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Investigation and Refinement of Palladium-Coupling Conditions for the Synthesis of Diarylethyne-Linked Multiporphyrin Arrays

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The synthesis of diarylethyne-linked multiporphyrin arrays requires Pd-mediated coupling conditions that are performed in dilute solution in the absence of copper and that give reaction mixtures that are easily purified. We previously developed copper-free Pd-mediated coupling conditions ($Pd_2(dba)_3$ and $AsPh_3$ in toluene/triethylamine (5:1) at 35 °C) but extensive chromatography was required to remove unidentified porphyrinic byproducts. We have used laser-desorption mass spectrometry (LD-MS) and analytical size-exclusion chromatography (SEC) to assay the products from the coupling reaction of a zinc(II) iodophenylporphyrin (ZnI) and a zinc(II) ethynylphenylporphyrin (ZnU′). Analysis of the crude reaction mixture revealed the diphenylethyne-linked dimer (Zn_2U) as the major product, byproducts plausibly derived from phenyl−aryl exchange processes (a phenylated derivative of ZnU′, a Ph_2As-substituted derivative of ZnI), byproducts believed to originate from direct phenylation processes (a phenylated derivative of ZnI, the phenylated dimer Ph-Zn_2U), and higher molecular weight material (HMWM) comprised of undefined porphyrin oligomers. The HMWM is readily removed but the phenylated dimer causes severe purification problems. Our observations concerning the phenylation processes are as follows: (1) The phenylated dimer was observed in significant quantity (∼7:1 ratio of Zn_2U/Ph-Zn_2U by LD-MS). (2) Control experiments showed that direct phenylation of free base (Fb) porphyrins or zinc porphyrins occurred with $Pd_2(dba)_3$ and $AsPh_3$ in the absence of iodo- or ethynylporphyrins. (3) Phenylation occurred at the earliest stage of the reaction (3 min time point). (4) The inclusion of CuI (with $Pd_2(dba)_3$ and PPh_3) accelerated formation of Zn_2U but did not reduce the amount of phenylation. (5) The use of P(*o*-tol)$_3$ in conjunction with $Pd_2(dba)_3$ caused slower reaction, a slight increase in HMWM, and significantly diminished arylation (Zn_2U/Ar-Zn_2U ratio ∼65:1). (6) Replacement of $Pd_2(dba)_3$ with $Pd(OAc)_2$ gave the same arylation ratio (65:1) but slightly lower yield. Application of the refined conditions ($Pd_2(dba)_3$ and P(*o*-tol)$_3$ in toluene/triethylamine (5:1) at 35 °C) to the stepwise synthesis of porphyrin trimers having metalation states of Zn and Fb (ZnZnFbU) or Mg, Zn, and Fb (MgZnFbU) afforded coupling efficiencies of 45−55% and a substantially simpler chromatographic purification process.

Introduction

One approach for the fabrication of molecular materials with nanometer dimensions has been the joining of modular building blocks via arylethyne units. Arylethynes afford a relatively rigid molecular framework and are conveniently constructed via repetitive stepwise coupling procedures. The diversity of materials prepared with arylethyne units includes nanometer-sized dendrimers,[1] linear oligomers,[2] and shape-persistent macrocycles.[3] We have used arylethyne-substituted porphyrins as building blocks[4,5] for the construction of molecular wires,[6] light-harvesting arrays,[7−9] electron-storage reservoirs,[10] amphipathic bilayer spanning molecules,[11] and optoelectronic gates.[12]

Preparation of diarylethyne-linked multiporphyrin arrays using free base (Fb) porphyrin and metallopor-

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phyrin building blocks imposes stringent constraints on the choice of coupling conditions.[13] The conditions must be nonacidic to avoid demetalation of metalloporphyrins and must avoid reagents that cause metalation of free base porphyrins. The latter constraint specifically excludes the use of many copper reagents as copper readily inserts into porphyrins. (Copper porphyrins are demetalated with exceptional difficulty.) The conditions must be sufficiently mild to suppress transmetalation of metalloporphyrins. The limited solubility of porphyrins generally causes couplings to be performed at modest concentration (0.01−0.001 M). Because most Pd-mediated coupling conditions have been developed for reactions at high concentration in the presence of a copper cocatalyst, we were prompted to develop modified conditions suitable for the preparation of arrays comprised of Fb and metalloporphyrins.

The conditions we devised in the early 1990s for the coupling of ethynylphenylporphyrins and iodophenylporphyrins include the use of tris(dibenzylideneacetone)-dipalladium(0) ($Pd_2(dba)_3$) and the ligand $AsPh_3$ in the absence of any copper reagents.[13] Reactions are performed at ∼2.5 mM ethynylporphyrin with the molar ratios of ethynylporphyrin (1.2), iodoporphyrin (1.0), $AsPh_3$ (1.2), and $Pd_2(dba)_3$ (0.15) in the mixed solvent toluene/triethylamine (5:1). This reaction medium is slightly basic and generally is an effective solvent for the porphyrinic starting materials, intermediates, and products. Reaction occurs smoothly at 35 °C; dimer- and trimer-forming reactions are complete in 1−2 h, and pentamer-forming reactions are complete in ∼6 h, with typical yields of 50−80%. Palladium insertion and transmetalation have not been observed under the mild reaction temperatures of 35 °C. These Pd-coupling conditions have been used in the syntheses of a variety of arrays containing porphyrinic pigments.[7−12,14,15]

The preparation of multiporphyrin arrays for studies of electronic and photonic properties requires the highest possible purity, preferably ≥99%. We developed a purification protocol that employs a combination of adsorption chromatography and preparative size exclusion chromatography (SEC).[9] The sequence of one silica column, one preparative SEC column, and one silica column gave dimers and trimers with 95−98% purity.[16] In applying the Pd-mediated coupling conditions to the preparation of larger multiporphyrin arrays, we found that the number of chromatographic procedures needed for purification increased almost linearly with the number of porphyrins in the array. The reaction byproducts which originated in the Pd-mediated coupling process were clearly porphyrinic in nature as evidenced by their absorption spectra. Although these vexing byproducts were uncharacterized, we surmised that they might originate from aryl−aryl interchange reactions which are known to occur in various Pd-mediated reactions (Heck,[17−21] Stille,[22,23] Suzuki[18,19,24,25]). While byproducts of aryl−aryl interchange are usually removed without difficulty upon workup in the coupling of small molecules, this would not necessarily be the case with the large size and hydrophobic nature of the porphyrin building blocks. The ability to suppress the formation of the porphyrinic byproducts is essential for the facile preparation of high-purity multiporphyrin arrays, especially as the number of porphyrins in the arrays increases.

In this paper we have used the reaction of zinc(II) 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin (ZnU′) and zinc(II) 5,10,15-trimesityl-20-(4-iodophenyl)porphyrin (ZnI) as the test case for examining the nature of the porphyrinic byproducts generated in the Pd-mediated coupling process affording a zinc porphyrin dimer, Zn_2U (Scheme 1). In our previous development of the Pd-coupling conditions, reactions were monitored by analytical SEC, and the final product purity was assessed using a combination of analytical SEC and laser desorption mass spectrometry (LD-MS). In this study, we have probed the reaction products by direct examination of crude reaction mixtures by both analytical SEC and LD-MS. A variety of porphyrinic byproducts have been identified, including those of mass in the region of that of the dimer Zn_2U. We surveyed conditions that minimize the formation of such byproducts, which are generally quite difficult to remove chromatographically. Over the past few years, studies of related Pd-mediated cross coupling chemistries have revealed that use of tri-*o*-tolylphosphine [$P(o\text{-tol})_3$] in place of $AsPh_3$ affords diminished aryl exchange.[18,20,21,25] We have characterized the product distribution obtained upon use of $P(o\text{-tol})_3$ in conjunction with $Pd_2(dba)_3$ in the synthesis of the porphyrin dimer Zn_2U. These conditions afford a cleaner reaction and have been applied to the synthesis of the trimers ZnZnFbU and MgZnFbU.

Results and Discussion

A. Characterization of the Product Distribution. To investigate the product composition we reexamined the reaction of ZnU′ and ZnI leading to the dimer Zn_2U (Scheme 1). The reaction was carried out using the

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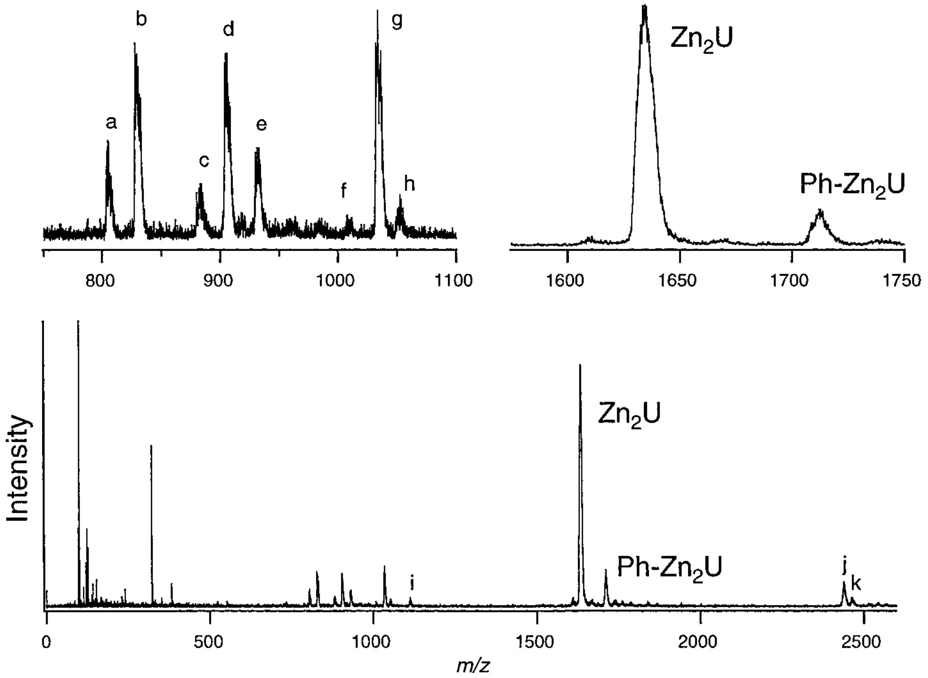
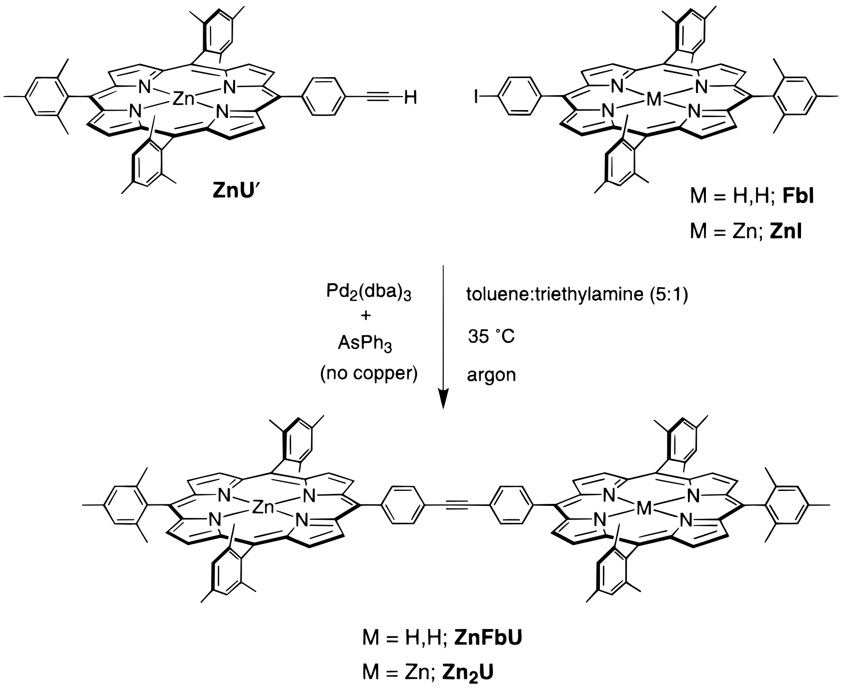


Figure 1. LD-MS spectrum of a sample from the crude reaction mixture from Zn_2U formation with $Pd_2(dba)_3$ and $AsPh_3$ after 2 h. The insets show expanded mass regions. The peaks at $m/z = 1634.6$ and 1712.1 are due to Zn_2U (calcd 1631) and Ph-Zn_2U (calcd 1707), respectively. Other peaks are assigned as follows: (a) $m/z = 804.8$, ZnI − I (due to laser photolysis; calcd 803.4); (b) $m/z = 827.9$, ZnU′ (calcd 828.4) (c) $m/z = 884.1$ Ph-ZnI − I (due to laser photolysis; calcd 880.4); (d) $m/z = 906.1$, Ph-ZnU′ (calcd 904.5); (e) $m/z = 931.4$, ZnI (calcd 930.3); (f) $m/z = 1010$, Ph-ZnI (calcd 1007.3); (g) $m/z = 1034$, Ph_2As-ZnU″ (calcd 1032); (h) $m/z = 1053$, unknown; (i) $m/z = 1113$, phenylated derivative of Ph_2As-ZnU″ (calcd 1109); (j) $m/z = 2437$, derivatization of Zn_2U with one phenylporphyrin unit (calcd 2433); (k) $m/z = 2462$, derivatization of Zn_2U with one ethynylphenylporphyrin unit (calcd 2457). Peak j is observed both upon laser photolysis of a mixture of ZnI and Zn_2U and in the HMWM fraction obtained from SEC separation.[27] (Note that the calculated masses are average masses.)

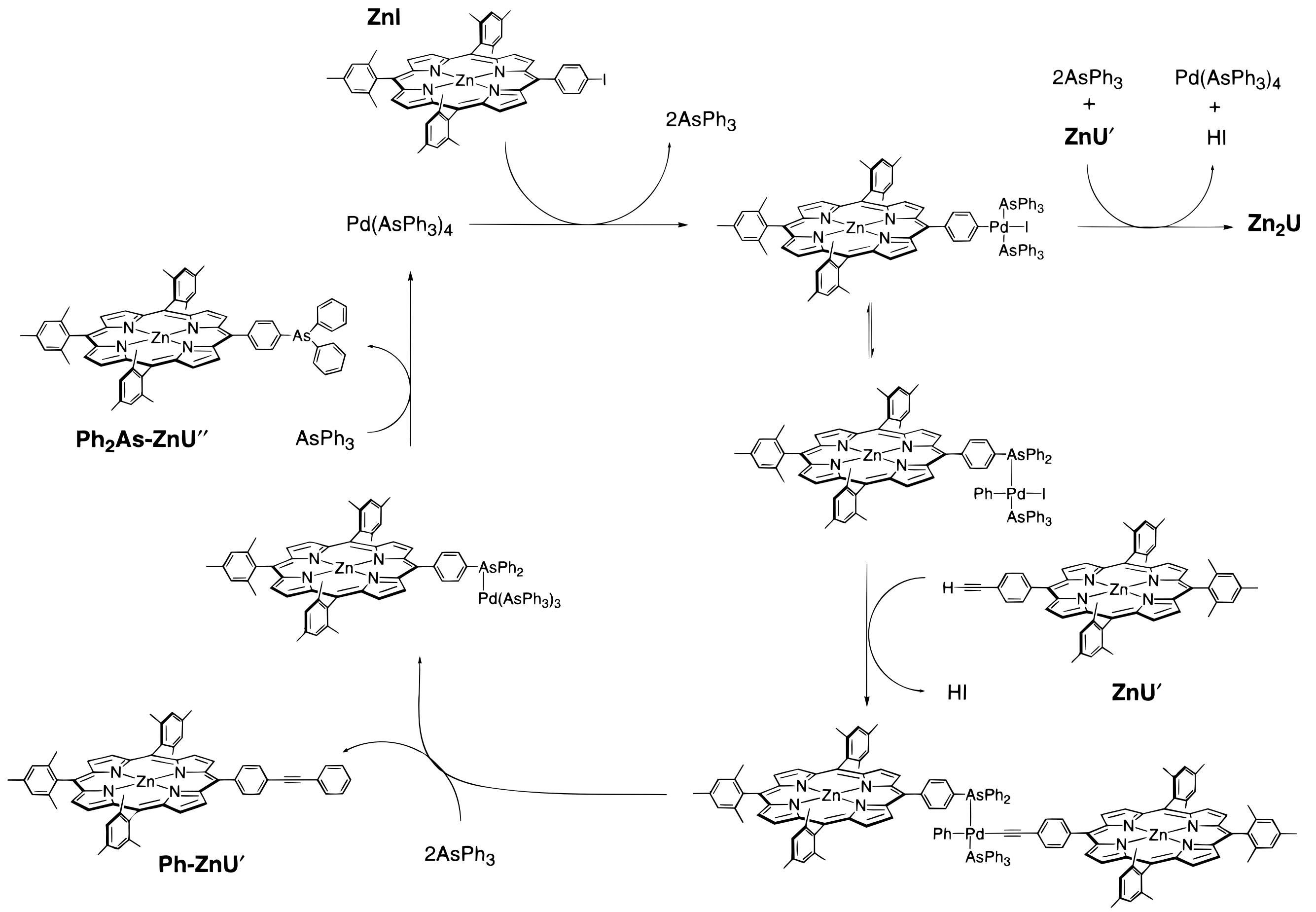
Scheme 1. Pd-Mediated Coupling of ZnU′ and ZnI to Make Zn_2U



conditions similar to those identified previously [~2.5 mM ethynylporphyrin with molar ratios of ethynylporphyrin (1), iodoporphyrin (1), $AsPh_3$ (1.2), and $Pd_2(dba)_3$ (0.15) in toluene/triethylamine (5:1) at 35 °C].[13] Reactions were performed at the microscale level in a glovebox or on a Schlenk line. Reaction mixtures were sampled and analyzed directly by LD-MS (Figure 1) and analytical SEC (Figure 2).

The LD-MS spectrum of a sample from the crude reaction mixture is dominated by the desired Zn_2U but a number of additional peaks also appear (Figure 1). The following assignments can be made: (1) The peaks at $m/z = 828$ and $m/z = 931$ correspond to unreacted ZnU′ and ZnI, respectively. (2) The peak at $m/z = 906$ can be assigned to the byproduct formed upon transfer of a phenyl group from $AsPh_3$ to ZnU′ ($828 + 77 = 905$)

Scheme 2. Simplified Catalytic Cycle Accounting for the Formatioin of Porphyrin Byproducts Ph-ZnU′ and Ph_2As-ZnU″ (Adapted from Novak et al.)[25]



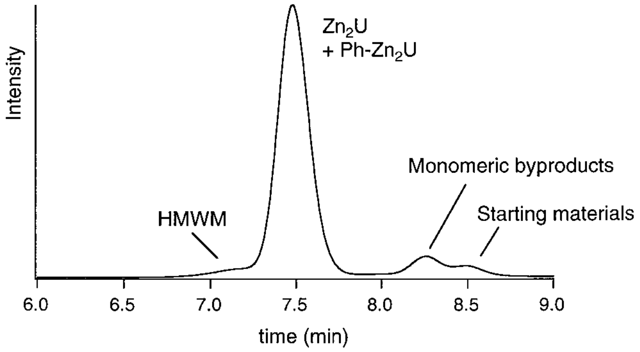


Figure 2. Analytical size exclusion chromatogram of the crude reaction mixture from the $Pd_2(dba)_3/AsPh_3$ mediated coupling of ZnU′ and ZnI.[27] Analysis was performed in toluene (100 Å column, 0.8 mL/min) with absorption spectral detection at 550 nm.

(Scheme 2).[26] (3) The peak at $m/z = 1034$ can be assigned to the byproduct formed upon substitution of the Ph_2As group for the iodo group in ZnI ($930 + 229 - 127 = 1032$) forming Ph_2As-ZnU″ (Scheme 2). (4) The peak at $m/z = 1712$ corresponds to transfer of a phenyl group from $AsPh_3$ to Zn_2U ($1631 + 77 = 1708$), affording the phenylated product Ph-Zn_2U. The ratio of Zn_2U:(Ph-Zn_2U) as determined from the peak heights is ~7:1.

The analytical SEC trace of the crude reaction mixture shows one dominant band and three small bands (Figure 2).[27] Bands in the chromatogram due to Zn_2U and unreacted monomers are assigned on the basis of known samples. The peak assigned to monomeric byproducts is based on retention time and corroborative LD-MS data. All materials eluting before Zn_2U are assigned as higher molecular weight material (HMWM).[27] Because Ph-Zn_2U and Zn_2U cochromatograph, they cannot be quantitated individually by analytical SEC (see Experimental Section). The assignment and integrated intensities are dimers Zn_2U and Ph-Zn_2U (91%), monomeric porphyrin byproducts (6%), and unreacted starting material (3%). The HMWM is not included in this quantitation. These results show that thorough analysis of the reaction product composition requires use of SEC in conjunction with LD-MS data.

The formation of phenyl−aryl exchange byproducts can be accounted for in a catalytic cycle[25] as shown in Scheme 2. These byproducts include Ph_2As-ZnU″ and Ph-ZnU′.[26] However, the phenylated byproducts (Ph-ZnI

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[26] Phenylated derivatives of ZnU′ can form via phenyl−aryl exchange (Ph-ZnU′, Scheme 2) or by direct phenylation (unspecified structure).

[27] Fractionation of the crude reaction mixture by preparative SEC followed by LD-MS analysis revealed the following. In the HMWM fraction, in addition to the peaks of mass higher than that of Zn_2U, some lower mass peaks also were observed including one at $m/z = 1034$ assigned to Ph_2As-ZnU″ (calcd 1032), indicating coelution with the porphyrin trimers, tetramers, and higher oligomers (HMWM). In the monomer byproduct fraction, most species anticipated on the basis of the masses in the low molecular weight region of the LD-MS spectrum obtained from the crude reaction mixture (Figure 1, peaks a−d) were observed. These results confirm the assignments for the various components observed in the SEC traces. (See Supporting Information.)

and Ph-Zn_2U)[28] cannot be accounted for by this catalytic cycle.

We performed control experiments to examine the extent of phenylation due merely to the combination of $Pd_2(dba)_3$ and $AsPh_3$, in the absence of a catalytic cycle involving the coupling of iodophenyl- and ethynylphenylporphyrins. Tetraphenylporphyrin (FbTPP, 5 mM) was treated with $Pd_2(dba)_3$ and $AsPh_3$ under the standard reaction conditions. After 2 h, LD-MS analysis of the crude reaction mixture showed the presence of a phenylated derivative of tetraphenylporphyrin, Ph-FbTPP, with a FbTPP/Ph-FbTPP ratio of 10:1.[29] The phenylated product was not separable from FbTPP on either silica or alumina TLC. Similar results were observed for ZnTPP, where the ZnTPP/Ph-ZnTPP ratio was 12:1. The sites of phenyl incorporation are not known. The results of these two experiments show that phenylation of the tetraphenylporphyrin occurs directly in the presence of $Pd_2(dba)_3$ and $AsPh_3$. While phenylation can occur as a consequence of phenyl−aryl exchange in a catalytic cycle, phenylation can also occur directly in the presence of $Pd_2(dba)_3$ and $AsPh_3$. Comparison of the peak ratios indicates a greater extent of phenylation during the course of the catalytic cycle (7:1 ratio of Zn_2U:Ph-Zn_2U) than in the absence (10:1 ratio of Ph-FbTPP:FbTPP). The phenylation of olefins has been observed in the presence of $Pd(OAc)_2$ and PPh_3[30,31] or $AsPh_3$[32] without any halogenated species present. The phenylation of FbTPP and ZnTPP is similar in that phenylation (from $AsPh_3$) occurs in the absence of any iodophenyl group and, therefore, without requiring the existence of species formed in a catalytic coupling cycle.

The nature of the HMWM observed by SEC was examined by LD-MS analysis. The LD-MS spectrum of the crude reaction mixture shows peaks at $m/z = 2437$ and 2462 (~4:1 ratio), consistent with the derivatization of Zn_2U with one additional phenyl-porphyrin unit (derived from ZnI) and one additional ethynylphenylporphyrin unit (derived from ZnU′), respectively (Figure 1). LD-MS analysis of the HMWM fraction obtained from a preparative SEC column exhibited a number of peaks, including a strong peak at $m/z = 2440$ (with accompanying higher mass shoulder at ~2460 plus other peaks at 2517, 2550, 2567), a less intense peak at $m/z = 3269$ (with accompanying higher mass shoulders), and an even weaker broad peak at $m/z \sim 4100$ (see Supporting Information).[27] This progression of peaks with increment of ~810 (830) is consistent with the addition of one, two, or three phenylporphyrin (ethynylphenylporphyrin) units to Zn_2U. Other less intense peaks in the shoulders are not readily assignable. We have frequently observed this type of pattern in LD-MS analyses of crude samples from Pd-mediated coupling reactions in the synthesis of multiporphyrin arrays (Figure 1). Such peaks are absent in purified samples. The HMWM byproducts are readily separated by preparative SEC and are clearly distinguished from the phenylated target molecules (e.g., Ph-Zn_2U). The latter are quite difficult to separate by chromatography, especially as the size of the arrays increases.

Table 1. Effects of Reaction Conditions on the Extent of Zn_2U Phenylation with $AsPh_3$ as Ligand[a]

entry	[ZnU′], [ZnI] (mM)	[$Pd_2(dba)_3$] (mM)	$AsPh_3$ (mM)	T (°C)	ratio (LD-MS)[b] of Zn_2U:Ph-Zn_2U	% yield (SEC)[c] of Zn_2U + Ph-Zn_2U (t, min)[d]
1[e]	2.5	0.38	3.0	35	7:1	91 (60)
2[e]	2.5	0.2	1.6	35	15:1	85 (60)
3	2.5	0.38	3.0	50	10:1	91 (20)
4[f]	7.5	0.37	3.0	50	25:1	80 (90)

[a] All reactions were performed in toluene/triethylamine 5:1 under argon in a glovebox. See Supporting Information for LD-MS data, SEC data, and kinetic plots. [b] Determined by ratioing the LD-MS peak heights for Zn_2U and Ph-Zn_2U. [c] Determined by comparison of the integrated area of the SEC band of the dimers with that of the internal standard ZnTPP (see Experimental Section). [d] Time points for collection of the SEC and LD-MS data are indicated in parentheses. The times do not indicate the end point of the reaction. [e] The $t_{1/2}$ is ~10 min. [f] The $t_{1/2}$ is ~30 min.

B. Investigation of Improved Coupling Conditions. We explored minor changes to the coupling conditions in an effort to suppress both phenyl−aryl exchange and direct phenylation processes while maintaining the attractive features of these conditions. Quantitative studies were enabled by including a known quantity of ZnTPP in each reaction, which allowed determination of the yield of dimers (sum of Zn_2U and Ph-Zn_2U due to coelution) by SEC. The results from the standard coupling conditions are displayed in Table 1 (entry 1). Upon decreasing the concentrations of $Pd_2(dba)_3$ and $AsPh_3$ by a factor of 2, the amount of phenylated dimer was decreased 2-fold but was still present at unacceptable levels (entry 2, Table 1). Although reduction of the $Pd_2(dba)_3$ and $AsPh_3$ concentration indicated a desirable trend, further reduction of $Pd_2(dba)_3$ and $AsPh_3$ posed sample-handling problems at these concentrations and scale. The reaction at 50 °C was complete by the first time point (3 min) but the Ph-Zn_2U contaminant was still present (entry 3, Table 1). At 3-fold higher concentration of the porphyrin monomers (ZnI and ZnU′) without changing the $Pd_2(dba)_3$ and $AsPh_3$ concentrations, the amount of Ph-Zn_2U declined but the level was still unacceptable (entry 4, Table 1).

We examined the time course for the formation of Zn_2U at 35 °C. A large burst of reaction occurred within the first time point (3 min), then the yield increased more slowly, and then a smaller burst occurred between 15 and 18 min, resulting in completion of the reaction (see Supporting Information). The erratic kinetics suggested aggregation or precipitation of the active species.

Studies over the past few years have shown that phenyl−aryl exchange can be suppressed by using *ortho*-substituted triarylphosphines such as tris(*o*-methoxyphenyl)phosphine in Suzuki or Heck reactions,[18] and

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(28) The mass spectral data do not distinguish whether Ph-Zn_2U is formed by direct phenylation or by coupling with a phenylated porphyrin monomer.

(29) In the phenylation experiment with FbTPP, a peak of comparable intensity to that of Ph-FbTPP was observed that corresponded to PdTPP. In the phenylation experiment with ZnTPP, no PdTPP was observed. In a large number of coupling reactions of iodophenyl or ethynylphenyl Fb porphyrins, no Pd porphyrins have been observed. These contrasting results suggest that the composition of available Pd species is different in the coupling reactions and the phenylation control experiments.

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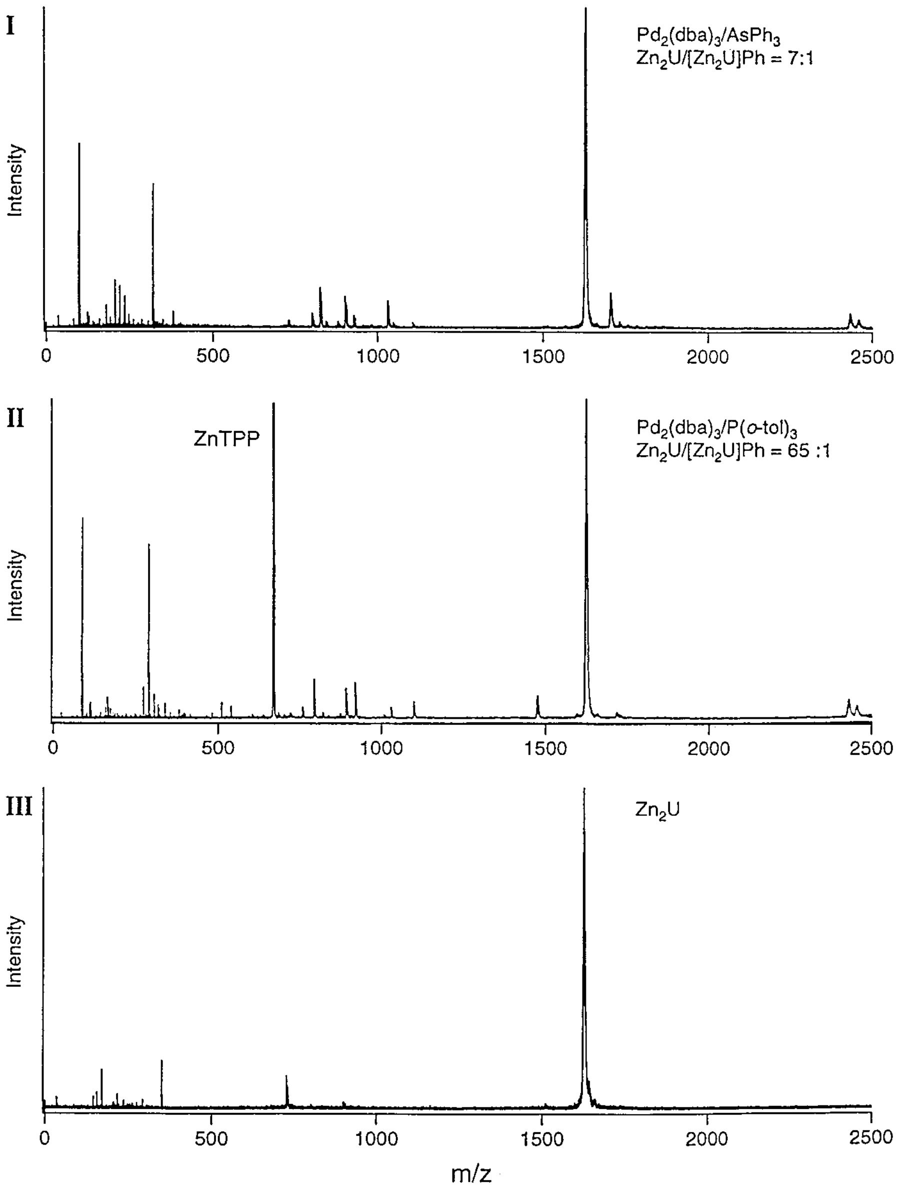

Figure 3. Comparison of LD-MS spectra: (I) crude reaction mixture for Zn_2U formation using $Pd_2(dba)_3$ and $AsPh_3$; (II) crude reaction mixture for Zn_2U formation using $Pd_2(dba)_3$ and P(*o*-tol)$_3$ (ZnTPP was included as a standard); and (III) purified Zn_2U from the reaction using $Pd_2(dba)_3$ and P(*o*-tol)$_3$.

Table 2. Effects of Reaction Conditions on the Extent of Zn_2U Arylation with P(*o*-tol)$_3$ as Ligand[a]

entry	[ZnU′], [ZnI] (mM)	[$Pd_2(dba)_3$] (mM)	P(*o*-tol)$_3$ (mM)	*T* (°C)	ratio (LD-MS)[b] of Zn_2U:Ar-Zn_2U	% Yield (SEC)[c] of Zn_2U + Ar−Zn_2U (*t*, min)[d]
1[e]	2.5	0.38	3.0	35	65:1	83 (360)
2	2.5	0.38	3.0	35	65:1	85 (1320)
3	2.5	0.38	3.0	50	65:1	81 (10)
4	7.5	0.37	3.0	50	65:1	61 (90)

[a] All reactions were performed in toluene/triethylamine 5:1 under argon in a glovebox. See Supporting Information for LD-MS data, SEC data, and kinetic plots. [b] Determined by ratioing the LD-MS peak heights for the Zn_2U and Ar-Zn_2U. [c] Determined by comparison of the integrated area of the SEC band of the dimers with that of the internal standard ZnTPP (see Experimental Section). [d] The times indicate when the SEC and LD-MS data were obtained. The times do not indicate the end point of the reaction. [e] The $t_{1/2}$ is ~35 min.

P(*o*-tol)$_3$ in Heck[20,21] or Suzuki[25] reactions. To overcome both the phenyl−aryl exchange and the direct phenylation side reactions, we investigated the use of P(*o*-tol)$_3$ in conjunction with $Pd_2(dba)_3$ for the coupling of ZnU′ and ZnI (Scheme 1). Using P(*o*-tol)$_3$ in place of $AsPh_3$ under otherwise identical conditions gave slower reaction but greatly diminished the amount of arylated side product (derived from transfer of an *o*-tolyl group), from a 7:1 ratio of Zn_2U:(Ph-Zn_2U) to a 65:1 ratio for Zn_2U:(Ar−Zn_2U) (entry 1, Table 2; Figure 3). Slightly higher yields of dimers were observed with $AsPh_3$ in the SEC trace, but this reflects in part the larger amount of undesired Ph-Zn_2U (entry 1 in both Tables 1 and 2). Higher temperature (entry 3, Table 2) or lower catalyst concentrations (entry 4, Table 2) did not alter the Zn_2U:(Ar-Zn_2U) ratio. In these reactions, the amount of HMWM is often slightly higher with P(*o*-tol)$_3$ than with $AsPh_3$. However, the HMWM is easily removed upon workup. In summary, the diminished yield of arylated byproducts (which are removed with difficulty

Table 3. Effects of Catalyst and Ligand on ZnFbU Formation[a]

entry	[ZnU′], [FbI] (mM)	[catalyst] (mM)	ligand (mM)	*t* (h)	ratio (LD-MS)[b] of ZnFbU:Ar-ZnFbU	% yield (SEC)[c] of ZnFbU + Ar−ZnFbU
1	2.5	Pd(OAc)$_2$, (0.52)	None	22	NA[d]	30[e]
2[f]	2.5	Pd(OAc)$_2$, (0.52)	AsPh$_3$, (2.0)	22	9:1[g]	66
3	2.5	Pd(OAc)$_2$, (0.53)	P(*o*-tol)$_3$, (2.1)	4	65:1	70
				22	65:1	71
4[h]	2.5	Pd(OAc)$_2$, (0.53)	P(*o*-tol)$_3$, (2.1)	5	20:1	59
				22	25:1	55
5[i]	2.5	Pd(OAc)$_2$, (0.50)	P(*o*-tol)$_3$, (2.0)	5	30:1	62
				22	30:1	67
6[i]	2.5	Pd(OAc)$_2$, (0.25)	P(*o*-tol)$_3$, (1.0)	5	45:1	41
				22	65:1	50
7	2.5	Pd(O$_2$CCF$_3$)$_2$, (0.51)	P(*o*-tol)$_3$, (2.1)	6	65:1	60
				23	65:1	64
8	2.5	palladacycle[j]	None	5	0.9:1	35
				23	0.8:1	42

[a] All reactions were performed under argon in a glovebox in toluene/triethylamine 5:1 at 60 °C unless noted otherwise. See Supporting Information for LD-MS data, SEC data, and kinetic plots. [b] Determined by ratioing the LD-MS peak heights for Zn$_2$U and Ar-Zn$_2$U. [c] Determined by comparison of the integrated area of the SEC band of the dimers with that of the internal standard ZnTPP (see experimental). [d] Not applicable as no ligands were used. [e] The yield represents only Zn$_2$U because no ligands were used. [f] Performed at 35 °C for 3.5 h, and then at 60 °C for the remainder. [g] ZnFbU:Ph-ZnFbU ratio. [h] The solvent was toluene/triethylamine 19:1. [i] A toluene stock solution which was 0.06 M in Pd(OAc)$_2$ and 0.26 M in P(*o*-tol)$_3$ was used. [j] *trans*-Di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II).

upon workup) obtained with P(*o*-tol)$_3$ makes this the ligand of choice for these types of coupling reactions.

To avoid ligands altogether, we investigated the use of Pd(OAc)$_2$ for the coupling of ZnU′ and FbI (Scheme 1). Pd(OAc)$_2$ gave no detectable phenylation but the reaction was sluggish and the yield was low (entry 1, Table 3). Pd(OAc)$_2$ with AsPh$_3$ gave improved yields (entry 2), but the ratio of ZnFbU:(Ph-ZnFbU) was nearly the same as with Pd$_2$(dba)$_3$ (entry 1, Table 1). With P(*o*-tol)$_3$, the yield was slightly lower but the amount of arylated dimer was the same as with Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$ (entry 3, Table 3). The amount of higher molecular weight material formed was 2−3 times greater with Pd(OAc)$_2$ versus Pd$_2$(dba)$_3$. Other variations such as the use of toluene:triethylamine 19:1 (entry 4) or stock solutions of the Pd(OAc)$_2$ and P(*o*-tol)$_3$ (entries 5 and 6) gave increased arylation and/or decreased yields. The use of Pd(O$_2$CCF$_3$)$_2$ and P(*o*-tol)$_3$ gave results comparable to those with Pd(OAc)$_2$ and P(*o*-tol)$_3$ (entry 7). The palladacycle *trans*-di(μ-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), which has been used in Heck reactions,[33] gave poor yields and a low ZnFbU:(Ar-ZnFbU) ratio (entry 8). In summary, the use of Pd(OAc)$_2$ and P(*o*-tol)$_3$ gives an equivalent level of arylation, a comparable yield of dimer, and an increased amount of higher molecular weight material compared with Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$.

Stille-coupling reactions can be accelerated by a factor of ∼250 upon inclusion of CuI in reactions that are catalyzed with Pd$_2$(dba)$_3$ and PPh$_3$.[34] While copper is to be avoided in general in porphyrin building block chemistry due to transmetalation of metalloporphyrins and metalation of free base porphyrins,[13] we sought to examine the effect of copper in the Pd-mediated coupling reaction yielding Zn$_2$U. Accordingly, we performed reactions of ZnU′ and ZnI with Pd$_2$(dba)$_3$ and PPh$_3$ with and without CuI. In the presence of CuI, the reaction was finished in 3 h, the yield of dimers was 94% (SEC), the ratio of Zn$_2$U:(Ph-Zn$_2$U) was 15:1 (LD-MS), and there was an intense unknown peak at m/z = 1063. The experiment without CuI was unfinished at 24 h with a 28% yield of dimers (SEC). The addition of CuI did not reduce the amount of phenylated product to an acceptable level, even though the reaction rate was significantly accelerated.

C. Applications. To explore the efficacy of these refined coupling conditions (using Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$), we scaled up the preparation of Zn$_2$U. The coupling reaction of ZnU′ and ZnI was performed with Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$ for 10 h at 35 °C with 0.12 mmol of each porphyrin. One silica gel column afforded a mixture of porphyrins free of ligand and Pd species, one preparative SEC column afforded a fraction consisting largely of the desired Zn$_2$U, and one final silica column gave 107 mg (55% yield) of the purified Zn$_2$U. The LD-MS analysis showed no peaks due to phenylated product (Ph-Zn$_2$U) (Figure 3).

We next prepared the trimers ZnZnFbU and MgZnFbU, which are of interest for studies of electronic communication between the different pigments in an array (Scheme 3). Coupling of ZnU′ and the TMS-ethynyliodoporphyrin **1**, followed by chromatography (silica, preparative SEC, silica) afforded 105 mg (65% yield) of TMS-ethynyl ZnFb dimer (**2**). Deprotection of **2** with tetrabutylammonium fluoride on silica gel gave the desired ethynyl ZnFb dimer (**3**). Coupling of **3** with ZnI using the same procedure and chromatographic workup gave the desired trimer ZnZnFbU in 50% yield. Similar coupling of ethynyl ZnFb dimer **3** with MgI followed by chromatographic workup (alumina, preparative SEC, alumina) gave the desired trimer MgZnFbU in 45% yield. Chromatography of the magnesium porphyrin containing array was performed on alumina because magnesium porphyrins are readily demetalated on silica.[35] The syntheses of ZnZnFbU and MgZnFbU show that these coupling conditions are compatible with Fb and metalloporphyrins, including magnesium por-

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[33] (a) Herrmann, W. A.; Brossner, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844−1847. (b) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossner, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849. (c) Herrmann, W. A.; Reisinger, C.-P.; Öfele, K.; Brossmer, C.; Beller, M.; Fischer, H. *J. Mol. Catal. A: Chem.* **1996**, *108*, 51−56.

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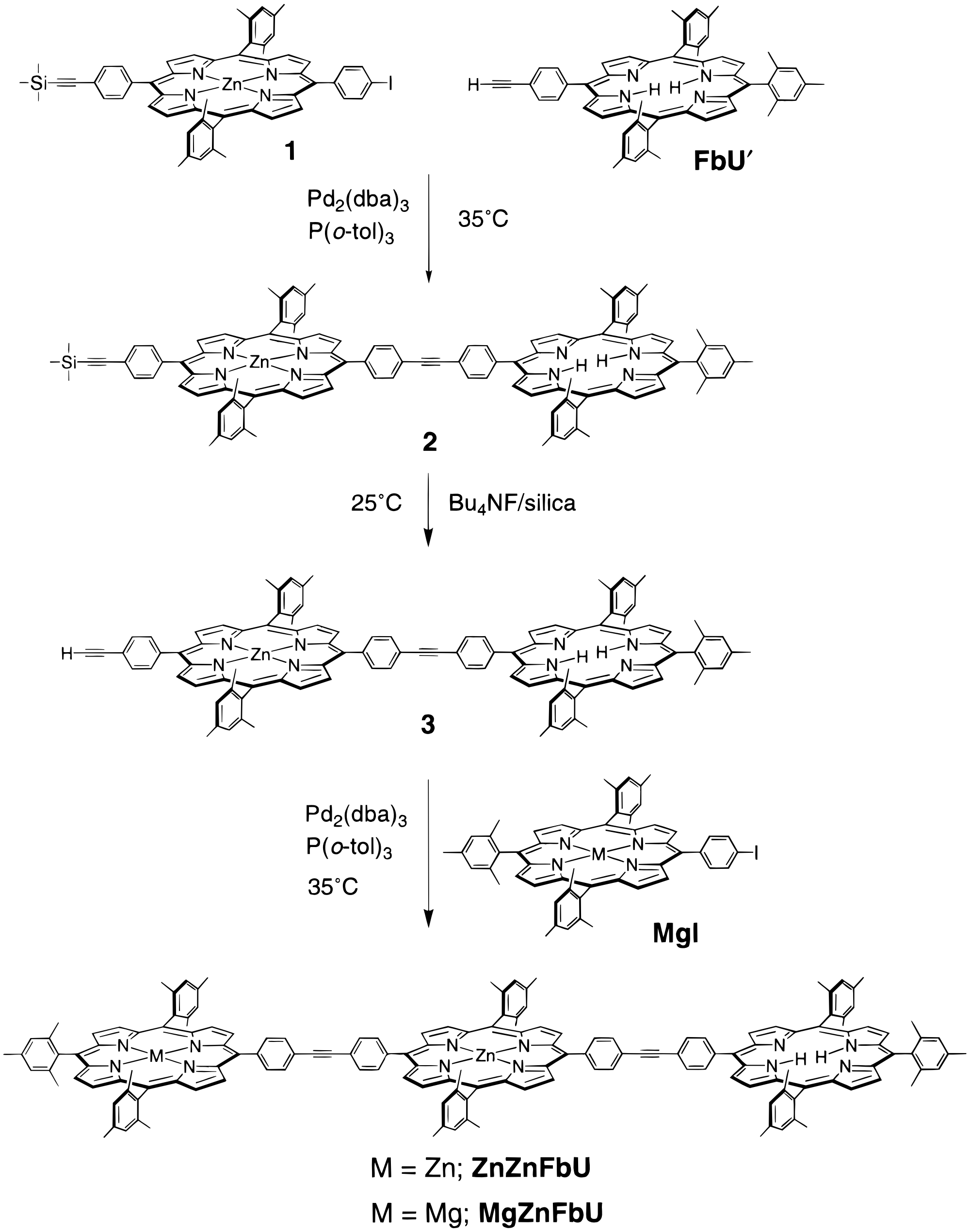
Scheme 3. Synthesis of Trimers ZnZnFbU and MgZnFbU



phyrins. In each case, the LD-MS analysis of the purified products showed no detectable phenylated species.

In summary, these refined conditions are suitable for the synthesis of diarylethyne-linked multiporphyrin arrays in dilute solution without metalation, demetalation, or transmetalation side reactions. The use of P(*o*-tol)$_3$ in place of AsPh$_3$ affords a slower reaction, slightly lower yields (45−55% vs 60−80%), and fewer byproducts derived from phenyl−aryl exchange or direct phenylation processes. The sharply decreased amount of phenylated target molecules (and only slight increase in amount of HMWM) provides a more facile purification procedure. The methodology described herein should be applicable in searches for further improvements in Pd-coupling conditions for the synthesis of multiporphyrin arrays.

Experimental Section

General. Triphenylarsine, tri-*o*-tolylphosphine, palladium(II) acetate, palladium(II) trifluoroacetate, tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$), and tetrabutylammonium fluoride on silica gel (1.0−1.5 mmol F/g resin) were purchased from Aldrich and used as received. Triethylamine was distilled from CaH$_2$. Toluene was distilled from LiAlH$_4$. CH$_2$Cl$_2$ (Fisher, reagent grade) and hexanes (Fisher, reagent grade) were used as received. Alumina (A540) and glass fiber filters (6G) were purchased from Fisher. Flash chromatography was performed on Baker flash silica. Preparative SEC was performed using BioRad Bio-Beads SX-1 beads. ^{1}H NMR spectra (300 MHz, General Electric GN 300NB), and absorption spectra (HP-8453) were collected routinely.

Laser Desorption Mass Spectrometry. Mass spectra were obtained via laser desorption using a Bruker Proflex II TOF mass spectrometer equipped with a 1.2-m flight tube, nitrogen laser (337 nm), multichannel plate detector, and 1 GHz transient recorder. The instrument provided a mass accuracy of 0.1% with external standards and mass resolution, $m/\Delta m$, (where Δm is the full width at the half-maximum of

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(35) Lindsey, J. S.; Woodford, J. N. *Inorg. Chem.* **1995**, *34*, 1063−1069.

the peak) of several thousand for species of ~2500 Da or less. Mass spectra were collected of porphyrin samples in the absence of an added matrix.[36] LD-MS of neat porphyrin samples affords spectra dominated by the porphyrin radical cation $M^{+\bullet}$ rather than the protonated molecule ion $[M + H]^+$. Intact molecule ions are generally observed for a wide variety of porphyrins and multiporphyrin arrays with minimal demetalation or fragmentation.[37] With iodo-substituted porphyrins, however, photolysis of the iodo group occurs upon LD-MS analysis. The photolysis products are readily assigned due to the characteristic peak from $[M - I]^{+\bullet}$.

Analysis of Product Distributions in the Formation of Zn_2U. Quantitation of the reaction products was achieved by incorporating a known quantity of ZnTPP (~2.5 mM) in each reaction mixture. The band on SEC due to ZnTPP was clearly distinct from those of the starting materials, product, and byproducts. Yield quantitation was achieved through the use of working curves, as described below.

During our initial studies, the product distributions in the formation of Zn_2U using $Pd_2(dba)_3$ with $AsPh_3$ were quantitated using a series of three analytical SEC columns. Subsequent analyses were performed equally well with one column (vide infra). Analytical SEC was performed on a Hewlett-Packard 1100 HPLC apparatus using 1000 Å (300 mm × 7.5 mm), 500 Å (300 mm × 7.8 mm), and 100 Å (300 mm × 7.5 mm) HP columns (5 μm) in series eluting with toluene (flow rate = 0.8 mL/min, void volume ~16.0 min) with quantitation at 550 nm (ref 475 nm) and an oven temperature at 30 °C. At specified intervals a 25-μL reaction aliquot was removed and placed in 2 mL of toluene. A 100-μL aliquot of this solution was injected into the HPLC. For each reaction the time points were 3, 6, 9, 12, 15, 18, 21, 25, 35, 45, 60, 90, 150, 210, 300, 360, 480, and 1320 min. The percentage of Zn_2U (and Ph-Zn_2U) was calculated on the basis of working curves (assuming Ph-Zn_2U and Zn_2U have equal molar absorptivities).

ZnTPP and Zn_2U working curves were established as follows: Samples of 1.8 mg of ZnTPP and 4.7 mg of Zn_2U were dissolved in 5 mL of toluene in separate volumetric flasks, and then serial dilutions were performed for each compound. Analytical SEC chromatograms were obtained, and the working curves were plotted as peak area vs concentration. For each compound, an excellent linearity and a Y intercept equal to zero were obtained. Within the range of linearity, the least-squares linear regression analysis provided the following regression equations and coefficients for ZnTPP and Zn_2U, respectively: $Y = 1.44 \times 10^8 X + 11$ ($R^2 = 1$) and $Y = 2.58 \times 10^8 X + 142$ ($R^2 = 1$). The percentage of Zn_2U formation (combined with Ph-Zn_2U or Ar-Zn_2U) was calculated on the basis of the peak area, and then corrected with the standard ZnTPP to scale to 100%.

During later studies, the product distributions in the formation of Zn_2U using $Pd_2(dba)_3$ and $AsPh_3$ or tri-*o*-tolylphosphine were quantitated as follows: Analytical SEC was performed on a Hewlett-Packard 1100 HPLC apparatus using a 100 Å (300 mm × 7.5 mm) HP column (5 μm) eluting with toluene (flow rate = 0.8 mL/min, void volume ~ 5 min) with quantitation at 550 nm (ref 475 nm) and an oven temperature at 30 °C. At specified intervals a 25-μL reaction aliquot was removed and placed in 2 mL of toluene. A 100-μL aliquot of this solution was injected onto the HPLC. The reaction monitoring times were the same as the analyses performed with three columns. The percentage of Zn_2U (and Ph-Zn_2U or Ar-Zn_2U) was calculated on the basis of the peak area, and then corrected with the standard ZnTPP to scale to 100%. Working curves were developed as described above. Least-squares linear regression analysis of the ZnTPP and Zn_2U provided the following regression equations and coefficients for ZnTPP and Zn_2U, respectively: $Y = 1.57 \times 10^8 X + 41.1$ ($R^2 = 1$) and $Y = 3.03 \times 10^8 X + 81.5$ ($R^2 = 1$).

While SEC analysis enabled quantitation of the yield of dimers, the coelution of Zn_2U and Ph-Zn_2U (or Ar-Zn_2U) precluded determination of their relative amount. A semiquantitative estimate of the ratio of Zn_2U:Ph-Zn_2U (or Ar-Zn_2U) was obtained by the peak heights in the LD-MS spectra.

Zinc(II) 5,10,15-Trimesityl-20-(4-iodophenyl)porphyrin (ZnI). Samples of mesitaldehyde (5.0 mL, 33.75 mmol), 4-iodobenzaldehyde (2.61 g, 11.25 mmol), and pyrrole (3.1 mL, 45 mmol) were condensed in 4.5 L of $CHCl_3$ with $BF_3{\cdot}O(Et)_2$ (1.8 mL, 14.9 mmol, 3.3 mM) at room temperature for 1 h. DDQ (7.66 g, 33.75 mmol) was then added, and the reaction mixture was stirred at room temperature for 1 h. At this point half of the reaction mixture was rotary evaporated to a black goo. The black goo was redissolved in 100 mL of CH_2Cl_2 and chromatographed on alumina (CH_2Cl_2, 6.8 × 10 cm). The mixture of six porphyrins eluted as one band. The other half of the reaction mixture was chromatographed in the same manner. All of the porphyrinic materials from the two columns were combined, dissolved in 750 mL of $CHCl_3$, and then a methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (3.4 g, 65 mmol, 30 mL methanol) was added. The reaction mixture was refluxed and monitored by fluorescence excitation spectroscopy. After stirring overnight, the reaction mixture was cooled to room temperature and washed with 10% $NaHCO_3$, H_2O, dried (Na_2SO_4), filtered, and concentrated, affording 6.56 g of a mixture of six porphyrins. A total of 450 mg of the porphyrin mixture was dissolved in 10 mL of CH_2Cl_2, and then 30 mL of hexanes was added. The solution was vacuum filtered through a funnel with a medium scintered frit. The filtrate was loaded onto a silica column (6.8 × 12 cm, hexanes/CH_2Cl_2, 3:1). Six bands due to the respective porphyrins were clearly visible on the column as the separation proceeded. The title porphyrin comprised the second band, affording 160 mg. ^1H NMR ($CDCl_3$): δ 1.83 (s, 12 H, $ArCH_3$), 1.84 (s, 6 H, $ArCH_3$), 2.63 (s, 9 H, $ArCH_3$), 7.27 (s, 6 H, ArH), 7.95 (AA′BB′, 2 H, ArH), 8.02 (AA′BB′, 2 H, ArH), 8.70 (s, 4 H, β-pyrrole), 8.76 (d, 2 H, $J = 4.5$ Hz, β-pyrrole); 8.83 (d, 2 H, $J = 4.5$ Hz, β-pyrrole). LD-MS ($C_{53}H_{45}IN_4Zn$): calcd av mass 930.2, obsd 931.4. λ_{abs} (toluene): 423, 550, 588 nm.

5,10,15-Trimesityl-20-(4-iodophenyl)porphyrin (FbI). A sample of ZnI (225 mg, 0.24 mmol) was dissolved in 50 mL of CH_2Cl_2 and treated with TFA (77 μL, 1 mmol). After 10 min another aliquot of TFA (77 μL, 1 mmol) was added because the demetalation was not complete as evidenced by alumina TLC. After the mixture was stirred for another 15 min, the reaction was judged to be complete by alumina TLC, absorption spectroscopy, and fluorescence excitation spectroscopy. Triethylamine (500 μL, 3.59 mmol) was added, and the reaction mixture was stirred for another 10 min. The solution was then washed three times with 10% $NaHCO_3$, once with H_2O, dried (Na_2SO_4), filtered, and rotary evaporated to give 200 mg (96%) of a purple solid. The analytical data were consistent with an authentic sample.[4]

Zinc(II) 5,10,15-Trimesityl-20-(4-ethynylphenyl)porphyrin (ZnU′). See refs 9 and 13 for the synthesis of this compound.

5,10,15-Trimesityl-20-(4-ethynylphenyl)porphyrin (FbU′). See ref 4 for the synthesis of this compound.

Magnesium(II) 5,10,15-Trimesityl-20-(4-iodophenyl)porphyrin (MgI). To a solution of FbI (208 mg, 0.24 mmol) in 50 mL of CH_2Cl_2 was added *N,N*-diisopropylethylamine (DIEA) (836 μL, 4.8 mmol) and MgI_2 (667 mg, 2.4 mmol).[35] The reaction mixture was stirred at room temperature. After 30 min the reaction was judged to be complete by fluorescence excitation spectroscopy. The reaction mixture was diluted with 50 mL of CH_2Cl_2, washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, concentrated, and chromatographed (alumina, poured in toluene/$CHCl_3$ 2:1, eluted with toluene/$CHCl_3$ 2:1) affording 200 mg (94%). ^1H NMR ($CDCl_3$): δ ^1H NMR ($CDCl_3$) δ 1.83 (s, 18 H, $ArCH_3$), 2.62 (s, 3 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.27 (s, 6 H, ArH), 7.95 (AA′BB′, 2 H, ArH), 8.04 (AA′BB′, 2 H, ArH), 8.60 (s, 4 H, β-pyrrole), 8.67 (d, 2 H, $J = 4.5$ Hz, β-pyrrole); 8.74 (d, 2 H, $J = 4.5$ Hz, β-pyrrole). LD-MS ($C_{53}H_{45}IN_4Mg$): calcd av mass 889.2, obsd 887.8. λ_{abs} (toluene): 428, 525, 566, 605 nm.

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(37) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.

Exemplary Procedure for Performing Pd-Coupling Reactions. Samples of ZnI (112 mg, 120 μmol), ZnU′ (99 mg, 120 μmol), $Pd_2(dba)_3$ (16.5 mg, 18 μmol), P(*o*-tol)$_3$ (44 mg, 144 μmol), and a stir bar were placed in a 200-mL Schlenk flask. The flask was attached, via thick-walled Tygon tubing, to a dual manifold. The flask was evacuated via a vacuum pump for 3 min and after the evacuation period the flask was back-flushed with argon for 3 min. The process of evacuation and flushing was performed a total of 3 times. At this point the argon flow rate was turned up and the threaded stopcock was removed. Deaerated toluene (40 mL) and deaerated triethylamine (8 mL) were added in succession to the flask by gastight syringe (the ratio of toluene/triethylamine was 5:1). The threaded stopcock was replaced, the argon flow rate was reduced, and the flask was immersed in an oil bath thermostated at 35 °C. The reaction was judged by analytical SEC to be complete at 10 h. At this point the reaction mixture was concentrated to dryness, redissolved in 20 mL of hexanes/CH_2Cl_2 (1:1), and poured on top of a flash silica chromatography column (4.8 × 5 cm). The P(*o*-tol)$_3$ was eluted with hexanes/CH_2Cl_2 (1:1) with gentle application of air pressure. The porphyrin species were eluted with hexanes/CH_2Cl_2 (1:1) steadily enriched with CH_2Cl_2. The Pd species remained bound to the top of the column, forming a black layer while the lower portion of the column was white. The mixture of porphyrins was then concentrated to dryness, dissolved in 5 mL of toluene, and then placed on top of a preparative SEC column (Bio-Beads SX-1 poured in toluene). Gravity elution afforded three major components (in order of elution): higher molecular weight material, desired dimer, and monomeric zinc porphyrin byproducts. The dimer-containing fraction was concentrated to dryness, dissolved in 10 mL of hexanes/CH_2Cl_2 (1:1), and chromatographed on silica (4.8 cm diameter x 10 cm, poured in hexanes/CH_2Cl_2, 1:1) with gravity elution. A small amount of monomeric zinc porphyrin eluted quickly, followed by the desired dimer. Concentration of the appropriate fractions gave 107 mg (55%). The analytical data were consistent with an authentic sample.[4]

Zinc(II) 5,15-Dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-iodophenyl)porphyrin (1). A sample of 5,15-dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-iodophenyl)porphyrin[5] (300 mg, 0.33 mmol) was dissolved in 75 mL of $CHCl_3$, and then a methanolic solution of $Zn(OAc)_2\cdot 2H_2O$ (110 mg, 0.50 mmol, 10 mL methanol) was added. The reaction mixture was stirred at room temperature and was monitored by fluorescence excitation spectroscopy. After stirring overnight, the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. Final purification via column chromatography (silica, hexanes/$CHCl_3$ 1:1) afforded 324 mg (100%) of the zinc chelate as a purple solid. ^{1}H NMR ($CDCl_3$): δ 0.37 (s, 9 H, $SiCH_3$), 1.82 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.97 (AA′BB′, 2 H, ArH), 8.08 (AA′BB′, 2 H, ArH), 8.08 (AA′BB′, 2 H, ArH), 8.18 (AA′BB′, 2 H, ArH), 8.77, 8.79 (m, 4 H, β-pyrrole), 8.84, 8.87 (m, 4 H, β-pyrrole). LD-MS ($C_{55}H_{47}N_4ISiZn$): calcd av mass 984.4, obsd 984.4. λ_{abs} (toluene): 424, 550, 590 nm.

Porphyrin Dimer 2. Samples of **1** (100 mg, 100 μmol) and FbU′ (76 mg, 100 μmol) were coupled using the Schlenk line technique. The reaction was followed by analytical SEC and was found to be complete at 12 h. The sequence of silica chromatography (hexanes/CH_2Cl_2, 1:1), preparative SEC (toluene), and silica chromatography (hexanes/$CHCl_3$, 1:1) afforded 105 mg (65%). A second reaction performed identically afforded 110 mg (68%). ^{1}H NMR ($CDCl_3$): δ −2.54 (bs, 2 H, NH), 0.38 (s, 9 H, $SiCH_3$), 1.85 (s, 12 H, $ArCH_3$), 1.87 (s, 18 H, $ArCH_3$), 2.62 (s, 3 H, $ArCH_3$), 2.64 (s, 6 H, $ArCH_3$), 2.65 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.30 (s, 6 H, ArH), 7.87 (AA′BB′, 2 H, ArH), 8.05 (AA′BB′, 2 H, ArH), 8.08 (AA′BB′, 2 H, ArH), 8.20 (AA′BB′, 2 H, ArH), 8.28 (AA′BB′, 2 H, ArH), 8.32 (AA′BB′, 2 H, ArH), 8.65 (s, 4 H, β-pyrrole), 8.74 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.80 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.83, 8.87 (m, 6 H, β-pyrrole), 8.97 (d, 2 H, J = 4.5 Hz, β-pyrrole). LD-MS ($C_{110}H_{94}N_8SiZn$): calcd av mass 1621.4, obsd 1620.3. λ_{abs} (toluene): 427, 516, 550, 593, 650 nm.

Porphyrin Dimer 3. A sample of **2** (105 mg, 0.065 mmol) was dissolved in 50 mL of toluene. Tetrabutylammonium fluoride on silica gel (120 mg, 1.0−1.5 mmol F^-/g) was added, and the reaction mixture was stirred at room temperature for 30 min. The organic layer was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to dryness. Column chromatography on silica ($CHCl_3$/hexanes (1:1), 4.8 × 7 cm) afforded 100 mg (100%). ^{1}H NMR ($CDCl_3$): δ −2.54 (bs, 2 H, NH), 1.85 (s, 12 H, $ArCH_3$), 1.87 (s, 18 H, $ArCH_3$), 2.63 (s, 3 H, $ArCH_3$), 2.64 (s, 6 H, $ArCH_3$), 2.65 (s, 6 H, $ArCH_3$), 3.32 (s, 1 H, CCH), 7.28 (s, 2 H, ArH), 7.29 (s, 4 H, ArH), 7.30 (s, 4 H, ArH), 7.89 (AA′BB′, 2 H, ArH), 8.05 (AA′BB′, 2 H, ArH), 8.08 (AA′BB′, 2 H, ArH), 8.22 (AA′BB′, 2 H, ArH), 8.28 (AA′BB′, 2 H, ArH), 8.32 (AA′BB′, 2 H, ArH), 8.65 (s, 4 H, β-pyrrole), 8.74 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.81 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.84, 8.88 (m, 6 H, β-pyrrole), 8.97 (d, 2 H, J = 4.5 Hz, β-pyrrole). LD-MS ($C_{107}H_{86}N_8Zn$): calcd av mass 1549.3, obsd 1551.6. λ_{abs} (toluene): 427, 516, 550, 592, 650 nm.

ZnZnFbU. Samples of ZnI (21 mg, 24 μmol), **3** (35 mg, 24 μmol), $Pd_2(dba)_3$ (3.1 mg, 3.4 μmol), and P(*o*-tol)$_3$ (9.5 mg, 31 μmol) in 9 mL toluene/triethylamine (5:1) were reacted using the Schlenk line technique. The reaction was followed by analytical SEC and was found to be complete at 18 h. Chromatography on one silica column (hexanes/CH_2Cl_2, 1:1), two preparative SEC columns (toluene), and one silica column ($CHCl_3$/hexanes, 2:1) afforded 28 mg (50%). Some precipitation occurred at the top of the first preparative SEC column with consequent streaking as the chromatography proceeded. A short period of sonication was required to obtain a homogeneous solution for the second preparative SEC column. ^{1}H NMR ($CDCl_3$): δ −2.53 (bs, 2 H, NH), 1.87 (s, 36 H, $ArCH_3$), 1.88 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 2.64 (s, 9 H, $ArCH_3$), 2.67 (s, 9 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.30 (s, 6 H, ArH), 7.33 (s, 6 H, ArH), 8.06, 8.10 (m, 8 H, ArH), 8.28 (AA′BB′, 4 H, ArH), 8.34 (AA′BB′, 4 H, ArH), 8.65 (s, 4 H, β-pyrrole), 8.73−8.75 (m, 6 H, β-pyrrole), 8.82 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.86 (d, 6 H, J = 4.5 Hz, β-pyrrole), 8.95 (d, 2 H, J = 5.4 Hz, β-pyrrole), 8.99 (d, 4 H, J = 3.6 Hz, β-pyrrole). LD-MS ($C_{160}H_{130}N_{12}Zn_2$): calcd av mass 2351.6, obsd 2356.4. λ_{abs} (toluene): 422, 431, 515, 551, 592, 650 nm.

MgZnFbU. Samples of MgI (20 mg, 24 μmol), **3** (35 mg, 24 μmol), $Pd_2(dba)_3$ (3.1 mg, 3.4 μmol), and P(*o*-tol)$_3$ (9.5 mg, 31 μmol) in 9 mL of toluene/triethylamine (5:1) were coupled using the Schlenk line technique. The reaction was followed by analytical SEC and was found to be complete at 24 h. Chromatography on one alumina column (toluene/$CHCl_3$, 1:1), one preparative SEC column (THF), and one final alumina column (toluene, and then toluene/$CHCl_3$, 1:1) afforded 25 mg (45%). ^{1}H NMR ($CDCl_3$): δ −2.53 (bs, 2 H, NH), 1.87 (s, 36 H, $ArCH_3$), 1.88 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 2.64 (s, 9 H, $ArCH_3$), 2.68 (s, 9 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.30 (s, 6 H, ArH), 7.33 (s, 6 H, ArH), 8.05, 8.10 (m, 8 H, ArH), 8.29 (AA′BB′, 4 H, ArH), 8.34 (AA′BB′, 4 H, ArH), 8.62 (s, 4 H, β-pyrrole), 8.65 (s, 6 H, β-pyrrole), 8.74 (d, 4 H, J = 4.5 Hz, β-pyrrole), 8.86 (d, 8 H, J = 5.1 Hz, β-pyrrole), 8.98−9.00 (m, 4 H, β-pyrrole). LD-MS ($C_{160}H_{130}MgN_{12}Zn$): calcd av mass 2310.5, obsd 2312.7. λ_{abs} (toluene): 432, 516, 553, 593, 603, 650 nm.

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Supporting Information Available: ^{1}H NMR and LD-MS spectra of the monomers, dimers, and trimers; LD-MS data, SEC traces, and kinetic plots from 21 experiments concerning the effects of reaction conditions on the reaction course and the identity of various byproducts including HMWM. This material is available free of charge via the Internet at http://pubs.acs.org.

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