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Porphyrin Dyads Bearing Carbon Tethers for Studies of High-Density Molecular Charge Storage on Silicon Surfaces

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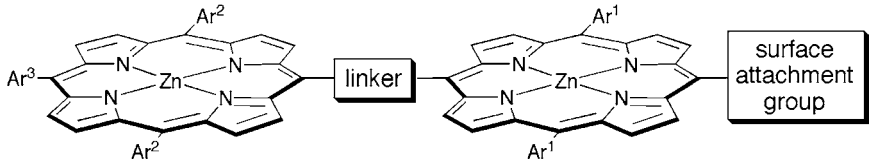

Redox-active molecules that afford high charge density upon attachment to an electroactive surface are of interest for use in molecular-based information-storage applications. One strategy for increasing charge density is to covalently link a second redox center to the first in an architecture that uses the vertical dimension in essentially the same molecular footprint. Toward this end, a set of four new porphyrin dyads have been prepared and characterized. Each dyad consists of two zinc porphyrins, an intervening linker (*p*-phenylene or 4,4′-diphenylethyne), and a surface attachment group (ethynyl or triallyl group). The porphyrin dyads were attached to an electroactive Si(100) surface and interrogated via electrochemical and FTIR techniques. The charge density obtainable for the ethynyl-functionalized porphyrin dyads is approximately double that observed for an analogously functionalized monomer, whereas that for the triallyl-functionalized dyads is at most 40% larger. These results indicate that the molecular footprint of the former dyads is similar to that of a monomer while that of the latter dyads is larger. For both the ethynyl- and triallyl-functionalized porphyrin dyads, higher charge densities (smaller molecular footprints) are obtained for the molecules containing the 4,4′-diphenylethyne versus the *p*-phenylene linker. This feature is attributed to the enhanced torsional flexibility of the former linker compared with that of the latter, which affords better packed monolayers. The FTIR studies indicate that the adsorption geometry of all the dyads is qualitatively similar and similar to that of monomers. However, the dyads containing the 4,4′-diphenylethyne linker sit somewhat more upright on the surface than those containing the *p*-phenylene linker, generally consistent with the smaller molecular footprint for the former dyads. Collectively, the high surface charge density (34−58 $\mu C \cdot cm^{-2}$) of the porphyrin dyads makes these constructs viable candidates for molecular-information-storage applications.

Introduction

Over the past few years we have been working to develop an approach for molecular-based information storage. In this approach, redox-active molecules are employed to store charge, where the presence of stored charge at a given potential represents the storage of information. This approach is amenable to implementation in a hybrid technology, where the charge-storage molecules replace the semiconductor material that serves as the charge-storage medium in existing memory or processing chips.[1] As part of this program, we have prepared a wide variety of redox-active molecular architectures as candidates for information-storage applications. The design of the information-storage molecules includes a redox-active unit and a tether for attachment to a surface. The molecules prepared to date, which are primarily porphyrinic in nature, have been designed for attachment to gold (via thiol groups),[2] silicon or germanium

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(1) (a) Roth, K. M.; Dontha, N.; Dabke, R. B.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. *J. Vac. Sci. Technol., B* **2000**, *18*, 2359−2364. (b) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543−1545.

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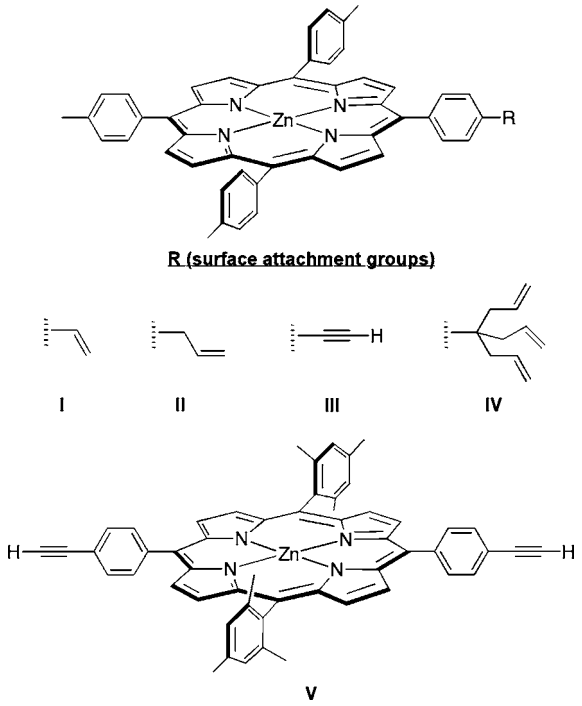
CHART 1



(via alcohol, thiol, selenol, or diverse carbon tethers),[3,4] and a wide variety of metal oxides (via phosphonic acid groups).[5]

A key advantage of employing molecules for charge storage is that redox-active molecules afford significantly higher charge density than semiconductors. For example, compounds **I**−**III** (Chart 1) each exhibit saturation surface coverages of ∼0.9×10^{-10} mol·cm^{-2} (molecular footprints, ∼190 Å^2), which afford a charge density of ∼17 μC·cm^{-2} (based on two electrons per porphyrin).[4,6] Compound **IV** (Chart 1), which bears a triallyl tether, exhibits an even higher saturation surface coverage of ∼2.2×10^{-10} mol·cm^{-2} (molecular footprint, ∼75 Å^2), which affords a charge density of ∼43 μC·cm^{-2}.[7] The charge-storage densities for all of these "molecular capacitors" are considerably higher than the 1−2 μC·cm^{-2} afforded by Si/SiO_2 capacitors currently used in dynamic random access memories.[8] Regardless, as feature sizes continue to shrink, still higher charge-storage densities are desirable.

To further increase the charge density, multilayer architectures composed of redox-active molecules are required, where the redox-active molecules remain electrochemically accessible from the electroactive surface. In this regard, we previously prepared porphyrin films by the polymerization of diethynylporphyrins such as compound **V**.[9] Electroactive films containing 10−50 or more porphyrins could be obtained by controlling the deposition procedure; however, fine control over a specific number of layers is not available via the polymerization approach. We have also previously prepared several porphyrin dyads bearing a single surface attachment group such as thioacetyl[10] or phosphonic acid[5] for attachment to gold or metal oxide surfaces, respectively. However, dyads bearing hydrocarbon tethers, as desired for attachment to silicon, have not been prepared.

In this paper, we describe the synthesis of a set of porphyrin dyads bearing hydrocarbon tethers. The tethers include an ethynyl group and a triallyl group. The dyads have been attached to silicon for studies of charge storage. This work illustrates the utility of presynthesized dyads for exploiting the vertical dimension to achieve increased charge density, as desired for use in information-storage applications.

Results and Discussion

Molecular Design and Synthesis Strategy. The target dyads are shown in Chart 2. The two porphyrins in each dyad are joined by a *p*-phenylene or a 1,4-diphenylethyne unit. The surface attachment group consists of an ethyne or a triallyl moiety. The synthesis of the diphenylethyne-linked dyads relies on well-established methodology, whereby iodo- and ethynyl-substituted porphyrin building blocks are joined via Sonogashira coupling reactions. Such reactions proceed under mild conditions, afford a good yield of the multiporphyrin array, and have been extensively used to prepare porphyrin-based light-harvesting arrays.[11] Phenylene-linked porphyrin dyads lacking surface attachment groups have been prepared by Suzuki coupling reactions in a strategy mirroring that for Sonogashira coupling.[12] However, we did not expect that the ethynyl or the triallyl groups would readily survive the Suzuki coupling process, which entails more forcing conditions. Accordingly, new synthetic routes to *p*-phenylene-linked porphyrin dyads were developed that avoid any Pd-mediated coupling reactions.

Two general strategies for the preparation of the *p*-phenylene-linked dyads are illustrated in Figure 1. Both routes rely on successive condensation reactions and extend approaches we have developed previously for *p*-phenylene-linked dyads and triads (lacking surface attachment).[13,14] The dyad bearing the ethyne was prepared via a linear sequence (A + B + C + D) from one end to the other along the axis of the molecule. The dyad bearing the triallyl moiety was prepared via a divergent strategy, beginning with the *p*-phenylene-linked core unit (A)

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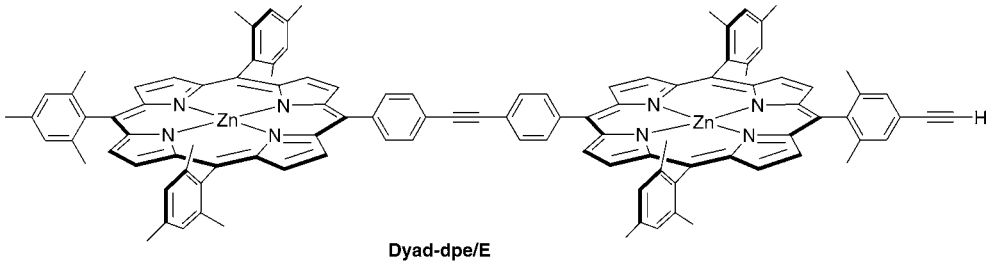
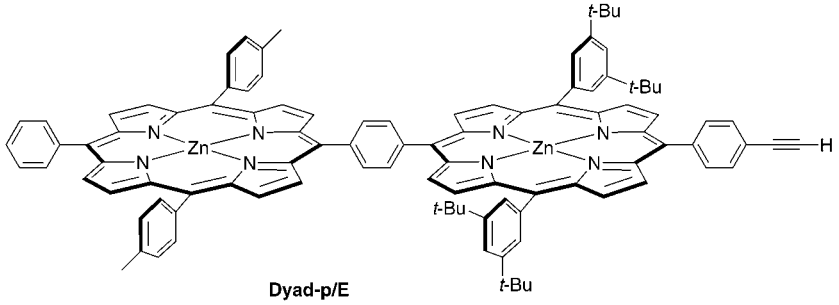
CHART 2



Dyad-dpe/E



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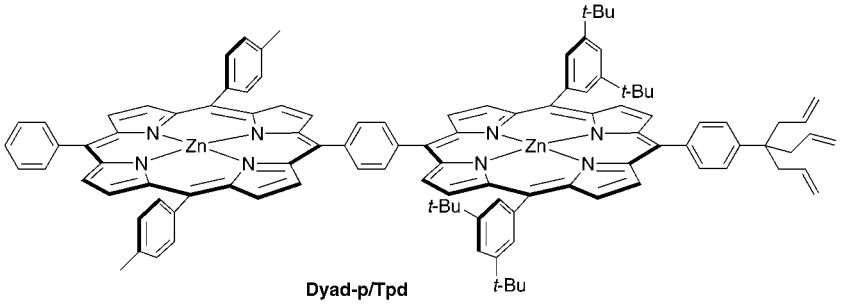

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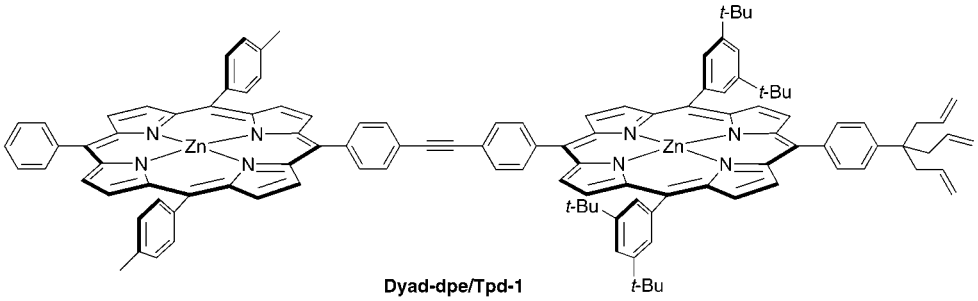
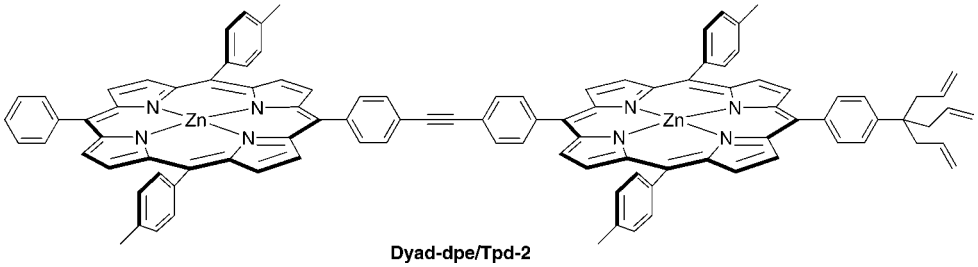


Dyad-dpe/Tpd-1



Dyad-dpe/Tpd-2

and then successively adding the end units (B, C) to create the two porphyrins. In this manner, the triallyl unit is added in the final stage of the synthesis. The syntheses are described in more detail below. Each new porphyrin was characterized by absorption and fluorescence spectroscopy, ^{1}H NMR spectroscopy, laser-desorption mass spectrometry (LD-MS),[15] and high-resolution FAB-MS. Each dyad was characterized by the same techniques as well as by analytical size exclusion chromatography.[16]

Synthesis. A. Linear Synthesis of a *p*-Phenylene-Linked Dyad. The synthesis of **Dyad-p/E** is shown in Scheme 1. The early stages of the synthesis (**1a**, **2**−**4**) have been described elsewhere[17] and are shown here for completeness and for a comparison of linear versus divergent strategies. Porphyrin

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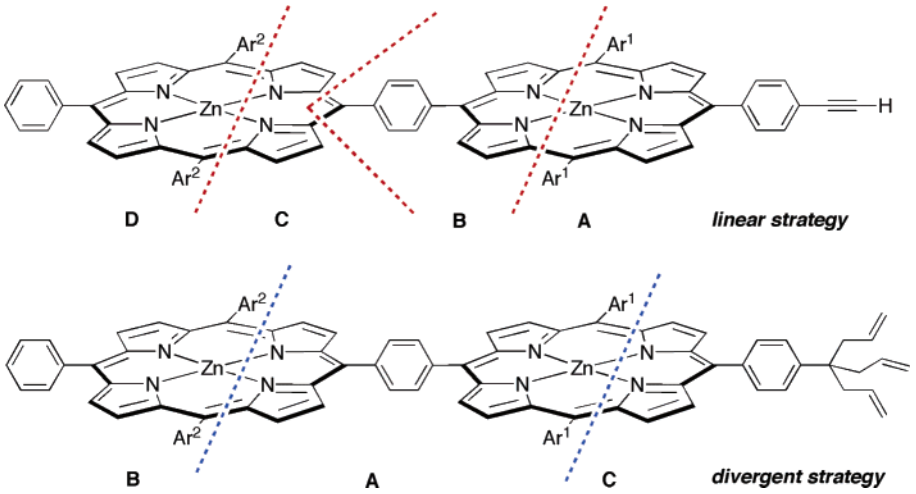
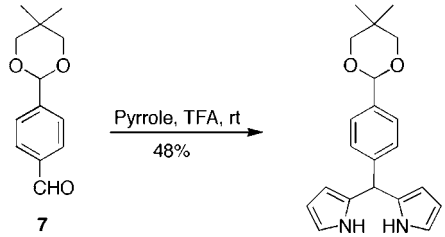


FIGURE 1. Successive condensation reactions are employed to create the *p*-phenylene-linked dyads. Upper: a linear sequence entails porphyrin formation (A + B), dipyrromethane formation (+ C), and porphyrin formation (+ D). Lower: a divergent approach employs the core unit in successive porphyrin-forming reactions (A + B; + C), thereby incorporating the triallyl tether in the final stage of the synthesis.

formation[18] was carried out by the condensation of dipyrromethane **1a**[18,19] and dipyrromethane−dicarbinol **2-diol**[13] in CH_2Cl_2 at room temperature, employing the mild Lewis acid[20] $Yb(OTf)_3$ for catalysis, followed by oxidation with DDQ. The resulting porphyrin−aldehyde **3** was obtained in 30% yield. This condensation proceeds successfully despite the presence of the carboxaldehyde group, illustrating the chemoselective reaction at the carbinol positions. Porphyrin **3** was previously prepared via the TFA-catalyzed condensation of **2-diol** and **1a** in acetonitrile, albeit in lower yield (13%).[13] The porphyrin−aldehyde **3** was treated to slightly modified conditions for dipyrromethane formation,[14,19] employing 300 equiv of pyrrole in CH_2Cl_2 (rather than using neat pyrrole) containing TFA at room temperature for 20 h. Porphyrin−dipyrromethane **4** was obtained in 68% yield.[17] Porphyrin−dipyrromethane **4** has been converted to the corresponding porphyrin−dipyrrin for studies of bis(porphyrin−dipyrrinato) metal complexes.[17] The condensation of **4** and **5-diol**[18,21] with $Yb(OTf)_3$ catalysis,[20] followed by oxidation with DDQ and metalation with zinc acetate, gave dyad **6** in 13% yield. TMS deprotection of the latter by tetrabutyl ammonium fluoride (TBAF) gave **Dyad-p/E** in 98% yield.

B. Divergent Synthesis of a *p*-Phenylene-Linked Dyad. The divergent synthesis of the dyad begins with the synthesis of the core unit (A, Figure 1), which consists of a dipyrromethane and a diacyldipyrromethane linked by a *p*-phenylene unit. The synthesis of a dipyrromethane bearing a protected aldehyde group is shown in eq 1. Compound **7** is available from *p*-cyanobenzaldehyde[22] or *p*-bromobenzaldehyde.[23] Treatment of **7** with excess pyrrole (25 equiv) and a catalytic amount of TFA (0.1 equiv) in a one-flask procedure[24] at room temperature for 5 min afforded dipyrromethane **1b** in 48% yield (∼20 g).



The 1,9-diacylation of dipyrromethane **1b** is shown in Scheme 2. To increase the solubilities of the porphyrins and the larger arrays derived therefrom, 3,5-di-*tert*-butylphenyl groups were employed for the 1,9-diacylation. We encountered difficulties in carrying out this apparently simple transformation with good efficiency using the standard procedures with 3,5-di-*tert*-benzoyl chloride (**8**)[25] or 2-pyridyl 3,5-di-*tert*-butylbenzothioate (**9**).[26] The standard conditions for direct 1,9-diacylation,[18] whereby dipyrromethane **1b** in toluene (50 mM) is treated with EtMgBr (5 equiv), followed by acid chloride **8** (2.5 equiv), afforded 1-acyldipyrromethane **10** (47% yield) and the desired 1,9-diacyldipyrromethane **11** in 25% yield. Alternatively, selective 1-acylation[27] was carried out by the treatment of **1b** in THF at −78 °C with EtMgBr (2.5 equiv), followed by pyridyl thioester **9** (1.0 equiv), affording 1-acyldipyrromethane **10** in 60% yield. 9-Acylation[18] of the 1-acyldipyrromethane **10** by treatment with EtMgBr (2, 2, 1 equiv) and acid chloride **8** (1, 1, 0.5 equiv) sequentially and repeatedly at 10 min intervals, afforded the

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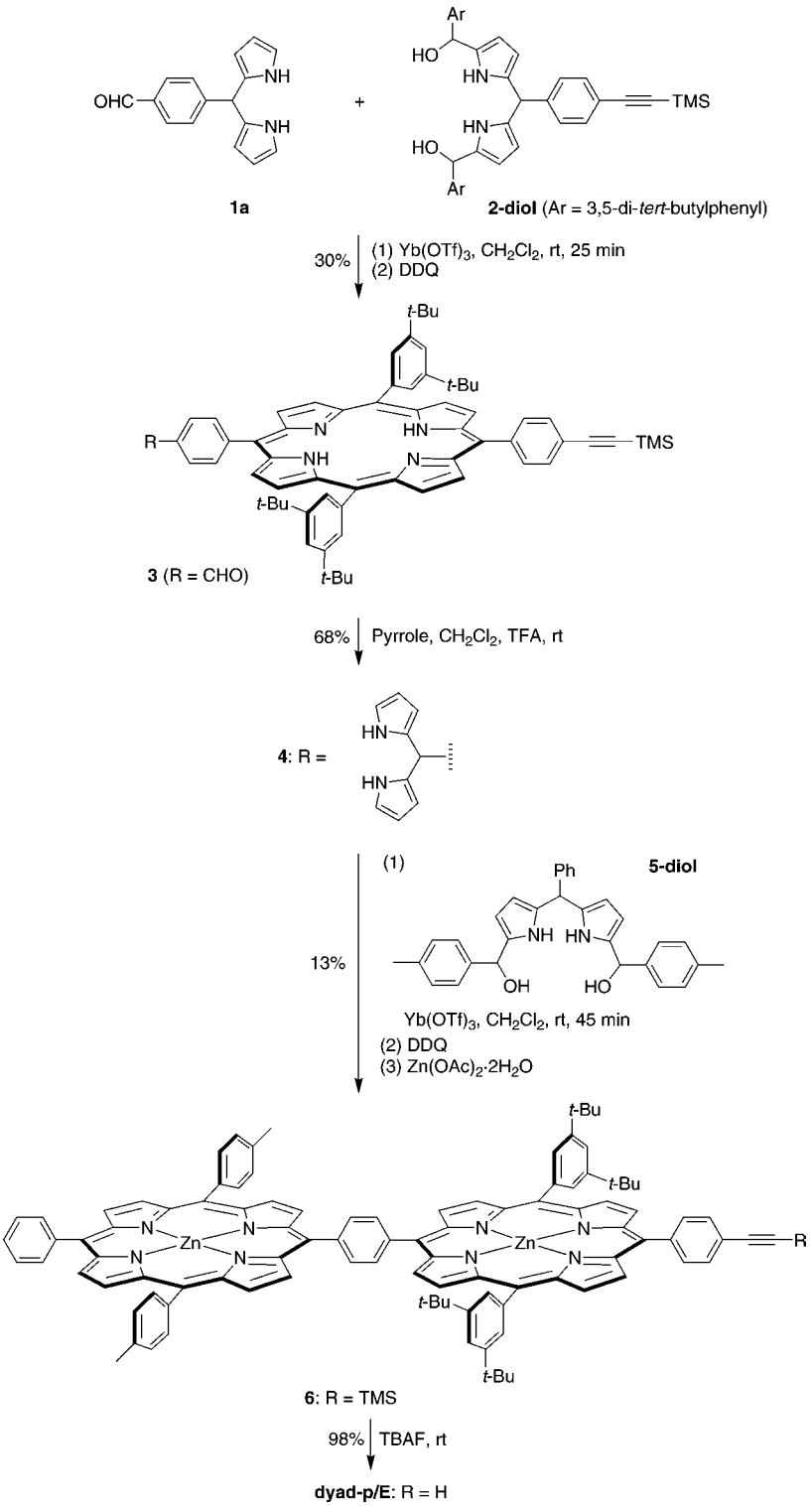
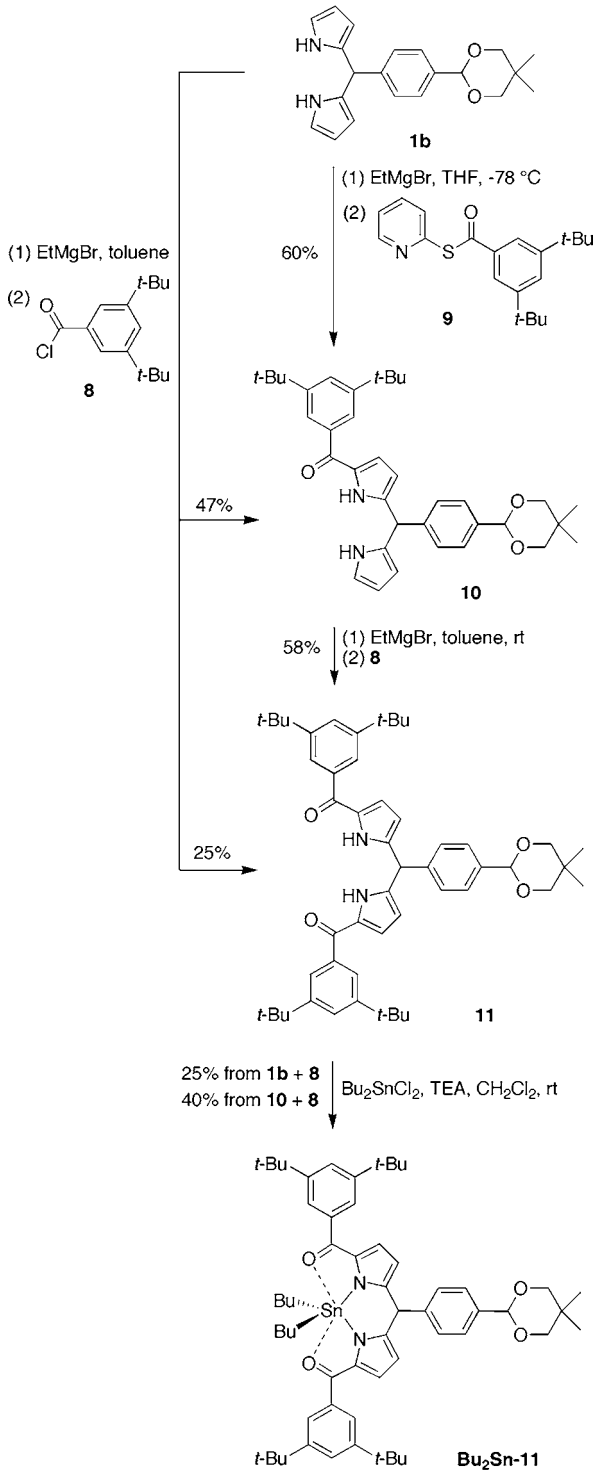
SCHEME 1



1,9-diacyldipyrromethane **11** in 58% yield after chromatographic purification. The overall yield of 1,9-diacyldipyrromethane **11** from dipyrromethane **1b** was 35%, which is similar to that obtained upon direct diacylation. Additional data concerning the 1,9-diacylation are provided in Supporting Information.

We recently discovered that dibutyltin dichloride (Bu_2SnCl_2) can selectively complex a 1,9-diacyldipyrromethane, affording the stable 1,9-diacyldipyrromethane−tin complex in high yield, while the dipyrromethane, 1-acyldipyrromethane, and 1,8-diacyldipyrromethane do not form the corresponding tin complexes.[21] Dialkyltin complexation in this manner affords a more facile means of purifying the desired 1,9-diacyldipyrromethane. This complexation process was applied to the reaction mixtures obtained in the synthesis of **11**. Thus, after a preliminary workup of the acylation reaction (quenching with aqueous NH_4Cl and washing with saturated aqueous $NaHCO_3$ and water), the crude reaction mixture was treated with Bu_2SnCl_2 and triethylamine (TEA) in CH_2Cl_2 at room temperature. The desired 1,9-

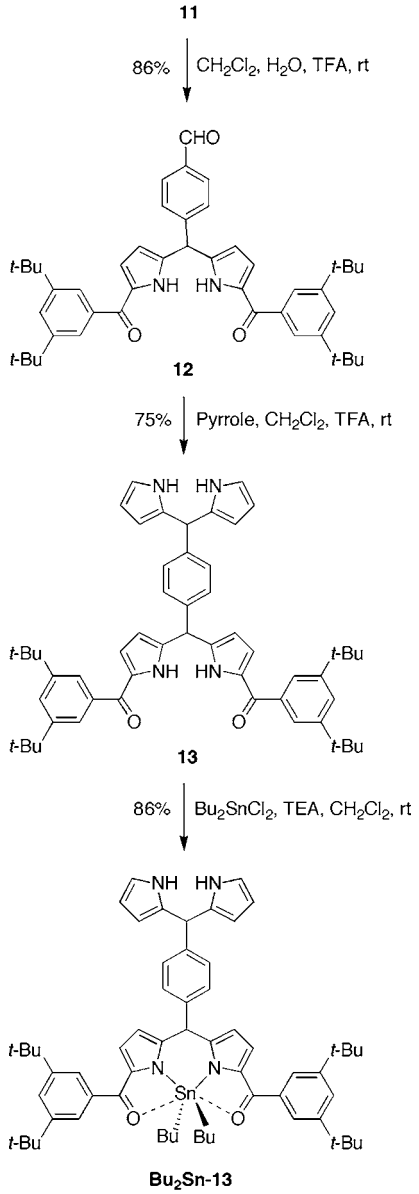
SCHEME 2



diacyldipyrromethane **11** was separated as the corresponding tin complex **Bu_2Sn−11** in 25% yield (direct diacylation of **1b**) and 40% yield (9-acylation of **10**). In each case, the hydrophobic **Bu_2Sn−11** was obtained in a straightforward manner upon passage of the crude reaction mixture over a silica pad. The dialkyltin complex can be decomplexed or used directly in porphyrin-forming reactions.

Deprotection of acetal **11** was achieved in CH_2Cl_2/TFA/water[28] at room temperature for 5.5 h, affording the aldehyde-substituted 1,9-diacyldipyrromethane (**12**) in 86% yield (Scheme 3). The conversion of the aldehyde to the corresponding dipyrromethane was carried out using a slightly modified procedure[14] that employs a mixture of CH_2Cl_2 and excess pyrrole rather than pyrrole alone. Thus, the formyl-substituted 1,9-diacyldipyrromethane **12** was dissolved in a minimum amount of CH_2Cl_2, excess pyrrole (100 equiv) was added, and the resulting mixture was treated with 0.1 equiv of TFA for 10 min at room temperature. Compound **13** was obtained in 75% yield. This synthesis relies on the chemoselective reaction at the aldehyde rather than at the keto groups. Treatment of **13** with Bu_2SnCl_2 and TEA afforded selective complexation of the diacyldipyrromethane moiety in the presence of the dipyrromethane. The hydrophobic product, **Bu_2Sn−13**, was isolated in 86% yield.

SCHEME 3



Condensation of **5-diol** and dipyrromethane−diacyldipyrromethane **13** in the presence of $Yb(OTf)_3$ followed by oxidation

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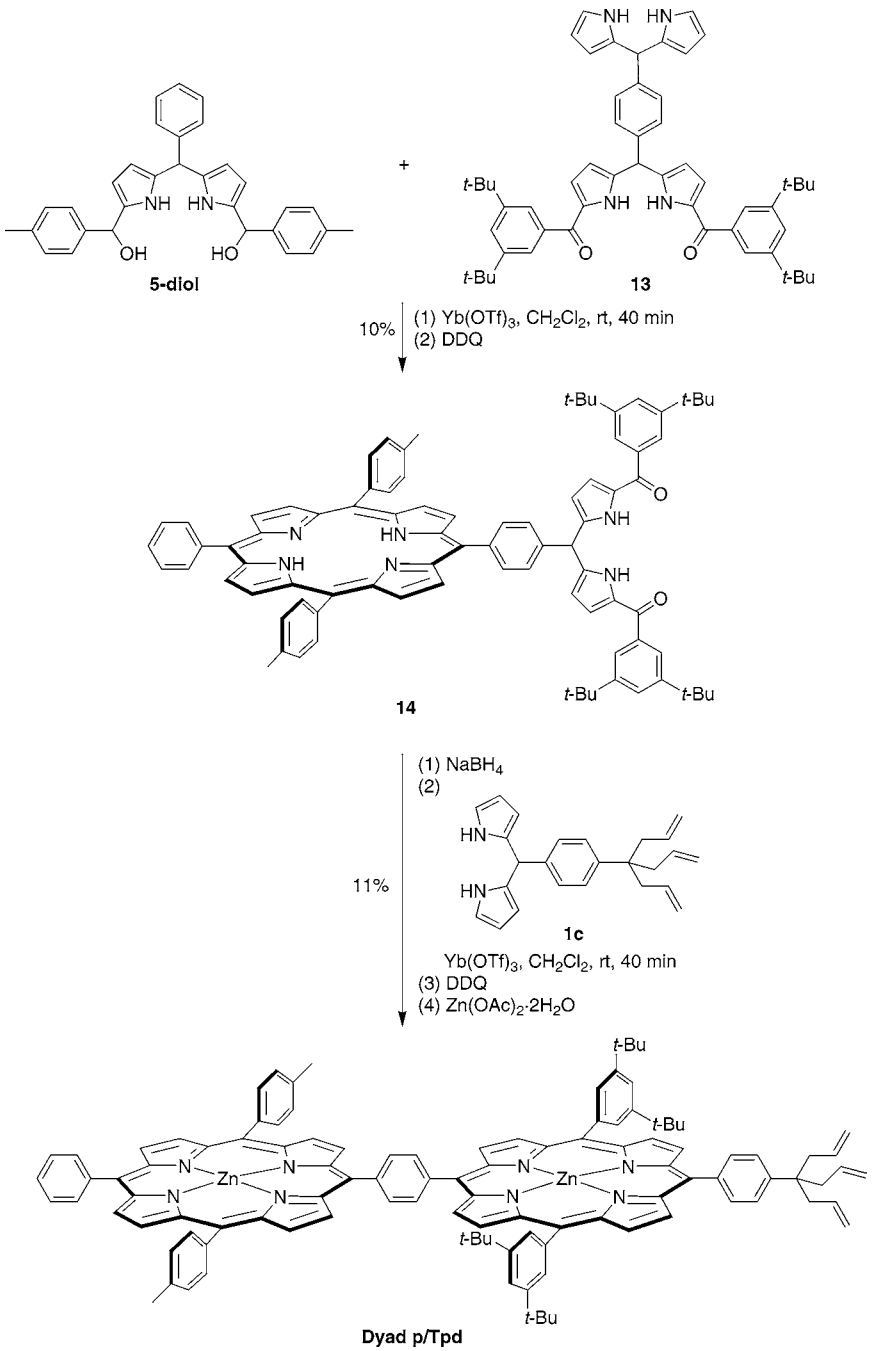
SCHEME 4



with DDQ gave porphyrin−diacyldipyrromethane **14** in 10% yield (Scheme 4). The latter was reduced with $NaBH_4$, and the resulting dipyrromethane−dicarbinol intermediate was reacted with triallyl−dipyrromethane **1c**[7] under $Yb(OTf)_3$-catalyzed conditions. Subsequent oxidation with DDQ and metalation with zinc acetate gave the *p*-phenylene-linked dyad bearing the triallyl tripod (**Dyad-p/Tpd**) in 11% yield.

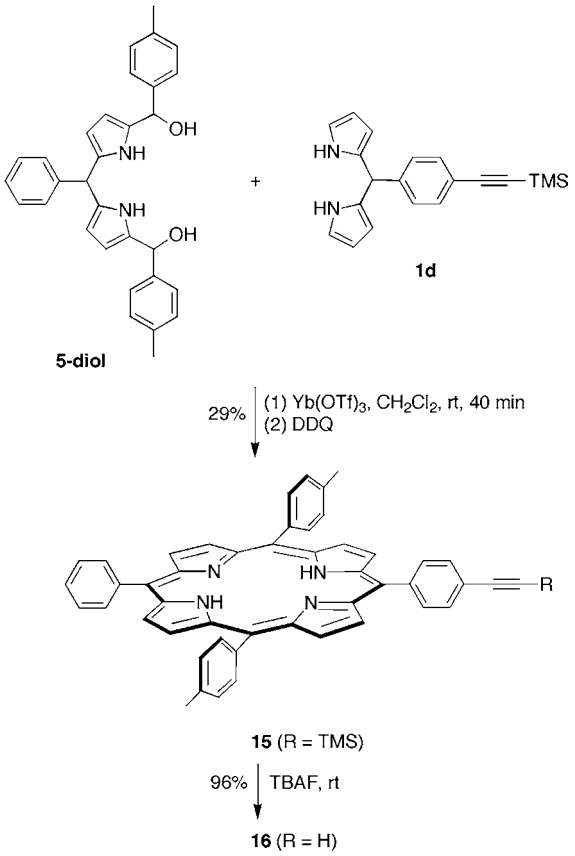
C. Synthesis of Diphenylethyne-Linked Dyads. The synthesis of diphenylethyne-linked dyads can be achieved by the Pd-mediated Sonogashira coupling of a porphyrin bearing a phenylethyne group with a porphyrin bearing a 4-iodophenyl group. The dyad **Dyad-dpe/E** (Chart 2) was prepared in this manner.[16]

The synthesis of an ethynylphenyl-substituted porphyrin is shown in Scheme 5. The condensation of **5-diol** and dipyrromethane **1d**[18,29] under $Yb(OTf)_3$ catalysis followed by oxidation with DDQ afforded the TMS-protected porphyrin **15** in 29% yield. Treatment of porphyrin **15** with TBAF gave ethynylphenyl−porphyrin **16** in 96% yield.

The synthesis of the complementary iodophenyl−porphyrin is shown in Scheme 6. The reduction of diacyldipyrromethane **17**[18] with $NaBH_4$ provided the corresponding dipyrromethane−dicarbinol, which was condensed with triallyl−dipyrromethane **1c** in the presence of $Yb(OTf)_3$ followed by oxidation with DDQ. The resulting porphyrin (**18**) bearing an iodophenyl group and the triallyl tripod was obtained in 33% yield. The Pd coupling of porphyrins **16** and **18** was carried out under standard

(29) Muthukumaran, K.; Ptaszek, M.; Noll, B.; Scheidt, W. R.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 5354−5364.

SCHEME 5



conditions that have been established for use with porphyrinic substrates [2.5 mM reactants in toluene/TEA (5:1) containing tris(dibenzylideneacetone)dipalladium(0), $Pd_2(dba)_3$, and tri(*o*-tolyl)phosphine, P(*o*-tol)$_3$, without any copper cocatalysts].[30] Our concern as to whether this reaction would proceed without Heck-type side reactions owing to the presence of the three allyl groups were unfounded, as the coupling reaction proceeded quite well. The crude mixture was metalated with zinc acetate, affording the desired diphenylethyne-linked dyad (**Dyad-dpe/Tpd-1**) in 51% yield.

Dyad-dpe/Tpd-1 incorporates a 3,5-di-*tert*-butylphenyl group at each of the flanking positions on the porphyrin that bears the tripod. These groups were employed to increase the solubility of the porphyrin dyad in organic solution. Subsequent surface studies (vide infra) raised the question as to whether the bulky *tert*-butyl groups might preclude tight packing of the dyads upon surface attachment. Such concerns prompted the synthesis of a second diphenylethyne-linked dyad lacking the bulky groups. The synthesis is shown in Scheme 7.

The treatment of 5-(4-iodophenyl)dipyrromethane (**1e**)[24,31] to the standard conditions for diacylation (EtMgBr, followed by the reaction with *p*-toluoyl chloride) afforded the corresponding 1,9-diacyldipyrromethane **19** in 27% yield. The reduction of **19** with $NaBH_4$ gave the corresponding dipyrromethane−dicarbinol, which was reacted with triallyl−dipyrromethane **1c** in the presence of Yb(OTf)$_3$ followed by oxidation with DDQ. The resulting free-base porphyrin **20** was obtained in 13% yield. The Pd coupling of ethynylphenyl−porphyrin **16** and iodophenyl−porphyrin **20** was carried out in the same manner as for **Dyad-dpe/Tpd-1**. The resulting all-free-base porphyrin dyad **21** was obtained in 91% yield. The metalation of **21** with zinc acetate afforded **Dyad-dpe/Tpd-2** in 97% yield.

Monolayer Characterization. Monolayers of the dyads were prepared on hydrogen-passivated Si(100) substrates by using a high-temperature (400 °C) "baking" procedure previously shown to give facile attachment of alkenyl- and alkynyl-functionalized porphyrins to Si(100) surfaces;[4] characterization included interrogation via electrochemical and FTIR techniques. The general electrochemical and vibrational characteristics of the dyad monolayers are similar to those we have previously reported for porphyrin monomers tethered to Si(100) via carbon tethers.[4,6,7] Consequently, we will not reiterate these general features herein but rather only describe key features that distinguish the dyads from the monomers.

Electrochemical Studies of Surface Coverage and Charge Density. The main objective of the electrochemical studies of the dyad monolayers was to determine the saturation surface coverages, which in turn determine the achievable charge density. To this end, representative fast scan (100 V s^{-1}) cyclic voltammograms of the saturation-coverage monolayers of the monopodal- and tripodal-functionalized dyads on Si(100) microelectrodes are shown in Figures 2 and 3, respectively. At oxidizing potentials, each dyad monolayer exhibits two resolved voltammetric waves. The redox potentials of these waves are similar to those of the monolayers of compounds **III** and **IV**, which are monomeric analogues of the monopodal- and tripodal-functionalized dyads, respectively (see Chart 1). For the monomeric porphyrins, the two redox waves correspond to the formation of the mono- and dications. In the case of the dyads, the first wave is attributed to the overlapping one-electron oxidations of each porphyrin that result in the formation of a monocation on each unit. The second redox wave of the dyads is attributed to the overlapping one-electron oxidations of each porphyrin that result in the formation of a dication on each unit.

The evidence in support of the above interpretation of the voltammetric data for the dyads stems from solution electrochemical studies of these dyads (not shown), as well as previous studies of related dyads that lack groups for surface attachment.[32,33] In particular, these studies reveal that the coupling between porphyrins linked via either phenylene or diphenylethynyl linkers is not sufficiently large to result in resolved splittings of the one-electron waves of the individual porphyrins. The coupling is sufficiently large, however, to result in rapid hole transfer (microsecond regime) between the two porphyrins in the dyad.[32,33] One observation of note is that the redox waves observed for the dyad monolayers are somewhat broader than those observed for the dyads in solution or for the monolayers of the monomeric reference compounds **III** and **IV**,[4,6,7] which suggests a slight inequivalence between the redox potentials of the porphyrin constituents. This inequivalence might arise because the two porphyrins in the dyad monolayer are not at the same distance from the working electrode.

The redox waves for the dyads were integrated to determine the charge density on the surface, which is related to the surface coverage. The charge densities and surface coverages for the five different dyads are summarized in Table 1; for comparison,

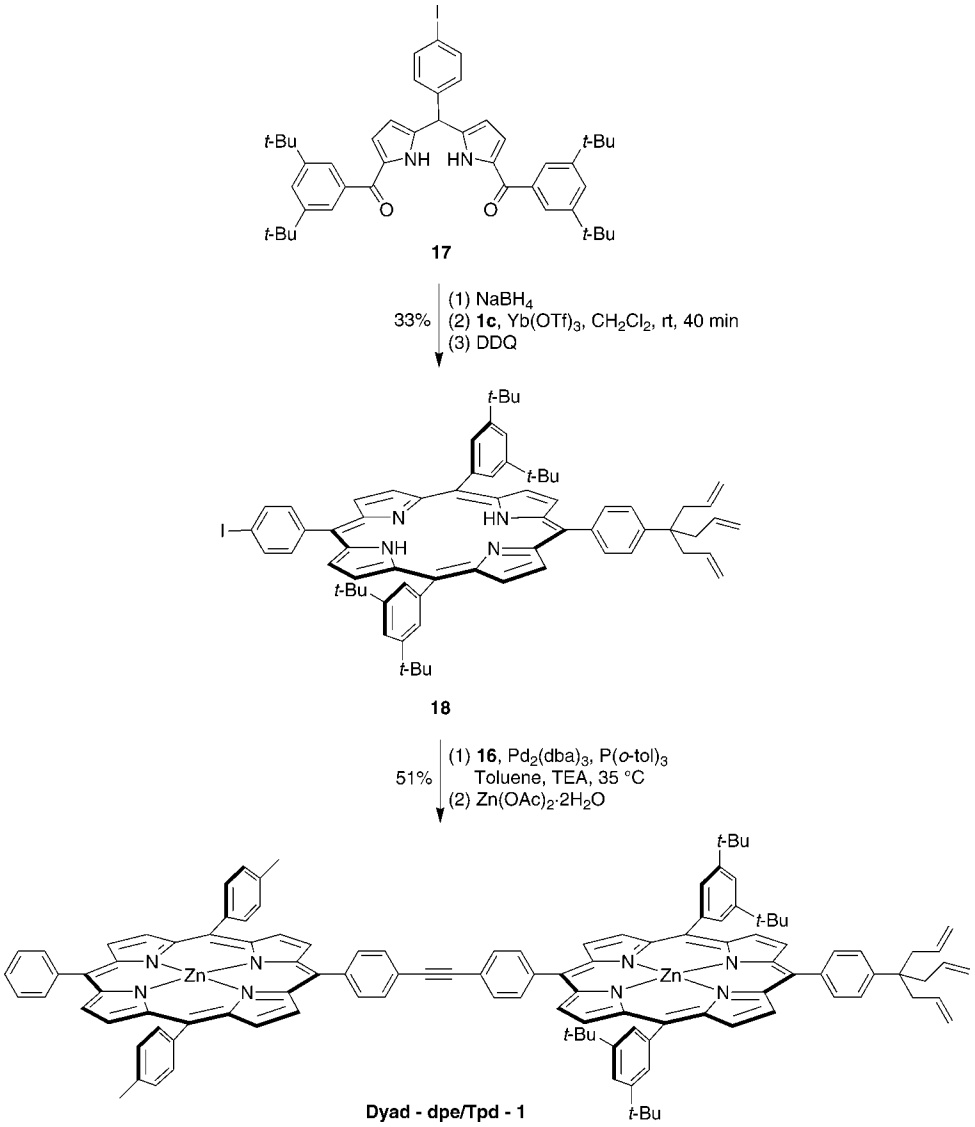
(30) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974−2983.

(31) Thamyongkit, P.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 5796−5799.

(32) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194−11207.

(33) Yang, S. I.; Seth, J.; Riggs, J. A.; Arai, T.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem. B* **1998**, *102*, 9426−9436.

SCHEME 6



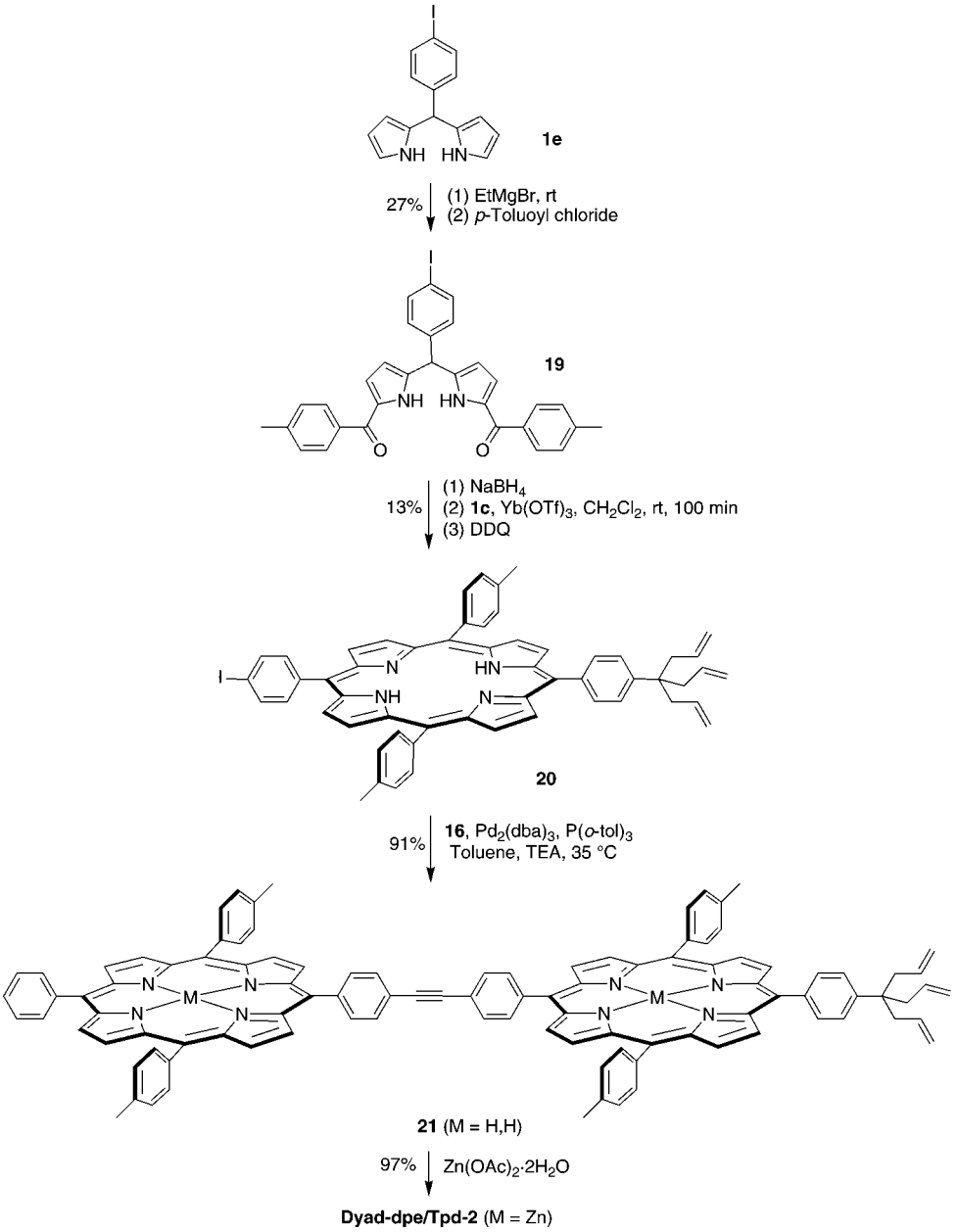
the values for the monomeric reference compounds **III** and **IV** are also included in the table. The entries in Table 1 include (1) the total charge density, σ, which is based on the integration of both voltammetric waves, (2) the surface coverage of the porphyrin units, Γ_p, which equals $^1/_2\sigma$, and (3) the surface coverage of the molecule, Γ_m, which is $^1/_4\sigma$ for the dyads and $^1/_2\sigma$ for the monomers. An inspection of Table 1 reveals the following features.

(1) For the monopodal-functionalized **Dyad-p/E** monolayer, the integrated charge is approximately twofold larger than that of the monomeric reference compound **III**. For the monopodal-functionalized **Dyad-dpe/E** monolayer, the integrated charge is more than double that of the reference monolayer. These observations suggest that the saturation surface coverage for the **Dyad-p/E** monolayer is comparable to that of compound **III**, whereas that of **Dyad-dpe/E** is larger.

(2) For all three of the tripodal-functionalized dyad monolayers, the charge densities are much less than the twofold increase expected relative to the monomeric reference compound **IV**. The charge density for the phenylene-linked **Dyad-p/Tpd** is less than 10% larger than that of compound **IV**. The charge densities for the diphenylethynyl-linked **Dyad-dpe/Tpd-1** and **Dyad-dpe/Tpd-2** are comparable to one another and approximately 40% larger than that of reference compound **IV**. These observations suggest that the surface coverages for the tripodal-functionalized dyads are in fact lower than that of the tripodal-functionalized monomer. In addition, no significant difference was observed between the use of 3,5-di-*tert*-butylphenyl versus the use of *p*-tolyl groups in **Dyad-dpe/Tpd-1** versus **Dyad-dpe/Tpd-2**, respectively.

FTIR Studies of Adsorption Geometry. The electrochemical studies indicate that the dyads afford larger charge densities than those of the monomeric porphyrins, regardless of whether the surface coverages are larger for the dyads. As an additional probe of the adsorption characteristics of the dyads, FTIR studies were conducted to investigate the orientation of the molecules on the surface. The mid-frequency (700−2000 cm^{-1}) IR spectra of the saturation coverage of monopodal- and tripodal-functionalized dyad monolayers are shown in Figures 4 and 5, respectively. In the figures, the bottom trace of each pair is the spectrum of the monolayer, and the top trace is the spectrum of a solid sample. The general features of the IR spectra of the dyads are similar to those we have previously reported for monomeric reference compounds **III** and **IV**.[4,6,7] The key

SCHEME 7



vibrational features relevant to our studies are the porphyrin in-plane ring-breathing mode near 998 cm^{-1} [34] and the out-of-plane hydrogen deformation at 797 cm^{-1}.[35] For the solid samples of the tripodal-functionalized dyads, other important features are the C═C stretching vibration, ν(C═C), of the alkene group in the linker at 1638 cm^{-1} and the out-of-plane C—H deformation, γ(CH), of this group in the 910−916-cm^{-1} range.[36] In the case of the monopodal-alkynyl-functionalized dyads, the C≡C stretching vibration of this group is also of potential interest, as is the C≡C stretch of the diphenylethynyl unit of the dyads containing this linker; however, these bands, which are expected in the 2100−2250-cm^{-1} range,[36] are extremely weak and cannot be used as reliable structural markers.

The salient features of the IR spectra of the dyads are as follows.

(1) The spectra for the monolayer and the solid samples of the dyads are similar, consistent with previous IR studies of other carbon-tethered porphyrin monolayers,[4,6,7] indicating that the structures of the porphyrin macrocycles and the substituent groups are retained upon monolayer formation.

(2) For all three tripodal-functionalized dyads, the absence of the bands associated with the ν(C═C) (1638 cm^{-1}) and γ-(CH) (910−916-cm^{-1} range) vibrations from the spectra of the monolayers indicate saturation of the double bond in each of the three legs of the tripod, similar to the behavior observed for the monomeric reference compound **IV** and consistent with an attachment to the surface via a hydrosilylation reaction.[37]

(34) Li, X. Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Su, Y. O.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 31−47.
(35) Li, X. Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 7012−7023.
(36) Silverstein, R. M.; Bassler, G. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1967.

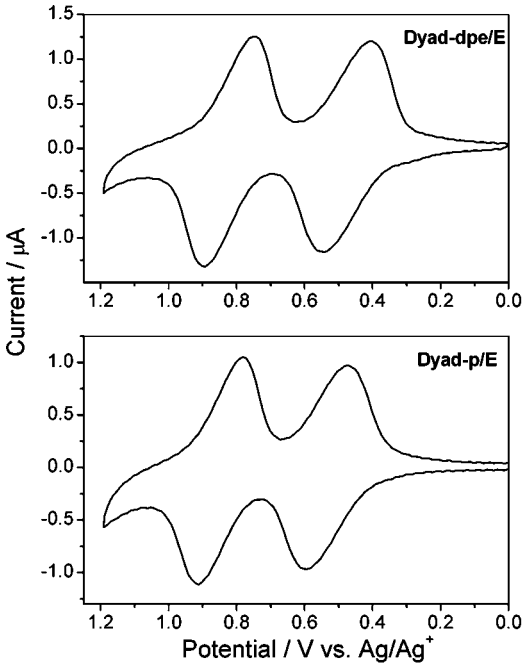


FIGURE 2. Fast-scan (100 V s^{-1}) voltammograms of the monopodal-functionalized monolayers on Si(100).

(3) The relative intensities of the in-plane (998 cm^{-1}) versus the out-of-plane (797 cm^{-1}) porphyrin modes can be used to determine the average tilt angles (α) of the porphyrin rings with respect to the surface normal.[38] We emphasize that the surface orientation obtained via this measurement is only meant as a qualitative comparison, particularly because the top and bottom porphyrins in the dyad can exhibit different orientations with respect to the surface, owing to torsional flexibility in the linker. The average tilt angles determined for the porphyrins in the dyad monolayers are included in Table 1 along with those of the monomeric reference compounds **III** and **IV**. An inspection of these data shows that the average angles for the porphyrins in all of the dyads are qualitatively similar to one another and similar to those of the porphyrins in the monomers. All of these angles fall in a 10° range centered near $\alpha \approx 40°$, suggesting that the adsorption geometries of all the molecules (monomers and dyads) are qualitatively similar. We do note, however, that the angles for the diphenylethyne-linked dyads are somewhat less than those of the phenylene-linked dyads, which could contribute to the higher surface coverage of the former dyads.

Concluding Remarks. Together, the electrochemical and the FTIR studies provide insights into the structural features that influence surface coverage and, thereby, charge density in the dyad monolayers. The first, somewhat surprising, observation is that the increased surface coverage afforded by the implementation of a tripodal versus a monopodal anchor in monomeric porphyrins does not scale to the dyads. Plausibly, increased steric interactions between the porphyrins in adjacent dyads compromise the ability of the tripodal anchor to achieve high coverage. The reduction in coverage observed for the tripodal-functionalized dyads versus the monomers cannot be obviously attributed to a large change in molecular orientation on the surface. Indeed, the average tilt angles for the tripodal dyads appear to be smaller than those for the monomeric reference compound (Table 1). The second observation is that, for a given type of surface attachment group, the dyads

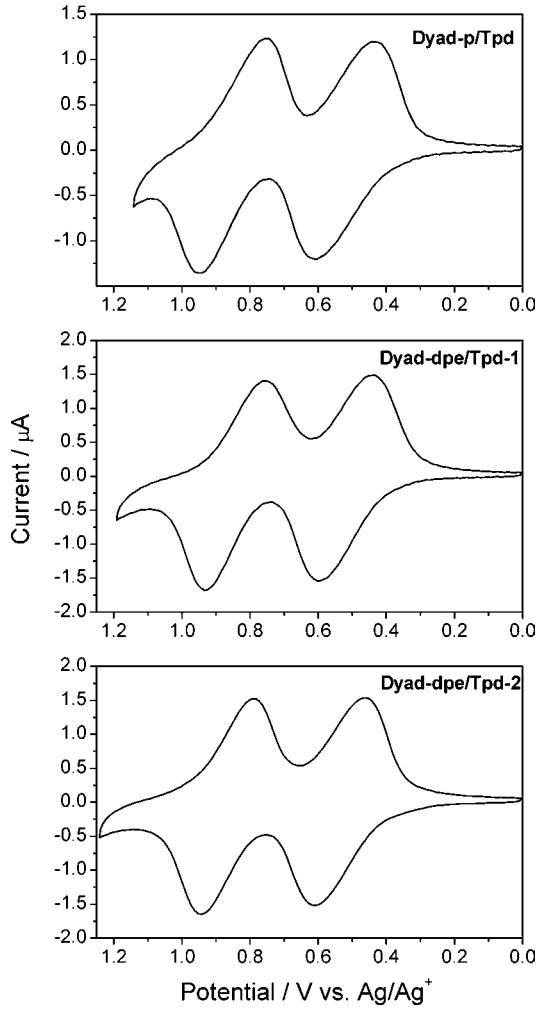


FIGURE 3. Fast-scan (100 V s^{-1}) voltammograms of the tripodal-functionalized monolayers on Si(100).

TABLE 1. Charge Densities,[a] Surface Coverage Values,[b] and Average Tilt Angles[c] for the Dyads and Reference Monomers

monolayer	σ ($\mu C \cdot cm^{-2}$)	$\Gamma_p \times 10^{-10}$ ($mol \cdot cm^{-2}$)	$\Gamma_m \times 10^{-10}$ ($mol \cdot cm^{-2}$)	tilt, α (deg)
cmpd **III**[d]	17	0.9	0.9	40
Dyad-p/E	34	1.8	0.9	42
Dyad-dpe/E	42	2.2	1.1	37
cmpd **IV**[e]	43	2.2	2.2	46
Dyad-p/Tpd	46	2.4	1.2	41
Dyad-dpe/Tpd-1	58	3.0	1.5	38
Dyad-dpe/Tpd-2	58	3.0	1.5	38

[a] Charge densities (σ) were determined via the integration of both voltammetric peaks. [b] Surface coverage of porphyrin units (Γ_p) equals $^1/_2\sigma$; surface coverage of molecules (Γ_m) is $^1/_2\sigma$ for the monomers and $^1/_4\sigma$ for the dyads. [c] Average tilt angle was 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] Taken from ref 4. [e] Taken from ref 7.

(37) (a) Buriak, J. M. *Chem. Commun*. **1999**, 1051−1060. (b) Buriak, J. M. *Chem. Rev*. **2002**, *102*, 1271−1308.

(38) (a) Painter, P. C.; Coleman, M. M.; Koenig, J. L. *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*; Wiley: New York, 1982. (b) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52−66. (c) Harrick, N. J.; Mirabella, F. M. *International Reflection Spectroscopy: Review and Supplement*; Harrick Scientific Corp.: New York, 1985. (d) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310−315. (e) Zaera, F. *Int. Rev. Phys. Chem.* **2002**, *21*, 433−471.

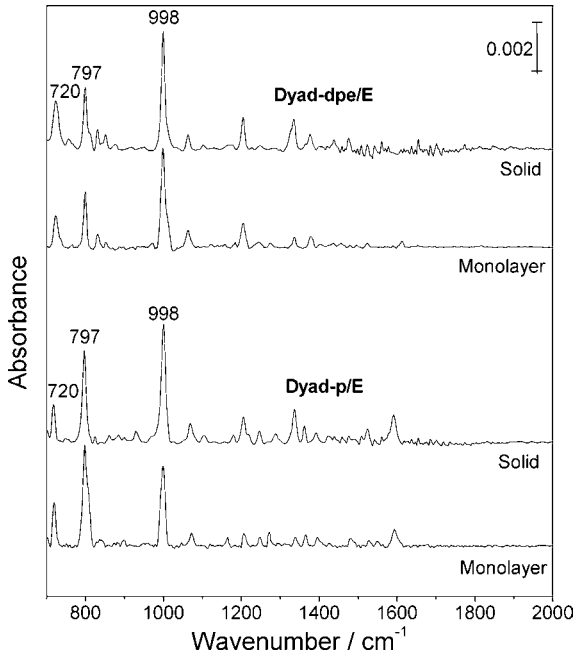


FIGURE 4. FTIR spectra of the monopodal-functionalized porphyrins in solid form (KBr pellet) and in monolayers on Si(100).

containing the diphenylethynyl linker exhibit higher surface coverage than those containing a phenylene linker. Plausibly, the enhanced torsional flexibility of the diphenylethynyl linker affords better packing of the molecules on the surface, although steric differences between the 3,5-di-*tert*-butylphenyl versus the *p*-tolyl groups do not appear to significantly alter the surface coverage. The diphenylethynyl-linked dyads also exhibit a somewhat smaller average tilt angle than do the phenylene-linked dyads (Table 1), which would tend to give a smaller molecular footprint and a higher surface coverage.

Regardless of how molecular structure affects packing and surface adsorption geometry, the studies reported herein indicate that the utilization of a dyad motif is effective for achieving increased charge density relative to that accessible via a similarly tethered monomeric porphyrin. In the case of monopodal linkers, the charge density can be doubled versus that obtainable for a monomeric species, indicating that this linking strategy takes full advantage of the vertical dimension for achieving increased charge density in a particular molecular footprint. The charge density achievable for a monopodal-functionalized dyad is at best comparable to that of a tripodal-functionalized monomeric species, owing to the superior packing density of the latter molecules. Although dyads constructed with a tripodal anchor do not afford a doubling of the charge density versus a similarly functionalized monomer, the increased charge density afforded by certain dyad architectures (e.g., the diphenylethyne-linked motif) is sufficiently large that a dyad has clear advantages over a monomer. The nature of the linker architecture between the porphyrins in the dyad also appears to play some role in the ability to achieve high charge density, with the more torsionally flexible diphenylethyne linker being superior to the more torsionally constrained phenylene linker. Collectively, these results have important implications for the construction of molecule-based charge-storage devices for electronics applications.

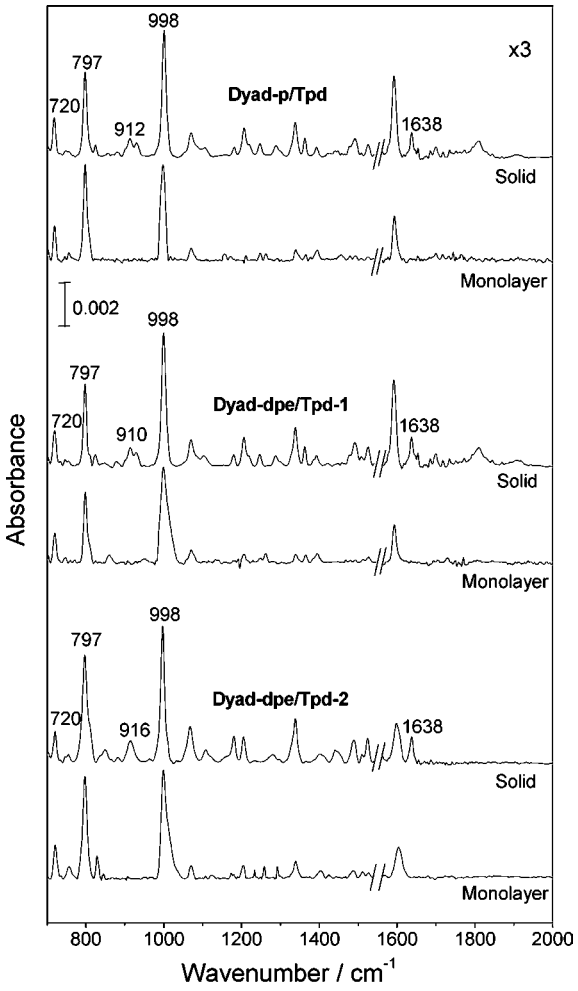


FIGURE 5. FTIR spectra of the tripodal-functionalized porphyrins in solid form (KBr pellet) and in monolayers on Si(100).

Experimental Section

5-[4-(5,5-Dimethyl-1,3-dioxan-2-yl)phenyl]dipyrromethane (1b). A general procedure was followed.[24] A solution of **7** (26.4 g, 0.120 mol) in pyrrole (210 mL, 3.00 mol, 25 equiv) was treated with TFA (0.925 mL, 12.0 mmol) at room temperature for 5 min. The reaction was quenched with 0.1 M aqueous NaOH (50 mL). Ethyl acetate was added. The organic phase was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (silica, CH_2Cl_2), affording a slightly yellow solid, which upon recrystallization (ethanol/water, 9:1) gave a colorless solid (19.5 g, 48%): mp 139−140 °C; ^{1}H NMR δ 0.80 (s, 3H), 1.29 (s, 3H), 3.65 (d, J = 10.8 Hz, 2H), 3.76 (d, J = 10.8 Hz, 2H), 5.38 (s, 1H), 5.48 (s, 1H), 5.91−5.92 (m, 2H), 6.14−6.15 (m, 2H), 6.66−6.67 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.89 (br, 2H); ^{13}C NMR δ 21.8, 23.0, 30.2, 43.6, 77.6, 101.5, 107.2, 108.2, 117.1, 126.4, 128.3, 132.2, 137.2, 142.7. FAB-MS: calcd for $C_{21}H_{24}N_2O_2$, 336.1838; found, 336.1848. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.94; H, 7.17; N, 8.32.

5,15-(3,5-Di-*tert*-butylphenyl)-10-[4-(5-phenyl-10,20-di-*p*-tolylporphinatozinc(II)-15-yl)phenyl]-20-[4-(2-(trimethylsilyl)ethynyl)phenyl]porphinatozinc(II) (6). A general procedure was followed.[18,20] A solution of **5** (283 mg, 0.411 mmol) in THF/methanol (16 mL, 10:1) was reacted with $NaBH_4$ (621 mg, 16.4 mmol) at room temperature for 3.5 h. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (20 mL) and CH_2Cl_2 (20 mL), and the resulting mixture was stirred for 5 min.

The organic phase was separated, washed with water, and concentrated. The resulting dipyrromethane−dicarbinol and **4** (443 mg, 0.410 mmol) were dissolved in CH_2Cl_2 (164 mL). $Yb(OTf)_3$ (336 mg, 0.542 mmol) was added, and the reaction mixture was stirred at room temperature for 45 min. Then DDQ (279 mg, 1.23 mmol) was added, and the mixture was stirred for 1 h. TEA (1 mL) was added to neutralize the reaction mixture. The mixture was filtered through a silica pad (CH_2Cl_2), and the purple band was collected. After removal of the solvent, the crude product was chromatographed [silica, CH_2Cl_2/hexanes (1:1)], affording the free-base dyad as a purple solid (88.0 mg), which was directly used in the metalation step.

A solution of the free-base dyad (44.0 mg) in $CHCl_3$ (5 mL) was reacted overnight with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (64.6 mg, 0.294 mmol) in methanol (1 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (1:1)], affording a purple solid (45 mg, 13% from **4**): ^{1}H NMR δ 0.40 (s, 9H), 1.55 (s, 36H), 2.77 (s, 6H), 7.52−7.66 (m, 7H), 7.76−7.88 (m, 4H), 7.89−7.91 (m, 2H), 7.98−8.06 (m, 2H), 8.10−8.30 (m, 8H), 8.64 (br, 4H), 8.94−9.10 (m, 8H), 9.16−9.24 (m, 4H), 9.38−9.48 (m, 4H). LD-MS: calcd for $C_{105}H_{94}N_8SiZn_2$, 1626.8; found, 1625.9. λ_{abs} 423, 434, 552, 592 nm. The quality of the NMR spectrum for the title compound was poor (though key features were evident); however, the dyad prepared from the title compound exhibited an NMR spectrum of excellent quality.

1-(3,5-Di-*tert*-butylbenzoyl)-5-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]dipyrromethane (10). A general procedure for 1-acylation was followed.[27] A solution of **1b** (3.36 g, 10.0 mmol) in dry THF (10 mL) was treated with EtMgBr (25.0 mL, 25 mmol, 1.0 M in THF) at room temperature for 10 min. The mixture was then cooled to −78 °C, and a solution of pyridyl thioester **9** (3.27 g, 10.0 mmol) in dry THF (10 mL) was added. The mixture was stirred for 10 min at −78 °C and then allowed to warm to room temperature with stirring for 20 min. The reaction mixture was quenched with saturated aqueous NH_4Cl. Ethyl acetate was added. The organic phase was washed with brine and water, dried (Na_2SO_4), and chromatographed [silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$/ethyl acetate (90:10)], affording a brown solid (3.31 g, 60%). The characterization data were consistent with those obtained for the product of the direct diacylation procedure.

1,9-Bis(3,5-di-*tert*-butylbenzoyl)-5-[4-(5,5-dimethyl-1,3-dioxan-2-yl)]phenyldipyrromethane (11). A procedure for 1,9-diacylation was followed.[18] A solution of **1b** (1.68 g, 5.00 mmol) in toluene (100 mL) was treated with EtMgBr (25 mL, 25 mmol, 1.0 M solution in THF) at room temperature for 30 min. Then a solution of acid chloride **8** (3.16 g, 12.5 mmol) in toluene (10 mL) was added at room temperature. The mixture was stirred for 10 min. The standard workup and chromatography [silica, hexanes/ethyl acetate (8:1 → 5:1)] afforded two fractions. The first fraction (containing the title compound) was concentrated to dryness. The residue was suspended in methanol and sonicated three times, affording a slightly brown solid (0.98 g, 25%): mp 158 °C (dec); ^{1}H NMR δ 0.80 (s, 3H), 1.28 (s, 3H), 1.29 (s, 36H), 3.65 (d, J = 10.8 Hz, 2H), 3.76 (d, J = 10.8 Hz, 2H), 5.39 (s, 1H), 5.69 (s, 1H), 5.98−5.99 (m, 2H), 6.54−6.55 (m, 2H), 7.52−7.56 (m, 8H), 7.64 (d, J = 7.6 Hz, 2H), 11.48 (br, 2H); ^{13}C NMR δ 21.9, 23.0, 30.2, 31.4, 34.8, 45.3, 77.6, 101.5, 111.0, 120.9, 124.1, 125.3, 126.8, 129.0, 131.1, 137.4, 137.9, 140.9, 141.9, 150.2, 185.4. FAB-MS: calcd for $C_{51}H_{64}N_2O_4$, 768.4866; found, 768.4854. Anal. Calcd for $C_{51}H_{64}N_2O_4$: C, 79.65; H, 8.39; N, 3.64. Found: C, 79.48; H, 8.42; N, 3.61.

The second fraction was concentrated, affording the 1-acyldipyrromethane **10** as a slightly yellow solid (1.32 g, 47%): mp 102−104 °C; ^{1}H NMR δ 0.80 (s, 3H), 1.29 (s, 3H), 1.36 (s, 18H), 3.64 (d, J = 11.2 Hz, 2H), 3.76 (d, J = 11.2 Hz, 2H), 5.40 (s, 1H), 5.54 (s, 1H), 6.00−6.05 (m, 2H), 6.16−6.18 (m, 1H), 6.70−6.75 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.61−7.62 (m, 1H), 7.67−7.68 (m, 2H), 7.92 (br, 1H), 9.35 (br, 1H); ^{13}C NMR δ 21.8, 22.9, 30.1, 31.3, 34.8, 43.9, 77.5, 101.3, 107.5, 108.1, 110.3, 117.7, 120.9, 123.3, 125.7, 126.4, 128.3, 130.8, 137.3, 137.8, 141.5, 150.6, 185.6. FAB-MS: calcd for $C_{36}H_{44}N_2O_3$, 552.3352; found, 552.3334. Anal. Calcd for $C_{36}H_{44}N_2O_3$: C, 78.22; H, 8.02; N, 5.07. Found: C, 77.92; H, 8.04; N, 5.00.

Dibutyl[1,9-bis(3,5-di-*tert*-butylbenzoyl)-5-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-5,10-dihydrodipyrrinato]tin(IV) (Bu_2Sn−11). A general procedure was followed.[21] A solution of EtMgBr (75.0 mL, 75 mmol, 1.0 M solution in THF) was added slowly to a tap-water-cooled flask containing a solution of **1b** (5.05 g, 15.0 mmol) in toluene (180 mL) under argon. An exothermic reaction with gas evolution ensued. The resulting mixture was stirred at room temperature for 30 min. A solution of **8** (9.48 g, 37.5 mmol) in toluene (20 mL) was added over 10 min. The resulting mixture was stirred for 30 min. The reaction mixture was poured into saturated aqueous NH_4Cl and ethyl acetate. The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to dryness. The residue was treated with TEA (4.2 mL, 30.0 mmol) and Bu_2SnCl_2 (4.56 g, 15.0 mmol) in CH_2Cl_2 (100 mL) at room temperature for 30 min. The mixture was filtered over a silica pad (CH_2Cl_2). The first band was collected and concentrated to dryness. The residue was dissolved in a minimum amount of diethyl ether. Methanol was added, yielding a precipitate. Filtration afforded a colorless solid (3.80 g, 25%): mp 199−200 °C (dec); ^{1}H NMR δ 0.71−0.79 (m, 9H), 1.14−1.19 (m, 2H), 1.22−1.26 (m, 2H), 1.28 (s, 3H), 1.32−1.36 (m, 2H), 1.38 (s, 36 H), 1.46−1.50 (m, 2H), 1.54−1.59 (m, 2H), 1.68−1.72 (m, 2H), 3.63 (d, J = 10.8 Hz, 2H), 3.75 (d, J = 10.8 Hz, 2H), 5.36 (s, 1H), 5.60 (s, 1H), 6.12 (d, J = 3.6 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.61−7.62 (m, 2H), 7.70−7.71 (m, 4H); ^{13}C NMR δ 13.60, 13.63, 21.8, 22.9, 24.22, 24.77, 26.00, 26.25, 27.20, 27.24, 30.0, 31.4, 34.9, 45.6, 77.5, 101.4, 115.1, 123.22, 123.70, 125.66, 126.39, 128.1, 135.9, 136.89, 137.05, 144.7, 150.72, 151.10, 185.6. FAB-MS obsd, 1001.5268; calcd, 1001.5218 [$(M + H)^+$; M = $C_{59}H_{80}N_2O_4Sn$]. Anal. Calcd for $C_{59}H_{80}N_2O_4Sn$: C, 70.86; H, 8.06; N, 2.80. Found: C, 70.97; H, 8.11; N, 2.89. The second band from the silica filtration was collected and rechromatographed (silica, CH_2Cl_2), affording **10** as a brown solid (3.98 g, 48%) with identical characterization data as described for **10** obtained by the direct diacylation of dipyrromethane **1b**.

9-Acylation of 1-Acyldipyrromethane 10, Affording 11. A procedure for the 9-acylation of 1-acyldipyrromethanes was followed.[18] A solution of **10** (9.70 g, 17.5 mmol) in anhydrous toluene (70 mL) was treated with EtMgBr (35.0 mL, 35 mmol, 1.0 M in THF) under argon at room temperature for 5 min. A solution of **8** (4.42 g, 17.5 mmol) in toluene (8.0 mL) was added. After 10 min, the same addition of EtMgBr and **8** was repeated once. After stirring for 10 min, the reaction mixture was treated with additional EtMgBr (17.5 mL, 17.5 mmol, 1.0 M in THF), followed by **8** (2.21 g, 8.7 mmol) in toluene (4.0 mL). After stirring at room temperature for 30 min, the reaction was quenched with saturated aqueous NH_4Cl. Ethyl acetate was added. The organic phase was separated, dried (Na_2SO_4), and chromatographed [silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$/ethyl acetate (90:10)], affording a brown solid (7.85 g, 58%). The characterization data were consistent with those obtained for the product from the direct diacylation.

9-Acylation of 1-Acyldipyrromethane 10 with Subsequent Tin Complexation, Affording Bu_2Sn−11. A solution of EtMgBr (35.3 mL, 35 mmol, 1.0 M solution in THF) was added slowly to a solution of **10** (3.90 g, 7.05 mmol) in toluene (30 mL) under argon. The resulting mixture was stirred at room temperature for 10 min. A sample of **8** (4.45 g, 17.6 mmol) was added, and the mixture was stirred for 30 min. The reaction mixture was poured into saturated aqueous NH_4Cl and ethyl acetate. The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated to dryness. Treatment of the residue with TEA (2.0 mL, 14.1 mmol) and Bu_2SnCl_2 (2.14 g, 7.05 mmol) in CH_2Cl_2 (50 mL) at room temperature for 30 min followed by the standard purification technique (as described above) afforded the title compound as a

colorless solid (2.82 g, 40%) with satisfactory characterization data (mp, ^{1}H NMR spectrum, and elemental analysis).

1,9-Bis(3,5-di-*tert*-butylbenzoyl)-5-(4-formylphenyl)dipyrromethane (12). A general procedure was followed.[28] A solution of **11** (18.5 g, 24.0 mmol) in CH_2Cl_2 (120 mL) was treated with a solution of TFA (40 mL) and water (20 mL) at room temperature. The reaction was stopped after 5.5 h. ^{1}H NMR analysis of the crude reaction mixture upon workup [wash with water and aqueous $NaHCO_3$, dry (Na_2SO_4), and concentrate] indicated the complete removal of the acetal group. The crude product thus obtained was chromatographed [CH_2Cl_2/ethyl acetate, 95:5 → 90:10], affording a brown solid (14.1 g, 86%): mp 167 °C dec; ^{1}H NMR δ 1.27 (s, 36H), 5.84 (s, 1H), 5.95−5.96 (m, 2H), 6.51−6.52 (m, 2H), 7.52−7.53 (m, 6H), 7.88 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 10.03 (s, 1H), 12.22 (br, 2H); ^{13}C NMR δ 31.3, 34.8, 45.5, 111.2, 121.0, 124.2, 125.6, 129.8, 130.4, 131.3, 135.4, 137.7, 139.9, 148.0, 150.3, 185.6, 191.7. FAB-MS: calcd for $C_{46}H_{54}N_2O_3$, 682.4134; found, 682.4121. Anal. Calcd for $C_{46}H_{54}N_2O_3$: C, 80.90; H, 7.97; N, 4.10. Found: C, 80.28; H, 8.16; N, 4.00.

5-[4-[1,9-Bis(3,5-di-*tert*-butylbenzoyl)dipyrromethan-5-yl]phenyl]dipyrromethane (13). A general procedure with slight modification was followed.[14] A solution of **12** (14.1 g, 20.6 mmol) in CH_2Cl_2 (25 mL) and pyrrole (143 mL, 2.06 mol, 100 equiv) was treated with TFA (159 μL, 2.06 mmol, 0.1 equiv) at room temperature for 10 min. The reaction was quenched with TEA (2 mL), and CH_2Cl_2 was added. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated to obtain a brown oily residue. Chromatography [silica, hexanes/ethyl acetate (5:1 → 3:1)] afforded a colorless solid (12.5 g, 75%): mp 174 °C (dec); ^{1}H NMR δ 1.30 (s, 36 H), 5.49 (s, 1H), 5.68 (s, 1H), 5.94−5.95 (m, 2H), 6.02−6.03 (m, 2H), 6.15−6.17 (m, 2H), 6.59−6.60 (m, 2H), 6.69−6.71 (m, 2H), 7.25−7.26 (m, 2H), 7.49−7.51 (m, 2H), 7.54−7.59 (m, 6H), 7.95 (br, 2H), 11.22 (br, 2H); ^{13}C NMR δ 31.4, 34.8, 43.6, 45.1, 107.2, 108.4, 111.1, 117.2, 120.9, 124.1, 125.4, 128.9, 129.2, 131.2, 132.3, 137.9, 139.7, 141.0, 141.1, 150.2, 185.4. FAB-MS: calcd for $C_{54}H_{62}N_4O_2$, 798.4873; found, 798.4902. Anal. Calcd for $C_{54}H_{62}N_4O_2$: C, 81.16; H, 7.82; N, 7.01. Found: C, 80.73; H, 7.82; N, 7.01.

Dibutyl[1,9-bis(3,5-di-*tert*-butylbenzoyl)-5-(4-(dipyrromethan-5-yl)phenyl)-5,10-dihydrodipyrrinato]tin(IV) (Bu_2Sn−13). A general procedure was followed.[21] A mixture of **13** (240 mg, 0.300 mmol), Bu_2SnCl_2 (91.0 mg, 0.300 mmol), and TEA (83 μL, 0.60 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 1 h. The mixture was concentrated. The resulting residue was chromatographed [silica, hexanes/ethyl acetate (5:1)], affording a colorless solid (266 mg, 86%): mp 107 °C (dec); ^{1}H NMR δ 0.70−0.76 (m, 6H), 1.11−1.25 (m, 4H), 1.32−1.53 (m, 6H), 1.38 (s, 36H), 1.69−1.73 (m, 2H), 5.44 (s, 1H), 5.58 (s, 1H), 5.90 (br, 2H), 6.12−6.15 (m, 2H), 6.19 (d, J = 4.0 Hz, 2H), 6.67−6.69 (m, 2H), 7.03 (d, J = 3.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 7.61−7.63 (m, 2H), 7.16−7.21 (m, 4H), 7.91 (br, 2H); ^{13}C NMR δ 13.61, 13.66, 24.0, 25.0, 26.02, 26.27, 27.25, 27.29, 31.4, 34.9, 43.5, 45.2, 107.2, 108.3, 115.0, 117.2, 123.2, 123.7, 125.8, 128.32, 128.50, 132.4, 136.1, 137.1, 140.3, 142.9, 150.8, 151.2, 185.6. Anal. Calcd for $C_{62}H_{78}N_4O_2Sn$: C, 72.30; H, 7.63; N, 5.44. Found: C, 72.32; H, 7.62; N, 5.50.

5-[4-[1,9-Bis(3,5-di-*tert*-butylbenzoyl)dipyrromethan-5-yl]phenyl]-15-phenyl-10,20-di-*p*-tolylporphyrin (14). A general procedure was followed.[18,20] A solution of **5** (0.900 g, 1.30 mmol) in THF/methanol (52 mL, 10:1) was treated with $NaBH_4$ (1.97 g, 52.1 mmol) at room temperature. After 3.5 h, the reaction mixture was poured in a mixture of saturated aqueous NH_4Cl (50 mL) and CH_2Cl_2 (50 mL). The organic phase was isolated, washed with water, dried (Na_2SO_4), and concentrated to dryness. A mixture of the resulting dipyrromethane−dicarbinol and **13** (1.04 g, 1.30 mmol) was dissolved in CH_2Cl_2 (520 mL) and stirred until a homogeneous solution was obtained. $Yb(OTf)_3$ (1.06 g, 1.71 mmol) was added at room temperature. After 40 min, the reaction mixture was treated with DDQ (0.885 g, 3.90 mmol) and stirred for 1 h. TEA (3 mL) was added, and the reaction mixture was filtered through a silica pad (CH_2Cl_2). A purple fraction was collected, concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The desired fraction was concentrated. The resulting crude product was suspended in hexanes and sonicated three times, affording a purple solid (0.159 g, 10%): ^{1}H NMR δ −2.78 (s, 2H), 1.43 (s, 36H), 2.71 (s, 6H), 5.95 (s, 1H), 6.52 (d, J = 3.6 Hz, 2H), 7.22 (d, J = 3.6 Hz, 2H), 7.56 (d, J = 8.0 Hz, 4H), 7.64−7.67 (m, 4H), 7.76−7.79 (m, 3H), 7.81−7.82 (m, 6H), 8.10 (d, J = 8.0 Hz, 4H), 8.17 (d, J = 8.0 Hz, 2H), 8.21−8.23 (m, 2H), 8.82−8.87 (m, 8H). LD-MS obsd, 1337.0 [(M + 2t − Bu)$^+$], 1395.1 [(M + 3t − Bu)$^+$, 1451.0 [(M + 4t − Bu)$^+$; calcd, 1218.6 (M = $C_{85}H_{82}N_6O_2$): λ_{abs} 421, 516, 550, 590, 647 nm; λ_{em} (λ_{ex} 550 nm) 654, 722 nm.

5-Phenyl-10,20-di-*p*-tolyl-15-[4-(2-(trimethylsilyl)ethynyl)-phenyl]porphyrin (15). A general procedure was followed.[18,20] A solution of **5** (1.40 g, 2.03 mmol) in THF/methanol (81 mL, 10:1) was treated with $NaBH_4$ (3.07 g, 81.2 mmol) at room temperature. After 3.5 h, the reaction mixture was poured in a mixture of saturated aqueous NH_4Cl (100 mL) and CH_2Cl_2 (100 mL). The organic phase was isolated, washed with water, dried (Na_2SO_4), and concentrated to dryness. A mixture of the resulting dipyrromethane−dicarbinol and **1d** (0.645 g, 2.03 mmol) was dissolved in CH_2Cl_2 (812 mL) and stirred until a homogeneous solution was obtained. $Yb(OTf)_3$ (1.61 g, 2.60 mmol) was added at room temperature. After 40 min, the reaction mixture was treated with DDQ (1.38 g, 6.08 mmol) and stirred for 1 h. Then TEA (3 mL) was added, and the reaction mixture was filtered through a silica pad (CH_2Cl_2). The purple band was collected, concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The desired fraction was concentrated. The crude product was suspended in methanol and sonicated three times, affording a purple solid (0.430 g, 29%): ^{1}H NMR δ −2.79 (s, 2H), 0.39 (s, 9H), 2.72 (s, 6H), 7.57 (d, J = 7.6 Hz, 4H), 7.76−7.78 (m, 3H), 7.88 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 7.6 Hz, 4H), 8.17 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 6.4 Hz, 2H), 8.80−8.88 (m, 8H). LD-MS obsd, 738.4. FAB-MS obsd, 739.3253; calcd, 739.3257 [(M + H)$^+$; M = $C_{51}H_{42}N_4Si$]: λ_{abs} 421, 516, 550, 596, 649 nm; λ_{em} (λ_{ex} 550 nm) 655, 722 nm.

5-(4-Ethynylphenyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (16). A solution of **15** (0.150 g, 0.203 mmol) in $CHCl_3$/THF (23 mL, 3:1) was treated with TBAF (0.305 mL, 0.31 mmol, 1.0 M in THF) at room temperature. After 1 h, TLC analysis [CH_2Cl_2/hexanes (3:1)] showed the complete consumption of **15**. The reaction mixture was diluted with CH_2Cl_2 and then washed with 10% aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The solid product was suspended in methanol and sonicated three times, affording a purple solid (0.131 g, 96%): ^{1}H NMR δ −2.78 (s, 2H), 2.72 (s, 6H), 3.34 (s, 1H), 7.57 (d, J = 7.2 Hz, 4H), 7.75−7.82 (m, 3H), 7.91 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 7.2 Hz, 4H), 8.19−8.24 (m, 4H), 8.82−8.90 (m, 8H). LD-MS obsd, 666.5. FAB-MS obsd, 667.2885; calcd, 667.2862 [(M + H)$^+$; M = $C_{48}H_{34}N_4$]: λ_{abs} 421, 516, 550, 596, 649 nm; λ_{em} (λ_{ex} 550 nm) 654, 721 nm.

5-[4-(1,1-Diallyl-3-buten-1-yl)phenyl]-10,20-bis(3,5-di-*tert*-butyl)-15-(4-iodophenyl)porphyrin (18). A general procedure was followed.[18,20] A solution of **17** (0.350 g, 0.448 mmol) in THF/methanol (18 mL, 10:1) was reacted with $NaBH_4$ (0.339 g, 8.97 mmol) at room temperature for 40 min. The reaction mixture was poured in a mixture of saturated aqueous NH_4Cl (20 mL) and CH_2Cl_2 (20 mL). The organic phase was isolated, washed with water, dried (Na_2SO_4), and concentrated to dryness. The resulting dipyrromethane−dicarbinol and **1c** (0.160 g, 0.449 mmol) were dissolved in CH_2Cl_2 (180 mL) and then treated with $Yb(OTf)_3$ (0.357 g, 0.576 mmol) at room temperature. After 40 min, DDQ (0.306 g, 1.35 mmol) was added, and the mixture was stirred for 1 h. The reaction mixture was neutralized with TEA (2 mL) and filtered through a silica pad (CH_2Cl_2). The purple band was collected, concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The crude product was suspended in methanol and sonicated three times, affording a purple solid (0.161 g, 33%): ^{1}H NMR δ −2.74 (s, 2H),

1.54 (s, 36H), 2.74 (d, J = 6.8 Hz, 6H), 5.19−5.24 (m, 6H), 5.83−5.93 (m, 3H), 7.70 (d, J = 7.6 Hz, 2H), 7.81 (s, 2H), 7.98 (d, J = 8.0 Hz, 2H), 8.10−8.11 (m, 6H), 8.19 (d, J = 8.0 Hz, 2H), 8.82−8.86 (m, 4H), 8.90−8.94 (m, 4H). LD-MS: calcd for $C_{70}H_{75}IN_4$, 1098.5; found, 1016.7 [(M − 2allyl)$^+$], 1058.8 [(M − allyl)$^+$], 1099.7 [M$^+$]. λ_{abs} 422, 516, 551, 596, 650 nm; λ_{em} (λ_{ex} 550 nm) 654, 722 nm.

5-(4-Iodophenyl)-1,9-bis(4-methylbenzoyl)dipyrromethane (19). A general procedure was followed.[24,31] A solution of EtMgBr (7.80 mL, 1.0 M in THF, 7.8 mmol) was added slowly to a flask containing a solution of **1e** (542 mg, 1.56 mmol) in toluene (30 mL) under argon. The resulting yellowish brown mixture was stirred at room temperature for 30 min. Then, a solution of *p*-toluoyl chloride (520 μL, 3.93 mmol) in toluene (3.9 mL) was added over a period of 3 min. The mixture was stirred at room temperature for 4 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (25 mL). Ethyl acetate (30 mL) was added. The layers were separated, and the organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed [silica, CH_2Cl_2/ethyl acetate (95:5)] to afford a brown amorphous solid (245 mg, 27%): ^{1}H NMR δ 2.39 (s, 6H), 5.62 (s, 1H), 5.88−5.95 (m, 2H), 6.45−6.52 (m, 2H), 7.18 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 8.4 Hz, 2H), 11.86 (br, 2H); ^{13}C NMR (75 MHz) δ 21.8, 44.9, 93.2, 111.4, 120.8, 128.9, 130.0, 131.2, 131.4, 135.6, 138.1, 140.4, 140.6, 142.5, 184.6. FAB-MS: calcd for $C_{31}H_{25}IN_2O_2$, 585.1039; found, 585.1046.

5-[4-(1,1-Diallyl-3-buten-1-yl)phenyl]-15-(4-iodophenyl)-10,20-di-*p*-tolylporphyrin (20). A general procedure was followed.[18,20] A solution of **19** (180 mg, 0.31 mmol) in THF/methanol (25 mL, 3:1) was reacted with $NaBH_4$ (59.0 mg, 1.54 mmol) at room temperature for 50 min. The reaction was monitored by TLC. Two additional portions of $NaBH_4$ (55.0 mg and 460 mg) were added at 50 min and at 1.25 h. The reaction was complete in 1h 45 min. The reaction was quenched with saturated aqueous NH_4Cl (20 mL). The reaction mixture was extracted with CH_2Cl_2. The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated. The resulting dipyrromethane−dicarbinol and **1c** (114 mg, 319 μmol) were dissolved in CH_2Cl_2 (124 mL) and then treated with $Yb(OTf)_3$ (248 mg, 400 μmol) at room temperature. After 1 h 40 min, DDQ (210 mg, 924 μmol) was added, and the mixture was stirred at room temperature for 1 h. Methanol (12 mL) and TEA (1.2 mL) were added to the reaction mixture. After stirring for 1 h, the mixture was concentrated and chromatographed (silica, CH_2Cl_2). The first purple band was collected and concentrated. The residue was dissolved in CH_2Cl_2 and treated with methanol, affording a precipitate upon the slow evaporation of approximately half of the solvent under reduced pressure. The precipitate was collected by centrifugation, suspended in hexanes, and sonicated three times to provide a purple solid (37.4 mg, 13%): ^{1}H NMR δ −2.78 (s, 2H), 2.62−2.76 (m, 12H), 5.10−5.25 (m, 6H), 5.75−5.95 (m, 3H), 7.53 (d, J = 7.6 Hz, 4H), 7.63 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 8.00−8.18 (m, 8H), 8.73−8.96 (m, 8H). LD-MS: calcd for $C_{56}H_{47}IN_4$, 902.3; found, 902.5. FAB-MS: calcd for $C_{56}H_{47}IN_4$, 902.2845; found, 902.2910. λ_{abs} 421, 516, 551, 591, 648 nm.

5-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-15-[4-[2-[4-(5-phenyl-10,20-di-*p*-tolylporphin-15-yl)phenyl]ethynyl]phenyl]-10,20-di-*p*-tolylporphyrin (21). A general procedure was followed.[30] A mixture of **20** (33.8 mg, 37.0 μmol), **16** (24.9 mg, 37.0 μmol), $Pd_2(dba)_3$ (5.50 mg, 5.98 μmol), and P(*o*-tol)$_3$ (13.4 mg, 44.3 μmol) in dry toluene/TEA (16 mL, 5:1) was reacted in a Schlenk flask at 35 °C. After 3.5 h, a second portion of $Pd_2(dba)_3$ (5.50 mg, 5.98 μmol) and P(*o*-tol)$_3$ (13.4 mg, 44.3 μmol) was added, and the reaction mixture was stirred for 2.5 h. The reaction was stopped after a total of 6 h. The solvent was removed, and the resulting residue was chromatographed [silica, CH_2Cl_2/hexanes (1:2) → CH_2Cl_2/hexanes (1:1)]. The resulting purple solid was dissolved in CH_2Cl_2. The addition of methanol and the slow evaporation of the solvent under reduced pressure afforded a precipitate. The precipitate was collected by centrifugation, suspended in hexanes, and sonicated three times to provide a purple solid (48.3 mg, 91%): ^{1}H NMR δ −2.74 (s, 4H), 2.60−2.90 (m, 18H), 5.05−5.15 (m, 6H), 5.78−6.00 (m, 3H), 7.58 (d, J = 7.9 Hz, 8H), 7.66−7.82 (m, 5H), 8.04−8.16 (m, 12H), 8.16−8.26 (m, 4H), 8.31 (d, J = 7.9 Hz, 4H), 8.78−9.00 (m, 16H). MALDI-MS (POPOP): calcd for $C_{104}H_{80}N_8$, 1441.7; found, 1441.1. FAB-MS: calcd for $C_{104}H_{80}N_8$, 1441.6584; found, 1441.6494. λ_{abs} 424, 516, 552, 593, 649 nm; λ_{em} (λ_{ex} 424 nm) 655, 722 nm.

Dyad-p/E. A solution of **6** (33.5 mg, 20.6 μmol) in $CHCl_3$/THF (3 mL, 3:1) was reacted with TBAF (31.0 μL, 31 μmol, 1.0 M solution in THF) at room temperature for 1 h. The reaction mixture was washed with 10% aqueous $NaHCO_3$, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (2:1)], affording a purple solid (31 mg, 98%): ^{1}H NMR δ 1.59 (s, 36 H), 2.77 (s, 6H), 3.34 (s, 1H), 7.62−7.63 (m, 5H), 7.79−7.87 (m, 4H), 7.93 (d, J = 8.0 Hz, 2H), 8.19−8.27 (m, 12H), 8.64 (s, 4H), 8.99−9.10 (m, 8H), 9.19 (d, J = 4.4 Hz, 2H), 9.22 (d, J = 4.4 Hz, 2H), 9.43 (d, J = 4.4 Hz, 2H), 9.46 (d, J = 4.4 Hz, 2H). LD-MS: calcd for $C_{102}H_{86}N_8Zn_2$, 1554.6; found, 1553.0. λ_{abs} 423, 433, 551, 592 nm.

Dyad-p/Tpd. A general procedure was followed.[18,20] A solution of **14** (0.135 g, 0.111 mmol) in THF/methanol (4.4 mL, 10:1) was reduced with $NaBH_4$ (84.0 g, 2.22 mmol) at room temperature for 40 min. The reaction mixture was poured in a mixture of saturated aqueous NH_4Cl (5 mL) and CH_2Cl_2 (5 mL). The organic phase was isolated, washed with water, dried (Na_2SO_4), and concentrated to dryness. A mixture of the resulting dipyrromethane−dicarbinol and **1c** in CH_2Cl_2 (44 mL) was treated with $Yb(OTf)_3$ (87.9 mg, 0.142 mmol) at room temperature for 40 min. DDQ (75.4 mg, 0.332 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 band was collected and concentrated, affording the crude free-base dyad (44.0 mg).

A solution of the crude free-base dyad (22.0 mg) in $CHCl_3$ (7.5 mL) was treated overnight with a solution of $Zn(OAc)_2\cdot 2H_2O$ (31.4 mg, 0.143 mmol) in methanol (2.5 mL) at room temperature. The reaction mixture was washed with water. The organic phase was isolated, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The residue was suspended in hexanes and sonicated three times, affording a purple solid (10.4 mg, 11%): ^{1}H NMR (THF-d_8) δ 1.60 (s, 36H), 2.73 (s, 6H), 2.80 (d, J = 6.8 Hz, 6H), 5.17−5.25 (m, 6H), 5.89−6.00 (m, 3H), 7.62 (d, J = 7.2 Hz, 4H), 7.76−7.81 (m, 5H), 7.92 (s, 2H), 8.17 (d, J = 7.6 Hz, 4H), 8.22−8.24 (m, 8H), 8.64 (s, 4H), 8.86 (d, J = 4.4 Hz, 2H), 8.89−8.92 (m, 4H), 8.94 (d, J = 4.4 Hz, 2H), 9.05 (d, J = 4.8 Hz, 2H), 9.08 (d, J = 4.4 Hz, 2H), 9.37−9.39 (m, 4H). LD-MS: calcd for $C_{110}H_{100}N_8Zn_2$, 1660.7; found, 1580.7 [(M − 2allyl)$^+$], 1624.0 [(M − allyl)$^+$], 1664.0 [M$^+$]. λ_{abs} 423, 432, 551, 590 nm; λ_{em} (λ_{ex} 550 nm) 601, 650 nm.

Dyad-dpe/Tpd-1. A general procedure was followed.[30] A mixture of **16** (49.5 mg, 72.7 μmol), **18** (80.0 mg, 72.8 μmol), $Pd_2(dba)_3$ (10.1 mg, 11.0 μmol), and P(*o*-tol)$_3$ (26.5 mg, 87.1 μmol) in dry toluene/TEA (29 mL, 5:1) was reacted in a Schlenk flask at 35 °C. After 5 h, the identical portions of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ were added, and the reaction mixture was stirred for 17 h. After removal of the solvent, the residue was purified by a three-column sequence: silica [CH_2Cl_2/hexanes (3:1)], size-exclusion chromatography (THF), and silica [CH_2Cl_2/hexanes (3:1)]. The resulting solid (70.5 mg), consisting of the free-base dyad, was used directly in the metalation step. A solution of free-base dyad residue (35.2 mg) in $CHCl_3$ (12 mL) was reacted overnight with a solution of $Zn(OAc)_2\cdot 2H_2O$ (49.0 mg, 223 μmol) in methanol (3 mL) at room temperature. The reaction mixture was washed with water, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The resulting solid was suspended in hexanes and sonicated three times, affording a purple solid (32.7 mg, 51%): ^{1}H NMR (THF-d_8) δ 1.57 (s, 36H), 2.71 (s, 6H), 2.74−2.82 (m, 6H), 5.12−5.26 (m, 6H), 5.84−6.00 (m, 3H), 7.58 (d, J = 8.0 Hz, 4H),

7.75−7.82 (m, 5H), 7.89 (s, 2H), 8.04−8.26 (m, 16H), 8.28−8.38 (m, 4H), 8.80−9.02 (m, 16H). LD-MS: calcd for $C_{118}H_{104}N_8Zn_2$, 1760.7; found, 1682.3 [(M − 2allyl)$^+$], 1725.3 [(M − allyl)$^+$], 1765.3 [M$^+$]. λ_{abs} 428, 552, 591 nm; λ_{em} (λ_{ex} 550 nm) 602, 651 nm.

Dyad-dpe/Tpd-2. A solution of **21** (20.0 mg, 13.9 μmol) in $CHCl_3$ (8 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (31.3 mg, 142 μmol) in methanol (2 mL) at room temperature. The reaction was monitored by TLC. After 7 h, the reaction mixture was washed with water, dried (Na_2SO_4), concentrated, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. The resulting solid was dissolved in THF. The addition of hexanes and the slow evaporation of approximately half of the solvent under reduced pressure afforded a precipitate. The precipitate was collected by centrifugation, suspended in hexanes, and sonicated three times, affording a purple solid (21.3 mg, 97%): ^{1}H NMR (THF-d_8) δ 2.71 (s, 12H), 2.74−2.84 (m, 6H), 5.10−5.30 (m, 6H), 5.58−6.08 (m, 3H), 7.58 (d, J = 7.6 Hz, 8H), 7.70−7.82 (m, 5H), 8.02−8.15 (m, 12H), 8.15−8.26 (m, 4H), 8.31 (d, J = 8.0 Hz, 4H), 8.80−8.90 (m, 8H), 8.90−8.98 (m, 8H). MALDI-MS (POPOP): calcd for $C_{104}H_{76}N_8Zn_2$, 1564.4; found, 1564.9. λ_{abs} 428, 551, 592 nm.

Physical Studies. Monolayer Preparation. All of the monolayers on Si(100) were prepared using a high-temperature (400 °C), short-time (2 min) "baking" attachment procedure described previously.[4] The surface coverage and the conditions for achieving saturation coverage were determined electrochemically in a series of experiments wherein the concentration of the porphyrin in the deposition solution (benzonitrile) was systematically varied. The experiments revealed that the surface coverage could be varied in a controlled fashion from the low 10^{-12} to 10^{-10} mol cm^{-2} range (saturation coverage) by varying the porphyrin concentration from ~2 μM to ~2 mM.

The monolayers for the electrochemical experiments were prepared by dispensing a 2 μL drop of the porphyrin solution onto the surface of a microelectrode (vide infra) contained in a sparged volatile organic compound vial sealed under Ar. The monolayers prepared for the FTIR experiments utilized a much larger platform (~1 cm^2) and, consequently, required a larger drop size, ~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 cooled to room temperature. Finally, the Si substrate was rinsed and sonicated five times with anhydrous CH_2Cl_2 and purged dry with Ar.

Electrochemical Measurements. The electrochemical measurements of the dyads in solution were made in a standard three-electrode cell using Pt working and counter electrodes 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 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.[39] Propylene carbonate containing 1.0 M n-Bu_4NPF_6 was used as the 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 of the dyads in the monolayer was determined by the integration of the total charge in both anodic waves and by using the geometrical dimensions of the microelectrode. The surface coverage of the porphyrins in the dyad or of the intact dyad was determined by scaling the charge density by a factor of two or four, respectively (vide supra).

FTIR Spectroscopy. The FTIR spectra of the porphyrin 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 a KBr pellet (~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: General experimental section, NMR spectra for selected compounds, and LD-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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