Synthesis and Film-Forming Properties of Ethynylporphyrins

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Thermal treatment of ethynyl porphyrin monomers on a surface has been found to yield robust porphyrin films. The scope of this in situ polymerization has been surveyed by the synthesis and characterization of a collection of 20 zinc porphyrins bearing diverse patterns of 1−4 ethyne (or protected ethyne) groups and a variety of nonlinking substituents. Films have been prepared on Si(100), SiO_2, Au(111), and glass. The films prepared on Si(100) have been examined by electrochemical methods, which indicate that surface coverages 50-fold greater than those of saturation-coverage monolayers are achievable, although the coverage varies appreciably (10-fold) among the survey group of molecules under a controlled set of film-forming conditions. Variation in these conditions affords control over the number of layers in the film (from a few to tens or more). The electrochemical characteristics of the multilayer films further indicate that the redox thermodynamics are of comparable homogeneity to those of monolayers. Examination of the films by FTIR and resonance Raman spectroscopy indicates the absence of an ethynyl or ethenyl linkage between the porphyrins. SEM analysis indicates the porphyrin polymer films range in thickness from tens to hundreds of nanometers. The in situ polymerization technique not only enables control over the thickness of the porphyrin polymer film but also sidesteps solubility problems that typically result upon solution polymerization. The ability to access the porphyrins in the films electrochemically to form porphyrin cation radicals affords increased surface charge density versus that with a monolayer, suggesting the application of the porphyrin films as materials for electrically addressable, molecular-based information storage.

Introduction

A longstanding challenge in the semiconductor industry has been to place an increasing number of functional devices in a chip. In dynamic random access memory (DRAM) chips, each memory cell contains a capacitor wherein the presence or absence of charge denotes the state of a bit (1 or 0). Approximately 200 000 electrons are stored per individual capacitor. The physical architecture of the capacitor typically is a vertical stack or trench containing a dielectric charge-storage material. The motivation for the stack and trench designs is to preserve critical real estate in the two-dimensional area of the chip, thereby achieving high memory density while accommodating the requisite charge storage in the dielectric material. The minimum feature size of production capacitors is ∼0.11 μm, which requires a vertical dimension in the several micrometer regime, giving aspect ratios of up to 100. The fabrication of such capacitors poses serious challenges. Indeed, next-generation devices having even greater memory density will require capacitors with larger aspect ratios or use of materials with higher charge-storage densities.[1]

Over the past few years, our laboratories have been engaged in a program to develop molecular materials for use as capacitors in information storage applications.[2] The molecular materials consist of redox-active molecules attached to an electroactive surface. The approach is inherently hybrid in design wherein standard semiconductor lithography is used to construct the circuitry and a collection of the redox-active molecules is used in lieu of the semiconductor charge-storage material. We have employed a variety of porphyrinic architectures for use as the redox-active molecules.[3−11] The

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porphyrins afford stable cationic redox states and participate in facile electron-transfer reactions. We have focused primarily on porphyrin monolayers attached to electroactive surfaces, though a number of efforts were aimed at building superstructures containing two,[5,6] three,[5] or an oligomeric array[12] of porphyrinic compounds for subsequent attachment to the surface.

Recently, we have developed two new methods for covalent attachment of porphyrins to silicon surfaces.[13a] In one method, deposition of a dilute solution of porphyrin (10 μM to 3 mM) onto a Si(100) surface and baking at 400 °C for 2 min (under inert atmosphere) results in the formation of porphyrin monolayers. A second method, which uses no solvent and involves direct sublimation of the porphyrin solid onto a heated Si(100) surface, also produces well-behaved porphyrin SAMs. Both the baking and sublimation procedures are attractive for preparing porphyrinic monolayers on Si(100) surfaces.[13a]

Application of the baking and sublimation procedures was found to be successful with porphyrins bearing diverse linkers, including ethynyl, vinyl, allyl, formyl, hydroxyl, acetylthio, acetylseleno, bromomethyl, bromo, and iodo groups.[13a] The all-carbon containing linkers afforded attachment via carbosilane linkages. We have recently reported FTIR studies of a number of carbon-anchored porphyrins that probe the adsorption geometry on the silicon surface.[13b] Upon examining a porphyrin bearing two ethynes, a polymeric film resulted that contained intact porphyrin macrocycles. This novel polymerization technique is of potential value for achieving increased charge density in a given footprint on the surface if porphyrins in the polymer can be accessed electrically. Although a wide variety of backbone,[12,14] pendant,[15] and two-dimensional polymers[16] containing porphyrins have been prepared, a chief challenge in preparing porphyrin polymers lies in obtaining a soluble, processable material suitable for characterization and application. The polymerization method that we discovered and describe herein sidesteps the solubility problems by achieving growth of the polymer on the electroactive surface.

In this paper, we describe our work to explore the scope of the polymerization approach. We first report the synthesis of a collection of porphyrins bearing two or more ethynyl groups in different patterns and with various nonlinking meso substituents. We then describe an investigation of the various polymeric films including characterization of the redox properties. Finally, we report studies aimed at identifying the composition of the linkers joining the porphyrins in the films. Collectively, this work defines an approach for preparing surface-bound porphyrin polymers for use in a variety of applications that rely on redox activity and electrical interrogation of the porphyrins.

Results and Discussion

Molecular Design. The porphyrins to be examined for exploring the scope of the surface-mediated polymerization process are shown in Charts 1−7.

• Chart 1 shows seven *trans*-A_2B_2 porphyrins bearing two ethynylphenyl moieties. All porphyrins are zinc chelates, except **Co-1**, which is a cobalt chelate. A cobalt porphyrin provides one additional cationic state compared with that of a zinc porphyrin. Porphyrins **Zn-2**-**Zn-4** differ in the steric bulk of the nonlinking meso substituents, which alters the facial encumbrance of the macrocycles. Porphyrin **Zn-4** employs a TMS-protected ethynyl group. Porphyrin **Zn-5** is electron-deficient owing to the presence of the two pentafluorophenyl groups. **Zn-6** is a derivative of **Zn-5** lacking the displaceable *p*-fluoro atom.

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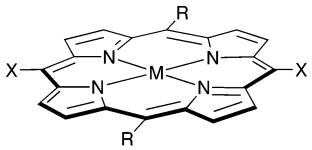
Chart 1



(M = Zn unless noted otherwise)

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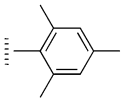
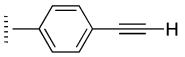
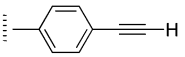
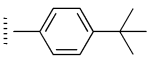
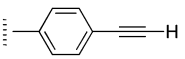
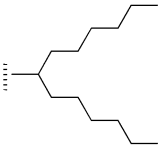
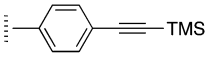
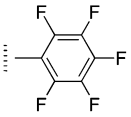
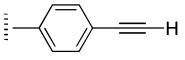
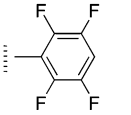
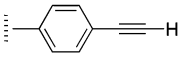
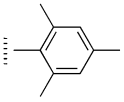
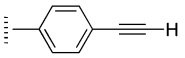
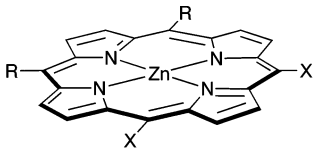
		**Zn-1**
		**Zn-2**
		**Zn-3**
		**Zn-4**
		**Zn-5**
		**Zn-6**
		**Co-1** (M = Co)

Chart 2



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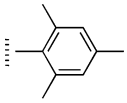
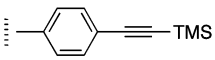
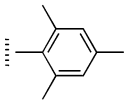
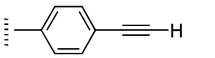
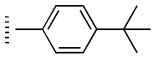
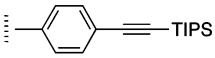
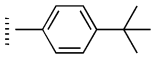
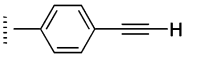
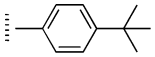
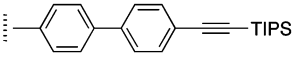
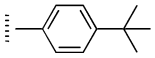
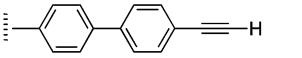
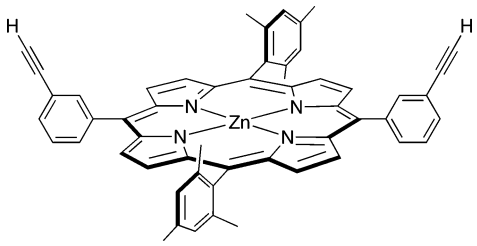
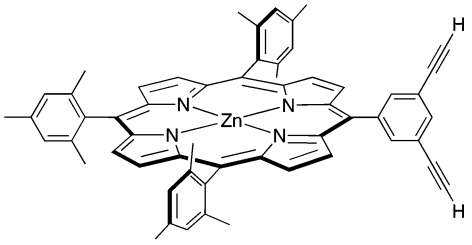
		**Zn-7**
		**Zn-8**
		**Zn-9**
		**Zn-10**
		**Zn-11**
		**Zn-12**

Chart 3



Zn-13



Zn-14

• Chart 2 shows six *cis*-A_2B_2-porphyrins containing either a protected ethynyl group (**Zn-7**, **Zn-9**, and **Zn-11**) or a free ethynyl group (**Zn-8**, **Zn-10**, and **Zn-12)**. Porphyrin **Zn-11** and **Zn-12** contain biphenyl groups to provide a longer distance between the macrocycles, and thereby potentially achieve a more porous film. Similarly, **Zn-7** and **Zn-9** differ in the degree of facial encumbrance.

• Chart 3 displays a *trans*-A_2B_2-porphyrin (**Zn-13**) and an A_3B-porphyrin (**Zn-14**), each bearing two ethynyl groups at the *m*-positions rather than the *p*-position of the phenyl group for comparative studies of film formation.

• Chart 4 exhibits an A_3B-porphyrin having three ethynyl groups (**Zn-15**).

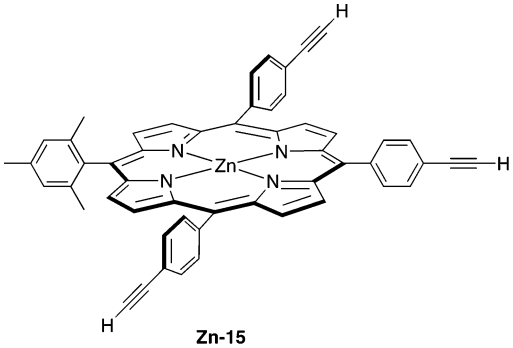
• Chart 5 shows an A_4-porphyrin bearing four ethynyl substituents (**Zn-16**).

• Chart 6 illustrates porphyrins having ethynyl and iodo groups (**Zn-17** and **Zn-19**) and those bearing two iodo groups (**Zn-18** and **Zn-20**) for attempting Sonogashira-type reactions. The two functional groups are positioned in either cis- (**Zn-19** and **Zn-20**) or trans-configurations (**Zn-17** and **Zn-18**).

• Chart 7 contains A_3B-porphyrins, each bearing a single surface attachment group, to be used as benchmarks for preparing porphyrin monolayers. The porphyrins include **Zn-21**, which bears one ethynyl group; **Zn-22**, which bears a $^{13}C_2$-labeled ethynyl moiety for investigation of the fate of the alkyne upon thermal reaction; and two porphyrins (**Zn-23** and **Zn-24**) that each bear a single hydroxymethyl group, which provides a means of attachment to the surface that is complementary to the ethyne.

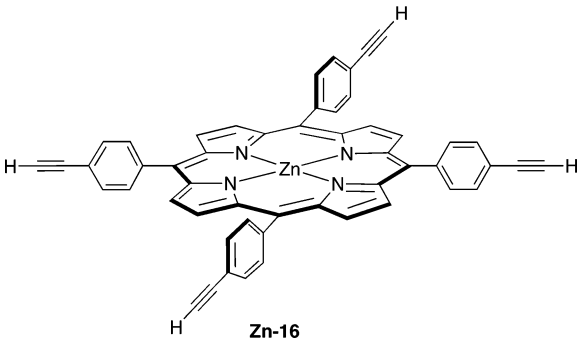
Synthesis of Porphyrin Monomers. A number of the porphyrins displayed in Charts 1−7 have been prepared previously including **Zn-1**,[17] **Zn-2**,[18] **Zn-3**,[18] **Zn-4**,[19] **Zn-7**,[20] **Zn-8**,[20] **Zn-14**,[21] **Zn-16**,[22] **Zn-18**,[23] **Zn-20**,[20] **Zn-21**,[24]

Chart 4



Zn-15

Chart 5



Zn-16

and **Zn-23**.[25] Some porphyrin precursors, including free base analogues, were synthesized earlier, including **1**,[17] **5**,[26] **9**,[27] **13**,[28] **15**,[29] **16**,[29] **18**,[30] **28**,[27] **31**,[27] **Zn-32**,[30] **35**,[31] **40**,[32] and **Zn40**.[32] Some of the previous syntheses employed statistical methods or high-temperature conditions. The syntheses described herein generally make use of mild rational methods

(17) Li, J.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927−8940.

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(21) Tomizaki, K.-Y.; Loewe, R. S.; Kirmaier, C.; Schwartz, J. K.; Retsek, J. L.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem*. **2002**, *67*, 6519−6534.

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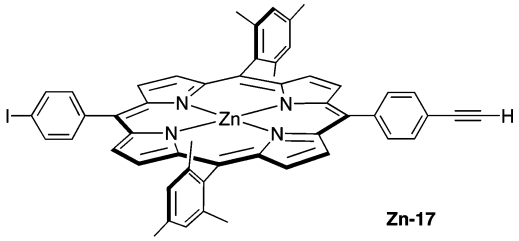
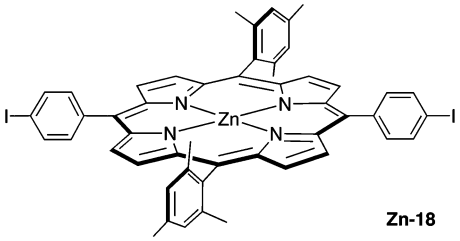
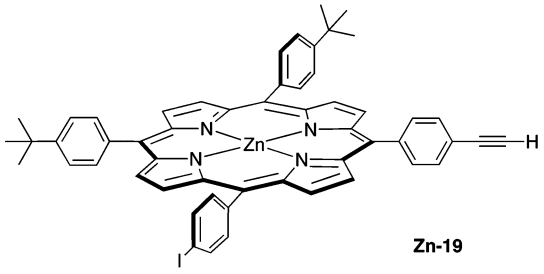
Chart 6



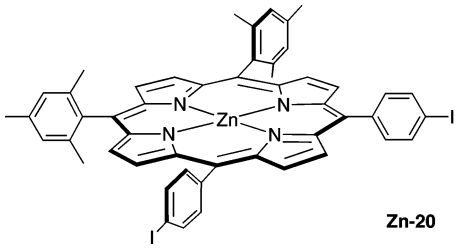
Zn-17



Zn-18

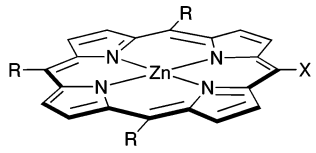


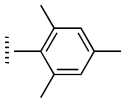
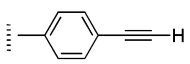
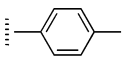
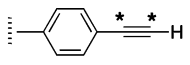
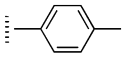
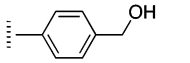
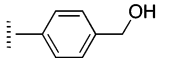
Zn-19



Zn-20

Chart 7

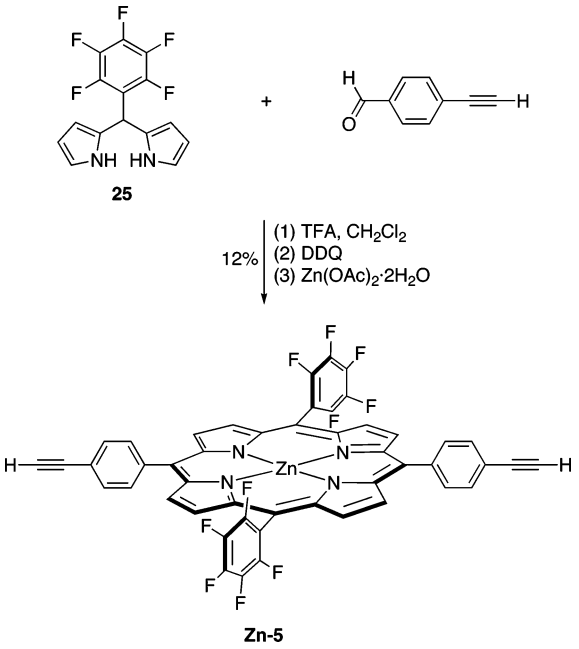


R	X	Compound
		**Zn-21**
		**Zn-22**
		**Zn-23**
		**Zn-24**

that have been developed over the past few years for preparing porphyrins bearing up to four different meso substituents.

The synthesis of the *trans*-diethynyl porphyrin **Zn-5** is shown in Scheme 1. Dipyrromethane **25**[33] was reacted with 4-ethynylbenzaldehyde in CH_2Cl_2 containing trifluoroacetic

Scheme 1



acid (TFA) under conditions[34] that afford minimal scrambling. Subsequent oxidation by DDQ and zinc insertion led to **Zn-5** in 12% yield.

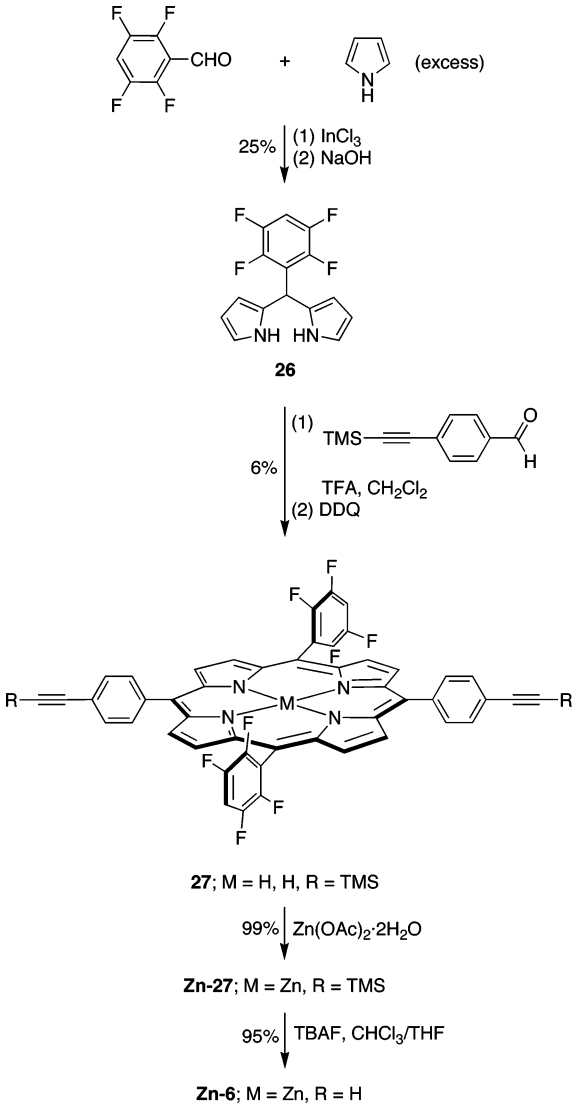
The synthesis of an analogous porphyrin bearing tetrafluorophenyl rather than pentafluorophenyl substituents is shown in Scheme 2. The rationale for the design of this porphyrin lies in the fact that the *p*-fluoro substituent of the pentafluorophenyl group is susceptible to nucleophilic substitution.[35] The reaction of 2,3,5,6-tetrafluorobenzaldehyde and pyrrole under refined conditions for dipyrromethane formation[33] (catalysis with $InCl_3$; chromatography-free workup) afforded the corresponding dipyrromethane **26** in 25% yield. Condensation of **26** and 4-(trimethylsilylethynyl)benzaldehyde in CH_2Cl_2 containing TFA[34] followed by oxidation with DDQ gave free base porphyrin **27** in 6% yield. Zinc insertion followed by cleavage of the TMS groups using tetrabutylammonium fluoride (TBAF) afforded **Zn-6** quantitatively.

Scheme 3 illustrates the metalation of porphyrins with an appropriate metal acetate. Treatment of porphyrin **1**[17] with $Co(OAc)_2 \cdot 4H_2O$ gave **Co-1** in 95% yield, while reaction of porphyrin **13**[28] with $Zn(OAc)_2 \cdot 2H_2O$ gave **Zn-13** in 93% yield.

The synthesis of an iodo-ethynyl porphyrin (**Zn-19**) for examination of Sonogashira-type reactions is shown in Scheme 4. Zinc insertion of free base porphyrin **28**[27] gave **Zn-28** in 96% yield. Removal of the TMS groups using TBAF afforded **Zn-19** in 97% yield.

The preparation of ethynylbiphenyl porphyrins **Zn-9** and **Zn-10** is shown in Scheme 5. Porphyrin **9**[27] was zincated to afford **Zn-9**, which upon treatment with TBAF gave **Zn-10** in high yield.

Scheme 2



The synthesis of **Zn-11** and **Zn-12** is outlined in Scheme 6. Esterification of 4-[2-(triisopropylsilyl)ethynyl]phenylboronic acid (**29**)[36] gave compound **30** in 96% yield. The Suzuki coupling reaction[37] of **30** and **31**[27] was carried out using $Pd(PPh_3)_4$ and K_2CO_3 in the solvent system[27] toluene/DMF (2:1). An excess (6 equiv) of compound **30** was employed to drive the reaction to completion. In this manner, porphyrin **Zn-11** was prepared in 48% yield. Porphyrin **Zn-11** was treated with TBAF in THF to furnish **Zn-12** in quantitative yield. The solubility of porphyrins **Zn-9** and **Zn-11** (TIPS group intact) was very good while that of **Zn-10** and **Zn-12** (free ethyne) was only moderate in common organic solvents.

An A_3B-porphyrin bearing three ethynyl groups was prepared by mixed-aldehyde condensation[38] using $BF_3 \cdot O(Et)_2$/ethanol cocatalysis[39] (Scheme 7). The reaction of mesitaldehyde, 4-ethynylbenzaldehyde, and pyrrole afforded a

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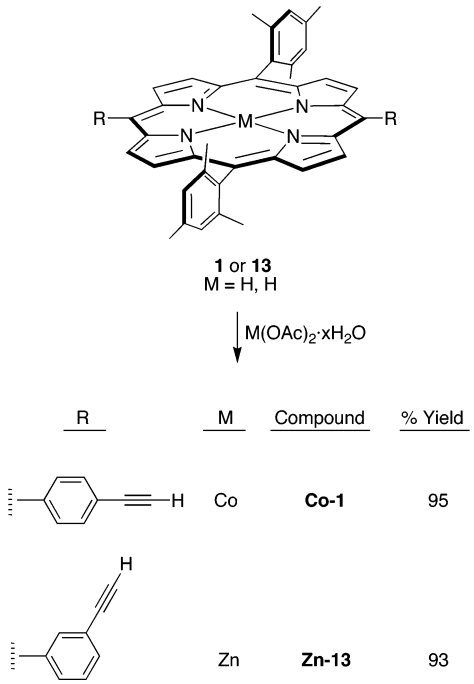
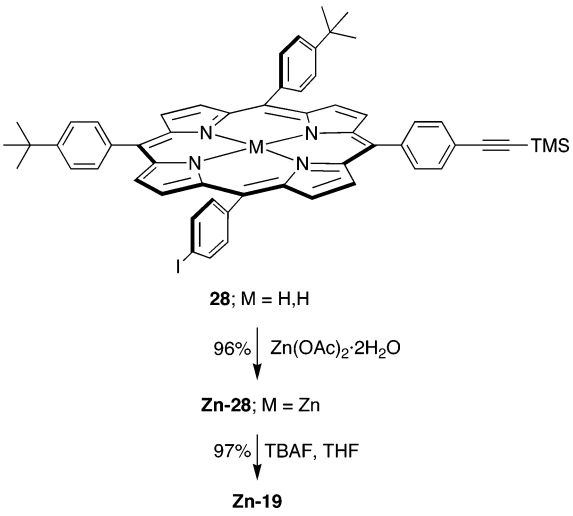
(39) Wagner, R. W.; Li, F.; Du, H.; Lindsey, J. S. *Org. Process Res. Dev.* **1999**, *3*, 28−37.

Scheme 3



Scheme 4



mixture of porphyrins, which upon chromatographic separation afforded porphyrin **Zn-15** in 10% yield.

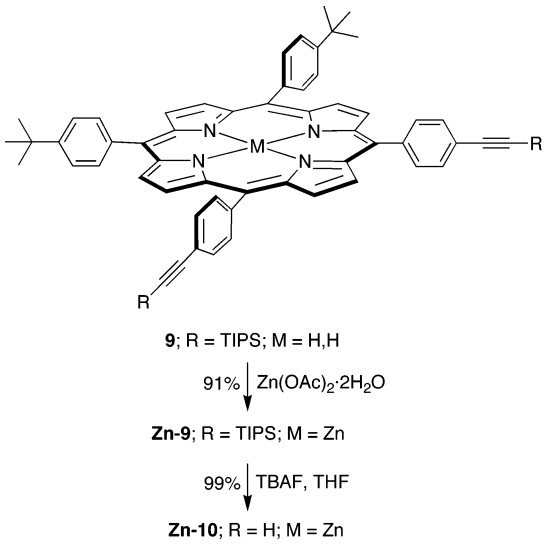
The synthesis of the A_4-porphyrin **Zn-16** was performed by condensation of pyrrole and 4-ethynylbenzaldehyde using $BF_3{\cdot}O(Et)_2$/NaCl cocatalysis[40] (Scheme 8). After oxidation with DDQ, the resulting free base porphyrin was metalated with $Zn(OAc)_2{\cdot}2H_2O$, affording **Zn-16** in 67% yield.

The removal of the TMS group of **Zn-32**[30] by treatment with TBAF gave Sonogashira-type porphyrin **Zn-17** in 89% yield (Scheme 9).

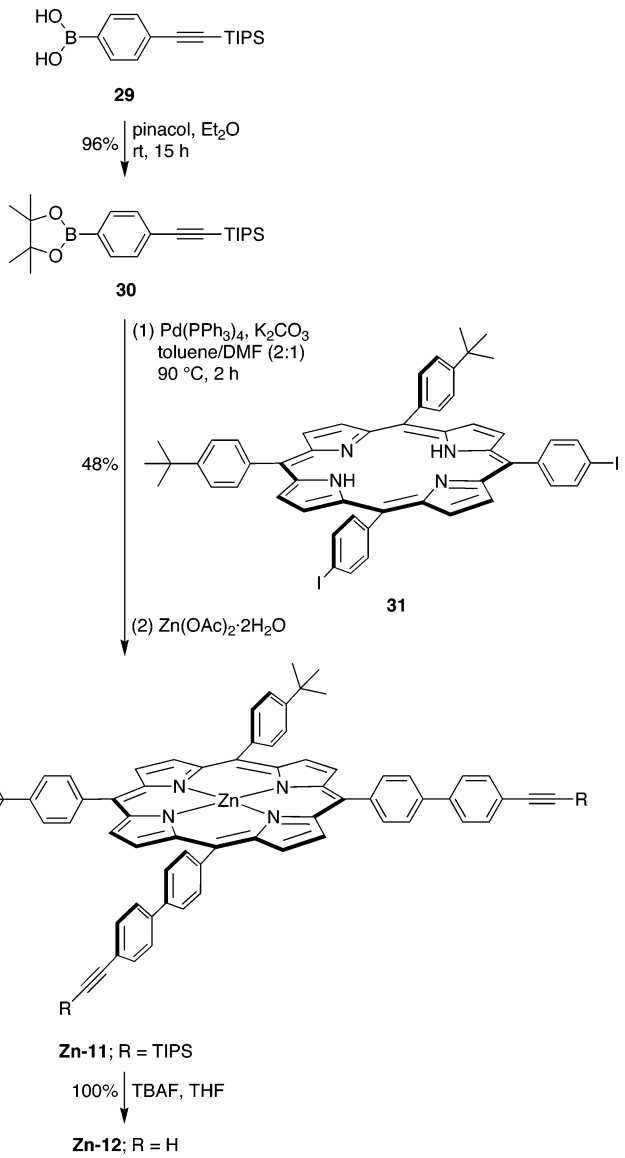
Synthesis of Porphyrins with Single Tethers. Zn-22 bears a $^{13}C_2$-labeled ethynyl moiety for investigation of the nature of the bond between the porphyrin and the surface as well as between porphyrins in model studies of film formation. The synthesis of the ^{13}C-labeled ethynyl porphyrin **Zn-22** is shown in Scheme 10. Reduction of 1,9-diacyl-

(40) Li, F.; Yang, K.; Tyhonas, J. S.; MacCrum, K. A.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 12339−12360.

Scheme 5

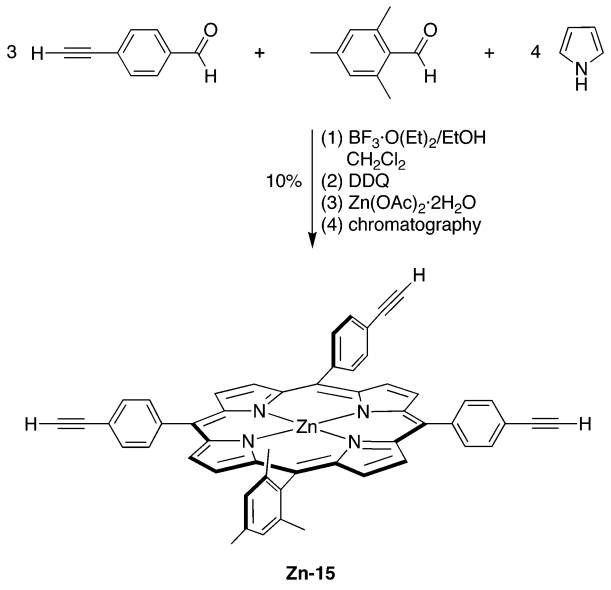


Scheme 6



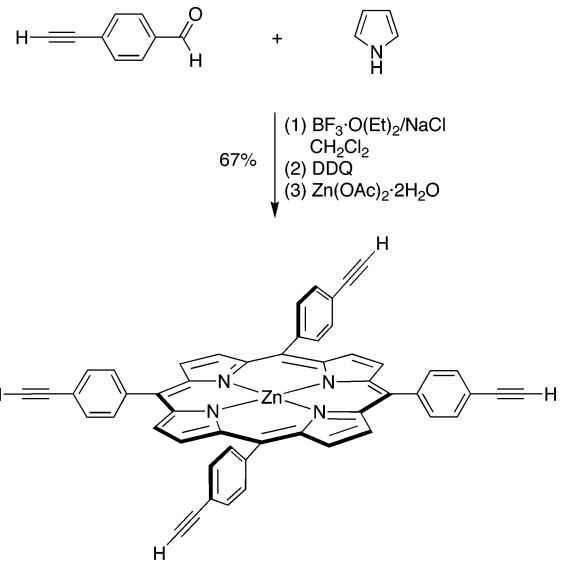
dipyrromethane **33**[41] with $NaBH_4$ afforded the corresponding dipyrromethane-dicarbinol, which was condensed with dipyrromethane **34**[26] in CH_2Cl_2 containing $Yb(OTf)_3$ under

Scheme 7



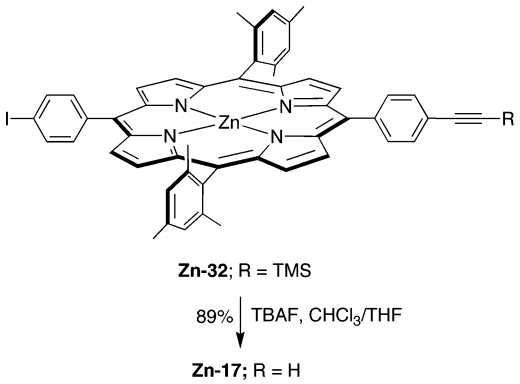
Zn-15

Scheme 8



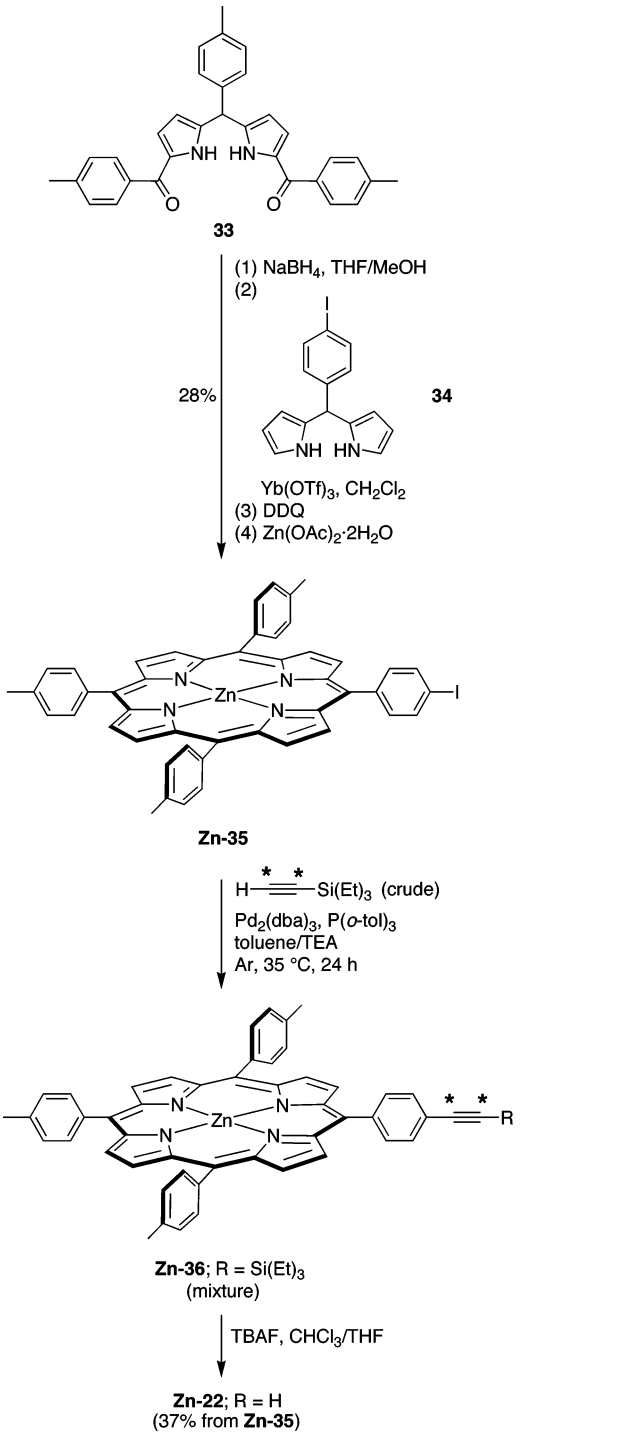
Zn-16

Scheme 9



conditions that proceed without detectable scrambling.[42] Subsequent oxidation by DDQ and zinc insertion afforded **Zn-35** in 28% yield.

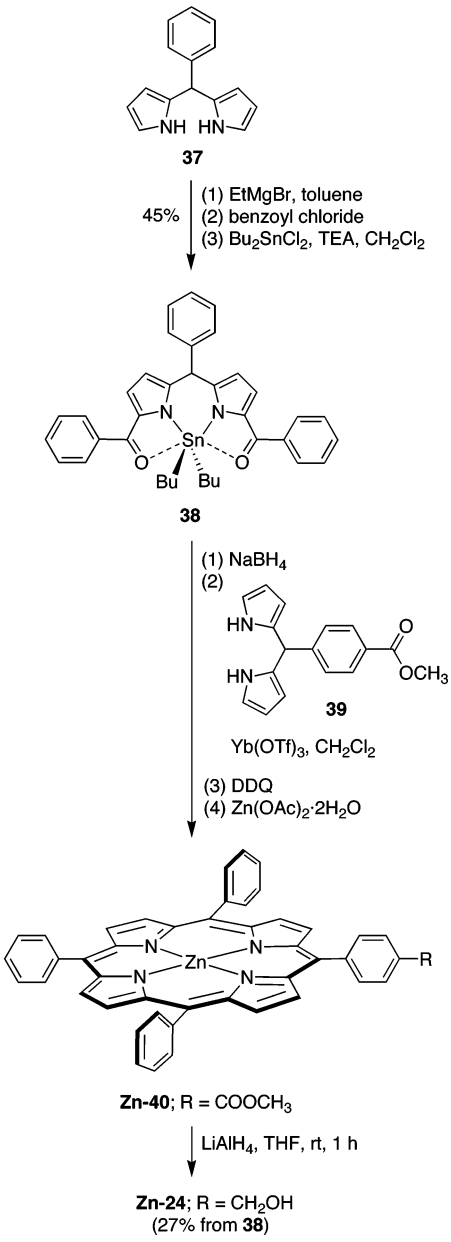
Scheme 10



According to a published procedure,[43] a solution of $^{13}C_2$-acetylene in THF was treated with EtMgBr at −78 °C and then with chlorotriethylsilane at room temperature, affording a mixture of (triethylsilyl)ethyne-[*1,2*-$^{13}C_2$] and its disilyl derivative (∼1:1 ratio by NMR analysis). Because the latter cannot undergo Sonogashira coupling, the mixture was used without purification in the coupling reaction with iodoporphyrin **Zn-35**. The reaction of **Zn-35** and (triethylsilyl)-ethyne-[*1,2*-$^{13}C_2$] was carried out under conditions used previously for Sonogashira reactions with porphyrins, which

(41) Gryko, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 2249−2252.
(42) Geier, G. R., III.; Callinan, J. B.; Rao, P. D.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810−823.
(43) Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177−1187.

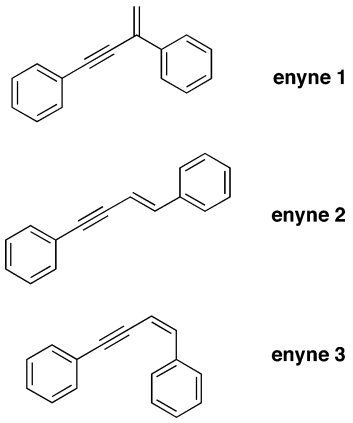
Scheme 11



employ reaction in dilute solution with catalysis by $Pd_2(dba)_3$ and P(*o*-tol)$_3$ in the absence of copper reagents.[30] **Zn-36** was obtained as a mixture with other porphyrinic byproducts having similar chromatographic retention. The crude mixture was treated with TBAF to give **Zn-22**, which was readily purified (37% overall yield from **Zn-35**). The ^{13}C NMR spectrum of **Zn-22** exhibits two enhanced doublets at δ = 79.4 ppm (J = 692.7 Hz) and 84.7 ppm (J = 690.9 Hz) owing to the presence of the two ethynyl ^{13}C atoms.

The synthesis of a porphyrin bearing a *p*-benzyl alcohol substituent is outlined in Scheme 11. Porphyrins **40** and **Zn-40** were previously prepared by a statistical route.[32] A rational approach was pursued by diacylation of dipyrromethane **37**[33] followed by tin-complexation[44] to obtain the 1,9-diacyldipyrromethane-tin complex **38** in 45% yield. Reduction by $NaBH_4$ of the latter afforded the corresponding dipyrromethane-dicarbinol, which upon reaction with dipyrromethane **39**[33] under Yb(OTf)$_3$ catalysis[42] followed by oxidation with DDQ gave porphyrin **40**. Zinc insertion of **40** gave ester-porphyrin **Zn-40**, which upon reaction with $LiAlH_4$ gave porphyrin **Zn-24** (27% overall yield from **38**).

Chart 8



Synthesis of Enyne Benchmarks. Three enyne benchmark compounds are shown in Chart 8. Each enyne is a known compound.[45,46] A synopsis of the synthesis of the three enynes is provided in the Experimental Section. The isolated enynes were stable to isomerization under ambient conditions.

Formation and Characterization of Porphyrin Films. All of the porphyrins containing multiple ethyne functionalities (Charts 1−5) were surveyed to determine the scope of polymeric film formation. Each porphyrin was subjected to an identical procedure: baking at 400 °C for 2 min after deposition (∼2 mM solution) onto a surface (see Experimental Section). These conditions were chosen because our previous studies have shown that porphyrins containing a single ethyne group undergo facile attachment to hydrogen-passivated Si(100) surfaces via a hydrosilylation process to produce monolayers at or near saturation coverage.[13a] The ability to covalently attach the porphyrins to Si permits electrochemical characterization, which provides a convenient assay of the density of the molecules on the surface (via the integrated charge in the voltammetric waves).

The electrochemical assays revealed that all of the multiply functionalized, unprotected ethynyl porphyrins (**Zn-1**-**Zn-3**, **Zn-5**, **Zn-6**, **Zn-8**, **Zn-10**, **Zn-12**, **Zn-14**-**Zn-16**, and **Co-1**) undergo thermal polymerization to produce films on the Si(100) surface, with the exception of one (**Zn-13**). A representative cyclic voltammogram of the porphyrin film formed by the *cis*-di-ethynyl-functionalized porphyrin, **Zn-8** (Chart 2), is shown in the bottom panel of Figure 1. For comparison, the voltammogram of a typical porphyrin monolayer at saturation coverage, formed from a mono-ethynyl-functionalized porphyrin, **Zn-21** (Chart 7), is shown in the top panel of the figure. The voltammograms of **Zn-8** and **Zn-21** were recorded at 1 V s^{-1} and 100 V s^{-1}, respectively. The slower scan rate was used for the film

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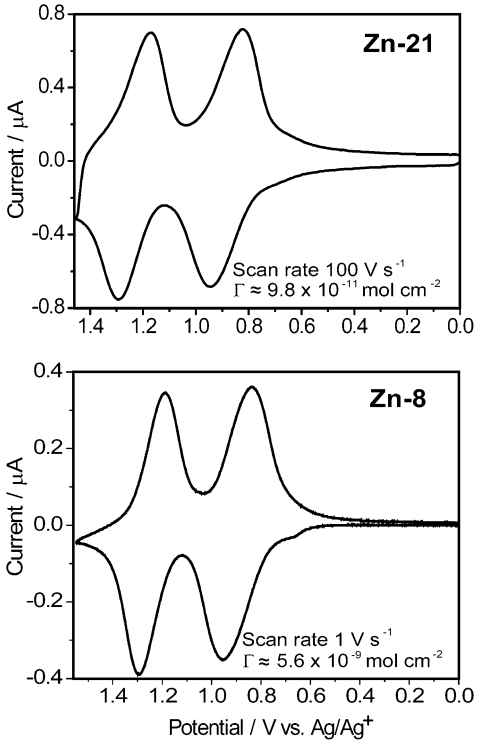

Figure 1. Representative cyclic voltammograms of the **Zn-21** monolayer (top panel) and the **Zn-8** film on a Si(100) microelectrode (bottom panel). The solvent overlayer was propylene carbonate containing 1.0 M *n*-Bu_4-PF_6 as the supporting electrolyte.

because the electron-transfer kinetics are much slower, resulting in extreme broadening at faster scan rates. The integrated current in the voltammogram of **Zn-8** gives a surface coverage, $\Gamma \sim 5.6 \times 10^{-9}$ mol cm^{-2}. This value is ~60 times larger than that of the saturation-coverage monolayer, $\Gamma \sim 9.8 \times 10^{-11}$ mol cm^{-2}. [Note that the 100-fold reduction in scan rate for **Zn-8** results in a 100-fold reduction in the integrated current.] A surface coverage of $\Gamma \sim 5.6 \times 10^{-9}$ mol cm^{-2} can only correspond to a film that grows off the surface because this surface concentration would correspond to a molecular footprint of ~3 Å^2 per molecule on a flat surface. Such a small footprint is unrealistic; the minimum footprint for porphyrins of this type in a close-packed monolayer is ~50 Å^2.[47] One surprising characteristic of the voltammetric signature of the **Zn-8** film is that the peak widths are comparable to those of the **Zn-21** monolayer, indicating that the redox thermodynamics of the porphyrins in the film are relatively homogeneous. Repeated redox cycling of the porphyrin films revealed that their stability was comparable to that of porphyrin monolayers. Under ambient conditions the films are robust for hundreds to a few thousand cycles.

The electrochemical assays of the films formed by the various porphyrins revealed that, under the conditions used for thermal polymerization, the surface coverage varied considerably among the molecules. The *cis*-diethynyl-functionalized porphyrin, **Zn-8**, and its trans analogue, **Zn-1** (Chart 1), gave the highest surface coverages ($\Gamma \sim 5.6 \times 10^{-9}$ mol cm^{-2} and $\Gamma \sim 7.5 \times 10^{-9}$ mol cm^{-2}, respectively).

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Table 1. Layer Type and Surface Coverage for the Porphyrins

molecule	layer type[a]	Γ[b] (mol/cm^2)
Zn-1	film	7.5×10^{-9}
Zn-2	film	*c*
Zn-3	film	2.1×10^{-10}
Zn-4	monolayer	7.0×10^{-11}
Zn-5	film	*c*
Zn-6	film	*c*
Zn-7	monolayer	5.3×10^{-11}
Zn-8	film	5.6×10^{-9}
Zn-9	monolayer	2.0×10^{-11}
Zn-10	film	5.0×10^{-10}
Zn-11	monolayer	2.1×10^{-11}
Zn-12	film	2.8×10^{-9}
Zn-13	monolayer	1.5×10^{-11}
Zn-14	film	9.9×10^{-10}
Zn-15	film	*c*
Zn-16	film	1.6×10^{-10}
Co-1	film	*c*

[a] Layers having surface coverages of 10^{-10} mol/cm^2 and greater are designated as films; layers of lesser surface coverage are designated as monolayers. [b] Determined via integration of the voltammetric waves. [c] Coverage could not be determined accurately owing to extreme breadth of the voltammetric waves.

The tetra-ethynyl-functionalized porphyrin, **Zn-16** (Chart 5), gave the lowest coverage ($\Gamma \sim 1.6 \times 10^{-10}$ mol cm^{-2}). The other porphyrins formed films wherein the coverage fell at various values within this range. These values are summarized in Table 1. There is no clear trend in the extent of surface coverage and the structure of the porphyrin. In addition, we did not attempt to optimize the conditions (initial solution concentration, baking temperature, or time) for any of the porphyrins. However, these features were investigated for **Zn-8**. For this porphyrin, little or no polymerization occurs at temperatures below 250 °C regardless of the baking time. As the temperature is increased for a given baking time, the extent of surface coverage monotonically increases. The surface coverage can also be controlled by the concentration of the initial deposition solution as is illustrated in Figure 2. Under the standard attachment conditions (400 °C, 2 min), deposition from solutions in the micromolar range results in very thin films of a few molecular layers, as indicated by the relatively low surface coverages. As the deposition solution concentration is increased to the millimolar regime, the films become progressively thicker.

In contrast to the unprotected ethynyl porphyrins, none of the multiply functionalized, protected ethynyl porphyrins (**Zn-4**, **Zn-7**, **Zn-9**, and **Zn-11**) formed films; these latter porphyrins, instead, formed monolayers. In this regard, we

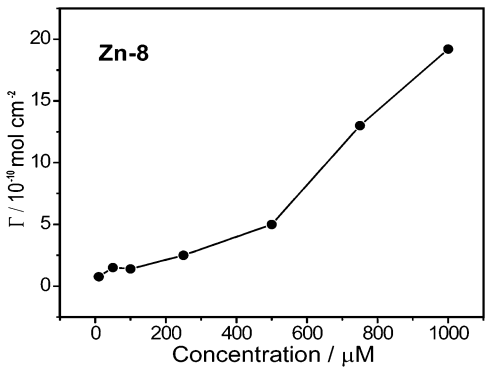

Figure 2. Effect of porphyrin concentration in the deposition solution on the surface coverage of the **Zn-8** film.

have previously shown that protected ethynyl porphyrins undergo facile attachment to Si(100) via cleavage of the protecting group.[13a] Apparently, the protecting group(s) on the other ethynyl functionalities of the surface-attached porphyrin block the reaction between these groups and protected ethynyl groups of porphyrins in the overlayer, effectively shutting off the thermal polymerization reaction that leads to film formation. The single unprotected porphyrin that does not appear to undergo polymerization, **Zn-13** (Chart 3), also exhibits a surface concentration consistent with monolayer formation. We have no explanation as to why this molecule does not form a film.

Several other series of experiments were conducted to better understand the nature of the polymerization process. In one series of experiments, we explored the possibility of thermally linking various iodo- and ethynyl-functionalized porphyrins (Chart 6) on the surface via a Sonogashira-type coupling process (without any palladium reagent). The reactant combinations for examination include self-condensation of iodo-ethynylporphyrin **Zn-17** or **Zn-19** or reaction of an admixture of a diiodo-porphyrin (**Zn-18** or **Zn-20**) and a diethynyl-porphyrin. This scheme was not successful; only monolayers formed on the surface. In another series of experiments, the substrate was altered from hydrogen-passivated Si(100) to the following: (1) Si(100) with a thick (3000 Å) thermal oxide layer, (2) Au(111), or (3) a glass slide. Film growth takes place on all of these other substrates, indicating that the polymerization is not unique to hydrogen-passivated Si(100), the only difference being that the porphyrins cannot covalently anchor to the alternative substrates, as evidenced by the fact that the porphyrins can be washed off (as an intact film), unlike the film formed on hydrogen-passivated Si(100). In a third series of experiments, a monolayer was first formed with a mono-ethynyl-functionalized porphyrin, **Zn-21**,[13a] or a mono-alcohol-functionalized porphyrin, **Zn-23** or **Zn-24** (Chart 7) as described previously.[48] The layer was then rinsed, dried, and deposited with a second solution containing a multiple-ethynyl-functionalized porphyrin, such as **Zn-8**, followed by baking (400 °C for 2 min). This two-step process resulted in formation of a **Zn-8** film overlayer on the porphyrin monolayer that is bound to the surface. Despite the fact that the film overlayer and the base monolayer have no typical sites for covalent linkage, the voltammetric characteristics of the **Zn-8** film overlayer (not shown) were similar to those of the **Zn-8** film grown in a single step (Figure 1), wherein all of the porphyrins are covalently linked to one another and the base layer is covalently bound to the surface. This observation indicates that multiple mixed layers can be readily prepared via the thermal process.

In another series of experiments, the nature of the linkage between the porphyrins in the film was investigated using FTIR and resonance Raman (RR) spectroscopy. These studies encompassed films of **Zn-8** as well as various benchmark compounds. The benchmark compounds included the three enynes shown in Chart 8 as well as a mono-ethynyl porphyrin wherein both carbon atoms in the ethynyl group are ^{13}C-labeled, **Zn-22** (Chart 7). The enynes were examined because we initially speculated that the thermal process might lead to enyne formation via linkage of the ethynyl groups of neighboring porphyrins. This type of linkage is reasonable because it is known that enynes can be formed at elevated temperatures, albeit typically in the presence of a metal reagent.[45,46,49] (Indeed, an enyne-linked porphyrin dyad derived from **Zn-21** has been prepared via palladium-mediated coupling at 100 °C.[24]) Furthermore, the process only involves a single addition reaction accompanied by a hydrogen shift, thus conserving mass. The ^{13}C-labeled compound, **Zn-22**, was prepared for comparative vibrational studies with the natural abundance partner, **Zn-21**. The goal of the experiments on these two compounds was to use the thermal process to prepare a porphyrin dyad linked via the single ethynyl groups on **Zn-21** (or **Zn-22**). We surmised that dyad formation would be the preferred reaction if the porphyrin was heated on an unreactive surface to which the ethynyl group could not covalently attach; Si(100) with the thick oxide layer was used for the experiment. We note that some dyad may also form during the process of attachment of monoethynyl-functionalized porphyrins to hydrogen-passivated Si(100); however, this material would be washed off during sample workup.

The FTIR and RR spectra of the solid **Zn-8** porphyrin prior to heating (not shown) exhibit bands typical of aryl porphyrins;[50−52] a band is also observed at 2109 cm^{-1} that is due to the C≡C stretching vibration, ν(C≡C), of the ethynyl group. Upon formation of the film from **Zn-8**, the spectral features due to the porphyrin modes do not change, whereas the ν(C≡C) mode is extremely weak and difficult to detect. This observation indicates that the thermal process does not affect the porphyrin ring, consistent with the electrochemical behavior (vide supra), whereas the ethynyl group is clearly affected. Regardless, neither the FTIR nor the RR spectra of the **Zn-8** film exhibit any new features that could be assigned to the ν(C≡C) mode of an enyne. Furthermore, no bands were observed in the region of the C═C stretching vibration, ν(C═C), that would also be expected upon enyne formation. These studies were guided by the vibrational studies on the three benchmark enynes, for all of which, both the ν(C≡C) and ν(C═C) bands are

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clearly visible in the spectra. Similar results were obtained upon heating the mono-ethynyl-functionalized porphyrin **Zn-21** (or **Zn-22**) on the unreactive oxide-covered Si(100) surface. The signature ν(C≡C) mode becomes extremely weak in the FTIR and RR spectra, but no new bands are observed that are consistent with enyne formation. Together, these results suggest that either (1) an enyne forms but the ν(C≡C) and ν(C═C) vibrations have negligible intensity or (2) the linkage between the porphyrins does not contain ethynyl or ethenyl functionalities, but rather another type of functionality. The first possibility seems unlikely given that the ν(C≡C) and ν(C═C) modes are easily detected in the vibrational spectra of the benchmark enynes. The second possibility seems more plausible for the following reasons.

(1) It is conceivable that the high temperatures necessary for film formation lead to a completely saturated linkage between the porphyrins. The detection of bands due to a new C−C single bond stretch, ν(C−C), would be difficult owing to spectral congestion in the lower frequency region. We attempted to address this issue via isotope-edited studies that compared the vibrational spectra of the films of ^{12}C versus ^{13}C ethynyl-labeled porphyrins, **Zn-21** and **Zn-22**. However, these studies also failed to reveal any new bands that could be clearly attributed to a new ν(C−C) vibration. If a fully saturated linkage forms between the porphyrins, the question that remains is what is the origin of the additional hydrogen that is required to saturate the ethynyl groups. In the case of the hydrogen-passivated Si(100), some of the hydrogen may come from the surface. However, this cannot be the case for the films formed on the unreactive surfaces, where some (or all) of the additional hydrogen would have to originate from adventitious sources that become reactive during the high-temperature film-forming process.

(2) Comprehensive studies of the pyrolysis of ethynylbenzene have shown the formation of a variety of products, dominant among which are 1-phenylnaphthalene and 2-phenylnaphthalene.[53] Diphenylenynes are likely intermediates in the reactions. No change in mass occurs upon conversion of two phenylethynes via a diphenylenyne to the phenylnaphthalene. One likely mechanistic course of reaction involves radical species. Although the pyrolysis of ethynylbenzene and the corresponding diphenylenynes was carried out at 650−1100 °C, similar reaction processes may occur at lower temperatures with porphyrins owing to the ability of the porphyrin to stabilize radical species. The ethynylaryl groups can communicate with the porphyrin via the attachment at the porphyrin meso-site. Regardless, if such reactions do occur in our lower temperature film-forming process, the products must not give any clear vibrational signature.

Finally, we obtained SEM images of the films to gain insight into the bulk material characteristics. Several cross-sectional images of films that range in thickness from a few tens to a few hundreds of nanometers are shown in Figure 3. The growth and resulting thickness of the film could be controlled to some extent (tens of nanometers) by the successive addition of aliquots of the monomer solution. However, the growth in thickness of the polymer film generally leveled off after addition of several aliquots. Taken together, the SEM images are in full accord with the results obtained from electrochemical measurements.

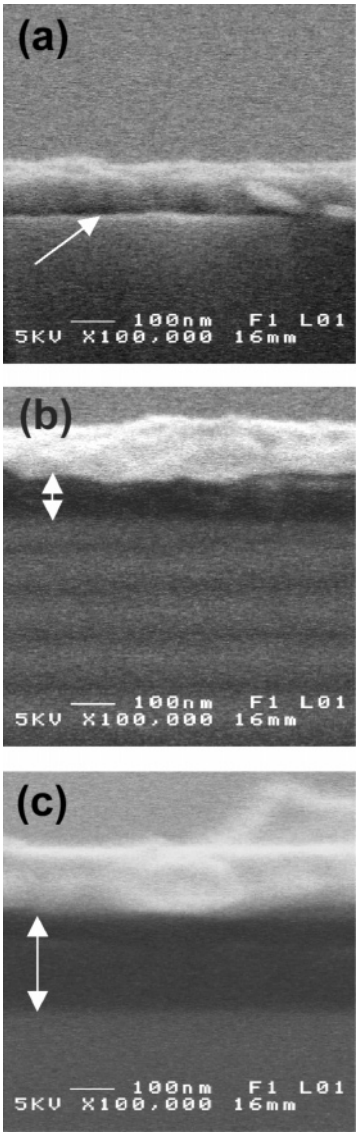

Figure 3. SEM images of films of **Zn-1**. The films were obtained by varying the number of aliquots [(a) = 1 drop, (b) = 2 drops, and (c) = 4 drops] of a ~1 mM solution of **Zn-1** in THF. Some variation in film thickness occurred due to variation in the attachment process. The arrows indicate the polymer layer thickness, which is found to range from a few tens of nanometers to several hundred nanometers.

Outlook. The ability to form porphyrin films on surfaces augurs well for a wide variety of applications in electronic materials chemistry. The porphyrins are accessible electrically, suggesting use of the porphyrin films for charge-storage purposes. The storage of an increased amount of charge in the vertical dimension (versus that available in a monolayer) is very attractive for applications as the active medium in molecular-based DRAM chips, thereby mitigating the daunting fabrication requirements of present-day trench capacitors. The fact that the electronic structure of the porphyrin is unperturbed by the film-forming process suggests a variety

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of other potential applications, ranging from solar energy to photonics. An additional intriguing feature concerns the ability to form multilayer films, suggesting the systematic construction of lamellar films of diverse composition. Finally, the success of the ethyne-based polymerization, particularly in avoiding the limitations of porphyrin solubility, should prompt investigation of a variety of reaction schemes for in situ polymerization to construct porphyrinic films.

Experimental Section

General. All ^{1}H NMR spectra (300 or 400 MHz) and ^{13}C NMR (75 MHz) were collected in $CDCl_3$ unless noted otherwise. Absorption and fluorescence spectra were collected in toluene at room temperature unless noted otherwise. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) without a matrix[54] and by high-resolution fast atom bombardment mass spectrometry (FAB-MS) using a matrix of nitrobenzyl alcohol and poly(ethylene glycol). Melting points are uncorrected. Silica gel (40 μm average particle size) was used for column chromatography. THF was freshly distilled from sodium as required. Toluene was distilled from CaH_2. $CHCl_3$ was stabilized with 0.8% ethanol. Pd-mediated coupling reactions were performed using inert atmosphere techniques on a Schlenk line.

Noncommercial Compounds. (Triethylsilyl)ethyne-[*1,2*-$^{13}C_2$],[43] porphyrins **1**,[17] **9**,[27] **13**,[28] **28**,[27] **31**,[27] **Zn-23**,[25] and **Zn-32**,[30] compound **29**,[36] and dipyrromethanes **25**,[33] **33**,[41] **34**,[26] **37**,[33] and **39**[33] were prepared as described in the literature.

5,15-Bis(4-ethynylphenyl)-10,20-dimesitylporphyrinatocobalt-(II) (Co-1). A solution of **1** (41 mg, 55 μmol) in $CHCl_3$ (20 mL) was treated with a solution of $Co(OAc)_2 \cdot 4H_2O$ (115 mg, 462 μmol) in methanol (5 mL). The mixture was heated to reflux under argon. After 12 h, the mixture was cooled and the solvent was then evaporated under reduced pressure. Column chromatography (silica, CH_2Cl_2) afforded a red solid (42 mg, 95%): ^{1}H NMR δ 3.80 (br, 12H), 4.11 (s, 6H), 4.14 (s, 2H), 9.46 (br, 4H), 9.84 (br, 4H), 12.48 (br, 4H), 15.31 (br, 4H), 15.98 (br, 4H); LD-MS obsd 804.1; FAB-MS obsd, 803.2673; calcd, 803.2585 ($C_{54}H_{40}N_4Co$); λ_{abs} (CH_2Cl_2) 412, 529 nm.

10,20-Bis(4-ethynylphenyl)-5,15-bis(pentafluorophenyl)porphinatozinc(II) (Zn-5). Following a standard procedure,[34] a solution of **25** (500 mg, 1.60 mmol) and 4-ethynylbenzaldehyde (208 mg, 1.60 mmol) in CH_2Cl_2 (160 mL) was treated with TFA (219 μL, 2.85 mmol) under argon at room temperature. After 30 min, DDQ (545 mg, 2.40 mmol) was added and the mixture was stirred for 1 h. Triethylamine (TEA, 1 mL) was then added and the reaction mixture was filtered through a silica pad (CH_2Cl_2). The porphyrin-containing fractions were combined and concentrated. The residue was dissolved in $CHCl_3$ (100 mL) and treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (350 mg, 1.60 mmol) in methanol (15 mL) at room temperature. After 2 h, the reaction mixture was concentrated and purified by column chromatography [silica, $CHCl_3$/hexanes (3:2)], affording a purple solid (88 mg, 12%): ^{1}H NMR δ 3.34 (s, 2H), 7.92 (d, J = 8.1 Hz, 4H), 8.19 (d, J = 7.5 Hz, 4H), 8.93 (d, J = 4.8 Hz, 4H), 9.10 (d, J = 4.8 Hz, 4H); LD-MS obsd, 904.6; FAB-MS obsd 904.0696, calcd 904.0663 ($C_{48}H_{18}F_{10}N_4Zn$); λ_{abs} 424, 549, 581 nm.

5,15-Bis(2,3,5,6-tetrafluorophenyl)-10,20-bis(4-ethynylphenyl)-porphyrinatozinc(II) (Zn-6). A mixture of **Zn-27** (39 mg, 38 μmol) and TBAF (57 μL, 1.5 equiv, 1.0 M in THF) in THF/$CHCl_3$ (12 mL, 1:3) was stirred at room temperature for 3 h. The reaction mixture was washed with 10% aqueous $NaHCO_3$ and water. The organic phase was dried (Na_2SO_4), filtered, concentrated and chromatographed (silica, CH_2Cl_2). Precipitation (CH_2Cl_2/hexanes) yielded a purple powder (31 mg, 95%): ^{1}H NMR δ 3.33 (s, 2H), 7.61 (tt, ^3J = 9.6 Hz, ^4J = 7.2 Hz, 2H), 7.92 (d, J = 8.3 Hz, 4H), 8.20 (d, J = 8.3 Hz, 4H), 8.94 (d, J = 4.80 Hz, 4H), 9.03 (d, J = 4.65 Hz, 4H); LD-MS obsd 867.9; FAB-MS obsd 868.0971; calcd 868.0852 ($C_{48}H_{20}N_4F_8Zn$); λ_{abs} ($CHCl_3$) 423, 553 nm.

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis[4-[2-(triisopropylsilyl)-ethynyl]phenyl]porphinatozinc(II) (Zn-9). A solution of **9** (495 mg, 455 μmol) in $CHCl_3$ (200 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (500 mg, 2.28 mmol) in methanol (20 mL) and stirred at room temperature for 2 h. Column chromatography (silica, $CHCl_3$) afforded a purple solid (478 mg, 91%): ^{1}H NMR δ 1.27 (s, 42H), 1.63 (s, 18H), 7.76 (d, J = 8.4 Hz, 4H), 7.89 (d, J = 8.4 Hz, 4H), 8.14 (d, J = 8.4 Hz, 4H), 8.17 (d, J = 8.4 Hz, 4H), 8.93−8.95 (m, 4H), 8.99−9.02 (m, 4H); LD-MS obsd, 1149.6; FAB-MS obsd 1148.5540, calcd 1148.5526 ($C_{74}H_{84}N_4Si_2Zn$); λ_{abs} 427, 511, 552, 592 nm.

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis(4-ethynylphenyl)porphinatozinc(II) (Zn-10). A solution of **Zn-9** (370 mg, 322 μmol) in THF (50 mL) was treated with TBAF (773 μL, 773 μmol, 1.0 M solution in THF) under argon at room temperature. After 1.5 h, $CHCl_3$ was added and the solution was washed with water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$), affording a magenta solid (268 mg, 99%): ^{1}H NMR δ 1.62 (s, 18H), 3.32 (s, 2H), 7.75 (d, J = 7.8 Hz, 4H), 7.89 (d, J = 7.8 Hz, 4H), 8.14 (d, J = 7.8 Hz, 4H), 8.18 (d, J = 7.8 Hz, 4H), 8.90−8.93 (m, 4H), 8.99−9.02 (m, 4H); LD-MS obsd 837.2; FAB-MS obsd 836.2924, calcd 836.2857 ($C_{56}H_{44}N_4Zn$); λ_{abs} 426, 551, 590 nm.

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis[4′-[2-(triisopropylsilyl)-ethynyl]biphen-4-yl]porphinatozinc(II) (Zn-11). Following a published procedure,[37] a Schlenk tube containing samples of **30** (471 mg, 1.23 mmol), **31** (200 mg, 204 μmol), $[Pd(PPh_3)_4]$ (70 mg, 61 μmol), and K_2CO_3 (225 mg, 1.63 mmol) was treated with toluene/DMF [30 mL, (2:1)].[2] The mixture was stirred at 90 °C for 2 h, then cooled, and passed over a silica column ($CHCl_3$). A second column [silica, $CHCl_3$/hexanes (3:2)] gave a purple solid. The solid was dissolved in $CHCl_3$ (30 mL) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (200 mg, 911 μmol) in methanol (10 mL) was added. After 15 min, the solution was concentrated and chromatographed [silica, $CHCl_3$/hexanes (1:1)], affording a purple solid (128 mg, 48%): ^{1}H NMR δ 1.21 (s, 42H), 1.62 (s, 18H), 7.71 (d, J = 8.4 Hz, 4H), 7.76 (d, J = 8.4 Hz, 4H), 7.88 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.4 Hz, 4H), 8.15 (d, J = 8.0 Hz, 4H), 8.29 (d, J = 8.0 Hz, 4H), 8.99−9.02 (m, 8H); LD-MS obsd 1301.7; FAB-MS obsd 1300.6149, calcd 1300.6152 ($C_{86}H_{92}N_4Si_2Zn$); λ_{abs} 427, 551, 592 nm.

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis(4′-ethynylbiphen-4-yl)-porphinatozinc(II) (Zn-12). A solution of **Zn-11** (106 mg, 81.3 μmol) in THF (15 mL) was treated with TBAF (195 μL, 195 μmol, 1.0 M solution in THF) under argon at room temperature. After 1 h, the solution was washed with water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$), affording a purple solid (80 mg, 100%): ^{1}H NMR δ 1.62 (s, 18H), 3.21 (s, 2H), 7.72 (d, J = 8.4 Hz, 4H), 7.76 (d, J = 8.4 Hz, 4H), 7.91 (d, J = 8.0 Hz, 4H), 7.99 (d, J = 8.0 Hz, 4H), 8.15 (d, J = 8.0 Hz, 4H), 8.31 (d, J = 8.0 Hz, 4H), 9.00−9.03 (m, 8H); LD-MS obsd, 989.5; FAB-MS obsd 988.3514, calcd 988.3483 ($C_{68}H_{52}N_4Zn$); λ_{abs} 427, 513, 551, 590 nm.

5,15-Bis(3-ethynylphenyl)-10,20-dimesitylporphinatozinc(II) (Zn-13). A solution of **13** (50.0 mg, 67.0 μmol) in $CHCl_3$

(54) (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.

(5 mL) was reacted overnight with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (73.0 mg, 330 μmol) in methanol (1 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated. The resulting crude was sonicated with methanol and then filtered. The filtered material was dried under vacuum, affording a purple solid (50 mg, 93%): ^{1}H NMR δ 1.83 (s, 12H), 2.64 (s, 6H), 3.15 (s, 2H), 7.28 (s, 4H), 7.70 (t, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 8.22 (d, J = 7.5 Hz, 2H), 8.35−8.39 (m, 2H), 8.78 (d, J = 4.8 Hz, 4H), 8.85 (d, J = 4.8 Hz, 4H); LD-MS obsd, 808.8; FAB-MS obsd 808.2614, calcd 808.2544 ($C_{54}H_{40}N_4Zn$); λ_{abs} 423, 549, 588 nm.

10,15,20-Tris(4-ethynylphenyl)-5-mesitylporphinatozinc(II) (Zn-15). Following a standard procedure,[39] a mixture of 4-ethynylbenzaldehyde (250 mg, 1.92 mmol), mesitaldehyde (95.0 mg, 0.641 mmol), and pyrrole (178 μL, 2.57 mmol) in CH_2Cl_2 (256 mL) containing ethanol (1.49 mL) was treated with $BF_3 \cdot O(Et)_2$ (103 μL, 0.813 mmol) at room temperature. After 1 h, DDQ (436 mg, 1.92 mmol) was added and the reaction mixture was stirred for 1 h. TEA (1 mL) was added and the reaction mixture was filtered through a silica pad (CH_2Cl_2). The purple fraction was concentrated. The resulting residue was dissolved in THF/$CHCl_3$ (120 mL, 1:1) and treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (475 mg, 2.16 mmol) in methanol (20 mL) at room temperature. After 4 h, the mixture was concentrated and chromatographed [silica, CH_2Cl_2/hexanes (1:1)], affording a purple solid (52 mg, 10%): ^{1}H NMR δ 1.83 (s, 6H), 2.64 (s, 3H), 3.33 (s, 3H), 7.30 (s, 2H), 7.90 (d, J = 7.6 Hz, 6H), 8.19 (t, J = 7.2 Hz, 6H), 8.82 (d, J = 4.8 Hz, 2H), 8.88 (d, J = 4.8 Hz, 2H), 8.93 (s, 4H); LD-MS obsd, 790.6; FAB-MS obsd 790.2136, calcd 790.2075 ($C_{53}H_{34}N_4Zn$); λ_{abs} 426, 551, 590 nm.

***meso*-Tetrakis(4-ethynylphenyl)porphinatozinc(II) (Zn-16).** Following a standard procedure,[40] a solution of 4-ethynylbenzaldehyde (225 mg, 1.73 mmol) and pyrrole (121 μL, 1.73 mmol) in CH_2Cl_2 (173 mL) was treated with NaCl (2.52 g, 43.3 mmol) and $BF_3 \cdot O(Et)_2$ (22.0 μL, 0.173 mmol) at room temperature. After 1 h, DDQ (295 mg, 1.30 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was passed through a silica column (CH_2Cl_2) and the purple fraction was concentrated. The crude mixture was dissolved in THF/$CHCl_3$ (100 mL, 2:1) and then treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (475 mg, 2.16 mmol) in methanol (15 mL) at room temperature. After 2 h, the mixture was concentrated and chromatographed (silica, $CHCl_3$), affording a purple solid (226 mg, 67%): ^{1}H NMR δ 3.32 (s, 4H), 7.90 (d, J = 8.0 Hz, 8H), 8.18 (d, J = 8.0 Hz, 8H), 8.95 (s, 8H); LD-MS obsd, 772.5; FAB-MS obsd 772.1655, calcd 772.1605 ($C_{52}H_{28}N_4Zn$); λ_{abs} 427, 552, 591 nm.

5-(4-Ethynylphenyl)-15-(4-iodophenyl)-10,20-dimesitylporphinatozinc(II) (Zn-17). A solution of **Zn-32** (115 mg, 117 μmol) in $CHCl_3$/THF (23 mL, 3:1) was treated with TBAF (175 μL, 175 μmol, 1.0 M in THF) at room temperature for 1 h. The reaction mixture was washed with 10% aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed [silica, $CHCl_3$/hexanes (3:1)], affording a purple solid (95 mg, 89%): ^{1}H NMR δ 1.83 (s, 12H), 2.65 (s, 6H), 3.32 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 8.0 Hz, 2H), 8.79−8.81 (m, 6H), 8.87−8.88 (m, 6H); MALDI-MS (dithranol) obsd 783.8 [$(M - I)^+$], 911.6 [M^+]; FAB-MS obsd 910.1531, calcd 910.1511 ($C_{52}H_{39}IN_4Zn$); λ_{abs} 424, 550, 589 nm; λ_{em} (λ_{ex} 550 nm) 604, 651 nm.

5,10-Bis(4-*tert*-butylphenyl)-15-(4-ethynylphenyl)-20-(4-iodophenyl)porphinatozinc(II) (Zn-19). A solution of **Zn-28** (238 mg, 235 μmol) in THF (30 mL) was treated with TBAF (266 μL, 266 μmol, 1.0 M solution in THF) under argon at room temperature. After 2 h, $CHCl_3$ was added and the solution was washed with water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$), affording a magenta solid (204 mg, 97%): ^{1}H NMR (THF-d_8) δ 1.63 (s, 18H), 3.79 (s, 1H), 7.81 (d, J = 8.0 Hz, 4H), 7.86 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 8.11−8.15 (m, 6H), 8.19 (d, J = 8.0 Hz, 2H), 8.83−8.90 (m, 8H); LD-MS obsd 938.5; FAB-MS obsd 939.1902, calcd 939.1936 [$(M + H)^+$; M = $C_{54}H_{43}IN_4Zn$]; λ_{abs} 425, 514, 551, 590 nm.

5-(4-Ethynylphenyl[*ethynyl*-$^{13}C_2$])-10,15,20-tri-*p*-tolylporphinatozinc(II) (Zn-22). A sample of (triethylsilyl)ethyne-[*1,2*-$^{13}C_2$] was prepared following a reported procedure[43] wherein acetylene-[*1,2*-$^{13}C_2$] was condensed in THF that was cooled with a liquid-nitrogen bath. The mixture was placed in a dry ice/acetone bath and then treated with EtMgBr followed by triethylsilyl chloride. The product consisted of a 1:1 mixture of (triethylsilyl)ethyne-[*1,2*-$^{13}C_2$] and 1,2-bis(triethylsilyl)ethyne-[*1,2*-$^{13}C_2$], which was used without purification in the following reaction.

Following a standard procedure,[30] a mixture of **Zn-35** (150 mg, 177 μmol), $Pd_2(dba)_3$ (24.4 mg, 26.6 μmol), and P(*o*-tol)$_3$ (64.0 mg, 210 μmol) in toluene/TEA (70 mL, 5:1) was treated with a crude sample (80.0 mg) of the 1:1 mixture of (triethylsilyl)ethyne-[*1,2*-$^{13}C_2$] and 1,2-bis(triethylsilyl)ethyne under argon in a Schlenk flask at 35 °C. After 16 h, identical portions of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ were added, followed by (triethylsilyl)ethyne-[*1,2*-$^{13}C_2$] (40.0 mg, ∼50% mixture with its disilyl derivative). After 8 h of stirring, TLC analysis showed the completion of the reaction. After removal of the solvent, the reaction mixture was purified by column chromatography [silica, CH_2Cl_2/hexanes (2:1 → 1:1)], which failed to give pure **Zn-36**. Hence, the mixture was directly used in the deprotection step described below.

The crude mixture was dissolved in $CHCl_3$/THF (20 mL, 3:1) and treated with TBAF (349 μL, 349 μmol, 1.0 M in THF) at room temperature. After 1 h of stirring, the reaction mixture was washed with 10% aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated. Purification by column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a purple solid (49 mg, 37% from **Zn-35**): ^{1}H NMR (THF-d_8) δ 2.56 (s, 6H), 2.69 (s, 3H), 3.79 (dd, J = 245.2 Hz, J = 56.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 6H), 7.86 (dd, J = 7.6 Hz, J = 4.8 Hz, 2H), 8.07 (d, J = 8.0 Hz, 6H), 8.18 (d, J = 8.0 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.84 (s, 4H), 8.86 (d, J = 4.8 Hz, 2H); ^{13}C NMR (THF-d_8) δ 21.6, 79.4 (enh, d, J = 692.7 Hz), 84.7 (enh, d, J = 690.9 Hz), 120.2, 121.6, 121.8, 123.1, 127.9, 130.9, 131.8, 132.2, 132.3, 132.5, 135.3, 135.4, 137.7, 141.7, 145.3, 150.6, 151.1, 151.2, 151.3; LD-MS obsd 744.4; FAB-MS obsd 744.2101, calcd 744.2142 ($C_{47}{}^{13}C_2H_{34}N_4Zn$); λ_{abs} 425, 551, 592 nm; λ_{em} (λ_{ex} 550 nm) 600, 649 nm.

5-[4-(Hydroxymethyl)phenyl]-10,15,20-triphenylporphinatozinc(II) (Zn-24). Following a standard procedure,[44] a solution of **38** (264 mg, 400 μmol) in dry THF/MeOH (15 mL, 10:1) was treated with $NaBH_4$ (303 mg, 8.0 mmol) in small portions with rapid stirring at room temperature. After 2 h, TLC analysis [hexanes/ethyl acetate (3:1)] indicated incomplete reduction. Therefore, an identical amount of $NaBH_4$ was added in the same manner. After another 2 h, TLC showed complete reduction of **38**. The reaction was quenched by slow addition of saturated aqueous NH_4Cl. The reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (K_2CO_3) and concentrated, affording **38-diol** as a slightly yellow foamlike solid. The freshly prepared **38-diol** was condensed with **39** (112 mg, 400 μmol) in CH_2Cl_2 (160 mL) under Yb(OTf)$_3$ catalysis[40] (317 mg, 512 μmol) at room temperature for 30 min. DDQ (272 mg, 1.2 mmol) was added and the reaction mixture was stirred for 1 h, then neutralized with TEA, and filtered through a pad of silica (CH_2Cl_2). The first fraction was collected and concentrated, affording a purple solid. A solution of the crude product (**40**) in $CHCl_3$ (15 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (230 mg, 1.0 mmol) in methanol (5 mL). The mixture

was stirred at room temperature for 4 h. The mixture was concentrated to dryness. The residue was dissolved in CH_2Cl_2 and chromatographed (silica, CH_2Cl_2). Compound **Zn-40** (5-[4-(methoxycarbonyl)phenyl]-10,15,20-triphenylporphyrinatozinc(II))[32] was obtained as a purple solid and carried forward without further purification. A solution of **Zn-40** in dry THF (30 mL) was treated with $LiAlH_4$ (16.5 mg, 430 μmol) under argon at room temperature for 1 h. Methanol was slowly added to destroy the excess $LiAlH_4$ and the solvent was evaporated under reduced pressure. Chromatography (silica, CH_2Cl_2) and then precipitation (CH_2Cl_2/hexanes) afforded a purple powder (81.8 mg, 27% from **38**): ^{1}H NMR δ 4.91 (d, $J = 6.3$ Hz, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.82−7.72 (m, 9H), 8.24−8.18 (m, 8H), 8.97−8.92 (m, 8H); LD-MS obsd 706.0; FAB-MS obsd 706.1711; calcd 706.1734 ($C_{45}H_{30}N_4ZnO$); λ_{abs} ($CHCl_3$) 422, 550 nm.

5-(2,3,5,6-Tetrafluorophenyl)dipyrromethane (**26**)**.** Following a known procedure,[33] a mixture of pyrrole (34.7 mL, 500 mmol) and 2,3,5,6-tetrafluorobenzaldehyde (0.58 mL, 5.0 mmol) was degassed with a stream of argon for 10 min. $InCl_3$ (111 mg, 500 μmol) was added, and the mixture was stirred under argon at room temperature for 1.5 h. Powdered NaOH (600 mg, 150 mmol) was added to quench the reaction. After 45 min of stirring, the mixture was filtered. The filtrate was concentrated. The remaining pyrrole was removed by entrainment with hexanes. The resulting solid was dissolved in ethanol/water (15 mL, 4:1) with heating on a water bath. The resulting mixture was filtered. The filtrate was set aside overnight at room temperature, affording white crystals (850 mg, 25% yield; 96.7% purity by GC): mp 147−149 °C; ^{1}H NMR δ 5.95 (s, 1H), 6.05 (m, 2H), 6.17 (dd, $J = 6.56$ Hz, $J = 6.03$ Hz, 2H), 6.74 (m, 2H), 7.00 (tt, $^3J = 9.8$ Hz, $^4J = 7.2$ Hz, 1H), 8.16 (br, 2H); ^{13}C NMR δ 33.7, 104.8, 105.0, 105.3, 107.8, 108.9, 118.2, 121.6, 128.6; FAB-MS obsd 249.0794; calcd 294.0780 ($C_{15}H_{10}N_2F_4$). Anal. Calcd for $C_{15}H_{10}N_2F_4$: C, 61.23; H, 3.43; N, 9.52. Found: C, 61.13; H, 3.37; N, 9.43.

5,15-Bis(2,3,5,6-tetrafluorophenyl)-10,20-bis[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (27). Following a standard procedure,[34] 4-(trimethylsilylethynyl)benzaldehyde (202 mg, 1.0 mmol) and **26** (249 mg, 1.0 mmol) were reacted in CH_2Cl_2 (1.0 L) with TFA catalysis (1.37 mL, 17.8 mmol). After 30 min, DDQ (0.8 g, 3.6 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized by TEA and filtered through a pad of alumina (CH_2Cl_2). The solvent was removed under reduced pressure. Chromatography [silica, CH_2Cl_2/hexanes (2:1)] afforded a purple solid (56.5 mg, 6%): ^{1}H NMR δ −2.85 (s, 2H), 0.39 (s, 18H), 7.61 (tt, $^3J = 9.6$ Hz, $^4J = 7.2$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 4H), 8.17 (d, $J = 8.3$ Hz, 4H), 8.85 (d, $J = 4.7$ Hz, 4H), 8.91 (d, $J = 4.7$ Hz, 4H); LD-MS obsd 950.1; FAB-MS obsd 950.2507; calcd 950.2567 ($C_{54}H_{38}N_4F_8Si_2$); λ_{abs}($CHCl_3$) 418, 512, 545, 589, 643 nm.

5,15-Bis(2,3,5,6-tetrafluorophenyl)-10,20-bis[4-[2-(trimethylsilyl)ethynyl]phenyl]porphinatozinc(II) (**Zn-27**)**.** A solution of **27** (40 mg, 42 μmol) in $CHCl_3$ (15 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (92 mg, 420 μmol) in methanol (5 mL). The mixture was stirred at room temperature for 12 h. The mixture was concentrated. The residue was dissolved in CH_2Cl_2 and chromatographed (silica, CH_2Cl_2), affording a purple solid (42.3 mg, 99%): ^{1}H NMR δ 0.39 (s, 18H), 7.60 (tt, Hz, $^3J = 9.6$ Hz, $^4J = 7.2$ Hz, 2H), 7.89 (d, $J = 8.1$ Hz, 4H), 8.17 (d, $J = 8.1$ Hz, 4H), 8.93 (d, $J = 4.7$ Hz, 4H), 9.00 (d, $J = 4.7$ Hz, 4H); LD-MS obsd 1013.9; FAB-MS obsd 1012.1668; calcd 1012.1642 ($C_{54}H_{36}N_4F_8Si_2Zn$); λ_{abs} ($CHCl_3$) 423, 553 nm.

5,10-Bis(4-*tert*-butylphenyl)-15-[4-[2-(trimethylsilyl)ethynyl]-phenyl]-20-(4-iodophenyl)porphinatozinc(II) (Zn-28). A solution of **28** (233 mg, 246 μmol) in $CHCl_3$ (50 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (269 mg, 1.23 mmol) in methanol (8 mL) and stirred at room temperature for 2 h. Column chromatography (silica, $CHCl_3$) afforded a purple solid (238 mg, 96%): ^{1}H NMR δ 0.38 (s, 9H), 1.62 (s, 18H), 7.76 (d, $J = 7.6$ Hz, 4H), 7.87 (d, $J = 8.0$ Hz, 2H), 7.95 (d, $J = 8.0$ Hz, 2H), 8.09 (d, $J = 8.0$ Hz, 2H), 8.13 (d, $J = 7.6$ Hz, 4H), 8.16 (d, $J = 8.0$ Hz, 2H), 8.90−8.94 (m, 4H), 8.99−9.02 (m, 4H); LD-MS obsd 1010.5; FAB-MS obsd 1010.2237, calcd 1010.2219 ($C_{57}H_{51}IN_4SiZn$); λ_{abs} 426, 484, 514, 551, 591 nm.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-[2-(triisopropylsilyl)ethynyl]benzene (30). A solution of **29** (2.33 g, 7.76 mmol) in diethyl ether (30 mL) containing pinacol (1.10 g, 9.31 mmol) was stirred under argon at room temperature for 15 h. Water was then added. The organic layer was separated, dried (Na_2SO_4), concentrated, and chromatographed (silica, $CHCl_3$), affording a white solid (2.87 g, 96%): mp 88−90 °C; ^{1}H NMR δ 1.13 (s, 21H), 1.34 (s, 12H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR δ 11.3, 18.7, 24.8, 83.9, 92.0, 107.2, 126.2, 131.1, 134.4; FAB-MS obsd 384.2670, calcd 384.2656. Anal. Calcd for $C_{23}H_{37}BO_2Si$: C, 71.86; H, 9.70. Found: C, 72.03; H, 9.77.

5-(4-Iodophenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II) (Zn-35). Following a standard procedure[27] with improved acid catalysis conditions,[42] a solution of **33** (400 mg, 0.846 mmol) in THF/MeOH (33 mL, 10:1) was reacted with $NaBH_4$ (640 mg, 16.9 mmol) at room temperature for 40 min. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (75 mL) and CH_2Cl_2 (75 mL). The mixture was stirred for 10 min and then extracted with CH_2Cl_2. The resulting organic phase was washed with water, dried (Na_2SO_4), and concentrated to dryness. A solution of the resulting foamlike solid and **34** (295 mg, 0.847 mmol) in CH_2Cl_2 (340 mL) was treated with $Yb(OTf)_3$ (696 mg, 1.12 mmol) at room temperature. After stirring for 40 min, DDQ (579 mg, 2.55 mmol) was added and the stirring was continued for 1 h. TEA (1 mL) was added and the reaction mixture was filtered through a silica pad (CH_2Cl_2). The purple fraction was collected. After removal of the solvent, the crude mixture was dissolved in $CHCl_3$ (200 mL) and reacted overnight with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (929 mg, 4.23 mmol) in methanol (50 mL) at room temperature. The reaction mixture was washed with water. The organic phase was dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (2:1)], affording a purple solid (199 mg, 28%): ^{1}H NMR (THF-d_8) δ 2.53 (s, 6H), 2.69 (s, 3H), 7.56 (d, $J = 7.8$ Hz, 6H), 7.96 (d, $J = 7.8$ Hz, 2H), 8.06 (d, $J = 7.8$ Hz, 6H), 8.11 (d, $J = 7.8$ Hz, 2H), 8.81−8.87 (m, 8H); ^{13}C NMR (THF-d_8) δ 21.6, 119.6, 121.6, 121.8, 127.9, 131.7, 132.2, 132.3, 132.5, 135.3, 136.5, 137.2, 137.6, 137.7, 141.6, 144.3, 150.6, 151.1, 151.2, 151.3; LD-MS obsd 846.6, 1565.5 [$(2M - I)^+$]; FAB-MS obsd 844.1063, calcd 844.1041 ($C_{47}H_{33}IN_4Zn$); λ_{abs} 425, 551, 592 nm; λ_{em} (λ_{ex} 550 nm) 599, 649 nm.

Dibutyl(1,9-dibenzoyl-5,10-dihydro-5-phenyldipyrrinato)tin-(IV) (**38**)**.** Following a standard procedure,[44] EtMgBr (50 mL, 50 mmol, 1.0 M in THF) was added slowly to a tap-water-cooled flask containing a solution of **37** (2.22 g, 10.0 mmol) in toluene (200 mL) under argon. The reaction mixture was stirred at room temperature for 30 min. A solution of benzoyl chloride (2.89 mL, 25.0 mmol) in toluene (25 mL) was added over 10 min. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (200 mL) and ethyl acetate (150 mL). The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to dryness. Treatment of the residue with TEA (4.18 mL, 30.0 mmol) and Bu_2SnCl_2 (3.04 g, 10.0 mmol) in CH_2Cl_2 (40 mL) at room temperature for 30 min followed by standard purification afforded a solid (2.98 g, 45% yield): mp 92 °C (dec); ^{1}H NMR δ 0.71 (t, $J = 7.2$ Hz, 3H), 0.75 (t, $J = 7.2$ Hz, 3H), 1.08−1.77 (m, 12H), 5.61 (s, 1H),

6.20 (d, $J = 3.7$ Hz, 2H), 7.09 (d, $J = 3.8$ Hz, 2H), 7.18−7.25 (m, 2H), 7.26−7.33 (m, 3H), 7.46−7.59 (m, 6H), 7.89−7.93 (m, 4H); ^{13}C NMR δ 13.80, 13.83, 24.2, 24.9, 26.2, 26.5, 27.4, 27.5 45.9, 115.5, 124.3, 127.0, 128.3, 128.6, 128.8, 129.2, 131.8, 136.0, 137.7, 144.3, 152.0, 184.8; FAB-MS obsd 663.2084; calcd 663.2034 ($C_{37}H_{38}N_2O_2Sn$). Anal. Calcd for $C_{37}H_{38}N_2O_2Sn$: C, 67.19; H, 5.79; N, 4.24. Found: C, 67.37; H, 5.93; N, 4.30.

Synthesis of Enyne Benchmarks. Enyne 1 was prepared by phenylacetylene self-addition in the presence of palladium catalysis according to a literature procedure.[45] **Enyne 2** and **enyne 3** were each prepared by a copper-catalyzed reaction of phenylacetylene and β-bromostyrene.[46] To favor one isomer over the other, we attempted to use the corresponding isomer of β-bromostyrene (or a mixture containing a larger fraction of the desired isomer). In the case of **enyne 2**, commercially available β-bromostyrene enriched in the E isomer (7:3 E/Z) was used, affording a mixture consisting predominantly of **enyne 2** and a trace of **enyne 3** (98:2 ratio respectively by GC analysis). Fractional crystallization of the mixture gave **enyne 2**. **Enyne 3** was prepared using a sample of β-bromostyrene enriched in the Z isomer (99:1 Z/E; prepared by a known procedure[55]). The product mixture consisted of the target **enyne 3** and the undesired **enyne 2** in ∼7:3 ratio (estimated by ^{1}H NMR analysis). **Enyne 3** was isolated by column chromatography on silica gel using petroleum ether as eluant.[56] Thus, regardless of the isomeric purity of the β-bromostyrene starting material, partial isomerization to the *E*-isomer was observed in both reactions. The isolated enynes were stable to isomerization under ambient conditions.

Film Studies. The conditions under which the porphyrin films are formed is identical to that we have previously reported for obtaining porphyrin monolayers on Si(100) surfaces, namely, deposition onto the surface followed by baking at 400 °C for 2 min (under inert atmosphere). This process has been previously described in detail.[13a] The preparation of the Si(100) microelectrodes and the substrates for the FTIR and RR spectroscopic studies have also been previously described, as have the methods and instrumentation for performing the electrochemical and spectroscopic studies.[48,50−52] The substrates for the SEM studies were prepared by using a ∼1 mM solution of the porphyrin monomer in THF. A 5-μL sample of this solution was placed on the substrate and subjected to heating at 400 °C for 2 min. Additional drops were added to obtain varying thicknesses of the resulting polymer film. After the attachment process, e-beam evaporation was used to deposit 10 nm of Ti followed by 100 nm of Au for SEM analysis.

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