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Porphyrin Architectures Tailored for Studies of Molecular Information Storage

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A molecular approach to information storage employs redox-active molecules tethered to an electroactive surface. Zinc porphyrins tethered to Au(111) or Si(100) provide a benchmark for studies of information storage. Three sets of porphyrins have been synthesized for studies of the interplay of molecular design and charge-storage properties: (1) A set of porphyrins is described for probing the effect of surface attachment atom on electron-transfer kinetics. Each porphyrin bears a *meso*-CH_2X group for surface attachment where X = OH, SAc, or SeAc. (2) A set of porphyrins is described for studying the effect of surface-charge density in monolayers. Each porphyrin bears a benzyl alcohol for surface attachment and three nonlinking meso substituents of a controlled degree of bulkiness. (3) A set of porphyrins is described that enables investigation of on-chip patterning of the electrolyte. Each porphyrin bears a formyl group distal to the surface attachment group for subsequent derivatization with a molecular entity that comprises the electrolyte. Taken together, this collection of molecules enables a variety of studies to elucidate design issues in molecular-based information storage.

Introduction

We have described an approach for information storage wherein molecules attached to an electroactive surface serve as the active medium. In this approach, information is stored in the discrete oxidation states of molecules. The ability to store charge in the surface-bound molecules allows the molecular medium to mimic the function of a semiconductor capacitor such as that found in a dynamic random access memory cell (which is comprised of a transistor−capacitor pair).[1] A system of particular interest is a hybrid architecture composed of information-storage molecules located in the memory cells of traditional, photolithographically constructed memory chips.

The generic design of the information-storage molecules includes a redox-active unit and a covalently attached tether; the tether is composed of a linker bearing a terminal functional group for surface attachment. Within this generic design, we have prepared a wide variety of molecular architectures as candidates for information-storage applications.[2−21] The molecules prepared to date have been employed to investigate the storage of multiple bits,[4−9,16] effects of tether structure on charge-storage properties and surface packing pat-

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(1) Roth, K. M.; Dontha, N.; Dabke, R. B.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. *J. Vac. Sci. Technol. B.* **2000**, *18*, 2359−2364.
(2) Gryko, D. T.; Clausen, P. C.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 8635−8647.
(3) Gryko, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7345−7355.
(4) Gryko, D. T.; Zhao, F.; Yasseri, A. A.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7356−7362.
(5) Clausen, C.; Gryko, D. T.; Dabke, R. B.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7363−7370.
(6) Clausen, C.; Gryko, D. T.; Yasseri, A. A.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7371−7378.
(7) Li, J.; Gryko, D.; Dabke, R. B.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7379−7390.
(8) Gryko, D.; Li, J.; Diers, J. R.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Mater. Chem.* **2001**, *11*, 1162−1180.
(9) Schweikart, K.-H.; Malinovskii, V. L.; Diers, J. R.; Yasseri, A. A.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 808−828.
(10) Li, Q.; Mathur, G.; Homsi, M.; Surthi, S.; Misra, V.; Malinovskii, V.; Schweikart, K.-H.; Yu, L.; Lindsey, J. S.; Liu, Z.; Dabke, R. B.; Yasseri, A.; Bocian, D. F.; Kuhr, W. G. *Appl. Phys. Lett.* **2002**, *81*, 1494−1496.
(11) Roth, K. M.; Gryko, D. T.; Clausen, C.; Li, J.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. *J. Phys. Chem. B* **2002**, *106*, 8639−8648.
(12) Roth, K. M.; Yasseri, A. A.; Liu, Z.; Dabke, R. R.; 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.
(13) Roth, K. M.; Liu, Z.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. *Molecules as Components of Electronic Devices*; ACS Symp. Ser. No. 844; American Chemical Society: Washington, DC, 2003; pp 51−61.
(14) 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.
(15) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543−1545.
(16) Li, Q.; Mathur, G.; Gowda, S.; Surthi, S.; Zhao, Q.; Yu, L.; Lindsey, J. S.; Bocian, D. F.; Misra, V. *Adv. Mater.* **2004**, *16*, 133−137.

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terns,[13,19,20] effect of molecular packing densities on charge-storage properties,[11,12] stability toward processing and operation (i.e., repeated redox cycling),[15] and incorporation of surface attachment groups for binding to Au,[1−9,11,13] Si or Ge,[10,12,17,21] or metal oxides (e.g., SiO_2, TiO_2).[14,18,19]

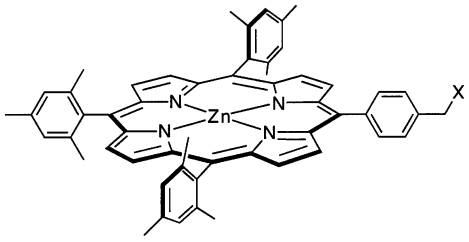
A number of issues remain to be addressed concerning the interplay of molecular design and charge-storage properties for use in memory devices. The motivation for the work described herein centers on three particular issues.

We have principally used thiols for attachment to Au and alcohols for attachment to Si (and Ge) surfaces. It is of interest to understand how the type of atom that is used for surface attachment affects the electron-transfer properties. In particular, theoretical studies by Ratner and co-workers have indicated that the conductivity through a molecule spanning two Au electrodes and attached via a chalcogenide monotonically increases down the group O < S < Se.[22] This hypothesis has not yet been tested.

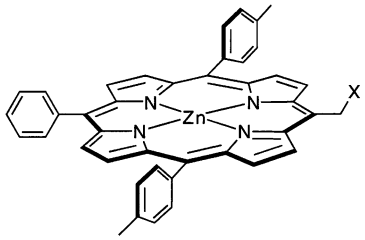
We have observed that the electron-transfer rates increase as the packing density in a self-assembled monolayer (SAM) decreases.[11,12] Such studies were performed by successive dilution of the SAMs. A factor of 10 difference in rate could be obtained for a given redox-active unit by control over the packing density. It is of interest to determine whether packing densities could be more effectively controlled by building in the desired level of steric bulk in the molecules employed to form the SAM.

Our present approach toward chip fabrication entails formation of the monolayer on a chip containing photolithographically defined memory cells, formation of a top contact to the molecules via an electrolyte drop (e.g., Bu_4NPF_6 in CH_2Cl_2) or a gel electrolyte (e.g., Bu_4NPF_6 in propylene carbonate), followed by solvent evaporation and deposition of the counter electrode. While this approach enables studies of the information-storage properties of the molecules, the methods for electrolyte deposition are not very amenable to device fabrication. In fabricating a hybrid chip containing molecular materials, it is essential to be able to (i) locate the electrolyte only in those regions of the chip where the molecules are located, (ii) control the thickness of the electrolyte layer, and (iii) introduce the counter electrode without creating shorts across the electrolyte/molecule region. At present, little control can be exercised over such "patterning of the electrolyte", which directly affects the methods employed for introducing the counter electrode. Consequently, it is of interest to explore molecular designs wherein the electrolyte is an integral part of the redox-active molecule. Such an approach may enable metal deposition directly on the electrolyte/molecule layer given that a liquid or gel electrolyte is no longer employed.

CHART 1



Zn-1a: X = OH
Zn-1b: X = SAc
Zn-1c: X = SeAc



Zn-2a: X = OH
Zn-2b: X = SAc
Zn-2c: X = SeAc

The ultimate design of molecules for use in information-storage applications requires consideration of all of the issues raised above. In this paper, we describe the synthesis of a number of porphyrins that can be used to address each issue. First, a set of porphyrins is described for probing the effect of surface attachment atom on electron-transfer kinetics. Each porphyrin bears a $-CH_2X$ group for surface attachment, where X = OH, SAc, or SeAc. Second, a series of porphyrins is described for probing the effect of surface-charge density in monolayers. Each porphyrin bears a benzyl alcohol for surface attachment and three nonlinking meso substituents of a controlled degree of bulkiness. Third, a set of porphyrins is described that can be employed in studies of electrolyte patterning. Each porphyrin bears a formyl group distal to the tether for subsequent derivatization with a molecular entity that comprises the electrolyte. This collection of molecules enables a variety of studies to elucidate design issues in molecular-based information storage. Examination of the charge-storage properties of the various molecules and the suitability of different designs for use in hybrid molecule−silicon memory chips is beyond the scope of this paper and will be described elsewhere.

Results and Discussion

I. Porphyrins for Investigation of Effects of Surface-Attachment Groups on Electron-Transfer Rates. Rationale: We previously prepared a set of porphyrins to examine the effects of the surface attachment group on the electron-transfer properties of the porphyrin in a SAM.[17] The porphyrins (**Zn-1a**−**c**, Chart 1) were attached to the surface via a benzyl-X group where X was an oxygen, sulfur, or selenium atom. (The *S*-acetyl or *Se*-acetyl protecting group undergoes cleavage

(17) Balakumar, A.; Lysenko, A. B.; Carcel, C.; Malinovskii, V. L.; Gryko, D. T.; Schweikart, K.-H.; Loewe, R. S.; Yasseri, A. A.; Liu, Z.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 1435−1443.

(18) Muthukumaran, K.; Loewe, R. S.; Ambroise, A.; Tamaru, S.-I.; Li, Q.; Mathur, G.; Bocian, D. F.; Misra, V.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 1444−1452.

(19) Loewe, R. S.; Ambroise, A.; Muthukumaran, K.; Padmaja, K.; Lysenko, A. B.; Mathur, G.; Li, Q.; Bocian, D. F.; Misra, V.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 1453−1460.

(20) Wei, L.; Padmaja, K.; Youngblood, W. J.; Lysenko, A. B.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2004**, *69*, 1461−1469.

(21) Liu, Z.; Yasseri, A. A.; Loewe, R. S.; Lysenko, A. B.; Malinovskii, V. L.; Zhao, Q.; Surthi, S.; Li, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2004**, *69*, 5568−5577.

(22) Yaliraki, S. N.; Kemp, M.; Ratner, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 3428−3434.

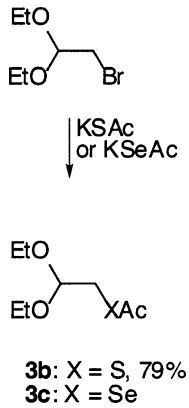
upon exposure to the Si surface, resulting in attachment via the S or Se atom.[17]) We found that the electron-transfer properties of the porphyrins were similar to one another. We considered the absence of any observable difference in the electron-transfer properties with O/S/Se groups might be attributed to the presence of the intervening phenyl unit, which limits the electron-transfer rate. We have now redesigned the molecules to contain only a $-CH_2X$ group (**Zn-2a**−**c**).

A variety of porphyrins bearing one or more *meso*-hydroxymethyl groups have been prepared.[23−25] The synthetic approach generally employed entails Vilsmeier formylation of an acid-stable metalloporphyrin (e.g., Ni, Cu) followed by (optional: demetalation and) reduction of the formyl group to give the hydroxymethyl group. Most porphyrins contained multiple β substituents. Indeed, the only example of a porphyrin bearing one free meso site, three nonlinking meso substituents, and no β substituents was prepared by a statistical process.[24] To our knowledge, no porphyrins with a directly attached *S*-acetylthiomethyl or *Se*-acetylselenomethyl group have been prepared.

Synthesis: The synthesis of porphyrins bearing distinct patterns of meso substituents can be achieved by reaction of a dipyrromethane and a dipyrromethane-dicarbinol.[26] Accordingly, we have investigated an approach wherein the $-CH_2X$ group is incorporated at the meso position of the dipyrromethane. The synthesis of the dipyrromethanes requires a hydroxy, *S*-acetylthio, or *Se*-acetylseleno group at the α-position of acetaldehyde. The diethyl acetal of α-hydroxyacetaldehyde (**3a**) is commercially available. Treatment of commercially available α-bromoacetaldehyde diethylacetal with KSAc afforded acetal **3b** in 79% yield (Scheme 1). The requisite KSeAc[27] was prepared from diacetylselenide[28] and reacted directly with α-bromoacetaldehyde diethylacetal in DMF at room temperature, affording *Se*-acetylseleno-acetaldehyde diethylacetal **3c** in crude form. The latter was used without further purification in the synthesis of the dipyrromethane.

The one-flask reaction of an aldehyde with excess pyrrole affords the dipyrromethane. We recently developed refined conditions that employ a mild Lewis acid as catalyst and refined workup conditions to give the dipyrromethane with minimal or no chromatography.[29] Thus, condensation of glycolaldehyde diethylacetal (**3a**)

SCHEME 1



3b: X = S, 79%
3c: X = Se

with excess pyrrole (100 equiv) in the presence of 0.1 equiv of $InCl_3$ at room temperature gave the desired dipyrromethane **4a** as well as the *N*-confused dipyrromethane (upon GC analysis after 24 h). Workup of this mixture gave **4a** in 29% yield. The same reaction at 60 °C for 2 h afforded dipyrromethane **4a** as a white solid in 61% yield and the *N*-confused dipyrromethane in 15% yield (Scheme 2). The reaction of acetal **3b** with excess pyrrole (100 equiv) in the presence of 0.3 equiv of $InCl_3$ at room temperature resulted in 50% starting material after 24 h. Refinement of the conditions [$InCl_3$ (0.3 equiv), pyrrole (100 equiv), 60 °C, 10 h] afforded dipyrromethane **4b** as an oil in 48% yield. Compound **4b** was found to be >99% pure by GC analysis, though the elemental analysis of **4b** (and the precursor **3b**) deviated slightly from the expected values. The analogous condensation of crude **3c** for 12 h followed by chromatography afforded dipyrromethane **4c** as an oil (8% yield from diacetylselenide).

The synthesis of free base porphyrin **2a** was pursued by condensation of dipyrromethane **4a** with dipyrromethane-dicarbinol **5-diol**[30] at room temperature (Scheme 2). The synthesis was investigated with use of TFA in CH_3CN[26] or a Lewis acid catalyst [$InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, or $Dy(OTf)_3$][31] in CH_2Cl_2. With TFA catalysis, the maximum spectroscopic yield reached 6%. The Lewis acids gave yields of 0%, 10%, 12%, and 8%, respectively. A scaled-up synthesis with $Yb(OTf)_3$ afforded **2a** in 17% isolated yield. Analysis of the crude reaction mixture by laser-desorption mass spectrometry (LD-MS)[32] did not reveal the formation of any porphyrin species derived from acidolysis of dipyrromethane species (i.e., scrambling). The similar reaction of **5-diol** with dipyrromethane **4b** or **4c** under $Yb(OTf)_3$ catalysis afforded free-base porphyrin **2b** or **2c** in 29% or 18% yield, respectively. In each case, LD-MS did not reveal any scrambling. Porphyrins **2a**−**c** were treated separately with $Zn(OAc)_2 \cdot 2H_2O$ to afford **Zn-2a**−**c**.

II. Porphyrins with Controlled Facial Encumbrance for Studies of Surface Charge Density on

(23) (a) Smith, K. M.; Bisset, G. M. F. *J. Org. Chem*. **1979**, *44*, 2077−2081. (b) Ogoshi, H.; Saita, K.; Sakurai, K.-I.; Watanabe, T.; Toi, H.; Aoyama, Y. *Tetrahedron Lett*. **1986**, *27*, 6365−6368. (c) Ponomarev, G. V.; Borovkov, V. V.; Shul'ga, A. M.; Sakata, Y. *J. Chem. Soc., Chem. Commun*. **1994**, 1927−1928. (d) Higuchi, H.; Shimizu, K.; Ojima, J.; Sugiura, K.-I.; Sakata, Y. *Tetrahedron Lett*. **1995**, *36*, 5359−5362. (e) Torpey, J. W.; Ortiz de Montellano, P. R. *J. Org. Chem*. **1995**, *60*, 2195−2199. (f) Higuchi, H.; Shimizu, K.; Takeuchi, M.; Ojima, J.; Sugiura, K.-I.; Sakata, Y. *Bull. Chem Soc. Jpn*. **1997**, *70*, 1923−1933. (g) Balaban, T. S.; Bhise, A. D.; Fischer, M.; Linke-Schaetzel, M.; Roussel, C.; Vanthuyne, N. *Angew. Chem., Int. Ed*. **2003**, *42*, 2140−2144.

(24) Tkachenko, N. V.; Lemmetyinen, H.; Sonoda, J.; Ohkubo, K.; Sato, T.; Imahori, H.; Fukuzumi, S. *J. Phys. Chem. A* **2003**, *107*, 8834−8844.

(25) Xu, Y.; Jaquinod, L.; Wickramasinghe, A.; Smith, K. M. *Tetrahedron Lett*. **2003**, *44*, 7753−7756.

(26) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem*. **2000**, *65*, 7323− 7344.

(27) Kageyama, H.; Takagi, K.; Murai, T.; Kato, S. *Z. Naturforsch*. **1989**, *44b*, 1519−1523.

(28) Koketsu, M.; Nada, F.; Hiramatsu, S.; Ishihara, H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 737−740.

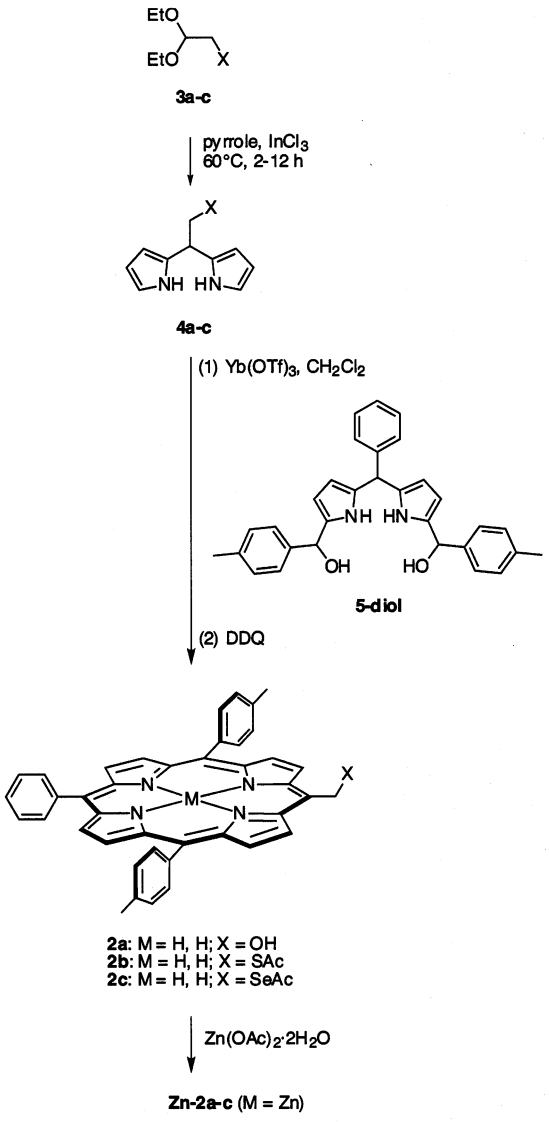
(29) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Proc. Res. Dev*. **2003**, *7*, 799−812.

(30) Tamaru, S.-I.; Yu, L.; Youngblood, W. J.; Muthukumaran, K.; Taniguchi, M.; Lindsey, J. S. *J. Org. Chem*. **2004**, *69*, 765−777.

(31) Geier, G. R., III; Callinan, J. B.; Rao, P. D.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810−823.

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

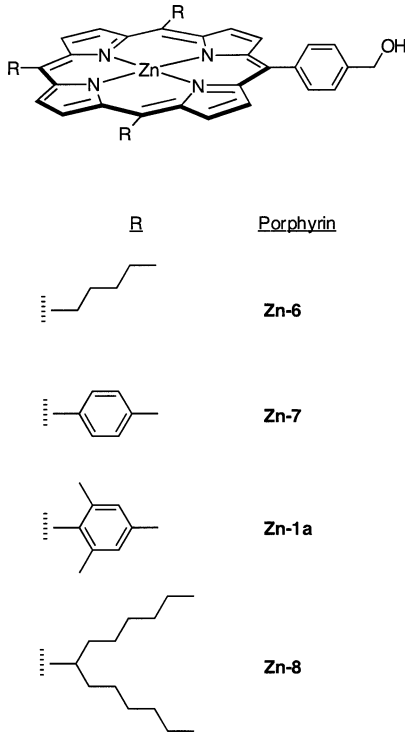
SCHEME 2



Charge-Storage Properties. Rationale: We sought to prepare a series of porphyrin−benzyl alcohols wherein the size of the nonlinking groups could be used to control the distance of separation of the porphyrins in self-assembled monolayers on the silicon surface. We previously have prepared porphyrin−benzyl alcohols bearing mesityl (**Zn-1a**) or pentyl (**Zn-6**) groups at the three nonlinking meso positions. We now describe the synthesis of zinc porphyrins that bear *p*-tolyl (**Zn-7**) or swallowtail (**Zn-8**) groups at the nonlinking meso positions (Chart 2). Several different synthetic routes have been pursued to prepare the porphyrins.

Synthesis: (1) *p*-Tolyl Porphyrins. The target zinc porphyrin (**Zn-7**) bears one *p*-benzyl alcohol and three meso *p*-tolyl substituents. The corresponding free base porphyrin (**7**) has been prepared by statistical routes.[33,34] A rational approach was pursued by reduction of 1,9-diacyldipyrromethane **9**[35] to give the dicarbinol, which upon reaction with dipyrromethane **10**[36,37] under TFA catalysis followed by oxidation with DDQ gave porphyrin **11** in 16% yield. Porphyrin **11** also has been prepared previously via statistical (mixed-aldehyde) condensations.[34,38] Treatment of **11** with $Zn(OAc)_2 \cdot 2H_2O$ gave **Zn-11**, which was reduced with $LiAlH_4$ to give **Zn-7** in quantitative yield (Scheme 3). The direct conversion of **11** to **Zn-7** (via **Zn-11** but without isolation) was achieved in 95% overall yield.

CHART 2

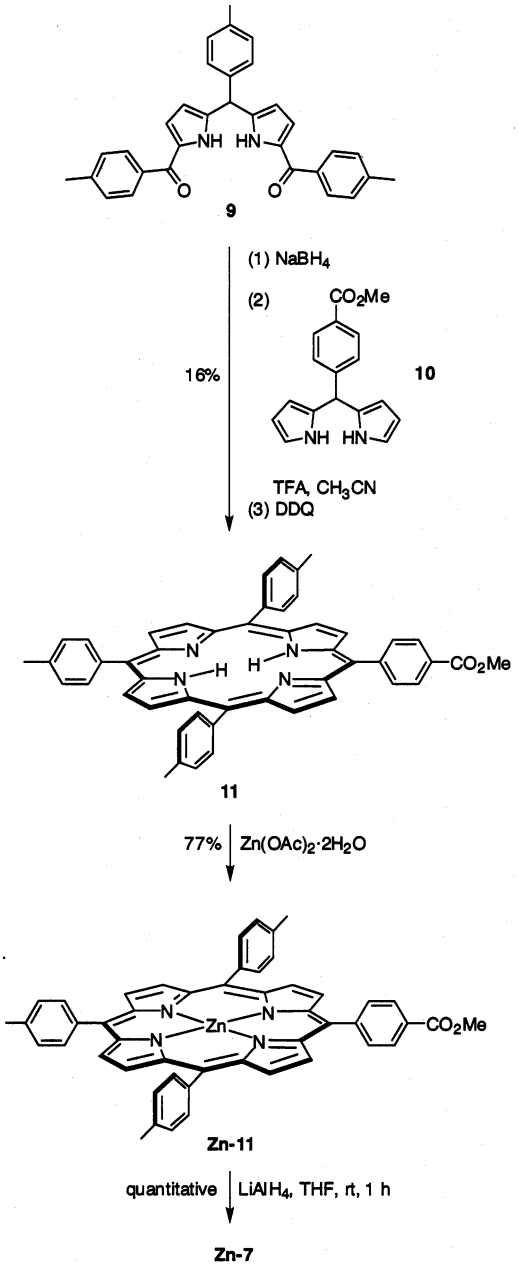


(2) Swallowtail Porphyrins. We recently prepared a series of porphyrin building blocks that incorporate tridec-7-yl (i.e., "swallowtail") substituents at the meso positions.[39] The hexyl chains project above and below the plane of the porphyrin macrocycle, with the C−H bond of the branching carbon (C7) lying in the plane of the macrocycle. Porphyrin building blocks with 1−4 swallowtail substituents were prepared; however, it was necessary to employ statistical approaches to gain access to porphyrins bearing three swallowtail substituents owing to the inability to reduce 1,9-diacyldipyrromethanes bearing swallowtail groups at the acyl positions. The statistical approach we employed herein to prepare **Zn-8** is shown in Scheme 4.

The condensation of aldehyde **12**,[40] dipyrromethane **13**,[39] and methyl 4-formylbenzoate in a stoichiometric

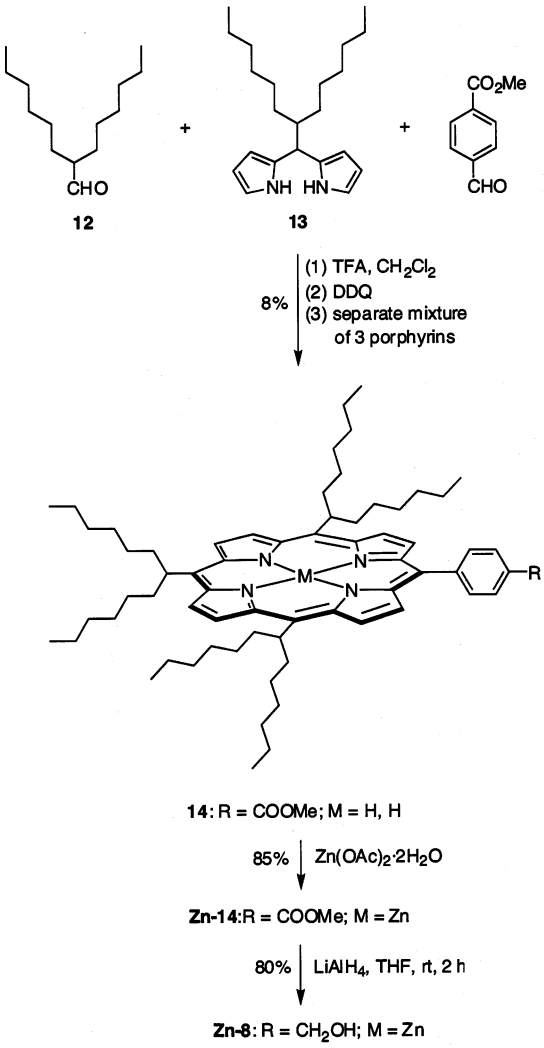
(33) Takahashi, Y.; Guillet, J. E.; Winnik, M. A. *Can. J. Chem.* **1989**, *67*, 411−416.
(34) Hombrecher, H. K.; Ohm, S. *Tetrahedron* **1993**, *49*, 2447−2456.
(35) Gryko, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 2249−2252.
(36) (a) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *263*, 279−286. (b) Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 4609−4613. (c) Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6535−6551.
(37) Balaban, T. S.; Eichhöfer, A.; Lehn, J.-M. *Eur. J. Org. Chem.* **2000**, 4047−4057.
(38) (a) Anton, J. A.; Loach, P. A. *J. Heterocycl. Chem.* **1975**, 573−576. (b) Williamson, D. A.; Bowler, B. E. *Tetrahedron* **1996**, *52*, 12357−12372.
(39) Thamyongkit, P.; Speckbacher, M.; Diers, J. R.; Kee, H. L.; Kirmaier, C.; Holten, D.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 3700−3710.
(40) Kato, M.; Komoda, K.; Namera, A.; Sakai, Y.; Okada, S.; Yamada, A.; Yokoyama, K.; Migita, E.; Minobe, Y.; Tani, T. *Chem. Pharm. Bull.* **1997**, *45*, 1767−1776.

SCHEME 3



ratio of 1:2:1 afforded the three expected porphyrins. The diester−porphyrin was the dominant porphyrin product and porphyrin **14** was isolated in 2% yield. Statistical considerations alone indicate the desired porphyrin **14** should be formed in maximum amounts when the ratio of reactants is equal to the stoichiometry required for formation of **14**, but the different reactivity of the various components can skew the actual product ratio. Upon increasing the amount of aldehyde **12** to a reactant ratio of 2:2:1, **14** was obtained in 8% yield (Scheme 4). We also investigated two other statistical routes. The condensation of swallowtail dipyrromethane **13**, aldehyde **12**, and 5-(4-carbomethoxyphenyl)dipyrromethane (**10**) in 1:2:1 ratio gave **14** in <1% yield, and the condensation of pyrrole, **12**, and methyl 4-formylbenzoate in 4:3:1 ratio gave **14** in 4% yield. No substantial improvements were obtained upon varying the ratios of the reactants.

SCHEME 4

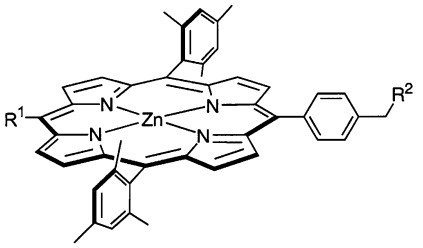


Metalation of porphyrin **14** with $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-14** in 85% yield. Treatment of **Zn-14** with $LiAlH_4$ in THF at room temperature for 2 h gave porphyrin−alcohol **Zn-8** in 80% yield.

III. Porphyrins for On-Chip Patterning of the Electrolyte. Rationale: An approach toward patterning the electrolyte is to attach an entity having a fixed charge (i.e., the electrolyte) to the charge-storage molecule. In this manner, the electrolyte is confined to the same locations as the charge-storage molecules, and the use of a liquid electrolyte is avoided altogether. The charged group can entail a fixed cation and mobile anion, a fixed anion and a mobile cation, or multiple charged groups of one or both types.

The use of a bipartite molecule composed of an electrolyte and charge-storage moiety leads to a design wherein the bipartite structure is assembled on a memory chip in a two-step process. In step one, the charge-storage molecule is attached to the electroactive surface of memory storage cells in the chip. In step two, the electrolyte unit is attached to the charge-storage molecules. The two-step approach for electrolyte attachment requires conditions such that (i) the surface, surface

CHART 3



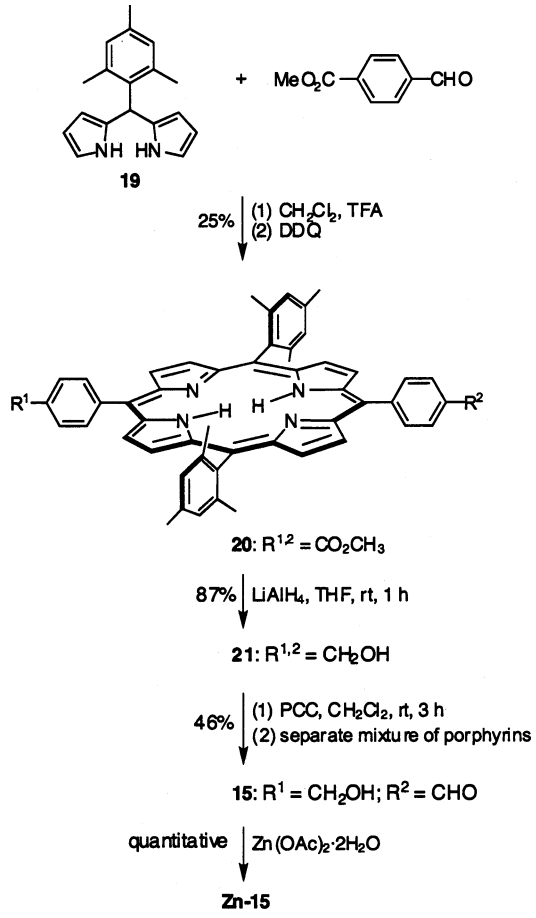
R^1	R^2	Compound
OHC—	—OH	**Zn-15**
OHC—	—SAc	**Zn-16**
OHC—	—OH	**Zn-17**
OHC—	—SAc	**Zn-18**

attachment linkage, redox-active molecule, and any other components on the chip are unaffected by the electrolyte attachment procedure and (ii) reaction occurs essentially quantitatively. Reactions that meet these criteria typically occur under mild conditions. Among the possible reactions, imine formation by condensation of an aldehyde (attached to the information-storage molecule) and a hydrazide (bearing the charged group) is particularly attractive. Indeed, hydrazide reagents bearing charged pyridinium or trimethylammonium groups (Girard's reagents P or T) have been used extensively for gentle derivatization[41] of aldehydes with rich functionality such as chlorophyll *b*,[42] carotenoids,[43] and other complex molecules.[44]

Four target molecules (**Zn-15**−**Zn-18**) were identified that meet the molecular design criteria (Chart 3). Each molecule incorporates a zinc porphyrin as the redox-active molecule. The porphyrin can be attached to an electroactive surface via a benzyl linker bearing an S or O atom. The distal formyl or 4-formylphenyl group provides a site for attachment of the electrolyte at a fixed distance from the porphyrin.

Synthesis: Each target compound (**Zn-15**−**Zn-18**) is a *trans*-AB_2C-porphyrin. Many *trans*-AB_2C-porphyrins can be synthesized in a rational manner by reaction of a dipyrromethane-dicarbinol and a dipyrromethane.[26] However, given the presence of two mesityl groups and two sensitive substituents (formyl and alcohol or *S*-acetylthio) per porphyrin, we chose a synthesis that employs an aldehyde + dipyrromethane reaction to construct the porphyrin macrocycle in conjunction with one statistical step (either during or after porphyrin formation) to achieve the *trans*-AB_2C substitution pattern.

SCHEME 5

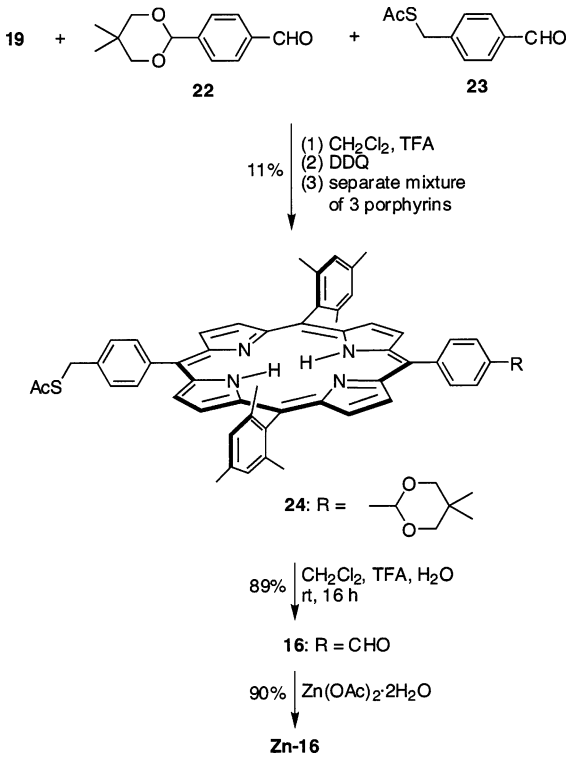


The synthesis of target molecule **Zn-15** is shown in Scheme 5. The condensation of 5-mesityldipyrromethane (**19**)[29,45] and methyl 4-formylbenzoate was carried out under the standard conditions[46] for forming *trans*-A_2B_2-porphyrins from sterically hindered dipyrromethanes (17.8 mM TFA in CH_2Cl_2 at room temperature). Subsequent oxidation with DDQ afforded the desired free base porphyrin **20** in 25% yield. Compound **20** has been reported with characterization data but without description of a synthetic procedure.[47] Reduction of **20** with excess $LiAlH_4$ afforded porphyrin−diol **21** in 87% yield. Treatment of **21** with 1 equiv of PCC afforded a statistical mixture, which was readily separated chromatographically affording the desired monoaldehyde **15** in 46% yield. A related route to a porphyrin with undecyl rather than mesityl substituents has been described.[37] Zinc insertion gave the target porphyrin **Zn-15**.

The synthesis of porphyrin **Zn-16** is shown in Scheme 6. The chosen route to porphyrin **Zn-16**, which bears an *S*-acetylthiomethyl functionality and a formylphenyl group, requires protection of the formyl group during the porphyrin-forming process. A statistical reaction of acetal-aldehyde **22** (available from 4-cyanobenzaldehyde[48]

(41) Wheeler, O. H. *Chem. Rev.* **1961**, *61*, 205−221.
(42) (a) Wetherell, H. R.; Hendrickson, M. J. *J. Org. Chem.* **1959**, *24*, 710−711. (b) Kenner, G. W.; McCombie, S. W.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2517−2523. (c) Losev, A.; Mauzerall, D. *Photochem. Photobiol.* **1983**, *38*, 355−361.
(43) Kanofsky, J. R.; Sima, P. D. *Photochem. Photobiol.* **2001**, *73*, 349−358.
(44) Caldwell, A. G. *J. Chem. Soc.* **1952**, 2035−2041.
(45) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.
(46) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.
(47) Liddell, P. A.; Kodis, G.; de la Garza, L.; Bahr, J. L.; Moore, A. L.; Moore, T. A.; Gust, D. *Helv. Chim. Acta* **2001**, *84*, 2765−2783.
(48) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827−836.

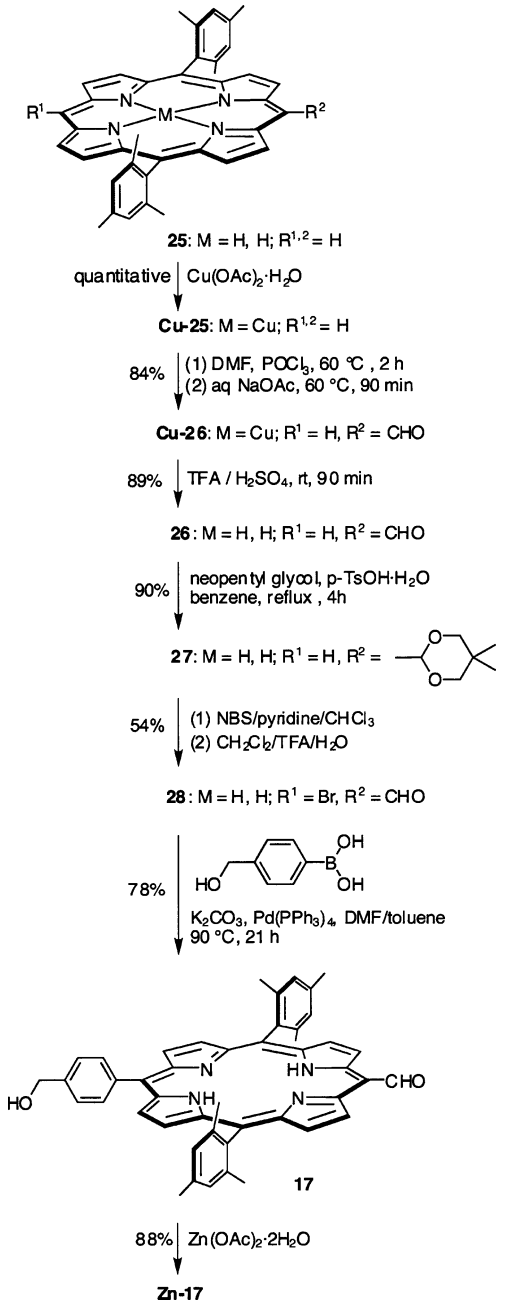
SCHEME 6



or methyl 4-formylbenzoate[49]), 4-(*S*-acetylthiomethyl)-benzaldehyde (**23**),[3] and 5-mesityldipyrromethane (**19**) under the standard conditions for reactions of sterically hindered dipyrromethanes[46] followed by oxidation with DDQ gave the expected mixture of three porphyrins. Chromatographic workup yielded the desired *trans*-AB_2C porphyrin **24** in 11% yield. Hydrolysis of the acetal group in **24** was achieved in a biphasic solution of CH_2Cl_2/TFA/H_2O[50] for 16 h to give porphyrin−aldehyde **16** in 89% yield. Metalation with $Zn(OAc)_2 \cdot 2H_2O$ at room temperature gave **Zn-16** in 90% yield.

The synthesis of porphyrin **Zn-17** can be divided essentially in three steps: meso-formylation, bromination of the remaining free meso position, and attachment of the hydroxymethylphenyl group by Suzuki coupling (Scheme 7). Metalation of porphyrin **25**[51] with copper acetate afforded the copper chelate **Cu-25**, which upon Vilsmeier formylation[52] gave the *meso*-formyl product **Cu-26** in 84% yield. It is noteworthy that monoformylation resulted even upon use of excess formylation reagent, indicating that the remaining meso position was deactivated. However, application of the standard conditions for meso-bromination (1 equiv of NBS in $CHCl_3$ and pyridine at room temperature)[53,54] resulted in partial bromination at a β-position rather than the desired meso site.

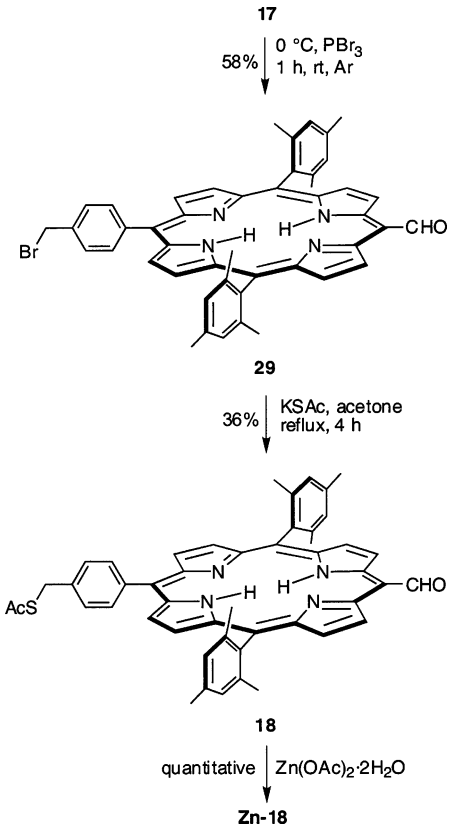
SCHEME 7



To suppress the deactivation caused by the presence of the *meso*-formyl group, **Cu-26** was demetalated with concentrated H_2SO_4 in TFA to give the free base *meso*-formyl porphyrin **26** in 89% yield. [Note that analogues of **Cu-26** (and **26**) with 3,5-di-*tert*-butylphenyl[25,55] or phenyl[56] in place of mesityl groups have been prepared.] Porphyrin **26** was treated with neopentyl glycol in the presence of *p*-TsOH·H_2O in refluxing benzene to give the acetal−porphyrin **27** in 90% yield. Bromination of **27** with NBS in the presence of pyridine[54] gave a mixture of the corresponding bromo-acetal−porphyrin and a small amount (∼5%) of porphyrin **28**. Treatment of the mixture

(49) Nagata, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3005−3016.
(50) Lindsey, J. S.; Brown, P. A.; Siesel, D. A. *Tetrahedron* **1989**, *45*, 4845−4866.
(51) Yu, L.; Muthukumaran, K.; Sazanovich, I. V.; Kirmaier, C.; Hindin, E.; Diers, J. R.; Boyle, P. D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *Inorg. Chem.* **2003**, *42*, 6629−6647.
(52) Johnson, A. W.; Oldfield, D. *J. Chem. Soc. (C)* **1966**, 794−798.
(53) Nudy, L. R.; Hutchinson, H. G.; Schieber, C.; Longo, F. R. *Tetrahedron* **1984**, *40*, 2359−2363.
(54) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983−5993.
(55) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399−8402.
(56) Yeung, M.; Ng, A. C. H.; Drew, M. G. B.; Vorpagel, E.; Breitung, E. M.; McMahon, R. J.; Ng, D. K. P. *J. Org. Chem.* **1998**, *63*, 7143−7150.

SCHEME 8



with CH_2Cl_2/TFA/H_2O led to porphyrin **28** in 54% overall yield. Suzuki coupling of **28** and 4-hydroxymethylphenylboronic acid under conditions[57] known to succeed with porphyrin substrates gave the porphyrin (**17**) bearing a hydroxymethylphenyl group in 78% yield upon chromatographic workup. Metalation with zinc acetate gave the desired target molecule **Zn-17** in 88% yield.

The synthesis of target porphyrin **Zn-18** was achieved as shown in Scheme 8. Treatment of porphyrin **17** with PBr_3 under conditions for reaction of benzyl alcohols[58] gave bromomethyl-porphyrin **29** in 58% yield. Reaction of the latter with potassium thioacetate[2,5] gave the free base porphyrin **18** in 36% yield. Subsequent metalation with zinc acetate afforded the desired porphyrin **Zn-18**.

IV. Outlook. The design of molecules for information-storage applications in a hybrid molecule-chip architecture requires consideration of a number of factors. Some factors bear on performance, such as electron-transfer rates and charge-retention times, while others concern fabrication, such as ensuring the electrolyte is located adjacent to the charge-storage molecules in the memory cells. The charge-storage molecules described herein have been designed to probe several of these factors. Tailoring the nature of the surface attachment group (O, S, Se) and the facial encumbrance of the porphyrin will enable studies of charge-storage properties. Porphyrins with a derivatizable functional group distal to the surface may facilitate fabrication and enable studies of electrolyte placement and how different electrolytes alter charge-storage properties. The ability to readily achieve different molecular designs through straightforward syntheses augurs well for the systematic identification of molecules suitable for use in hybrid information-storage constructs.

Experimental Section

Noncommercial Compounds. Compounds **5**,[30] **9**,[35] **10**,[36,37] **12**,[40] **13**,[39] **19**,[29,45] **22**,[48,49] **23**,[3] **25**,[51] **Zn-1a**−**c**,[17] and diacetylselenide[28] were prepared as described in the literature.

5-(Hydroxymethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (2a). Following a general procedure,[30] a sample of **5** (1.72 g, 2.50 mmol) was reduced with $NaBH_4$ in dry THF/methanol (9:1) and the resulting **5-diol** was condensed with **4a** (443 mg, 2.50 mmol) in CH_2Cl_2 (500 mL) containing $Yb(OTf)_3$ (1.00 g, 1.60 mmol) at room temperature for 4 min. DDQ (1.71 g, 7.50 mmol) was added. The reaction mixture was concentrated and passed over a silica column [CH_2Cl_2 → CH_2Cl_2/ethyl acetate (98:2)] to afford a purple solid (260 mg, 17%): ^{1}H NMR δ −2.84 (br s, 2H), 2.73 (s, 6H), 6.98 (d, J = 5.2 Hz, 2H), 7.57 (d, J = 8.0 Hz, 4H), 7.75 (m, 3H), 8.08 (d, J = 8.0 Hz, 4H), 8.19 (d, J = 8.2 Hz, 2H), 8.81 (d, J = 4.4 Hz, 2H), 8.82 (d, J = 4.4 Hz, 2H), 9.01 (d, J = 4.4 Hz, 2H), 9.61 (d, J = 4.4 Hz, 2H); LD-MS obsd 598.0; FAB-MS obsd 596.2598, calcd 596.2576 ($C_{41}H_{32}N_4O$); λ_{abs} 422, 516, 552, 589, 654 nm.

Zn(II)-5-(Hydroxymethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (Zn-2a). Porphyrin **2a** (258 mg, 0.432 mmol) was dissolved in $CHCl_3$ (50 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (474 mg, 2.16 mmol) in methanol (8 mL) was added. The reaction mixture was stirred at room temperature for 16 h, then concentrated and chromatographed [silica, CH_2Cl_2/ethyl acetate (98:2)]. The product was concentrated to dryness. The resulting solid was washed first with methanol and then with hexanes, affording a purple solid (125 mg, 44%): ^{1}H NMR δ 2.74 (s, 6H), 6.37 (s, 2H), 7.56 (d, J = 8.0 Hz, 4H), 7.72 (m, 3H), 8.06 (d, J = 8.0 Hz, 4H), 8.18 (d, J = 8.2 Hz, 2H), 8.90−8.95 (m, 4H), 9.00 (d, J = 4.5 Hz, 2H), 9.27 (d, J = 4.5 Hz, 2H); LD-MS obsd 660.5, 643.3 [(M − OH)$^+$]; FAB-MS obsd 658.1711, calcd 658.1713 ($C_{41}H_{30}N_4OZn$); λ_{abs} 422, 551, 589 nm.

5-(*S*-Acetylthiomethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (2b). As described for **2a**, condensation of **5-diol** (derived from **5**; 0.62 g, 0.90 mmol) and **4b** (210 mg, 0.900 mmol) in CH_2Cl_2 (360 mL) containing $Yb(OTf)_3$ (720 mg, 1.16 mmol) at room temperature for 4 min, oxidation with DDQ (610 mg, 2.68 mmol), and chromatography [silica, CH_2Cl_2/ethyl acetate (19:1)] afforded a purple solid (0.17 g, 29%): ^{1}H NMR δ −2.78 (br s, 2H), 2.45 (s, 3H), 2.71 (s, 6H), 6.62 (s, 2H), 7.55 (d, J = 7.8 Hz, 4H), 7.73 (m, 3H), 8.06 (d, J = 8.3 Hz, 4H), 8.16 (d, J = 8.0 Hz, 2H), 8.79 (dd, J = 4.8, 13.1 Hz, 4H), 8.95 (d, J = 4.8 Hz, 2H), 9.47 (d, J = 4.8 Hz, 2H); MALDI-MS (POPOP) obsd 579.8 [(M − SAc)$^+$]; FAB-MS obsd 654.2484, calcd 654.2453 ($C_{43}H_{34}N_4OS$); λ_{abs} 420, 519, 553, 596, 654 nm.

Zn(II)-5-(*S*-Acetylthiomethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (Zn-2b). A solution of porphyrin **2b** (88 mg, 0.13 mmol) in $CHCl_3$ (15 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (147 mg, 0.676 mmol) in methanol (3 mL) at room temperature for 2 h. Chromatography [CH_2Cl_2/ethyl acetate (98:2)] afforded a purple solid (81 mg, 84%): ^{1}H NMR δ 2.42 (s, 3H), 2.73 (s, 6H), 6.61 (s, 2H), 7.56 (d, J = 8.0 Hz, 4H), 7.75 (m, 3H), 8.07 (d, J = 8.0 Hz, 4H), 8.18 (d, J = 7.6 Hz, 2H), 8.88−8.92 (m, 4H), 9.03 (d, J = 4.4 Hz, 2H), 9.52 (d, J = 4.4 Hz, 2H); LD-MS obsd 642.7 [(M − SAc)$^+$]; FAB-MS obsd 717.1693, calcd 717.1667 [(M + H)$^+$] (M = $C_{43}H_{32}N_4OSZn$); λ_{abs} 427, 555, 593 nm.

5-(*Se*-Acetylselenomethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (2c). As described for **2a**, condensation of **5-diol** (derived from **5**; 138 mg, 0.200 mmol) with **4c** (57 mg, 0.20 mmol) in CH_2Cl_2 (80 mL) containing $Yb(OTf)_3$ (160 mg, 0.257 mmol) at room temperature for 4 min followed by oxidation with DDQ (136 mg, 0.60 mmol) and chromatography [silica, CH_2Cl_2/ethyl acetate (19:1)] afforded a purple solid (25 mg, 18%): ^{1}H NMR δ −2.65 (br s, 2H), 2.53 (s, 3H), 2.71 (s, 6H),

(57) Yu, L.; Lindsey, J. S. *Tetrahedron* **2001**, *57*, 9285−9298.
(58) Sellner, H.; Faber, C.; Rheiner, P. B.; Seebach, D. *Chem. Eur. J.* **2000**, *6*, 3692−3705.

6.70 (s, 2H), 7.55 (d, J = 8.0 Hz, 4H), 7.73 (m, 3H), 8.06 (d, J = 8.0 Hz, 4H), 8.17 (d, J = 8.0 Hz, 2H), 8.77 (dd, J = 4.7, 11.0 Hz, 4H), 8.87 (d, J = 4.7 Hz, 2H), 9.48 (d, J = 4.7 Hz, 2H); MALDI-MS (POPOP) obsd 579.3 [(M − SeAc)$^+$]; FAB-MS obsd 703.2001, calcd 703.1976 ($C_{43}H_{34}N_4OSe$); λ_{abs} 424, 521, 557, 599, 655 nm.

Zn(II)-5-(*Se*-Acetylselenomethyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (Zn-2c). A solution of **2c** (23 mg, 0.03 mmol) in CH_2Cl_2 (6 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (47 mg, 0.32 mmol) in methanol (2 mL) at room temperature for 15 min. The reaction mixture was washed with water and brine, dried (Na_2SO_4), and concentrated. Chromatography [CH_2Cl_2/hexanes (7:3)] afforded a purple solid (22 mg, 87%): ^{1}H NMR δ 2.48 (s, 3H), 2.72 (s, 6H), 6.63 (s, 2H), 7.55 (d, J = 7.7 Hz, 4H), 7.73 (m, 3H), 8.06 (d, J = 7.7 Hz, 4H), 8.17 (m, 2H), 8.88 (dd, J = 4.7, 11.5 Hz, 4H), 8.98 (d, J = 4.7 Hz, 2H), 9.49 (d, J = 5.1 Hz, 2H); MALDI-MS (POPOP) obsd 643.6 [(M − SeAc)$^+$]; FAB-MS obsd 765.1105, calcd 765.1111 ($C_{43}H_{32}N_4OSeZn$); λ_{abs} 429, 557, 597 nm.

***S*-Acetylthioacetaldehyde Diethylacetal (3b).** Following a procedure with slight modification,[3] KSAc (2.56 g, 22.4 mmol) was added to a solution of bromoacetaldehyde diethylacetal (2.95 g, 15.0 mmol) in acetone (50 mL). The mixture was refluxed, yielding a precipitate after a few minutes. After 24 h, the reaction mixture was cooled and filtered. Concentration of the filtrate gave a tan liquid. Chromatography [silica, hexanes/ethyl acetate (95:5)] gave a colorless liquid (2.27 g, 79%): ^{1}H NMR δ 1.21 (t, J = 7.0 Hz, 6H), 2.35 (s, 3H), 3.11 (d, J = 5.5 Hz, 2H), 3.55−3.67 (m, 4H), 4.50 (t, J = 5.4 Hz, 1H); ^{13}C NMR δ 15.1, 30.4, 32.2, 62.3, 101.1, 195.4. Anal. Calcd for $C_8H_{16}O_3S$: C, 49.97; H, 8.39; S, 16.68. Found: C, 49.42; H, 8.30; S, 16.56.

5-(Hydroxymethyl)dipyrromethane (4a). Following a new procedure,[29] a solution of glycolaldehyde diethylacetal (2.70 g, 20.1 mmol) and pyrrole (139 mL, 2.00 mol) was degassed with a stream of argon for 5 min. $InCl_3$ (0.45 g, 2.0 mmol) was added and the mixture was heated at 60 °C for 2 h. The heat source was removed, and a sample of solid NaOH (0.24 g, 6.0 mmol) was added. The mixture was stirred for 30 min and then filtered. The filtrate was concentrated and excess pyrrole was removed. The resulting dark brown solid was extracted with ethyl acetate/hexanes (1:1). The ethyl acetate/hexanes extract was concentrated affording a pale yellow solid. Chromatography [silica, 6.0 × 10 cm, ethyl acetate/hexanes (1:1); (400−1000 mL)] followed by concentration of the eluted product gave a white solid (2.16 g, 61%): mp 83 °C; >99% purity by GC; ^{1}H NMR δ 1.93 (t, J = 6.3 Hz, 1H), 4.10 (d, J = 5.6 Hz, 2H), 4.26 (t, J = 5.0 Hz, 1H), 6.09 (m, 2H), 6.19 (m, 2H), 6.73 (m, 2H), 8.29 (br s, 2H); ^{13}C NMR δ 40.2, 65.8, 106.0, 108.6, 117.7, 130.5. Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 67.98; H, 6.87; N, 15.85.

5-(*S*-Acetylthiomethyl)dipyrromethane (4b). As described for **4a**, a mixture of **3b** (1.87 g, 9.73 mmol), pyrrole (67.5 mL, 0.97 mol), and $InCl_3$ (0.65 g, 2.9 mmol) was heated at 60 °C for 10 h. Workup including addition of solid NaOH (0.35 g, 8.8 mmol), recovery of excess pyrrole, extraction with ethyl acetate/hexanes (1:1), and chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a viscous liquid (1.09 g, 48% yield, >99% purity by GC): ^{1}H NMR δ 2.31 (s, 3H), 3.45 (d, J = 7.7 Hz, 2H), 4.24 (t, J = 7.5 Hz, 1H), 6.08 (m, 2H), 6.16 (m, 2H), 6.66 (m, 2H), 7.91 (br s, 2H); ^{13}C NMR δ 30.7, 33.9, 38.0, 106.2, 108.3, 117.7, 131.4, 196.4. Anal. Calcd for $C_{12}H_{14}N_2OS$: C, 61.51; H, 6.02; N, 11.96, S, 13.68. Found: C, 62.69; H, 6.03; N, 12.20; S, 12.33.

5-(*Se*-Acetylselenomethyl)dipyrromethane (4c). Following a procedure with a slight modification,[27] KOMe (0.25 g, 3.6 mmol) was added to a solution of diacetylselenide (0.62 g, 3.8 mmol) in a mixed solvent (10 mL) of anhydrous ether/hexanes (1:1) at 0 °C. The mixture was stirred for 3 h. The supernatant liquid was removed by syringe and the resulting precipitate was washed with hexanes (2 × 3 mL), affording 437 mg (72%) of KSeAc as a white solid; mp 120−130 °C dec (lit.[27] mp 110−120 °C).

A mixture of bromoacetaldehyde diethylacetal (0.41 g, 2.1 mmol) and KSeAc (437 mg, 2.71 mmol) in anhydrous DMF (3 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated. The crude product was dried under vacuum to obtain *Se*-acetylselenomethylacetaldehyde diethylacetal (**3c**) as a liquid (ca. 85% pure by ^{1}H NMR). This material was used directly in the next reaction.

As described for **4a** with modified workup, a mixture of crude **3c** (0.30 g), pyrrole (8.70 mL, 125 mmol), and $InCl_3$ (83 mg, 0.37 mmol) was heated at 60 °C for 12 h. Without adding NaOH, the mixture was filtered. The filtrate was concentrated and excess pyrrole was recovered. The resulting dark brown solid was extracted with ethyl acetate/hexanes (1:1). Concentration of the extract gave a viscous, pale yellow liquid. Chromatography [silica, ethyl acetate/hexanes (1:4)] afforded a viscous liquid (83 mg, 8% overall yield from diacetylselenide, >99% purity by GC): ^{1}H NMR δ 2.38 (s, 3H), 3.45 (d, J = 7.4 Hz, 2H), 4.28 (t, J = 7.5 Hz, 1H), 6.09 (m, 2H), 6.17 (m, 2H), 6.63 (m, 2H), 7.85 (br s, 2H); ^{13}C NMR δ 30.3, 34.6, 38.6, 105.9, 108.2, 117.4, 132.0, 197.1. Anal. Calcd for $C_{12}H_{14}N_2OSe$: C, 51.25; H, 5.02; N, 9.96. Found: C, 51.59; H, 5.21; N, 10.23.

Zn(II)-5-[4-(Hydroxymethyl)phenyl]-10,15,20-tri-*p*-tolylporphyrin (Zn-7). A sample of **11** (180 mg, 0.25 mmol) was metalated with $Zn(OAc)_2{\cdot}2H_2O$ (275 mg, 1.25 mmol) at room temperature for 24 h. The resulting crude **Zn-11** (195 mg, 0.25 mmol) in dry THF (30 mL) was treated with $LiAlH_4$ (29 mg, 0.75 mmol) under argon at room temperature for 1 h. Methanol and water were then added slowly. The mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried (Na_2SO_4), concentrated, and chromatographed ($CHCl_3$, containing 0−10% THF). The resulting product was washed with methanol, affording a purple solid (178 mg, 95%): ^{1}H NMR (THF-d_8) δ 2.69 (s, 9H), 4.44 (t, J = 6.0 Hz, 1H), 4.93 (d, J = 6.0 Hz, 2H), 7.55 (d, J = 7.8 Hz, 6H), 7.73 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 7.2 Hz, 6H), 8.14 (d, J = 7.8 Hz, 2H), 8.83 (s, 8H); LD-MS obsd 747.97; FAB-MS obsd 748.2217, calcd 748.2181 ($C_{48}H_{36}N_4OZn$); λ_{abs} 420, 549, 587 nm.

Zn(II)-5-[4-(Hydroxymethyl)phenyl]-10,15,20-tris(tridec-7-yl)porphyrin (Zn-8). A solution of **Zn-14** (90.0 mg, 85.3 μmol) in dry THF (10 mL) was treated with $LiAlH_4$ (11.0 mg, 290 μmol) at room temperature for 2 h. Methanol (5 mL) was slowly added and the mixture was filtered. The filtrate was concentrated and chromatographed [silica, $CHCl_3$/hexanes (3:1)], affording the title compound in the first major band followed by a small amount of (demetalated) free base porphyrin alcohol in a second band. The first band was concentrated, affording the title compound as a purple solid (35 mg, 80%): ^{1}H NMR δ 0.68−0.74 (m, 18H), 1.04−1.38 (m, 48H), 1.97 (br s, 1H), 2.70−2.83 (m, 6H), 2.88−3.01 (m, 6H), 5.07 (s, 2H), 5.15−5.27 (m, 3H), 7.73 (d, J = 7.6 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 8.86−8.88 (m, 2H), 9.58−9.80 (m, 6H); MALDI-MS (POPOP) obsd 1027.5, 942.7 [(M − *n*-hexyl)$^+$]; FAB-MS obsd 1024.6888, calcd 1024.6876 ($C_{66}H_{96}N_4OZn$); λ_{abs} 424, 555, 593 nm; λ_{em} (λ_{ex} = 550 nm) 611, 659 nm.

5-[4-(Methoxycarbonyl)phenyl]-10,15,20-tri-*p*-tolylporphyrin (11). Following a general procedure,[26] a sample of **9** (3.31 g, 7.00 mmol) was reduced with $NaBH_4$ (5.30 g, 140 mmol) in dry THF/methanol (154 mL, 10:1) and the resulting **9-diol** was condensed with **10** (1.96 g, 7.00 mmol) in acetonitrile (1.4 L) containing TFA (3.22 mL) at room temperature. Subsequent oxidation with DDQ (3.18 g, 14.0 mmol) and workup afforded a purple solid (798 mg, 16%): ^{1}H NMR (THF-d_8) δ −2.71 (s, 2H), 2.68 (s, 9H), 4.05 (s, 3H), 7.58 (d, J = 7.5 Hz, 6H), 8.08 (d, J = 7.2 Hz, 6H), 8.31 (d, J = 7.4 Hz, 2H), 8.43 (d, J = 9.0 Hz, 2H), 8.77 (d, J = 4.5 Hz, 2H), 8.84 (d, J = 7.5 Hz, 6H); LD-MS obsd 714.53; FAB-MS obsd 715.3069, calcd 715.3073 ($C_{49}H_{38}N_4O_2$); λ_{abs} 419, 516, 552, 591, 647 nm.

Zn(II)-5-[4-(Methoxycarbonyl)phenyl]-10,15,20-tri-*p*-tolylporphyrin (Zn-11). A solution of **11** (72 mg, 0.10 mmol) in $CHCl_3$ (30 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (110 mg, 0.50 mmol) in methanol (1 mL) at room temperature for 4 h. The mixture was washed with saturated aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$). The resulting product was washed with methanol, affording a purple solid (60 mg, 77%): ^{1}H NMR (THF-d_8) δ 2.69 (s, 9H), 4.05 (s, 3H), 7.55 (d, J = 7.5 Hz, 6H), 8.07 (d, J = 8.1 Hz, 6H), 8.30 (d, J = 8.1 Hz, 2H), 8.41 (d, J = 8.7 Hz, 2H), 8.78 (d, J = 4.5 Hz, 2H), 8.84 (s, 4H), 8.86 (d, J = 5.1 Hz, 2H); LD-MS obsd 776.0; FAB-MS obsd 776.2181, calcd 776.2130 ($C_{49}H_{36}N_4O_2Zn$); λ_{abs} 421, 549, 588 nm.

5-[4-(Methoxycarbonyl)phenyl]-10,15,20-tris(tridec-7-yl)porphyrin (14). Following a general procedure,[4] a solution of dipyrromethane **13** (100 mg, 304 μmol), aldehyde **12** (64.6 mg, 304 μmol), and methyl 4-formylbenzoate (25.0 mg, 152 μmol) in CH_2Cl_2 (15 mL) was treated with TFA (20.8 μL, 270 μmol, 17.8 mM) at room temperature for 30 min. DDQ (104 mg, 457 μmol) was added and the reaction mixture was stirred for 1 h. TEA (38.0 μL) was added. The reaction mixture was filtered through a silica pad (CH_2Cl_2) and the collected fraction was concentrated. Chromatography [silica, $CHCl_3$/hexanes (3:1)] afforded a purple solid (25 mg, 8%): ^{1}H NMR δ −2.48 (s, 2H), 0.69−0.74 (m, 18H), 1.08−1.35 (m, 48H), 2.70−2.80 (m, 6H), 2.90−2.98 (m, 6H), 4.13 (s, 3H), 5.10−5.20 (m, 3H), 8.25 (d, J = 8.4 Hz, 2H), 8.42 (d, J = 7.6 Hz, 2H), 8.69 (m, 2H), 9.46−9.68 (m, 6H); MALDI-MS (POPOP) obsd 990.8, 905.7 [(M − *n*-hexyl)$^+$]; FAB-MS obsd 990.7755, calcd 990.7690 ($C_{67}H_{98}N_4O_2$); λ_{abs} 422, 519, 555, 600 nm; λ_{em} (λ_{ex} = 550 nm) 664, 728 nm.

Zn(II)-5-[4-(Methoxycarbonyl)phenyl]-10,15,20-tris-(tridec-7-yl)porphyrin (Zn-14). A solution of **14** (50 mg, 50 μmol) in $CHCl_3$ (8 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (55.0 mg, 252 μmol) in methanol (2 mL) at room temperature for 16 h. The reaction mixture was washed with water, dried (Na_2SO_4), concentrated, and chromatographed [silica, $CHCl_3$/hexanes (3:1)], affording a purple solid (45 mg, 85%): ^{1}H NMR δ 0.69−074 (m, 18H), 1.05−1.11 (m, 48H), 2.74−2.84 (m, 6H), 2.92−3.01 (m, 6H), 4.13 (s, 3H), 5.21−5.24 (m, 3H), 8.10 (s, 2H), 8.27 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.79−8.82 (m, 2H), 9.60−9.80 (m, 4H); MALDI-MS (dithranol) obsd 1057.0, 969.6 [(M − *n*-hexyl)$^+$]; FAB-MS obsd 1052.6875, calcd 1052.6825 ($C_{67}H_{96}N_4O_2Zn$); λ_{abs} 425, 555, 593 nm; λ_{em} (λ_{ex} = 550 nm) 613, 659 nm.

5-(4-Formylphenyl)-15-[4-(hydroxymethyl)phenyl]-10,20-dimesitylporphyrin (15). A solution of porphyrin **21** (42 mg, 0.056 mmol) in CH_2Cl_2 (40 mL) under argon was treated with PCC (13 mg, 0.060 mmol). The resulting green mixture was stirred under argon at room temperature. After 3 h, the mixture was concentrated and chromatographed [silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$/ethyl acetate (2:1)]. The second band (purple) afforded a purple powder (19.2 mg, 46%): ^{1}H NMR δ −2.63 (s, 2H), 1.83 (s, 12H), 1.99 (m, 1H), 2.63 (s, 6H), 5.07 (d, J = 3.6 Hz, 2H), 7.28 (s, 4H), 7.75 (d, J = 8 Hz, 2H), 8.22 (d, J = 8 Hz, 2H), 8.27 (d, J = 8 Hz, 2H), 8.41 (d, J = 8 Hz, 2H), 8.70 (m, 6H), 8.80 (d, J = 4.8 Hz, 2H), 10.38 (s, 1H); LD-MS obsd 757.82; FAB-MS obsd 756.3492, calcd 756.3464 ($C_{52}H_{44}N_4O_2$); λ_{abs} 421, 515, 549, 593, 649 nm.

Zn(II)-5-(4-Formylphenyl)-15-[4-(hydroxymethyl)phenyl]-10,20-dimesitylporphyrin (Zn-15). A solution of porphyrin **15** (19 mg, 0.025 mmol) in $CHCl_3$ (11 mL) and methanol (2 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (450 mg, 2.05 mmol) in methanol (6 mL) for 2.5 h at room temperature. Standard workup including chromatography (silica, CH_2Cl_2) gave a purple solid (20.6 mg, quantitative): ^{1}H NMR δ 1.83 (s, 12H), 2.63 (s, 6H), 4.77 (s, 2H), 7.28 (s, 4H), 7.57 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8 Hz, 2H), 8.78 (d, J = 4.8 Hz, 2H), 8.80 (d, J = 4.4 Hz, 2H), 8.82 (d, J = 4.8 Hz, 2H), 8.86 (d, J = 4.8 Hz, 2H), 10.34 (s, 1H); LD-MS obsd 821.16; FAB-MS obsd 818.2607, calcd 818.2599 ($C_{52}H_{42}N_4O_2Zn$); λ_{abs} 424, 550, 593 nm.

5-[4-(*S*-Acetylthiomethyl)phenyl]-15-(4-formylphenyl)-10,20-dimesitylporphyrin (16). Following a standard procedure,[50] a sample of porphyrin **24** (51.4 mg, 0.057 mmol) in CH_2Cl_2 (14 mL) was treated with TFA/H_2O (1.4 mL, 1:1 v/v) at room temperature for 16 h. The solution was taken up in additional CH_2Cl_2. The organic layer was washed with 5% aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and chromatographed [silica, ether/hexanes (1:2)], affording a purple powder (41.5 mg, 89%): ^{1}H NMR δ −2.61 (s, 2H), 1.84 (s, 12H), 2.50 (s, 3H), 2.63 (s, 6H), 4.47 (s, 2H), 7.29 (s, 4H), 7.67 (d, J = 8.1 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 7.8 Hz, 2H), 8.41 (d, J = 7.6 Hz, 2H), 8.70−8.73 (m, 6H), 8.81 (d, J = 4.8 Hz, 2H), 10.38 (s, 1H); LD-MS obsd 813.50, 738.48 [(M − SAc)$^+$]; FAB-MS obsd 815.3420, calcd 815.3420 ($C_{54}H_{46}N_4O_2S$); λ_{abs} 422, 515, 550, 592 nm.

Zn(II)-5-[4-(*S*-Acetylthiomethyl)phenyl]-15-(4-formylphenyl)-10,20-dimesitylporphyrin (Zn-16). A solution of porphyrin **16** (30.7 mg, 0.0376 mmol) in $CHCl_3$ (15 mL) and methanol (6 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (825 mg, 3.76 mmol) in methanol (4 mL) at room temperature for 16 h. The mixture was taken up in ethyl acetate, washed with 5% aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and chromatographed (silica, CH_2Cl_2) to afford a purple powder (29.8 mg, 90%): ^{1}H NMR δ 1.82 (s, 12H), 2.48 (s, 3H), 2.63 (s, 6H), 4.46 (s, 2H), 7.28 (s, 4H), 7.65 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 8.26 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.77−8.82 (m, 6H), 8.89 (d, J = 4.8 Hz, 2H), 10.36 (s, 1H); LD-MS obsd 875.58, 800.81 [(M − SAc)$^+$]; FAB-MS obsd 876.2460, calcd 876.2476 ($C_{54}H_{44}N_4O_2SZn$); λ_{abs} 424, 550, 589 nm.

5-Formyl-15-(4-hydroxymethylphenyl)-10,20-dimesitylporphyrin (17). Following a standard procedure,[57] a mixture of porphyrin **28** (31 mg, 0.047 mmol), K_2CO_3 (63.3 mg, 0.458 mmol), $Pd(PPh_3)_4$ (8.4 mg, 7.2 μmol), and 4-hydroxymethylphenylboronic acid (15.6 mg, 0.103 mmol) in DMF (7.5 mL) and toluene (7.5 mL) was heated at 90 °C under argon for 21 h. Then, the reaction mixture was taken up in CH_2Cl_2, washed several times with water, dried (Na_2SO_4), and chromatographed (silica, CH_2Cl_2) to afford a purple solid (25.2 mg, 78%): ^{1}H NMR δ −1.76 (s, 2H), 1.84 (s, 12H), 2.63 (s, 6H), 5.05 (s, 2H), 7.29 (s, 4H), 7.75 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 8.56 (d, J = 4.4 Hz, 2H), 8.72 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 4.8 Hz, 2H), 9.98 (d, J = 4.8 Hz, 2H), 12.46 (s, 1H); LD-MS obsd 679.64; FAB-MS obsd 680.3159, calcd 680.3151 ($C_{46}H_{40}N_4O_2$); λ_{abs} 426, 526, 567, 599, 656 nm.

Zn(II)-5-Formyl-15-(4-hydroxymethylphenyl)-10,20-dimesitylporphyrin (Zn-17). A solution of porphyrin **17** (24 mg, 0.035 mmol) in $CHCl_3$ (10 mL) and methanol (6 mL) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (580 mg, 2.64 mmol) at room temperature for 2.5 h. Standard workup including chromatography (silica, CH_2Cl_2) gave a purple-green solid (23.5 mg, 88%): ^{1}H NMR (THF-d_8) δ 1.86 (s, 12H), 2.64 (s, 6H), 4.50 (m, 1H), 4.92 (d, J = 5.6 Hz, 2H), 7.31 (s, 4H), 7.72 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 8.52 (d, J = 4.4 Hz, 2H), 8.70 (d, J = 4.4 Hz, 2H), 8.76 (d, J = 4.4 Hz, 2H), 10.10 (d, J = 4.8 Hz, 2H), 12.53 (s, 1H); LD-MS obsd 743.88; FAB-MS obsd 742.2278, calcd 742.2286 ($C_{46}H_{38}N_4O_2Zn$); λ_{abs} 431, 562, 601 nm.

5-[4-(*S*-Acetylthiomethyl)phenyl]-15-formyl-10,20-dimesitylporphyrin (18). Following a general procedure,[2,5] a solution of porphyrin **29** (10 mg, 0.013 mmol) in acetone (1.5 mL) was treated with potassium thioacetate (22 mg, 0.19 mmol). The reaction mixture was heated to reflux and followed by TLC. After 4 h, the starting porphyrin **29** was consumed. The mixture was allowed to cool to room temperature, then CH_2Cl_2 and water were added. The organic layer was washed with 10% aqueous $NaHCO_3$ and water and dried (Na_2SO_4). Purification by chromatography (silica, CH_2Cl_2/hexanes) gave a purple solid (3.6 mg, 36%): ^{1}H NMR δ −1.80 (br s, 2H), 1.84 (s, 12H), 2.49 (s, 3H), 2.64 (s, 6H), 4.45 (s, 2H), 7.29 (s, 4H), 7.66 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 8.55 (d, J =

4.4 Hz, 2H), 8.71 (d, J = 4.4 Hz, 2H), 8.83 (d, J = 5.2 Hz, 2H), 9.97 (d, J = 4.8 Hz, 2H), 12.45 (s, 1H); LD-MS obsd 738.97, 664.05 [(M − SAc)$^+$]; FAB-MS obsd 738.3066, calcd 738.3028 ($C_{48}H_{42}N_4O_2S$); λ_{abs} 427, 525, 566, 659 nm.

Zn(II)-5-[4-(*S*-Acetylthiomethyl)phenyl]-15-formyl-10,20-dimesitylporphyrin (Zn-18). A solution of porphyrin **18** (3 mg, 0.004 mmol) in $CHCl_3$/MeOH (5 mL, 3:2) was treated with $Zn(OAc)_2 \cdot 2H_2O$ (90 mg, 0.41 mmol) at room temperature for 4 h. Standard workup including chromatography [silica, CH_2Cl_2/ethyl acetate (8:1)] gave a purple-green solid (3.2 mg, quantitative): ^{1}H NMR (THF-d_8) δ 1.85 (s, 12H), 2.44 (s, 3H), 2.62 (s, 6H), 4.46 (s, 2H), 7.31 (s, 4H), 7.66 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 7.6 Hz, 2H), 8.52 (d, J = 4.4 Hz, 2H), 8.69 (d, J = 4.4 Hz, 2H), 8.75 (d, J = 4.8 Hz, 2H), 10.10 (d, J = 4.8 Hz, 2H), 12.53 (s, 1H); LD-MS obsd 798.08, 723.20 [(M − SAc)$^+$]; FAB-MS obsd 800.2186, calcd 800.2163 ($C_{48}H_{40}N_4O_2SZn$); λ_{abs} 431, 560, 601 nm.

5,15-Dimesityl-10,20-bis[4-(methoxycarbonyl)phenyl]-porphyrin (20). Following a standard procedure,[46] a solution of **19** (203 mg, 0.769 mmol) and methyl 4-formylbenzoate (126 mg, 0.768 mmol) in CH_2Cl_2 (76 mL) was treated with TFA (150 μL, 1.95 mmol) at room temperature. After 40 min, DDQ (262 mg, 1.15 mmol) was added. After 60 min, TEA (150 μL) was added. The reaction mixture was concentrated and chromatographed [silica, CH_2Cl_2/hexanes (1:1)], affording a purple powder (76.9 mg, 25%): ^{1}H NMR δ −2.64 (s, 2H), 1.83 (s, 12H), 2.63 (s, 6H), 4.11 (s, 6H), 7.28 (s, 4H), 8.31 (d, J = 8.0 Hz, 4H), 8.43 (d, J = 8.0 Hz, 4H), 8.71 (d, J = 4.8 Hz, 4H), 8.74 (d, J = 5.2 Hz, 4H); LD-MS obsd 813.84; FAB-MS obsd 815.3599, calcd 815.3597 ($C_{54}H_{46}N_4O_4$); λ_{abs} 421, 515, 548, 593, 649 nm.

5,15-Bis[4-(hydroxymethyl)phenyl]-10,20-dimesitylporphyrin (21). A solution of porphyrin **20** (76 mg, 0.093 mmol) in dry THF (20 mL) was treated with $LiAlH_4$ (28 mg, 0.74 mmol) at room temperature under argon. The progress of the reaction was monitored by TLC and LD-MS. After 1 h, methanol was added slowly. The reaction mixture was filtered and the filtrate was concentrated. Purification by chromatography [silica, CH_2Cl_2 → CH_2Cl_2/ethyl acetate (2:1)] afforded a dark purple powder (61.5 mg, 87%): ^{1}H NMR δ −2.61 (s, 2H), 1.84 (s, 12H), 2.00 (m, 2H), 2.63 (s, 6H), 5.06 (s, 4H), 7.28 (s, 4H), 7.74 (d, J = 8.0 Hz, 4H), 8.22 (d, J = 8.0 Hz, 4H), 8.69 (d, J = 4.4 Hz, 4H), 8.80 (d, J = 4.4 Hz, 4H); LD-MS obsd 757.67; FAB-MS obsd 758.3666, calcd 758.3621 ($C_{52}H_{46}N_4O_2$); λ_{abs} 420, 515, 548, 592, 650 nm.

5-[4-(*S*-Acetylthiomethyl)phenyl]-10,20-dimesityl-15-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]porphyrin (24). Following a general procedure,[4] a solution of aldehyde **22** (113 mg, 0.513 mmol), aldehyde **23** (99 mg, 0.51 mmol), and 5-mesityldipyrromethane (**19**) (270 mg, 1.02 mmol) in CH_2Cl_2 (100 mL) was treated with TFA (140 μL, 1.82 mmol) at room temperature for 30 min. DDQ (348 mg, 1.53 mmol) was added. After 90 min, TEA (150 μL) was added. The reaction mixture was filtered through a short silica column (CH_2Cl_2). The resulting mixture of three porphyrins was concentrated, dissolved in toluene, and chromatographed (silica, toluene). The second purple band was isolated and precipitated (CH_2Cl_2/MeOH) to give a purple powder (51.4 mg, 11%): ^{1}H NMR δ −2.65 (s, 2H), 0.92 (s, 3H), 1.46 (s, 3H), 1.83 (s, 12H), 2.50 (s, 3H), 2.63 (s, 6H), 3.86 (d, J = 10.8 Hz, 2H), 3.97 (d, J = 10.5 Hz, 2H), 4.47 (s, 2H), 5.75 (s, 1H), 7.28 (s, 4H), 7.66 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 8.15 (d, J = 8.1 Hz, 2H), 8.24 (d, J = 7.8 Hz, 2H), 8.65−8.69 (m, 4H), 8.79 (d, J = 5.1 Hz, 4H); LD-MS obsd 900.59, 825.51 [(M − SAc)$^+$]; FAB-MS obsd 900.4100, calcd 900.4073 ($C_{59}H_{56}N_4O_3S$); λ_{abs} 420, 515, 548, 593 nm.

Cu(II)-5,15-Dimesitylporphyrin (Cu-25). A solution of porphyrin **25** (365 mg, 0.668 mmol) in $CHCl_3$/methanol (2:1 v/v, 60 mL) was treated with $Cu(OAc)_2 \cdot H_2O$ (2.08 g, 10.4 mmol) at room temperature for 2.5 h. Standard workup including chromatography (silica, CH_2Cl_2) gave a red-purple powder (406 mg, quantitative): LD-MS obsd 607.92; FAB-MS obsd 607.1942, calcd 607.1923 ($C_{38}H_{32}CuN_4$); λ_{abs} 406, 530, 564 nm.

Cu(II)-5-Formyl-10,20-dimesitylporphyrin (Cu-26). Following a standard procedure,[52] a solution of porphyrin **Cu-25** (333 mg, 0.547 mmol) in 1,2-dichloroethane (130 mL) was added dropwise to the Vilsmeier reagent (freshly prepared at 0 °C from 3.2 mL of anhydrous DMF and 3.8 mL of $POCl_3$) and the mixture was then heated at 60 °C. After 2 h, TLC analysis indicated the absence of any starting porphyrin **Cu-25**. A solution of saturated aqueous NaOAc (60 mL) was added dropwise and the mixture was heated for another 90 min. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The organic layers were combined, washed with water, dried (Na_2SO_4), and concentrated. Purification by chromatography (silica, CH_2Cl_2/hexanes) afforded a purple powder (291 mg, 84%): LD-MS obsd 635.45; FAB-MS obsd 635.1885, calcd 635.1872 ($C_{39}H_{32}CuN_4O$); λ_{abs} 420, 548, 589 nm.

5-Formyl-10,20-dimesitylporphyrin (26). Following a standard procedure,[52] a solution of porphyrin **Cu-26** (287 mg, 0.451 mmol) in TFA (25 mL) was treated with concentrated H_2SO_4 (10 mL) and stirred at room temperature. After 90 min, an aliquot of the solution was removed and treated with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. TLC analysis revealed that the copper complex was consumed. The reaction mixture was worked up with saturated aqueous $NaHCO_3$ and CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2) to give a purple powder (232 mg, 89%): ^{1}H NMR δ −2.24 (s, 2H), 1.86 (s, 12H), 2.68 (s, 6H), 7.34 (s, 4H), 8.74 (d, J = 4.4 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.23 (d, J = 4.4 Hz, 2H), 10.06 (br s, 2H), 10.17 (s, 1H), 12.57 (s, 1H); LD-MS obsd 574.38; FAB-MS obsd 574.2740, calcd 574.2733 ($C_{39}H_{34}N_4O$); λ_{abs} 423, 520, 559, 597, 652 nm.

5,15-Dimesityl-10-(5,5-dimethyl-1,3-dioxan-2-yl)porphyrin (27). Following a literature procedure,[49] a mixture of porphyrin **26** (168 mg, 0.292 mmol), neopentyl glycol (36.5 mg, 0.350 mmol), and *p*-toluenesulfonic acid monohydrate (5.5 mg, 0.029 mmol) in benzene (50 mL) was heated to reflux. After 4 h, TLC analysis showed almost no starting material. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, and washed with 10% aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (alumina, CH_2Cl_2/hexanes) to afford a purple solid (174 mg, 90%): ^{1}H NMR δ −3.02 (s, 2H), 1.13 (s, 3H), 1.85 (s, 12H), 1.94 (s, 3H), 2.68 (s, 6H), 4.34 (d, J = 11.2 Hz, 2H), 4.38 (d, J = 11.6 Hz, 2H), 7.34 (s, 4H), 8.03 (s, 1H), 8.83 (d, J = 4.4 Hz, 2H), 8.91 (d, J = 4.4 Hz, 2H), 9.28 (d, J = 4.4 Hz, 2H), 9.98 (br s, 2H), 10.17 (s, 1H); LD-MS obsd 660.53, 574.42 [(M − $C_5H_{10}O$)$^+$]; FAB-MS obsd 660.3499, calcd 660.3464 ($C_{44}H_{44}N_4O_2$); λ_{abs} 414, 507, 583, 636 nm.

5-Bromo-15-formyl-10,20-dimesitylporphyrin (28). Following a standard procedure,[54] a solution of **27** (140 mg, 212 μmol) in $CHCl_3$ (47 mL) was cooled in an ice bath and treated with pyridine (190 μL) and NBS (38.0 mg, 213 μmol). After 15 min, the reaction was quenched by acetone (10 mL) and the solvent was evaporated. TLC analysis [CH_2Cl_2/hexanes (1:1)] of the resulting crude mixture exhibited the formation of a brominated product and a small amount of porphyrin **28**. The crude mixture was dissolved in CH_2Cl_2 (53 mL) and the solution was treated with a solution of TFA/water (5.3 mL, 1:1) at room temperature. After 16 h, the organic phase was separated, washed with 5% aqueous $NaHCO_3$ and water, and concentrated to dryness. Chromatography [silica, CH_2Cl_2/hexanes (1:1)] followed by trituration of the resulting solid in methanol gave a purple solid (75 mg, 54%): ^{1}H NMR δ −1.78 (s, 2H), 1.85 (s, 12H), 2.66 (s, 6H), 7.31 (s, 4H), 8.62 (d, J = 4.8 Hz, 2H), 8.82 (d, J = 5.2 Hz, 2H), 9.52 (d, J = 4.4 Hz, 2H), 9.94 (d, J = 4.4 Hz, 2H), 12.43 (s, 1H); LD-MS obsd 653.4; FAB-MS obsd 652.1857, calcd 652.1838 ($C_{39}H_{33}BrN_4O$); λ_{abs} 426, 529, 569, 604, 663 nm.

5-(4-Bromomethylphenyl)-15-formyl-10,20-dimesitylporphyrin (29). Following a general procedure,[58] a solution of porphyrin **17** (24 mg, 0.035 mmol) in anhydrous ether (10 mL) at 0 °C under argon was treated dropwise with PBr_3 (30 μL,

0.32 mmol). The purple solution immediately became green and then a precipitate appeared. The mixture was stirred at room temperature for 1 h. Then CH_2Cl_2 was added to give a green solution, which was washed with saturated aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and chromatographed (silica, CH_2Cl_2/hexanes), affording a purple solid (15.3 mg, 58%): ^{1}H NMR δ −1.81 (br s, 2H), 1.84 (s, 12H), 2.64 (s, 6H), 4.83 (s, 2H), 7.29 (s, 4H), 7.77 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 7.6 Hz, 2H), 8.56 (d, J = 4.4 Hz, 2H), 8.71 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 5.2 Hz, 2H), 9.97 (d, J = 4.4 Hz, 2H), 12.46 (s, 1H); LD-MS obsd 741.80, 660.17 [$(M - Br)^+$]; FAB-MS obsd 742.2335, calcd 742.2307 ($C_{46}H_{39}BrN_4O$); λ_{abs} 427, 526, 566, 658 nm.

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Supporting Information Available: General experimental section and characterization data for new compounds, including ^{1}H NMR and ^{13}C NMR spectra for all new nonporphyrin compounds, and ^{1}H NMR spectra and LD-MS or MALDI-MS spectra for all new porphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

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