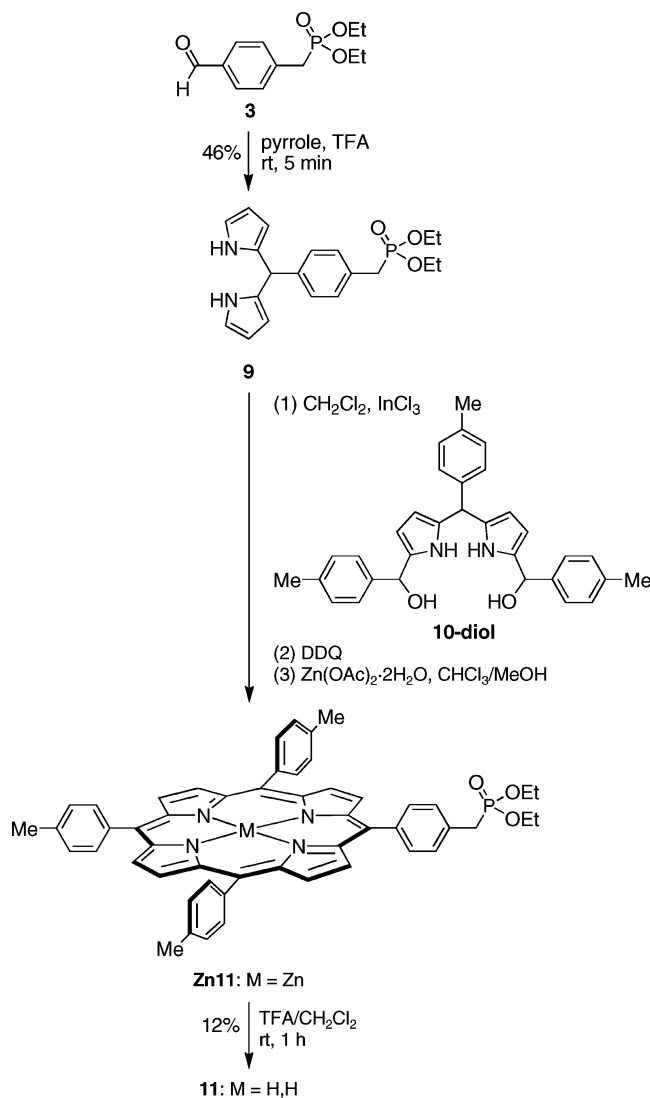
The synthesis of a porphyrin-phosphonic acid bearing *p*-tolyl groups at all nonlinking meso positions is shown in Scheme 3. The synthesis relies on the rational condensation of a dipyrromethane and a dipyrromethane-dicarbonyl.³⁰ Reaction of **3** with excess pyrrole under TFA catalysis afforded dipyrromethane **9** in 46% yield. The condensation of **9** and **10-diol**³¹ in CH_2Cl_2 using InCl_3 as catalyst³² followed by oxidation with DDQ afforded the free base porphyrin. The reaction of crude free base porphyrin with $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ gave the zinc porphyrin **Zn11**. However, the insolubility of **Zn11** in typical solvents (CHCl_3 , THF, toluene, and mixtures thereof) prevented analysis. A suspension of **Zn11** in CH_2Cl_2 was treated with TFA, affording the free base porphyrin **11** in 12% overall yield. Free base porphyrin **11** showed good solubility and was readily characterized.

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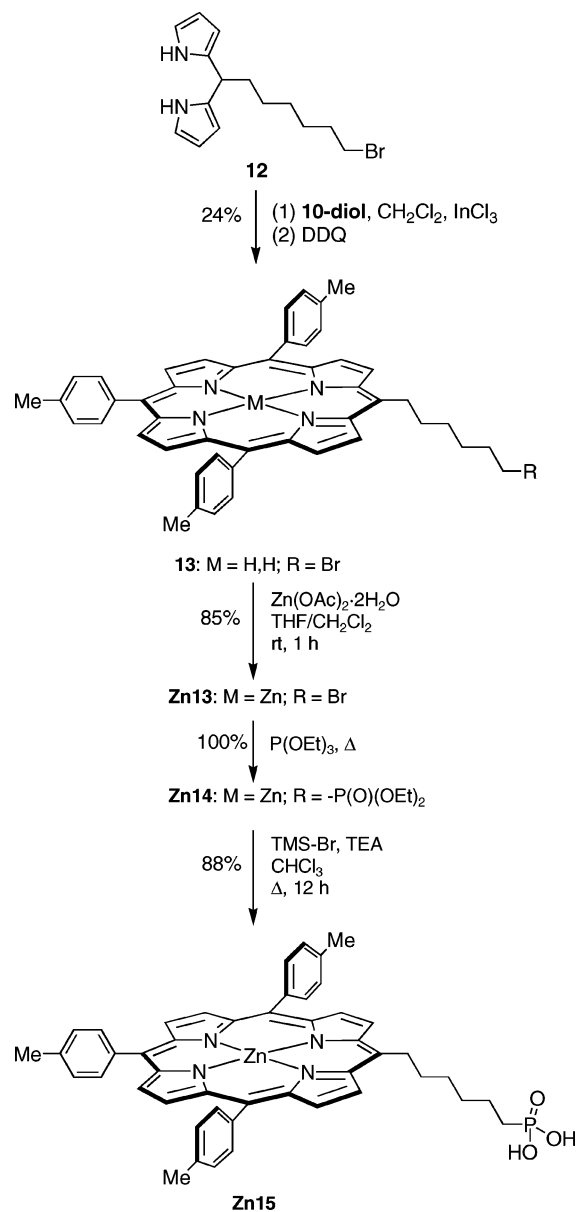
SCHEME 3



(b) Hexylphosphonic Acid Tether. To explore the effect of tether length on the electron-transfer properties of porphyrin SAMs, we prepared a porphyrin that bears a hexylphosphonic acid tether (Scheme 4). Condensation of dipyrromethane **12**³³ and **10-diol** using InCl_3 followed by oxidation with DDQ afforded porphyrin **13** in 24% yield. Metalation furnished **Zn13** in 85% yield. An Arbuzov reaction of **Zn13** and triethyl phosphite afforded porphyrin **Zn14** in quantitative yield. Treatment with TMS-Br/TEA in refluxing CHCl_3 gave porphyrin-hexylphosphonic acid **Zn15** in 88% yield.

Porphyrin Architectures for Increased Memory Density. Molecules with an increased number of cationic oxidation states can afford increased memory density. We have employed this approach in the construction of *S*-acetylthio-derivatized ferrocene-porphyrins³⁴ as well as other multiredox arrays.³⁵ A ferrocene-porphyrin can

SCHEME 4



store two bits of information³⁴ provided the porphyrin and ferrocene are weakly coupled electronically: the porphyrin macrocycle can be cycled between three states (neutral, monocation, dication) while the ferrocene provides access to a fourth state (ferrocene monocation).

The synthesis of a ferrocene-porphyrin bearing a dimethyl phosphonate group is outlined in Scheme 5. Condensation of 4-ferrocenylbenzaldehyde (**16**),^{34,36} α -bromo-*p*-tolualdehyde (**6**), and 5-mesityldipyrromethane (**17**)³⁷ afforded a mixture of three porphyrins, which was treated with trimethyl phosphite in an Arbuzov reaction. Chromatography afforded the dimethyl ferrocene-porphyrin-phosphonate **18** in 20% yield. Metalation of **18** with $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ gave the zinc chelate (~40%), but this

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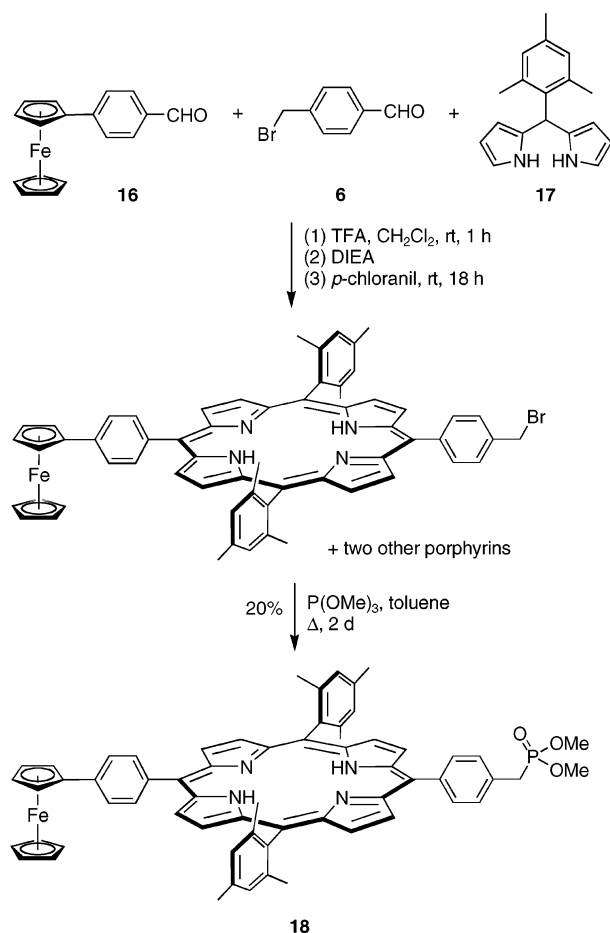
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SCHEME 5



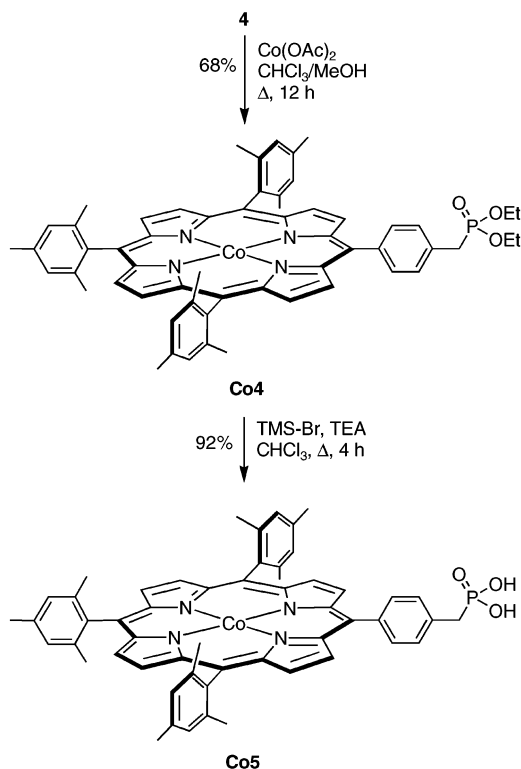
compound proved difficult to characterize because of its insolubility in CHCl₃, THF, and toluene. Attempted deprotection of the zinc porphyrin-phosphonate also afforded an intractable solid.

We have also explored the use of cobalt(II)porphyrins to serve as molecules that can provide three cationic oxidation states: the mono- and dication porphyrin radicals and a metal-centered Co(II)/Co(III)³⁸ oxidation. The synthesis of a cobalt porphyrin-phosphonic acid is shown in Scheme 6. Porphyrin **4** was treated with Co(OAc)₂ to yield the cobalt porphyrin **Co4** in 68% yield. Cleavage of the ethyl protecting groups using the same procedure described above (TMS-Br/TEA in refluxing CHCl₃) furnished the porphyrin-phosphonic acid **Co5** in 92% yield.

Porphyrins Bearing Tripodal Phosphonic Acid Tethers. Our design for porphyrins bearing tripodal phosphonic acid tethers incorporates a *p*-phenylene group between the porphyrin and the methane-carbon vertex of the tripod. The three legs of the tripod are provided by benzylphosphonic acid groups. The synthesis we developed proceeds via a dipyrromethane bearing the tripod with protected phosphonic acid groups (Scheme 7).

The synthesis begins with 1-(4-bromophenyl)-1,1,1-tri-*p*-tolylmethane (**19**).¹⁴ Rosenmund–von Braun reaction

SCHEME 6



of **19** with CuCN afforded **20** in 60% yield (76% based on recovery of starting material **19**). Radical bromination of **20** using NBS (1.1 equiv per methyl group) and AIBN in refluxing benzene furnished crude tribromo nitrile **21** in ~90% purity. ¹H NMR spectroscopy showed the presence of unreacted *p*-tolyl resonances, indicating incomplete bromination. The mono and dibromo products were not easily removed from the reaction mixture; thus, the crude material was carried forward. Reduction of crude **21** with DIBALH gave aldehyde **22**, which was converted to the acetal (**23**) using TiCl₄ in CH₂Cl₂/methanol. Subsequent reaction with triethyl phosphite at 100 °C for 6 h afforded **24** in 54% yield (from **20**). The acetal was cleaved during the acidic workup that was employed to convert the odorous triethyl phosphite to diethyl phosphite. Although each member of the series of compounds **21**–**23** was ~90% pure owing to the presence of partially brominated species, **24** was obtained in pure form. Condensation of **24** with excess pyrrole under new reaction conditions (InCl₃ as catalyst)³⁹ afforded dipyrromethane **25** in 77% yield.

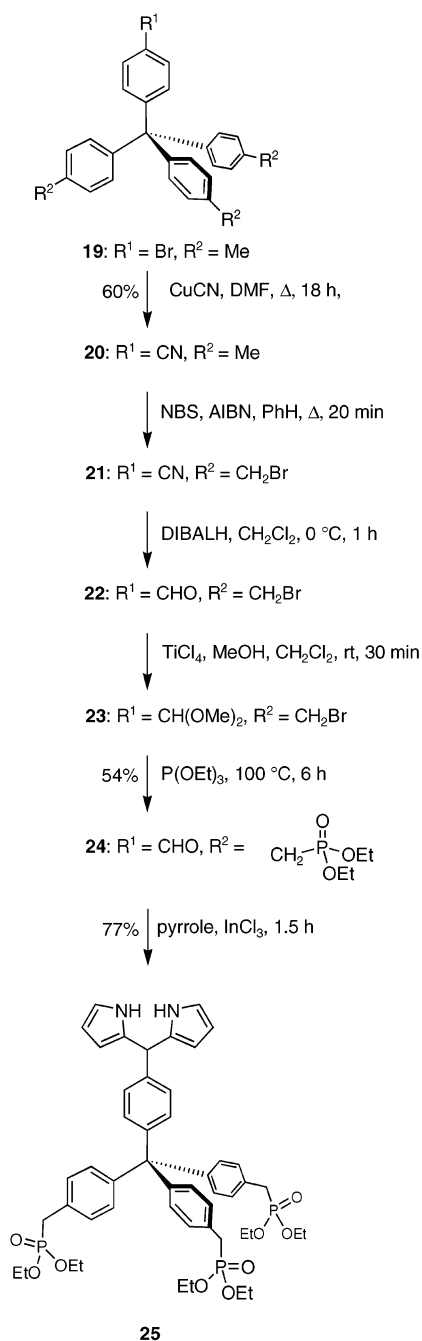
Dipyrromethane **25** serves as a valuable synthetic intermediate for condensation with dipyrromethane-dicarbonyls³⁰ to afford porphyrins bearing a tripodal phosphonate tether. Thus, condensation of **25** and dipyrromethane-dicarbonyl **10-diol**³¹ with catalysis by InCl₃ followed by oxidation with DDQ gave the free base porphyrin. Metalation gave zinc porphyrin **Zn26** in 11.3% overall yield. Deprotection using 5 equiv of TMS-Br and 6.7 equiv of TEA per phosphonate group afforded porphyrin **Zn27** in 82% yield (Scheme 8).

Similarly, a porphyrin was prepared that bears a free ethynyl group, which could be used for Sonogashira

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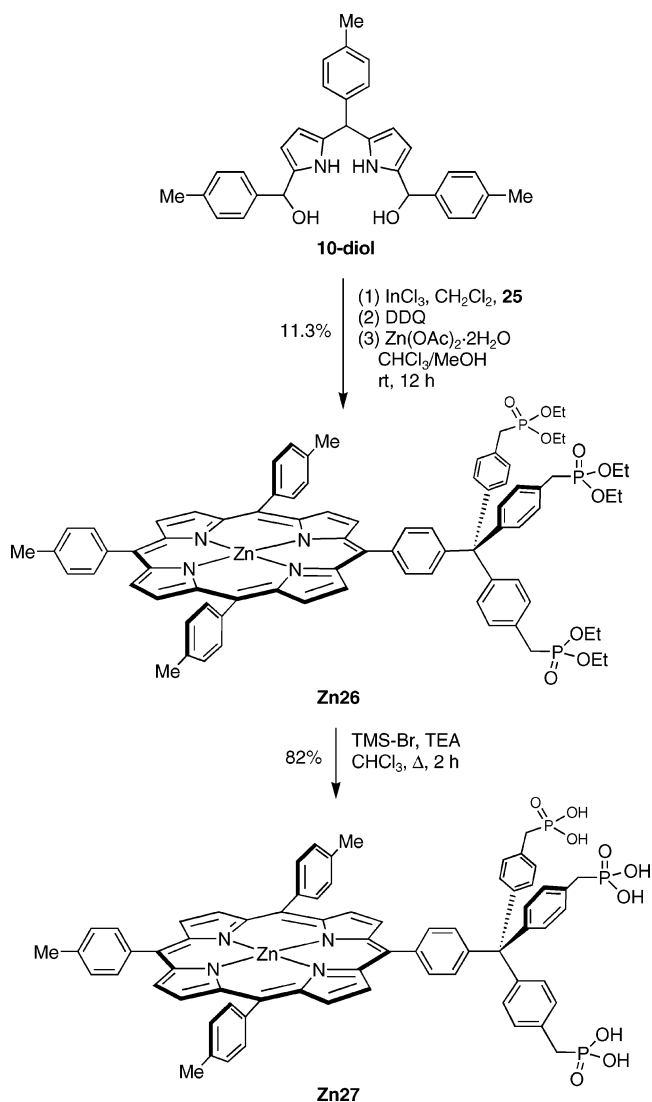
SCHEME 7



oligomerization with porphyrin monomers. The ethynyl unit was incorporated via **29-diol**, which was obtained by treatment of ethynyl diacyldipyrromethane **28**⁴⁰ with TBAF to give **29** followed by reduction with NaBH₄. The condensation of **25** and **29-diol** in CH₂Cl₂ with Yb(OTf)₃ as catalyst³² followed by oxidation with DDQ gave the free base porphyrin. Metalation afforded zinc porphyrin **Zn30** in 24% yield (Scheme 9).

Chemical Characterization and Solubility Properties. All porphyrins were characterized by absorption spectroscopy, ¹H NMR spectroscopy, LDMS,⁴¹ and FABMS. The phosphonate-containing compounds generally were

SCHEME 8

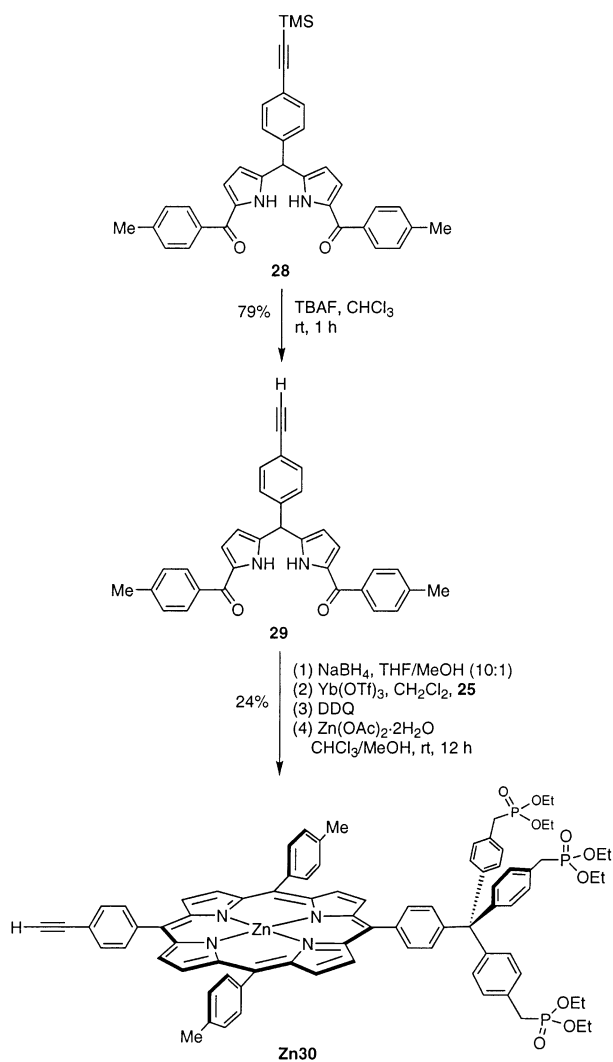


also characterized by ³¹P NMR spectroscopy using H₃PO₄ as an external standard. In a few cases, solubility limited purification and analysis. Tri-*p*-tolylporphyrin **Zn11** was sparingly soluble (CHCl₃, THF, or toluene), and trimesitylporphyrin **Zn4** displayed good solubility in these solvents. The greater bulk of the mesityl versus *p*-tolyl group suppresses cofacial aggregation between porphyrins. The free base analogues of both porphyrins display good solubility. Porphyrin **Zn18** was of such poor solubility that no characterization data could be obtained, whereas the free base analogue, **18**, displayed good solubility. The limited solubility of **Zn11** and **Zn18** but not their free base analogues is attributed to coordination of the dialkyl phosphonate of one porphyrin to the apical site of the zinc porphyrin of another porphyrin. Each porphyrin bearing a tripodal phosphonate tether displayed good solubility in common organic solvents. Porphyrin **Zn27**, which bears three phosphonic acid groups, was quite soluble in water as well as organic solvents.

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SCHEME 9



2. Electrochemical Studies of Monolayers on SiO₂. The electrochemical behavior was investigated for the porphyrin tripod **Zn27** tethered to a thin layer of SiO₂ grown on (100) p-type Si substrates (doping density $1 \times 10^{18} \text{ cm}^{-3}$). The surface-attachment procedure (described in the Supporting Information) entailed the deposition of a solution of **Zn27** in DMF on the SiO₂ substrate followed by (1) brief heating to 170 °C and (2) washing with organic solvents. A solution of propylene carbonate containing 1.0 M Bu₄NPF₆ was placed on top of the monolayer of molecules. A silver electrode was immersed in electrolyte to provide the reference electrode.

Representative fast-scan cyclic voltammograms of monolayers of **Zn27** on the SiO₂ layer (thickness, $T_{\text{ox}} = 1.3 \text{ nm}$) are shown in Figure 1 as a function of two scan rates (20 and 100 V s⁻¹). Two distinct anodic and cathodic current peaks are observed at both scan rates, which correspond to the formation/neutralization of the mono- and dication radicals of the porphyrin. The oxidation of **Zn27** appears to occur at slightly lower voltages as compared to an analogous porphyrin (**Zn31**)¹ bearing a *p*-phenylphosphonic acid tether. At lower scan rates, the integrated oxidation and reduction current in each of the waves is approximately the same, indicating that the same amount of charge is being transferred in and out

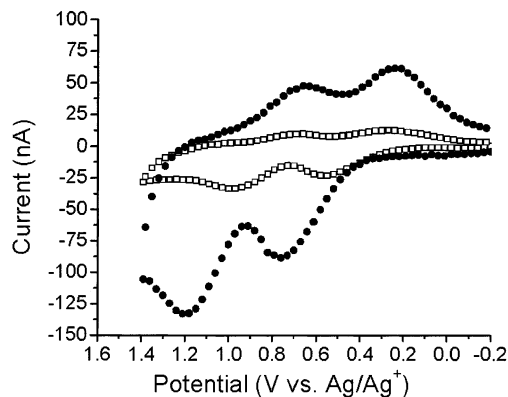
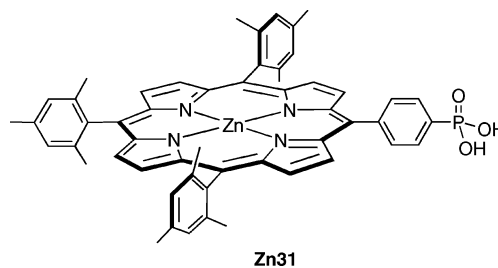


FIGURE 1. Cyclic voltammetry of **Zn27** on SiO₂ ($T_{\text{ox}} = 1.3 \text{ nm}$) with scan rates of 20 (lower amplitude) and 100 (higher amplitude) V s⁻¹.

of the monolayers. However, at higher scan rates, the reduction currents are lower than the oxidation currents. The diminished reduction current is attributed to limited minority carriers available in the p-type semiconductor at high scan rates. The integrated current ($\sim 2.25 \times 10^{13}$ electrons/cm²) corresponds to a molecular coverage on the SiO₂ surface of $3.7 \times 10^{-11} \text{ mol/cm}^2$. These voltammetric characteristics indicate that the porphyrin bearing a tripodal phosphonic acid tether forms a robust, electrically well-behaved monolayer on the SiO₂ surface.



The data shown in Figure 1 indicates that porphyrin tripod **Zn27** has a larger dependence on scan rates, as demonstrated by the peak splitting, compared to the analogous porphyrin **Zn31** bearing a *p*-phenylphosphonic acid tether. This larger scan-rate dependence is attributed to slower redox kinetics, which stems from the longer length of the tripodal tether. The linker joining the porphyrin to a phosphonic acid surface attachment group in the tripod encompasses a *p*-phenylene, saturated carbon atom, and a *p*-benzyl motif. At present, we are investigating the electron-transfer and charge-retention characteristics of various redox-active molecules tethered to SiO₂ as a function of SiO₂ thickness. Both the oxide thickness and the tether length are expected to affect the redox kinetics. Understanding such effects is essential for the rational design of molecular-based information storage devices.

Conclusions

A set of porphyrins bearing dialkyl phosphonate groups or phosphonic acids has been prepared for attachment to metal oxide surfaces. The phosphonate groups are tethered to the porphyrins via benzyl or hexyl linkers, thereby constituting analogues of the porphyrins de-

scribed in the previous paper where phenylphosphonic acid tethers were employed. The tripodal tether is built around a compact, robust tetraarylmethane component. The phosphonic acid group can be introduced to the porphyrin by Arbuzov reaction of a bromoalkyl porphyrin or via an appropriately derivatized precursor in a porphyrin-forming reaction. Tripodal porphyrin-phosphonic acid **Zn27** formed a robust, electrochemically active SAM on SiO₂. The ability to readily attach redox-active molecules to metal oxide surfaces and exercise some control over distance and orientation via the tether architecture (including single versus tripodal surface attachment groups) opens a number of opportunities for studies of molecular-based information storage. We have extended our work with tripodal tethers by attaching diverse redox-active molecules to a thiol-derivatized tripod for comparative studies of electron-transfer properties, as described in the following paper.⁴²

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Supporting Information Available: Complete experimental procedures and relevant spectral data (¹H, ¹³C, and ³¹P NMR spectra and LD-MS spectra) for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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