JOC Article

Porphyrins Bearing Arylphosphonic Acid Tethers for Attachment to Oxide Surfaces

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Synthetic molecules bearing phosphonic acid groups can be readily attached to oxide surfaces. As part of a program in molecular-based information storage, we have developed routes for the synthesis of diverse porphyrinic compounds bearing phenylphosphonic acid tethers. The routes enable (1) incorporation of masked phosphonic acid groups in precursors for use in the rational synthesis of porphyrinic compounds and (2) derivatization of porphyrins with masked phosphonic acid groups. The precursors include dipyrromethanes, monoacyldipyrromethanes, and diacyldipyrromethanes. The *tert*-butyl group has been used to mask the dihydroxyphosphoryl substituent. The di-*tert*-butyloxyphosphoryl unit is stable to the range of conditions employed in syntheses of porphyrins and multiporphyrin arrays yet can be deprotected under mild conditions (TMS-Cl/TEA or TMS-Br/TEA in refluxing $CHCl_3$) that do not cause demetalation of zinc or magnesium porphyrins. The porphyrinic compounds that have been prepared include (1) A_3B-, *trans*-AB_2C-, and ABCD-porphyrins that bear a single phenylphosphonic acid group, (2) a *trans*-A_2B_2-porphyrin bearing two phenylphosphonic acid groups, (3) a chlorin that bears a single phenylphosphonic acid group, and (4) a porphyrin dyad bearing a single phenylphosphonic acid group. For selected porphyrin-phosphonic acids, the electrochemical characteristics have been investigated for molecules tethered to SiO_2 surfaces grown on doped Si. The voltammetric behavior indicates that the porphyrin-phosphonic acids form robust, electrically well-behaved monolayers on the oxide surface.

Introduction

We recently described a new design for a molecular-based memory device wherein a layer of redox-active molecules is tethered to an ultrathin dielectric surface, which in turn is deposited on a semiconductor.[1] The dielectric layer and the molecular tether (linker and surface attachment group) both provide barriers to electron transfer between the semiconductor and the redox-active molecule. The design can be implemented as the gate region of a field effect transistor, as shown in Figure 1. In this type of molecular-based field effect transistor, the charge stored in the molecules can change the current level in the transistor, thereby affording a nondestructive means by which the charge state of the molecules can be detected.

In contrast with conventional semiconductor-based devices, the use of charge-storage molecules exploits the power of synthetic design to tailor molecules that operate at low voltage and that provide multiple charged states.

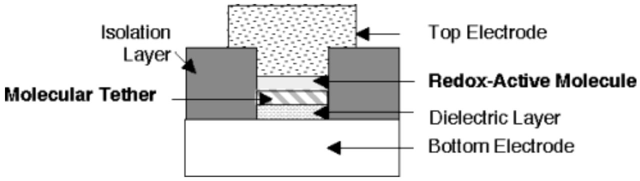

FIGURE 1. Schematic of an electrode-molecule-oxide-electrode device for potential memory applications. The molecule is composed of a redox-active unit and a tether (linker and surface attachment group).

Great latitude also exists in the design of the barriers presented by both the tether and the dielectric layer. The barrier presented by the tether can be tuned via synthetic organic chemistry, and that of the dielectric can be tuned by semiconductor-processing techniques. In particular, the composition (and length) of the tether can be varied from insulating aliphatic groups to more conducting conjugating species. Likewise the composition of the dielectric layer can be a commonly used SiO_2 layer or a metal oxide such as HfO_2, ZrO_2, etc.

Our preliminary studies of the design shown in Figure 1 employed ferrocenylmethylphosphonic acid as the charge-storage molecule.[1] The phosphonic acid group anchors the charge-storage molecule to the oxide surface. The initial success of this approach has prompted us to

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[1] Li, Q.; Surthi, S.; Mathur, G.; Gowda, S.; Sorenson, T. A.; Tenent, R. C.; Kuhr, W. G.; Tamaru, S.-I.; Lindsey, J. S.; Liu, Z.; Bocian, D. F.; Misra, V. *Appl. Phys. Lett.* **2003**, *83*, 198−200.

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investigate the synthesis of a much wider variety of charge-storage molecules, particularly porphyrinic molecules, which bear phosphonic acid terminated linkers. Porphyrins bearing phosphonic acid tethers have been synthesized and attached to oxide surfaces for a variety of other applications including solar energy, oxidative catalysis, sensing, and recognition of polysaccharides.[2−14]

The synthetic approaches that have been employed to prepare porphyrins bearing phosphonic acid/phosphonate units can be characterized by (1) whether the phosphonate unit is introduced into precursors to the porphyrin or by derivatization of a preexisting porphyrin, (2) whether statistical or rational routes are employed, (3) the number and pattern of phosphonate groups at the perimeter of the porphyrin, (4) the type of phosphonic acid protecting group employed, (5) the nature of the central metal, and (6) the method of cleavage of the phosphonic acid protecting groups.

A_4-Porphyrins bearing four arylphosphonic acids have been prepared by condensation of a dialkoxyphosphorylbenzaldehyde with pyrrole followed by deprotection of the free base porphyrin.[2] Alternatively, the free base porphyrin can be metalated followed by deprotection.[4,5] A_4-Porphyrins bearing four alkylphosphonic acids have been prepared by derivatization of a reactive halo-substituted porphyrin.[5−7] A_3B-Porphyrins bearing a single phosphonic acid have been prepared by a mixed-aldehyde condensation of a dialkoxyphosphorylbenzaldehyde, benzaldehyde, and pyrrole[4] or by derivatization of a porphyrin bearing a single reactive halo group.[6,14] *trans*-A_2B_2-Porphyrins bearing two phosphonic acid groups have been prepared by condensation of a dialkoxyphosphorylbenzaldehyde and dipyrromethane.[12] Chlorins bearing two phosphonic acids have been prepared by derivatization of a deuterochlorin-dibromide with tris(trimethylsilyl)phosphite.[9] In each case, the porphyrinic species were employed as the free base or as a metal chelate that is rather robust toward the acidic conditions for cleavage of the dialkyl phosphonate. The metals include Mn,[4,5] Fe,[9] Co,[9] Ni,[9] Pd,[6] and Os,[7] which are all categorized in the porphyrin field as class I or class II metals, affording chelates that are exceptionally resilient toward acids.[15] In general, phosphonic acids combine with metals to give extended, often insoluble, metal phosphonates. A rare case wherein metalation was performed in the presence of a free phosphonic acid employed a porphyrin superstructure containing a hindered phosphonic acid.[14]

In this paper, we first describe new strategies for the synthesis of porphyrins bearing phenylphosphonic acid tethers. This extends our prior work where diverse porphyrinic compounds bearing alcohol, thiol, or selenol tethers (in free or protected form) have been prepared for attachment to metals or silicon.[16] We employ the di-*tert*-butyl group as a masking group for the phosphonic acid, with predominant use of strategies wherein the di-*tert*-butyl phosphonate is incorporated in precursors of the porphyrin. In the course of this work, we have also developed methods for unveiling the free phosphonic acid that are compatible with zinc (class III) or magnesium (class IV) chelates of porphyrins. We then describe the electrochemical characteristics of selected porphyrin-phosphonic acids tethered to SiO_2 dielectric layers on Si platforms. Collectively, these studies provide the basis for the rational synthesis of a wide variety of porphyrins, including porphyrin building blocks and multiporphyrin arrays, bearing phenylphosphonic acid tethers and demonstrate the robust electrical characteristics of the molecule-oxide-semiconductor architectures.

Results and Discussion

1. Approach. A variety of protecting groups have been used for phosphonic acids, including methyl, ethyl, allyl, and *tert*-butyl groups.[2−14,17−23] For our application, a key issue concerns the stability of the metalloporphyrin toward conditions employed for protecting group removal, as inadvertent demetalation of the porphyrin would complicate the synthesis of mixed-metal multiporphyrin arrays. Accordingly, the ideal masking agent should meet the following requirements: (1) compatibility with porphyrin forming conditions, including acid catalysis and DDQ oxidation conditions, (2) stability toward a variety of metalation conditions, (3) compatibility with Pd-mediated coupling reactions, and (4) ability to undergo cleavage without demetalation of the metalloporphyrins.

Mild conditions for the cleavage of a dialkyl phosphonate to give the phosphonic acid originate with Rabinowitz, who first used trimethylsilyl chloride (TMS-Cl) followed by hydrolysis of the resulting bis(trimethylsilyl) phosphonate.[24] Modifications of this approach have led

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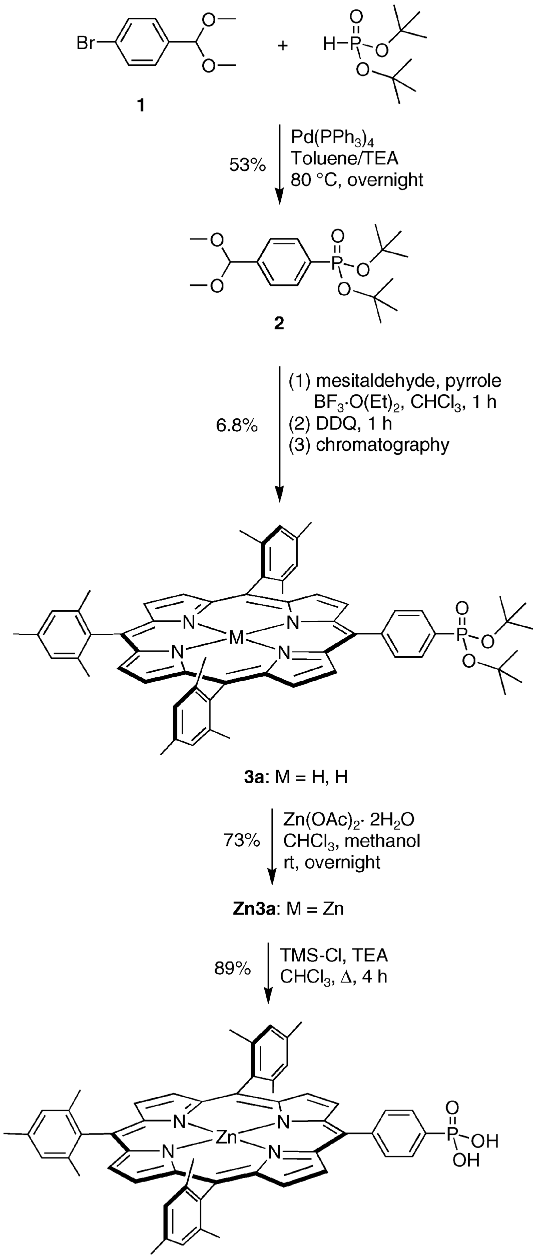
SCHEME 1



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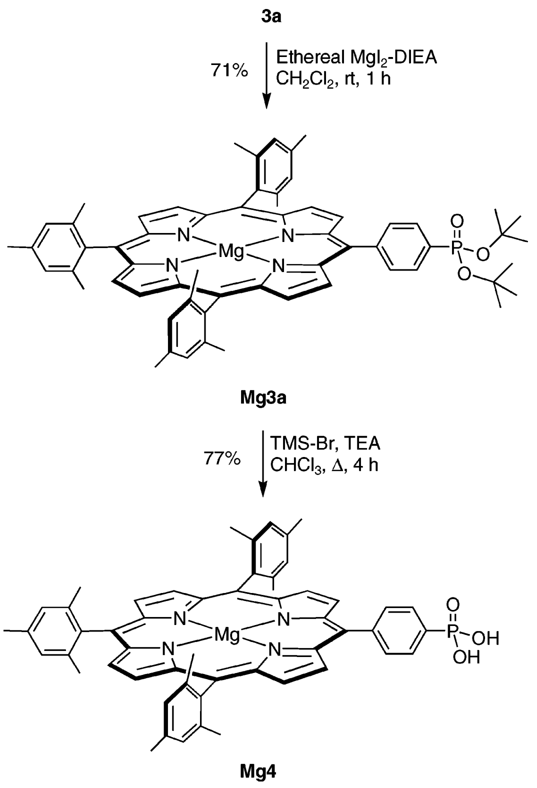

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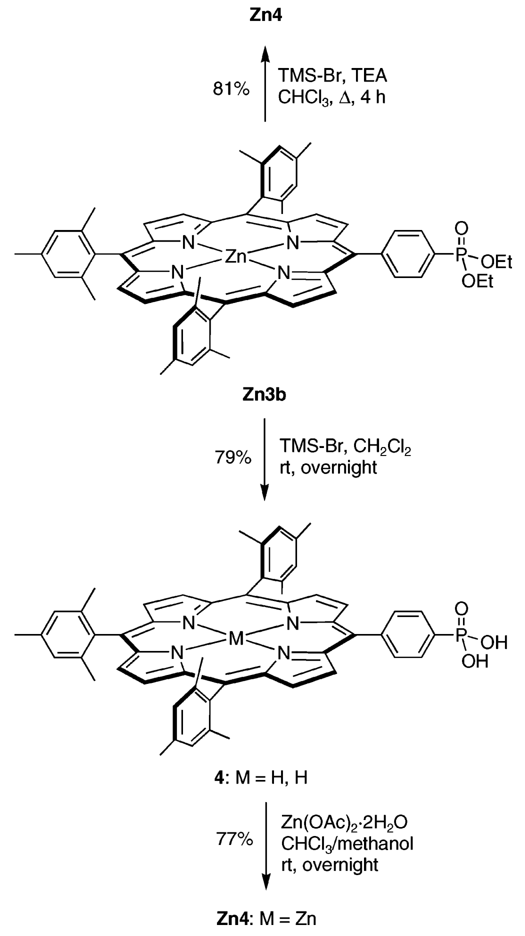

to the following conditions: (1) TMS-Br (neat);[17] (2) TMS-Br/CH_3CN[22] or CH_2Cl_2;[20] (3) TMS-Cl/TEA;[25] and (4) TMS-Br/TEA/CH_2Cl_2.[21] Some of these approaches have been applied to the cleavage of a diethyl porphyrin-phosphonate: (1) TMS-Br/CH_2Cl_2 (free base porphyrins);[6,7,12] (2) TMS-Br/TEA/DMF (Mn-porphyrin);[13] and (3) NaBr/TMS-Cl/TEA/DMF (Mn-porphyrin).[4]

In this and the accompanying paper,[26] we have examined methods for the introduction and cleavage of various phosphonic acid protecting groups that are compatible with the preparation of diverse porphyrinic compounds. Several possible masking agents [2-trimethylsilylethyl,

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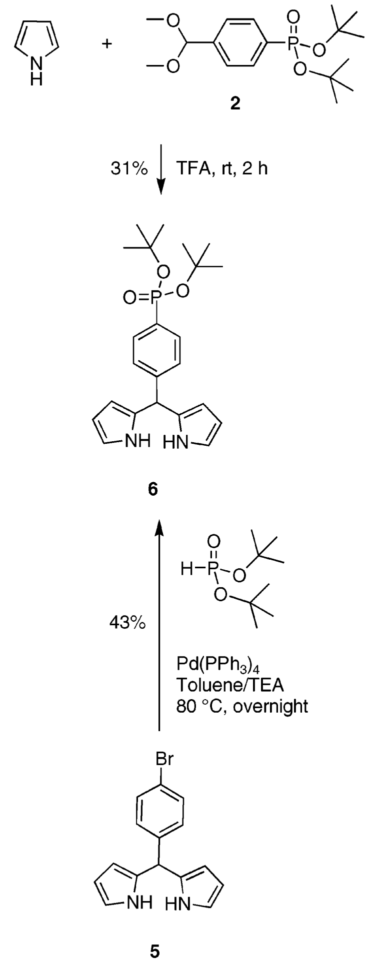
SCHEME 4

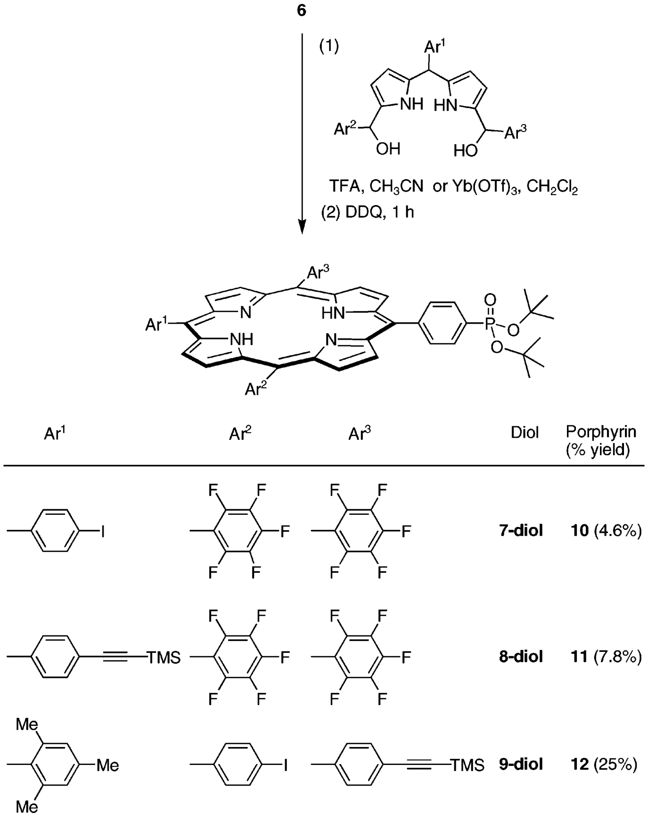


2-cyanoethyl, 2-chloroethyl, methyl] were examined but found inapplicable for the preparation of porphyrin-phosphonic acids (see Supporting Information). The *tert*-butyl group has been used for the protection of phosphates in nucleotide syntheses with facile removal under mild nonacidic conditions (TMS-Cl/TEA).[25] We therefore employed the *tert*-butyl group as masking agent in the work described herein.

2. Synthesis. The synthesis of porphyrins bearing a phosphonate group was achieved following three different strategies: (1) a mixed-aldehyde condensation of a phosphonate-derivatized benzaldehyde and an aldehyde of choice (mesitaldehyde) with pyrrole, (2) condensation of a phosphonate-derivatized dipyrromethane with a dipyrromethane-dicarbinol, and (3) derivatization of a bromo- or iodo-substituted porphyrin with a phosphonate reagent.

A. Functionalization of Precursors of the Porphyrin. For porphyrin formation using a mixed-aldehyde condensation, we required a phosphonate-derivatized benzaldehyde. Thus, the Pd-mediated coupling of 4-bromobenzaldehyde dimethylacetal (**1**)[27] with di-*tert*-butyl phosphite afforded 4-(di-*tert*-butyloxyphosphoryl)benzaldehyde dimethylacetal (**2**) in 53% yield following a procedure used for the synthesis of 4-(diethoxyphosphoryl)benzaldehyde[4] (Scheme 1). Acetals can be used directly (like aldehydes) in the synthesis of porphyrins[28] and dipyrromethanes.[29] The mixed-aldehyde condensation[30] of acetal **2**, mesitaldehyde, and pyrrole with $BF_3 \cdot O(Et)_2$/ethanol cocatalysis[31] afforded porphyrin **3a** in 6.8% yield after chromatography. Metalation of **3a** using $Zn(OAc)_2 \cdot 2H_2O$ in $CHCl_3$/methanol gave zinc porphyrin **Zn3a** in 73% yield (Scheme 1). Cleavage of the *tert*-butyl groups was achieved by following the known procedure[25] with TMS-Cl/TEA in refluxing $CHCl_3$ (stabilized with amylenes). In this manner, the zinc porphyrin-phosphonic acid **Zn4** was obtained without demetalation in 89% yield. Note that $CHCl_3$ stabilized with amylenes rather than ethanol was used to avoid the possible reaction of ethanol with TMS-Cl.

SCHEME 5



The synthesis of magnesium porphyrin **Mg3a** was first tried using the heterogeneous magnesium insertion procedure.[32] Porphyrin **3a** was treated with MgI_2 and DIEA in CH_2Cl_2 at room temperature, but these conditions resulted in cleavage of the *tert*-butyl groups. However, magnesium insertion using the homogeneous procedure[33] (ethereal MgI_2-DIEA reagent in CH_2Cl_2) gave

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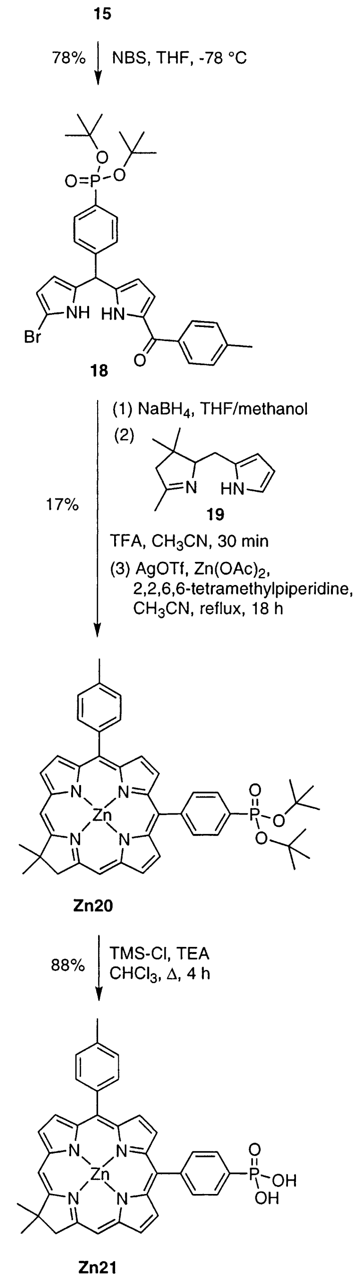
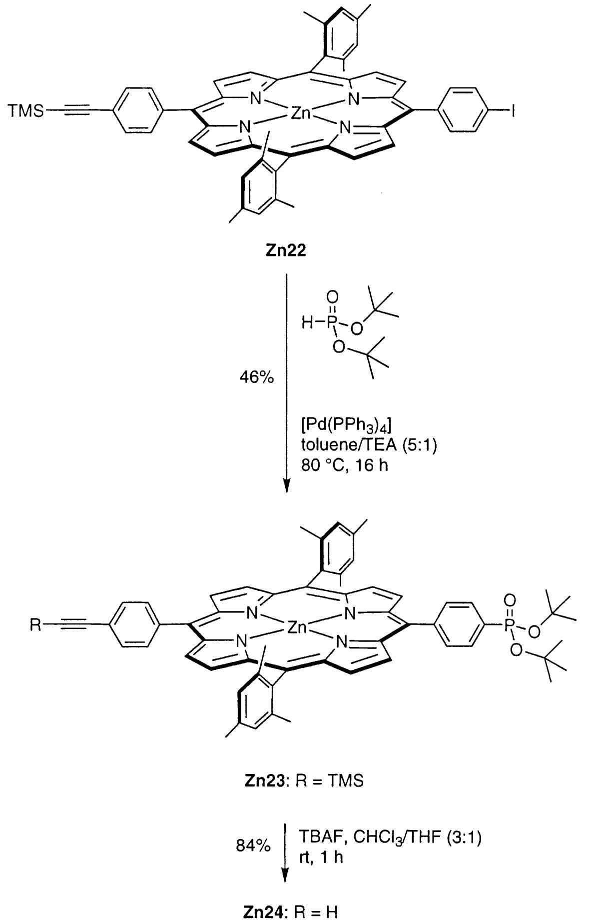
SCHEME 6



SCHEME 7



Mg3a in 71% yield. Treatment of **Mg3a** with TMS-Cl/TEA in refluxing $CHCl_3$ or THF did not cause cleavage of the *tert*-butyl groups. However, use of TMS-Br/TEA in refluxing $CHCl_3$ gave porphyrin-phosphonic acid **Mg4** in 77% yield (Scheme 2).

We also examined the diethyl porphyrin-phosphonate **Zn3b**, which was prepared from 4-(diethoxyphosphoryl)-benzaldehyde[4] in the same manner as for **Zn3a**. We found that **Zn3b** could be deprotected without affecting the metalation state by using the TMS-Br/TEA reagent in refluxing $CHCl_3$. On the other hand, treatment of **Zn3b** with TMS-Br in the absence of TEA (employed for the deprotection of diethyl phosphonates)[6] at room temperature caused demetalation in addition to cleavage of the ethyl groups, affording the free base porphyrin-phosphonic acid **4** in 79% yield (Scheme 3). Porphyrin **4** was metalated with $Zn(OAc)_2$•$2H_2O$ under standard conditions, giving **Zn4** in 77% yield. The successful metalation of a porphyrin bearing a free phosphonic acid was surprising and may stem in part from the suppression of aggregation afforded by the three mesityl groups.

The success of the above studies prompted us to employ the di-*tert*-butyl phosphonate in a variety of porphyrin precursors. Accordingly, reaction of acetal **2** with excess pyrrole following a standard procedure[34] afforded dipyrromethane **6** in 31% yield (Scheme 4). Alternatively, Pd-mediated coupling of 5-(4-bromophenyl)dipyrromethane (**5**)[34] with di-*tert*-butyl phosphite under conditions similar to those for the synthesis of **2** gave **6**. Dipyrromethane **6** is a valuable synthon for use in porphyrin chemistry.

Dipyrromethane **6** was treated with various dipyrromethane-dicarbinols (**7-diol**, **8-diol**, and **9-diol**)[35] in a rational route[35] to afford the corresponding porphyrins **10**, **11**, and **12** in 4.6%, 7.8%, and 25% yields, respectively (Scheme 5). The synthesis of **10** was achieved in CH_2Cl_2 containing $Yb(OTf)_3$ for acid catalysis,[36] and that of **11** and **12** was carried out in CH_3CN containing TFA.

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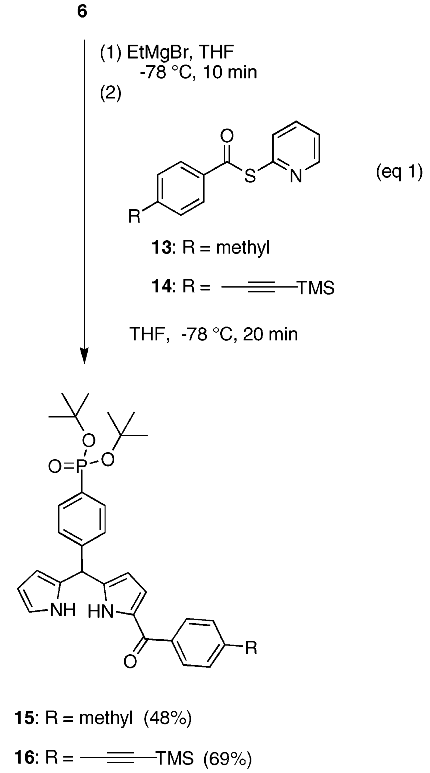
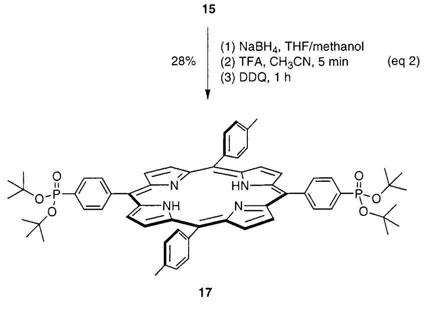
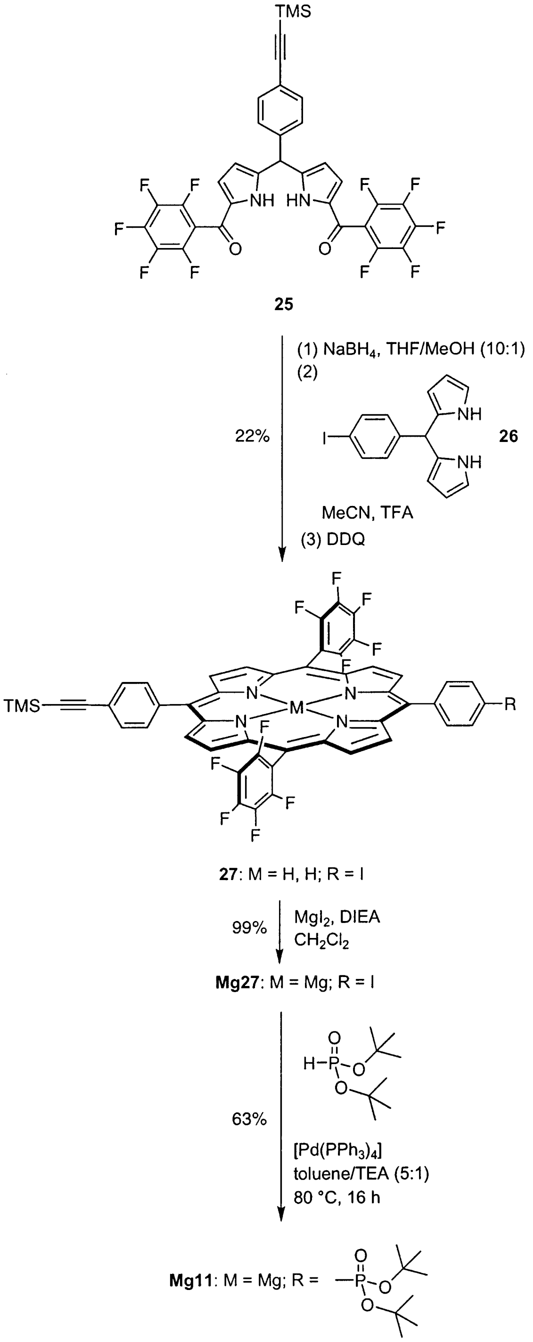
Application of the procedure for monoacylation of a dipyrromethane[37] to **6** by treatment with EtMgBr and pyridyl thioester **13**[37] or **14**[35] gave the corresponding monoacyl product **15** or **16** in 48% or 69% yield, respectively (eq 1). Reduction of **15** with $NaBH_4$ in THF/methanol afforded the monocarbinol **15-OH**. Self-condensation[37] of **15-OH** on treatment with TFA in CH_3CN followed by oxidation with DDQ afforded the bis-phosphonate-porphyrin **17** in 28% yield (eq 2). The self-condensation of **15-OH** using $InCl_3$ as catalyst[36] resulted in a very low yield (3%) of the required porphyrin **17**.





A chlorin bearing a phenylphosphonic acid tether also was prepared. Monoacyl-dipyrromethane **15** was treated with NBS to afford **18** in 78% yield. Reduction of **18** with $NaBH_4$ gave the monocarbinol **18-OH** (Eastern half), which on reaction with tetrahydrodipyrrin **19**[38] (Western half) under one-flask chlorin-forming conditions[38] gave the phosphonate-substituted zinc chlorin **Zn20** in 17% yield (Scheme 6). Treatment of **Zn20** with TMS-Cl/TEA in $CHCl_3$ at reflux afforded the zinc chlorin-phosphonic acid **Zn21** in 88% yield.

SCHEME 8



B. Functionalization of the Porphyrin. An alternative approach for preparing porphyrin-phenylphosphonic acids entails the Pd-mediated coupling of di-*tert*-butyl phosphite with a bromophenyl- or iodophenyl-substituted porphyrin. Thus, reaction of iodophenyl-porphyrin **Zn22**[39] and di-*tert*-butyl phosphite in toluene/TEA (5:1) containing $Pd(PPh_3)_4$ at 80 °C afforded phosphonate-porphyrin **Zn23** in 46% yield. The TMS-ethyne group in **Zn23** was cleaved with TBAF in $CHCl_3$/THF, giving ethynyl-porphyrin **Zn24** in 84% yield (Scheme 7). Porphyrin **Zn24**

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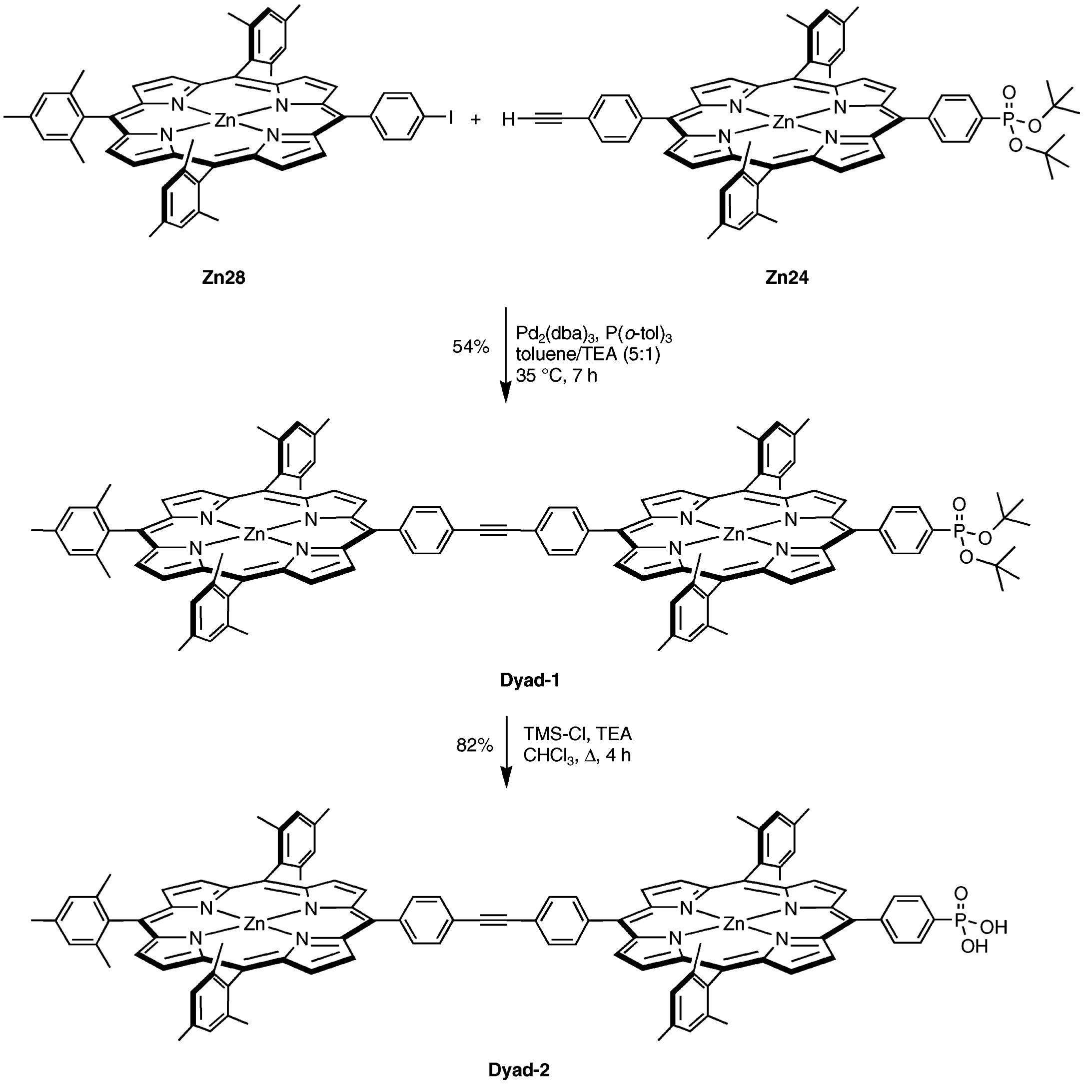
SCHEME 9



is an important building block as the free ethyne group can be exploited in the construction of multiporphyrin arrays.

The same derivatization approach was applied to a magnesium porphyrin. Dipyrromethane-dicarbinol **25-diol** (derived from diacyldipyrromethane **25**[35]) and dipyrromethane **26**[34] were subjected to the standard sequence of condensation and oxidation, affording porphyrin **27** in 22% yield. Use of the heterogeneous magnesium insertion conditions gave **Mg27**, which was chromatographed on alumina rather than silica to avoid demetalation.[40] The Pd-mediated coupling of di-*tert*-butyl phosphite with **Mg27** afforded **Mg11** in 63% yield (Scheme 8).

C. Porphyrin Dyads Bearing a Phenylphosphonic Acid Tether. The synthesis of a porphyrin dyad bearing a single phosphonic acid tether is shown in Scheme 9. The Sonogashira coupling of **Zn24** with **Zn28** was carried out under the conditions developed for synthesis of multiporphyrin arrays.[41] The conditions employ equimolar amounts of the two porphyrins in relatively dilute solution (5 mM each in toluene/TEA) at 35 °C with catalysis by Pd$_2$(dba)$_3$ and tri-*o*-tolylphosphine [P(*o*-tol)$_3$] without any copper cocatalysts. Thus, the coupling of **Zn24** with **Zn28**[42] afforded **Dyad-1** in 54% yield upon chromatographic workup including size exclusion chromatography[43] (SEC). Treatment of **Dyad-1** with TMS-Cl/TEA in refluxing CHCl$_3$ afforded **Dyad-2** bearing a free phosphonic acid in 82% yield. No demetalation of the zinc porphyrins was observed.

D. Benchmark Compound. For comparison with the properties of the various porphyrinic phosphonic acids, we sought an analogous ferrocene-phosphonic acid. Ferrocenes bearing alkylphosphonic acid groups have been prepared previously.[20,21] The reaction of 4-iodophenylferrocene[44] with bis(trimethylsilyl)phosphite in the presence of Pd(PPh$_3$)$_4$ followed by treatment with water afforded 4-(ferrocenyl)phenylphosphonic acid (**29**) in 40% yield (eq 3). Because no further synthetic transformations were

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[40] Li, F.; Gentemann, S.; Kalsbeck, W. A.; Seth, J.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Mater. Chem.* **1997**, *7*, 1245−1262.

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[43] Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166−11180.

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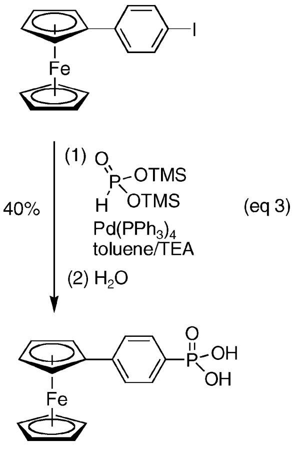

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required and the ferrocene-phosphonic acid was readily purified by crystallization, the trimethylsilyl protecting group could be employed. This situation is in contrast to that with the porphyrins, where the dialkyl protecting group for the phenylphosphonic acid facilitates synthetic transformations and purification yet can be readily removed when desired.

E. Characterization. The porphyrins and chlorins were characterized by absorption spectroscopy, ^{1}H NMR spectroscopy, LDMS,[45] and FABMS. The phosphonate-containing compounds were also characterized by ^{31}P NMR spectroscopy using H_3PO_4 as an external standard. The ^{31}P NMR spectrum of each of the phosphonate-containing compounds yielded a singlet. The ^{1}H NMR and ^{13}C NMR spectra of the molecules bearing phosphonate groups showed splitting of some signals originating from atoms in the adjacent phenylene or alkyl phosphonate unit due to coupling with the phosphorus nucleus. ^{1}H NMR and ^{31}P NMR spectra for **Zn21** were not obtained (in $CDCl_3$, THF-d_8, CD_3OD, or DMSO-d_6) due to aggregation.

3. Electrochemical Studies of Monolayers on SiO$_2$.

The electrochemical behavior was investigated for a variety of porphyrin-phosphonic acid complexes tethered to thin layers of SiO_2 grown on (100) p-type Si substrates (doping density 1×10^{18} cm^{-3}). Representative fast-scan cyclic voltammograms of monolayers of **Zn4** on the SiO_2 layer (thickness, $T_{ox} = 1.3$ nm) are shown in Figure 2 as a function of scan rate (2−20 V s^{-1}). Two distinct anodic and cathodic current peaks are observed at all scan rates, which correspond to the formation/neutralization of the mono- and dication radicals of the porphyrin. At a given scan rate, the integrated current in each of the waves is approximately the same, indicating that the same amount of charge is being transferred in and out of the monolayers during both oxidation and reduction steps. The integrated current corresponds to a molecular coverage on the SiO_2 surface of $\sim 1.7 \times 10^{-11}$ mol cm^{-2}. The electrochemical behavior of **Mg4** is very similar to that of **Zn4**. These voltammetric characteristics indicate that the porphyrin-phosphonic acids form robust, electrically well-behaved monolayers on the SiO_2 surface.

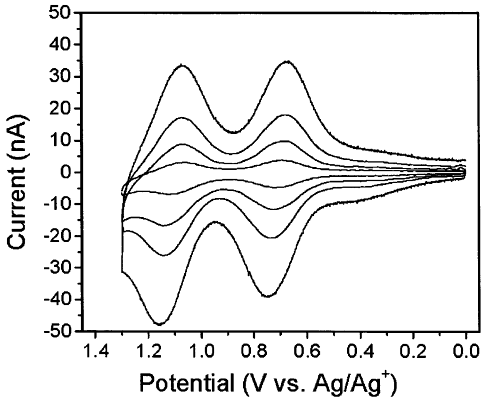

FIGURE 2. Cyclic voltammetry of **Zn4** on SiO_2 ($T_{ox} = 1.3$ nm) with scan rates of 2, 5, 10, and 20 V s^{-1} (from lowest to highest amplitude).

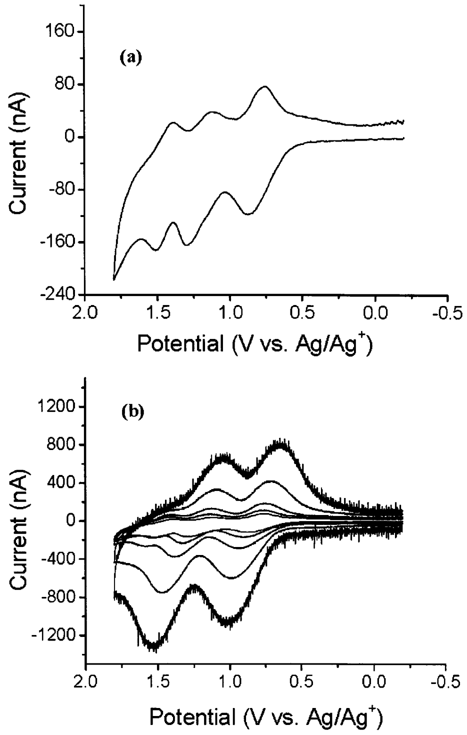

FIGURE 3. Cyclic voltammetry of **Dyad-2** on SiO_2 (T_{ox} = 1.3 nm). (a) Voltammetry at a scan rate of 5 V s^{-1}. (b) Voltammetry with scan rates of 5, 10, 20, 50, and 100 V s^{-1} (from lowest to highest amplitude). Note that three peaks are observed at slower scan rates, whereas two peaks are observed at higher scan rates.

Figure 3 shows the voltammetric characteristics of a monolayer of **Dyad-2** on SiO_2. In the monolayer, the two porphyrins may be electrically inequivalent if there is a voltage drop across the long axis of the dyad. This electrical inequivalence could afford the possibility of doubling the number of accessible redox states. As can be seen in Figure 3a, three distinct waves are indeed observed in the voltammogram. However, at higher scan rates (Figure 3b), the third peak disappears and only two peaks are observed. A plausible explanation for this observation is that (1) the porphyrin distal to the surface undergoes slower electron-transfer kinetics than the proximal porphyrin, and (2) the higher scan rates over-

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[45] (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.

take the slower kinetic component but not the faster component. At present, we are investigating in detail the electron-transfer and charge-retention characteristics of the porphyrin-phosphonic acids tethered to SiO_2. A key objective is to understand how these properties are affected by the SiO_2 thickness (i.e., the dielectric barrier) as well as the tether barrier. The next paper in this series describes porphyrinic molecules bearing longer tethers, including benzylphosphonic acid and tripodal benzylphosphonic acid tethers.[26] Gaining an understanding of how both the dielectric barrier and the tether barrier affect the electron-transfer and charge-retention characteristics is essential for applications in molecular information storage.

Conclusion

The di-*tert*-butyl-masked phenylphosphonic acid group shows high stability toward the diverse reaction conditions that are employed in the synthesis of porphyrins and chlorins. The mild nonacidic deprotection conditions (TMS-Br or TMS-Cl/TEA in refluxing $CHCl_3$) enable cleavage of the *tert*-butyl group without affecting the metalation state of class III or IV metalloporphyrins (zinc or magnesium chelates) or a zinc chlorin. Two complementary routes were developed for preparing di-*tert*-butyl porphyrinic phenylphosphonates: (1) use of phosphonate-substituted precursors in the rational synthesis of porphyrinic compounds and (2) derivatization of an iodophenyl-substituted porphyrin with di-*tert*-butyl phosphite in a Pd-mediated coupling process. The voltammetric characteristics of monolayers of the porphyrin-phosphonic acids indicate that these molecules are robust, electrically well-behaved species when tethered to an oxide layer deposited on a (semi)conducting medium.

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Supporting Information Available: Complete experimental procedures, description of screening experiments for possible protecting groups, and NMR and mass spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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