Rational Syntheses of Cyclic Hexameric Porphyrin Arrays for Studies of Self-Assembling Light-Harvesting Systems

Lianhe Yu and Jonathan S. Lindsey*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

jlindsey@ncsu.edu

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Two new cyclic hexameric arrays of porphyrins have been prepared in a rational, convergent manner. The porphyrins in each cyclic hexamer are joined by diphenylethyne linkers affording a wheel-like array with a diameter of ∼35 Å. One array is comprised of five zinc (Zn) porphyrins and one free base (Fb) porphyrin (***cyclo*-Zn$_5$FbU**) while the other is comprised of an alternating sequence of two Zn porphyrins and one Fb porphyrin (***cyclo*-Zn$_2$FbZn$_2$FbU**). The prior synthesis employed a one-flask template-directed process and afforded alternating Zn and Fb porphyrins or all Zn porphyrins. More diverse metalation patterns are attractive for manipulating the flow of excited-state energy in the arrays. The rational synthesis of each array employed three Pd-mediated coupling reactions with four tetraarylporphyrin building blocks bearing diethynyl, diiodo, bromo/iodo, or iodo/ethynyl groups. The final ring closure yielding the cyclic hexamer was achieved by reaction of a porphyrin pentamer + porphyrin monomer or the joining of two porphyrin trimers. In the presence of a tripyridyl template, the yields of the 5 + 1 and 3 + 3 reactions ranged from 10 to 13%. The 5 + 1 reaction in the absence of the template proceeded in 3.5% yield, thereby establishing the structure-directed contribution to cyclic hexamer formation. The 3 + 3 route relied on successive ethyne + iodo/bromo coupling reactions. One template-directed route to ***cyclo*-Zn$_2$FbZn$_2$FbU** employed a magnesium porphyrin, affording ***cyclo*-Zn$_2$FbZn$_2$MgU** from which magnesium was selectively removed. The arrays exhibit absorption spectra that are nearly the sum of the spectra of the component parts, indicating weak electronic coupling. Fluorescence spectroscopy showed that the quantum yield of energy transfer in toluene at room temperature from the Zn porphyrins to the Fb porphyrin(s) was 60% in ***cyclo*-Zn$_5$FbU** and 90% in ***cyclo*-Zn$_2$FbZn$_2$FbU**. Two dipyridyl-substituted porphyrins, a Zn tetraarylporphyrin and a Fb oxaporphyrin, have been synthesized for use as guests in the cyclic hexamers, affording self-assembled arrays for light-harvesting studies.

Introduction

The ability to design and construct molecular architectures in which the flow of excited-state energy can be directed in a controlled manner, as occurs in the photosynthetic light-harvesting complexes, is expected to have substantial impact in materials chemistry.[1] The photosynthetic light-harvesting complexes consist of up to hundreds of porphyrinic pigments organized in elaborate three-dimensional structures.[2,3] An attractive approach for meeting the daunting synthetic challenge of organizing a large number of pigments is to design small- or medium-sized multichromophoric arrays which self-assemble into light-harvesting architectures.[4,5] As one example of this hybrid approach, we prepared a shape-persistent cyclic hexameric array of covalently linked porphyrins with a cavity diameter of ∼35 Å.[6] This work was motivated by the finding that pigments in the photosynthetic antenna complexes are arranged in cyclic architectures[3] and inspired by the extensive work of Sanders on the chemistry of cyclic multiporphyrin arrays.[7−32] The 35 Å cavity size proved ideal for binding

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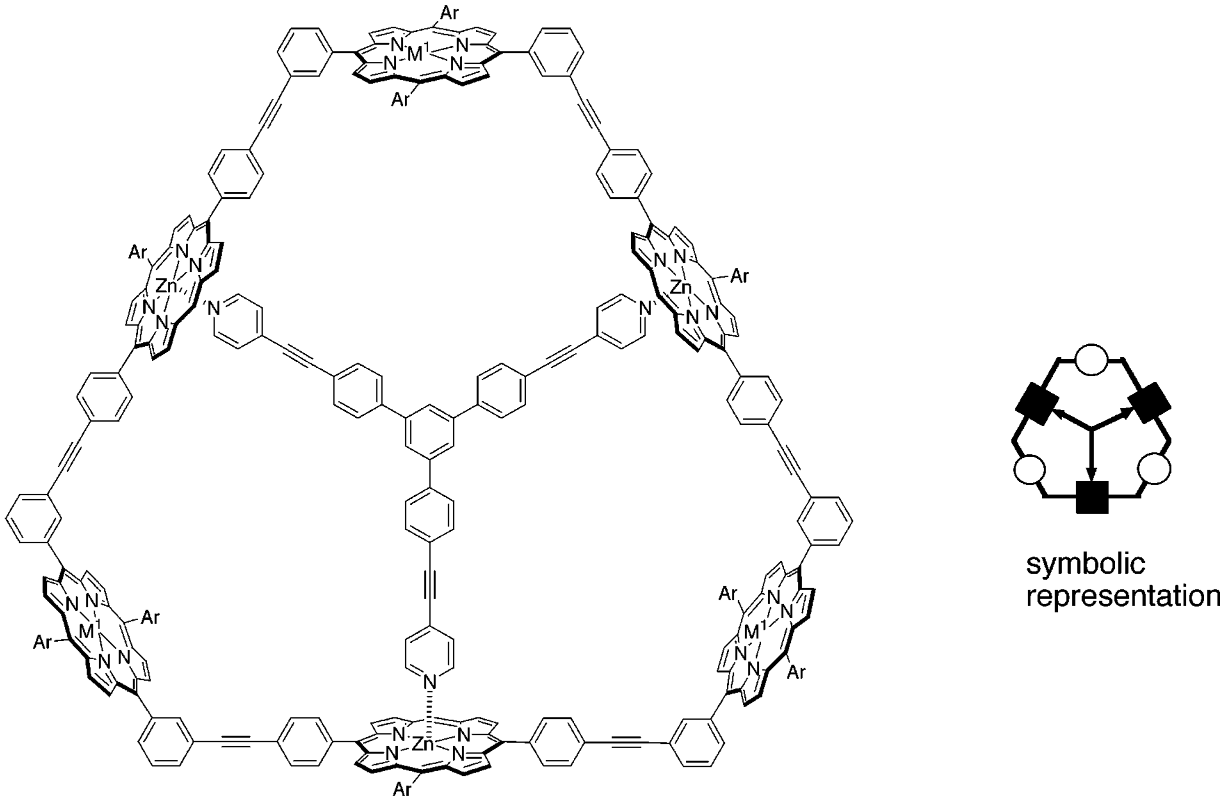
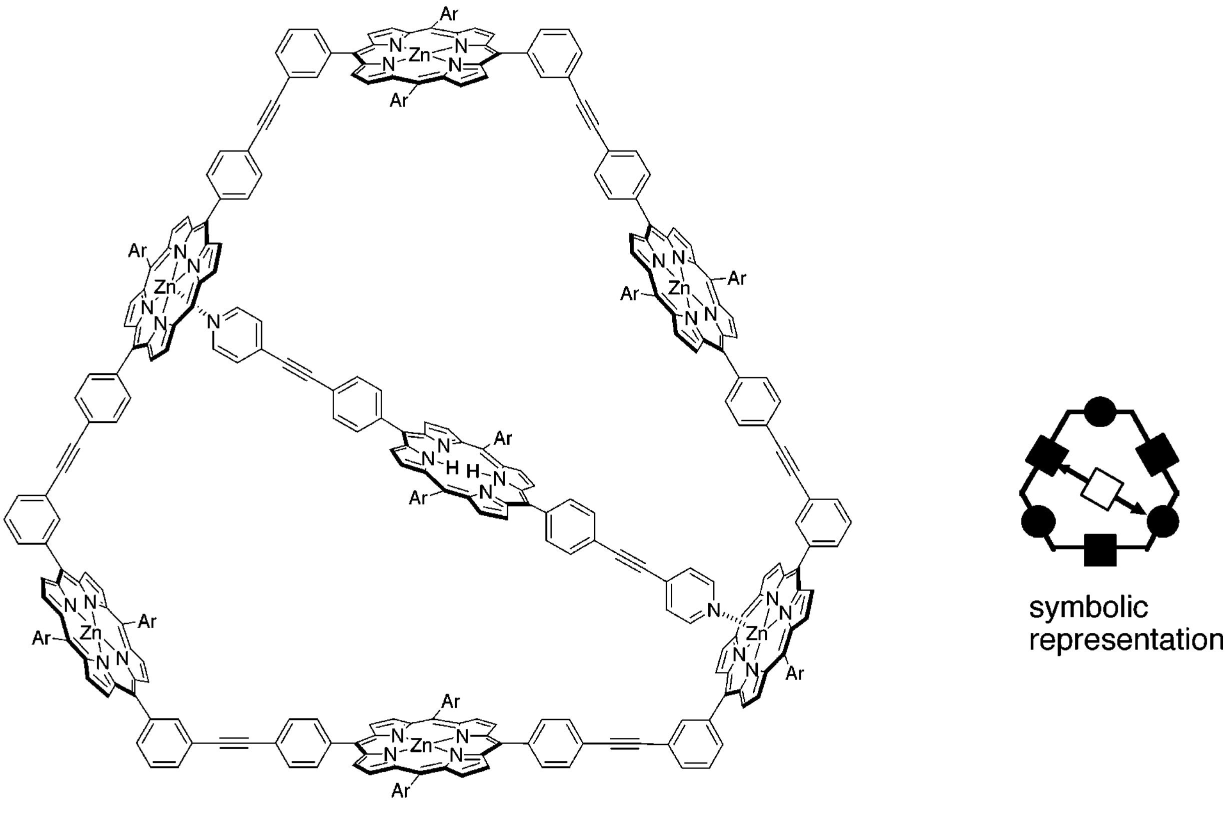
Chart 1. Self-Assembled Arrays Prepared Previously[a]



***cyclo*-Zn_3Fb_3U-1** Ar = mesityl; M^1 = H,H



***cyclo*-Zn_6U-2** Ar = mesityl

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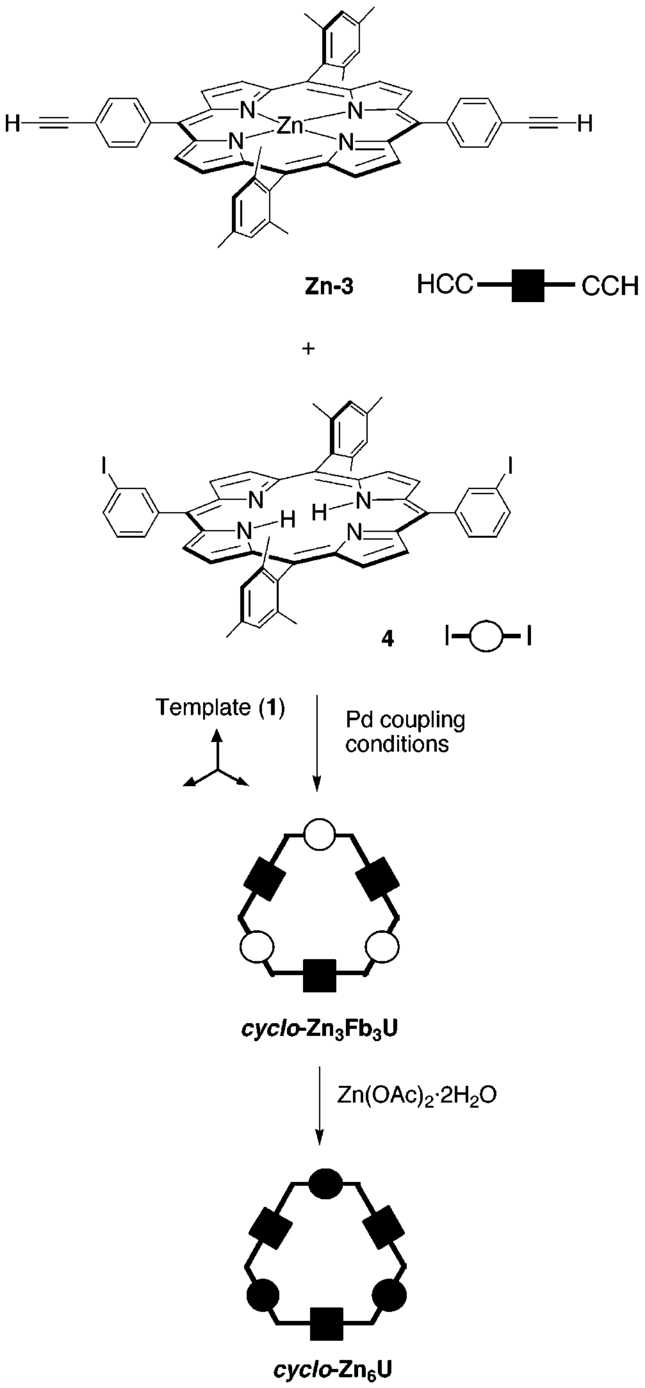
[a] In both structures, a mesityl group is present at each non-linking meso position (not displayed on coordinated metalloporphyrins for clarity).

tripyridyl template **1** or *trans*-dipyridyl substituted porphyrin **2** with high affinity (Chart 1). The binding of the dipyridyl-substituted free base (Fb) porphyrin **2** in the cyclic host comprised of six zinc (Zn) porphyrins (***cyclo*-Zn$_6$U**) yielded a self-assembled light-harvesting array in a wheel and spoke architecture.[33]

The synthesis of the cyclic hexameric porphyrin array was achieved in a one-flask template-directed reaction of two porphyrin building blocks (Scheme 1).[6] This method relied on the Pd-mediated coupling of a *p*/*p*-substituted ethynylphenyl Zn porphyrin (**Zn-3**) and a *m*/*m*-substituted iodophenyl Fb porphyrin (**4**) in the presence of a tripyridyl template (**1**). The template was readily removed on workup but could be reinserted into the purified cyclic hexamer. Because the template-directed synthesis with the tripyridyl template requires coordination of the three *p*/*p*-substituted Zn porphyrins, the only cyclic hexamers that were accessible incorporated alternating Zn porphyrins and Fb porphyrins (***cyclo*-Zn$_3$Fb$_3$U**) or all Zn porphyrins (***cyclo*-Zn$_6$U**). Other desirable patterns of metalloporphyrins, such as those present in the new cyclic hexamers ***cyclo*-Zn$_5$FbU** and ***cyclo*-Zn$_2$FbZn$_2$FbU** (Chart 2), were not available using this one-flask synthesis.

The motivation for preparing cyclic hexamers with various metalation patterns is to study and ultimately control the flow of excited-state energy in the self-assembled light-harvesting arrays. In the arrays, energy transfer proceeds very rapidly between covalently linked porphyrins via a through-bond process.[1] Binding of the guest via pyridyl ligation to a Zn porphyrin causes a red-shift (~10 nm) in the absorption spectrum, in effect lowering the excited-state energy of the pyridyl-coordinated Zn porphyrin. For example, in ***cyclo*-Zn$_6$U-1**, photoexcitation of the Zn porphyrins is followed by energy transfer to the pyridyl-coordinated Zn porphyrins.[33] In ***cyclo*-Zn$_6$U-2**, energy transfer can occur via a through-space process from any porphyrin in the wheel to the Fb porphyrin guest. However, the more rapid through-bond energy-transfer process among porphyrins in the wheel of the array results in localization of energy on the pyridyl-coordinated Zn porphyrins. Energy transfer from the latter to the guest Fb porphyrin apparently is slow, occurring in a yield commensurate with a through-space process.[33] The flow of energy in ***cyclo*-Zn$_6$U-2** is illustrated in Figure 1. The sluggish transfer from the pyridyl-coordinated Zn porphyrins to the guest Fb porphyrin limits the performance of the self-assembled complex as a light-harvesting system.

Scheme 1



In an array containing five Zn porphyrins and one Fb porphyrin (***cyclo*-Zn$_5$FbU**), pyridyl coordination of two of the Zn porphyrins creates a cascade wherein the excited-state energy levels decrease in the following order: Zn porphyrin > pyridyl-coordinated Zn porphyrin

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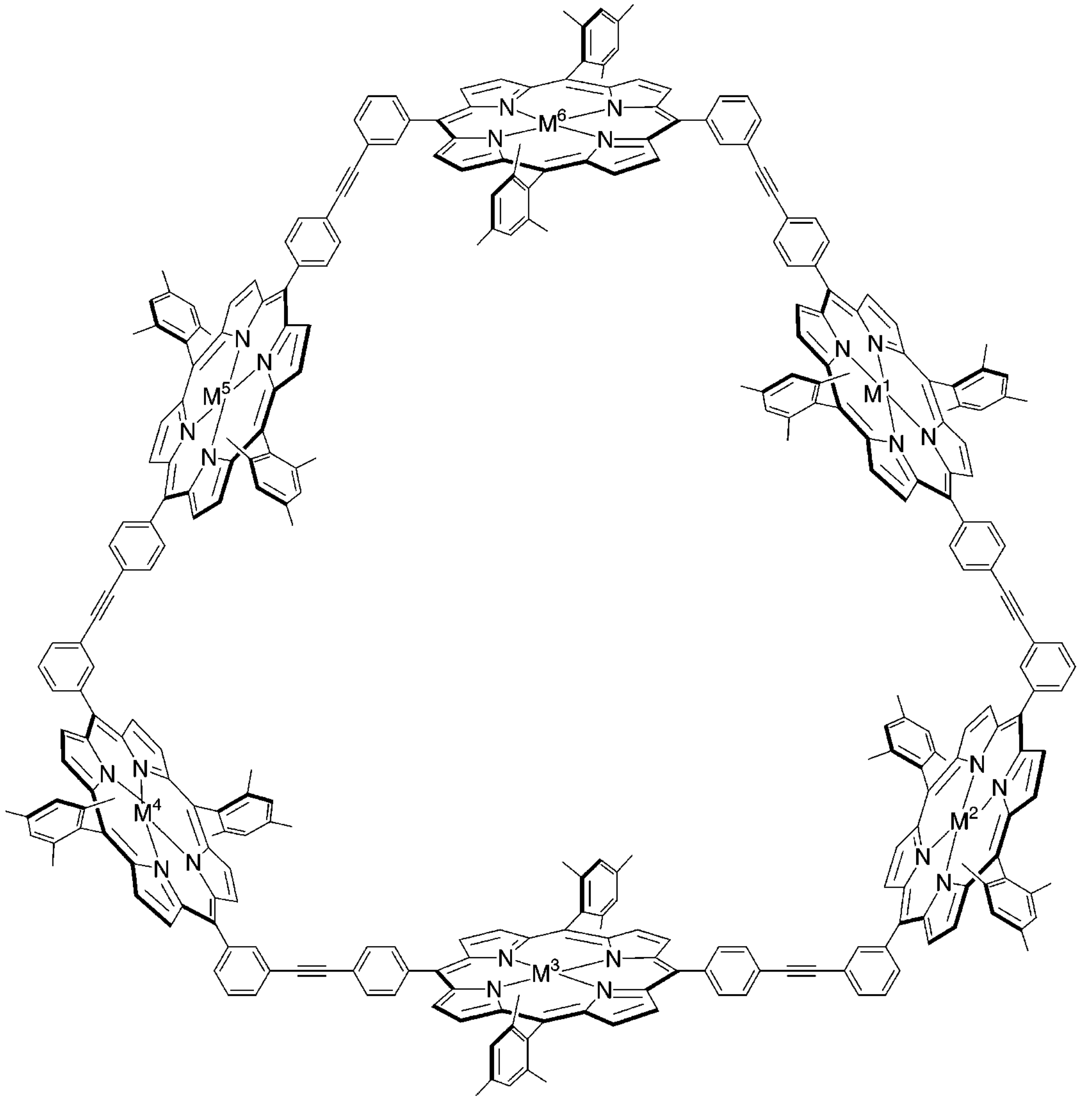
Chart 2



***cyclo*-Zn_5FbU** M^1 - M^5 = Zn; M^6 = H, H

***cyclo*-Zn_2FbZn_2FbU** M^1, M^2, M^4, M^5 = Zn; M^3, M^6 = H, H

> Fb porphyrin. With a guest having an excited-state of lower energy than that of the Fb porphyrin (e.g., phthalocyanine, bacteriochlorin, heteroatom-substituted Fb porphyrin), excited-state energy should rapidly reach the Fb porphyrin via through-bond transfer among porphyrins in the wheel and then transfer to the guest via a through-space process. Three paths of energy transfer for ***cyclo*-Zn_5FbU-guest** are displayed in Figure 1. Paths 1 and 2 proceed downhill in energy in a stepwise manner and are unremarkable. Path 3 proceeds along the wheel from Zn porphyrin → pyridyl-coordinated Zn porphyrin → Fb porphyrin; the transfer from the nonadjacent pyridyl-coordinated Zn porphyrin to the Fb porphyrin occurs via the intermediacy of a Zn porphyrin. We have shown that through-bond energy transfer can occur efficiently among distant (i.e., nonadjacent) sites in covalently linked arrays via a superexchange process.[1,34] In ***cyclo*-Zn_2FbZn_2FbU**, two Fb porphyrins can serve as funnels for energy transfer to a suitable guest (Figure 1). Two paths for energy transfer in the wheel lead to the Fb porphyrins, from which through-space transfer to the guest can occur. The objective of the work described in this paper has been to gain efficient access to arrays such as ***cyclo*-Zn_5FbU** and ***cyclo*-Zn_2FbZn_2FbU**, thereby enabling studies of the energy-transfer dynamics and light-harvesting properties.

To gain access to cyclic hexamers containing diverse patterns of metalloporphyrins requires a stepwise synthesis of one or more linear arrays followed by cyclization to give the desired cyclic structure. Gossauer recently reported the synthesis of very large shape-persistent hexameric arrays of porphyrins (46 Å diameter), including an array comprised of five Zn porphyrins and one Fb porphyrin.[35,36] The synthesis employed the iterative divergent/convergent construction of linear hexamers, which were

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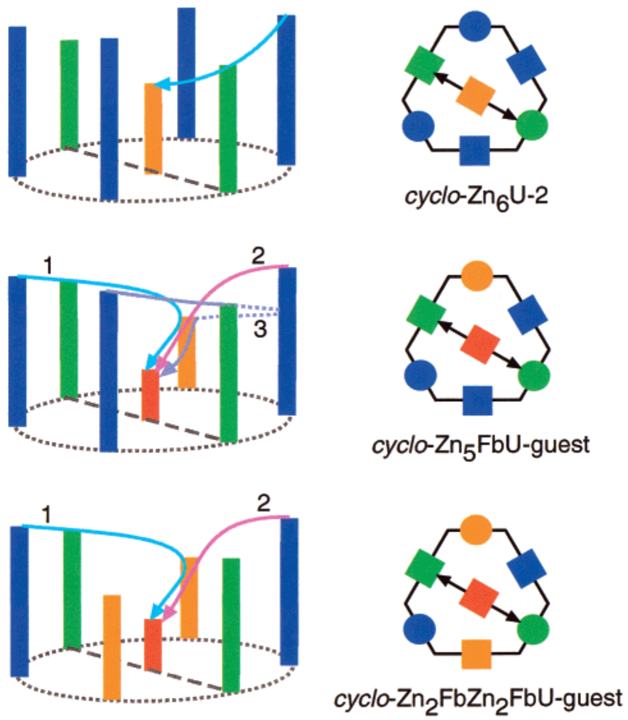


Figure 1. Paths for the flow of excited-state energy in self-assembled light-harvesting arrays. The color and height of the bars in the histograms on the left indicate the relative excited-state energy level of the various components. Code: Zn porphyrin (blue), pyridyl-coordinated Zn porphyrin (green), Fb porphyrin (orange), guest chromophore (red). (Top) In ***cyclo*-Zn$_6$U-2**, energy flows from the Zn porphyrin to the pyridyl-coordinated Zn porphyrin to the guest Fb porphyrin. (Middle) In ***cyclo*-Zn$_5$FbU**-guest, energy flows from the Zn porphyrins via several paths to the Fb porphyrin, which can funnel energy to the guest. The dashed line in path 3 indicates the super-exchange process from a pyridyl-coordinated Zn porphyrin to a Fb porphyrin via the intermediacy of a Zn porphyrin. (Bottom) In ***cyclo*-Zn$_2$FbZn$_2$FbU**-guest, energy flows to the Fb porphyrins from which energy is funneled to the guest.

cyclized to the corresponding cyclic hexamers. Although templating was not observed during the cyclization process of the linear hexamers, the cyclic hexamers exhibited very high affinity for a number of polydentate ligands.

In this paper, we first describe a refined synthesis of the tripyridyl template (**1**). We then consider several rational, stepwise strategies with differing degrees of convergence for the preparation of cyclic hexamers. Several such strategies are implemented, affording the two new cyclic hexamers ***cyclo*-Zn$_5$FbU** and ***cyclo*-Zn$_2$FbZn$_2$FbU**. The recent availability of porphyrin building blocks bearing up to four different meso substituents enables both the synthesis of the porphyrin building blocks and the stepwise synthesis of the cyclic arrays to be carried out in a rational manner (i.e., without any statistical reactions at any step). A *trans*-dipyridyl substituted oxaporphyrin has been prepared as one example of a low-energy chromophore for binding inside the host. The studies of energy transfer in the complexes formed upon binding various guests in the cyclic hexamers will be presented elsewhere.

Results and Discussion

Synthetic Strategy. The cyclic hexamers have 3-fold rather than 6-fold symmetry due to the presence of three *p*/*p*-substituted porphyrins and three *m*/*m*-substituted porphyrins. The distances are such that template **1** binds to the *p*/*p*-substituted porphyrins rather than the *m*/*m*-substituted porphyrins. Therefore, for template-directed synthesis with **1**, the three *p*/*p*-substituted porphyrins must be employed in the metalated state. Three approaches for the template-directed formation of ***cyclo*-Zn$_5$FbU** are shown in Figure 2. (A) 5 + 1 route: All three *p*/*p*-substituted Zn porphyrins are located in the linear pentamer **Zn$_5$-*p*/*p*-CCH**. The sixth porphyrin is a *m*/*m*-substituted Fb porphyrin. While the template cannot facilitate intermolecular reaction yielding the linear Zn$_5$-Fb hexamer, binding of the template to the linear Zn$_5$Fb hexamer can facilitate intramolecular ring closure. (B) 5 + 1 route: Only two *p*/*p*-substituted Zn-porphyrins are located in the linear pentamer **Zn$_2$FbZn$_2$-*m*/*m*-CCH**. The sixth porphyrin is a *p*/*p*-substituted Zn porphyrin. For the template to assist formation of the linear hexamer, the template must bis-ligate to **Zn$_2$FbZn$_2$-*m*/*m*-CCH** and mono-ligate with the *p*/*p*-substituted Zn porphyrin monomer. The template can also facilitate intramolecular ring closure in the last step. In both routes A and B, the templated ring closure is effectively the same.[37] (C) 3 + 3 route: Two *p*/*p*-substituted Zn porphyrins are located in one trimeric building block (**ZnFbZn-*p*/*p*-Br**) while

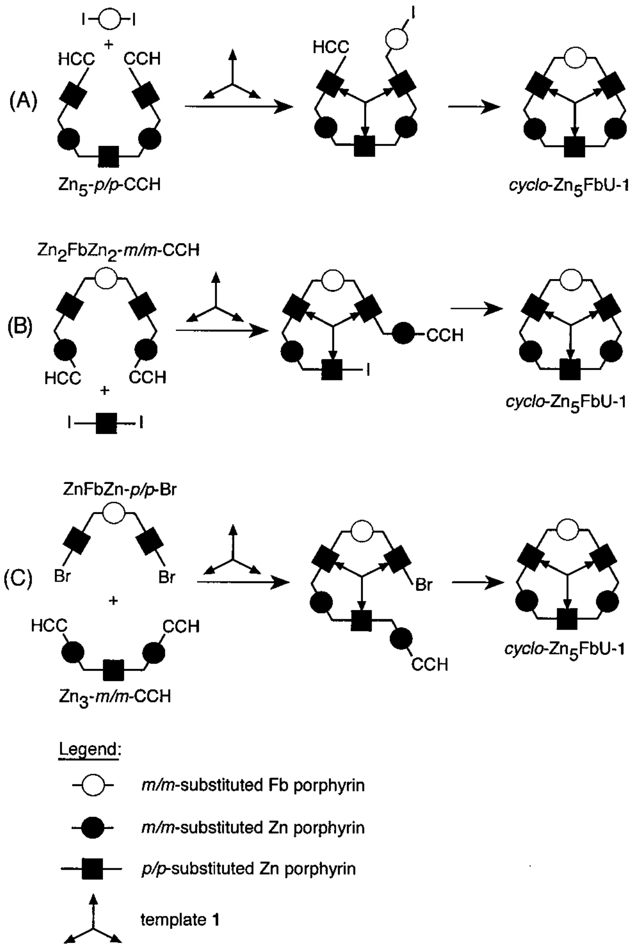


Figure 2. Possible roles of the template in different routes to the cyclic hexamer ***cyclo*-Zn$_5$FbU**. (A) A 5 + 1 route with triligation of the pentamer **Zn$_5$-*p*/*p*-CCH** prior to reaction with the Fb-*m*/*m*-diiodo-porphyrin. (B) A 5 + 1 route with only di-ligation possible of the pentamer **Zn$_2$FbZn$_2$-*m*/*m*-CCH**; triligation occurs upon reaction with the Zn-*p*/*p*-diiodo-porphyrin. (C) A 3 + 3 route with triligation possible upon reaction of the two trimers, **Zn$_3$-*m*/*m*-CCH** and **ZnFbZn-*p*/*p*-Br**. The legend employed here also applies to Schemes 7−10.

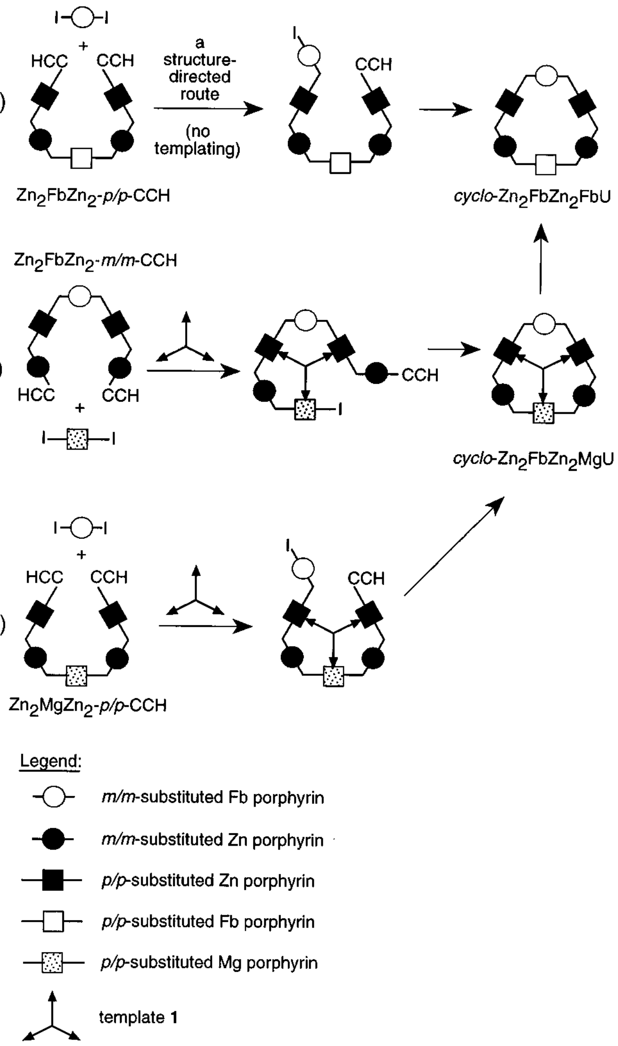


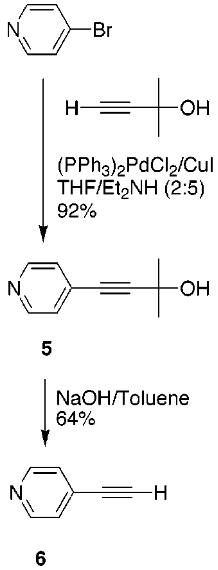
Figure 3. Possible roles of the template in different routes to the cyclic hexamer ***cyclo*-Zn$_2$FbZn$_2$FbU**. (A) A structure-directed 5 + 1 route wherein triligation is not possible due to the metalation states of the pentamer **Zn$_2$FbZn$_2$-*p/p*-CCH** and the Fb-*m*/*m*-diiodo-porphyrin. (B) A 5 + 1 route with triligation upon reaction of the pentamer **Zn$_2$FbZn$_2$-*m/m*-CCH** and the monomer Mg-*p*/*p*-diiodo-porphyrin. (C) A 5 + 1 route with triligation of the pentamer **Zn$_2$MgZn$_2$-*p/p*-CCH** prior to reaction with the Fb-*m*/*m*-diiodo-porphyrin. The legend employed here also applies to Schemes 7−10.

the third *p*/*p*-substituted Zn porphyrin is located in the other trimeric building block (**Zn$_3$-*m/m*-CCH**). For the template to assist formation of the linear hexamer, the template must bis-ligate and mono-ligate to the respective trimers. As in cases A and B, the template can facilitate intramolecular ring closure of the linear hexamer. We chose routes A and C to synthesize the target molecule ***cyclo*-Zn$_5$FbU**.

Examples of 5 + 1 routes for the rational synthesis of ***cyclo*-Zn$_2$FbZn$_2$FbU** are outlined in Figure 3. (A) All three *p*/*p*-substituted porphyrins are located in the linear pentamer **Zn$_2$FbZn$_2$-*p/p*-CCH**. However, only two are Zn porphyrins and one is a Fb porphyrin. In this case triligation with the tripyridyl template is not possible due to the absence of the third binding site. Thus, this route constitutes a structure-directed synthesis. (B) One approach to achieve a template-directed synthesis is to construct a linear pentamer (**Zn$_2$FbZn$_2$-*m/m*-CCH**) for reaction with a Mg porphyrin. In this case, the tripyridyl template can bind to two *p*/*p*-substituted Zn porphyrins in **Zn$_2$FbZn$_2$-*m/m*-CCH** and the incoming *p*/*p*-substituted Mg porphyrin. The resulting Zn$_2$FbZn$_2$Mg cyclic hexamer can be selectively demetalated to give the desired hexamer ***cyclo*-Zn$_2$FbZn$_2$FbU**. Mg porphyrins (but not Zn porphyrins) readily demetalate upon exposure to silica gel.[38] (C) An alternate route is to introduce magnesium into **Zn$_2$FbZn$_2$-*p/p*-CCH**. The resulting Zn$_2$-MgZn$_2$-pentamer incorporates three *p*/*p*-substituted metalloporphyrins (two Zn porphyrins and one Mg porphyrin) for binding with the template in the cyclization step. Demetalation of the Mg-porphyrin again affords ***cyclo*-Zn$_2$FbZn$_2$FbU**. We chose routes A and B for preparing ***cyclo*-Zn$_2$FbZn$_2$FbU**.

Tripyridyl Template. For large-scale synthesis, we sought a more efficient preparation of template **1** than that employed previously.[6] Key starting materials for the construction of the tripyridyl template are 4-ethynylpyridine (**6**) and 1,3,5-tris(4-iodophenyl)benzene (**7**). In our hands, the synthesis of ethynylpyridine intermediate **5** in diethylamine following a reported method[39] gave a 50% yield in contrast to the reported 84%. To overcome the poor solubility of the starting material 4-bromopyridine hydrochloride in diethylamine, we performed the reaction in the mixed solvent system of THF/diethylamine (2:5), obtaining a 92% yield. Treatment of **5** in a suspension of NaOH/toluene gave **6** in 64% yield (Scheme 2). Compound **6** darkens on storage at room temperature over 2 days and should be used immediately.

Scheme 2



Preparation of 1,3,5-tris(4-iodophenyl)benzene (**7**) was first carried out by condensation of 4-iodoacetophenone in alcoholic hydrogen chloride, affording 17% yield after 30 days of reaction.[40] The same acid-catalyzed reaction using trimethyl orthoformate in chloroform instead of

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[37] The linear hexamers formed via the two routes differ only in whether the iodo or ethynyl group is attached to the *m*/*m*- or *p*/*p*-substituted porphyrin or vice versa.

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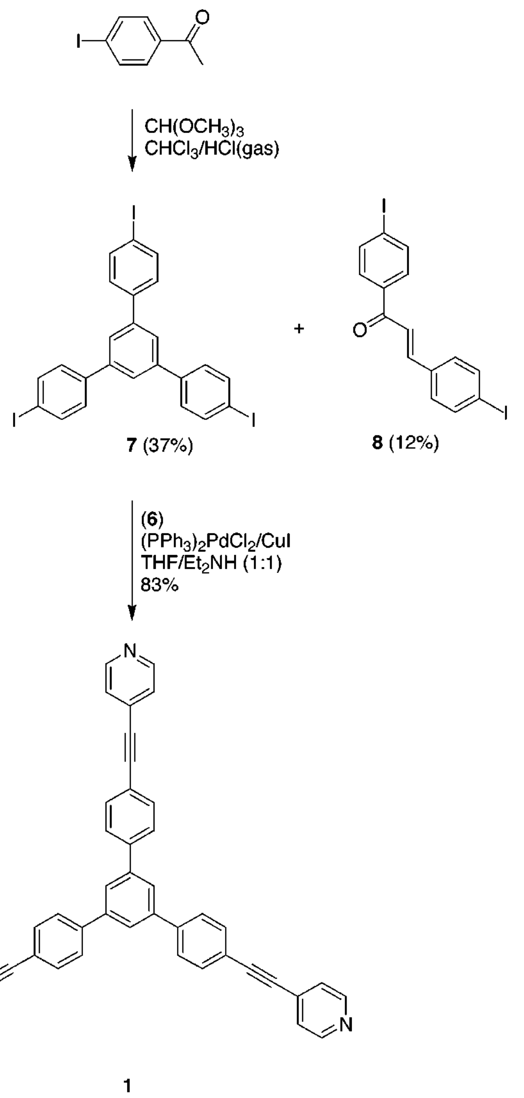
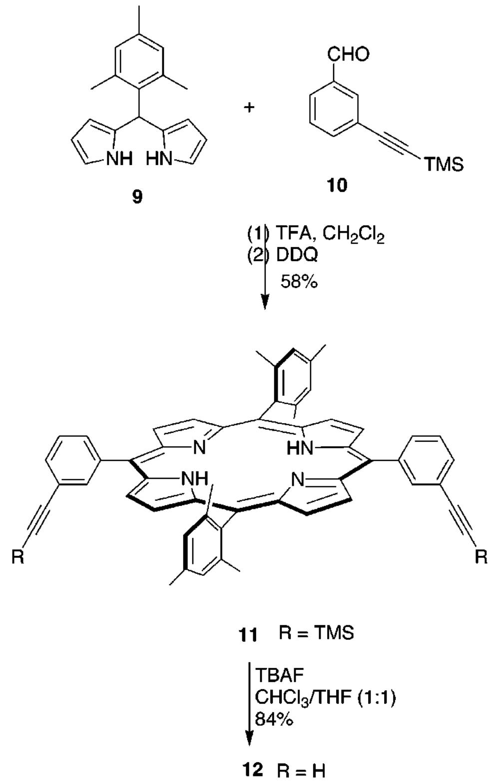
Scheme 3



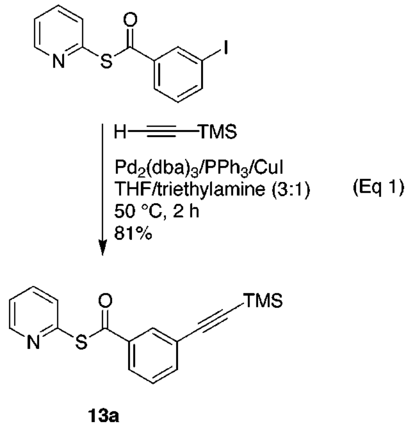
Scheme 4



alcohol gave a yield of 37% after 15 h. The byproduct **8** was also isolated in 12% yield. The Pd-mediated coupling of 4-ethynylpyridine (**6**) and **7** in THF/diethylamine (1:1) at 45 °C afforded the tripyridyl template **1** in 83% yield (Scheme 3), compared with the previous 71% yield.[6]

Porphyrin Building Blocks. *Trans*-A_2B_2-porphyrins are readily formed by reaction of an aldehyde with a sterically hindered dipyrromethane.[41] We chose 5-mesityldipyrromethane (**9**) as a convenient starting material for the synthesis of the various porphyrins. The mesityl group imparts good solubility and 5-mesityldipyrromethane is especially resistant to acidolytic scrambling in porphyrin syntheses.[41] The mesityl substituted *trans*-A_2B_2-porphyrins **Zn-3** and **4** have been prepared previously.[6] A slightly refined synthesis of **3** is provided in the Supporting Information. Condensation of 5-mesityldipyrromethane (**9**) with 3-[2-(trimethylsilyl)ethynyl] benzaldehyde (**10**)[43] followed by oxidation with DDQ afforded *m*/*m*-TMS-protected ethynylphenyl porphyrin **11** in 58% yield (Scheme 4). Cleavage of the TMS groups by using tetra-*n*-butylammonium fluoride (TBAF) afforded **12** in 84% yield.

Porphyrin building blocks bearing iodophenyl groups and/or ethynylphenyl groups in a trans architecture are essential for the preparation of the cyclic hexameric arrays. Porphyrins bearing one iodophenyl group and one ethynylphenyl group have been prepared using mixed aldehyde condensations[43] affording a mixture of three porphyrins which were separated by column chromatography. A rational synthesis is now available that makes use of a diacyldipyrromethane and a dipyrromethane to construct the desired *trans*-AB_2C-porphyrin.[44,45] The monoacylation of dipyrromethanes is readily achieved with *S*-2-pyridyl benzothioates. Thioester **13a** was prepared in 81% yield by coupling *S*-2-pyridyl 3-iodobenzothioate[46] and trimethylsilylacetylene using $Pd_2(dba)_3$ in THF/triethylamine (3:1) (eq 1). Thioesters **13b** and **13c** were prepared as described in the literature.[44]



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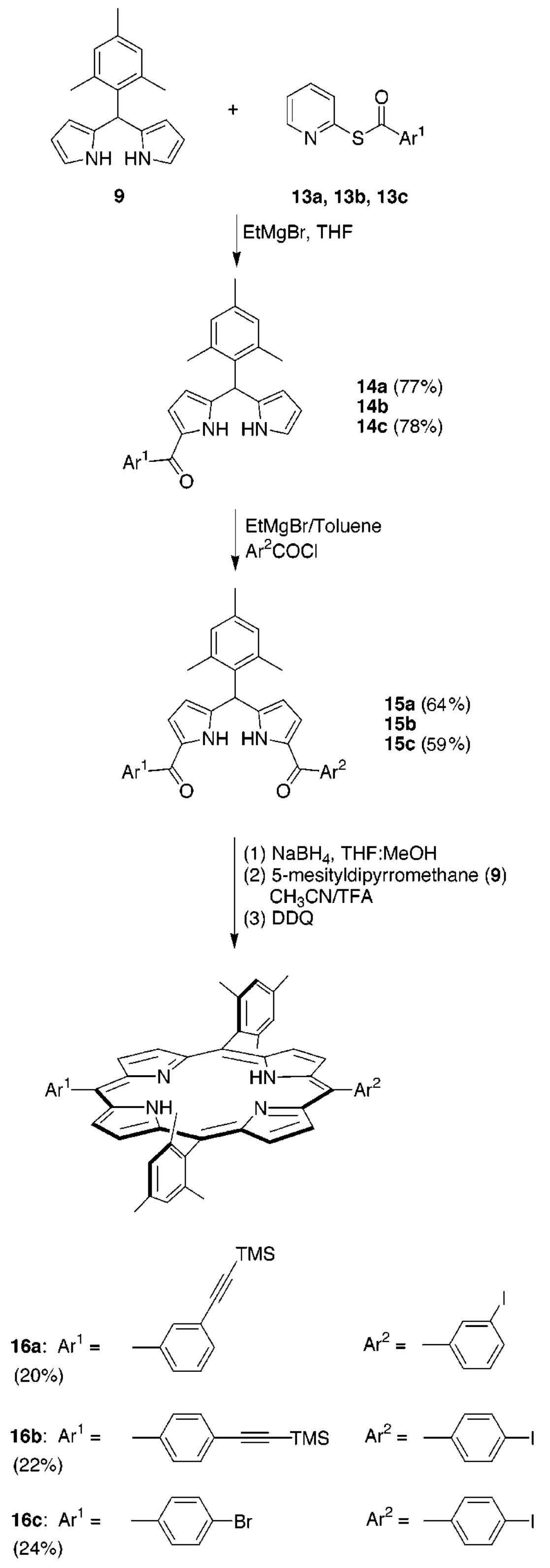
(41) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

(42) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.

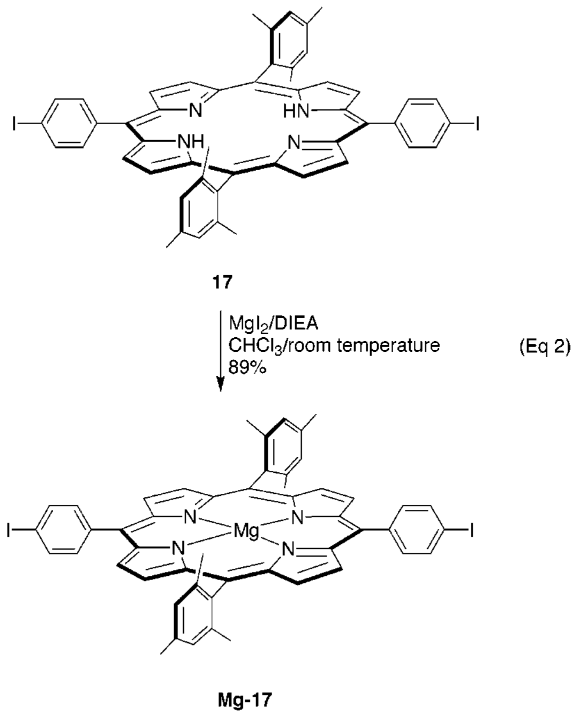
(43) Ravikanth, M.; Strachan, J.-P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, *54*, 7721−7734.

Scheme 5



The reaction of 5-mesityldipyrromethane (**9**) with EtMgBr followed by a pyridyl benzothioate (**13a**–**c**) gave the corresponding monoacyldipyrromethane **14a**–**c** in good yield (Scheme 5). The second acyl group was introduced by reaction of a monoacyldipyrromethane (**14a**–**c**) with an iodobenzoyl chloride, affording the corresponding diacyldipyrromethane **15a**–**c**. Treatment of a diacyldipyrromethane with $NaBH_4$ gives the corresponding dipyrromethanedicarbinol.[44] Condensation of **15a-dicarbinol** and 5-mesityldipyrromethane (**9**) under nonscrambling conditions (30 mM TFA in CH_3CN at room temperature) followed by oxidation with DDQ gave the single porphyrin product **16a**. Metalation with zinc acetate gave **Zn-16a.** The analogous diacyldipyrromethanes **15b**,**c** were treated in the same manner, affording porphyrins **16b**,**c** without scrambling. Sizable quantities (0.5–0.7 g) of pure porphyrins were prepared with only minimal chromatography by this rational route.

The Mg porphyrin monomer (**Mg-17**) was prepared with the room temperature, heterogeneous magnesium-insertion procedure.[38] Treatment of Fb porphyrin **17**[41] with *N*,*N*-diisopropylethylamine (DIEA) and MgI_2 in $CHCl_3$ gave **Mg-17** in 89% yield after chromatography on alumina (eq 2).



Porphyrin Guests. The guest in the cyclic hexamers ***cyclo*-Zn_5FbU** and ***cyclo*-Zn_2FbZn_2FbU** must be able to serve as the energy-transfer acceptor from Zn or Fb porphyrin energy donors. Free base oxaporphyrins (i.e., an N_3O-porphyrin) have slightly red-shifted absorption bands compared with the normal (i.e., N_4-) porphyrins.[47] Thus, a dipyridyl-substituted N_3O-porphyrin was attractive for use as a guest that would function as an energy-transfer acceptor in the self-assembled cyclic hexameric arrays. We previously developed methods for preparing

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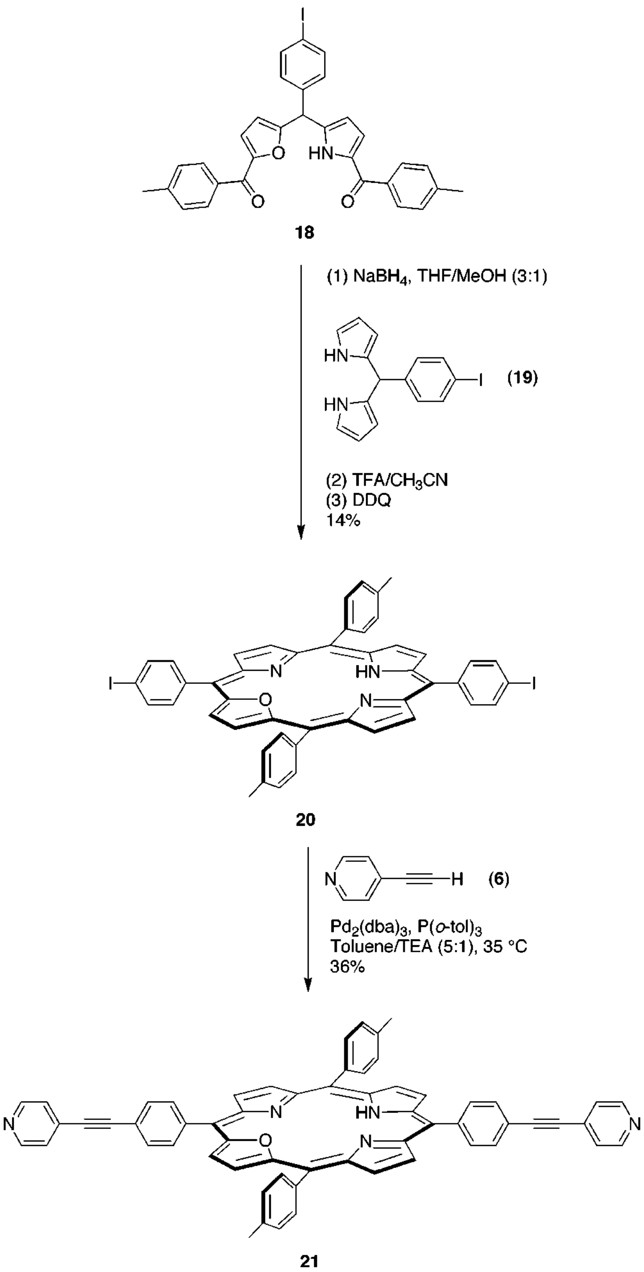
(44) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344.

(45) Retrosynthetic analysis shows several different routes for constructing a given *trans*-AB_2C-porphyrin: (1) An A-dipyrromethane can be diacylated to give the BAB-dipyrromethane, which is then reacted with a C-dipyrromethane. (2) A B-dipyrromethane is monoacylated to give an AB-dipyrromethane, followed by a second monoacylation to give an ABC-dipyrromethane. Reaction of the latter with a B-dipyrromethane gives the *trans*-AB_2C-porphyrin. While the former route is expedient and generally superior, conditions have not been identified for reducing the mesitoyl dipyrromethane to the corresponding carbinol. Accordingly, the latter route wherein B is mesityl constitutes the appropriate fallback approach for preparing the desired *trans*-AB_2C-porphyrins.

(46) Rao, P. D.; Littler, B. J.; Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 1084–1092.

(47) Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, C.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890–7901.

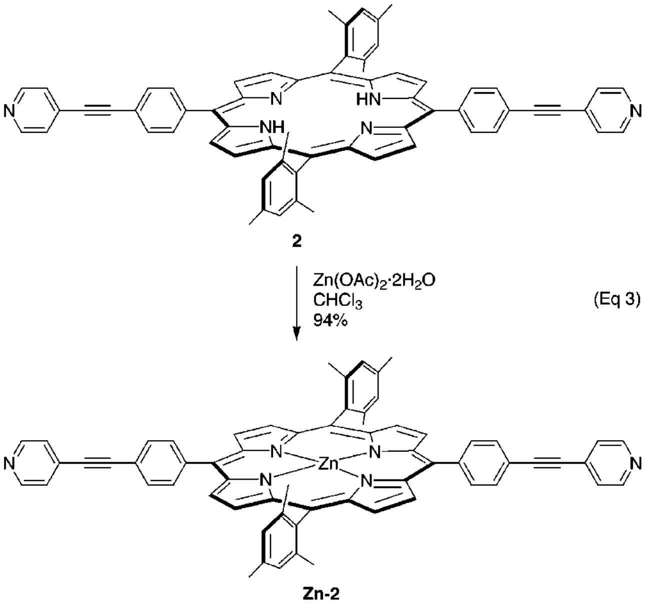
Scheme 6



heteroatom-substituted porphyrin building blocks.[47] The synthesis began with 5-(4-iodophenyl)furylpyrromethane which was acylated under Friedel–Crafts conditions, affording the diacyl derivative **18**.[47] Reduction of **18** with $NaBH_4$ in THF/methanol (3:1) gave the furylpyrromethanedicarbinol, which was condensed with 5-(4-iodophenyl)dipyrromethane (**19**) under nonscrambling condensation conditions (30 mM TFA in CH_3CN at room temperature)[44] followed by oxidation with DDQ. The yield of the desired N_3O-porphyrin **20** from the reaction of **18** and **19** was 14%. The Pd-mediated coupling of **20** and 4-ethynylpyridine (**6**) was performed under conditions similar to those for the preparation of multiporphyrin arrays.[48] The desired dipyridyl N_3O-porphyrin **21** was obtained in 36% yield after purification by column chromatography on basic alumina (Scheme 6).

As is typical of oxaporphyrins, **20** and **21** are significantly more basic than normal N_4-porphyrins. Indeed, the absorption spectrum of **20** or **21** in neat CH_2Cl_2 showed a long-wavelength shoulder on the Soret band (~440 nm) due to the formation of the protonated N_3O-porphyrin. Addition of triethylamine caused disappearance of this shoulder. The ^1H NMR spectrum of the N_3O-porphyrin **20** or **21** recorded in $CDCl_3$ showed no NH peak even when the $CDCl_3$ was treated overnight with K_2CO_3. However, the ^1H NMR spectrum of each N_3O-porphyrin revealed the nonsymmetric structure of the macrocycle, with clear resolution of all of the resonances arising from the β-protons on the furan and pyrrole rings.

For comparison purposes, we also prepared a dipyridyl-substituted Zn porphyrin (**Zn-2**) as shown in eq 3.



Synthesis of *cyclo*-Zn_5FbU via the 5 + 1 Route. We initially pursued the 5 + 1 route outlined in Figure 2A. The synthesis employs four porphyrin building blocks, three Pd-mediated coupling reactions, and two deprotection steps. The coupling reactions were performed using refined conditions suitable for joining porphyrin building blocks but at slightly higher concentration:[48] ~3.6–5 mM [ethyne] and [iodo], ~15 mol % $Pd_2(dba)_3$ based on [ethyne], and ~120 mol % $P(o\text{-tol})_3$ based on [ethyne], in toluene/triethylamine (5:1) at 35 °C under argon. Each purified product was characterized by TLC, analytical SEC, LD-MS, UV–vis spectroscopy, fluorescence spectroscopy, and ^1H NMR spectroscopy.

The synthesis began by coupling *p*/*p*-diethynyl Fb porphyrin **3** with 2 mol equiv of *m*/*m*-iodo/TMS-ethynyl Zn porphyrin **Zn-16a** (Scheme 7). The distribution of products observed by analytical SEC was typical, consisting of desired trimer, mono-coupled byproduct (dimer), and high molecular weight material (HMWM). Purification by one silica column, one preparative SEC column, and one silica column afforded trimer **ZnFbZn-*m/m*-CCTMS** in 47% yield. Deprotection of the TMS-ethynyl groups using TBAF[49] gave the diethynyl trimer **ZnFbZn-*m/m*-CCH** in 90% yield. A similar sequence of reactions was employed to prepare the pentamer. The coupling of **ZnFbZn-*m/m*-CCH** and 2 mol equiv of the *p*/*p*-iodo/TMS-ethynyl **Zn-16b** gave the TMS-protected pen-

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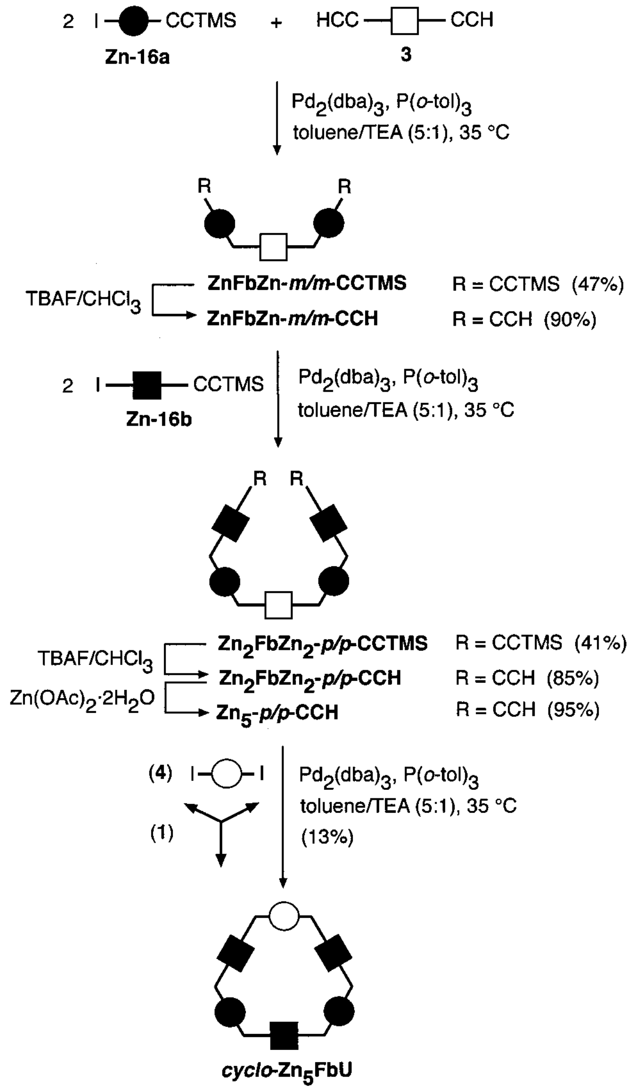
(48) Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974–2983.

Scheme 7

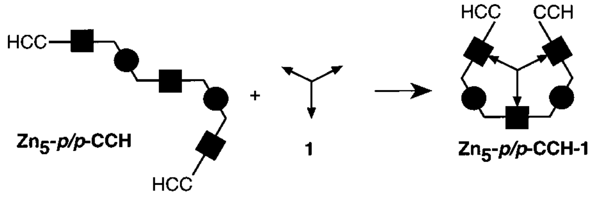


tamer **Zn$_2$FbZn$_2$-*p/p*-CCTMS** in 41% yield after silica chromatography and SEC. Cleavage of the TMS groups gave the ethynyl substituted pentamer **Zn$_2$FbZn$_2$-*p/p*-CCH** in 85% yield. Metalation of **Zn$_2$FbZn$_2$-*p/p*-CCH** with Zn(OAc)$_2$•2H$_2$O afforded **Zn$_5$-*p/p*-CCH** in 95% yield.

A survey reaction of **Zn$_5$-*p/p*-CCH** and *m*/*m*-diiodo Fb porphyrin **4** was performed in the presence of a stoichiometric amount of the template (Scheme 7). The reaction required 2.5 h for complete consumption of the starting porphyrins. The analytical SEC trace of the crude reaction mixture showed a sharp peak assigned as the desired hexamer (see Supporting Information).[50] LD-MS analysis of the same reaction mixture showed the molecule ion peak at $m/z = 4645.4$ (calcd avg mass 4642.3 for $C_{312}H_{230}N_{24}Zn_5$) as the only significant peak in the region $m/z = 3000-10000$. The preparative synthesis of ***cyclo*-Zn$_5$FbU** was carried out in the same manner. Chromatography on one silica column (CHCl$_3$) removed non-porphyrin species and some of the HMWM; four repetitive preparative SEC columns (THF) removed most of the HMWM. A final silica column afforded the pure ***cyclo*-Zn$_5$FbU** in 13% yield.

Binding of the Linear Pentamer Zn$_5$-*p/p*-CCH and the Tripyridyl Template (1). The cyclic hexamers such as ***cyclo*-Zn$_6$U** have high affinity for template **1**, effectively giving quantitative association at concentrations typically employed for static electronic spectroscopy (i.e., 10^{-6} to 10^{-7} M).[33] We investigated whether the less-structured linear pentamer **Zn$_5$-*p/p*-CCH** exhibited similar affinity for **1** (Scheme 8). Upon addition of 1 mol equiv of the tripyridyl template **1** to a solution of **Zn$_5$-*p/p*-CCH** in toluene (3.0 × 10^{-7} M each), the Soret band red-shifted from 423 to 432 nm, indicating the binding of the template with **Zn$_5$-*p/p*-CCH** (Figure 4A). Illumination of

Scheme 8



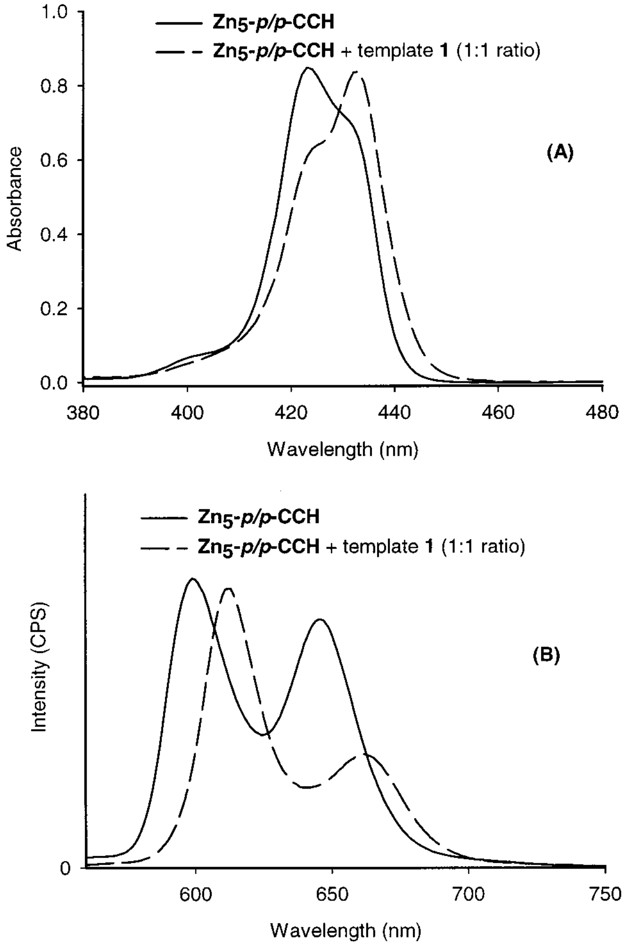


Figure 4. Template binding effect of **Zn$_5$-*p/p*-CCH** with tripyridyl template **1** in toluene at room temperature (3.0 × 10^{-7} M each). (A) UV–vis absorption spectra before and after adding template **1**. (B) Fluorescence emission spectra before and after adding template **1**.

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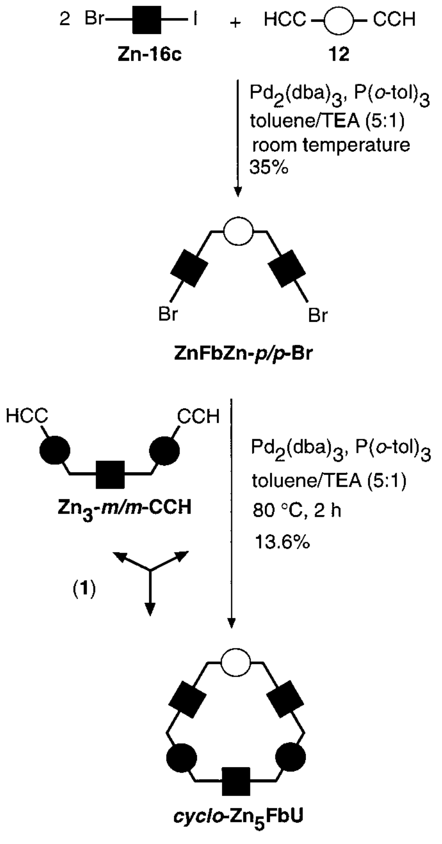
(49) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166–11180.

(50) Analytical SEC generally is a very effective tool for monitoring array-forming reactions.[49] However, in this reaction a significant amount of precipitation occurred. The analytical SEC traces of aliquots from the crude reaction mixture can be misleading because typically only the soluble species are sampled. Such precipitation was not observed in our prior work.[6] The analytical SEC trace of the soluble fraction from this reaction, and that of the purified product, are shown in the Supporting Information.

Zn_5-*p/p*-CCH at 550 nm in toluene resulted in emission typical of a Zn porphyrin, with $\lambda_{em} = 598$ and 642 nm. However, illumination at 550 nm of the solution containing a 1:1 ratio of **Zn_5-*p/p*-CCH** and template **1** resulted in a red-shifted emission ($\lambda_{em} = 612$ and 662 nm) characteristic of pyridyl-coordinated Zn porphyrins, with no emission observed from the uncoordinated Zn porphyrin (Figure 4B). Given that fluorescence from the fully uncoordinated array (**Zn_5-*p/p*-CCH**) at a level of 5% would be readily detected, the association constant for formation of **Zn_5-*p/p*-CCH-1** must be $>10^9$ M^{-1}. These results suggest that the linear pentamer and the template must be quantitatively associated under the conditions of the Pd-coupling reactions, which are performed at a concentration 4 orders of magnitude higher than in this binding experiment.

Synthesis of *cyclo*-Zn_5FbU via the 3 + 3 Route. We recently developed methodology for successive Sonogashira coupling reactions of iodo and bromo groups on porphyrin building blocks.[51] This method enabled investigation of a 3 + 3 route for preparing ***cyclo*-Zn_5FbU** (Figure 2C). This route requires the preparation of two trimer precursors, a diethynyl trimer **Zn_3-*m/m*-CCH** and a dibromo trimer **ZnFbZn-*p/p*-Br**. The latter was prepared by the selective reaction of 2 mol equiv of bromo/iodo porphyrin **Zn-16c** with diethynyl porphyrin **12** at room temperature (Scheme 9). SEC analysis of an aliquot removed after 2.5 h showed the presence of 7% HMWM, 58% trimer, 7% dimer, and 28% monomers (uncorrected data). No additional catalyst was added for this reaction. Chromatographic workup (silica, SEC, silica) afforded the pure trimer **ZnFbZn-*p/p*-Br** in 35% yield. This approach affords good selectivity for the iodo + ethyne reaction in the presence of a bromo group.

Scheme 9



The 3 + 3 reaction of **ZnFbZn-*p/p*-Br** and **Zn_3-*m/m*-CCH** (Scheme 9) was carried out using the conditions for the bromo + ethyne coupling reaction, which are essentially identical to those of the iodo + ethyne reaction but with reaction at 80 °C.[51] Purification of this mixture required an SEC column (THF) to remove the undissolved Pd species and some of the HMWM, three preparative SEC columns to remove the remaining HMWM which chromatographed closely with the desired cyclic hexamer, and a final silica column chromatography.[50] Some insoluble materials remained on top of the first short SEC column, which upon dissolution in pyridine and analysis by SEC were found to consist mostly of HMWM. The desired product ***cyclo*-Zn_5FbU** was obtained in 13.6% yield. The precipitate in this reaction appears to be associated with the template.[52]

Synthesis of *cyclo*-Zn_2FbZn$_2$FbU. All approaches envisaged in Figure 3 for the synthesis of ***cyclo*-Zn_2FbZn$_2$FbU** construct the array in a 5 + 1 route. We initially investigated the approach shown in Figure 3B, which employs four porphyrin building blocks, three Pd-coupling reactions, and three functional group deprotection steps (including magnesium demetalation). Coupling of *m*/*m*-diethynyl porphyrin **12** and 2 mol equiv of *p*/*p*-iodo/TMS-ethynyl Zn porphyrin **Zn-16b** afforded the desired trimer (**ZnFbZn-*p/p*-CCTMS**) and byproduct (dimer) in 36% and 3.7% yield, respectively, after purification by chromatography (silica, SEC, silica). Cleavage of the TMS groups (TBAF) afforded the diethynyl trimer **ZnFbZn-*p/p*-CCH** in 80% yield (Scheme 10). Coupling of the latter with 2 mol equiv of *m*/*m*-iodo/TMS-ethynyl **Zn-16a** afforded the TMS-protected porphyrin pentamer **Zn_2FbZn$_2$-*m/m*-CCTMS** in 51% yield after chromatography (silica, SEC, silica). Cleavage of the TMS groups with TBAF afforded **Zn_2FbZn$_2$-*m/m*-CCH** in 85% yield.

The coupling reaction of **Zn_2FbZn$_2$-*m/m*-CCH** and *p*/*p*-diiodo Mg porphyrin (**Mg-17**) in the presence of template **1** was complete within 1.5 h. The analytical SEC trace of the crude reaction mixture exhibited a sharp peak assigned as the hexamer ***cyclo*-Zn_2FbZn$_2$MgU**.[50] LD-MS analysis also showed an intense molecule ion peak at $m/z = 4602.9$ (calcd avg mass 4601.2 for $C_{312}H_{230}MgN_{24}Zn_4$). Demetalation of magnesium was achieved by treatment of the crude reaction mixture with silica gel in $CHCl_3$. Chromatography on silica removed Pd species and some of the HMWM, repetitive preparative SEC removed most of the HMWM, and a final silica chromatography followed by precipitation from $CHCl_3$/methanol afforded ***cyclo*-Zn_2FbZn$_2$FbU** in 10% yield.

We also investigated the coupling reaction of **Zn_2FbZn$_2$-*p/p*-CCH** and *m*/*m*-diiodo Fb porphyrin (**4**) in the absence of the template (route A, Figure 3). A survey reaction required 3 h for the complete consumption of the starting porphyrins (see Supporting Information for the SEC trace of the crude reaction mixture). LD-MS analysis of this crude reaction mixture exhibited an

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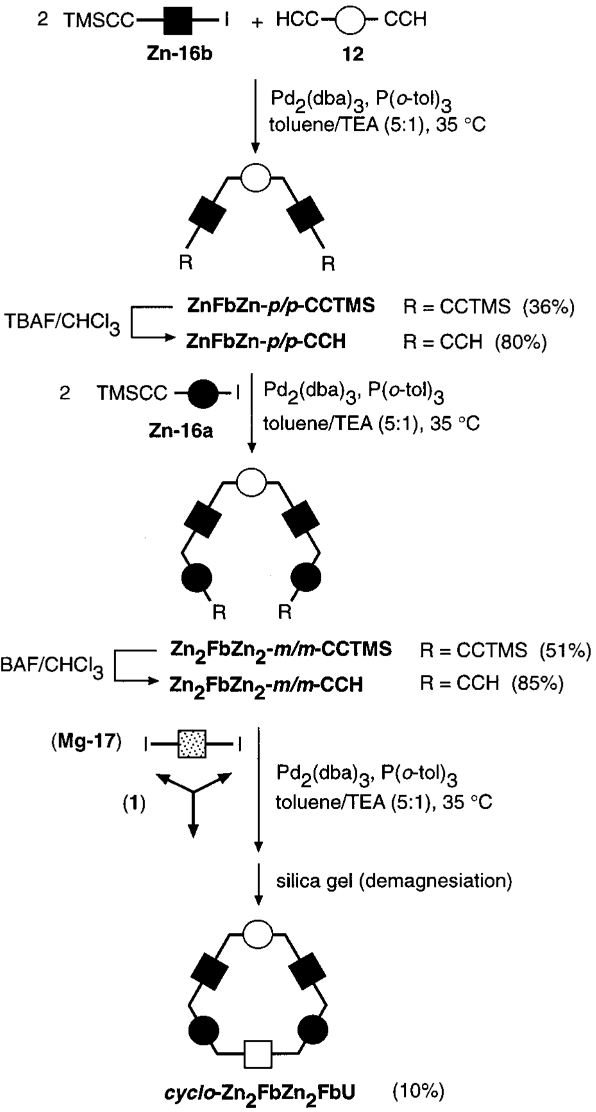
(51) Loewe, R. S.; Lammi, R. K.; Diers, J. R.; Kirmaier, C.; Bocian, D. F.; Holten, D.; Lindsey, J. S. Manuscript in preparation.

(52) The reaction in the absence of the template resulted in complete consumption of the starting porphyrin trimers after 2 h (analytical SEC). No precipitation was noticed in this reaction. The integrated intensity (uncorrected) of the desired hexamer only accounted for 4.4% of the total, and LD-MS analysis of this crude mixture showed a weak peak at $m/z = 4630.1$ (calcd 4642.2 for $C_{312}H_{230}N_{24}Zn_5$). This material was not isolated.

Scheme 10



intense molecule ion peak at $m/z = 4583.8$. The ***cyclo*-Zn$_2$FbZn$_2$FbU** was isolated by chromatography (silica; three SEC columns) in 3.5% yield with 95% purity as judged by analytical SEC. This reaction without the template establishes the structure-directed contribution to cyclic hexamer formation. Although the yield was low, the appropriate comparison is the one-flask synthesis without a template, which afforded no isolated cyclic hexamer (a trace was detected by LD-MS). The one-flask synthesis with a template afforded ***cyclo*-Zn$_3$Fb$_3$U** in 5.3% yield.[6] Thus, the rational syntheses can be carried out to obtain cyclic hexamers with diverse metalation patterns for which a template-directed synthesis is not possible, obtaining yields comparable to those in the one-flask synthesis with a template. A detailed comparison of the synthesis and purification methods employed in the one-flask and stepwise syntheses is shown in a Table in the Supporting Information.

Spectroscopic Characterization. The absorption and fluorescence spectra of the cyclic arrays were collected in toluene at room temperature. The absorption spectrum of each array (***cyclo*-Zn$_5$FbU**, ***cyclo*-Zn$_2$FbZn$_2$FbU**) exhibits a slightly broadened Soret band while the visible bands are essentially identical to those of the component Zn and Fb porphyrins. The close similarity of the spectra of the component parts and that of the array are typical of a weakly coupled set of chromophores.[1] Illumination of ***cyclo*-Zn$_5$FbU** at 550 nm, where the Zn porphyrins absorb over 90% of the light, results in emission from both the Zn and Fb porphyrins (integrated $\Phi_f = 0.085$). The emission from the Zn porphyrins is decreased to 40% of that of a benchmark Zn porphyrin, commensurate with a quantum yield of 60% for energy transfer reaching the Fb porphyrin. For ***cyclo*-Zn$_2$FbZn$_2$FbU**, illumination at 550 nm, where the Zn porphyrins absorb 85% of the light, results in emission predominantly from the Fb porphyrins (integrated $\Phi_f = 0.098$). The Zn porphyrin emission is decreased to 10% of that of a benchmark Zn porphyrin, commensurate with a quantum yield of 90% for energy transfer reaching the Fb porphyrin (see fluorescence spectra in the Supporting Information). Thus, for both arrays the dominant excited singlet-state process is energy transfer from the Zn to the Fb porphyrins. The spectroscopic characterization of the self-assembled arrays derived from ***cyclo*-Zn$_5$FbU** and ***cyclo*-Zn$_2$FbZn$_2$FbU** with various guests will be presented elsewhere.

Consideration of Synthetic Strategies. The synthesis of multiporphyrin light-harvesting arrays is a relatively new area of materials chemistry. A diversity of synthetic methods is required for this field to flourish. The arrays produced by Gossauer have 6-fold symmetry with six *p*/*p*-substituted porphyrins joined via a 1,3-bis(phenylethynyl)phenylene linker.[36] The synthesis reported by Gossauer employs an iterative divergent/convergent strategy. This approach begins with one porphyrin building block (prepared via earlier statistical methods), employs four Pd-coupling reactions (one site per coupling reaction), and requires six functional group transformations as the array grows in size. Two advantages of this strategy are as follows: (1) The metalation state of each porphyrin can be controlled. (2) The linear hexamers bearing iodo and ethynyl functional groups enable cyclization to be performed in dilute solution. Such large relatively rigid molecules, which have rarely been accessible, can be used in fundamental studies of macrocyclization. The cyclizations (untemplated) were performed at 0.25 mM and afforded up to 0.39−1.8 mg of cyclic hexamer in yields of 8−31%.

The arrays described herein have 3-fold symmetry with alternating *p*/*p*- and *m*/*m*-substituted porphyrins. Each synthetic route is performed in a stepwise manner, employs four porphyrin monomers, and requires three Pd coupling reactions (two sites per coupling reaction) and one to three functional group deprotection steps. Reaction at two coupling sites with each Pd-coupling step affords rapid synthesis but restricts the range of patterns of distinct porphyrins that can be produced. The final ring-forming step also entails reaction at two sites (the first an intermolecular reaction, the second an intramolecular reaction) for which the conditions have yet to be optimized. The cyclizations (templated) were performed at 1.7−1.8 mM of each reactant and afforded 7.8−9.8 mg of cyclic hexamer in yields of 10−13.6%. Two advantages of this approach are as follows: (1) The desired functional groups are introduced at the earliest stage in the synthesis, during the construction of the porphyrin monomers, for which powerful methodology is now available. (2) A high degree of convergence minimizes synthetic manipulations of the growing arrays.

Conclusions. For studies of the flow of excited-state energy in self-assembled light-harvesting systems, two new cyclic hexamers (***cyclo*-Zn$_5$FbU**, ***cyclo*-Zn$_2$FbZn$_2$FbU**) were prepared. Several convergent approaches for constructing the macrocyclic arrays were examined. The major findings from this work are as follows: (1) The yields in the ring-forming reaction in the template-directed 5 + 1 route were 13% (***cyclo*-Zn$_5$FbU**, Figure 2A) and 10% (***cyclo*-Zn$_2$FbZn$_2$FbU**, Figure 3B), while that in the template-directed 3 + 3 route was 13.6% (***cyclo*-Zn$_5$FbU**, Figure 2C). The yield in the structure-directed (i.e., no template) 5 + 1 route was 3.5% (***cyclo*-Zn$_2$FbZn$_2$FbU**, Figure 3A). For comparison, the overall yield of the template-directed one-flask synthesis was 5.3% (***cyclo*-Zn$_3$Fb$_3$U**) while the structure-directed one-flask synthesis gave only a trace of product. (2) The template-directed one-flask route is superior for those cyclic hexamers with a suitable pattern of metalation states (e.g., ***cyclo*-Zn$_3$Fb$_3$U** and ***cyclo*-Zn$_6$U**), affording a simple and expedient synthesis. On the other hand, the stepwise synthesis is applicable to those cyclic hexamers with metalation patterns incompatible with a one-flask synthesis (e.g., ***cyclo*-Zn$_5$FbU** and ***cyclo*-Zn$_2$FbZn$_2$FbU**). The stepwise syntheses can be implemented with or without a template whereas the one-flask synthesis can be performed only with a template. (3) Both the 5 + 1 route and the 3 + 3 route afford convergent syntheses. The 3 + 3 route employs the reaction of a diethynyl trimer and a dibromo trimer; the latter is available via successive iodo + ethyne and bromo + ethyne coupling reactions. (4) The linear pentamer exhibits high affinity for the tripyridyl template with association constant > 10^9 M^{-1}. (5) The rational synthesis of the cyclic hexamer employs *trans*-AB$_2$C-porphyrins and *trans*-A$_2$B$_2$-porphyrins bearing ethyne, iodo, and/or bromo functional groups. The availability of ample quantities of the requisite porphyrin building blocks enabled the cyclic hexamers to be obtained in quantities of ~10 mg, which is sufficient for spectroscopic studies.

Experimental Section

General. ^{1}H NMR spectra (300 or 500 MHz) and ^{13}C NMR spectra (75 MHz) were collected in CDCl$_3$. Absorption spectra and fluorescence spectra (corrected) were collected in toluene at room temperature. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix,[53] or by high-resolution fast atom bombardment mass spectrometry (FAB-MS). All reagents were obtained from Aldrich and were used as received. The known compounds **2**,[33] **Zn-3**,[6] **4**,[6] **9**,[42] **10**,[43] **11**,[43] **13b**,[44] **13c**,[44] **14b**,[44] **15b**,[44] **Zn-16b**,[48] **17**,[41] **18**,[47] **19**,[42] 3-iodobenzoyl chloride,[44] and *S*-2-pyridyl 3-iodobenzothioate[46] were prepared according to literature procedures.

Solvents. Solvents were dried by standard methods. Diethylamine, triethylamine and toluene were distilled from CaH$_2$. The solvents CH$_3$CN, CH$_2$Cl$_2$, and CHCl$_3$ (stabilized with 0.8% ethanol) were reagent-grade and were used as received from Fisher.

Chromatography. Adsorption column chromatography was performed using flash silica gel (Baker, 60−200 mesh) or alumina (alumina basic, Brockman activity I, Fisher). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1 in THF (Fisher HPLC grade). Analytical SEC[49] (λ_{det} = 420 nm) was performed to monitor the progress of the coupling reactions and assess the purity of the porphyrin oligomers and cyclic hexameric arrays.

Fluorescence Spectroscopy. Fluorescence quantum yields were determined in toluene at room temperature as described previously.[6] Tetraphenylporphyrin (TPP, Φ_f = 0.11),[54] zinc tetraphenylporphyrin (ZnTPP, Φ_f = 0.033),[54] and ***cyclo*-Zn$_6$U** (Φ_f = 0.039)[6] were used as quantitative standards.

1,3,5-Tris{4-[2-(4-pyridyl)ethynyl]phenyl}benzene (1). Following a standard method,[55] samples of **6** (0.84 g, 8.1 mmol), **7** (1.37 g, 2.0 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (428 mg, 0.60 mmol), and CuI (8 mg, 0.04 mmol) were weighed into a 100 mL Schlenk flask. The flask was pump-purged with argon three times. THF/diethylamine (60 mL, 1:1) was added, and the mixture was stirred at 45 °C under argon. TLC analysis [silica, CHCl$_3$/ethyl acetate (1:1)] showed the product as the second bright fluorescent spot upon UV illumination. Additional 4-ethynylpyridine (90 mg, 0.87 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (60 mg, 0.093 mmol), and CuI (3.0 mg, 0.015 mmol) were added after a total of 3 h and stirring was continued for another 3 h. The reaction mixture was cooled in a freezer overnight. The precipitate was filtered, and the filtrate was concentrated and purified by chromatography [silica, CH$_2$Cl$_2$/methanol (96.5:3.5)]. The second band (bright fluorescence) was collected, which afforded a slightly yellow solid (1.01 g, 83%): mp > 260 °C; ^{1}H NMR δ 8.63 (d, J = 5.7 Hz, 6H), 7.84 (s, 3H), 7.74 (d, J = 8.1 Hz, 6H), 7.69 (d, J = 8.1 Hz, 6H), 7.42 (d, J = 5.7 Hz, 6H); FAB-MS obsd 610.2306, calcd 610.2283 ($C_{45}H_{27}N_3$). Anal. Calcd: C, 88.64; H, 4.46; N, 6.89. Found: C, 87.86; H, 4.53; N, 6.87.

Zn(II)-5,15-Dimesityl-10,20-bis{4-[2-(4-pyridyl)ethynyl]-phenyl}porphyrin (Zn-2). A solution of **2**[33] (15.0 mg, 16.6 μmol) in CHCl$_3$ (5 mL) was treated with a solution of Zn(OAc)$_2$·2H$_2$O (18.3 mg, 83.3 μmol) in methanol (0.5 mL) at room temperature for 4 h. The standard workup and chromatography [silica, CHCl$_3$/methanol (95:5)] afforded a purple solid (15.2 mg, 94%): ^{1}H NMR δ 8.70−8.66 (m, 8H), 8.12 (d, J = 8.1 Hz, 4H), 7.66 (d, J = 7.8 Hz, 4H), 7.25 (m, 8H), 6.58 (s, br, 4H), 2.60 (s, 6H), 1.78 (s, 12H); LD-MS obsd 960.1, FAB-MS obsd 963.3130, calcd 963.3154 ($C_{64}H_{46}N_6Zn$); λ_{abs} (log ϵ) 426 (5.42), 551 (4.27), 593 (3.74) nm; λ_{em} (λ_{ex} = 550 nm) 600, 646 nm (Φ_f = 0.046).

2-Methyl-4-(4-pyridyl)-3-butyn-2-ol (5). Following a standard method,[55,56] 4-bromopyridine hydrochloride (5.01 g, 25.7 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (180 mg, 0.26 mmol), and CuI (29 mg, 0.15 mmol) were weighed into a 100 mL Schlenk flask which was then pump-purged with argon three times. 2-Methyl-3-butyn-2-ol (2.60 g, 31.0 mmol) and diethylamine/THF (60 mL, 5:2) were added under argon. After stirring for 4.5 h at room temperature, the reaction was judged to be complete by TLC analysis [silica, CHCl$_3$/ethyl acetate (1:1)]. The solvent was evaporated to dryness. The crude product was dissolved in CHCl$_3$ (100 mL) and washed with water. The organic layer was dried (Na$_2$SO$_4$), and the solvent was removed. The residue was purified by chromatography [silica, CHCl$_3$/ethyl acetate (1:1)], affording a yellow solid (4.01 g). Recrystallization (CHCl$_3$/hexanes) afforded a slightly yellow solid (3.80 g, 92%): mp 113−114 °C; ^{1}H NMR δ 8.54 (d, J = 5.1 Hz, 2H), 7.25 (d, J = 5.1 Hz, 2H), 3.60 (br s, 1H), 1.63 (s, 6H); ^{13}C NMR δ 149.3, 131.4, 125.7, 99.2, 79.3, 65.1, 31.2. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.46; H, 6.96; N, 8.71.

4-Ethynylpyridine (6). A solution of **5** (3.00 g, 18.6 mmol) in toluene (90 mL) was treated with finely powdered NaOH (0.80 g, 20 mmol), and the mixture was refluxed for 3 h. TLC [silica, ethyl acetate/CHCl$_3$ (1:1)] indicated the reaction was complete. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated taking care to minimize the loss of the product, which is quite volatile.

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Kugelrohr distillation (0.01 mmHg, 30 °C) afforded a white solid (1.22 g, 64%): mp 96−97 °C; ^{1}H NMR δ 8.60 (d, $J = 5.9$ Hz, 2H), 7.35 (d, $J = 5.9$ Hz, 2H), 3.30 (s, 1H); ^{13}C NMR δ 149.6, 130.1, 125.9, 81.8, 80.7; HRMS (EI) obsd 103.0418, calcd 103.0422 (C_7H_5N).

1,3,5-Tris(4-iodophenyl)benzene (7). 4-Iodoacetophenone (25.0 g, 0.10 mol) and trimethyl orthoformate (17.1 g, 0.16 mol) were dissolved in $CHCl_3$ (200 mL) in a three-necked round-bottomed flask fitted with a gas inlet and a gas outlet; the latter was connected to an aqueous sodium hydroxide trap. The solution was purged with HCl gas for 30 min at 0 °C and then was stirred overnight at room temperature. TLC [silica, $CHCl_3$/hexanes (1:3)] showed complete consumption of 4-iodoacetophenone. The solvent was removed, and the residue was purified by chromatography [silica, 7.5 × 30 cm, $CHCl_3$/hexanes (1:3)]. The first band (yellow) was the desired product followed by the byproduct **8** as the second band. Recrystallization ($CHCl_3$/methanol) afforded a slightly yellow solid (8.6 g, 37%): mp >260 °C; ^{1}H NMR δ 7.78 (d, $J = 8.1$ Hz, 6H), 7.67 (s, 3H), 7.39 (d, $J = 8.1$ Hz, 6H); ^{13}C NMR δ 141.6, 140.1, 138.0, 129.1, 124.9, 93.6. Anal. Calcd for $C_{24}H_{15}I_3$: C, 42.12; H, 2.21. Found: C, 42.13; H, 2.20. Data for compound **8** (2.98 g, 12%): mp 96−98 °C; ^{1}H NMR δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 1.5$ Hz, 1H), 2.54 (s, 3H); ^{13}C NMR δ 190.4, 154.4, 141.8, 138.2, 137.7, 137.6, 129.5, 128.1, 121.4, 100.5, 95.4, 18.6. Anal. Calcd for $C_{16}H_{12}OI_2$: C, 40.54; H, 2.55. Found: C, 40.55; H, 2.50.

5,15-Bis(3-ethynylphenyl)-10,20-dimesitylporphyrin (12). Following an early method for preparing **11** at one-fifth the scale,[43] a solution of **10** (955 mg, 4.73 mmol) and 5-mesityldipyrromethane (**9**) (1.25 g, 4.73 mmol) in $CHCl_3$ (625 mL) was treated with $BF_3{\cdot}O(Et)_2$ (260 μL, 3.3 mM). After 1 h, DDQ (1.68 g, 7.40 mmol) was added, and the mixture was stirred for another 1 h at room temperature. The reaction mixture was filtered through a pad of alumina, washed with $CHCl_3$, and the porphyrin fraction was collected. Chromatography [silica, CH_2Cl_2/hexanes (1:1)] gave TMS-protected porphyrin **11** as a purple solid (1.25 g, 58%). ^{1}H NMR and LD-MS data were identical to those previously reported.[43] A solution of **11** (1.20 g, 1.34 mmol) in $CHCl_3$ (150 mL) was treated with TBAF on silica gel (2.68 g, 2.68 mmol, 1.0−1.5 mmol F^-/g resin) at room temperature for 2 h. The mixture was washed with 10% aqueous $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated. Chromatography [silica, $CHCl_3$/hexanes (1:1)] afforded a purple solid (0.84 g, 84%): ^{1}H NMR δ 8.76 (d, $J = 5.1$ Hz, 4H), 8.70 (d, $J = 5.1$ Hz, 4H), 8.35 (d, $J = 1.5$ Hz, 2H), 8.20 (d, $J = 7.5$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H), 7.28 (s, 4H), 3.16 (s, 2H), 2.63 (s, 6H), 1.83 (s, 12H), −2.68 (s, br, 2H); LD-MS obsd 747.7; FAB-MS obsd 746.3442, calcd 746.3409 ($C_{54}H_{42}N_4$); λ_{abs} 420, 514, 548, 591, 647 nm; λ_{em} ($\lambda_{ex} = 520$ nm) 649, 717 nm.

***S*-2-Pyridyl 3-[2-(trimethylsilyl)ethynyl]benzenethioate (13a).** Following a refined procedure,[44] samples of *S*-2-pyridyl 3-iodobenzenethioate[46] (17.1 g, 50.1 mmol), $Pd_2(dba)_3$ (0.83 g, 0.90 mmol), PPh_3 (1.97 g, 7.51 mmol), and CuI (0.95 g, 5.0 mmol) were weighed into a 250 mL Schlenk flask. The flask was pump-purged with argon three times, and then THF/triethylamine (140 mL, 3:1) and trimethylsilylacetylene (11.0 mL, 76.9 mmol) were added. The flask was sealed tightly. The mixture was stirred for 2 h at 50 °C, at which point TLC analysis [silica, hexanes/ethyl acetate (4:1)] showed incomplete consumption of *S*-2-pyridyl 3-iodobenzenethioate. The flask was cooled to room temperature and additional trimethylsilylacetylene (7.00 mL, 49.6 mmol) was added. Stirring was continued at 50 °C for another 1 h, affording complete reaction. The mixture was filtered, and the filtered material was washed with ethyl acetate. The filtrate was concentrated and purified by chromatography [silica, hexanes/ethyl acetate (4:1)], affording a slightly brown solid. Recrystallization from hexanes/ethyl acetate gave pale yellow crystals (12.58 g, 81%): mp 90−92 °C; ^{1}H NMR δ 8.70−8.68 (m, 1H), 8.10 (m, 1H), 7.96−7.93 (m, 1H), 7.84−7.78 (m, 2H), 7.73−7.68 (m, 2H), 7.44 (t, $J = 8.1$ Hz, 1H), 7.38−7.33 (m, 1H), 0.27 (s, 9H); ^{13}C NMR δ 188.6, 150.9, 150.5, 137.1, 136.8, 136.5, 130.8, 130.7, 128.7, 127.2, 124.0, 123.7, 103.3, 96.1, 0.3; FAB-MS obsd 312.0898, calcd 312.0878 ($C_{17}H_{17}NOSSi$). Anal. Calcd: C, 65.55; H, 5.50; N, 4.50. Found: C, 65.53; H, 5.55; N, 4.45.

5-Mesityl-1-{3-[2-(trimethylsilyl)ethynyl]benzoyl}dipyrromethane (14a). Following a published procedure,[44] EtMgBr (44.0 mL, 44.0 mmol, 1.0 M in THF) was added to a solution of **9** (5.28 g, 20.0 mmol) in dry THF (20 mL) at room temperature under argon. The mixture was stirred for 10 min at room temperature and then cooled to −78 °C. A solution of **13a** (6.22 g, 20.0 mmol) in THF (30 mL) was then added. The mixture was stirred at −78 °C for 10 min and then allowed to warm to room temperature. TLC analysis [silica gel, CH_2Cl_2/ethyl acetate (98:2)] showed complete consumption of **13a** after 40 min. The reaction mixture was poured into a mixture of CH_2Cl_2 (200 mL) and saturated aqueous NH_4Cl (100 mL). The organic phase was separated, washed with brine and water, dried (Na_2SO_4), and concentrated to give a dark foamlike solid. Chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] afforded an amorphous yellow solid (7.16 g, 77%): mp 95−97 °C; ^{1}H NMR δ 9.21 (s, br, 1H), 7.92 (m, 1H), 7.84 (s, br, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.40 (t, $J = 8.1$ Hz, 1H), 6.90 (s, 2H), 6.84−6.82 (m, 1H), 6.70−6.68 (m, 1H), 6.24−6.21 (m, 1H), 6.15−6.12 (m, 2H), 5.96 (s, 1H), 2.30 (s, 3H), 2.09 (s, 6H), 0.26 (s, 9H); ^{13}C NMR δ 183.0, 141.3, 138.5, 137.4, 137.1, 134.7, 132.9, 132.1, 130.5, 129.5, 128.9, 128.6, 128.2, 123.2, 120.8, 116.9, 110.1, 108.8, 107.1, 104.1, 95.1, 38.5, 20.7, 20.6, 0.2; FAB-MS obsd 464.2311, calcd 464.2284 ($C_{30}H_{32}N_2OSi$). Anal. Calcd: C, 77.54; H, 6.94; N, 6.03. Found: C, 77.39; H, 6.83; N, 5.91.

1-(4-Bromobenzoyl)-5-mesityldipyrromethane (14c). Following the procedure for the preparation of **14a**, the reaction of **9** (1.85 g, 7.00 mmol) in THF (10 mL) with EtMgBr (15.4 mL, 15.4 mmol, 1.0 M in THF) followed by *S*-2-pyridyl 4-bromobenzenethioate[44] (2.06 g, 7.00 mmol) afforded, upon standard workup and chromatography (silica, CH_2Cl_2), a yellow foamlike solid (2.46 g, 78%): mp 120−122 °C; ^{1}H NMR δ 9.24 (s, br, 1H), 7.84 (s, br, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 8.1$ Hz, 2H), 7.00 (s, 2H), 6.80−6.78 (m, 1H), 6.69−6.68 (m, 1H), 6.23−6.20 (m, 1H), 6.15−6.12 (m, 2H), 5.95 (s, 1H), 2.29 (s, 3H), 2.09 (s, 6H); ^{13}C NMR δ 182.7, 141.3, 137.4, 137.2, 137.1, 132.9, 131.5, 130.5, 130.3, 129.5, 128.9, 126.3, 120.5, 116.9, 110.2, 108.9, 107.2, 38.6, 20.7; FAB-MS obsd 446.0979, calcd 446.0994 ($C_{25}H_{23}BrN_2O$). Anal. Calcd: C, 67.12; H, 5.18; N, 6.26. Found: C, 67.11; H, 5.23; N, 6.23.

1-(3-Iodobenzoyl)-5-mesityl-9-{3-[2-(trimethylsilyl)ethynyl]benzoyl}dipyrromethane (15a). Following a standard procedure,[44] a solution of monoacyldipyrromethane **14a** (7.03 g, 14.2 mmol) in toluene (60 mL) was treated with EtMgBr (28.4 mL, 28.4 mmol, 1.0 M in THF) under argon. After stirring at room temperature for 5 min, a solution of 3-iodobenzoyl chloride (3.78 g, 15.1 mmol) in toluene (2 mL) was added under argon. Stirring was continued at room temperature for 10 min. EtMgBr (28.4 mL, 28.4 mmol) was again added followed by stirring for 5 min, and then 3-iodobenzoyl chloride (3.78 g, 14.2 mmol) in toluene (2 mL) was added. After 15 min, TLC analysis [silica, CH_2Cl_2/ethyl acetate (98:2)] indicated complete consumption of **14a**. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (200 mL) and ethyl acetate (300 mL). The organic phase was separated, washed with brine and water, dried (Na_2SO_4), and concentrated. Chromatography (silica, CH_2Cl_2) followed by recrystallization (CH_2Cl_2/methanol) afforded a brown solid (6.76 g, 64%): mp 100−102 °C; ^{1}H NMR δ 10.18 (s, br, 2H), 8.08 (m, 1H), 7.86−7.83 (m, 2H), 7.75−7.69 (m, 2H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.36 (t, $J = 8.1$ Hz, 1H), 7.17 (t, $J = 8.1$ Hz, 1H), 6.94 (s, 2H), 6.77−6.72 (m, 2H), 6.12 (s, 1H), 6.10 (s, 2H), 2.32 (s, 3H), 2.19 (s, 6H), 0.25 (s, 9H); ^{13}C NMR δ 182.5, 181.7, 140.8, 140.5, 140.1, 139.8, 138.4, 138.0, 137.4, 137.0, 134.0, 133.1, 133.0, 130.2, 130.0, 129.8, 129.6, 129.1, 128.2, 127.9, 122.9, 121.5, 121.4, 110.8, 110.7, 104.2, 94.8, 93.5, 39.2, 20.9, 0.2; FAB-MS obsd 694.1531, calcd 694.1513 ($C_{37}H_{35}IN_2O_2Si$). Anal. Calcd: C, 63.97; H, 5.08; N, 4.03. Found: C, 63.81; H, 5.18; N, 3.98.

1-(4-Bromobenzoyl)-9-(4-iodobenzoyl)-5-mesityldipyrromethane (15c). Following the procedure for the synthesis of **15a**, a solution of monoacyldipyrromethane **14c** (2.46 g, 5.50 mmol) in toluene (25 mL) was treated with EtMgBr (11.0 mL, 11.0 mmol, 1.0 M in THF) under argon for 5 min at room temperature. Then 4-iodobenzoyl chloride (1.47 g, 5.50 mmol) was added under argon, and the mixture was stirred for 10 min at room temperature. This procedure was repeated twice [EtMgBr (11.0 mL, 11.0 mmol), 4-iodobenzoyl chloride (1.47 g, 5.50 mmol); EtMgBr (5.5 mL, 5.5 mmol), 4-iodobenzoyl chloride (0.74 g, 2.78 mmol)]. The mixture was stirred at room temperature for 30 min, followed by standard workup and chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)]. Precipitation of the product from CH_2Cl_2/methanol afforded a yellow solid (2.21 g, 59%): mp 233−235 °C (dec); ^{1}H NMR δ 10.35 (s, br, 2H), 7.78 (d, $J = 8.7$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 2H), 7.56 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.7$ Hz, 2H), 6.93 (s, 2H), 6.70−6.68 (m, 2H), 6.10−6.07 (m, 3H), 2,32 (s, 3H), 2.18 (s, 6H); ^{13}C NMR δ 182.7, 182.4, 140.5, 137.4, 137.2, 136.9, 132.9, 131.2, 130.8, 130.3, 130.0, 126.4, 121.1, 110.7, 98.9, 39.2, 20.8; FAB-MS obsd 676.0245, calcd 676.0222 ($C_{32}H_{26}BrIN_2O_2$). Anal. Calcd: C, 56.74; H, 3.87; N, 4.14. Found: C, 56.96; H, 4.08; N, 3.94.

5-(3-Iodophenyl)-10,20-dimesityl-15-{3-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (16a). Following a standard procedure,[44] a solution of diacyldipyrromethane **15a** (2.78 g, 4.00 mmol) in dry THF/methanol (176 mL, 10:1) was treated with $NaBH_4$ (3.02 g, 80.0 mmol) in portions, and the mixture was stirred at room temperature. TLC analysis [alumina, ethyl acetate/CH_2Cl_2 (1:1)] showed that the reduction was complete after 30 min. The reaction mixture was poured into a mixture of saturated aqueous NH_4Cl (200 mL) and CH_2Cl_2 (300 mL). The organic phase was washed with brine and water, dried (Na_2SO_4), and concentrated. The resulting residue was dried under vacuum for 15 min. To the freshly prepared dipyrromethanedicarbinol (4.00 mmol) were added **9** (1.06 g, 4.00 mmol) and CH_3CN (1600 mL) at room temperature. TFA (3.68 mL, 48.0 mmol, 30 mM) was added. The solution instantly turned dark. After 3.5 min, the spectroscopic yield of porphyrin had leveled off. Then DDQ (2.72 g, 12.0 mmol) was added and the mixture was stirred for 1 h at room temperature. Triethylamine (6.80 mL, 48.0 mmol) was then added. The mixture was filtered through a pad of alumina (eluted with CH_2Cl_2). Removal of the solvent gave a dark solid which was redissolved in CH_2Cl_2 (30 mL) and chromatographed (silica, CH_2Cl_2), affording a purple solid (0.75 g, 20%). The ^{1}H NMR data were identical to those reported for the product obtained from a mixed aldehyde condensation.[43]

Zn(II)-5-(3-Iodophenyl)-10,20-dimesityl-15-{3-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (Zn-16a). A solution of **16a** (0.71 g, 0.77 mmol) in $CHCl_3$ (150 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.85 g, 3.88 mmol) in methanol (5 mL) at room temperature for 3 h. The standard workup afforded a purple solid (0.72 g, 95%): ^{1}H NMR δ 8.86−8.83 (m, 4H), 8.80−8.77 (m, 4H), 8.60−8.59 (m, 1H), 8.35 (m, 1H), 8.22−8.16 (m, 2H), 8.11 (d, $J = 8.7$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.67 (t, $J = 8.1$ Hz, 1H), 7.47 (t, $J = 8.1$ Hz, 1H), 7.29 (s, 4H), 2.64 (s, 6H), 1.82 (m, 12H), 0.25 (s, 9H); LD-MS obsd 985.9; FAB-MS obsd 982.1916, calcd 982.1906 ($C_{55}H_{47}IN_4SiZn$); λ_{abs} 424, 550, 590 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 645, 595 nm.

5-(4-Iodophenyl)-10,20-dimesityl-15-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (16b). Following the procedure for preparing **16a**, a solution of diacyldipyrromethane **15b** (2.30 g, 3.31 mmol) in THF/methanol (146 mL, 10:1) was treated with $NaBH_4$ (2.51 g, 66.4 mmol). Standard workup and condensation with **9** (0.874 g, 3.31 mmol) in CH_3CN (1300 mL) at room temperature using TFA (3.05 mL, 39.7 mmol, 30 mM) was followed by oxidation with DDQ (2.25 g, 9.93 mmol). Treatment with triethylamine (5.60 mL, 39.7 mmol), filtration through a pad of alumina (eluted with CH_2Cl_2) and chromatography (silica, CH_2Cl_2) afforded a purple solid (0.665 g, 22%). The ^{1}H NMR data were identical to those reported for the product obtained from a mixed aldehyde condensation.[43]

5-(4-Bromophenyl)-15-(4-iodophenyl)-10,20-dimesitylporphyrin (16c). Following the procedure described for the preparation of **16a**, a solution of diacyldipyrromethane **15c** (1.90 g, 2.80 mmol) in THF/methanol (160 mL, 3:1) was treated with $NaBH_4$ (5.18 g, 137 mmol). Standard workup and condensation with 5-mesityldipyrromethane (**9**) (0.74 g, 2.80 mmol) in CH_3CN (1120 mL) using TFA (2.60 mL, 30 mM) was followed by oxidation with DDQ (1.93 g, 8.5 mmol). The standard workup, including chromatography (silica, CH_2Cl_2) followed by sonication with methanol afforded a purple solid (613 mg, 24%): ^{1}H NMR δ 8.78−8.76 (m, 4H), 8.70 (d, $J = 4.5$ Hz, 4H), 8.08 (d, $J = 8.1$ Hz, 4H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.88 (d, $J = 8.1$ Hz, 2H), 7.29 (s, 4H), 2.63 (s, 6H), 1.82 (s, 12H), −2.68 (s, br, 2H); LD-MS obsd 902.8; FAB-MS obsd 902.1478, calcd 902.1481 ($C_{50}H_{40}BrIN_4$); λ_{abs} 420, 515, 548, 592, 648 nm; λ_{em} ($\lambda_{ex} = 520$ nm), 650, 719 nm.

Zn(II)-5-(4-Bromophenyl)-15-(4-iodophenyl)-10,20-dimesitylporphyrin (Zn-16c). A solution of porphyrin **16c** (506 mg, 0.56 mmol) in $CHCl_3$ (140 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (613 mg, 2.80 mmol) overnight at room temperature. Standard workup and sonication with methanol afforded a purple solid (515 mg, 95%): ^{1}H NMR δ 8.86 (d, $J = 4.5$ Hz, 2H), 8.85 (d, $J = 4.5$ Hz, 2H), 8.78 (d, $J = 4.5$ Hz, 4H), 8.10 (d, $J = 6.6$ Hz, 2H), 8.07 (d, $J = 6.6$ Hz, 2H), 7.97 (d, $J = 8.1$ Hz, 2H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.28 (s, 4H), 2.63 (s, 6H), 1.82 (s, 12H); LD-MS obsd 964.0; FAB-MS obsd 964.0646, calcd 964.0616 ($C_{50}H_{38}BrIN_4Zn$); λ_{abs} 423, 549, 589 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 594, 645 nm.

Mg(II)-5,15-Bis(4-iodophenyl)-10,20-dimesitylporphyrin (Mg-17). Following a standard procedure,[38] a solution of 5,15-bis(4-iodophenyl)-10,20-dimesitylporphyrin[41] (190 mg, 0.20 mmol) in $CHCl_3$ (15 mL) was treated with *N*,*N*-diisopropylethylamine (695 μL, 4.0 mmol) and MgI_2 (556 mg, 2.0 mmol) at room temperature. Fluorescence excitation spectroscopy indicated complete metalation after 20 min. The mixture was washed with 10% aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated to afford a purple residue. Chromatography (alumina, $CHCl_3$) afforded a purple solid (174 mg, 89%): ^{1}H NMR δ 8.76 (d, $J = 4.5$ Hz, 4H), 8.69 (d, $J = 4.5$ Hz, 4H), 8.05 (d, $J = 8.1$ Hz, 4H), 7.95 (d, $J = 8.1$ Hz, 4H), 7.27 (s, 4H), 2.63 (s, 6H), 1.81 (s, 12H); LD-MS obsd 970.8; FAB-MS obsd 972.1030, calcd 972.1036 ($C_{50}H_{38}I_2MgN_4$); λ_{abs} 406, 428, 526, 564, 605 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 609, 661 nm.

5,15-Bis(4-iodophenyl)-10,20-di-*p*-tolyl-23*H*-21-oxaporphyrin (20). To an ice-cooled solution of **18**[47] (0.59 g, 1.0 mmol) in THF/methanol (40 mL, 3:1) was added $NaBH_4$ (1.90 g total, 50.0 mmol) in small portions over 10 min. The reduction was followed by TLC analysis [alumina, CH_2Cl_2/ethyl acetate (2:1)] and was complete after stirring for 40 min at room temperature. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4), and the solvent was removed affording a foamlike solid. The freshly prepared furylpyrromethane-dicarbinol was then condensed with **19** (0.35 g, 1.0 mmol) in CH_3CN (180 mL) containing TFA (920 μL, 30 mM) at room temperature. After 3.5 min the spectroscopic yield of porphyrin had stopped increasing. DDQ (0.68 g, 3.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h, and then triethylamine (2.40 mL) was added with stirring for 10 min. The reaction mixture was then combined with water and extracted with $CHCl_3$. The organic phase was dried (Na_2SO_4) and concentrated. Chromatography [silica, THF/CH_2Cl_2 (1:9)] removed a fast-moving black band (non-porphyrin species) from the slowly eluting porphyrin. The column was eluted until no red fluorescence was observed in the eluent using a UV lamp (365 nm). Further chromatography (basic alumina, Brockman activity I, CH_2Cl_2) afforded a light blue band (non-porphyrin species), and then elution with CH_2Cl_2/ethyl acetate (98:2) gave the desired porphyrin as a slow-moving green band. Removal of the solvent and washing the residue with ethanol afforded a black-purple solid (130 mg, 14%): ^{1}H NMR δ 9.21 (d, $J = 4.2$ Hz, 1H), 9.14 (d, $J = 4.2$ Hz, 1H), 8.91 (d, $J = 5.1$ Hz, 1H), 8.84 (d, $J = 4.2$ Hz, 1H), 8.64 (d, $J = 4.5$ Hz, 1H), 8.57 (s, 2H), 8.50 (d, $J = 4.2$ Hz, 1H), 8.10−8.03 (m, 8H), 7.90 (dd, $J^1 = 8.1$ Hz, $J^2 = 1.5$ Hz, 4H), 7.55 (d, $J = 7.2$ Hz, 4H), 2.70 (s, 3H), 2.69 (s, 3H); LD-MS obsd 896.5; FAB-MS obsd 896.0650, calcd 896.0635 ($C_{46}H_{31}I_2N_3O$); λ_{abs}, 423, 509, 541, 613, 673 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 679, 750 nm.

5,15-Bis{4-[2-(4-pyridyl)ethynyl]phenyl}-10,20-di-*p*-tolyl-23*H*-21-oxaporphyrin (21). Following a standard method for Pd-mediated coupling,[48] samples of N_3O-porphyrin **20** (90.0 mg, 0.10 mmol), 4-ethynylpyridine **6** (41.6 mg, 0.40 mmol), $Pd_2(dba)_3$ (55.1 mg, 0.060 mmol), and $P(o\text{-tol})_3$ (146.2 mg, 0.48 mmol) were added to a 50 mL Schlenk flask. The flask was evacuated and purged with argon three times, taking care to avoid the loss of 4-ethynylpyridine by vacuum sublimation. Degassed toluene/triethylamine (24 mL, 5:1) was added, and the mixture was stirred at 35 °C. The reaction was followed by LD-MS and TLC analysis [alumina, $CHCl_3$/methanol (98:2)]. After 4 h, the starting porphyrin had been consumed. Chromatography [basic alumina, Brockman activity I, packed with $CHCl_3$; eluted with $CHCl_3$/ethyl acetate (98:2)] gave a trace of the mono-coupled byproduct (confirmed by LD-MS analysis), followed by the desired product as the second band. The solvent was removed, and the residue was placed on top of a cotton plug in a Pasteur pipet. After washing with methanol, the purple material on top of the cotton plug was dissolved in $CHCl_3$, concentrated and dried, affording a purple solid (30.2 mg, 36%): ^{1}H NMR δ 9.24 (d, $J = 4.2$ Hz, 1H), 9.16 (d, $J = 5.1$ Hz, 1H), 8.93 (d, $J = 5.1$ Hz, 1H), 8.86 (d, $J = 4.5$ Hz, 1H), 8.69 (d, $J = 6.0$ Hz, 4H), 8.66 (d, $J = 4.2$ Hz, 1H), 8.60 (s, 2H), 8.52 (d, $J = 4.5$ Hz, 1H), 8.21 (d, $J = 8.1$ Hz, 4H), 8.06 (d, $J = 6.6$ Hz, 4H), 7.96−7.93 (m, 4H), 7.57−7.52 (m, 8H), 2.71 (s, 3H), 2.70 (s, 3H); LD-MS obsd 847.6; FAB-MS obsd 846.3248, calcd 846.3233 ($C_{60}H_{39}N_5O$); λ_{abs} (log ϵ), 425 (5.47), 510 (4.44), 542 (3.90), 616 (3.52), 675 (3.71) nm; λ_{em} ($\lambda_{ex} = 510$ nm) 680, 751 nm ($\Phi_f = 0.060$).

ZnFbZn-*m*/*m*-CCTMS. Following the refined Pd-coupling procedure for the preparation of multiporphyrin arrays,[48] samples of **3** (243 mg, 0.32 mmol), **Zn-16a** (640 mg, 0.65 mmol), $Pd_2(dba)_3$ (90 mg, 0.098 mmol), and $P(o\text{-tol})_3$ (241 mg, 0.78 mmol) were weighed into a 250 mL Schlenk flask which was then pump-purged three times with argon. Toluene/triethylamine (132 mL, 5:1) was added, and the flask was stirred at 35 °C. Monitoring by analytical SEC and LD-MS showed the reaction had leveled off after 7 h. The solvent was removed, and the residue was chromatographed [silica, hexanes/$CHCl_3$ (1:2)] affording unreacted porphyrin monomers followed by a mixture of mono-coupled dimer, desired trimer and high molecular weight materials (HMWM). The mixture of porphyrins was concentrated to dryness, dissolved in 20 mL of THF, and chromatographed in two equal portions (SEC, THF). Gravity elution afforded four major components (in order of elution): HMWM, desired trimer, mono-coupled byproduct (dimer, LD-MS obsd *m*/*z* at 1604.5, calcd 1604.0 for $C_{109}H_{88}N_8SiZn$) and unreacted monomeric porphyrins. The trimer-containing fractions were combined and chromatographed [silica, hexanes/$CHCl_3$ (1:1)], affording the title compound as a purple solid (373 mg, 47%). Similar purification of the dimer fraction gave the byproduct dimer as a purple solid (33 mg, 6%). Data for the title compound: ^{1}H NMR δ 8.97 (d, $J = 4.5$ Hz, 4H), 8.85−8.83 (m, 8H), 8.80−8.78 (m, 8H), 8.68 (d, $J = 4.5$ Hz, 4H), 8.56 (d, $J = 5.5$ Hz, 2H), 8.35 (d, $J = 7.0$ Hz, 2H), 8.27−8.26 (m, 2H), 8.20−8.17 (m, 2H), 8.08 (d, $J = 7.8$ Hz, 2H), 7.93 (d, $J = 8.1$ Hz, 4H), 7.88 (d, $J = 8.1$ Hz, 2H), 7.80 (m, 2H), 7.68 (m, 2H), 7.30 (s, 12H), 2.64 (s, 12H), 2.60 (s, 6H), 1.85 (s, 24H), 1.80 (s, 12H), 0.25 (s, 18H), −2.65 (s, br, 2H); LD-MS obsd 2459.6; calcd avg mass 2459.9 ($C_{164}H_{134}N_{12}Si_2Zn_2$); λ_{abs} 423, 514, 550, 589, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 653, 720 nm. Data for the dimer (byproduct): ^{1}H NMR δ 8.96 (d, $J = 4.7$ Hz, 2H), 8.84−8.82 (m, 4H), 8.80−8.78 (m, 4H), 8.76 (d, $J = 4.5$ Hz, 2H), 8.69 (d, $J = 4.7$ Hz, 4H), 8.56 (d, $J = 6.0$ Hz, 1H), 8.36 (d, $J = 6.0$ Hz, 1H), 8.28−8.25 (m, 1H), 8.20 (d, $J = 8.1$ Hz, 2H), 8.18 (d, $J = 7.9$ Hz, 2H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.94 (d, $J = 7.9$ Hz, 2H), 7.89−7.86 (m, 4H), 7.80 (m, 1H), 7.67 (m, 1H), 7.30 (s, 4H), 7.26 (s, 4H), 3.30 (s, 1H), 2.64 (s, 6H), 2.61 (s, 6H), 1.86 (s, 12H), 1.82 (s, 12H), 0.26 (s, 9H), −2.65 (s, br, 2H); LD-MS obsd 1602.6; FAB-MS obsd 1600.63, calcd 1600.62 ($C_{109}H_{88}N_8SiZn$); λ_{abs} 421, 515, 549, 592, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 652, 720 nm.

ZnFbZn-*m*/*m*-CCH. A solution of **ZnFbZn-*m*/*m*-CCTMS** (370 mg, 0.15 mmol) in $CHCl_3$/THF (44 mL, 10:1) was treated with TBAF on silica gel (1.20 g, 1.0−1.5 mmol F^-/g resin), and the mixture was stirred at room temperature. After 2 h, LD-MS and TLC analysis [silica, $CHCl_3$/hexanes (1:1)] showed the deprotection was complete. The reaction mixture was washed with water and dried (Na_2SO_4), and the solvent was removed. Chromatography (silica, $CHCl_3$/hexanes 1:1) afforded a purple solid, which was washed (by sonication) with methanol, filtered, and dried, affording a purple solid (312 mg, 90%): ^{1}H NMR δ 8.96 (d, $J = 4.5$ Hz, 4H), 8.86−8.83 (m, 8H), 8.80−8.78 (m, 8H), 8.68 (d, $J = 4.5$ Hz, 4H), 8.56 (s, 2H), 8.38 (d, $J = 7.0$ Hz, 2H), 8.28 (d, $J = 7.0$ Hz, 2H), 8.23 (t, $J = 7.0$ Hz, 2H), 8.19 (d, $J = 8.1$ Hz, 4H), 8.08 (d, $J = 7.8$ Hz, 2H), 7.93 (d, $J = 8.1$ Hz, 4H), 7.90 (d, $J = 7.8$ Hz, 2H), 7.81 (m, 2H), 7.71 (m, 2H), 7.30 (s, 8H), 7.25 (s, 4H), 3.15 (s, 2H), 2.65 (s, 12H), 2.60 (s, 6H), 1.85 (s, 24H), 1.80 (s, 12H), −2.65 (s, br, 2H); LD-MS obsd 2315.8; FAB-MS obsd 2314.85, calcd 2314.82 ($C_{158}H_{118}N_{12}Zn_2$); λ_{abs} 421, 515, 549, 592, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 652, 720 nm.

Zn$_3$-*m*/*m*-CCH. A solution of **ZnFbZn-*m*/*m*-CCH** (119 mg, 0.051 mmol) in $CHCl_3$ (10 mL) was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (56.0 mg, 0.26 mmol) in methanol (0.5 mL) overnight at room temperature. Standard workup and chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a purple solid (110 mg, 91%): ^{1}H NMR δ 8.97 (d, $J = 5.1$ Hz, 4H), 8.88−8.83 (m, 12H), 8.80 (d, $J = 5.4$ Hz, 4H), 8.76 (d, $J = 5.4$ Hz, 4H), 8.57 (m, 2H), 8.39−8.37 (m, 2H), 8.27 (d, $J = 8.7$ Hz, 4H), 8.20 (d, $J = 8.1$ Hz, 4H), 8.08 (d, $J = 8.1$ Hz, 2H), 7.95−7.89 (m, 6H), 7.81 (m, 2H), 7.71 (m, 2H), 7.30 (s, 12H), 3.14 (s, 2H), 2.64 (s, 12H), 2.60 (s, 6H), 1.85 (s, 24H), 1.79 (s, 12H); LD-MS obsd 2376.8, calcd avg mass 2378.9 ($C_{158}H_{116}N_{12}Zn_3$); λ_{abs} 422, 550, 590 nm, λ_{em} ($\lambda_{ex} = 550$ nm) 603, 650 nm.

Zn$_2$FbZn$_2$-*p*/*p*-CCTMS. Following the procedure described for the preparation of **ZnFbZn-*m*/*m*-CCTMS**, samples of **ZnFbZn-*m*/*m*-CCH** (280 mg, 0.12 mmol) and **Zn-16b** (238 mg, 0.24 mmol) were coupled using $Pd_2(dba)_3$ (34 mg, 0.037 mmol) and $P(o\text{-tol})_3$ (91.2 mg, 0.30 mmol) in toluene/triethylamine (48 mL, 5:1) at 35 °C under argon. Analytical SEC and LD-MS analysis showed a leveling off of the pentamer yield after 5 h. Chromatography (silica, $CHCl_3$) removed the Pd species and afforded a mixture of porphyrins. Further chromatography in two equal portions (SEC, THF) afforded four major components (in order of elution): HMWM, the desired pentamer, a trace amount of mono-coupled byproduct (tetramer LD-MS obsd at 3176.5, calcd for $C_{213}H_{164}N_{16}SiZn_3$ $m/z = 3171.9$) and unreacted monomeric porphyrins. The pentamer-containing fractions were combined and chromatographed [silica, hexanes/$CHCl_3$ (1:2)], affording a purple solid (201 mg, 41%): ^{1}H NMR δ 8.98−8.97 (m, 8H), 8.88−8.82 (m, 16H), 8.80−8.75 (m, 12H), 8.69−8.66 (m, 4H), 8.58 (d, $J = 6.5$ Hz, 4H), 8.30−8.28 (m, 4H), 8.23−8.15 (m, 12H), 8.09 (d, $J = 7.5$ Hz, 4H), 7.95−7.93 (m, 8H), 7.86−7.80 (m, 8H), 7.32 (s, 8H), 7.27−7.24 (m, 12H), 2.66 (s, 12H), 2.62 (s, 12H), 2.61 (s, 6H), 1.89 (s, 24H), 1.82 (s, 24H), 1.80 (s, 12H), 0.37 (s, 18H), −2.66 (s, br, 2H); LD-MS obsd 4023.4; calcd avg mass 4028.4 ($C_{268}H_{210}N_{20}Si_2Zn_4$); λ_{abs} 422 (br), 515, 550, 592, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 599, 653, 720 nm

Zn$_2$FbZn$_2$-*p*/*p*-CCH. Following the procedure described for the synthesis of **ZnFbZn-*m*/*m*-CCH**, a mixture of **Zn$_2$FbZn$_2$-*p*/*p*-CCTMS** (201 mg, 0.050 mmol) and TBAF on silica gel (400 mg, 1.0−1.5 mmol F^-/g resin) in $CHCl_3$/THF (33 mL, 10:1) was stirred at room temperature for 2 h. The standard workup followed by chromatography [silica, $CHCl_3$/hexanes (1:1)] gave a purple solid, which was washed (sonicated) with methanol, filtered, and dried, affording a purple solid (166 mg, 85%): ^{1}H NMR δ 9.00−8.97 (m, 8H), 8.90−8.83 (m, 16H), 8.79−8.76 (m, 12H), 8.70−8.66 (m, 4H), 8.59−8.57 (m, 4H), 8.30−8.28 (m, 4H), 8.24−8.17 (m, 12H), 8.10 (d, $J = 7.5$ Hz, 4H), 7.94 (d, $J = 7.2$ Hz, 8H), 7.88−7.80 (m, 8H), 7.32 (s, 8H), 7.27−7.25 (m, 12H), 3.30 (s, 2H), 2.66 (s, 12H), 2.62 (s, 12H), 2.60 (s, 6H), 1.88 (s, 24H), 1.81 (s, 24H), 1.80 (s, 12H), −2.66 (s, br, 2H); LD-MS obsd 3882.5; calcd avg mass 3884.0 ($C_{262}H_{194}N_{20}Zn_4$); λ_{abs} 422 (br), 516, 551, 592, 649 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 600, 653, 721 nm.

Zn$_5$-*p*/*p*-CCH. A solution of **Zn$_2$FbZn$_2$-*p*/*p*-CCH** (66.2 mg, 17.0 μmol) in $CHCl_3$ (10 mL) was treated with a solution of

$Zn(OAc)_2 \cdot 2H_2O$ (37.3 mg, 170 μmol) in methanol (0.5 mL), and the mixture was stirred overnight at room temperature under argon. The reaction mixture was diluted with $CHCl_3$, washed with 10% aqueous $NaHCO_3$, H_2O, dried (Na_2SO_4), filtered, and concentrated to give a purple solid (63.7 mg, 95%): ^{1}H NMR δ 8.98 (d, $J = 5.4$ Hz, 8H), 8.89−8.82 (m, 20H), 8.78−8.74 (m, 12H), 8.58 (d, $J = 5.1$ Hz, 4H), 8.28−8.27 (m, 4H), 8.22−8.16 (m, 12H), 8.09 (d, $J = 7.8$ Hz, 4H), 7.94 (d, $J = 7.5$ Hz, 8H), 7.88-7.79 (m, 8H), 7.32 (s, 8H), 7.25 (s, 12H), 3.29 (s, 2H), 2.65 (s, 12H), 2.62 (s, 12H), 2.60 (s, 6H), 1.88 (s, 24H), 1.80 (s, 24H), 1.79 (s, 12H); LD-MS obsd 3946.1; calcd avg mass 3947.4 ($C_{262}H_{192}N_{20}Zn_5$); λ_{abs} 424, 432 (br), 551, 592 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 599, 646 nm.

***Cyclo*-Zn$_5$FbU via the 5 + 1 Route.** Samples of **Zn$_5$-*p/p*-CCH** (63.7 mg, 16.1 μmol), **4** (18.4 mg, 19.4 μmol), tripyridyl template **1** (9.8 mg, 16.1 μmol), $Pd_2(dba)_3$ (4.5 mg, 4.8 μmol), and P(*o*-tol)$_3$ (11.8 mg, 38.6 μmol) were added to a 25 mL Schlenk flask. The flask was evacuated and purged with argon three times, and then deaerated toluene/triethylamine (9 mL, 5:1) was added. The flask was immersed in an oil bath at 35 °C. The reaction was followed by analytical SEC and found to be complete after 2.5 h. Chromatography (silica, $CHCl_3$) removed the Pd species and the tripyridyl template, affording a mixture of the monomeric porphyrin, the desired hexamer, and HMWM as the first band. Further chromatography (SEC, 5 × 65 cm, THF) afforded the desired hexamer as the second band contaminated with HMWM. Four repetitive chromatography (SEC, THF) runs afforded fractions containing the pure hexamer, which were combined and chromatographed [silica, $CHCl_3$/hexanes (2:1)]. The hexamer fraction was collected, and the solvent was removed. The residue was placed on top of a cotton plug in a Pasteur pipet and washed with methanol. The purple material on top of the cotton plug was dissolved in $CHCl_3$, concentrated, and dried, affording a purple solid (9.8 mg, 13%): ^{1}H NMR δ 8.97 (d, $J = 4.5$ Hz, 8H), 8.88 (d, $J = 5.1$ Hz, 4H), 8.84 (d, $J = 5.1$ Hz, 20H), 8.76 (d, $J = 5.1$ Hz, 4H), 8.73 (d, $J = 5.1$ Hz, 12H), 8.53−8.50 (m, 4H), 8.32 (d, $J = 7.5$ Hz, 6H), 8.18 (d, $J = 8.7$ Hz, 12H), 8.08 (d, $J = 7.5$ Hz, 6H), 7.91 (d, $J = 7.8$ Hz, 12H), 7.82 (m, 8H), 7.31 (s, br, 12H), 7.22 (s, br, 12H), 2.65 (s, br, 12H), 2.58 (s, 24H), 1.88 (s, 12H), 1.86 (s, 12H), 1.76 (s, 48H), −2.61 (s, br, 2H); LD-MS obsd 4645.4, calcd avg mass 4642.3 ($C_{312}H_{230}N_{24}Zn_5$); λ_{abs} (log ϵ) 428 (6.45), 512 (4.71), 550 (5.23), 591 (4.47), 649 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 599, 651, 719 nm ($\Phi_f = 0.085$).

ZnFbZn-*p/p*-Br. Following the procedure for the first step in the successive iodo/bromo coupling approach,[51] samples of **Zn-16c** (493 mg, 0.51 mmol) and **12** (174 mg, 0.23 mmol) were coupled using $Pd_2(dba)_3$ (63 mg, 0.069 mmol) and P(*o*-tol)$_3$ (168 mg, 0.55 mmol) in toluene/triethylamine (96 mL, 5:1) at room temperature under argon. Analytical SEC and LD-MS analysis showed the reaction was complete after 3 h. Standard workup and chromatography (silica, $CHCl_3$) afforded a mixture of porphyrins. Further purification by chromatography (preparative SEC, THF) afforded four major bands (in order of elution): HMWM, desired trimer, mono-coupled byproduct (dimer) and monomeric species. The trimer-containing fraction was chromatographed [silica, $CHCl_3$/hexanes (3:1)], affording a purple solid (195 mg, 35%): ^{1}H NMR δ 8.93 (d, $J = 4.5$ Hz, 4H), 8.91 (d, $J = 2.7$ Hz, 2H), 8.89 (d, $J = 2.7$ Hz, 2H), 8.86 (d, $J = 2.7$ Hz, 2H), 8.85 (d, $J = 2.7$ Hz, 2H), 8.81−8.78 (m, 2H), 8.60−8.58 (m, 2H), 8.34−8.28 (m, 2H), 8.26 (d, $J = 2.4$ Hz, 2H), 8.23 (d, $J = 2.4$ Hz, 2H), 8.13−8.09 (m, 6H), 7.97 (dd, $J^1 = 1.5$ Hz, $J^2 = 8.1$ Hz, 4H), 7.88 (dd, $J^1 = 2.4$ Hz, $J^2 = 7.8$ Hz, 4H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.34 (s, 4H), 7.29 (s, 4H), 7.28 (s, 4H), 2.68 (s, 6H), 2.64 (s, 6H), 2.63 (s, 6H), 1.91 (s, 12H), 1.83 (s, 12H), 1.82 (s, 12H), −2.54 (s, br, 2H); LD-MS obsd 2420.5, calcd avg mass 2425.2 ($C_{154}H_{116}Br_2N_{12}Zn_2$); λ_{abs} 423, 515, 550, 591, 649 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 601 (w), 649, 718 nm.

***Cyclo*-Zn$_5$FbU via the 3 + 3 Route.** Following the procedure for the second step in the successive iodo/bromo coupling approach,[51] samples of **Zn$_3$-*m/m*-CCH** (35.7 mg, 0.015 mmol) and **ZnFbZn-*p/p*-Br** (40.0 mg, 0.016 mmol) were coupled using $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol), P(*o*-tol)$_3$ (10.9 mg, 0.036 mmol), and template **1** (9.2 mg, 0.015 mmol) in toluene/triethylamine (9.0 mL, 5:1) at 80 °C under argon. Analytical SEC and LD-MS analysis showed the reaction was complete after 2 h. The reaction mixture was loaded directly on a short SEC column (THF), and all the porphyrin-containing fractions were collected. Chromatography (silica, $CHCl_3$) gave a porphyrin mixture, which was purified by preparative SEC (THF), removing most of the HMWM. Repetitive preparative SEC (three columns) gave a purple solid. Final chromatography [silica, $CHCl_3$/hexanes (4:1)] and washing with methanol gave a purple solid (9.5 mg, 13.6%). LD-MS, ^{1}H NMR, UV−vis, and fluorescence spectral data were identical with those obtained by the 5 + 1 route.

ZnFbZn-*p/p*-CCTMS. Following the procedure described for the preparation of **ZnFbZn-*m/m*-CCTMS**, samples of porphyrin **12** (187 mg, 0.25 mmol) and **Zn-16b** (512 mg, 0.52 mmol) were coupled using $Pd_2(dba)_3$ (75 mg, 0.082 mmol) and P(*o*-tol)$_3$ (201 mg, 0.66 mmol) in toluene/triethylamine (110 mL, 5:1) at 35 °C under argon for 5 h. The standard workup and chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a mixture of porphyrins, which was purified by SEC in two equal portions (THF), affording four major bands (in order of elution): HMWM, desired trimer, mono-coupled byproduct (dimer), and unreacted monomeric porphyrins. The trimer-containing fractions were combined and chromatographed [silica, hexanes/$CHCl_3$ (1:2)], affording the desired trimer as a purple solid (220 mg, 36%). The same purification gave byproduct (dimer) as a purple solid (15 mg, 3.7%). Data for the title compound: ^{1}H NMR δ 8.92−8.87 (m, 8H), 8.85−8.82 (m, 4H), 8.79−8.78 (m, 12H), 8.58−8.56 (d, $J = 6.5$ Hz, 2H), 8.29−8.25 (m, 2H), 8.24 (d, $J = 6.6$ Hz, 4H), 8.17 (d, $J = 6.6$ Hz, 4H), 8.10 (d, $J = 7.5$ Hz, 2H), 7.96 (dd, $J^1 = 6.6$ Hz, $J^2 = 2.6$ Hz, 4H), 7.86−7.83 (m, 6H), 7.33 (s, 4H), 7.27 (s, 8H), 2.66 (s, 6H), 2.62 (s, 6H), 2.61 (s, 6H), 1.90 (s, 12H), 1.81 (s, 12H), 1.80 (s, 12H), 0.37 (s, 18H), −2.57 (s, br, 2H); LD-MS obsd 2452.8, calcd avg mass 2459.9 ($C_{164}H_{134}N_{12}Si_2Zn_2$); λ_{abs} 428, 515, 551, 593, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 600, 649, 718 nm. Data for byproduct (dimer): ^{1}H NMR δ 8.87 (d, $J = 4.5$ Hz, 4H), 8.82 (d, $J = 4.5$ Hz, 2H), 8.77−8.73 (m, 8H), 8.65 (m, 4H), 8.54 (m, 1H), 8.22 (d, $J = 8.1$ Hz, 4H), 8.17 (d, $J = 8.1$ Hz, 2H), 8.09 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 2H), 7.84 (d, $J = 8.1$, 2H), 7.80 (m, 1H), 7.30 (s, 4H), 7.27 (m, 6H), 2.64 (s, 6H), 2.62 (s, 6H), 1.87 (s, 12H), 1.81 (s, 12H), 0.37 (s, 9H), −2.54 (s, 2H); LD-MS obsd 1613.7; FAB-MS obsd 1618.67 calcd 1618.63 ($C_{109}H_{88}N_8SiZn$); λ_{abs} 427, 515, 553, 595, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 604, 649, 719 nm.

ZnFbZn-*p/p*-CCH. A solution of **ZnFbZn-*p/p*-CCTMS** (220 mg, 0.089 mmol) in THF/$CHCl_3$ (12 mL, 1:1) was treated with TBAF (270 μL, 0.27 mmol, 1.0 M in THF) for 30 min at room temperature. The solvent was removed, and the resulting residue was dissolved in $CHCl_3$ (20 mL), washed with 10% aqueous $NaHCO_3$, and dried (Na_2SO_4). Chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a purple solid (163 mg, 80%): ^{1}H NMR δ 8.92−8.87 (m, 8H), 8.86−8.84 (m, 4H), 8.79−8.76 (m, 12H), 8.57 (d, $J = 6.6$ Hz, 2H), 8.29−8.17 (m, 10H), 8.10 (d, $J = 8.1$ Hz, 2H), 7.96 (dd, $J^1 = 6.6$ Hz, $J^2 = 2.6$ Hz, 4H), 7.86 (dd, $J^1 = 8.1$ Hz, $J^2 = 2.6$ Hz, 4H), 7.81 (d, $J = 7.8$ Hz, 2H), 7.32 (s, 4H), 7.27 (s, 8H), 3.30 (s, 2H), 2.66 (s, 6H), 2.62 (s, 6H), 2.61 (s, 6H), 1.90 (s, 12H), 1.81 (s, 12H), 1.80 (s, 12H), −2.57 (s, br, 2H); LD-MS obsd 2317.0; FAB-MS obsd 2314.85, calcd 2314.82 ($C_{158}H_{118}N_{12}Zn_2$); λ_{abs} 428, 515, 556, 597, 648 nm; λ_{em} ($\lambda_{ex} = 550$ nm) 604, 649, 717 nm.

Zn$_2$FbZn$_2$-*m/m*-CCTMS. Following the procedure described for the preparation of **ZnFbZn-*p/p*-CCTMS**, samples of **ZnFbZn-*p/p*-CCH** (160 mg, 0.069 mmol) and **Zn-16a** (143 mg, 0.14 mmol) were coupled using $Pd_2(dba)_3$ (21 mg, 0.022 mmol) and P(*o*-tol)$_3$ (56 mg, 0. 18 mmol) in toluene/triethylamine (28 mL, 5:1) for 3 h at 35 °C under argon. The standard workup and chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a mixture of porphyrins, which was purified by SEC in two equal portions (THF), affording four major bands (in order of elution): HMWM, desired pentamer, mono-coupled byproduct (tetramer), and unreacted monomeric porphyrins. The pentamer-containing fractions were combined and chromatographed [silica, hexanes/$CHCl_3$ (1:2)], affording the desired pentamer as a purple solid (142 mg, 51%): ^{1}H NMR δ 8.97 (d,

J = 5.1 Hz, 4H), 8.91−8.83 (m, 20H), 8.80−8.75 (m, 16H), 8.56 (d, J = 6.5 Hz, 4H), 8.34 (d, J = 7.1 Hz, 2H), 8.29−8.17 (m, 14H), 8.09 (d, J = 7.2 Hz, 4H), 7.96−7.92 (m, 8H), 7.88 (d, J = 8.1 Hz, 2H), 7.84−7.78 (m, 4H), 7.67 (m, 2H), 7.32 (s, 4H), 7.30 (s, 6H), 7.25 (m, 10H), 2.64 (s, 18H), 2.61 (s, 6H), 2.60 (s, 6H), 1.89 (s, 12H), 1.85 (s, 24H), 1.80 (s, 12H), 0.26 (s, 18H), −2.58 (s, br, 2H); LD-MS obsd 4015.5, calcd avg mass 4028.4 ($C_{268}H_{210}N_{20}Si_2Zn_4$); λ_{abs} 425, 432, 514, 556, 596, 649 nm; λ_{em} (λ_{ex} = 550 nm) 603, 649, 718 nm.

Zn$_2$FbZn$_2$-*m/m*-CCH. Following the procedure described for the preparation of **ZnFbZn-*p/p*-CCH**, a solution of **Zn$_2$FbZn$_2$-*m/m*-CCTMS** (140 mg, 0.034 mmol) in THF/$CHCl_3$ (10 mL, 1:1) was treated with TBAF (87 μL, 0.087 mmol, 1.0 M/THF) for 30 min at room temperature. The solvent was removed, and the resulting residue was dissolved in $CHCl_3$ (20 mL); the latter was then washed with 10% aqueous $NaHCO_3$ and dried (Na_2SO_4). Chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a purple solid (112 mg, 85%): ^{1}H NMR δ 8.96 (d, J = 5.1 Hz, 4H), 8.90 (d, J = 5.1 Hz, 4H), 8.88−8.82 (m, 16H), 8.80−8.74 (m, 16H), 8.56 (m, 4H), 8.38 (d, J = 7.5 Hz, 2H), 8.29−8.20 (m, 14H), 8.11−8.08 (m, 4H), 7.95−7.89 (m, 10H), 7.84−7.79 (m, 4H), 7.70 (m, 2H), 7.32 (s, 4H), 7.30 (s, 4H), 7.25 (m, 12H), 3.15 (s, 2H), 2.64 (s, 18H), 2.61 (s, 6H), 2.60 (s, 6H), 1.89 (s, 12H), 1.85 (s, 24H), 1.80 (s, 12H), 1.79 (s, 12H), −2.58 (s, br, 2H); LD-MS obsd 3883.8, calcd avg mass 3884.0 ($C_{262}H_{194}N_{20}Zn_4$); λ_{abs} 425, 432, 516, 556, 597, 650 nm; λ_{em} (λ_{ex} = 550 nm) 605, 649, 717 nm.

***Cyclo*-Zn$_2$FbZn$_2$FbU.** Following the general procedure described for the preparation of ***cyclo*-Zn$_5$FbU** via the 5 + 1 route, samples of **Zn$_2$FbZn$_2$-*m/m*-CCH** (67.6 mg, 0.017 mmol), **Mg-17** (18.2 mg, 0.019 mmol) and template **1** (10.4 mg, 0.017 mmol) were coupled using $Pd_2(dba)_3$ (4.8 mg, 5.2 μmol) and P(*o*-tol)$_3$ (12.4 mg, 0.041 mmol) in toluene/triethylamine (9.6 mL, 5:1) at 35 °C under argon for 1.5 h. LD-MS analysis of this crude reaction mixture showed an intense peak corresponding to the desired hexamer ***cyclo*-Zn$_2$FbZn$_2$MgU** at m/z = 4602.9 (calcd avg mass 4601.2 for $C_{312}H_{230}MgN_{24}Zn_4$). The solvent was removed, the residue was dissolved in $CHCl_3$ (80 mL), and silica gel (Fisher, 200−425 mesh, 20 g) was added to demetalate the Mg porphyrin. The mixture was stirred at room temperature for 2 days. The mixture was then filtered through a pad of silica gel, and the porphyrin species were collected and concentrated. Chromatography (silica, $CHCl_3$) afforded a mixture of porphyrins (monomeric porphyrin, the desired hexamer, and HMWM). Chromatography (SEC, THF) afforded the desired demagnesiated hexamer as the second band contaminated with HMWM. Repetitive chromatography (SEC, THF) afforded fractions containing the pure hexamer, which were combined and chromatographed [silica, $CHCl_3$/hexanes (4:1)], affording a purple solid, which was precipitated from $CHCl_3$/methanol (7.8 mg, 10%): ^{1}H NMR δ 8.97 (d, J = 4.5 Hz, 4H), 8.91−8.83 (m, 20H), 8.81−8.75 (m, 20H), 8.70 (d, J = 7.8 Hz, 4H), 8.56 (m, 4H), 8.39−8.37 (m, 2H), 8.29−8.20 (m, 16H), 8.07 (d, J = 8.1 Hz, 6H), 7.96−7.89 (m, 12H), 7.81 (m, 4H), 7.71 (m, 4H), 7.31, 7.30, 7.28 (three s, 24H), 2.63, 2.61, 2.60, 2.59 (four s, 36H), 1.89, 1.85, 1.82, 1.79 (four s, 72H), −2.58 (s br, 2H), −2.69 (s br, 2H); LD-MS obsd 4572.0, calcd avg mass 4578.9 ($C_{312}H_{232}N_{24}Zn_4$); λ_{abs} (log ϵ) 428 (6.37), 515 (5.02), 550 (5.29), 591 (4.97), 647 (4.01); λ_{em} (λ_{ex} = 550 nm) 600, 650, 718 nm (Φ_f = 0.098).

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Supporting Information Available: ^{1}H NMR spectra for all new compounds; ^{13}C NMR spectra for **5**−**8**, **13a**, **14a**, **14c**, **15a**, **15c**; LD-MS spectra for all porphyrins and porphyrin arrays; absorption and fluorescence spectra of cyclic hexamers; SEC traces of cyclic hexamers; a table comparing synthesis and purification methods in one-flask and stepwise syntheses; and structural diagrams for each scheme in which compounds are displayed as icons. This material is available free of charge via the Internet at http://pubs.acs.org.

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