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Investigation of Stepwise Covalent Synthesis on a Surface Yielding Porphyrin-Based Multicomponent Architectures

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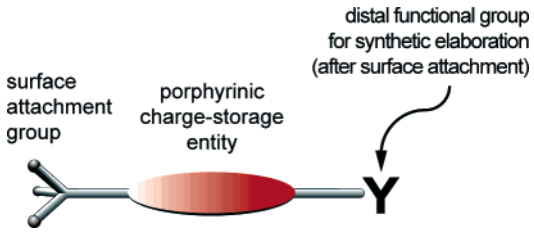

Porphyrins have been shown to be a viable medium for use in molecular-based information storage applications. The success of this application requires the construction of a stack of components ("electroactive surface/tether/charge-storage molecule/linker/electrolyte/top contact") that can withstand high-temperature conditions during fabrication (up to 400 °C) and operation (up to 140 °C). To identify suitable chemistry that enables in situ stepwise synthesis of covalently linked architectures on an electroactive surface, three sets of zinc porphyrins (22 altogether) have been prepared. In the set designed to form the base layer on a surface, each porphyrin incorporates a surface attachment group (triallyl tripod or vinyl monopod) and a distal functional group (e.g., pentafluorophenyl, amine, bromo, carboxy) for elaboration after surface attachment. A second set designed for in situ dyad construction incorporates a single functional group (alcohol, isothiocyanato) that is complementary to the functional group in the base porphyrins. A third set designed for in situ multad construction incorporates two identical functional groups (bromo, alcohol, active methylene, amine, isothiocyanato) in a trans configuration (5,15-positions in the porphyrin). Each porphyrin that bears a surface attachment group was found to form a good quality monolayer on Si(100) as evidenced by the voltammetric and vibrational signatures. One particularly successful chemistry identified for stepwise growth entailed reaction of a surface-tethered porphyrin-amine with a dianhydride (e.g., 3,3′,4,4′-biphenyltetracarboxylic dianhydride), forming the monoimide/monoanhydride. Subsequent reaction with a diamine (e.g., 4,4′-methylene-bis(2,6-dimethylaniline)) gave the bis(imide) bearing a terminal amine. Repetition of this stepwise growth process afforded surface-bound oligo-imide architectures composed of alternating components without any reliance on protecting groups. Taken together, the ability to prepare covalently linked constructs on a surface without protecting groups in a stepwise manner augurs well for the systematic preparation of a wide variety of functional molecular devices.

Introduction

Over the past few years, we have been working to develop approaches for molecular-based information storage. In this approach, redox-active molecules are employed to store charge; the presence of stored charge at a given potential represents the storage of information. This approach is amenable to implementation in a hybrid technology wherein the charge-storage molecules replace the material that presently serves as the charge-storage medium in existing memory chips. As part of this program, we have prepared a wide variety of redox-active molecular architectures, particularly porphyrinic molecules, as candidates for information-storage applications.[1−8] The reader is referred to refs 1−8 for recent studies; references to earlier work can be found in these papers.

The design of the information-storage molecules includes a redox-active unit and a tether for attachment to a surface. In laboratory studies, the information-storage molecule is attached

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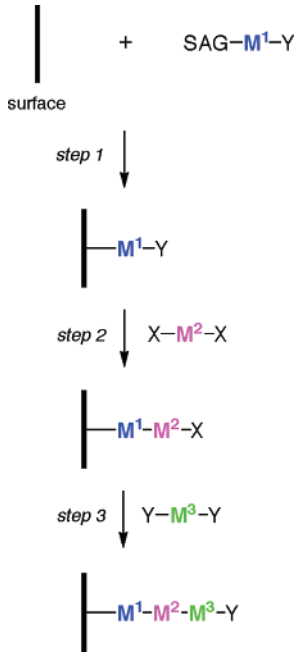
to an electroactive surface. A liquid or gel electrolyte is added, and a counterelectrode is contacted to the electrolyte to complete the electrochemical cell that constitutes the memory device.[9,10] For real-world implementation in a hybrid molecular-semiconductor device, the fabrication of the memory device presents a number of challenges: (1) The charge-storage molecules must be incorporated as components in a stack that consists of electroactive surface/tether/charge-storage molecule/linker/electrolyte/top contact. (2) The electrolyte should be sufficiently thin to afford rapid electron-transfer reactions yet sufficiently thick to minimize electric shorts (via pinholes) between the electroactive surface and the top contact. The ideal dimensions of the electrolyte are considered to be ~10 nm. (3) Sufficient charge density must be present to reliably read the stored information.[11] For the feature sizes in current memory cells, the requisite charge density can be achieved with a monolayer of monomeric porphyrins on a planar substrate.[12,13] Nevertheless, as feature sizes for memory cells become smaller, assemblies of monomeric porphyrins will not have the requisite charge density for reliable read out.[8] Accordingly, multilayer architectures of redox-active molecules will be needed to maintain the required amount of charge stored in each cell.

Two distinct methods can be considered for construction of the stack of components in a memory cell:

(1) Attach a presynthesized molecular architecture to the electroactive surface. We have explored this approach at length; although porphyrin dyads and triads have been prepared, such constructs attach to the surface with an increased molecular footprint that partially attenuates the greater charge density expected from the multad design.[8,14]

(2) Build the stack in a stepwise process on the electroactive surface. A number of multilayer assembly procedures have been developed over the years, epitomized by the Langmuir−Blodgett method.[15] Most such approaches afford noncovalent assemblies.

SCHEME 1



Given the excursions in temperature to which the chip is exposed, during both fabrication (up to 400 °C) and operation (up to 140 °C),[12] we focused on the fabrication of covalently linked architectures.

A conceptual outline for in situ formation of covalently linked architectures is shown in Scheme 1. A charge-storage molecule that bears a surface attachment group (SAG) and distal functional group (Y) is attached to an electroactive surface (step 1). A monomer bearing a functional group (X) complementary to Y is then attached (step 2). In considering approaches for further elaboration of the stack, we realized that the stepwise growth process might be carried out with a pair of difunctional monomers wherein each monomer bears two identical functional groups. For example, with monomers X−M^1−X and Y−M^2−Y, the coupling could be carried out step-by-step *without use of protecting groups* to generate oligomers composed of −M^1−M^2−M^1−M^2...M^i−. The success of this method would stem from (1) growth on a surface, which effectively blocks one site of reactivity on the initial monomer, (2) monomers that are inherently symmetrical with respect to their two functional groups, and (3) the use of relatively rigid monomers wherein reactivity between components at different sites on the surface is effectively suppressed. This approach differs from the synthesis of biomolecules on a polymeric resin (e.g., solid-phase peptide synthesis) or on a surface (e.g., DNA chip fabrication). In the synthesis of peptides, for example, each amino acid contains an amino group and a carboxylic acid moiety (x−m−y), one of which must be protected to prevent self-condensation while the other is activated. The advantage of avoiding protecting groups lies in synthetic convenience and efficiency, where every reaction carried out contributes to the growth of the stack of components necessary to construct the memory cell. Note that in principle the monomer M can comprise a charge-storage entity, a spacer, an electrolyte, a tether for surface attachment, and so forth.

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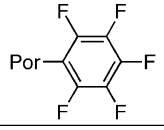
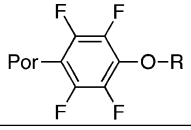
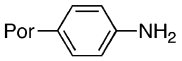
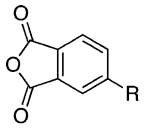
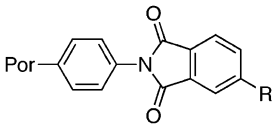
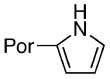
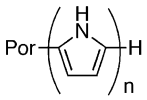
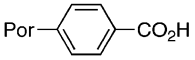
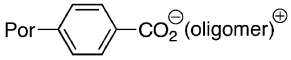
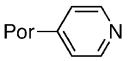
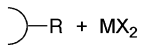
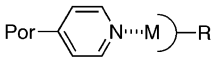
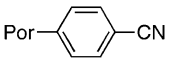
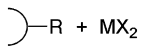
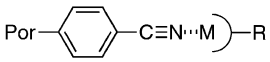
TABLE 1. Prototypical Reactions for Stepwise Synthesis on a Surface

Entry	Surface reactant Porphyrin-Y	Reactant X-M	Surface attached product Porphyrin-M
1		HO−R	
2			
3[a]	Por−H	Nu−R	Por−Nu−R
4[a]			
5	Por−Br	HO−R	Por−OR
6		$(oligomer)^{\oplus}$	
7			
8			

[a] Reaction requires an oxidant.

To successfully implement the in situ covalent synthesis method, the following criteria must be met: (1) The Y group in the compound forming the base layer must not attach to the surface and must survive the surface attachment process. In this regard, the method of attachment of the porphyrinic-based charge-storage molecules to Si(100) entails a high-temperature (300−400 °C) baking or sublimation process.[5,10] (2) The Y group must enable derivatization with the next layer. (3) The derivatization chemistry must be compatible with the surface, the components in the preceding layer (e.g., the porphyrinic charge-storage material), and the modular components that will be attached or deposited in subsequent layers. (4) The entire construct must be compatible with device operation. There is little precedent in organic chemistry to guide the selection of Y groups and derivatization chemistries that satisfy the aforementioned criteria, particularly the high temperatures of surface attachment and device operation. Indeed, an early effort toward this goal encountered inadequate selectivity of the SAG vs the Y group in the base porphyrin upon attempted surface attachment as well as competing surface reactions upon addition of the components designated to form the second layer.[16] Accordingly, we embarked on a program to examine a set of porphyrins for suitability in these applications. The porphyrins of interest include the base porphyrin, which is attached to the electroactive surface, and porphyrins that can be attached to the base porphyrin in building a stack of redox-active compounds for increased charge density.

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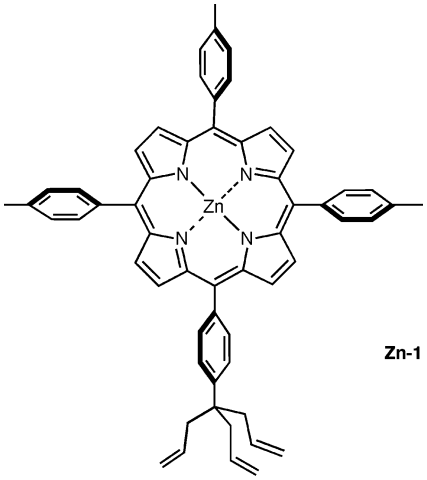
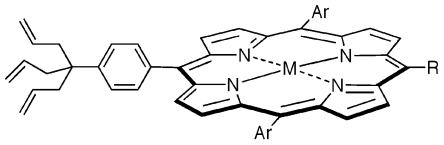
CHART 1



Zn-1

Herein, we describe the preparation of a series of 22 porphyrins for studies of in situ covalent synthesis accompanied by a survey of their use. The paper is divided into three parts. Part I describes the synthesis of a family of molecules built around a zinc porphyrin bearing a tripodal allyl tether (for surface attachment) and a distal functional group (for subsequent elaboration). We previously prepared a porphyrin bearing a "triallyl" tether (Chart 1), which was found to afford a compact molecular footprint upon attachment to Si(100).[13] Part II describes the synthesis of porphyrins that bear one or two functional groups for use in the in situ construction of porphyrin dyads or multads, respectively, to give high-charge density

CHART 2



M = Zn, Ar = *p*-tolyl unless noted otherwise

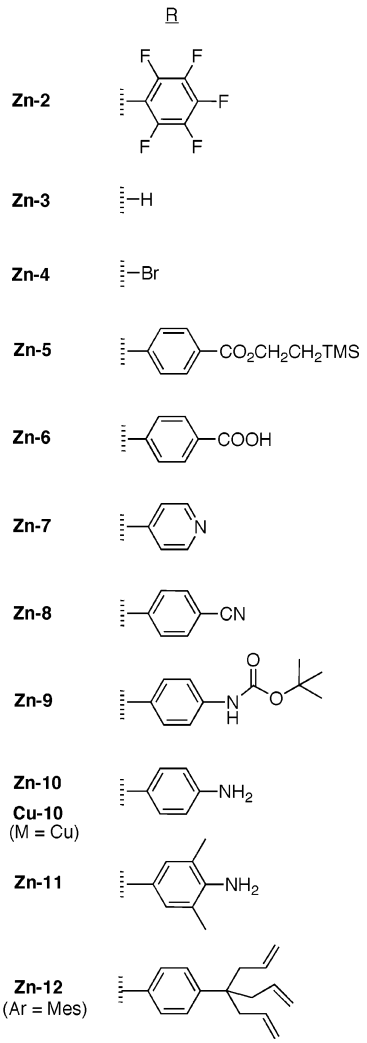
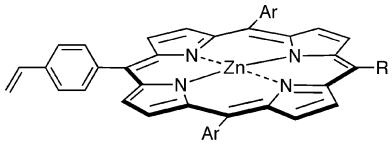
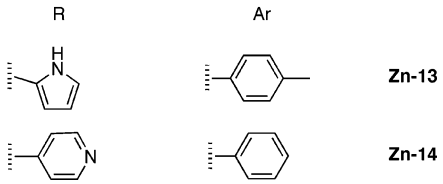


CHART 3





architectures. Part III describes the results of studies that assess the suitability of the functional groups for derivatization purposes. This work establishes a new approach for building molecular architectures on a surface that is particularly appropriate for creating the vertical stack of components required for hybrid molecular-semiconductor information-storage devices.

Results and Discussion

Part I. Porphyrins for Surface Attachment and Subsequent Elaboration. A. Molecular Design. The key reactions we sought to examine are shown in Table 1. The reactions selected for examination require few or no added reagents. The reactions are primarily aimed at derivatization of porphyrins, although a number may have a broader scope. Most of the reactions are well precedented. For example, pentafluorophenyl-substituted porphyrins are known to undergo nucleophilic displacement of the *p*-fluoro substituent (entry 1).[17] The reaction of an amine with an anhydride can afford the acid-amide (not shown), which proceeds to the imide (entry 2).[18] Porphyrins upon electrochemical oxidation are known to undergo nucleophilic substitution (entry 3).[19] In the same vein, a pyrrole attached to a porphyrin can undergo oxidative oligomerization with pyrrole in solution (entry 4).[20] A porphyrin bearing a directly attached halo substituent may undergo nucleophilic displacement (entry 5).[19] A carboxylic acid substituent may enable electrostatic assembly of a cationic oligomer, as required for placement of the electrolyte material (entry 6). The lone pair of electrons on nitrogen in a pyridyl or benzonitrile group can be exploited for binding a metal coordination complex (entries 7 and 8).[21]

A set of porphyrins (**Zn-2**−**Zn-12**) for investigation of these derivatization processes is shown in Chart 2. Each molecule incorporates a zinc porphyrin as an electroactive unit, a triallyl tether, and a distal functional group. The members of a second set of porphyrins (**Zn-13**, **Zn-14**) each bear a single vinyl tether and a distal functional group (Chart 3).

B. Synthesis. The syntheses described herein generally make use of mild rational methods developed over the past few years for preparing porphyrins bearing up to four different meso substituents.[22−25] Each of **Zn-2**−**Zn-14** is a *trans*-AB_2C-porphyrin. The core porphyrin-forming reaction requires access to dipyrromethanes and 1,9-diacyldipyrromethanes. The synthesis of dipyrromethanes proceeds by condensation of an aldehyde with excess pyrrole in the presence of an acid catalyst (e.g., TFA or $InCl_3$) at room temperature.[26,27] In this manner, aldehydes **15a**−**j** afforded the corresponding dipyrromethanes

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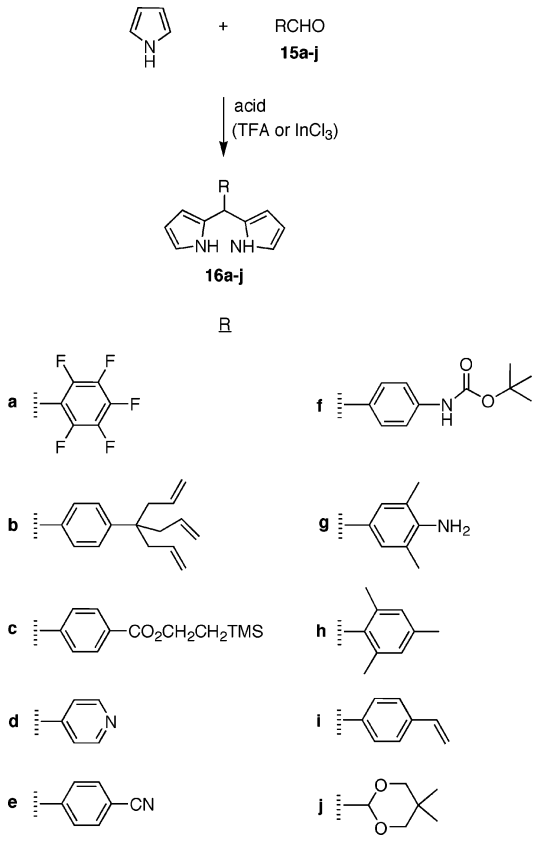
SCHEME 2

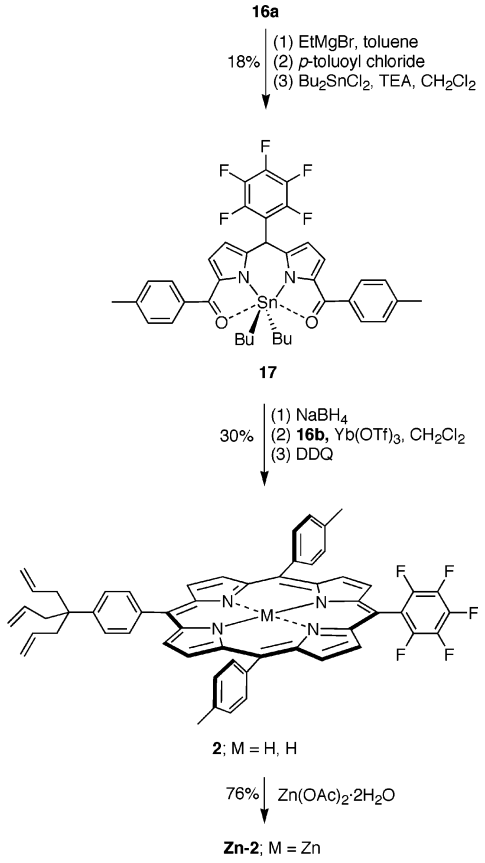


16a, **16b**,[13] **16c**,[28] **16d**,[29] **16e**,[23] **16f**, **16g**, **16h**,[27] **16i**,[5] and **16j**,[30] of which **16f** and **16g** are new compounds (Scheme 2). Commercially available aldehydes were employed with the exception of **15b**,[13] **15f**,[31] and **15g**,[32] which were prepared as described in the literature.

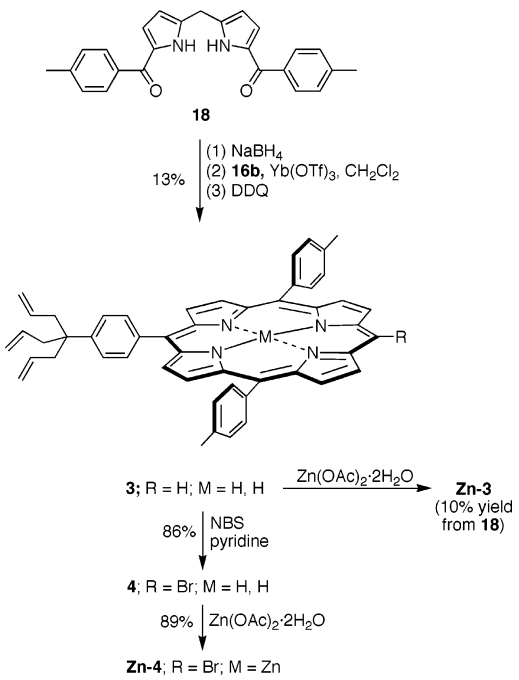
The synthesis of porphyrin **Zn-2** is shown in Scheme 3. Diacylation[33] of 5-(pentafluorophenyl)dipyrromethane (**16a**) followed by complexation with dibutyltin dichloride (to facilitate workup) afforded the dipyrromethane−tin complex **17** in 18% yield. Reduction of **17** with $NaBH_4$ afforded the corresponding dipyrromethane-dicarbinol. Reaction of the latter with the triallyl dipyrromethane **16b** in CH_2Cl_2 containing $Yb(OTf)_3$ followed by oxidation with DDQ gave porphyrin **2** in 30% yield. Zinc metalation of **2** afforded **Zn-2** in 76% yield.

The synthesis of porphyrin **Zn-3** is shown in Scheme 4. Reduction of the meso-unsubstituted 1,9-diacyldipyrromethane **18**[33] with $NaBH_4$ afforded the corresponding dipyrromethane-dicarbinol. The latter was condensed with **16b** in the presence of $Yb(OTf)_3$ followed by oxidation with DDQ, affording the free-base porphyrin **3**. Treatment of **3** with NBS[34,35] at 0 °C

SCHEME 3



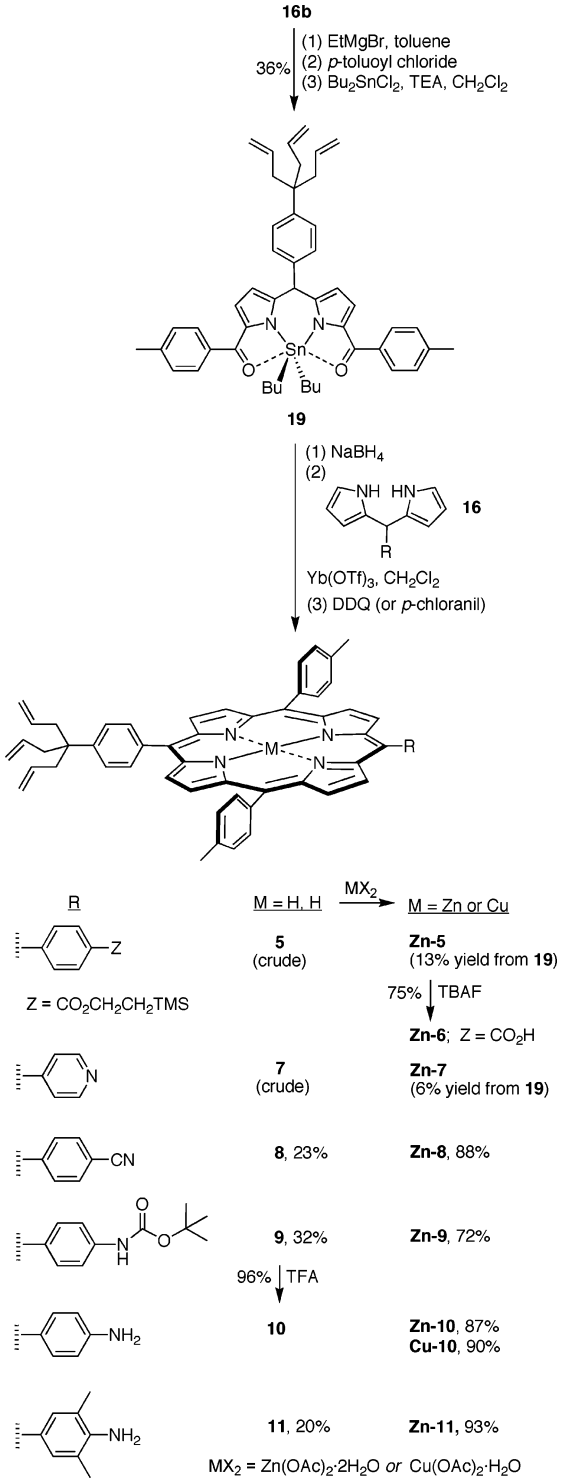
SCHEME 4



afforded the *meso*-bromo porphyrin **4** in 86% yield, showing the chemoselectivity of the porphyrin meso-position vs the three allyl groups. Zinc metalation of **3** or **4** afforded **Zn-3** or **Zn-4**, respectively.

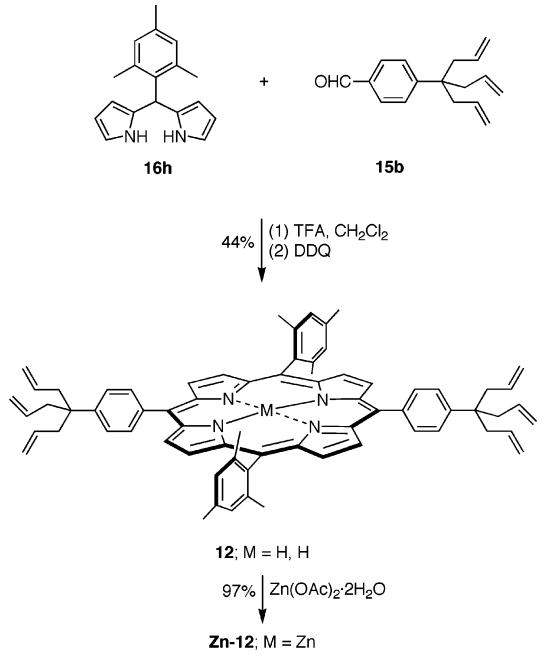
(28) Tomizaki, K.-y.; Yu, L.; Wei, L.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2003**, *68*, 8199−8207.
(29) Gryko, D.; Lindsey, S. J. *J. Org. Chem.* **2000**, *65*, 2249−2252.
(30) Balakumar, A.; Muthukumaran, K.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 5112−5115.
(31) Rai, R.; Katzenellenbogen, J. A. *J. Med. Chem.* **1992**, *35*, 4150−4159.
(32) Lal, B.; Gidwani, R. M.; Reden, J.; de Souza, N. J. *Tetrahedron Lett.* **1984**, *25*, 2901−2904.
(33) Tamaru, S. I.; Yu, L.; Youngblood, W. J.; Muthukumaran, K.; Taniguchi, M.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 765−777.
(34) (a) Nudy, L. R.; Hutchinson, H. G.; Schieber, C.; Longo, F. R. *Tetrahedron* **1984**, *40*, 2359−2363. (b) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983−5993.
(35) 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.

SCHEME 5



The strategy for preparing porphyrins **Zn-2**, **Zn-3**, and **Zn-4** entailed use of the triallyl dipyrromethane and the diacyldipyrromethane bearing the distal functional group. The preparation of the porphyrins bearing sensitive functional groups destined for the distal site required reversal of this strategy, wherein the triallyl dipyrromethane carried the 1,9-diacyl moieties. The sole consideration in the two approaches centers around the compatibility of the functional group with the conditions for 1,9-diacylation (EtMgBr/ArCOCl) and reduction to the dicarbinol ($NaBH_4$ in THF/MeOH).

SCHEME 6



Diacylation of triallyl dipyrromethane **16b** followed by tin complexation afforded the dipyrromethane−tin complex **19** (Scheme 5). This valuable compound was reduced with $NaBH_4$ to give the corresponding dipyrromethane-dicarbinol. Condensation of the latter with a dipyrromethane (**16c**, **16d**, **16e**, **16f**, or **16g**) followed by oxidation and metalation gave the corresponding porphyrin (**Zn-5**, **Zn-7**, **Zn-8**, **Zn-9**, or **Zn-11**). Treatment of **Zn-5** with TBAF cleaved the trimethylsilylethyl group, thereby providing **Zn-6**. Treatment of BOC-protected aminoporphyrin **9** with TFA afforded the free-base aminoporphyrin **10** in quantitative fashion. Metalation of **10** afforded **Zn-10** or **Cu-10** in 87% or 90% yield.

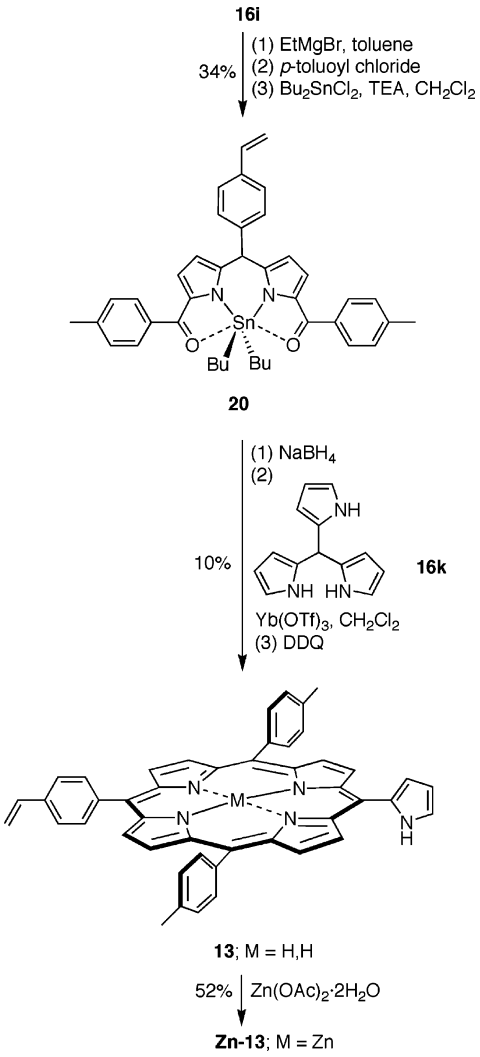
The condensation of 5-mesityldipyrromethane (**16h**) with the aldehyde tripod **15b** using TFA catalysis[22] followed by oxidation with DDQ afforded the free-base porphyrin **12** in 44% yield. Subsequent metalation with $Zn(OAc)_2 \cdot 2H_2O$ afforded **Zn-12** in 97% yield (Scheme 6).

The synthesis of a porphyrin bearing a 2-pyrrolyl group and a 4-vinylphenyl tether is outlined in Scheme 7. Tri(pyrrol-2-yl)methane (**16k**) was prepared by the known reaction of triethyl orthoformate and pyrrole with chloroacetic acid.[36] Diacylation of 5-(4-vinylphenyl)dipyrromethane (**16i**) followed by tin complexation provided the dipyrromethane−tin complex **20** in 34% yield. Reduction of **20** with $NaBH_4$ afforded the corresponding dipyrromethane-dicarbinol, which upon $Yb(OTf)_3$-mediated condensation with **16k** followed by oxidation with DDQ gave porphyrin **13** in 10% yield. Treatment of **13** with $Zn(OAc)_2 \cdot 2H_2O$ provided **Zn-13** in 52% yield.

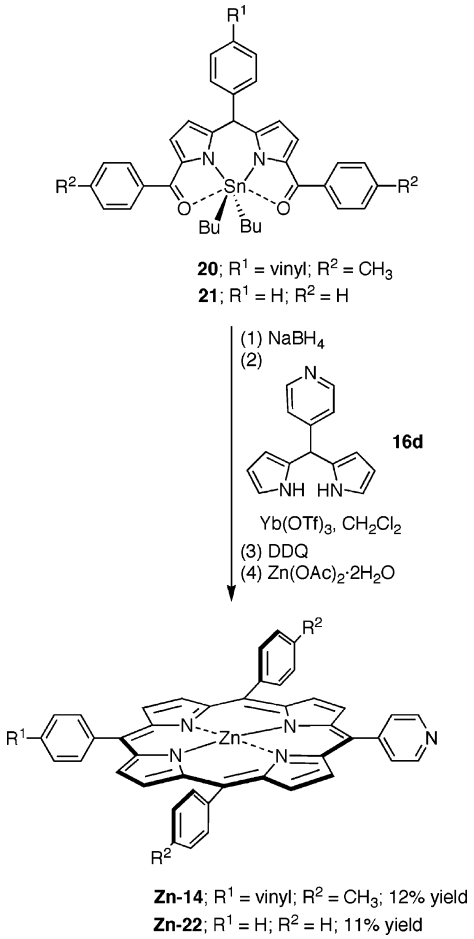
The synthesis of two pyridyl-substituted porphyrins (**Zn-14** and **Zn-22**) is outlined in Scheme 8. Porphyrin **Zn-14** bears a vinyl group for surface attachment, a pyridyl group for subsequent elaboration, and two *p*-tolyl groups. Porphyrin **Zn-22** is a control compound that bears a pyridyl group and three phenyl groups. Attempts to diacylate 5-(4-pyridyl)dipyrromethane (**16d**) were unsuccessful. Accordingly, the dipyrromethane representing the distal side of the porphyrin was

(36) Reese, C. B.; Yan, H. *Tetrahedron Lett.* **2001**, *42*, 5545−5547.

SCHEME 7



SCHEME 8



subjected to diacylation. The diacyldipyrromethane−tin complex **20** was described above, and diacyldipyrromethane−tin complex **21**[37] has been reported previously. Reduction of **20** or **21** with $NaBH_4$ afforded the corresponding dipyrromethane-dicarbinol, which upon reaction with the pyridyl-dipyrromethane **16d** in CH_2Cl_2 containing $Yb(OTf)_3$, oxidation with DDQ, and zinc metalation afforded **Zn-14** or **Zn-22**, respectively. It is noteworthy that the free-base analogue (**22**)[29,38] and **Zn-22**[39] were previously prepared by different routes.

Part II. Porphyrins for in Situ Synthesis. A. Porphyrins for in Situ Dyad Formation. Two porphyrins were designed for studies of in situ dyad formation, where the porphyrin would be attached to the distal functional group of the base porphyrin. Each porphyrin bears one reactive group and three nonlinking substituents. A porphyrin containing an alcohol group can be used for in situ reaction with a porphyrin containing a pentafluorophenyl or bromo substituent (**Zn-2** or **Zn-4**, respectively) to form ether-linked dyads on the surface. A porphyrin bearing an isothiocyanatophenyl group can be used for in situ reaction with an aminoporphyrin (**Zn-10** or **Zn-11**) to form thiourea-linked dyads on the surface.

We have prepared several porphyrins, each bearing a single alcohol substituent (**Zn-23**,[40] **Zn-24**,[1] and **Zn-25**,[1] Chart 4). A porphyrin bearing a biphenylmethanol group was attractive given the ample distance between the porphyrin and the reactive functional group. The Suzuki coupling reaction of porphyrin **Zn-26**[41] and 4-(hydroxymethyl)phenylboronic acid (**27**) was carried out using $Pd(PPh_3)_4$ and K_2CO_3 in toluene/DMF, affording porphyrin-biphenylmethanol **Zn-28** (eq 1). The conditions employed were typical of those for Suzuki reactions with porphyrins, where limited solubility requires reaction in dilute solution.[42]

Porphyrins bearing isothiocyanato groups have been described by Boyle for use in bioconjugation procedures.[43] Porphyrin **29**[44] was metalated with zinc, and the zinc chelate was treated with

(37) Liu, Z.; Schmidt, I.; Thamyongkit, P.; Loewe, R. S.; Syomin, D.; Diers, J. R.; Lindsey, J. S.; Bocian, D. F. *Chem. Mater.* **2005**, *17*, 3728−3742.

(38) Barton, M. T.; Rowley, N. M.; Ashton, P. R.; Jones, C. J.; Spencer, N.; Tolley, M. S.; Yellowlees, L. J. *New J. Chem.* **2000**, *24*, 555−560.

(39) Barton, M. T.; Rowley, N. M.; Ashton, P. R.; Jones, C. J.; Spencer, N.; Tolley, M. S.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **2000**, 3170−3175.

(40) (a) Yasseri, A. A.; Syomin, D.; Loewe, R. S.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 15603−15612. (b) Erratum: *J. Am. Chem. Soc.* **2005**, *127*, 9308.

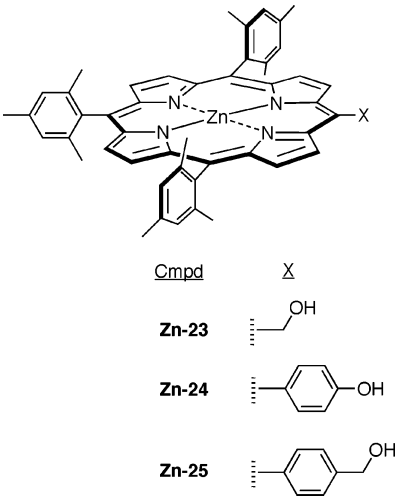
(41) Loewe, R. S.; Lammi, R. K.; Diers, J. R.; Kirmaier, C.; Bocian, D. F.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 1530−1552.

(42) (a) Yu, L.; Lindsey, J. S. *Tetrahedron* **2001**, *57*, 9285−9298. (b) Zhou, X.; Chan, K. S. *J. Chem. Soc., Chem. Commun.* **1994**, 2493−2494.

(43) Sutton, J. M.; Clarke, O. J.; Fernandez, N.; Boyle, R. W. *Bioconjugate Chem.* **2002**, *13*, 249−263.

(44) Sazanovich, I. V.; Balakumar, A.; Muthukumaran, K.; Hindin, E.; Kirmaier, C.; Diers, J. R.; Lindsey, J. S.; Bocian, D. F.; Holten, D. *Inorg. Chem.* **2003**, *42*, 6616−6628.

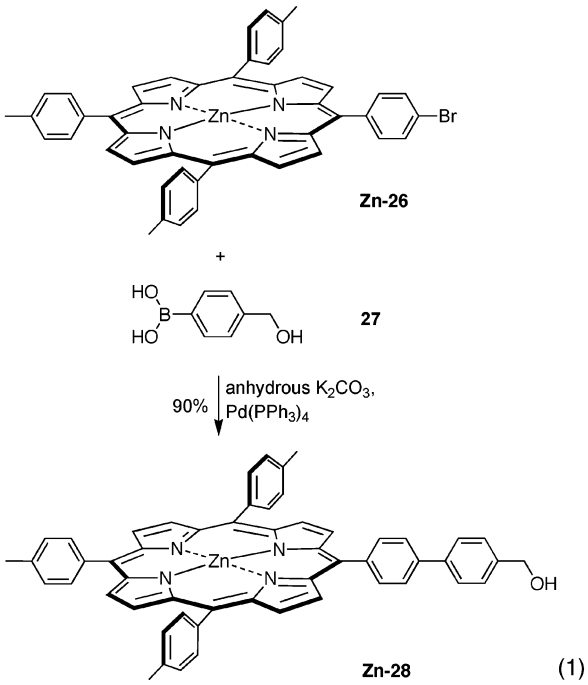
CHART 4

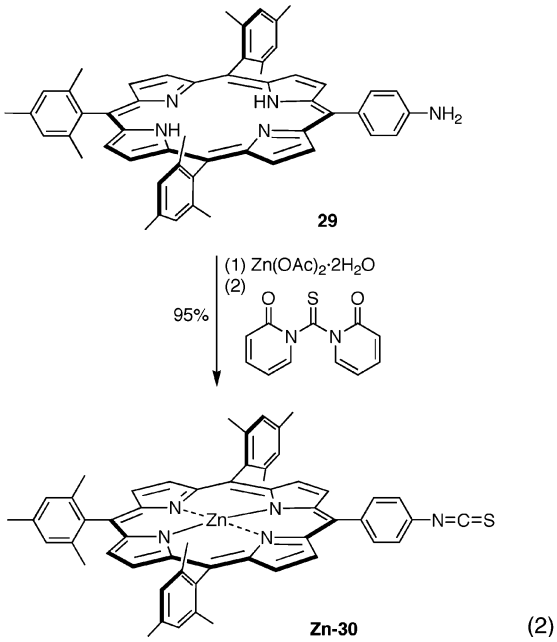


1,1′-thiocarbonyldi-2(1*H*)-pyridone (TDP) to give the isothiocyanatoporphyrin **Zn-30** (eq 2).

B. Porphyrins for in Situ Oligomer Formation without Protecting Groups. The porphyrins for in situ synthesis of oligomers bear two identical functional groups on opposing sides of the porphyrin. A set of seven such *trans*-A_2-porphyrins (**Zn-31**−**Zn-37**) is shown in Chart 5. The functional groups were chosen for complementarity to the distal functional group in the set of base porphyrins (Chart 2). The syntheses of *trans*-A_2-porphyrins **Zn-31**−**Zn-36** were initiated by condensation of an aldehyde and a dipyrromethane that is resistant to acidolysis (e.g., 5-mesityldipyrromethane (**16h**) or dipyrromethane itself).[22] The *trans*-A_2-porphyrin **Zn-37** relied on self-condensation of an acetal-substituted dipyrromethane-carbinol.[30] The syntheses are described in more detail below.

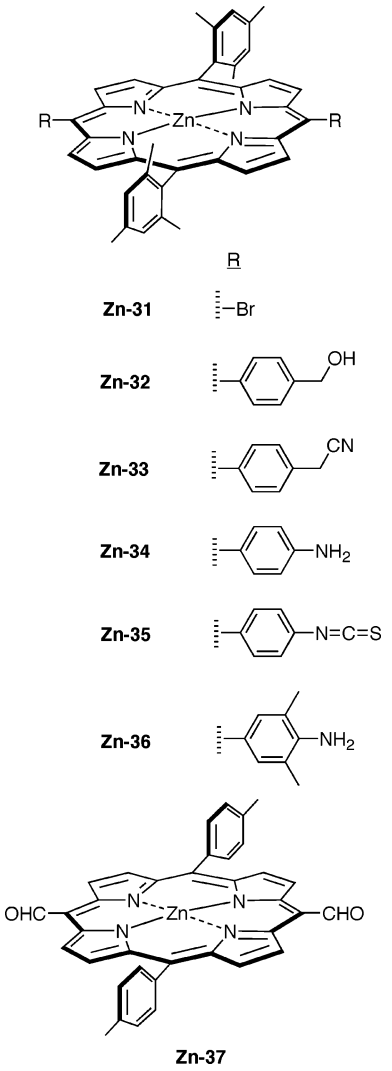
The synthesis of dibromoporphyrin **Zn-31** is shown in eq 3. Treatment of porphyrin **38** (available by condensation of dipyrromethane and mesitaldehyde)[35] with NBS afforded crude dibromoporphyrin **31**,[35] which was directly metalated with Zn(OAc)$_2$·2H$_2$O to give **Zn-31** (71% yield from **38**).

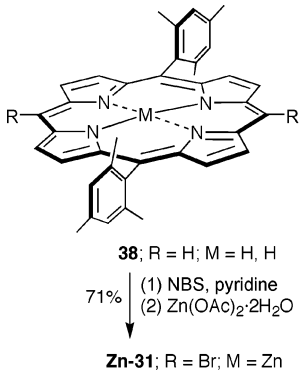




The synthesis of bis(hydroxymethyl)porphyrin **Zn-32** and bis(cyanomethyl)porphyrin **Zn-33** is shown in Scheme 9. The

CHART 5





(3)

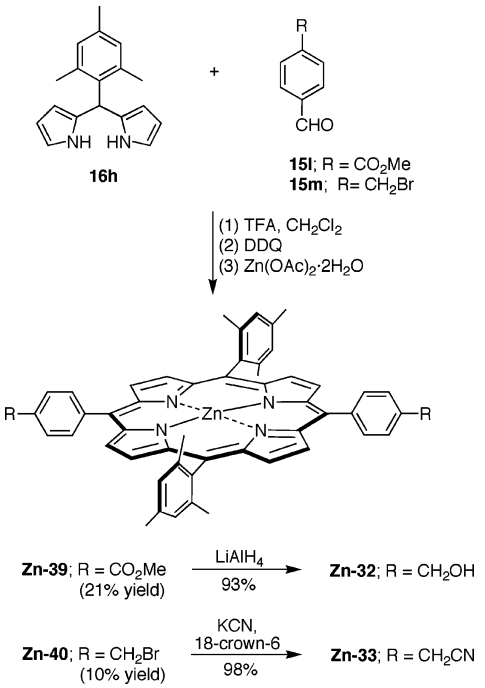
condensation of 5-mesityldipyrromethane (**16h**) and aldehyde **15l** or **15m**[45] in CH_2Cl_2 containing TFA followed by oxidation with DDQ and zinc insertion led to **Zn-39** or **Zn-40** in 21% or 10% yield, respectively. Free-base porphyrin **39** is known.[16] Porphyrin **Zn-40** has been prepared previously in higher yield using different reaction conditions.[46] Reaction of **Zn-39** with $LiAlH_4$ gave **Zn-32** in 93% yield. Treatment of **Zn-40** with KCN in the presence of 18-crown-6[47] afforded **Zn-33** in 98% yield.

The synthesis of diaminoporphyrin **Zn-34** and diisothiocyanatoporphyrin **Zn-35** is outlined in Scheme 10. The condensation of 5-mesityldipyrromethane with **15f** using TFA catalysis followed by oxidation with DDQ afforded **41** in 40% yield. Treatment of this BOC-protected free-base porphyrin with TFA afforded free-base diaminoporphyrin **34** in quantitative fashion. Zinc metalation of the latter afforded **Zn-34** in 92% yield. The isothiocyanato group was introduced to porphyrin **34** using a different reagent than that employed for porphyrin **29**. Following an older literature procedure,[48] treatment of **34** with di-2-pyridyl thiocarbonate (DPTC) gave diisothiocyanatoporphyrin **35** in 73% yield. Zinc metalation of **35** afforded **Zn-35** in 93% yield.

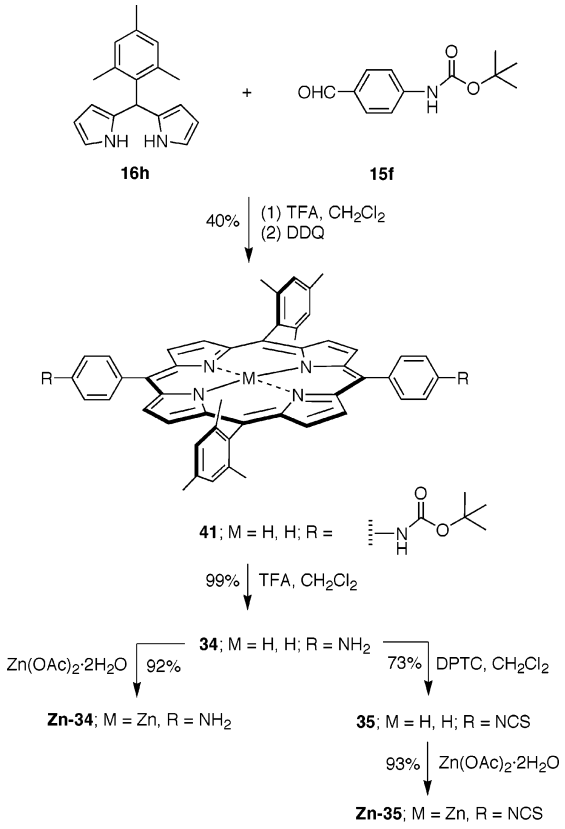
The synthesis of a sterically hindered diaminoporphyrin (**Zn-36**) is shown in Scheme 11. The condensation of dipyrromethane **16h** and aldehyde **15g**[32] in CH_2Cl_2 containing TFA followed by oxidation with *p*-chloranil led to **36** in 5% yield. Zinc metalation of **36** afforded **Zn-36** in 93% yield.

The synthesis of diformylporphyrin **Zn-37** is shown in eq 4. Porphyrin **42** was obtained by self-condensation of the carbinol

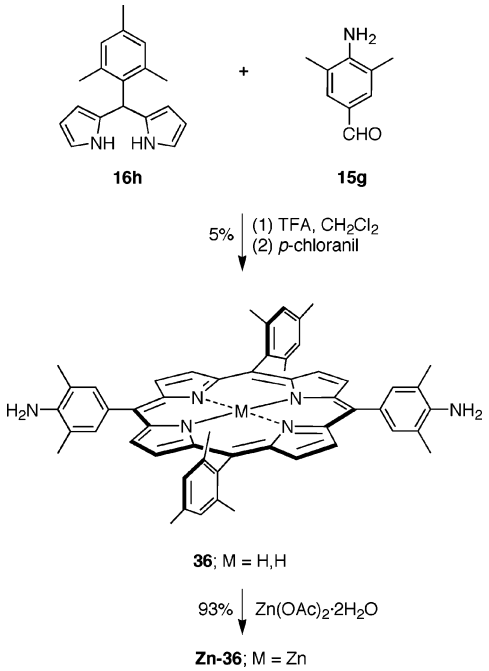
SCHEME 9



SCHEME 10



SCHEME 11

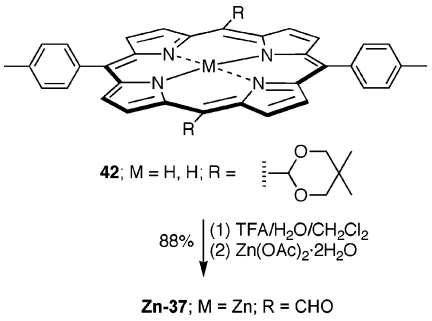


(4)

(45) Wen, L.; Li, M.; Schlenoff, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 7726−7733.

(46) Jiang, B.; Jones, W. E., Jr. *Macromolecules* **1997**, *30*, 5575−5581.

derived from a 1-acyldipyrromethane bearing a 5-acetal substituent.[30] An alternative synthesis of **42** is described in the Supporting Information. Hydrolysis of the two acetal groups of **42** with CH_2Cl_2/TFA/H_2O gave crude 5,15-diformylporphyrin **37**[30] which upon metalation gave **Zn-37** (88% yield from **42**).



(4)

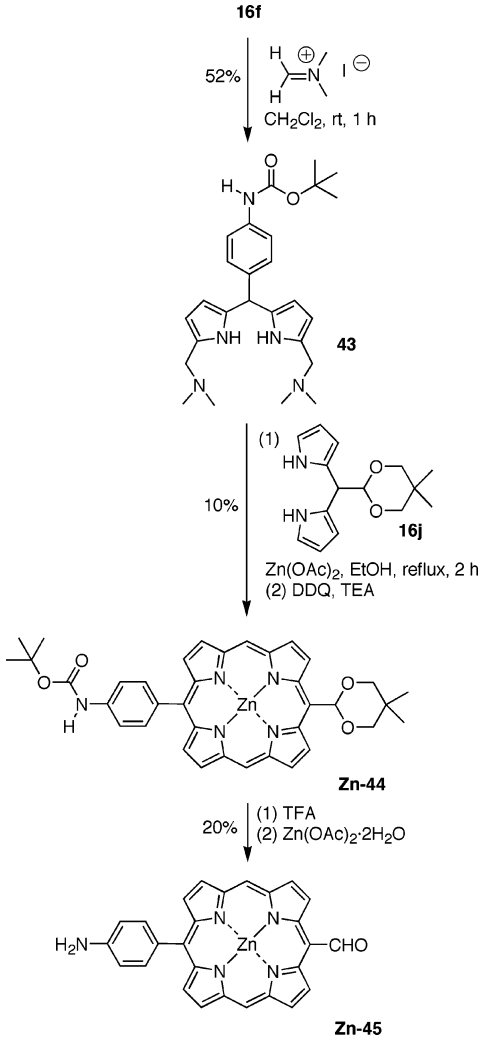
A porphyrin containing one amino group and one formyl substituent was prepared for examination of in situ polymerization as a complement to in situ stepwise growth. A new synthesis of *trans*-AB-porphyrins was employed.[25] Reaction of **16f** with Eschenmoser's reagent at room temperature followed by hydrolysis with aqueous $NaHCO_3$ gave the 1,9-bis(*N*,*N*-dimethylaminomethyl)dipyrromethane (**43**) in 52% yield (Scheme 12). Condensation of **43** and **16j** in ethanol containing $Zn(OAc)_2$ under reflux for 2 h followed by oxidation with DDQ afforded the porphyrin **Zn-44** in 10% yield. Treatment of **Zn-44** with TFA and subsequent zinc metalation afforded **Zn-45** in 20% yield. Porphyrin **Zn-45** was unstable on chromatography and was isolated in ~95% purity in low yield.

Part III. Physical Studies. A. Surface Coverage, Adsorption Geometry, and Binding Motif of the Zn Porphyrin Monolayers. Prior to investigating the suitability of the surface-tethered Zn porphyrins as base layers for in situ formation of covalent architectures, the redox characteristics, surface coverage, adsorption geometry, and binding motif of each porphyrin (**Zn-2**−**Zn-14**, Charts 2 and 3) were examined on Si(100). The surface coverage was evaluated using electrochemical methods; the adsorption geometry and binding motif were examined using FTIR spectroscopy. Voltammetric and FTIR data for two representative molecules, **Zn-2** and **Zn-10**, are shown in Figures 1 and 2, respectively. A summary of the redox potentials, surface coverage, adsorption geometry (expressed as the average tilt angle with respect to the surface normal), and binding motif of each molecule is provided in Table 2.

The general electrochemical and vibrational characteristics of the Zn porphyrin monolayers are similar to those we have previously reported for other carbon-tethered porphyrin monolayers on Si(100) and will not be elaborated on herein.[7,8,13] Instead, we summarize the general characteristics and focus on the key features of the molecules that are germane to their suitability for in situ covalent synthesis. These characteristics and features are as follows.

(1) All of the Zn porphyrins that bear a surface attachment group form good quality monolayers on Si(100) as evidenced by both their voltammetric and their vibrational signatures. The surface coverage of all the Zn porphyrins (with the exception

SCHEME 12



of **Zn-7** and **Zn-14**) is in the range of $(1-2) \times 10^{-10}$ mol cm^{-2}, which is comparable to that of other carbon-tethered Zn porphyrins on Si(100).[7,8,13] The surface coverages for **Zn-7** and **Zn-14**, both of which are functionalized with pyridine, are 3−4-fold lower; we have no explanation for this observation.

(2) The adsorption geometries of all the Zn porphyrins are similar to one another and similar to those of other carbon-tethered Zn porphyrins on Si(100) as determined by their vibrational signatures.[7,8,13] In particular, the average tilt angle of the porphyrin plane with respect to the surface normal is ~38° for all the molecules.

(3) For a number of the Zn porphyrins, it appears that binding can occur via either the targeted triallyl (T) (or vinyl (V)) group or the functional group (Y); only **Zn-2**, **Zn-3**, **Zn-5**, and **Zn-6** (and **Zn-12**, for which Y is also a T group) bind exclusively via the targeted alkenyl group. This assessment is based on features observed in the FTIR spectra as is illustrated by the spectra shown for **Zn-2** vs **Zn-10** in Figure 2. In particular, the spectra of the **Zn-2** and **Zn-10** solids exhibit bands characteristic of the alkenyl group near 1638 (C═C stretch) and 917 cm^{-1} (CH deformation). Attachment to the surface via a hydrosilylation reaction eliminates these bands,[7,8,13] as is observed for the **Zn-2** (and **Zn-3**, **Zn-5**, and **Zn-6**) monolayer(s). In contrast, bands due to the alkenyl C═C stretch and CH deformation clearly remain in the spectrum of the **Zn-10** (and other)

(47) Cook, F. L.; Bowers, C. W.; Liotta, C. L. *J. Org. Chem.* **1974**, *39*, 3416−3418.

(48) (a) Kim, S.; Yi, K. Y. *Tetrahedron Lett.* **1985**, *26*, 1661−1664. (b) Han, W.; Li, S.; Lindsay, S. M.; Gust, D.; Moore, T. A.; Moore, A. L. *Langmuir* **1996**, *12*, 5742−5744.

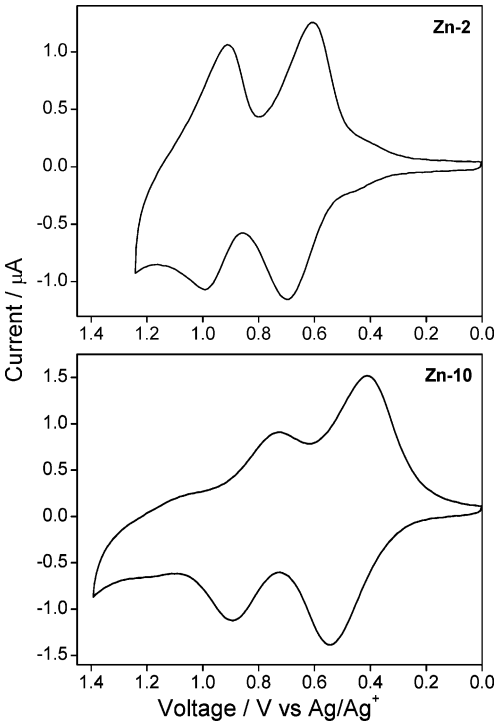


FIGURE 1. Fast-scan (100 V s^{-1}) voltammograms of the **Zn-2** (top panel) and **Zn-10** (bottom panel) monolayers on Si(100).

monolayer(s), indicating that some of the porphyrins bind via an alternative motif, namely, the functional group. The relative number of molecules that bind via the alkenyl vs the functional group cannot be readily determined from the FTIR data because the intensities of the vibrational bands for the monolayer are sensitive to the orientation of the transition dipoles with respect to the surface as well as the relative number of dipoles. For example, the strong residual alkenyl features that appear in the spectrum of the **Zn-10** monolayer would nominally suggest that the majority of the molecules bind via the NH_2 group. However, the in situ synthesis studies described below show that this cannot be the case (vide infra).

(4) Most of the functional groups (that do not bind to the surface) remain intact under the high-temperature conditions

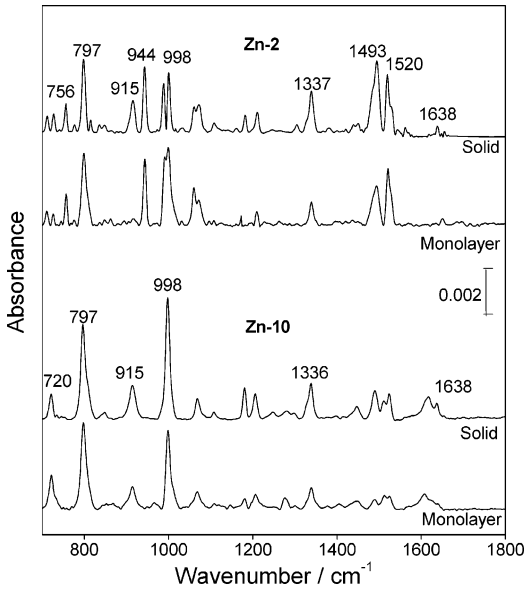


FIGURE 2. FTIR spectra of solid **Zn-2** and **Zn-10** in KBr pellets and the corresponding **Zn-2** and **Zn-10** monolayers on Si(100).

used for surface attachment, as evidenced by their vibrational signatures in the spectrum of the monolayer (e.g., C−F stretch at 944 cm^{-1} for **Zn-2**; C≡N stretch for **Zn-8** at 2213 cm^{-1}). One clear exception is the carboxyl functional group. The spectra of the monolayers of **Zn-5**, **Zn-6**, and **Zn-9** show no evidence of the characteristic C═O stretches (∼1700 cm^{-1}) that are observed for these molecules in the solids.

The observation that the functional groups of many of the Zn porphyrins that appear to bind and/or react with the surface thermally decompose limits the choices for the base porphyrins in the studies of in situ formation of vertical architectures. Indeed, the only porphyrins that bind exclusively via the alkenyl group and exhibit thermally stable functional groups are **Zn-2** and **Zn-3**. From this pair, **Zn-2** was selected for studies of in situ porphyrin dyad formation because the *p*-fluorine atom (of the pentafluorophenyl group) should be more reactive than the *meso*-H atom (of the porphyrin macrocycle) toward ipso substitution. We also chose to investigate dyad formation using

TABLE 2. Redox Potentials,[a] Surface-Coverage Values,[b] Average Tilt Angles,[c] and Binding Motif[d] for the Zn−Porphyrin Monolayers on Si(100)

	$E^{0/+1}$ (V)		$E^{+1/+2}$ (V)		surface coverage	tilt	
porphyrin	soln	monolayer	soln	monolayer	(10^{-10} mol cm^{-2})	(deg)	binding motif
Zn-2	0.61	0.64	0.90	0.95	2.1	36	T
Zn-3	0.56	0.59	0.88	0.99	1.8	38	T
Zn-4	0.54	0.56	0.87	0.90	1.7	39	T or Y
Zn-5	0.59	0.66	0.86	0.99	1.8	37	T
Zn-6[e]	0.53	0.55	0.84	0.88	1.7	39	T
Zn-7	0.54	0.62	0.86	0.90	0.4	37	T or Y
Zn-8	0.54	0.55	0.85	0.87	2.2	38	T or Y
Zn-9	0.55	0.65	0.87	0.94	2.1	41	T or Y
Zn-10[f]	0.52	0.58	0.80	0.88	2.1	38	T or Y
Zn-11[g]	0.55	0.58	0.87	0.92	2.0	37	T or Y
Zn-12	0.52	0.55	0.85	0.93	1.4	36	T or Y
Zn-13[h]	0.48	0.52	0.73	0.80	1.3	41	V or Y
Zn-14	0.52	0.58	0.89	0.94	0.6	40	V or Y

[a] Solution potentials were obtained in CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6; scan rate = 0.1 V s^{-1}. Values are referenced vs Ag/Ag^+; $FeCp_2/FeCp_2^+$ 0.20 V. Monolayer potentials were obtained in propylene carbonate containing 1.0 M *n*-Bu_4NPF_6; scan rate = 100 V s^{-1}. [b] Porphyrin surface concentration was calculated from the integrated area of the $E^{0/+1}$ and $E^{+1/+2}$ anodic waves and using the geometrical area of the microelectrode (10^{-4} cm^2). [c] Average tilt angle determined on the basis of the intensity ratio of the in-plane pyrrole breathing (998 cm^{-1}) and the out-of-plane β-pyrrole hydrogen deformation (797 cm^{-1}) bands in the IR spectra. [d] Binding motif: T = tripod; V = vinyl; Y = functional group (Charts 2 and 3). [e] A third redox wave is observed at ∼1.18 V in solution that is absent in the monolayer. [f] A third redox wave is observed at ∼1.17 V for both solution and monolayer. [g] A third redox wave is observed at ∼1.35 V for both solution and monolayer. [h] Two additional redox waves are observed at ∼1.18 and ∼1.30 V for both solution and monolayer.

Zn-4, which is functionalized with a *meso*-Br atom, as the base porphyrin. In another series of studies, we investigated in situ formation of polyimides on a porphyrin base layer. These studies used **Zn-10**, which is functionalized with a *p*-aminophenyl group. These studies are described in more detail below.

B. In Situ Formation of Zn Porphyrin Dyad Monolayers. We attempted to form porphyrin dyads by reacting the surface-attached monolayers of **Zn-2** and **Zn-4** with the three alcohol-functionalized Zn porphyrins shown in Chart 4. The porphyrin alcohol was deposited on the monolayer and heated at 400 °C (see Experimental Section for details). The samples were then interrogated using both voltammetry and FTIR spectroscopy. The voltammetric signatures showed modest increases in charge density (20−40%) depending on the choice of porphyrin base layer and alcohol. In no case was dyad formation quantitative. The changes in the FTIR spectra were less apparent, and no signature bands could be identified that are characteristic of formation of an ether linkage between the two porphyrins. However, these bands would be difficult to detect because they would fall in a spectrally congested region. We have not yet attempted to optimize the conditions for in situ dyad formation because this will require exploration of a relatively large parameter space.

C. In Situ Formation of Polyimide Functionalized Zn Porphyrin Monolayers. We examined in situ formation of polyimides by reacting the surface-attached **Zn-10** monolayers with successive applications of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPTC) and either 4,4′-methylenedianiline (MDA) or 4,4′-methylene-bis(2,6-dimethylaniline) (MMDA). The porphyrin dianhydride and dianiline ("imide reagents") were successively deposited on the monolayer and heated at 280 °C (see Experimental Section for details). The samples were then interrogated using both voltammetry and FTIR spectroscopy. The voltammetric and FTIR data for the stepwise addition of one−four aliquots of imide reagents are shown in Figures 3 and 4, respectively. The structures of the molecules that would result from the imide formation reaction are shown in Scheme 13.

Inspection of the voltammetric data in Figure 3 shows that subjecting the **Zn-10** monolayer to BPTC and MDA/MMDA results in an apparent successive loss of signal. The signal loss is particularly large upon addition of MDA to the BPTC-modified monolayer but far less severe when MMDA is added. The attenuation of the voltammetric signal suggests that the imide reagents may partially compromise the integrity of the monolayer. However, these data do not provide structural information.

The FTIR spectra shown in Figure 4 provide a much clearer picture of the effects of the imide reagents on the porphyrin monolayer and indeed confirm that the imide formation reaction occurs. Upon addition of the BPTC, the vibrational signatures of the porphyrin remain and a number of new features appear due to the appended BPTC. The key bands are observed at 1723, 1778, and 1852 cm^{-1}, all of which are due to C═O stretches of the anhydride and/or imide. The 1853-cm^{-1} band is due to the symmetric C═O stretch of the anhydride; the 1778-cm^{-1} band is due primarily to the asymmetric C═O stretch of the anhydride, which overlaps the weaker symmetric C═O stretch of the imide; the 1723-cm^{-1} band is due to the asymmetric C═O stretch of the imide. This latter feature provides direct evidence that a significant number of **Zn-10** molecules bind to the surface via the triallyl group, leaving the porphyrin amino

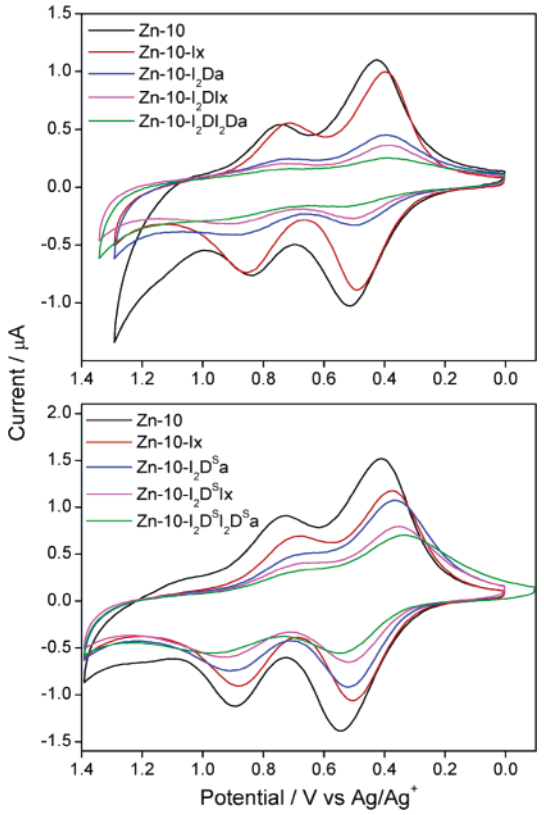


FIGURE 3. Fast-scan (100 V s^{-1}) voltammograms of the **Zn-10** monolayers on Si(100) before and after successive stepwise additions of BPTC and MDA (top panel) or MMDA (bottom panel).

group free to couple to one end of the BPTC molecule. [Neat BPTC only exhibits bands at 1852 and 1778 cm^{-1} due to the anhydride.] Upon addition of MDA/MMDA, the 1853-cm^{-1} band of the anhydride disappears; the intensity of the 1778-cm^{-1} band is greatly attenuated, and the intensity of the 1723-cm^{-1} band of the imide increases, consistent with loss of anhydride and formation of an additional imide linkage. Upon addition of the next aliquots of BPTC and MDA/MMDA, the band-intensity pattern exhibits a similar alteration. As the number of imide linkages increases, the imide band at 1723 cm^{-1} gains intensity relative to the porphyrin bands. These data do not, however, address the issue of whether the imide-forming reaction is quantitative. Finally, we note that the successive addition of imide reagents appears to result in an overall loss of the intensity of the porphyrin vibrational bands, qualitatively consistent with the loss of voltammetric data and reinforcing the notion that the conditions used for polyimide formation are not totally benign toward the porphyrin base monolayer. We are continuing to investigate strategies for mitigating the deleterious processes.

Outlook

A major impediment to the development of hybrid molecular-semiconductor devices resides in the identification of molecular chemistry that is compatible with the daunting temperatures encountered in semiconductor fabrication (up to 400 °C) and operation (up to 140 °C). Our prior work has established that porphyrins (1) bearing appropriate tethers undergo attachment to surfaces at elevated temperatures (200−400 °C), (2) operate at elevated temperatures (100 °C), and (3) can be cycled repeatedly ($>10^{10}$ cycles).[49] Little precedent is available,

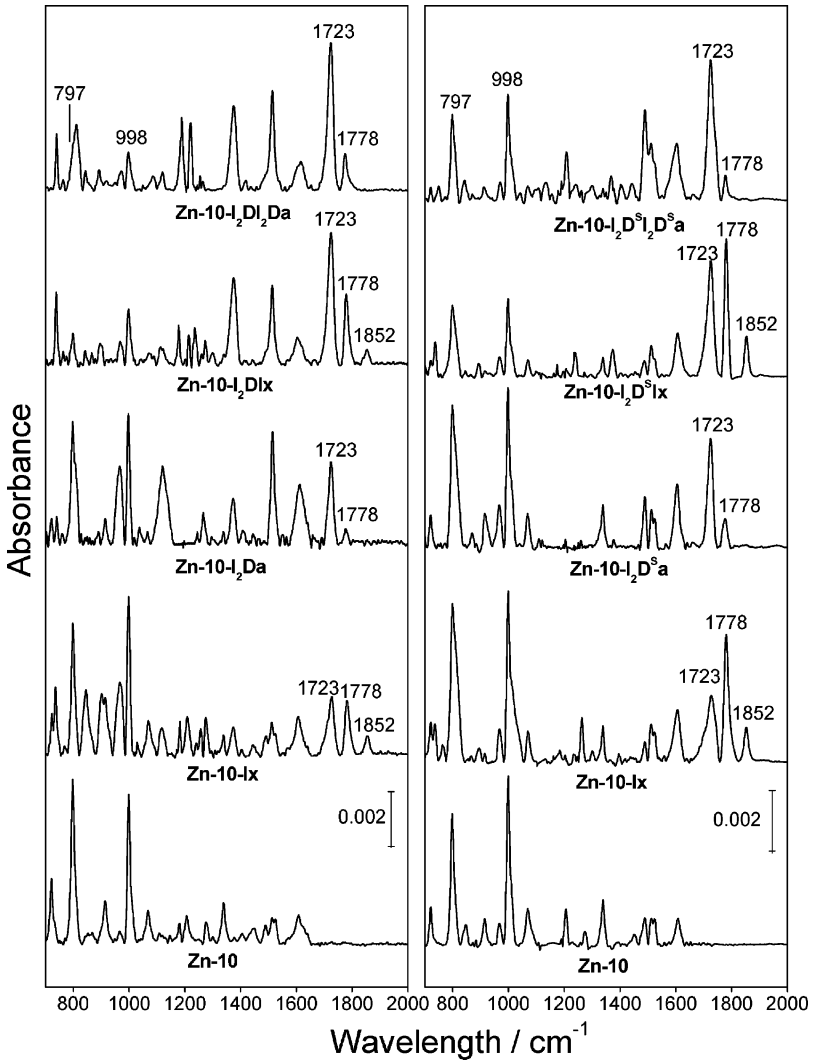


FIGURE 4. FTIR spectra of the **Zn-10** monolayers on Si(100) before and after successive stepwise additions of BPTC and MDA (left panel) or MMDA (right panel).

however, concerning chemistry suitable for in situ synthesis of covalently linked molecular architectures on an electroactive surface, particularly where the first step requires a high-temperature attachment procedure.

The library of porphyrins prepared herein has enabled an initial survey of a variety of chemistries for in situ synthesis of molecular architectures on an electroactive surface. More extensive studies and examination of reaction conditions with this library are now possible. A chief finding is that multads of porphyrinic macrocycles (and/or spacers of various composition) can be constructed in a stepwise manner without the use of protecting groups. Such a synthesis process has heretofore required the use of protecting groups, wherein one cycle of coupling has entailed three reactions: protecting group introduction, coupling, and protecting group removal. The avoidance of protecting groups provides a more efficient process and lessens the burden of identifying suitable conditions for protecting group removal that are compatible with the components in the nascent molecular architecture as well as the underlying substrate.

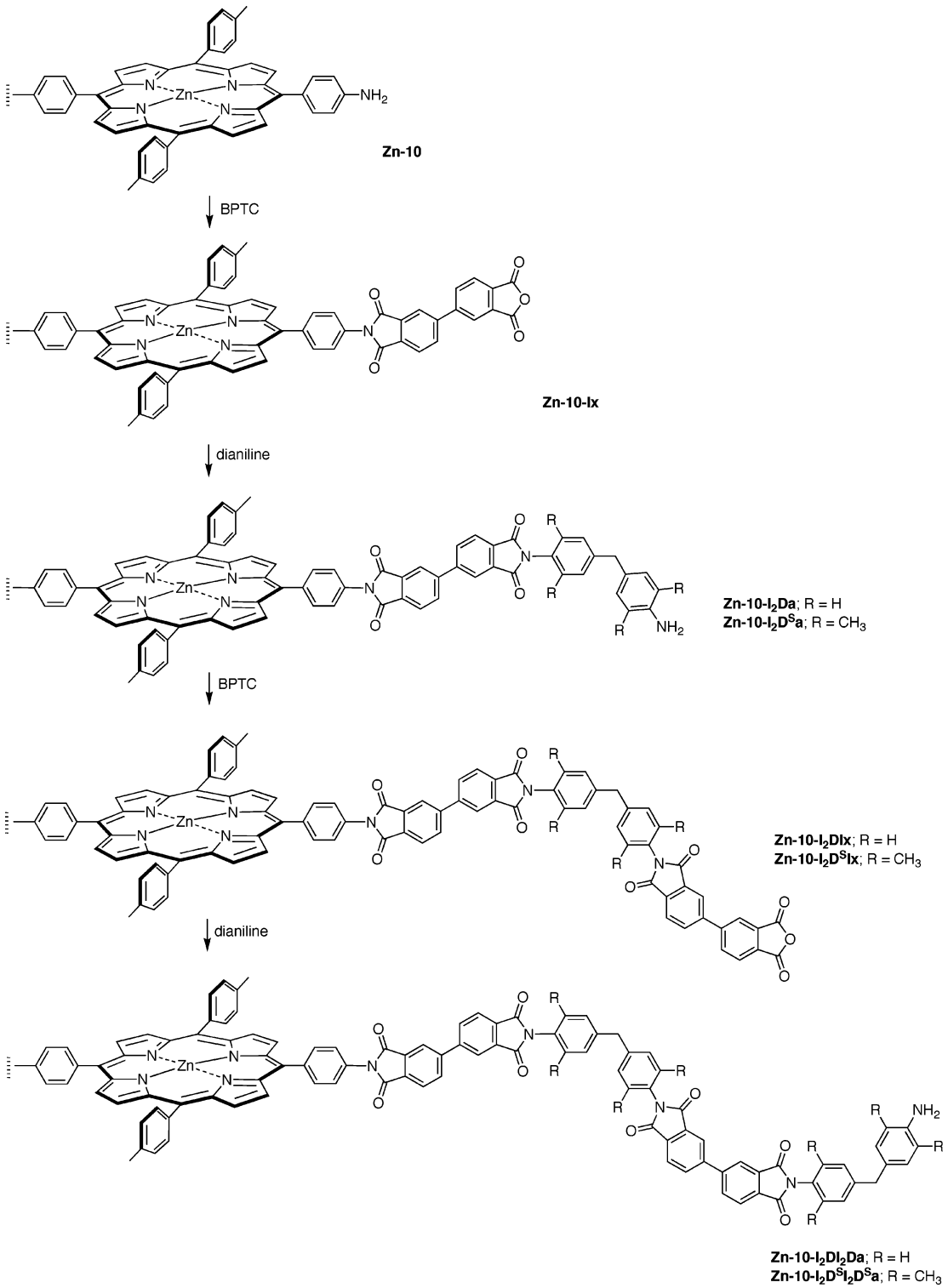
The current studies further demonstrate that, among the various chemistries explored for covalent multad synthesis, the imide-forming reaction is particularly attractive. Coupling to the surface-tethered molecule is readily achieved using this reaction, and the stepwise growth of the overlayers is conveniently monitored via the IR signatures of the building blocks. Polyimides are well established as polymers with high thermal stability and a wide range of applications.[18] We are currently in the process of exploring this reaction as a means of preparing covalently linked multiporphyrin architectures. In this approach, a diamino-functionalized porphyrin, such as **Zn-34** or **Zn-36**, is substituted for MDA/MMDA and BPTC is retained as the dianhydride. The results of these studies are beyond the scope of the current work and will be the subject of a separate publication.

Experimental Section

A. General Procedures for Porphyrin Formation. 5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-10,20-di-*p*-tolyl-15-(pentafluorophenyl)porphyrin (2). Following a standard procedure[23] with improved acid catalysis conditions,[24] a solution of tin complex **17**

(49) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543−1545.

SCHEME 13



(108 mg, 0.139 mmol) in dry THF/MeOH (10 mL, 10:1) was treated with $NaBH_4$ (303 mg, 8.01 mmol) in small portions with rapid stirring at room temperature. After 3 h, the reaction was quenched by slow addition of saturated aqueous NH_4Cl. The reaction mixture was extracted with CH_2Cl_2. The organic solution was dried (K_2CO_3) and concentrated, affording **17-diol** as a slightly yellow foamlike solid. The freshly prepared **17-diol** was condensed with **16b** (50 mg, 0.14 mmol) in CH_2Cl_2 (55 mL) containing $Yb(OTf)_3$ (109 mg, 0.176 mmol) at room temperature for 30 min. DDQ was added, and the reaction mixture was stirred for 1 h. TEA was added. The mixture was filtered through a pad of alumina (CH_2Cl_2). The eluted crude product was chromatographed (silica, CH_2Cl_2), affording a purple solid (36 mg, 30%): ^{1}H NMR δ −2.55 (s, 2H), 2.74−2.71 (overlapping peaks, 12H), 5.22−5.18 (m, 6H), 5.92−5.81 (m, 3H), 7.56 (d, J = 7.6 Hz, 4H), 7.69 (d, J = 7.9 Hz, 2H), 8.10 (d, J = 7.6 Hz, 4H), 8.15 (d, J = 7.9 Hz, 2H), 8.76 (d, J = 4.6 Hz, 2H), 8.83 (d, J = 4.6 Hz, 2H), 8.88 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.6 Hz, 2H); LD-MS obsd 866.2; FAB-MS obsd 866.3432, calcd 866.3422 ($C_{56}H_{43}F_5N_4$); λ_{abs} 418, 485, 515, 548, 588, 644 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-10,20-di-*p*-tolyl-15-[4-[2-(trimethysilyl)ethoxycarbonyl]phenyl]porphinatozinc(II) (Zn-5). Following a standard procedure,[23,24] a solution of tin complex **19** (170 mg, 0.206 mmol) in dry THF/MeOH (20 mL, 10:1) was treated with $NaBH_4$ (390 mg, 10.3 mmol) in small portions with rapid stirring at room temperature. After 4 h, the reaction was quenched by slow addition of saturated aqueous NH_4Cl. The reaction mixture was extracted with CH_2Cl_2. The organic solution was dried (Na_2SO_4) and concentrated, affording **19-diol** as a slightly yellow foamlike solid. The freshly prepared **19-diol** was condensed with **16c** (75.9 mg, 0.206 mmol) in CH_2Cl_2 (82 mL) containing $Yb(OTf)_3$ (162 mg, 3.2 mM, 0.261 mmol) at room temperature for 20 min. DDQ (139 mg, 0.61 mmol) was added, and the reaction mixture was stirred for 1 h. TEA was added. The reaction mixture was filtered through a pad of alumina (CH_2Cl_2). The first fraction was collected and concentrated. The purple solid was dissolved in $CHCl_3$ (20 mL), and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (300 mg, 1.37 mmol) in methanol (10 mL) was added. The reaction mixture was stirred overnight at room temperature. Chromatography (silica, CH_2Cl_2) afforded a purple solid. Methanol was added, and the resulting suspension was sonicated. Filtration afforded a purple solid (24.4 mg, 12%): ^{1}H NMR δ 0.18 (s, 9H), 1.25−1.32 (m, 2H), 2.72 (s, 6H), 2.74 (d, J = 7.0 Hz, 6H), 4.59 (t, J = 8.42 Hz, 2H), 5.18−5.23 (m, 6H), 5.83−5.92 (m, 3H), 7.56 (d, J = 7.7 Hz, 4H), 7.68 (d, J = 8.1 Hz, 2H), 8.11 (d, J = 7.7 Hz, 4H), 8.16 (d, J = 8.1 Hz, 2H), 8.30 (d, J = 8.4 Hz, 2H), 8.41 (d, J = 8.1 Hz, 2H), 8.87 (d, J = 4.8 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.00 (d, J = 4.8 Hz, 4H); LD-MS obsd 982.0; FAB-MS obsd 982.3628, calcd 982.3621 ($C_{62}H_{58}N_4O_2SiZn$); λ_{abs} 422, 549, 589 nm.

5,15-Bis[4-(4-allylhepta-1,6-dien-4-yl)phenyl]-10,20-dimesitylporphyrin (12). Following a standard procedure,[22] samples of **15b** (17.9 mg, 0.074 mmol) and **16h** (19.7 mg, 0.074 mmol) were reacted at room temperature in CH_2Cl_2 (7.5 mL) containing TFA (10 μL, 18 mM, 0.130 mmol). After 30 min, DDQ (30 mg, 15 mM, 0.13 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized by addition of TEA. The mixture was filtered through a pad of alumina (CH_2Cl_2). The filtrate was concentrated under reduced pressure. The residue was chromatographed (silica, CH_2Cl_2) to give a purple solid. The solid was suspended in methanol. The suspension was sonicated with methanol and filtered, affording a purple solid (16 mg, 44%): ^{1}H NMR δ −2.61 (s, 2H), 1.84 (s, 12H), 2.62 (s, 6H), 2.72 (d, J = 7.3 Hz, 12H), 5.16−5.23 (m, 12H), 5.80−5.90 (m, 6H), 7.27 (s, 4H), 7.67 (d, J = 8.2 Hz, 4H), 8.17 (d, J = 8.4 Hz, 4H), 8.70 (d, J = 4.8 Hz, 4H), 8.78 (d, J = 4.8 Hz, 4H); LD-MS obsd 966.5; FAB-MS obsd 966.5612, calcd 966.5600 ($C_{70}H_{70}N_4$); λ_{abs} 419, 516, 550, 593, 647 nm.

5-[4-(*N*-(*tert*-Butyloxycarbonyl)amino)phenyl]-15-(5,5-dimethyl-1,3-dioxan-2-yl)porphinatozinc(II) (Zn-44). Following a standard procedure,[25] a solution of **16f** (168 mg, 0.500 mmol) in CH_2Cl_2 (5.0 mL) was treated with *N*,*N*-dimethylmethyleneammonium iodide (Eschenmoser's reagent, in fine powder form; 194 mg, 1.05 mmol) at room temperature for 1 h. After standard workup, addition of hexanes/CH_2Cl_2 to the crude product afforded a precipitate, which upon filtration gave 5-[4-(*N*-(*tert*-butyloxycarbonyl)amino)phenyl]-1,9-bis(*N*,*N*-dimethylaminomethyl)dipyrromethane (**43**) as a pale yellow solid (112 mg, 52%): ^{1}H NMR δ 1.49 (s, 9H), 2.24 (s, 12H), 3.40−3.51 (m, 4H), 5.33 (s, 1H), 5.74−5.76 (m, 2H), 5.92−5.94 (m, 2H), 6.58 (s, 1H), 7.12 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 8.68 (br, 1H); ^{13}C NMR δ 28.4, 43.8, 44.8, 56.6, 107.0, 108.4, 118.9, 127.5, 129.1, 133.4, 137.1, 137.3; FAB-MS (LR) obsd 450.29, calcd 451.2947 ($C_{26}H_{37}N_5O_2$). A solution of **43** (230 mg, 0.500 mmol) and **16j** (110 mg, 0.500 mmol) in ethanol (50 mL) at room temperature was treated with $Zn(OAc)_2$ (915 mg, 5.00 mmol) and heated to reflux. After 2 h, the reaction mixture was allowed to cool to room temperature. A sample of DDQ (340 mg, 1.50 mmol) was added, and the mixture was stirred for 15 min. TEA (0.348 mL, 2.50 mmol) was added. The reaction mixture was concentrated and chromatographed [column 1; silica, CH_2Cl_2/ethyl acetate (3:2); column 2: silica, CH_2Cl_2/MeOH/TEA (50:20:1)] to give a purple solid (32 mg, 10%): ^{1}H NMR (THF-d_8) δ 1.15 (s, 3H), 1.64 (s, 9H), 2.00 (s, 3H), 4.27 (d, J = 11.3 Hz, 2H), 4.44 (d, J = 11.0 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 8.17 (s, 1H), 8.92 (s, 1H), 9.08 (d, J = 4.4 Hz, 2H), 9.36 (d, J = 4.4 Hz, 2H), 9.45 (d, J = 4.8 Hz, 2H), 10.22 (d, J = 4.8 Hz, 2H), 10.24 (s, 2H); LD-MS obsd 677.7; FAB-MS obsd 677.2037, calcd 677.1981 ($C_{37}H_{35}N_5O_4Zn$); λ_{abs} 406, 536, 571 nm.

B. General Procedure for Porphyrin Metalation. 5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-10,20-di-*p*-tolyl-15-(pentafluorophenyl)porphinatozinc(II) (Zn-2). A solution of **2** (27 mg, 0.031 mmol) in $CHCl_3$ (30 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (200 mg, 0.911 mmol) in methanol (6 mL). After stirring overnight at room temperature, the mixture was concentrated. The residue was dissolved in CH_2Cl_2. Chromatography (silica, CH_2Cl_2) afforded a purple powder (22 mg, 76%): ^{1}H NMR δ 2.75−2.72 (overlapping peaks, 12H), 5.23−5.17 (m, 6H), 5.89−5.84 (m, 3H), 7.57 (d, J = 7.6 Hz, 4H), 7.69 (d, J = 7.9 Hz, 2H), 8.10 (d, J = 7.6 Hz, 4H), 8.16 (d, J = 7.9 Hz, 2H), 8.85 (d, J = 4.6 Hz, 2H), 8.94 (d, J = 4.6 Hz, 2H), 8.99 (d, J = 4.6 Hz, 2H), 9.07 (d, J = 4.6 Hz, 2H); LD-MS obsd 928.2; FAB-MS obsd 928.2527, calcd 928.2543 ($C_{56}H_{41}F_5N_4Zn$); λ_{abs} 419, 547 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-bromo-10,20-di-*p*-tolylporphinatozinc(II) (Zn-4). A solution of **4** (24 mg, 0.03 mmol) in $CHCl_3$ (25 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (300 mg, 1.37 mmol) in methanol (10 mL). The mixture was stirred overnight at room temperature. The mixture was poured into water, and the porphyrin product was extracted with CH_2Cl_2. The organic extracts were washed (aqueous $NaHCO_3$ and water) and dried (Na_2SO_4). Chromatography (silica, hexanes/CH_2Cl_2 1:1) afforded a purple solid (23 mg, 89%): ^{1}H NMR δ 2.72−2.75 (overlapping peaks, 12H), 5.17−5.22 (m, 6H), 5.83−5.91 (m, 3H), 7.56 (d, J = 7.7 Hz, 4H), 7.67 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 7.7 Hz, 4H), 8.12 (d, J = 8.1 Hz, 2H), 8.87 (d, J = 4.8 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.03 (d, J = 4.8 Hz, 2H), 9.77 (d, J = 4.8 Hz, 2H); LD-MS obsd 840.9; FAB-MS obsd 840.1868, calcd 840.1806 ($C_{50}H_{41}N_4BrZn$); λ_{abs} 421, 552, 591 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-(4-aminophenyl)-10,20-di-*p*-tolylporphinatocopper(II) (Cu-10). A solution of **10** (7 mg, 0.009 mmol) in $CHCl_3$ (20 mL) was treated with a solution of $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol) in methanol (6 mL). The mixture was stirred overnight at room temperature. The mixture was poured into water, and the porphyrin product was extracted with CH_2Cl_2. The organic extract was washed (aqueous $NaHCO_3$ and water), dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2), affording a purple solid (7 mg, 90%): ^{1}H NMR δ 2.54 (s, 6H), 2.63 (br, 6H), 3.89 (s, 2H), 5.11 (br, 6H), 5.76 (br, 3H), 6.83 (br, 2H), 7.26 (br, 6H), 7.45 (br, 8H); MALDI-MS (dithranol) obsd 852.8; FAB-MS obsd 852.3193, calcd 852.3127 ($C_{56}H_{47}N_5Cu$); λ_{abs} 419, 541, 578 nm.

C. Other Synthetic Procedures. 5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-bromo-10,20-di-*p*-tolylporphyrin (4). Following a standard procedure,[34,35] a solution of **3** (25.0 mg, 0.035 mmol) in $CHCl_3$ (12 mL) and pyridine (60 μL) was treated with NBS (10.0 mg, 0.057 mmol) at 0 °C. After 30 min, the reaction was quenched with acetone (10 mL). The reaction mixture was washed with H_2O and dried (Na_2SO_4). Chromatography (silica, CH_2Cl_2) afforded a purple solid (24.0 mg, 87%): ^{1}H NMR δ −2.73 (s, 2H), 2.71−2.73 (m, 12H), 5.17−5.22 (m, 6H), 5.80−9.91 (m, 3H), 7.57 (d, J = 7.7 Hz, 4H), 7.66 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 7.7 Hz, 4H), 8.12 (d, J = 8.1 Hz, 2H), 8.77 (d, J = 4.8 Hz, 2H), 8.85 (d, J = 4.8 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.66 (d, J = 4.8 Hz, 2H); LD-MS obsd 779.3; FAB-MS obsd 778.2721, calcd 778.2671 ($C_{50}H_{43}N_4Br$); λ_{abs} 421, 519, 555, 597, 653 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-(4-carboxyphenyl)-10,20-di-*p*-tolylporphinatozinc(II) (Zn-6). A solution of **Zn-5** (12 mg, 12 mmol) in DMF (10 mL) was treated with TBAF (60 μL, 1.0 M solution in THF) at room temperature for 3 h. The reaction mixture was washed with 10% $NaHCO_3$ and water. The organic

layer was dried (Na_2SO_4), concentrated, and chromatographed [silica, $CHCl_2$, then CH_2Cl_2/MeOH (3:1)]. The eluent was concentrated. The residue was treated with a mixture of hexanes/EtOH (1:1) yielding a suspension that was sonicated. Filtration afforded a purple solid (8.0 mg, 75%): ^{1}H NMR (THF-d_8) δ 2.68 (s, 6H), 2.78 (d, J = 7.0 Hz, 6H), 5.15−5.23 (m, 6H), 5.87−5.97 (m, 3H), 7.56 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 8.4 Hz, 4H), 8.07 (d, J = 7.7 Hz, 4H), 8.16 (d, J = 8.1 Hz, 2H), 8.27 (d, J = 7.7 Hz, 2H), 8.41 (br, 2H), 8.82−8.87 (overlapping peaks, 8H); LD-MS obsd 881.8; FAB-MS obsd 882.2912, calcd 882.2912 ($C_{57}H_{46}N_4O_2Zn$); λ_{abs} (THF) 424, 557, 587 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-(4-aminophenyl)-10,20-di-*p*-tolylporphyrin (10). A solution of **9** (20.0 mg, 0.022 mmol) in $CHCl_3$ (20 mL) was treated with TFA (5 mL) at 0 °C. The mixture was stirred for 45 min. Then, the mixture was poured into water, and the porphyrin product was extracted with CH_2Cl_2. The organic extract was washed (aqueous $NaHCO_3$ and water), dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2), affording a purple solid (17 mg, 96%): ^{1}H NMR δ −2.75 (s, 2H), 2.71 (s, 6H), 2.73 (d, J = 7.0 Hz, 6H), 4.01 (s, 2H), 5.17−5.22 (m, 6H), 5.83−5.92 (m, 3H), 7.06 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 4H), 7.68 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 7.7 Hz, 4H), 8.16 (d, J = 8.1 Hz, 2H), 8.81 (d, J = 4.8, 2H), 8.86−8.88 (m, 4H), 8.91 (d, J = 4.8, 2H); LD-MS obsd 791.4; FAB-MS obsd 792.4125, calcd 792.4066 [$(M + H)^+$; $C_{56}H_{49}N_5$]; λ_{abs} 422, 519, 555, 593, 649 nm.

5-[4-(*N*-(*tert*-Butoxycarbonyl)amino)phenyl]dipyrromethane (16f). Following a general procedure,[26] a mixture of **15f** (2.00 g, 9.04 mmol) and pyrrole (16 mL, 0.23 mol) was treated with TFA (70 μL, 0.90 mmol) and stirred at room temperature for 30 min. NaOH (0.1 M, 20 mL) and ethyl acetate (50 mL) were added, and the organic layer was separated. After washing with brine and water, the organic extract was dried (Na_2SO_4) and concentrated. The resulting brown residue was chromatographed (silica, CH_2Cl_2) to obtain a pale yellow solid (2.48 g, 81%): mp 141−144 °C (dec); ^{1}H NMR δ 1.51 (s, 9H), 7.43 (s, 1H), 5.92 (m, 2H), 6.14−6.16 (m, 2H), 6.46 (m, 1H), 6.69−6.70 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.93 (br, 2H); ^{13}C NMR δ 28.3, 43.3, 80.6, 107.1, 108.4, 117.1, 118.9, 128.9, 132.5, 136.7, 137.1, 152.8; FAB-MS obsd 337.1791; calcd 337.1790 ($C_{20}H_{23}N_3O_2$).

5-(4-Amino-3,5-dimethylphenyl)dipyrromethane (16g). Following a general procedure,[26] a mixture of aldehyde **15g** (500 mg, 3.35 mmol) and pyrrole (16 mL, 0.23 mol) was treated with TFA (70 μL, 0.90 mmol) and stirred at room temperature for 16 h. The mixture was concentrated. Chromatography (silica, CH_2Cl_2) gave unreacted aldehyde followed by the title compound as a pale yellow solid (175 mg, 20%): mp 137−143 °C (dec); ^{1}H NMR δ 2.14 (s, 6H), 3.47 (s, 2H), 5.34 (s, 1H), 5.94−5.95 (m, 2H), 6.15−6.16 (m, 2H), 6.67−6.68 (m, 2H), 6.81 (s, 2H), 7.90 (br, 2H); ^{13}C NMR δ 17.9, 43.4, 106.9, 108.5, 117.0, 122.2, 128.4, 133.5, 141.8; FAB-MS obsd 265.1572; calcd 265.1579 ($C_{17}H_{19}N_3$).

Dibutyl[5,10-dihydro-5-(pentafluorophenyl)-1,9-di-*p*-toluoyldipyrrinato]tin(IV) (17). Following a standard procedure,[33] EtMgBr (6.4 mL, 6.4 mmol, 1.0 M in THF) was added slowly to a tap-water cooled flask containing a solution of **16a** (400 mg, 1.28 mmol) in toluene (25 mL) under argon. The reaction mixture was stirred at room temperature for 30 min. A sample of *p*-toluoyl chloride (0.42 mL, 3.2 mmol) was added over 10 min. The mixture was stirred for an additional 1 h and then was poured into a mixture of saturated aqueous NH_4Cl and ethyl acetate. The organic layer was washed (water and brine), dried (Na_2SO_4), and concentrated to dryness. The residue was treated with TEA (0.4 mL) and Bu_2SnCl_2 (389 mg, 1.28 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for 30 min and then concentrated. Chromatography [silica, hexanes/CH_2Cl_2 (1:3)] and then crystallization (diethyl ether/methanol) afforded pale pink crystals (180 mg, 18%): mp 139−142 °C (dec); ^{1}H NMR δ 0.72 (t, J = 7.3 Hz, 3H), 0.75 (t, J = 7.3 Hz, 3H), 1.25−1.15 (m, 4H), 1.48−1.34 (m, 4H), 1.63−1.55 (m, 4H), 2.45 (s, 6H), 7.01 (d, J = 3.8 Hz, 2H), 6.12 (s, 1H), 7.01 (d, J = 3.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 4H), 7.83 (d, J = 8.0 Hz, 4H); ^{13}C NMR δ 13.7, 13.8, 21.8, 24.4, 24.7, 26.3, 26.4, 27.2, 25.5, 34.1, 114.0, 123.7, 129.3, 129.4, 134.9, 135.7, 142.6, 147.3, 185.2; FAB-MS obsd 781.1915, calcd 781.1875 [$(M + H)^+$; M = $C_{39}H_{37}F_5N_2O_2Sn$]. Anal. Calcd for $C_{39}H_{37}F_5N_2O_2Sn$: C, 60.10; H, 4.78; N, 3.59. Found: C, 60.12; H, 4.76; N, 3.67.

5-(4-Hydroxymethylbiphen-4′-yl)-10,15,20-tri-*p*-tolylporphyrinatozinc(II) (Zn-28). Following a standard procedure,[42] a mixture of **Zn-26** (100 mg, 0.125 mmol), 4-(hydroxymethyl)phenylboronic acid (**27**) (38.0 mg, 0.250 mmol), anhydrous K_2CO_3 (138 mg, 0.998 mmol), and $Pd(PPh_3)_4$ (21.7 mg, 0.0188 mmol) in DMF/toluene (12.5 mL) was reacted at 85 °C for 16 h using Schlenk techniques. The reaction mixture was concentrated to dryness. The resulting crude product was chromatographed (silica, CH_2Cl_2), affording a purple solid (93.0 mg, 90%): ^{1}H NMR (THF-d_8) δ 2.54 (s, 6H), 2.69 (s, 3H), 4.32 (t, J = 6.0 Hz, 1H), 4.71 (d, J = 6.0 Hz, 2H), 7.56 (d, J = 7.6 Hz, 8H), 7.93 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 8.08 (d, J = 8.0 Hz, 6H), 8.26 (d, J = 7.6 Hz, 2H), 8.84 (s, 4H), 8.87 (d, J = 4.8 Hz, 2H), 8.92 (d, J = 4.8 Hz, 2H); LD-MS obsd 824.5; FAB-MS obsd 824.2430, calcd 824.2494 ($C_{54}H_{40}N_4OZn$); λ_{abs} (toluene) 425, 552, 593 nm; λ_{em} (λ_{ex} 550 nm) 603, 650 nm.

5-(4-Isothiocyanatophenyl)-10,15,20-trimesitylporphinatozinc-(II) (Zn-30). A solution of **29** (40 mg, 0.053 mmol) in $CHCl_3$ (5 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (58 mg, 0.26 mmol) in methanol (1 mL) with stirring at room temperature for 15 h. Chromatography [silica, $CHCl_3$/THF (98:2)] afforded 5-(4-aminophenyl)-10,15,20-trimesitylporphinatozinc(II) (**Zn-29**) as a purple solid (41 mg, 95%). Following a literature procedure,[43] a solution of this sample of **Zn-29** (40 mg, 0.049 mmol) in dry CH_2Cl_2 (10 mL) was treated with 1,1′-thiocarbonyldi-2(1*H*)-pyridone (TDP) (23 mg, 0.098 mmol) with stirring at room temperature under argon for 2 h. Chromatography (silica, CH_2Cl_2) afforded a purple solid (42 mg, 100%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.83−1.86 (overlapping peaks, 18H), 2.63 (s, 9H), 7.31 (s, 6H), 7.65 (d, J = 8.4 Hz, 2H), 8.24 (d, J = 8.1 Hz, 2H), 8.70−8.75 (m, 4H), 8.77 (d, J = 4.8 Hz, 2H), 8.84 (d, J = 4.5 Hz, 2H); LD-MS obsd 860.1; FAB-MS obsd 859.2712, calcd 859.2687 ($C_{54}H_{45}N_5SZn$); λ_{abs} (toluene) 423, 550 nm.

5,15-Dibromo-10,20-dimesitylporphinatozinc(II) (Zn-31). Following a standard procedure,[34,35] a solution of **38** (50 mg, 0.091 mmol) in $CHCl_3$ (30 mL) and pyridine (40 μL) was treated with NBS (40 mg, 0.23 mmol) at 0 °C. After 1 h, the reaction was quenched by addition of acetone (5 mL). The reaction mixture was washed with H_2O, dried (Na_2SO_4), and concentrated. The crude solid was dissolved in $CHCl_3$ (20 mL) and treated overnight at room temperature with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (200 mg, 0.911 mmol) in methanol (6 mL). Chromatography [silica, hexanes/$CHCl_3$ (2:1)] afforded a purple solid (50 mg, 71%): ^{1}H NMR (THF-d_8) δ 1.84 (s, 12H), 2.64 (s, 6H), 7.33 (s, 4H), 8.67 (d, J = 4.8 Hz, 4H), 9.59 (d, J = 4.4 Hz, 4H); LD-MS obsd 767.4; FAB-MS obsd 764.0140, calcd 764.0129 ($C_{38}H_{30}Br_2N_4Zn$); λ_{abs} (THF) 428, 565, 607 nm.

5,15-Bis[(4-hydroxymethyl)phenyl]-10,20-dimesitylporphinatozinc(II) (Zn-32). A solution of **Zn-39** (28 mg, 0.032 mmol) in dry THF (15 mL) was treated with $LiAlH_4$ (20 mg, 0.53 mmol) under argon at room temperature for 1 h. Methanol was slowly added to destroy the excess $LiAlH_4$. The solvent was evaporated under reduced pressure. Chromatography (silica, CH_2Cl_2) afforded a purple powder (21 mg, 80%): ^{1}H NMR δ 1.83 (s, 12H), 2.63 (s, 6H), 4.95 (d, J = 5.12 Hz, 4H), 7.28 (s, 4H), 7.68 (d, J = 7.7 Hz, 4H), 8.22 (d, J = 8.1 Hz, 4H), 8.77 (d, J = 4.4 Hz, 4H), 8.87 (d, J = 4.8 Hz, 4H); LD-MS obsd 820.3; FAB-MS obsd 820.2736, calcd 820.2756 ($C_{52}H_{44}N_4O_2Zn$); λ_{abs} 420, 548 nm.

5,15-Bis[4-(cyanomethyl)phenyl]-10,20-dimesitylporphinatozinc-(II) (Zn-33). Following a standard procedure,[47] a solution of **Zn-40** (20 mg, 0.022 mmol) in acetonitrile/THF [20 mL, 1:1] was treated with KCN (24 mg, 0.37 mmol) and 18-crown-6 (3 mg, 0.01 mmol) with stirring at room temperature for 2 days. The reaction

mixture was concentrated and chromatographed (silica, CH_2Cl_2) to give a purple solid (17 mg, 96%): ^{1}H NMR δ 1.83 (s, 12H), 2.61 (s, 6H), 4.24 (s, 4H), 7.30 (s, 4H), 7.75 (d, J = 7.7 Hz, 4H), 8.21 (d, J = 8.1 Hz, 4H), 8.67 (d, J = 4.4 Hz, 4H), 8.78 (d, J = 4.4 Hz, 4H); LD-MS obsd 838.5; FAB-MS obsd 838.2768, calcd 838.2762 ($C_{54}H_{42}N_6Zn$); λ_{abs} (THF) 423, 557, 596 nm; λ_{abs} 421, 549 nm.

5,15-Bis(4-aminophenyl)-10,20-dimesitylporphyrin (34). A solution of **41** (60 mg, 0.065 mmol) in $CHCl_3$ (20 mL) was treated with TFA (5 mL) at 0 °C with stirring for 45 min at room temperature. The mixture was poured into water, and the porphyrin product was extracted with CH_2Cl_2. The organic extract was washed (aqueous $NaHCO_3$ and water), dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2) to give a purple solid (47 mg, 99%): ^{1}H NMR δ −2.59 (s, 2H), 1.84 (s, 12H), 2.63 (s, 6H), 4.02 (s, 4H), 7.06 (d, J = 8.1 Hz, 4H), 7.28 (s, 4H), 7.99 (d, J = 8.1 Hz, 4H), 8.66 (d, J = 4.8 Hz, 4H), 8.87 (d, J = 4.8 Hz, 4H); LD-MS obsd 728.9; FAB-MS obsd 729.3712, calcd 729.3706 [(M + H)$^+$; M = $C_{50}H_{44}N_6$); λ_{abs} 423, 519, 556, 595, 652 nm.

5,15-Bis(4-isothiocyanatophenyl)-10,20-dimesitylporphyrin (35). Following a literature procedure,[48] a solution of **34** (32 mg, 0.044 mmol) in $CHCl_3$ (20 mL) was treated with di-2-pyridyl thiocarbonate (DPTC) (21 mg, 0.090 mmol) with stirring at room temperature. TLC analysis (silica, CH_2Cl_2) after 2 h indicated incomplete reaction, whereupon additional DPTC (10 mg, 0.043 mmol) was added. The reaction mixture was stirred for 1 h. The reaction mixture was concentrated and chromatographed (silica, CH_2Cl_2) to give a purple solid (26 mg, 73%): ^{1}H NMR δ −2.65 (s, 2H), 1.84 (s, 12H), 2.64 (s, 6H), 7.30 (s, 4H), 7.62 (d, J = 8.1 Hz, 4H), 8.21 (d, J = 8.4 Hz, 4H), 8.73−8.75 (m, 8H); LD-MS obsd 812.7; FAB-MS obsd 813.2823, calcd 813.2834 [(M + H)$^+$; M = $C_{52}H_{40}N_6S_2$]; λ_{abs} (THF) 420, 516, 551, 559, 647, 601 nm.

5,15-Diformyl-10,20-di-*p*-tolylporphinatozinc(II) (Zn-37). Following a standard procedure,[30] a solution of **42** (20.0 mg, 0.028 mmol) in CH_2Cl_2 (24 mL) was treated with TFA/H_2O (2.8 mL, 2:1) at room temperature. TLC analysis after 16 h indicated incomplete reaction. An additional amount of TFA/H_2O [5 mL (2:1)] was added, and the reaction mixture was stirred at room temperature for 16 h. After standard workup, the crude **37** was dissolved in $CHCl_3$ (20 mL) and treated overnight with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (100 mg, 0.456 mmol) in methanol (6 mL) at room temperature. The product obtained upon chromatography (silica, CH_2Cl_2) was washed with hexanes and with ethanol, affording a purple powder (10.0 mg, 60%): ^{1}H NMR (THF-d_8) δ 2.73 (s, 6H), 7.62 (d, J = 7.3 Hz, 4H), 8.07 (d, J = 8.1 Hz, 4H), 8.97 (d, J = 4.8 Hz, 4H) 10.16 (d, J = 4.8 Hz, 4H), 12.65 (s, 2H) LD-MS obsd 608.7; FAB-MS obsd 608.1211, calcd 608.1191 ($C_{36}H_{24}N_4O_2Zn$); λ_{abs} (THF) 432, 633 nm.

5-(4-Aminophenyl)-15-formylporphinatozinc(II) (Zn-45). A solution of **Zn-44** (20 mg, 0.029 mmol) in CH_2Cl_2 (20 mL) was treated with TFA/H_2O (1.4 mL, 1:1) at room temperature for 16 h. The organic layer was washed (5% aqueous $NaHCO_3$ and water), dried (Na_2SO_4), and concentrated. The ^{1}H NMR spectrum showed incomplete deprotection of the amino group. The solid was dissolved in CH_2Cl_2 (20 mL), and TFA (4 mL) was slowly added. After 1 h, the organic layer was washed (5% aqueous $NaHCO_3$ and water), dried (Na_2SO_4), and concentrated. The resulting residue was dissolved in $CHCl_3$ (20 mL) and treated with $Zn(OAc)_2 \cdot 2H_2O$ (200 mg, 0.911 mmol) at room temperature for 16 h. Chromatography (silica, CH_2Cl_2) afforded a purple-green solid, which proved somewhat unstable on chromatography (3 mg, 20%): ^{1}H NMR (THF-d_8) δ 5.00 (br, 2H), 7.01 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 9.07 (d, J = 4.4, 2H), 9.25 (d, J = 4.4 Hz, 2H), 9.48 (d, J = 4.4 Hz, 2H), 10.20 (s, 2H), 10.30 (d, J = 4.8 Hz, 2H), 12.61 (s, 1H); MALDI-MS (dithranol) obsd 491.3, calcd 491.1 ($C_{27}H_{17}N_5O$); λ_{abs} (THF) 421, 557, 597 nm.

D. Physical Studies. Materials. The substrates for surface attachment were prepared from commercially available highly doped p-type Si(100) wafers. The anhydrous solvents and chemicals used in the preparation of the porphyrin monolayers, the in situ synthesis studies, and the electrochemical and FTIR characterization include benzonitrile, CH_2Cl_2, *N*,*N*-dimethylacetamide (DMAc), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPTC), 4,4′-methylenedianiline (MDA), and 4,4′-methylene-bis(2,6-dimethylaniline) (MMDA); all were used as received. The propylene carbonate used for the electrochemical studies was dried on molecular sieves before use. The Bu_4NPF_6 supporting electrolyte was recrystallized three times from methanol and dried at 110 °C under vacuum.

Porphyrin Monolayer Preparation. The porphyrin monolayers on Si(100) were prepared using a high-temperature (400 °C), short time (2 min) "baking" attachment procedure described previously.[5] The monolayers for the electrochemical experiments were prepared by dispensing a 2 μL drop of the porphyrin solution onto the surface of a microelectrode contained in a sparged VOC vial sealed under Ar. The monolayers prepared for the FTIR experiments utilized much larger platforms ($\sim$1 cm^2) and consequently required a larger drop size, $\sim$50 μL. After deposition, the vial containing the Si substrate was heated on a hotplate at 400 °C for 2 min and then removed and purged with Ar until cooling to room temperature. Finally, the Si substrate was rinsed, sonicated five times with anhydrous CH_2Cl_2, and purged dry with Ar.

In Situ Synthesis Studies. The studies of in situ formation of porphyrin dyads were performed by first preparing a particular porphyrin monolayer as described above. The cleaned and washed substrate was then placed in a sealed vial and purged with Ar, and a drop of the solution containing the second porphyrin was introduced (5 and 50 μL for the electrochemical and FTIR substrates, respectively). After deposition, the vial containing the Si substrate was heated on a hotplate at 400 °C for 2 min and then removed and purged with Ar until cooling to room temperature. Finally, the Si substrate was rinsed, sonicated five times with anhydrous CH_2Cl_2, and purged dry with Ar.

The studies of in situ formation of polyimides on the **Zn-10** monolayers followed the same general procedure as that described above for the porphyrin dyads with the following modifications. (1) After deposition of the BPTC solution (5 mM in DMAc) onto the porphyrin-modified substrate, the substrate was heated on a hotplate at 280 °C for 2 min, removed and purged under Ar until cooling to room temperature, washed and sonicated with CH_2Cl_2, and dried with Ar. (2) After electrochemical or spectroscopic interrogation, the sample was again washed and dried, and a solution of MDA/MMDA (5 mM in DMAc) was introduced onto the substrate. The sample was then heated at 280 °C for 2 min, removed and purged under Ar until cooled to room temperature, washed and sonicated with CH_2Cl_2, and dried with Ar. (3) After the second electrochemical and spectroscopic interrogation, the sample was rewashed and dried, and the above procedure was repeated with alternating doses of BPTC and MDA/MMDA.

Electrochemical Measurements. The electrochemical measurements of the porphyrins in solution were made in a standard three-electrode cell using Pt working and counterelectrodes and a Ag/Ag$^+$ reference electrode. The solvent/electrolyte was CH_2Cl_2 containing 0.1 M *n*-Bu_4NPF_6.

The electrochemical measurements on the porphyrin monolayers were performed in a two-electrode configuration using highly doped p-type Si(100) working electrodes (100 × 100 μm) and a Ag counter-/reference electrode, fabricated as described earlier.[10] Propylene carbonate containing 1.0 M *n*-Bu_4NPF_6 was used as solvent/electrolyte. The cyclic voltammograms were recorded using a Gamry Instruments PC4−FAS1 femtostat running PHE 200 framework and Echem Analyst software. The charge density in the monolayer was determined by integration of the total charge of both anodic waves and by using the geometrical dimensions of the microelectrode. The surface coverage of the porphyrin monomers and dyads was determined by scaling the charge density by a factor of 2 or 4, respectively.

FTIR Spectroscopy. The FTIR spectra of the porphyrins in both solid and monolayer forms were collected at room temperature with

a spectral resolution of 4 cm^{-1}. The spectra of the solid porphyrin samples were obtained in KBr pellets (∼1−2 wt % porphyrin). These spectra were collected in transmission mode using a room-temperature DTGS detector by averaging over 32 scans.

The IR spectra of the monolayers were obtained using a Harrick Scientific horizontal reflection Ge-attenuated total reflection accessory (GATR, 65° incidence angle). The Si substrates were placed in contact with the flat surface of a semispherical Ge crystal that serves as the optical element, and IR spectra were collected with p polarized light using a liquid-nitrogen cooled medium-bandwidth MCT detector (600−4000 cm^{-1}) and averaging 256 scans. The Ge crystal was cleaned with neat 2-butanone before every experiment, and the GATR accessory was purged with dry N_2 during data acquisition. The spectra of porphyrin monolayers were referenced against that of a hydrogen-terminated Si(100) surface previously subjected to the same deposition conditions as those used to obtain the monolayer but using only the neat deposition solvent.

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Supporting Information Available: Complete Experimental Section including an alternative synthesis of **42**; ^1H NMR and ^{13}C NMR spectra for selected compounds; and LD-MS and/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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