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Formation of Porphyrins in the Presence of Acid-Labile Metalloporphyrins: A New Route to Mixed-Metal Multiporphyrin Arrays

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The ability to incorporate distinct metalloporphyrins at designated sites in multiporphyrin arrays is essential for diverse applications in materials and biomimetic chemistry. The synthesis of such mixed-metal arrays via acid catalyzed reactions has largely been restricted to metalloporphyrins of stability class II (e.g., Cu, Co, Ni) or I. We describe routes for the rational synthesis of mixed-metal arrays via acid-catalyzed condensations that are compatible with metalloporphyrins of stability class III (e.g., Zn) and IV (e.g., Mg). The routes are demonstrated for *p*-phenylene-linked arrays. The key finding is that several mild Lewis acids [$InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, and $Dy(OTf)_3$], which are known to catalyze the dipyrromethane + dipyrromethane–dicarbinol condensation in CH_2Cl_2 at room temperature without acidolysis, do not demetalate zinc or magnesium porphyrins under the same conditions. Rational routes to porphyrin dyads and triads employ reaction of a (porphyrin)–dipyrromethane and a (porphyrin)–dipyrromethane–dicarbinol. The porphyrin-forming reactions (six examples) proceed in yields of 18–28%. The metalation states of the arrays prepared in this manner include Zn-free base (ZnFb), MgFb, ZnFbMg, ZnFbZn, and ZnFbFb. Studies of the catalysis process indicate that the dipyrromethane + dipyrromethane–dicarbinol condensation is catalyzed by both the Lewis acid and a Brønsted acid derived in situ from the Lewis acid. Taken together, the ability to employ otherwise "acid-labile" metalloporphyrins as precursors in condensation procedures should broaden the scope of accessible mixed-metal multiporphyrin arrays and motivate further studies of the application of mild Lewis acid catalysts in porphyrin chemistry.

Introduction

The organization of multiple porphyrins into arrays has provided the basis for a variety of functional molecular architectures including light-harvesting systems,[1] reaction centers,[2] optoelectronic gates,[3] multistate information-storage devices,[4] host−guest assemblies,[5] and multielectron-redox enzymes.[6] Attaining the desired function requires the ability to incorporate porphyrins with particular attributes (redox potentials, orbital composition, excited-state dynamics, conformational properties, metal coordination, etc.) at designated sites in the array. The attributes of the porphyrin are largely determined by the nature and pattern of substituents at the perimeter of the macrocycle and the nature and oxidation state of the central metal.

The type of metalloporphyrins in an array has a profound impact on the synthetic strategy that can be employed. A major factor is that metalloporphyrins can undergo demetalation upon exposure to acid. The stability of metalloporphyrins toward acids of various strengths is described by a characteristic "stability class" as shown in Table 1.[7] For example, a metalloporphyrin of stability class III (e.g., Zn) would undergo demetalation in the presence of aqueous HCl in CH_2Cl_2 and also under conditions that define class II or

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Table 1. Stability Classes of Metalloporphyrins[7]

stability class	reagent[a]	effect	metallo-porphyrin[b]
I	H_2SO_4 (neat)	partial demetalation	Al,[c] Pd, V
II	H_2SO_4 (neat)	demetalation	Co, Cu, Ni
III	$HCl/H_2O-CH_2Cl_2$	demetalation	Fe, In, Zn
IV	AcOH (neat)	demetalation	Mg, Mn, Pb
V	$H_2O-CH_2Cl_2$	demetalation	Ba, Ca, Sr

[a] Treatment at 25 °C for 2 h. [b] Representative metal chelates. Each metal is divalent unless noted otherwise. [c] Al(III).

I metalloporphyrins (neat H_2SO_4) but is stable toward the conditions of stability class IV or V (AcOH or H_2O).

Two distinct approaches have been developed for the stepwise synthesis of multiporphyrin arrays joined by covalent linkers: (1) coupling of intact metalloporphyrin building blocks via Pd-mediated, Sonogashira or Glaser reactions; (2) acid-catalyzed condensation forming one or more new porphyrins in the process. The two approaches are quite complementary. The former approach is compatible with a wide variety of metalloporphyrins (stability classes I−IV) as well as free base (Fb) porphyrins owing to the mild, basic conditions of the Pd coupling reactions for use with porphyrins.[8,9] However, the porphyrin−porphyrin linker is constructed in the joining process and thus is limited in scope by the nature of the Pd-mediated coupling reaction: a directed coupling of iodo and ethyne groups yielding an ethyne linker (Sonogashira reaction) or an undirected dimerization of ethynes yielding a butadiyne linker (Glaser reaction). The acid-catalyzed condensation approach has much greater latitude toward linkers because the new porphyrin is formed around a preexisting linker. The reactions have included "aldehyde + pyrrole" and "aldehyde + dipyrromethane" condensations. However, the acid-catalysis conditions in such reactions typically have entailed propionic acid at reflux,[10] *p*-toluenesulfonic acid in methanol at room temperature,[11] trifluoroacetic acid (TFA) or $BF_3{\cdot}O(Et)_2$ in CH_2Cl_2 at room temperature,[12,13] or trichloroacetic acid in acetonitrile at room temperature.[14] Such acid-catalysis conditions restrict application of this approach to free base porphyrins or to metalloporphyrins that are quite acid-resistant (i.e., stability class I or II).

In addition to the limitation on choice of metal, the use of acid catalysis also imposes limits on the type of synthetic components that can be employed. Dipyrromethanes are common precursors to porphyrins[15] yet are susceptible to acidolysis. Acidolysis of dipyrromethanes followed by recombination of undesired fragments (i.e., "scrambling") leads to a mixture of porphyrins, which must be expressly avoided in any rational synthesis.[13] The propensity of dipyrromethanes toward scrambling depends on the substituents on the dipyrromethanes. Under the conditions for condensations with aldehydes, little or no scrambling is observed with dipyrromethanes that lack any meso substituents (regardless of β-substituents) or with β-unsubstituted dipyrromethanes that bear a hindered meso substituent (e.g., 5-mesityldipyrromethane), while extensive scrambling typically occurs with β-unsubstituted dipyrromethanes that bear an unhindered meso substituent (e.g., 5-phenyldipyrromethane).[16] The choice of dipyrromethane substituents is not necessarily innocent, as the substitution pattern plays a large role in determining the ordering of the molecular orbitals and thus the nature of the HOMO (a_{2u} or a_{1u}) of the resulting porphyrin.[17]

The strategies that employ acid-catalyzed condensations with a porphyrin precursor for preparing multiporphyrin arrays are diverse and include the following rational approaches: (1) Condensation of a porphyrincarboxaldehyde with pyrrole yields a star-shaped array.[18−21] (2) Condensation of a porphyrincarboxaldehyde with a dipyrromethane gives the corresponding triad[22−31] or of a multiporphyrin array bearing one carboxaldehyde with a dipyrromethane yields the larger array.[24,29,30] In the few cases that employed β-unsubstituted/meso-substituted dipyrromethanes,[25,28,31,32] scrambling was generally reported when the meso substituent was unhindered[25,28] but not when hindered.[31] (3) Condensation of a nickel porphyrin−dipyrromethane and a 1,9-diformyldipyrromethane gives the corresponding NiFb porphyrin dyad.[33] Of the few porphyrin−dipyrromethanes that have been prepared, all have incorporated β-substituents.[33−35] Statistical variants of most such strategies, wherein multiple

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aldehyde or dipyrromethanes species were employed leading to a mixture of products, have also been devised.[18,20,32,36−46] Regardless of approach, the only metalloporphyrins employed in the above routes were Co,[43] Cu,[21,43] or Ni[19,20,27,30,33,43] chelates. On the other hand, strategies that employ acid-catalyzed condensations of non-porphyrin precursors for preparing mixed-metal arrays generally suffer from reliance on at least one statistical reaction.[32,33,47−50] In summary, acid-catalyzed condensation methods have enabled the rational synthesis of M^1Fb porphyrin dyads and M^1FbM^1 porphyrin trimers, where M^1 is from stability class II. No routes have heretofore been developed that provide access to dyads and triads of composition M^1Fb and M^1FbM^3, where M^1 and M^3 include metals from stability class III or IV. The ability to employ a much broader expanse of metalloporphyrins in the acid-catalyzed condensations, particularly metals giving photochemically active porphyrins (e.g., Zn or Mg), would be exceptionally attractive for preparing functional multiporphyrin architectures.

Of particular interest are multiporphyrin arrays joined via the *p*-phenylene linker, because arrays with such linkers exhibit very fast excited-state energy-transfer rates between adjacent zinc and free base porphyrins [$>(10\ \text{ps})^{-1}$] while maintaining electronic spectra that are nearly identical to those of the monomeric components.[50] *p*-Phenylene-linked arrays have been prepared by acid-catalyzed condensations[15,18,20,21,23−26,29−33,36−48] or by the Suzuki reaction.[31,44] The Suzuki reaction entails a Pd-mediated coupling, employs basic conditions, and provides the basis for a rational synthesis of mixed-metal dyads owing to the directed coupling of a boronate group and a halogen. However, the reaction conditions require the presence of a strong base at elevated temperature for prolonged times, and stepwise syntheses of phenylene-linked multiporphyrin arrays larger than dyads have not been demonstrated using the Suzuki reaction.[31] Given the limitations of the Suzuki reaction and the acid-catalyzed condensations, new methods are needed that enable rational syntheses of *p*-phenylene-linked multiporphyrin arrays containing diverse free base and metalloporphyrins (stability classes I−IV) at designated sites.

We recently developed a strategy for the rational synthesis of porphyrins bearing up to four different meso substituents via the reaction of a dipyrromethane and a dipyrromethane−dicarbinol.[51] For nonscrambling acid catalysis conditions, we initially employed TFA in CH_3CN at room temperature. More recently, we found that a number of acids that were relatively inactive toward catalysis of the pyrrole + aldehyde condensation proved quite effective for catalyzing the condensation of a dipyrromethane and a dipyrromethane−dicarbinol. A subset of such acids was investigated in detail; these acids included $InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, and $Dy(OTf)_3$ in CH_2Cl_2 at room temperature.[52] The reactions proceeded without detectable acidolysis of the dipyrromethane species and afforded higher yields of porphyrin than obtained with TFA in CH_3CN. Our initial results in applying the new Lewis acids to reactions employing elaborate dipyrromethanes also gave good yields without detectable scrambling.[53] The exceptional results and apparent mildness of the acid catalysis achieved with $InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, and $Dy(OTf)_3$ prompted us to investigate whether these acids could be used in the presence of acid-labile (stability classes III and IV) metalloporphyrins.

In this paper, we report our findings concerning the use of the new Lewis acid catalysts in reactions of zinc and magnesium porphyrins yielding mixed-metal multiporphyrin arrays. The paper is divided into two parts. In part 1, we describe the rational synthesis of the mixed-metal multiporphyrin dyads and triads wherein adjacent porphyrins are joined via a *p*-phenylene linker. The synthesis of such arrays required the preparation of porphyrin−dipyrromethanes and porphyrin−dipyrromethane−dicarbinols, the joining of which occurs in a directed manner. In part 2, we report our studies of the catalytic conditions afforded by the new Lewis acids. Taken together, this work provides the foundation for the rational synthesis of mixed-metal multiporphyrin arrays incorporating metalloporphyrins of stability classes I−IV.

Results and Discussion

1. Synthesis. The synthesis of the porphyrin building blocks begins with methods that have been developed over the past few years, including the one-flask synthesis of a

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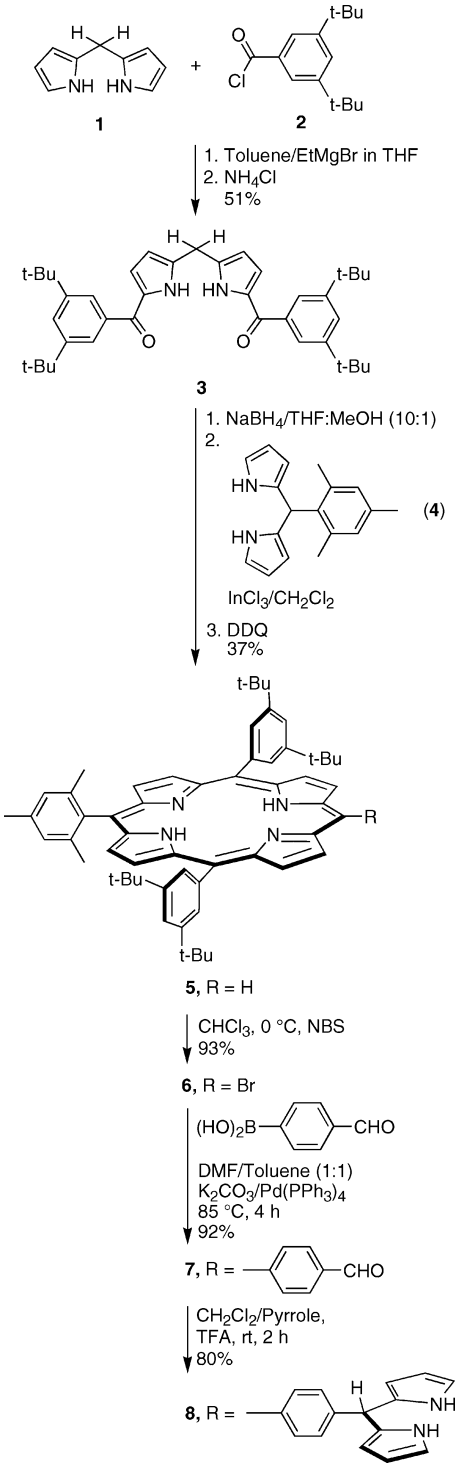
dipyrromethane from an aldehyde and excess pyrrole,[54] the 1,9-diacylation of a dipyrromethane,[51] and the reduction of a diacyldipyrromethane to the corresponding dipyrromethane−dicarbinol.[51] Each porphyrin building block (*trans*-AB_2C type) was prepared by condensation of a dipyrromethane + dipyrromethane−dicarbinol followed by oxidation with DDQ. The syntheses described herein make exclusive use of the Lewis acids [$InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, or $Dy(OTf)_3$ in CH_2Cl_2 at room temperature][52] for catalyzing the dipyrromethane + dipyrromethane−dicarbinol condensation.

Synthesis of Porphyrin−Dipyrromethanes. Treatment of dipyrromethane (**1**) with ethylmagnesium bromide followed by 3,5-di-*tert*-butylbenzoyl chloride (**2**) afforded diacyldipyrromethane **3** in 51% yield (4.70 g) (Scheme 1). Diacyldipyrromethane **3** is a known compound but was previously prepared in a smaller quantity (442 mg) and in lower yield (27%).[55] Compound **3** was reduced using $NaBH_4$ in THF/methanol to give the corresponding dicarbinol. Condensation of the latter with 5-mesityldipyrromethane (**4**) in the presence of $InCl_3$ in CH_2Cl_2 at room temperature for 40 min followed by oxidation with DDQ afforded porphyrin **5** in 37% yield. Porphyrin **5**[31] has been prepared previously in lower yield (23%) using TFA in CH_3CN. Treatment of porphyrin **5** with NBS (1.0 molar equiv) in $CHCl_3$ in the presence of pyridine at 0 °C[56] afforded the *meso*-bromoporphyrin **6** in 93% yield. Note that no β-brominated products were observed upon ^1H NMR analysis. A Suzuki coupling of *meso*-bromoporphyrin **6** and 4-formylphenyl boronic acid (2 equiv) in DMF/toluene (1:1)[31] using K_2CO_3 (8 molar equiv relative to **6**) containing $Pd(PPh_3)_4$ (15 mol % relative to **6**) at 85 °C for 4 h gave porphyrin **7** in 92% yield.

The conditions for the standard procedure for preparing dipyrromethanes employ the reaction of an aldehyde in excess pyrrole (25-fold) using TFA as catalyst.[54] More recently we have found that a larger excess of pyrrole (up to 400-fold) in conjunction with dilution in CH_2Cl_2 (2 or 3:1 v/v relative to pyrrole) affords a cleaner reaction and a higher yield, at least for the few elaborate aldehydes that have been examined.[53] Treatment of porphyrin−benzaldehyde **7** with pyrrole (300 molar equiv) and TFA (1.1 molar equiv) in CH_2Cl_2 for 2 h followed by column chromatography afforded porphyrin−dipyrromethane **8** in 80% yield (Scheme 1). The porphyrin−dipyrromethane gave considerable streaking on silica chromatography, but the impurities were more polar and bound to the top of the silica column and only one chromatography column was required for purification. To our knowledge, the few prior syntheses of porphyrin−dipyrromethanes have afforded a β-substituted dipyrromethane,[33−35] typically by reaction of a porphyrincarboxaldehyde with ethyl 3,4-dimethylpyrrolecarboxylate followed by ester hydrolysis and decarboxyation.[34,35] The synthesis of **8** shows that porphyrin−dipyrromethanes lacking β-substituents can be prepared in a one-flask process.

Scheme 1



Metalation of Porphyrin−Dipyrromethanes. Metalation of free base porphyrin **8** with $Zn(OAc)_2 \cdot 2H_2O$ was performed under standard conditions in $CHCl_3$/methanol (Scheme 2). The second fraction containing the desired compound was collected, giving **Zn-8** in 72% yield. The reported yield is slightly low for Zn insertions, which can be attributed to the propensity of the dipyrromethane moiety to cause streaking upon chromatographic workup.

The synthesis of magnesium porphyrins can be achieved at room temperature in high yield by two methods.[57,58] The milder of the two methods employs a homogeneous solution

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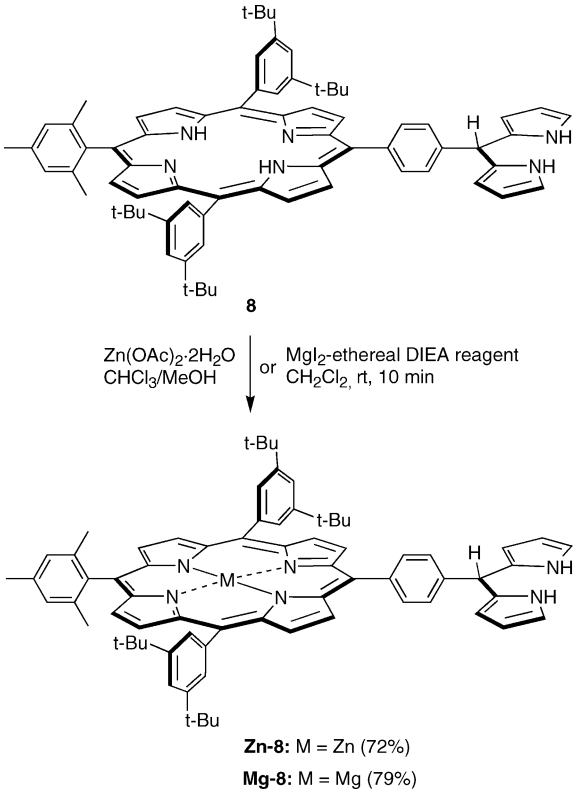
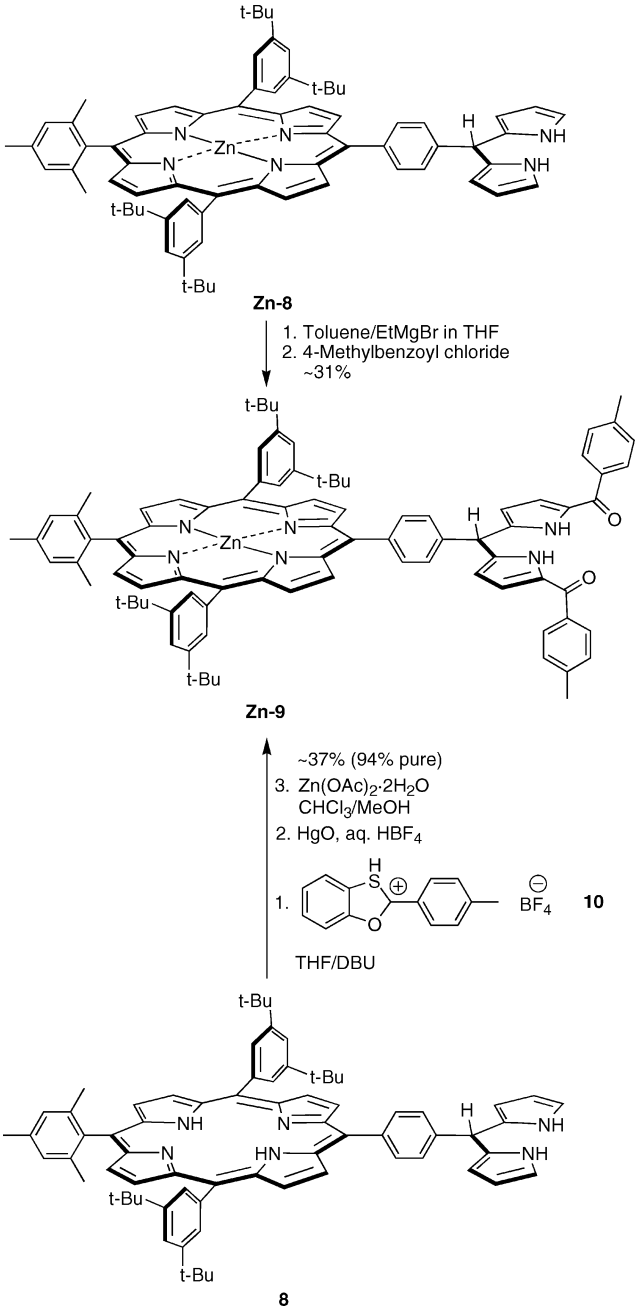
Scheme 2



of MgI_2 in diethyl ether containing DIEA.[58] Because of the anticipated lability of the dipyrromethane unit toward acid, the homogeneous method was employed. Thus, a solution of **8** in CH_2Cl_2 was treated with a freshly prepared solution of MgI_2 in diethyl ether containing DIEA, which was prepared following a known procedure[58] (Scheme 2). The standard workup including column chromatography (Al_2O_3, $CHCl_3$) afforded the desired magnesium porphyrin **Mg-8** in 79% yield. As with the zinc chelate, streaking of **Mg-8** on the column was observed and is a likely source of the less than quantitative yield.

Synthesis of Porphyrin−Diacyldipyrromethanes. Two routes are available for the 1,9-diacylation of a dipyrromethane: (1) treatment of the dipyrromethane with ethylmagnesium bromide followed by reaction with an acid chloride;[51] (2) alkylation of the dipyrromethane with a benzoxathiolium tetrafluoroborate followed by hydrolysis to unveil the acyl groups.[59] Both methods presented difficulties upon application to porphyrin−dipyrromethanes. We applied the former route to the zinc porphyrin due to the presence of the Grignard reagent and the latter to the free base porphyrin owing to the use of acidic conditions (Scheme 3): (1) Treatment of **Zn-8** with a solution of EtMgBr (1.0 M in THF) in anhydrous toluene followed by addition of *p*-toluoyl chloride (2.5 molar equiv) afforded the resulting monoacyl and diacyl products. Purification by successive column chromatography gave the relatively pure porphyrin−

Scheme 3



diacyldipyrromethane **Zn-9** (∼31% yield). (2) The alkylation procedure was performed by treating porphyrin−dipyrromethane **8** with 4 molar equiv of 2-(4-methylphenyl)-1,3-benzoxathiolium tetrafluoroborate (**10**)[60] and DBU[61] (4 molar equiv) in anhydrous THF for 1 h. Hydrolysis was performed in situ by adding HgO (4 molar equiv) and aqueous HBF_4 (8 molar equiv) for 2 h.[61] Standard workup and chromatography gave crude porphyrin−diacyldipyrromethane **9**, which was metalated using $Zn(OAc)_2{\cdot}2H_2O$ in $CHCl_3$/methanol. Purification by column chromatography on silica gave the relatively pure **Zn-9** (∼37% overall), but a rather broadened ^1H NMR spectrum was obtained. Analytical size exclusion

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chromatography (SEC) showed a dominant sharp peak (94% of total based on absorption at 420 nm) accompanied by a faster eluting small shoulder (6% of total). While later we found that preparative SEC in conjunction with silica chromatography could afford a product that was clean by analytical SEC, the material of 94% purity was used in the syntheses of the dyads and triads.

Synthesis of Porphyrin Dyads. The *p*-phenylene-linked porphyrin dyads were prepared by the dipyrromethane−dicarbinol + dipyrromethane condensation in CH_2Cl_2 using one of the new, mild Lewis acids followed by oxidation with DDQ. Thus, Zn−porphyrin−dipyrromethane **Zn-8** was reacted with dipyrromethane-dicarbinol **11-diol**[51] (2.5 mM each) in CH_2Cl_2 containing ytterbium(III) trifluoromethane sulfonate [$Yb(OTf)_3$] at an effective concentration of 3.2 mM (the catalyst does not dissolve completely, but we use concentration terms for clarity about how much material is employed). The progress of the reaction was monitored by treatment of reaction samples with a solution of DDQ (10 mM in toluene) followed by TLC analysis. A new fast-eluting band was observed to increase in intensity over time. Traditional UV−vis spectroscopic analysis[51] to follow the appearance of the porphyrin Soret band cannot be used to monitor the progress of the reaction because the starting material contains a porphyrin species, which shows a typical absorption pattern. After 50 min, DDQ (0.75 molar equiv/mol of pyrrole units) was added and the reaction mixture was stirred for 15 min. The resulting dyad **ZnFb-12** was very nonpolar compared to the starting compounds, moved as the first tight band close to the solvent front upon column chromatography (silica, CH_2Cl_2), and was readily isolated in 23% yield (Scheme 4).

For comparison purposes, the same dyad was prepared by the complementary reaction. Thus, reduction of porphyrin−diacyldipyrromethane **Zn-9** with $NaBH_4$ in dry THF/methanol (10:1) for 90 min gave the corresponding Zn−porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** (Scheme 4). The latter was condensed with 5-phenyldipyrromethane (**13**)[54] in CH_2Cl_2 containing $Yb(OTf)_3$ for 50 min. Oxidation with DDQ and purification by chromatography on silica afforded the desired dyad **ZnFb-12** in 22% yield.

The analogous dyad **MgFb-12** was prepared by condensation of porphyrin **Mg-8** and dipyrromethane−dicarbinol **11-diol** in CH_2Cl_2 containing $Yb(OTf)_3$ (Scheme 5). In early experiments the addition of DDQ followed by alumina chromatography led to the isolation of the demetalated dyad (**FbFb-12**). The addition of DDQ to cause oxidation of the porphyrinogen and polypyrromethane species results in formation of the hydroquinone product, namely $DDQH_2$ (2,3-dichloro-5,6-dicyano-1,4-dihydroxybenzene). The latter is weakly acidic ($pK_a = 5.14$)[62] and was considered to be the likely cause of demetalation. The same condensation was repeated and after 50 min pyridine was added to neutralize the acid. (Pyridine was chosen rather than TEA or DIEA, for example, because pyridine is electron-deficient and should not be oxidized by DDQ.) Then DDQ was added. Purification via column chromatography on alumina afforded **MgFb-12** in 28% yield. Note that alumina was employed rather than silica because magnesium porphyrins are stable on alumina but undergo demetalation on silica.

Dyad **MgFb-12** also was prepared by condensation of porphyrin **Mg-8** and dipyrromethane−dicarbinol **11-diol** in CH_2Cl_2 using $Dy(OTf)_3$ under the same conditions as for the reaction employing $Yb(OTf)_3$. However, the presence of several byproducts resulted in a difficult workup, and dyad **MgFb-12** was obtained accompanied by slight impurities in ~15% yield. Accordingly, $Dy(OTf)_3$ was not used to prepare further dyads or triads.

Synthesis of Porphyrin Triads. The successful synthesis of ZnFb and MgFb dyads prompted us to employ the same strategy to prepare mixed-metal triads. Thus, the condensation of porphyrin−dipyrromethane **Zn-8** and porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** was performed in CH_2Cl_2 containing $Yb(OTf)_3$ for 50 min followed by oxidation with DDQ (Scheme 6). Purification by column chromatography (silica, CH_2Cl_2) afforded the triad **ZnFbZn-14** in 21% yield. All byproducts were more polar and remained on top of the silica column, which is consistent with the results of the dyad-forming experiments.

Similarly, condensation of Zn−porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** and Mg−porphyrin−dipyrromethane **Mg-8** was performed in CH_2Cl_2 using $Yb(OTf)_3$ for 50 min, followed by the addition of pyridine and DDQ (Scheme 7). Column chromatography on alumina gave the triad **ZnFbMg-14** in 23% yield.

The related triad **ZnFbFb-14** was prepared via two different routes as shown in Scheme 8. First, treatment of a solution of **ZnFbMg-14** in CH_2Cl_2 with silica gel[63] and stirring overnight resulted in the selectively demagnesiated triad **ZnFbFb-14**. Second, condensation of Zn−porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** and Fb−porphyrin−dipyrromethane **8** was performed in CH_2Cl_2 containing $Yb(OTf)_3$ followed by oxidation with DDQ, affording the same triad **ZnFbFb-14** in 18% yield. The success of this porphyrin-forming reaction indicates that buffering of the acid by the free base porphyrin has little adverse effect on the reaction course. By contrast, the reactions of free base porphyrincarboxaldehydes with pyrrole or dipyrromethane species often require elevated concentrations of acid owing to the buffering effect of the porphyrin.[31]

Chemical Characterization. Each dyad and triad was characterized by TLC, analytical SEC, laser-desorption mass spectrometry (LD-MS),[64] absorption spectroscopy, fluorescence spectroscopy, and ^{1}H NMR spectroscopy. Each purified array was relatively homogeneous by TLC and analytical SEC, gave a strong molecule ion peak upon LD-MS analysis, and gave a readily assignable ^{1}H NMR spectrum. The

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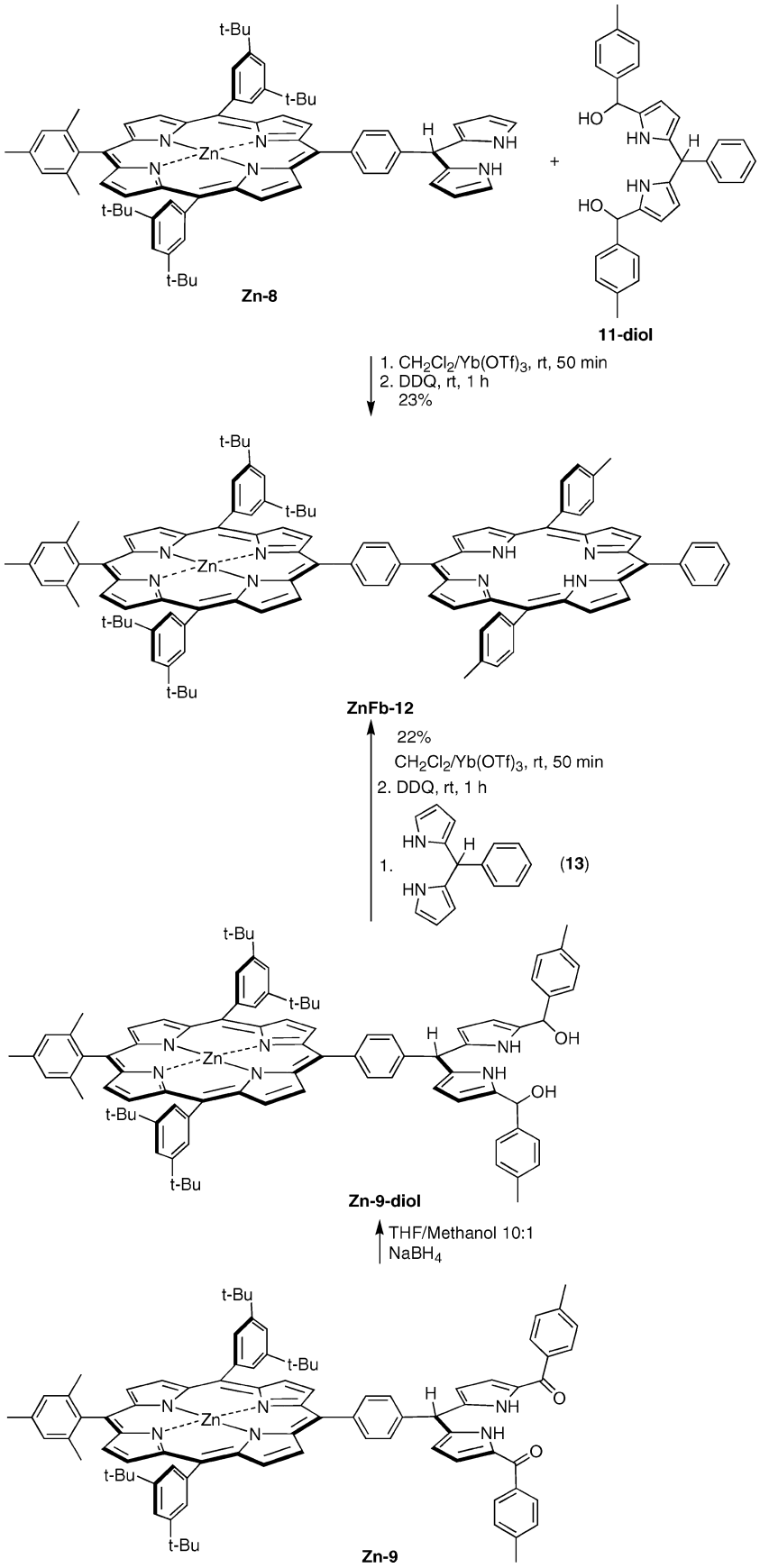
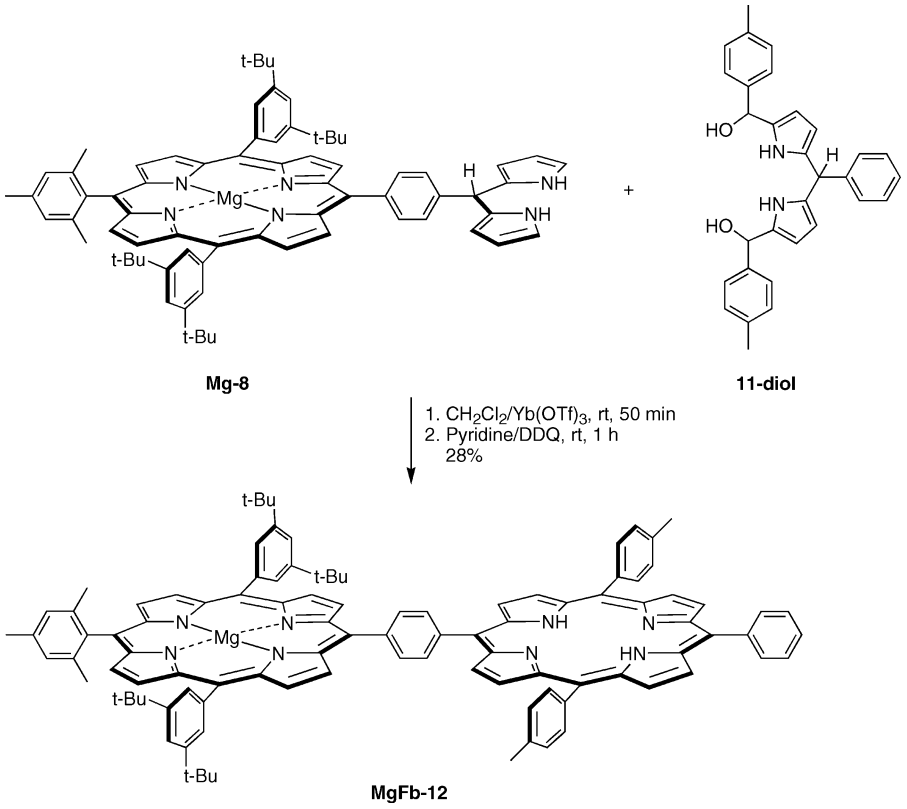
Scheme 4

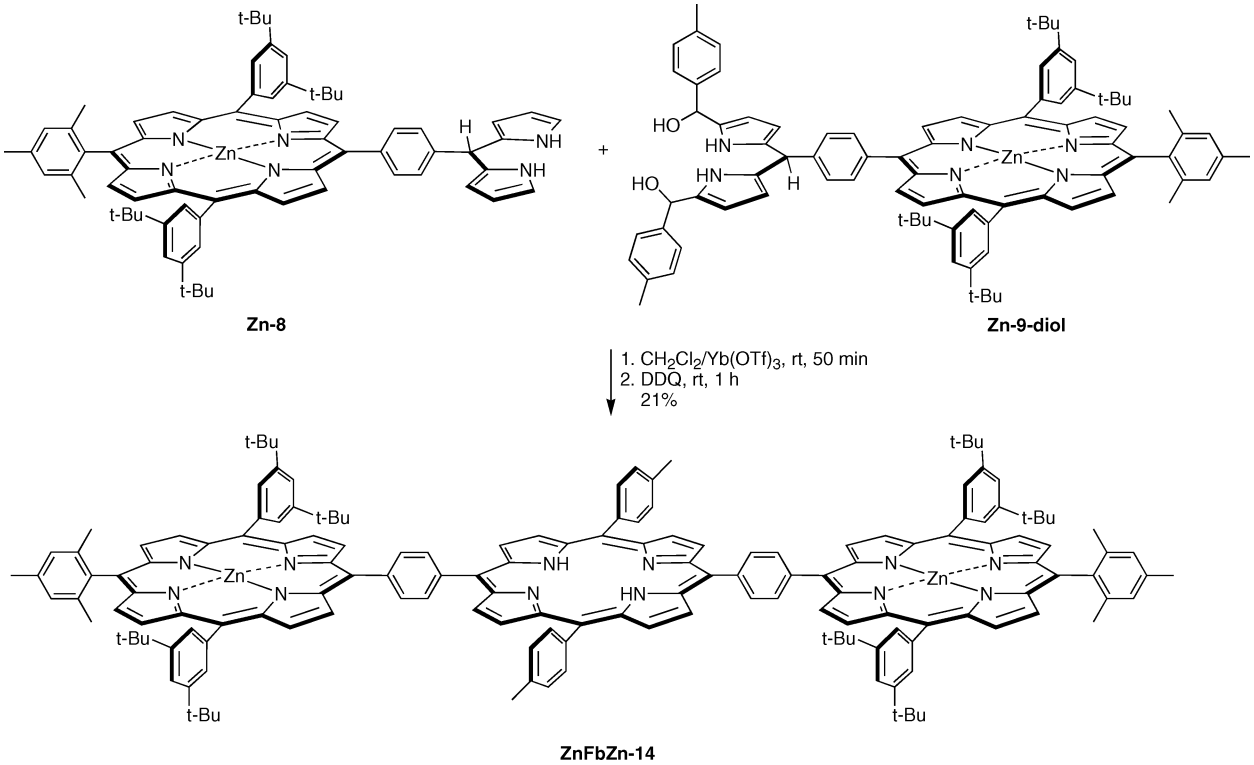


absorption spectrum of each array generally was the sum of the spectra of the component porphyrin monomers in the visible region, while splitting and broadening of the Soret peak was observed in the near-UV region. The splitting of

Scheme 5



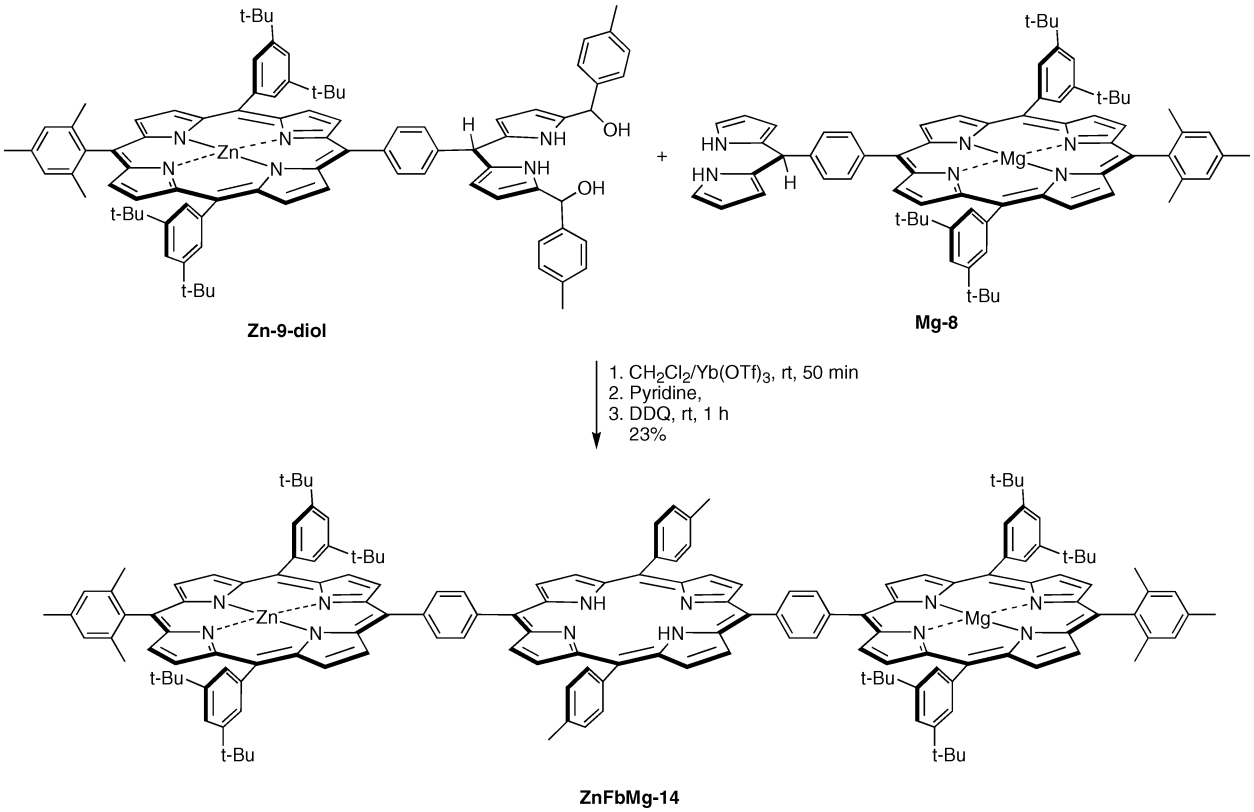
Scheme 6



the Soret band was typical for *p*-phenylene-linked arrays,[31,50] with maxima at 419 and 428 nm for **ZnFb-12**, at 420 and 431 nm for **MgFb-12**, at 419 and 435 nm for **ZnFbZn-14**, at 421 and 436 nm for **ZnFbMg-14**, and at 420 and 434 nm for **ZnFbFb-14**. The fluorescence emission spectrum of each array containing Zn and Fb chromophores showed emission exclusively from the Fb unit. The fluorescence emission spectrum of arrays containing a Mg chromophore showed the typical bands for Fb emission at 653 and 717 nm.

In no case was any sign of demetalation observed in the isolated products. Furthermore, no bands were observed during column chromatographic workup of the crude reaction

Scheme 7



Zn-9-diol + **Mg-8**

ZnFbMg-14

mixtures that could be attributed to the presence of a dyad or triad containing a demetalated porphyrin. Such demetalated porphyrins would be readily detected in the dyads and triads prepared herein. For example, TLC analysis of **ZnFbMg-14** and **ZnFbFb-14** on alumina using CH_2Cl_2/hexanes (2:1) gave $R_f = 0.12$ and 0.80, respectively. It is noteworthy that LD-MS could not be employed as a means of analyzing crude samples from reactions containing magnesium porphyrins due to demetalation of the magnesium porphyrins during the analytical process (see Supporting Information). However, LD-MS could be used for crude reaction samples containing zinc or free base porphyrins. For example, LD-MS analysis of a sample from the crude reaction mixture for the formation of **ZnFb-12** showed the expected intense molecule ion peak for **ZnFb-12** and no peak for the corresponding demetalated species, **FbFb-12**.

2. Examination of Acid Catalysis Conditions. Prior to, during the course of, and following the synthetic work described above we performed a series of experiments that explored the nature of the acid catalysis conditions for use with metalloporphyrins of stability classes III and IV. The studies were aimed initially at confirming the suitability of the acid catalysts and then turned toward gaining a deeper understanding of the acid catalysis process. The following sections describe the findings from a number of these experiments.

Stability of Metalloporphyrins toward Acids. We first examined the stability of a series of metalloporphyrins toward the mild Lewis acid catalysts [$InCl_3$, Yb(OTf)$_3$, Sc(OTf)$_3$, Dy(OTf)$_3$] that were found previously to be effective for the dipyrromethane + dipyrromethane−dicarbinol condensation. For stability studies we chose a series of porphyrins bearing substituents spanning a range of steric hindrance, including *meso*-tetrapentylporphyrin (H_2TPnP), *meso*-tetraphenylporphyrin (H_2TPP), and *meso*-tetramesitylporphyrin (H_2TMP) (Chart 1). The zinc and magnesium chelate of each porphyrin was examined. Each metalloporphyrin (2.5 mM in CH_2Cl_2) was treated with each of the four different catalysts using the concentration of the catalyst found optimal in studies of dipyrromethane−carbinol condensations:[52] $InCl_3$ (0.32 mM); Yb(OTf)$_3$ (3.2 mM); Sc(OTf)$_3$ (0.32 mM); Dy(OTf)$_3$ (1.0 mM). Note that although the acids do not dissolve completely in CH_2Cl_2, we use concentration terms nonetheless to describe the quantity employed. The reaction mixtures were stirred at room temperature for a specific period (1, 6 h) prior to analysis. Samples of fixed absorption at the Q(1,0) transition for the given metalloporphyrin (∼550 nm) were then analyzed by fluorescence spectroscopy with illumination of the Q_x(1,0) transition for the free base porphyrin (∼515 nm). The fluorescence emission of the Fb porphyrin was employed to determine the amount of free base porphyrin present, using a working curve for each metalloporphyrin (see Supporting Information). The limit of detection for each type of porphyrin ranged from 0.10% to 1.0% depending on the type of metal employed and the nature of the porphyrin substituents. The results obtained are summarized in Table 2.

The amount of demetalation over the course of 1 h generally ranged from relatively little to undetectable depending on the type of acid and the type of porphyrin. In general, the chelates of tetraphenylporphyrin were more prone to demetalation than those of tetrapentylporphyrin or

Scheme 8

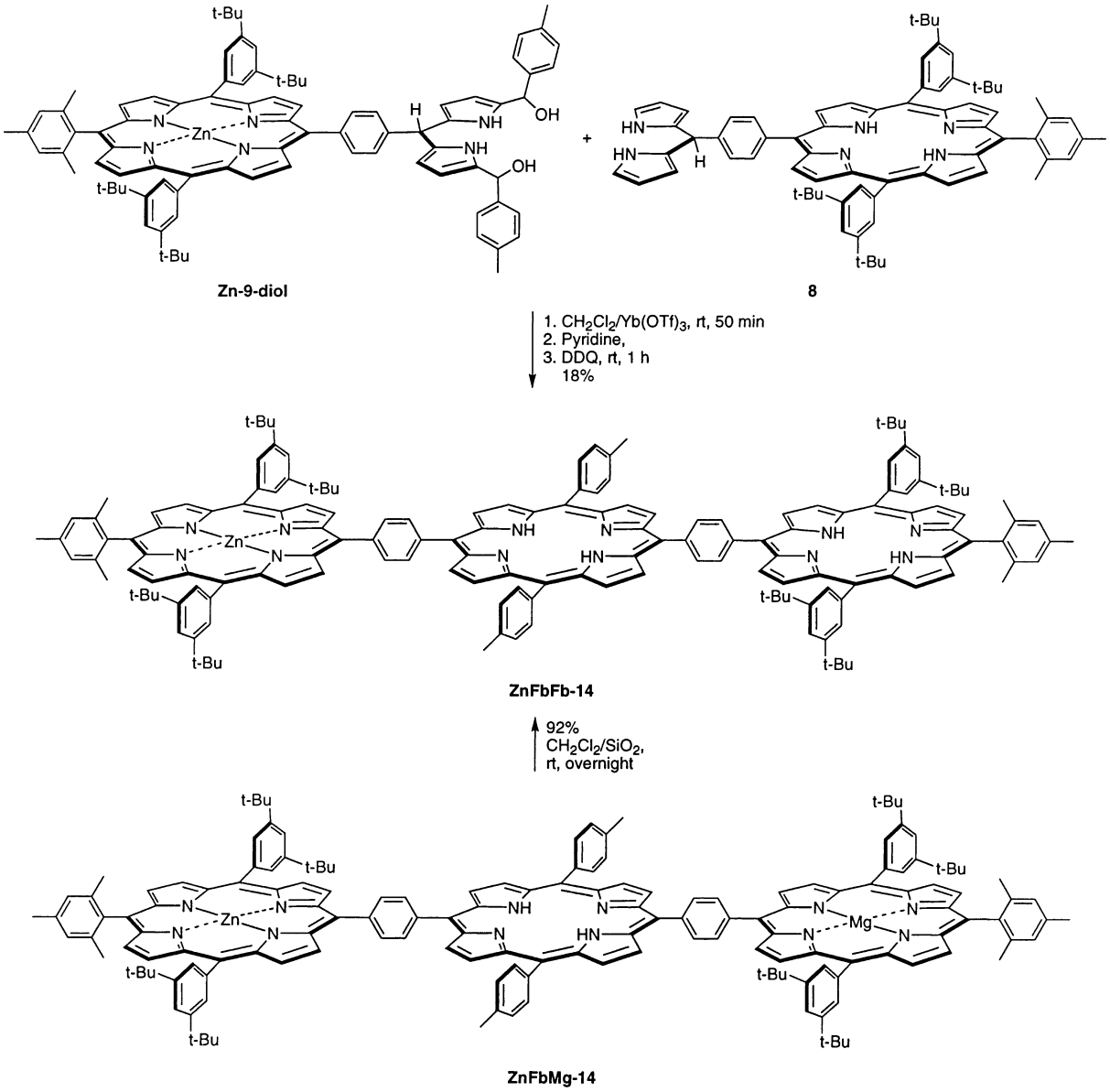
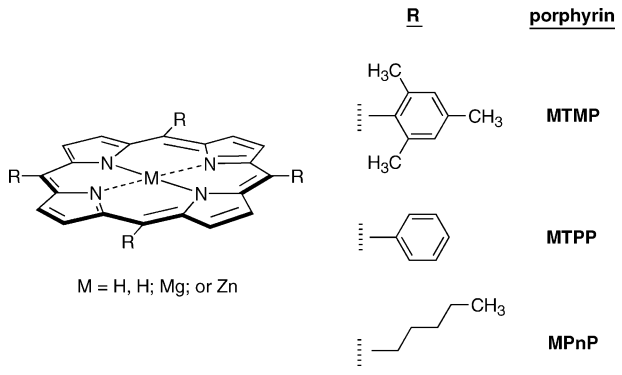


Chart 1



tetramesitylporphyrin. For ZnTPP, demetalation at 1 h was observed only with Sc(OTf)$_3$, and this was only at the ~0.3% level. At 6 h, a time period much longer than the dipyrromethane + dipyrromethane−dicarbinol condensation period but long enough to accentuate any differences between the catalysts, a small amount of demetalation was observed for $InCl_3$ and the level had increased for the sample with Sc(OTf)$_3$, but again no demetalation was detected for Dy(OTf)$_3$ and Yb(OTf)$_3$. No demetalation was observed for any acid at 6 h for ZnTPnP; the only demetalation observed with ZnTMP occurred at a trace level (0.54%) with Sc(OTf)$_3$ at 6 h.

For MgTPP at 1 h, a significant amount of demetalation (14%) was observed for Yb(OTf)$_3$, minor amounts (~3−4%) for Sc(OTf)$_3$ and Dy(OTf)$_3$, but no demetalation was observed for $InCl_3$. The extent of demetalation increased for the three acids over 6 h, but again no demetalation was detected for $InCl_3$. On the other hand, no demetalation was observed for MgTPnP or MgTMP at the 1 h timepoint with $InCl_3$, Yb(OTf)$_3$, or Dy(OTf)$_3$; only Sc(OTf)$_3$ gave demetalation, and this occurred at the ~1−2% level.

Of course, for porphyrin-forming reactions employed in the synthesis of mixed-metal arrays, demetalation at even the 0.1−1% level is unacceptable. The disparity in extent of demetalation among the three types of porphyrins must

Table 2. Stability of Metalloporphyrins toward the Four Acid Catalysts

			extent of metalloporphyrin demetalation with a given catalyst[c] (%)							
		limit of detection	$InCl_3$		$Yb(OTf)_3$		$Sc(OTf)_3$		$Dy(OTf)_3$	
entry	metalloporphyrin[a]	(LOD)[b] (%)	1 h	6 h	1 h	6 h	1 h	6 h	1 h	6 h
1	ZnTMP	0.10	<LOD	<LOD	<LOD	<LOD	<LOD	0.54	<LOD	<LOD
2	ZnTPP	0.10	<LOD	0.54	<LOD	<LOD	0.35	3.0	<LOD	<LOD
3	ZnTPnP	0.32	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
4	MgTMP	1.0	<LOD	<LOD	<LOD	1.5	1.1	7.7	<LOD	<LOD
5	MgTPP	0.32	<LOD	<LOD	14.0	60	3.9	5.5	2.7	7.3
6	MgTPnP	0.32	<LOD	1.0	<LOD	0.5	2.4	3.5	<LOD	<LOD

[a] Each metalloporphyrin was employed in a 2.5 mM solution in CH_2Cl_2 at room temperature. [b] Limit of detection in the fluorescence assay of the corresponding free base porphyrin derived by demetalation. [c] The amount of each catalyst employed is described in concentration terms (regardless of solubility) and is as follows: $InCl_3$, 0.32 mM; $Yb(OTf)_3$, 3.2 mM; $Sc(OTf)_3$, 0.32 mM; $Dy(OTf)_3$, 1.0 mM.

stem from differences in electronic properties and steric hindrance. In general, the rate of demetalation increases with the electron-richness of the porphyrin ring, as the mechanism of acid-induced demetalation entails protonation of the core nitrogen atoms.[65] The rate of demetalation generally decreases with increasing steric bulk protecting the metal site.[65] In the synthetic work described herein, each porphyrin was substituted with one mesityl group, two 3,5-di-*tert*-butylphenyl groups, and one *p*-phenylene group. The propensity toward demetalation of such metalloporphyrins would be expected to lie between that of the MTPP and MTMP benchmarks. To the extent that the acid-stability studies provide a realistic model of the conditions to which the metalloporphyrins are exposed during porphyrin formation, we should have observed some demetalated components in the $Yb(OTf)_3$-catalyzed syntheses using magnesium porphyrin building blocks.

The demetalation studies exposed the metalloporphyrin to the acid catalyst in CH_2Cl_2. In the porphyrin-forming reactions, other species are present that can interact with the acid catalyst, such as the dipyrromethane−dicarbinol. To examine whether the presence of a dipyrromethane−dicarbinol diminished the extent of demetalation, a solution of MgTPP (2.5 mM) and the dipyrromethane−dicarbinol **11-diol** (2.5 mM) in CH_2Cl_2 was treated with $Yb(OTf)_3$ (3.2 mM). After 1 h, the demetalation of MgTPP was only 0.8%, 17-fold less than the 14% observed when MgTPP alone was treated with $Yb(OTf)_3$. On the other hand, the same experiment using 5-phenyldipyrromethane (**13**, 2.5 mM) (which should not bind $Yb(OTf)_3$) rather than **11-diol** resulted in 13% demetalation of MgTPP. These results demonstrate that, under the porphyrin-forming conditions, the catalyst $Yb(OTf)_3$ likely causes less demetalation of the metalloporphyrin than observed in the more demanding control experiments performed herein.

Lewis Acids and Brønsted Acids. The observation of demetalation due to the presence of a Lewis acid prompted us to consider the mechanism of demetalation. The reaction for the demetalation of a metalloporphyrin requires a source of protons, shown as follows:

$$2H^+ + M{-}\text{porphyrin} \rightarrow H_2{-}\text{porphyrin} + M^{2+} \quad (1)$$

If the Lewis acid acted exclusively as a Lewis acid, a source of protons would not be available to participate in the demetalation. However, Lewis acids are known to engage in Lewis-acid-promoted formation of Brønsted acids, thereby providing a source of protons.[66] To assess the Brønsted acidity of the four catalysts, we treated solutions of H_2TPP (2.5 mM) in CH_2Cl_2 with each of the catalysts $InCl_3$ (0.32 mM), $Yb(OTf)_3$ (3.2 mM), $Sc(OTf)_3$ (0.32 mM), and $Dy(OTf)_3$ (1.0 mM) at room temperature. After 1 h, a sample from each reaction mixture (in CH_2Cl_2) was removed and then diluted in CH_2Cl_2 to give a solution for spectroscopic measurement ($\sim$3 μM total porphyrin species). The resulting spectra showed the presence of two bands, the Soret band and the band at $\sim$440 nm characteristic of H_4TPP^{2+}.[67] The spectrum obtained with $Yb(OTf)_3$ is shown in Figure 1, along with that of H_4TPP^{2+} formed by protonation of H_2TPP with TFA. The percentage of H_4TPP^{2+} present in these samples was as follows: $InCl_3$ (16%); $Yb(OTf)_3$ (47%); $Sc(OTf)_3$ (42%); $Dy(OTf)_3$ (<1%). In the case of $Yb(OTf)_3$, the spectrum also was recorded in a very thin film cell without dilution, giving a 39% yield of H_4TPP^{2+}, thereby indicating that the observed protonation is not a dilution artifact. The observation of the characteristic absorption spectrum of H_4TPP^{2+} under the conditions of the porphyrin-forming reaction implies that the presence of the Lewis acid results in the formation of a Brønsted acid (that protonates H_2TPP to give H_4TPP^{2+}). The source of protons is likely from H_2O, which is present in reagent-grade CH_2Cl_2 at a concentration of $\sim$8−10 mM.[68]

The presence of the Lewis acid and a Brønsted acid derived from the Lewis acid raised the question as to the nature of the catalysis that promotes the condensation of the dipyrromethane + dipyrromethane−dicarbinol. The hindered base 2,6-di-*tert*-butylpyridine,[69] which can act as a proton sponge but not bind to bulky Lewis acids, has been employed to discriminate Lewis and Brønsted acid catalysis. We examined the extent of demetalation of MgTPP in the

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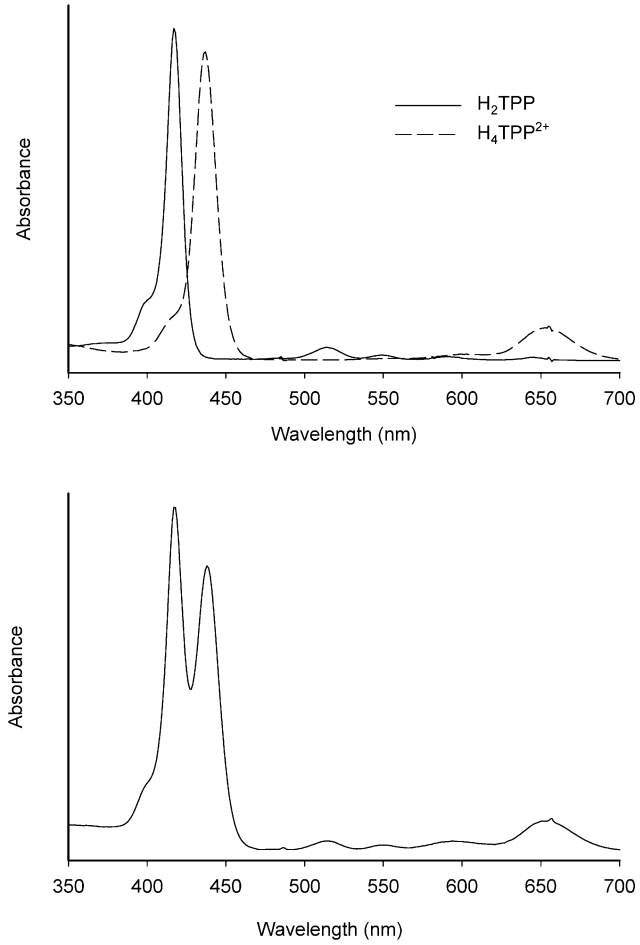


Figure 1. Top panel: Absorption spectra of H_2TPP and H_4TPP^{2+} (formed by acidification with TFA) in CH_2Cl_2 at room temperature. Bottom panel: Absorption spectrum of H_2TPP (2.5 mM) in CH_2Cl_2 after 1 h of treatment with $Yb(OTf)_3$ (3.2 mM) at room temperature, followed by dilution in CH_2Cl_2 to give a ~3 μM solution of total porphyrin species.

presence of $Yb(OTf)_3$ (3.2 mM) and various amounts of 2,6-di-*tert*-butylpyridine. In the absence of any 2,6-di-*tert*-butylpyridine, the extent of demetalation was 14% after 1 h in CH_2Cl_2. In the presence of 2,6-di-*tert*-butylpyridine (3.2 mM), only 0.44% demetalation was observed, while with 10 times as much 2,6-di-*tert*-butylpyridine (32 mM) the observable demetalation was below the limits of detection (<0.32%) after 1 h at room temperature. Thus, demetalation did not occur to a measurable extent in the presence of the mild Lewis acid and an agent that selectively neutralized any Brønsted acids.

Next, we examined whether the porphyrin-forming reaction would proceed with exclusive Lewis acid catalysis or whether the observed catalysis in the presence of the Lewis acids actually emanated from the Lewis-acid-derived Brønsted acid. A solution of dipyrromethane−dicarbinol **11-diol** (2.5 mM) and 5-phenyldipyrromethane (**13**, 2.5 mM) in CH_2Cl_2 was treated with $Yb(OTf)_3$ and various amounts of 2,6-di-*tert*-butylpyridine (3.2 or 32 mM) at room temperature (Scheme 9). The yield of the porphyrin over time was recorded by removing an aliquot and oxidizing the aliquot with DDQ, followed by UV−vis spectroscopy. The results are shown in Figure 2. In the absence of 2,6-di-*tert*-butylpyridine, the reaction was fast with near-maximal yield

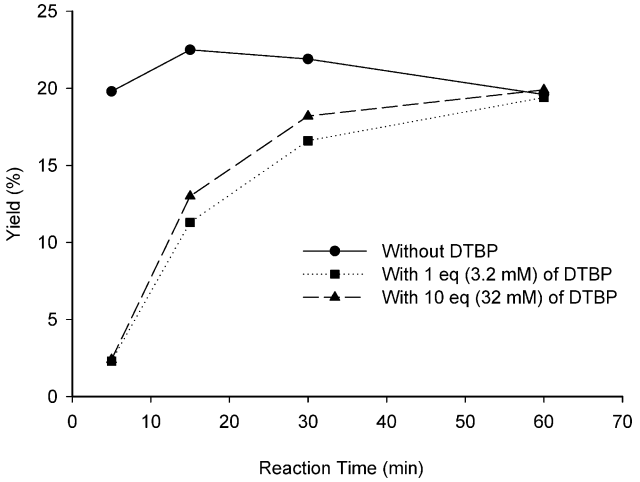
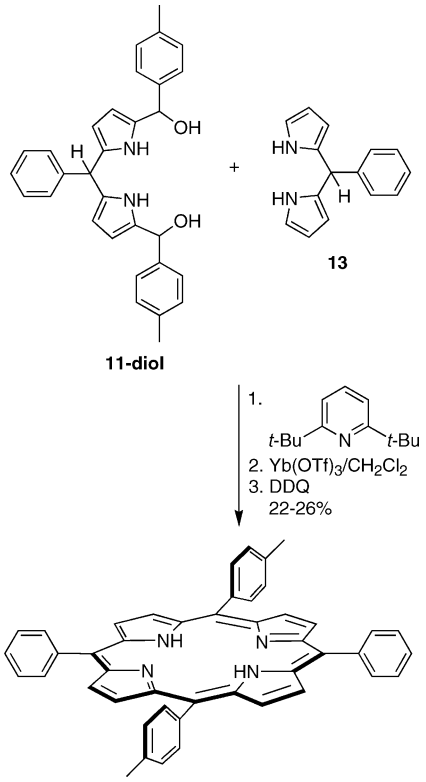


Figure 2. The yield of porphyrin as a function of time for dipyrromethane−dicarbinol + dipyrromethane condensation under catalysis by $Yb(OTf)_3$ in CH_2Cl_2. (The concentration of each reactant is 2.5 mM, and the concentration of the catalyst is 3.2 mM.) Each data point is the average from duplicate samples. Key: DTBP = 2,6-di-*tert*-butylpyridine.

Scheme 9



observed at the earliest time point (5 min). In the presence of 1 equiv of 2,6-di-*tert*-butylpyridine (relative to $Yb(OTf)_3$), the reaction was much slower and required 30−60 min to reach the same yield as without the base. The same slow reaction was observed with 10 equiv of 2,6-di-*tert*-butylpyridine. LD-MS analysis of each crude reaction mixture showed no scrambled porphyrin product. The isolated yield of porphyrin from each of the above reactions was consistent with the yield observed spectroscopically: 28% (in the absence of 2,6-di-*tert*-butylpyridine); 22% (in the presence of 3.2 mM 2,6-di-*tert*-butylpyridine); 26% (in the presence of 32 mM 2,6-di-*tert*-butylpyridine).

In summary, the presence of 2,6-di-*tert*-butylpyridine with the mild Lewis acid (1) greatly suppresses demetalation of a class IV metalloporphyrin and (2) does not diminish the yield of porphyrin obtained. One interpretation of these results is that the reaction in the presence of the 2,6-di-*tert*-butylpyridine derives predominantly from Lewis acid catalysis, while that in the absence of 2,6-di-*tert*-butylpyridine stems from a combination of Lewis acid catalysis and Lewis-acid-derived Brønsted acid catalysis. These observations suggest that further studies of the use of mild Lewis acid catalysts, in conjunction with bases that neutralize Brønsted acids, may lead to further improvements in catalysis for use with otherwise acid-labile metalloporphyrins.

Conclusions

The condensation of a dipyrromethane and a dipyrromethane−dicarbinol can be catalyzed with very mild acids. The reaction catalyzed by $Yb(OTf)_3$ proceeds without detectable acidolysis of the dipyrromethane species and without significant demetalation of zinc or magnesium tetraarylporphyrins. The catalytic conditions were used in the synthesis of *p*-phenylene-linked porphyrin dyads and triads containing zinc, magnesium, and free base porphyrins. The syntheses were carried out in a rational way owing to the inherent asymmetry of the joining reactions. The joining reactions include the following: porphyrin−dipyrromethane + dipyrromethane−dicarbinol; porphyrin−dipyrromethane−dicarbinol + dipyrromethane; porphyrin−dipyrromethane + porphyrin−dipyrromethane−dicarbinol. The porphyrin-forming reactions proceed in yields of 18−28%. A current limitation of this approach entails the methodology for diacylation of porphyrin−dipyrromethanes. Regardless, the acid-catalyzed condensation of a dipyrromethane and a dipyrromethane−dicarbinol is a valuable complement to the use of Pd-mediated coupling reactions with intact porphyrin building blocks. The former approach opens a pathway to multiporphyrin arrays comprised of free base porphyrins and diverse metalloporphyrins without apparent restrictions on the nature of the linker that joins adjacent porphyrins. Further studies of mild Lewis acid catalysts are warranted to explore the scope of application to elaborate substrates that incorporate diverse acid-labile components, including other metalloporphyrins of stability classes III and IV.

Experimental Section

Synthesis. General Methods. All ^{1}H NMR spectra (400 MHz) were collected in $CDCl_3$ unless noted otherwise. Absorption and fluorescence spectra were collected in chloroform at room temperature unless specified otherwise. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) without a matrix[64] or by high-resolution fast atom bombardment mass spectrometry (FAB-MS) using a matrix of nitrobenzyl alcohol and poly(ethylene glycol). The acid catalysts were used as received from Aldrich.

Solvents. THF was distilled from sodium benzophenone ketyl as required. Toluene was distilled from CaH_2. Anhydrous methanol (Aldrich), anhydrous DMF (Aldrich), CH_2Cl_2 (ACS), $CHCl_3$ (Fisher, certified ACS grade, stabilized with 0.8% ethanol), and $CHCl_3$ (Aldrich, 99.8%, certified ACS grade, stabilized with amylenes) were used as received. The $CHCl_3$ used was stabilized with ethanol unless noted otherwise.

Chromatography. Adsorption column chromatography was performed using flash silica gel (Baker, 60−200 mesh). Neutral alumina (80−200 mesh) was obtained from Fisher Scientific. Analytical SEC[70] was performed to assess the purity of multiporphyrin arrays.

Noncommercial Compounds. Dipyrromethanes **1**, **4**, and **13**,[54] acylating agents 2-(4-methylphenyl)-1,3-benzoxathiolium tetrafluoroborate (**10**)[60] and 3,5-di-*tert*-butylbenzoyl chloride (**2**),[71] and 1,9-bis(4-methylbenzoyl)-5-phenyldipyrromethane (**11**)[51] were obtained by literature procedures. The benchmark porphyrins for the acid catalysis studies H_2TPnP,[12] MgTPP,[57] H_2TMP,[72] MgTMP,[57] and ZnTMP[73] were prepared according to literature procedures. Porphyrins H_2TPP and ZnTPP are available from Aldrich; the syntheses of ZnTPnP and MgTPnP are described below.

1,9-Bis(3,5-di-*tert*-butylbenzoyl)dipyrromethane (3). From a known procedure[55] at 5.4 times the scale, reaction of dipyrromethane **1** (2.31 g, 15.8 mmol) and acid chloride **2** (10.0 g, 39.6 mmol) afforded a white powder (4.70 g, 51%) with analytical data consistent with those reported in the literature.[55]

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-mesitylporphyrin (5). From a standard procedure,[51] **3** (1.74 g, 3.00 mmol) was reacted with $NaBH_4$ (2.28 g, 60.0 mmol) in dry THF/methanol (240 mL, 10:1) for 90 min. After reduction was complete, the reaction was quenched with aqueous NH_4Cl (150 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with brine, and dried (K_2CO_3). Removal of the solvent afforded the dipyrromethane−dicarbinol as a colorless foam. The latter was condensed with **4** (0.790 g, 3.00 mmol) in CH_2Cl_2 (1200 mL) containing $InCl_3$ (86 mg, 0.39 mmol) for 40 min followed by oxidation with DDQ (2.04 g, 9.00 mmol). Filtration through a pad of silica and removal of the solvent gave a purple solid (883 mg, 37%): the analytical data were consistent with those reported in the literature for the synthesis employing other acid catalysis.[31]

5-Bromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphyrin (6). From a standard procedure,[56] a stirred solution of porphyrin **5** (427 mg, 0.530 mmol) in $CHCl_3$ (130 mL) was cooled in an ice bath for 15 min. Then NBS (94 mg, 0.53 mmol) was added. After 12 min, TLC analysis showed complete consumption of starting material. The reaction was quenched with acetone (20 mL), and the crude product was purified by column chromatography [silica, CH_2Cl_2/hexanes (1:1)]. Removal of the solvent afforded a purple solid (438 mg, 93%): ^{1}H NMR δ −2.64 (s, 2H), 1.54 (s, 36H), 1.85 (s, 6H), 2.61 (s, 3H), 7.26 (s, 2H), 7.80−7.81 (m, 2H), 8.06 (m, 4H), 8.64 (d, J = 4.8 Hz, 2H), 8.80 (d, J = 4.4 Hz, 2H), 8.92 (d, J = 4.4 Hz, 2H), 9.67 (d, J = 4.8 Hz, 2H); LD-MS obsd *m*/*e* 882.2; FAB-MS obsd *m*/*e* 882.4228, calcd *m*/*e* 882.4236 ($C_{57}H_{63}N_4Br$).

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-formylphenyl)-20-mesitylporphyrin via Suzuki Coupling (7). From a standard procedure,[31] porphyrin **6** (0.50 g, 0.57 mmol), 4-formylphenylboronic acid (0.17 g, 1.1 mmol), anhydrous K_2CO_3 (0.63 g, 4.5 mmol), and $Pd(PPh_3)_4$ (98 mg, 85 μmol, 15%) were weighed into a 100

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mL Schlenk flask. The flask was pump-purged with argon three times. Then toluene/DMF (57 mL, 1:1) was added and the reaction mixture was heated to 85 °C and stirred for 4 h. TLC analysis showed complete consumption of the starting material. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica, $CHCl_3$) affording a purple solid (474 mg, 92%): analytical data were consistent with those reported in the literature.[31]

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-(dipyrromethane-5-yl)-phenyl]-20-mesitylporphyrin (8). Following a modified procedure[53] for dipyrromethane synthesis,[54] a solution of porphyrin **7** (227 mg, 0.250 mmol) and pyrrole (5.0 g, 75 mmol) in CH_2Cl_2 (12 mL) was treated with TFA (22 μL, 0.28 mmol) at room temperature. TLC analysis [silica, $CHCl_3$/TEA (99:1)] showed complete consumption of the starting porphyrin−benzaldehyde after 2 h. The reaction mixture was neutralized with TEA. The solvent and the excess pyrrole were removed under reduced pressure. Chromatography [silica, $CHCl_3$/TEA (99:1)] afforded the desired product as a purple solid (205 mg, 80%): ^{1}H NMR δ −2.65 (br s, 2H), 1.53 (s, 36H), 1.86 (s, 6H), 2.62 (s, 3H), 5.84 (s, 1H), 6.18 (br s, 2H), 6.29−6.32 (m, 2H), 6.85−6.87 (m, 2H), 7.27 (s, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.78−7.79 (m, 2H), 8.08−8.09 (m, 4H), 8.18 (d, J = 8.1 Hz, 2H), 8.22 (br s, 2H), 8.69 (d, J = 4.8 Hz, 2H), 8.83−8.88 (m, 6H); LD-MS obsd *m*/*e* 1024.8; FAB-MS obsd *m*/*e* 1024.6115, calcd *m*/*e* 1024.6131 ($C_{72}H_{76}N_6$); λ_{abs} (toluene) 421, 516, 550, 593, 649 nm; λ_{em} (λ_{ex} = 515 nm, toluene) 652, 720 nm.

[5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-(dipyrromethan-5-yl)-phenyl]-20-mesitylporphinato]zinc(II) (Zn-8). A solution of **8** (0.30 g, 0.29 mmol) in $CHCl_3$ (32 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.32 g, 1.5 mmol) in methanol (5 mL). The reaction mixture was stirred overnight at room temperature, leaving only a small amount of free base species upon analysis by TLC and UV−visible spectroscopy. Purification by column chromatography (silica, $CHCl_3$) afforded two fractions owing to the significant difference in polarities of the free base porphyrin and the zinc chelate. The fraction containing the zinc chelate was concentrated, affording a purple solid (229 mg, 72%): ^{1}H NMR δ 1.53 (s, 36H), 1.86 (s, 6H), 2.62 (s, 3H), 5.84 (s, 1H), 6.17−6.19 (m, 2H), 6.29−6.31 (m, 2H), 6.86−6.87 (m, 2H), 7.28 (s, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.79−7.80 (m, 2H), 8.10−8.11 (m, 4H), 8.18 (d, J = 8.0 Hz, 2H), 8.22 (br s, 2H), 8.79 (d, J = 4.8 Hz, 2H), 8.95−8.99 (m, 6H); LD-MS obsd *m*/*e* 1085.8, FAB-MS obsd *m*/*e* 1086.5219, calcd *m*/*e* 1086.5266 ($C_{72}H_{74}N_6Zn$); λ_{abs} 424, 551, 592 nm; λ_{em} (λ_{ex} = 551 nm) 602, 649 nm.

[5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-(dipyrromethan-5-yl)-phenyl]-20-mesitylporphinato]magnesium(II) (Mg-8). Following a general procedure,[58] a solution of "ethereal MgI_2−DIEA" reagent (28 mL) was added via syringe to a stirred solution of porphyrin **8** (234 mg, 0.230 mmol) in CH_2Cl_2 (75 mL) under argon. After 10 min, TLC and UV−visible absorption spectral analysis showed complete metalation. Workup by extraction with $CHCl_3$, washing the organic phase with brine, and purification by column chromatography (alumina, $CHCl_3$) afforded a purple solid (189 mg, 79%): ^{1}H NMR δ 1.55 (s, 36H), 1.87 (s, 6H), 2.63 (s, 3H), 5.81 (s, 1H), 6.17−6.19 (m, 2H), 6.28−6.30 (m, 2H), 6.83−6.85 (m, 2H), 7.27−7.28 (m, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.77−7.78 (m, 2H), 8.13 (s, 4H), 8.19−8.21 (m, 4H), 8.72 (d, J = 4.4 Hz, 2H), 8.88−8.93 (m, 6H); LD-MS obsd *m*/*e* 1044.6, FAB-MS obsd *m*/*e* 1046.5857, calcd *m*/*e* 1046.5825 ($C_{72}H_{74}N_6Mg$); λ_{abs} 408 (sh), 430, 566, 607 nm; λ_{em} (λ_{ex} = 566 nm) 612, 666 nm.

[5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-(1,9-bis(4-methylbenzoyl)dipyrromethan-5-yl)phenyl]-20-mesitylporphinato]zinc-(II) (Zn-9). Route A. Following a dialkylation procedure,[59,61] a suspension of **10** (628 mg, 2.00 mmol) in anhydrous THF (9.7 mL) was degassed with a stream of Ar for 5 min. Then DBU (300 μL, 2.00 mmol) was added and the reaction mixture rapidly became clear and homogeneous. A solution of porphyrin **8** (511 mg, 0.50 mmol) in anhydrous THF (10 mL) was added via syringe. After the sample was stirred for 1 h, TLC analysis showed complete alkylation. Then HgO (435 mg, 2.00 mmol) and aqueous HBF_4 (523 μL, 4.00 mmol) were added and stirring was continued for further 2 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (150 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with $NaHCO_3$ and brine, and dried (Na_2SO_4). After removal of the solvent the crude product was purified by column chromatography [silica, $CHCl_3$/ethyl acetate (10:1)]. Some nonpolar byproducts could be separated as they appear in a slightly purple colored forerun. The product fraction came off as a very tight and concentrated band, affording a purple powder (252 mg, ∼40%). The ^{1}H NMR spectrum was broadened though the LD-MS spectrum showed the desired product as the dominant peak: LD-MS obsd *m*/*e* 1258.3; FAB-MS obsd *m*/*e* 1260.6940, calcd *m*/*e* 1260.6969 ($C_{88}H_{88}N_6O_2$); λ_{abs} 422, 518, 553, 593, 649 nm; λ_{em} (λ_{ex} = 518 nm) 651, 717 nm. The crude material obtained in this manner from several runs was pooled and metalated. In one run, a sample of the crude free base porphyrin (368 mg, 0.290 mmol) was dissolved in $CHCl_3$ (32 mL) and then a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.320 g, 1.46 mmol) in methanol (5 mL) was added. The reaction mixture was stirred at room temperature. After 2 h, TLC and UV−visible spectroscopic analysis showed complete metalation. Purification by column chromatography (silica, $CHCl_3$) gave a purple solid (356 mg, 92%; 37% overall). The R_f of **Zn-9** (silica, $CHCl_3$) is much higher than for the corresponding free base porphyrin **9**, implying the zinc chelate is less polar than the free base compound. Analytical SEC showed this material to be 94% pure: ^{1}H NMR δ 1.59 (s, 36H), 1.91 (s, 6H), 2.43 (s, 6H), 2.67 (s, 3H), 6.12 (s, 1H), 6.30−6.33 (m, 2H), 6.71−6.75 (m, 2H), 6.81 (s, 2H), 7.24−7.32 (m, 6H), 7.60−7.62 (m, 2H), 7.85−7.95 (m, 6H), 8.17 (s, 4H), 8.32−8.33 (m, 2H), 8.85−8.86 (m, 2H), 9.01−9.07 (m, 4H), 11.69 (br s, 2H); LD-MS obsd *m*/*e* 1325.2, FAB-MS obsd *m*/*e* 1322.6044, calcd *m*/*e* 1322.6104 ($C_{88}H_{86}N_6O_2Zn$); λ_{abs} 423, 551, 593 nm; λ_{em} (λ_{ex} = 551 nm) 602, 647 nm.

Route B. Following a standard procedure,[51] a solution of **Zn-8** (340 mg, 0.310 mmol) in anhydrous toluene (6.5 mL) was treated with a solution of EtMgBr (1.0 M solution in THF, 1.56 mL, 1.56 mmol) for 30 min. Then *p*-toluoyl chloride (100 μL, 0.780 mmol) was added and the mixture was stirred for an additional 45 min at room temperature. Then the reaction was quenched with saturated aqueous NH_4Cl (25 mL). Ethyl acetate was added, and the organic phase was washed with water and brine and then dried (Na_2SO_4). The solvent was removed and the crude product was purified by column chromatography (silica, CH_2Cl_2) to remove some nonpolar byproducts. Then the eluant was changed [CH_2Cl_2/ethyl acetate (20:1)] to obtain the monoacylated product. The desired diacylated compound was recovered by using the solvent mixture CH_2Cl_2/ethyl acetate (10:1). A final column (silica, $CHCl_3$) afforded a purple powder (128 mg, 31%) of comparable purity to that of the 94% pure material obtained from route A.

Dyad ZnFb-12. Following a common procedure,[51] reduction of **11** (57 mg, 0.13 mmol) with $NaBH_4$ (95 mg, 2.5 mmol) in anhydrous THF/methanol (10 mL, 10:1) and standard workup gave the dipyrromethane−dicarbinol **11-diol** as a yellow foam. The latter was then condensed with porphyrin−dipyrromethane **Zn-8** (136 mg, 0.130 mmol) in CH_2Cl_2 (50 mL) containing $Yb(OTf)_3$ (100 mg, 0.160 mmol) for 50 min followed by oxidation with DDQ (85 mg, 0.38 mmol). Filtration through a pad of silica and removal of

the solvent gave a purple solid (44 mg, 23%): ^{1}H NMR δ −2.61 (s, 2H), 1.58 (s, 36H), 1.91 (s, 6H), 2.65 (s, 3H), 2.75 (s, 6H), 7.25 (s, 2H), 7.31 (s, 2H), 7.61 (d, J = 7.2 Hz, 4H), 7.76−7.80 (m, 3H), 7.84−7.85 (m, 2H), 8.18−8.20 (m, 4H), 8.26 (d, J = 7.2 Hz, 4H), 8.60−8.65 (m, 4H), 8.84 (d, J = 4.4 Hz, 2H), 8.87 (d, J = 4.8 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.02 (d, J = 4.4 Hz, 2H), 9.06 (d, J = 4.4 Hz, 2H), 9.18 (d, J = 4.4 Hz, 2H), 9.31 (d, J = 4.4 Hz, 2H), 9.40 (d, J = 4.4 Hz, 2H); LD-MS obsd *m*/*e* 1509.6, FAB-MS obsd *m*/*e* 1506.6750, calcd *m*/*e* 1506.6893 ($C_{103}H_{94}N_8$Zn); λ_{abs} 419, 428, 516, 551, 590, 647 nm; λ_{em} (λ_{ex} = 551 nm) 654, 717 nm.

Dyad ZnFb-12 via Zn-9-diol. Following a standard procedure,[51] **Zn-9** (102 mg, 0.0800 mmol) was reacted with $NaBH_4$ (58 mg, 1.5 mmol) in dry THF/methanol (6.2 mL, 10:1) for 90 min. After reduction was complete, the reaction was quenched with aqueous NH_4Cl (40 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with brine, and dried (K_2CO_3). Removal of the solvent afforded the porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** as a purple solid. The latter was condensed with **13** (17 mg, 0.080 mmol) in CH_2Cl_2 (31 mL) containing Yb(OTf)$_3$ (62 mg, 0.10 mmol) for 50 min followed by oxidation with DDQ (52 mg, 0.23 mmol). Purification by column chromatography (silica, CH_2Cl_2) and precipitation with methanol gave a purple solid (25 mg, 22%): the analytical data were consistent with those from the previous experiment.

Dyad MgFb-12. Following a common procedure,[51] reduction of **11** (82 mg, 0.18 mmol) with $NaBH_4$ (137 mg, 3.60 mmol) in anhydrous THF/methanol (15 mL, 10:1) and standard workup gave the dipyrromethane−dicarbinol **11-diol** as a yellow foam. The latter was then condensed with porphyrin−dipyrromethane **Mg-8** (189 mg, 0.180 mmol) in CH_2Cl_2 (72 mL) containing Yb(OTf)$_3$ (144 mg, 0.230 mmol) for 50 min. Then pyridine (5 mL) was added followed by DDQ (122 mg, 0.540 mmol). Purification by column chromatography (alumina, CH_2Cl_2) afforded the desired dyad in the first fraction, which moved as a tight band close to the solvent front. Precipitation with methanol gave a purple solid (75 mg, 28%). A second preparation at smaller scale (0.079 mmol of **Mg-8**) afforded a 27% yield (31 mg): ^{1}H NMR ($CDCl_3$/THF-d_8) δ −2.61 (s, 2H), 1.58 (s, 36H), 1.92 (s, 6H), 2.64 (s, 3H), 2.75 (s, overlapped with water signal of THF, 6H), 7.30 (s, 2H), 7.45−7.46 (m, 2H), 7.60 (d, J = 6.4 Hz, 4H), 7.79−7.84 (m, 5H), 8.17 (s, 4H), 8.25 (d, J = 6.4 Hz, 4H), 8.59−8.65 (m, 4H), 8.75−8.77 (m, 2H), 8.87−8.95 (m, 6H), 9.06−9.10 (m, 4H), 9.32−9.33 (m, 4H); LD-MS obsd *m*/*e* 1465.4, FAB-MS obsd *m*/*e* 1466.7490, calcd *m*/*e* 1466.7452 ($C_{103}H_{94}N_8$Mg); λ_{abs} 420, 431, 517, 565, 606, 647 nm; λ_{em} (λ_{ex} = 566 nm) 653, 718 nm.

Triad ZnFbZn-14. Following a standard procedure,[51] **Zn-9** (155 mg, 0.117 mmol) was reacted with $NaBH_4$ (220 mg, 5.85 mmol) in dry THF/methanol (9.4 mL, 10:1). After reduction was complete, the reaction was quenched with aqueous NH_4Cl (50 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with brine, and dried (K_2CO_3). Removal of the solvent afforded the porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** as a purple solid. The latter was condensed with **Zn-8** (127 mg, 0.117 mmol) in CH_2Cl_2 (47 mL) containing Yb(OTf)$_3$ (94 mg, 0.15 mmol) for 50 min followed by oxidation with DDQ (79 mg, 0.35 mmol). Purification by column chromatography (silica, CH_2Cl_2) afforded one main fraction, which moved as a tight band close to the solvent front. Precipitation with methanol gave a purple solid (56 mg, 21%): ^{1}H NMR ($CDCl_3$/THF-d_8) δ −2.47 (s, 2H), 1.56 (s, 72H), 1.89 (s, 12H), 2.62 (s, 6H), 2.76 (s, overlapped with water signal of THF, 6H), 7.45−7.46 (m, 4H), 7.64 (d, J = 6.4 Hz, 4H), 7.81 (s, 4H), 8.15 (s, 8H), 8.23 (d, J = 6.4 Hz, 4H), 8.61−8.65 (m, 8H), 8.72−8.74 (m, 4H), 8.90−8.92 (m, 4H), 9.07−9.08 (m, 8H), 9.32−9.33 (m, 8H); LD-MS obsd *m*/*e* 2375.4, calcd average mass *m*/*e* 2371.1 ($C_{160}H_{154}N_{12}$Zn); λ_{abs} 419, 435, 518, 553, 593, 648 nm; λ_{em} (λ_{ex} = 553 nm) 654, 717 nm.

Triad ZnFbMg-14. Following a standard procedure,[51] **Zn-9** (165 mg, 0.124 mmol) was reacted with $NaBH_4$ (233 mg, 6.20 mmol) in dry THF/methanol (9.9 mL, 10:1) for 90 min. After reduction was complete, the reaction was quenched with aqueous NH_4Cl (60 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with brine, and dried (K_2CO_3). Removal of the solvent afforded the porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** as a purple solid. The latter was condensed with **Mg-8** (130 mg, 0.124 mmol) in CH_2Cl_2 (50 mL) containing Yb(OTf)$_3$ (99 mg, 0.16 mmol) for 50 min. Then pyridine (4 mL) was added followed by DDQ (83 mg, 0.37 mmol). Purification by column chromatography (Al_2O_3, CH_2Cl_2) and precipitation with methanol gave a purple solid (65 mg, 23%): ^{1}H NMR ($CDCl_3$/THF-d_8) δ −2.42 (s, 2H), 1.62 (s, 72H), 1.93 (s, 6H), 1.95 (s, 6H), 2.67 (s, 6H), 2.81 (s, overlapped with water signal of THF, 6H), 7.32 (s, 4H), 7.69 (d, J = 8.0 Hz, 4H), 7.85−7.87 (m, 4H), 8.18−8.21 (m, overlapped with signal of pyridine ligand, 8H), 8.29 (d, J = 8.0 Hz, 4H), 8.66−8.72 (m, 8H), 8.74 (d, J = 4.4 Hz, 2H), 8.78 (d, J = 4.4 Hz, 2H), 8.92 (d, J = 4.4 Hz, 2H), 8.96 (d, J = 4.4 Hz, 2H), 9.08 (d, J = 4.4 Hz, 2H), 9.12−9.15 (m, 6H), 9.34 (d, J = 4.4 Hz, 2H), 9.38−9.41 (m, 6H); LD-MS obsd *m*/*e* 2333.8, calcd average mass *m*/*e* 2331.2 ($C_{160}H_{154}$MgN$_{12}$Zn); λ_{abs} 421, 436, 519, 558, 605, 649 nm; λ_{em} (λ_{ex} = 558 nm) 654, 717 nm.

Triad ZnFbFb-14. Following a standard procedure,[51] **Zn-9** (123 mg, 0.093 mmol) was reacted with $NaBH_4$ (175 mg, 4.50 mmol) in dry THF/methanol (7.5 mL, 10:1) for 90 min. After reduction was complete, the reaction was quenched with aqueous NH_4Cl (40 mL). CH_2Cl_2 was added, and the organic phase was collected, washed with brine, and dried (K_2CO_3). Removal of the solvent afforded the porphyrin−dipyrromethane−dicarbinol **Zn-9-diol** as a purple solid. The latter was condensed with **8** (95 mg, 0.093 mmol) in CH_2Cl_2 (37 mL) containing Yb(OTf)$_3$ (74 mg, 0.12 mmol) for 50 min followed by oxidation with DDQ (62 mg, 0.27 mmol). Purification by column chromatography (silica, CH_2Cl_2) afforded one main fraction, which moved as a tight band close to the solvent front, followed by another, streaking fraction. The first band was isolated. Precipitation with methanol gave a purple solid (38 mg, 18%): ^{1}H NMR ($CDCl_3$) δ −2.47 (br s, 2H), −2.46 (br s, 2H), 1.59 (s, 72H), 1.91−1.92 (m, 12H), 2.65 (s, 6H), 2.79 (s, 6H), 7.32 (s, 4H), 7.67 (d, J = 8.0 Hz, 4H), 7.85−7.86 (m, 4H), 8.19−8.21 (m, 8H), 8.27 (d, J = 8.0 Hz, 4H), 8.66 (s, 8H), 8.76 (d, J = 4.4 Hz, 2H), 8.85 (d, J = 5.2 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 9.03 (d, J = 4.8 Hz, 2H), 9.09 (d, J = 4.8 Hz, 2H), 9.13 (d, J = 4.4 Hz, 4H), 9.20 (d, J = 4.4 Hz, 2H), 9.31−9.38 (m, 6H), 9.43 (d, J = 5.2 Hz, 2H); LD-MS obsd *m*/*e* 2304.5, calcd average mass *m*/*e* 2309.2 ($C_{160}H_{156}N_{12}$Zn); λ_{abs} 420, 434, 518, 554, 592, 649 nm; λ_{em} (λ_{ex} = 554 nm) 654, 719 nm.

Triad ZnFbFb-14 via Selective Demetalation of ZnFbMg-14. A sample of **ZnFbMg-14** (0.040 g, 0.017 mmol) was dissolved in 50 mL of CH_2Cl_2. Then silica gel (5 g) was added and the resulting mixture was stirred overnight at room temperature. The silica gel was removed by filtration. TLC analysis showed quantitative transformation of the Mg chelate to the Fb porphyrin. No further purification was necessary. The solvent was removed, and the desired triad **ZnFbFb-14** was obtained as a purple solid (36 mg, 92%): the analytical data were consistent with those from the experiment described above.

(*meso*-Tetrapentylporphinato)zinc(II) (ZnTPnP). A sample of H_2TPnP (236 mg, 0.40 mmol) in $CHCl_3$ (30 mL) was treated with

a solution of $Zn(OAc)_2 \cdot 2H_2O$ (439 mg, 2.0 mmol) in MeOH (2 mL) overnight at room temperature. Standard workup and chromatography (silica, CH_2Cl_2) afforded a purple solid (241 mg, 92%): ^{1}H NMR δ 1.01 (t, J = 7.6 Hz, 12H), 1.54−1.59 (m, 8H), 1.79−1.82 (m, 8H), 2.46 (br s, 8H), 4.71 (br s, 8H), 9.28 (s, 8H); LD-MS obsd *m*/*e* 651.1, FAB-MS obsd *m*/*e* 652.3508, calcd *m*/*e* 652.3483 ($C_{40}H_{52}N_4Zn$); λ_{abs} (toluene) 424, 558, 597 nm; λ_{em} (λ_{ex} = 558 nm, toluene) 602, 657 nm.

(*meso*-Tetrapentylporphinato)magnesium(II) (MgTPnP). Following a published procedure,[57] a sample of H_2TPnP (236 mg, 0.40 mmol) in $CHCl_3$ (30 mL, stabilized with amylenes) containing DIEA (1.39 mL, 8.0 mmol) was treated with MgI_2 (1.11 g, 4.0 mmol) for 10 min at room temperature. Standard workup and chromatography (alumina, CH_2Cl_2) afforded a purple solid (218 mg, 89%): ^{1}H NMR δ 1.03 (t, J = 7.6 Hz, 12H), 1.61 (br s, 8H), 1.87 (br s, 8H), 2.58 (br s, 8H), 4.99 (br s, 8H), 9.50 (s, 8H); LD-MS obsd *m*/*e* 610.9, FAB-MS obsd *m*/*e* 612.4060, calcd *m*/*e* 612.4042 ($C_{40}H_{52}N_4Mg$); λ_{abs} (toluene) 408, 428, 575, 615 nm; λ_{em} (λ_{ex} = 575 nm, toluene) 618, 678 nm.

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Supporting Information Available: Description of the metalloporphyrin acid-stability experiments, absorption spectra of H_2-TPP upon exposure to various Lewis acids in CH_2Cl_2, ^{1}H NMR and LD-MS (or MALDI-MS) of all new compounds, and analytical SEC traces for all arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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