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Synthesis of Cyclic Hexameric Porphyrin Arrays. Anchors for Surface Immobilization and Columnar Self-Assembly

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To investigate new architectures for the self-assembly of multiporphyrin arrays, a one-flask synthesis of a shape-persistent cyclic hexameric array of porphyrins was exploited to prepare six derivatives bearing diverse pendant groups. The new arrays contain 6−12 carboxylic acid groups, 12 amidino groups, 6 thiol groups, or 6 thiol groups and 6 carboxylic acid groups in protected form (*S*-acetylthio, TMS-ethyl, TMS-ethoxycarbonyl). The arrays contain alternating Zn and free base (Fb) porphyrins or all Zn porphyrins. The one-flask synthesis entails a template-directed, Pd-mediated coupling of a *p*/*p*′-substituted diethynyl Zn porphyrin and a *m*/*m*′-substituted diiodo Fb porphyrin. The porphyrin building blocks (*trans*-A_2B_2, *trans*-AB_2C) contain the protected pendant groups at nonlinking meso positions. A self-assembled monolayer (SAM) of a Zn_3Fb_3 cyclic hexamer containing one thiol group on each porphyrin was prepared on a gold electrode and the surface-immobilized architecture was examined electrochemically. Together, the work reported herein provides cyclic hexameric porphyrin arrays for studies of self-assembly in solution or on surfaces.

Introduction

A wide variety of multiporphyrin arrays have been prepared for studies related to biological and materials chemistry.[1−6] Cyclic architectures of porphyrins in defined 3-dimensional structures have been employed in diverse studies[7] and are members of a broader class of shape-persistent nanoscale molecular architectures that have elicited wide interest.[8] Anderson and Sanders pioneered the synthesis of cyclic arrays (primarily trimers and tetramers) of porphyrins joined by diphenylethyne or diphenylbutadiyne linkers and investigated their host−guest properties.[7,9] We extended this line of work to the synthesis of a cyclic hexameric porphyrin array comprised of alternating Zn porphyrins and free base (Fb) porphyrins joined via diphenylethyne linkers (Scheme 1).[10] This cyclic array is shape persistent with a cavity diameter of 30−35 Å. The cyclic hexamer was prepared by a one-flask reaction of a diethynyl zinc porphyrin (**Zn-2**) and a diiodo free base porphyrin (**3**) in the presence of a tripyridyl template (**4**). The cyclic hexamer also has been prepared in a stepwise manner where the template is used in the final reaction of components (pentamer + monomer, or trimer + trimer) to create the hexamer.[11] The template is essential for the one-flask synthesis and can be used to augment the stepwise synthesis. Regardless of approach, the template is displaced upon chromatographic workup of the reaction mixture. The cyclic hexamer (bearing mesityl groups at all nonlinking porphyrin meso-positions) is termed **Zn_3Fb_3-1a** (previously termed *cyclo*-Zn_3Fb_3U-*p*/*m*). The cyclic hexamer containing all Zn porphyrins (**Zn_6-1a**) is readily formed by metalation. Gossauer has prepared an even larger cyclic hexameric array incorporating arylethyne linkers.[12]

The primary motivation for preparing the cyclic hexamers was to study light-harvesting phenomena. The

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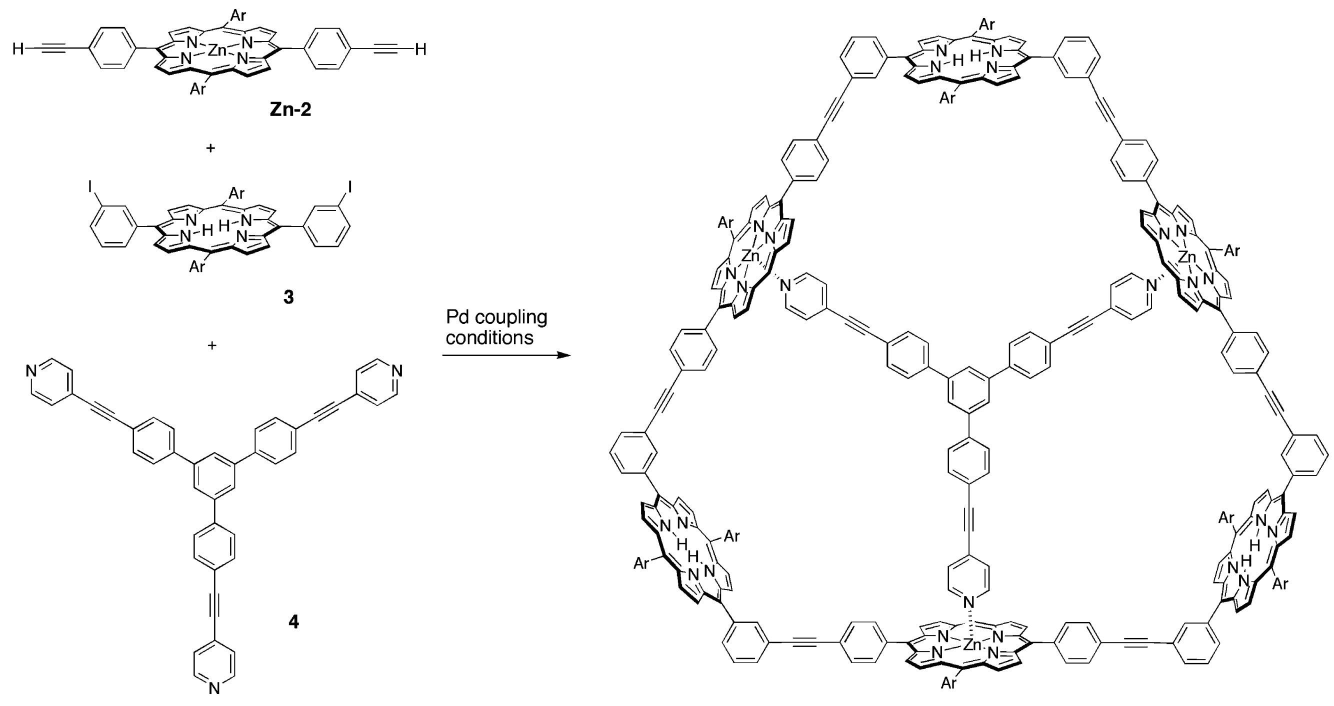
SCHEME 1. Cyclic Hexamer with the Bound Tripyridyl Template[a]



[a] Three nonlinking *meso*-aryl groups have been omitted for clarity.

tripyridyl template or a dipyridyl porphyrin can be bound as a guest in the cyclic hexameric host in a nearly quantitative manner at submicromolar concentrations ($K_{assoc} > 3 \times 10^8$ M^{-1}).[13] Photophysical studies of **Zn_3Fb_3-1a** characterized the energy-transfer dynamics from a Zn porphyrin to adjacent Fb porphyrins in the backbone of the wheel,[10] and from the porphyrins in the wheel to a dipyridyl-substituted Fb porphyrin bound in the cyclic hexamer in a wheel-and-spoke architecture.[13] The facile synthesis, shape-persistent architecture, avid host–guest binding phenomena, and efficient energy-transfer properties prompted consideration of applications for analogous cyclic hexamers in supramolecular and materials chemistry.

We felt that with appropriate derivatization, a cyclic hexamer would afford a corral-like architecture in a self-assembled monolayer (SAM) and that such a structure could be used as a baseplate or anchor for columnar self-assembly of cyclic hexamers yielding tubular structures. Encouragement for the latter notion was provided by preliminary X-ray scattering studies of **Zn_3Fb_3-1a** at high concentration in toluene, showing that at saturation the hexamer organizes into crystal-like arrays consistent with columnar stacking (Dr. David Tiede, unpublished data). Columnar or tubular structures constitute a characteristic motif in both biological and artificial systems.[14] The formation of SAMs occurs readily upon exposure of thiol-derivatized porphyrins to a gold substrate. A variety of porphyrin-containing compounds bearing free thiols[15–17] or *S*-acetylthio esters[16–21] have been prepared, as have porphyrin disulfides.[21,22] The *S*-acetylthio-derivatized compounds can be used in SAM formation as the ester undergoes cleavage upon exposure to the gold substrate, thereby obviating handling of free thiols.[17,23] To our knowledge, the largest multiporphyrin arrays that have been employed in the formation of SAMs contain three porphyrins anchored to the surface via two thio tethers.[20]

In this paper, we describe the design and synthesis of a family of cyclic hexamers bearing functional groups arrayed along the wheel. The functional groups (carboxylic acid, amidine, thiol) in protected form are incorporated in *trans*-AB$_2$C- and *trans*-A$_2$B$_2$-porphyrin building blocks.

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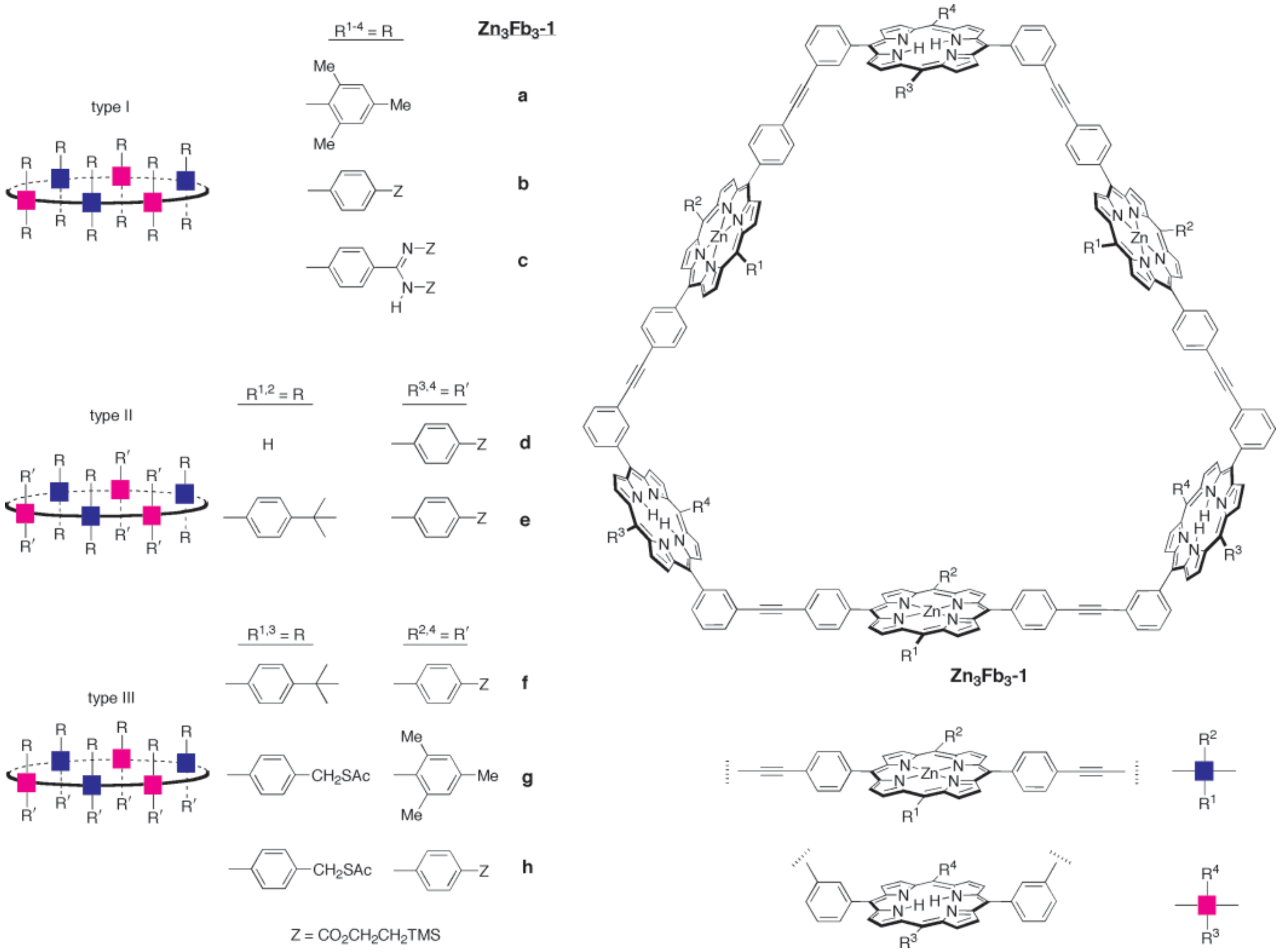
CHART 1



The porphyrins are used as substrates in the template-directed one-flask synthesis of cyclic hexamers. A cyclic hexamer bearing six thiol groups has been employed to form a SAM that has been characterized electrochemically. The examination of columnar architectures is beyond the scope of this paper and will be described elsewhere.

Results and Discussion

(1) Molecular Design. Cyclic hexamers with three distinct patterns of substituents were designed as shown in Chart 1. Each porphyrin possesses two nonlinking meso substituents. Because the cyclic hexamers are prepared by reaction of an R^1/R^2-diethynyl porphyrin and an R^3/R^4-diiodo-porphyrin, up to four distinct substituents can be introduced on the nonlinking meso-positions. In cyclic hexamers of type I, all nonlinking meso-substituents are identical ($R^{1-4} = R$). In type II, the two substituents on the diethynyl porphyrin are identical with one another (R^1, $R^2 = R$) and the two substituents on the diiodo porphyrin are identical with one another (R^3, $R^4 = R'$). In type III, the two porphyrins each bear the same two distinct substituents (R^1, $R^3 = R$; R^2, $R^4 = R'$). Note that the porphyrins can rotate about the diphenylethyne linker, enabling interchange of the groups that project

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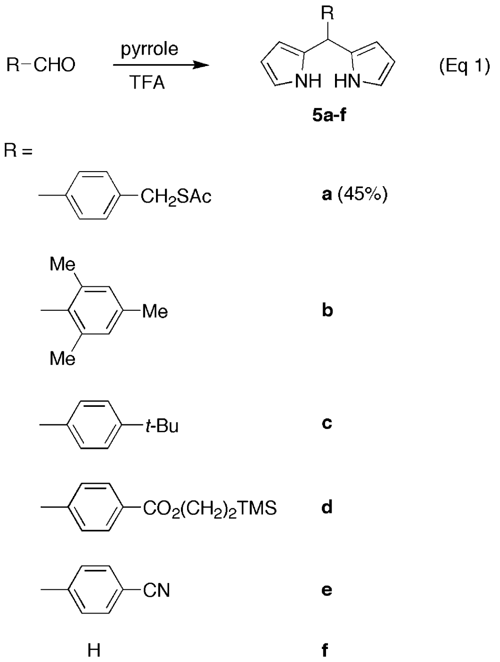
on each side of the array. Such rotation is inconsequential for types I and II, where a given porphyrin has two identical nonlinking substituents. In type III, each porphyrin has two distinct nonlinking substituents. Thus, the architecture displayed in Chart 1 for type III cyclic hexamers is only one possible accessible conformation.

The substituents of interest include groups that enable surface immobilization (thiol, carboxy, amidine) and possible columnar self-assembly (carboxy, amidine). The previous cyclic hexamer (**Zn$_3$Fb$_3$-1a**) employed mesityl groups at all nonlinking meso-positions. To determine the effects of lesser steric bulk, an aryl group lacking 2,6-dimethyl groups was employed (**Zn$_3$Fb$_3$-1b**). The designs of **Zn$_3$Fb$_3$-1d** and **Zn$_3$Fb$_3$-1e** (incorporating *meso*-H or *tert*-butylphenyl groups) also enable comparison of the effects of steric hindrance toward binding. The remaining cyclic hexamers contain one set of substituents for surface immobilization or binding (**Zn$_3$Fb$_3$-1d**−**g**) or two sets of substituents (**Zn$_3$Fb$_3$-1c**,**h**).

(2) Synthesis of Porphyrin Building Blocks. The cyclic hexamers of type I and II require *trans*-A$_2$B$_2$-porphyrins while type III requires *trans*-AB$_2$C-porphyrins. The rational synthesis of *trans*-A$_2$B$_2$-porphyrins is achieved by the reaction of a dipyrromethane + aldehyde or the self-condensation of a dipyrromethane-monocarbinol, while that of *trans*-AB$_2$C-porphyrins proceeds by the reaction of a dipyrromethane + dipyrromethane-dicarbinol. The protected forms of the carboxy, amidine, and thiol functional groups include the 2-(trimethylsilyl)ethyl ester, the bis[2-(trimethylsilyl)ethyl carbamate], and the *S*-acetylthio ester, respectively. Several monomeric porphyrins bearing amidino groups have been prepared, in which case protecting groups were not employed because further synthetic manipulations were not performed.[24]

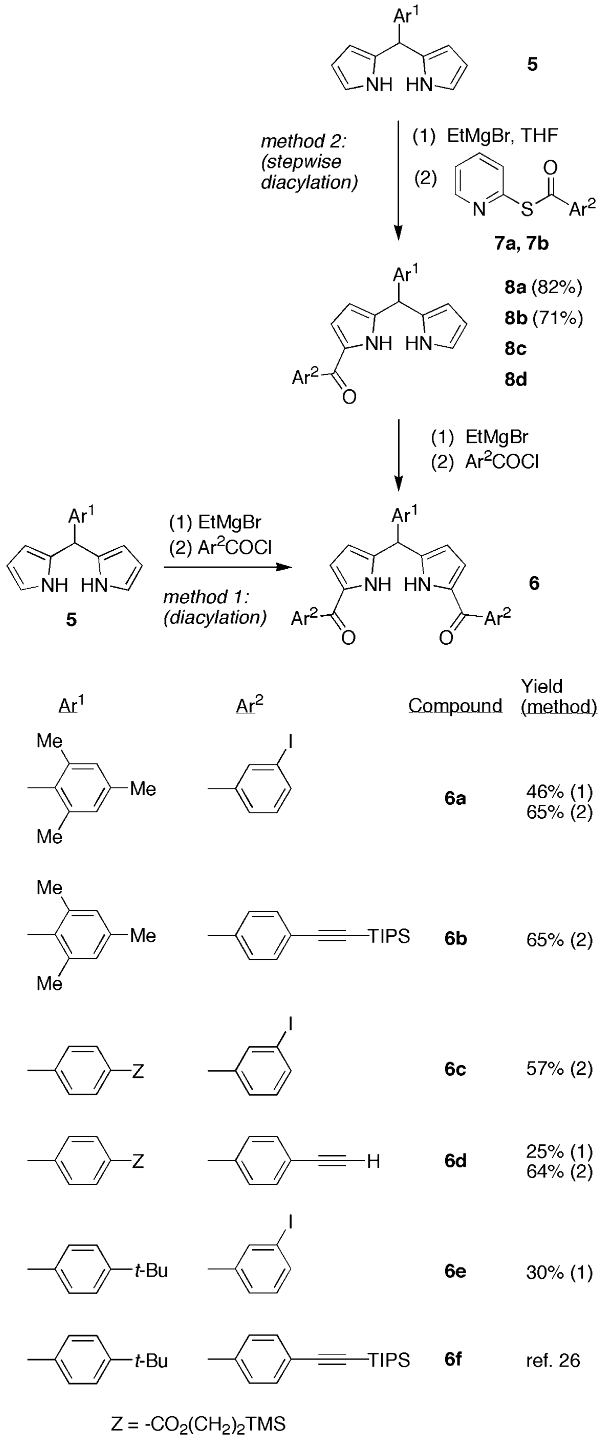
Dipyrromethane Precursors. The reaction of 4-(*S*-acetylthiomethyl)benzaldehyde[19] with excess pyrrole under TFA catalysis in a one-flask process[25] afforded dipyrromethane **5a** in 45% yield (eq 1). The known dipyrromethanes **5b**,[25] **5c**,[26,27] **5d**,[27] **5e**,[26] and **5f**[25] were prepared in the same manner.



(Eq 1)

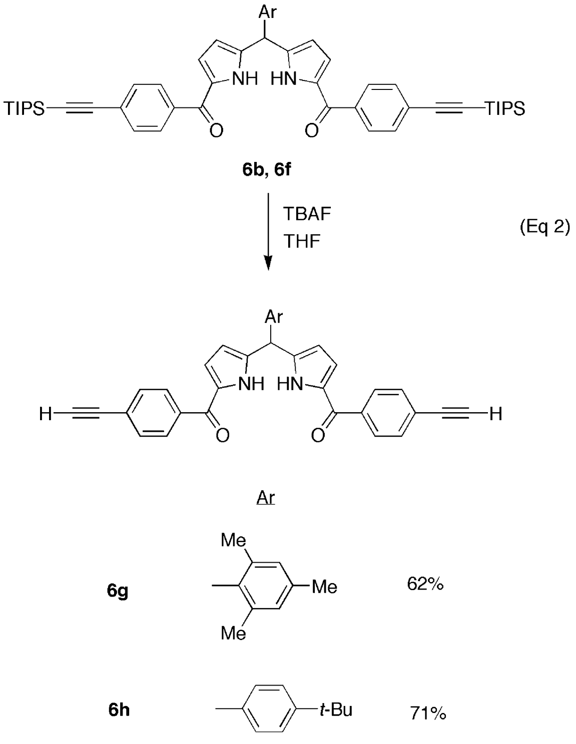
The introduction of acyl groups at the 1- and 9-positions of a dipyrromethane can be achieved in two ways: the direct diacylation of the dipyrromethane with identical substituents at the 1- and 9-positions in a one-flask process, or the stepwise acylation with two different substituents at the 1- and 9-positions (Scheme 2).[26] The direct diacylation method often affords a mixture of the diacyldipyrromethane and the monoacyldipyrromethane, which can be difficult to separate. The stepwise acylation method sometimes affords cleaner reactions than the

SCHEME 2

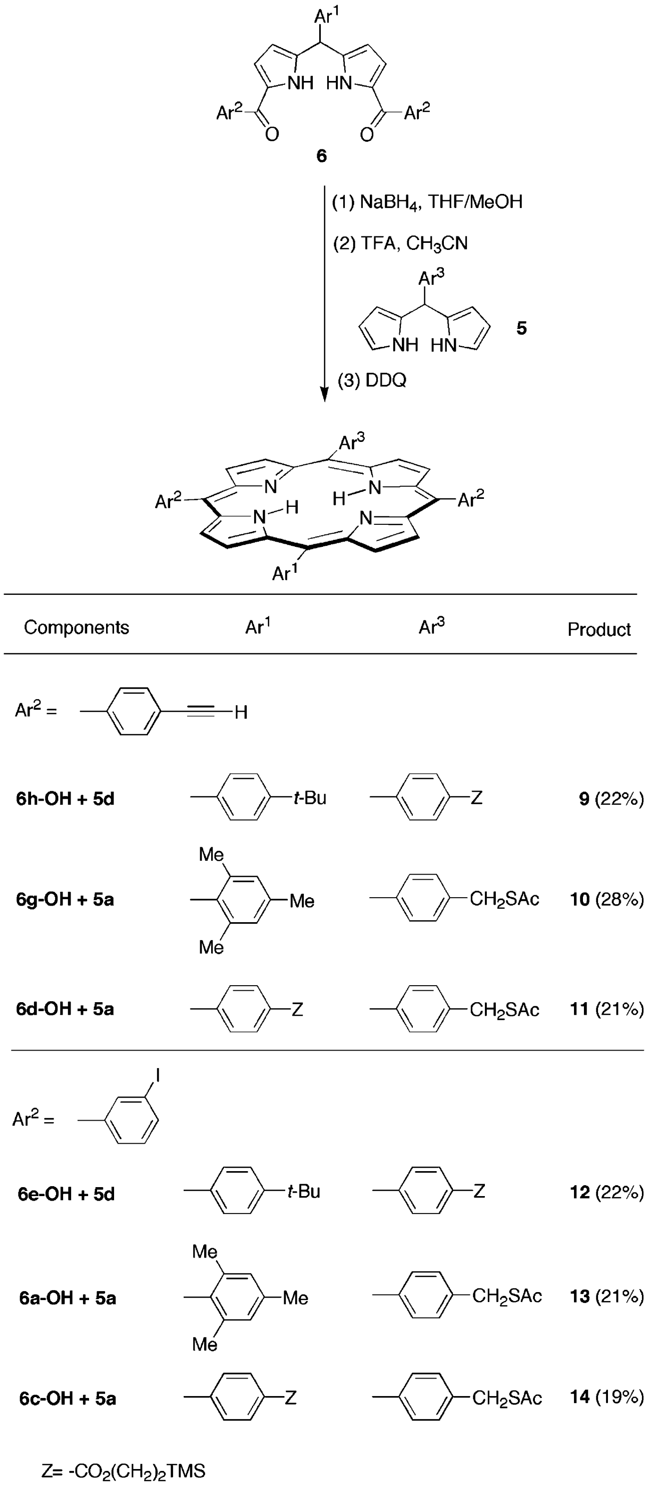


direct acylation method. While all diacyldipyrromethanes required herein incorporated the same acyl substituents at the 1- and 9-positions, we employed both the direct diacylation approach (method 1) and the stepwise acylation approach (method 2), the latter employing the same acyl component in both steps to obtain the requisite diacyldipyrromethanes. Thus, treatment of a dipyrromethane (**5**) with 5 equiv of EtMgBr in toluene followed by 2.5 equiv of the corresponding acid chloride produced a mixture of monoacyl and diacyldipyrromethanes, which was separated by column chromatography. In this manner (method 1), diacyldipyrromethanes **6a**, **6d**, **6e**, and **6f**[26] were obtained in modest yield.

Method 2 was applied in selected cases, requiring *S*-2-pyridyl benzothioates. *S*-2-Pyridyl 3-iodobenzothioate (**7a**) was made previously;[27] **7b** was prepared in 83% yield by reaction of 4-[2-(triisopropylsilyl)ethynyl]benzoyl chloride[26] and 2-mercaptopyridine. Thus, treatment of a dipyrromethane (**5**) with EtMgBr in THF followed by a pyridyl benzothioate (**7a**, **7b**) afforded the monoacyldipyrromethane (**8a**, **8b**) in good yield (82%, 71%, respectively). Monoacyldipyrromethanes **8c** and **8d** were prepared according to the literature.[27] The second acylation of **8a**−**d** with the requisite acid chloride afforded **6a**−**d** in 57−65% yield. The TIPS groups in diacyldipyrromethanes **6b** and **6f** were removed with TBAF in THF, affording **6g** and **6h** in 62% and 71% yield, respectively (eq 2).



SCHEME 3



***trans*-AB$_2$C-porphyrins.** The synthesis of the desired *trans*-AB$_2$C-porphyrins is shown in Scheme 3. The reduction of a diacyldipyrromethane (**6**) with NaBH$_4$ in THF/methanol afforded the corresponding dipyrromethane-dicarbinol (**6-OH**). The latter was directly condensed with a dipyrromethane (**5**) in acetonitrile in the presence of TFA, followed by oxidation with DDQ. The Fb porphyrins **9**−**14** were obtained in 19−28% yield. Treatment of the

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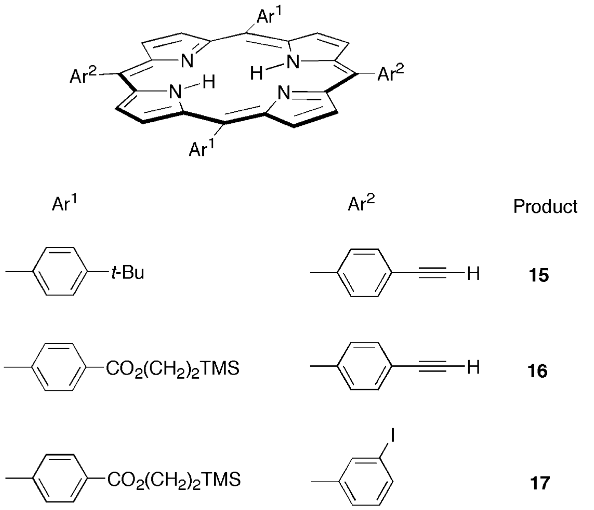
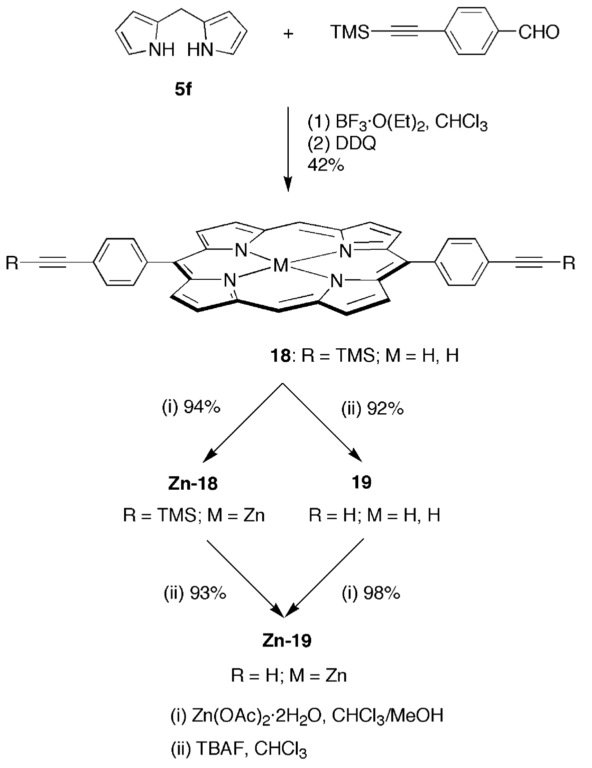
CHART 2



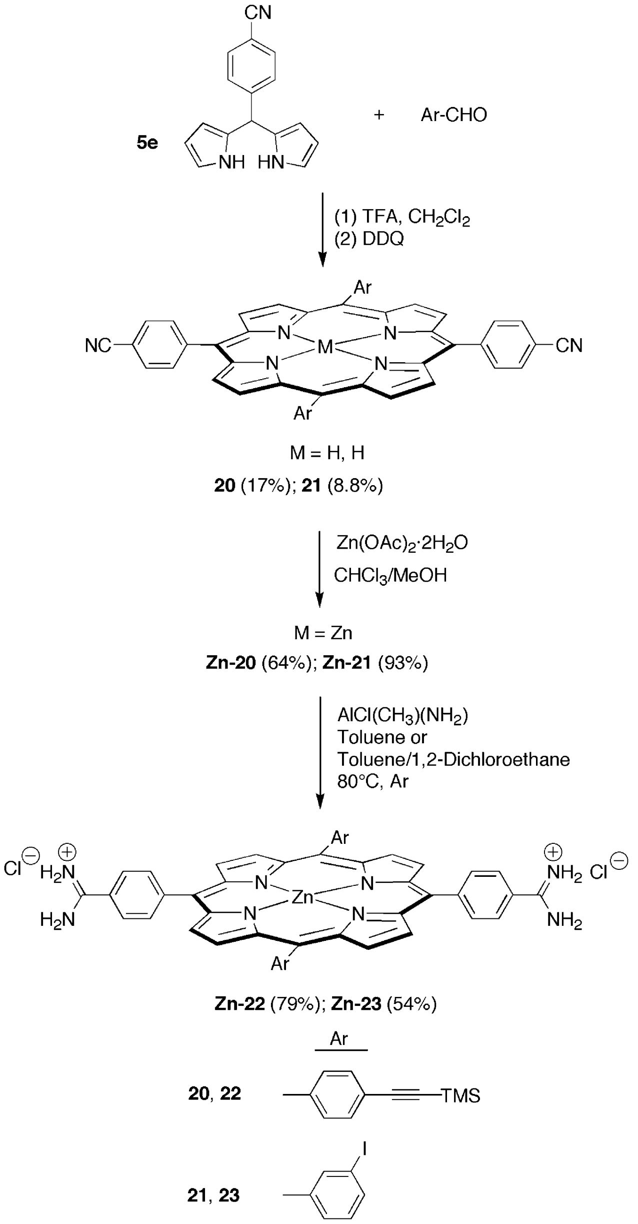
SCHEME 4



Fb porphyrins with methanolic zinc acetate afforded the corresponding zinc chelates in >90% yield.

***trans*-A$_2$B$_2$-Porphyrins.** Porphyrins **15**−**17** (Chart 2) were prepared by the self-condensation of a dipyrromethane-monocarbinol.[27] The synthesis of a *trans*-A$_2$B$_2$-porphyrin lacking nonlinking meso-substituents is shown in Scheme 4. A wide variety of related diarylporphyrins have been prepared by Boyle and co-workers.[28] The reaction of dipyrromethane **5f** and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde under minimal scrambling conditions[29] afforded the TMS-protected ethynyl porphyrin **18** in 42% yield. Deprotection of the TMS group with TBAF on silica gel afforded **19** in 92% yield. Treatment of **19** with methanolic zinc acetate afforded the zinc chelate **Zn-19**. Alternatively, porphyrin **Zn-19** was prepared by metalation of **18**, yielding **Zn-18**, followed by deprotection of the TMS group affording **Zn-19**. While the yield of each of these steps is >90%, the limited solubility of **19** in CH$_2$Cl$_2$/CHCl$_3$ makes the latter route (via **Zn-18**) preferred for the preparation of **Zn-19**.

SCHEME 5



A porphyrin bearing two amidino groups was prepared as shown in Scheme 5. Condensation of dipyrromethane **5e** with the appropriate aldehyde in CH$_2$Cl$_2$ under TFA catalysis afforded **20** or **21** in 17% or 8.8% yield, respectively. The solubility of **21** was extremely poor in CHCl$_3$, CH$_2$Cl$_2$, or toluene. The zinc chelates **Zn-20** and **Zn-21** were treated with Weinreb's amide transfer reagent [AlCl(CH$_3$)(NH$_2$), freshly prepared from equimolar amounts of ammonium chloride and Al(CH$_3$)$_3$ in toluene][30] at 80 °C for 3−4 days, affording **Zn-22** and **Zn-23**

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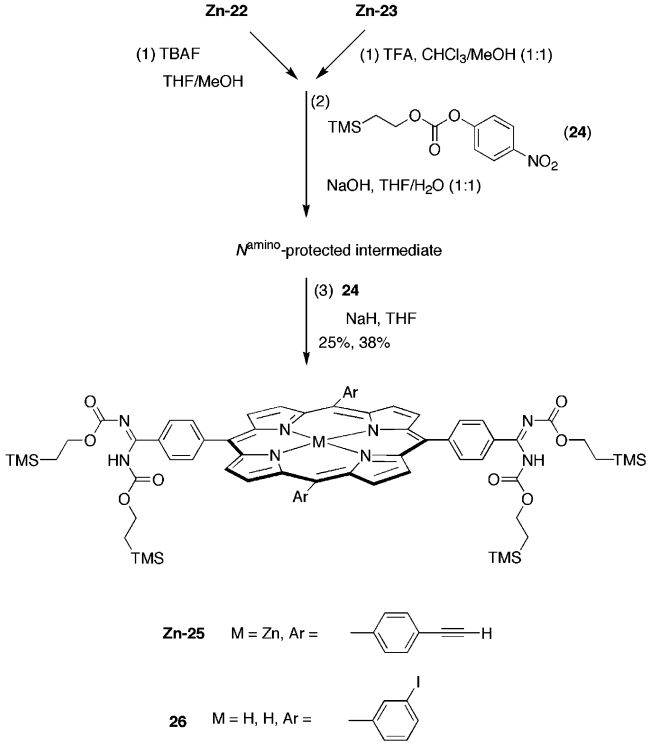
[28] (a) Elgie, K. J.; Scobie, M.; Boyle, R. W. *Tetrahedron Lett.* **2000**, *41*, 2753−2757. (b) Sutton, J. M.; Clarke, O. J.; Fernandez, N.; Boyle, R. W. *Bioconjugate Chem.* **2002**, *13*, 249−263.

[29] Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

SCHEME 6



in 79% and 54% yield, respectively. Metalation of **20** and **21** with zinc was essential to avoid production of the aluminum chelates **Al-20** and **Al-21** upon reaction with $AlCl(CH_3)(NH_2)$.

To improve the solubility of the amidino porphyrins, we considered the established acetyl,[31] ethoxycarbonyl,[32] and benzyloxycarbonyl[33] protecting groups for the amidino functionality, but our requirements for deprotection under gentle conditions at the cyclic hexamer stage led to use of the 2-(trimethylsilyl)ethoxycarbonyl group. The TMS-ethyne groups in **Zn-22** were deprotected with TBAF in methanol. The resulting ethynyl porphyrin was treated with 2-(trimethylsilyl)ethyl *p*-nitrophenyl carbonate (**24**)[34] in the presence of NaOH in THF/H_2O (1:1), affording the putative N^{amino}-protected porphyrin. Limited solubility of this species caused difficulties in chromatographic purification. Accordingly, treatment with **24** in the presence of NaH in THF afforded **Zn-25** in 25% overall yield. Similarly, **Zn-23** was demetalated with TFA and the amidino moieties were protected with 2-(trimethylsilyl)ethoxycarbonyl groups, affording **26** in 38% yield (Scheme 6).

(3) Synthesis of Cyclic Hexamers. The conditions for the one-flask reaction of diethynyl porphyrin **Zn-2** and diiodo porphyrin **3** with template **4** to give the cyclic hexamer $\mathbf{Zn_3Fb_3}$**-1a** employed each porphyrin at 2.5 mM with a molar ratio of **Zn-2**:**3**:**4**:$Pd_2(dba)_3$:$AsPh_3$ = 1.0/1.0/1.0/0.30/2.4 in toluene/TEA (5:1) at 35 °C (Scheme 1).[10] We investigated two changes to the reaction conditions: (1) We changed the ratio of **Zn-2**:**3**:**4** to 1.0/1.0/0.33. (2) We examined the use of $P(o\text{-tol})_3$ in place of $AsPh_3$, which afforded diminished side reactions in the synthesis of diarylethyne-linked multiporphyrin arrays, thereby facilitating separation and purification.[35] In the one case examined ($\mathbf{Zn_3Fb_3}$**-1e**), the isolated yield was 5.1% ($AsPh_3$) or 1.8% ($P(o\text{-tol})_3$). Accordingly, each Pd-mediated coupling was performed with use of the conditions previously employed for the synthesis of $\mathbf{Zn_3Fb_3}$**-1a** but with a 1.0/1.0/0.33 ratio of **Zn-2**:**3**:**4**.

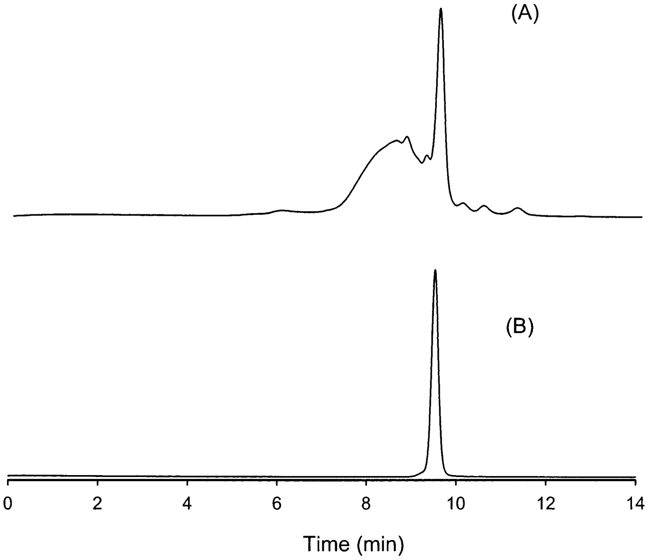


FIGURE 1. Analytical SEC traces in the synthesis of $\mathbf{Zn_3Fb_3}$**-1c**. (A) The crude reaction mixture obtained with $AsPh_3/Pd_2(dba)_3$. Peaks from t_R = 6−9 min are attributed to high molecular weight material (HMWM). (B) Purified cyclic hexamer $\mathbf{Zn_3Fb_3}$**-1c**.

A set of survey reactions (10-mL scale, Schlenk line) was performed for the synthesis of each of the cyclic hexamers. The reactions make use of a refined synthesis of template **4**.[11] Each reaction was completed within 1−3 h as indicated by analytical size exclusion chromatography (SEC). The SEC traces of each crude mixture showed high molecular weight material (HMWM) and the desired cyclic hexameric array (Figure 1). The molecule ion peak of most porphyrin monomers and multiporphyrin arrays was readily detected by laser desorption mass spectrometry (LDMS) without an added matrix,[36] as we have observed previously in the synthesis of $\mathbf{Zn_3Fb_3}$**-1a**.[10] However, LDMS spectra of the cyclic hexamers bearing ester groups could not be obtained. Among several LDMS matrices examined, only 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) and dithranol clearly gave the molecule ion peak for most of the cyclic hexamers. In general the observed mass was within ±0.2% of the expected mass.

The preparative syntheses of cyclic hexamers were performed in the same manner and gave product distributions that were essentially identical with those ob-

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[30] (a) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, 4171−4174. (b) Levin, J. I.; Turos, E.; Weinreb, S. M. *Synth. Commun.* **1982**, *12*, 989−993. (c) Garigipati, R. S. *Tetrahedron Lett.* **1990**, *31*, 1969−1972.

[31] Luckenbach, G. *Chem. Ber.* **1884**, *17*, 1421−1428.

[32] (a) Olin, J. F.; Dains, F. B. *J. Am. Chem. Soc.* **1930**, *52*, 3322−3327. (b) Massa, S.; Di Santo, R.; Artico, M. *J. Heterocycl. Chem.* **1990**, *27*, 1131−1133.

[33] Su, T.; Naughton, M. A. H.; Smyth, M. S.; Rose, J. W.; Arfsten, A. E.; McCowan, J. R.; Jakubowski, J. A.; Wyss, V. L.; Ruterbories, K. J.; Sall, D. J.; Scarborough, R. M. *J. Med. Chem.* **1997**, *40*, 4308−4318.

[34] Rosowsky, A.; Wright, J. E. *J. Org. Chem.* **1983**, *48*, 1539−1541.

[35] Wagner, R. W.; Ciringh, Y.; Clausen, C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974−2983.

[36] Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 282−291.

TABLE 1. Synthesis of Cyclic Hexamers

precursors	type	yield, %	cyclic hexamer
Zn-2 + **3**	I	5.3	**Zn$_3$Fb$_3$-1a**
Zn-16 + **17**	I	4.1	**Zn$_3$Fb$_3$-1b**
Zn-25 + **26**	I	0.7	**Zn$_3$Fb$_3$-1c**[a]
Zn-19 + **17**	II	5.9	**Zn$_3$Fb$_3$-1d**
Zn-15 + **17**	II	5.1	**Zn$_3$Fb$_3$-1e**
Zn-9 + **12**	III	8.7	**Zn$_3$Fb$_3$-1f**
Zn-10 + **13**	III	9.6	**Zn$_3$Fb$_3$-1g**
Zn-11 + **14**	III	3.6	**Zn$_3$Fb$_3$-1h**

[a] Characterization data were insufficient to establish identity.

tained in survey reactions. Chromatography on silica removed non-porphyrin species and some of the HMWM species, while preparative SEC (repetitive) removed the HMWM species and gave the pure cyclic hexamer. In this manner, the cyclic hexamers **Zn$_3$Fb$_3$-1b**,**d**−**g** were obtained in yields ranging from 3.6% to 9.6% (Table 1). The product of the reaction leading to cyclic hexamer **Zn$_3$Fb$_3$-1c** was obtained in 0.7% yield. Several all-Zn hexamers [**Zn$_6$-1b**,**d**,**f**,**g**] were prepared by treatment of the corresponding arrays with zinc acetate.

The cyclic hexameric porphyrin arrays **Zn$_3$Fb$_3$-1b**,**d**−**g** were characterized by TLC analysis, analytical SEC, MALDI-MS, UV−vis absorption spectroscopy, ^{1}H NMR spectroscopy, and fluorescence spectroscopy. The cyclic hexamers were sufficiently soluble in THF-d_8 [**Zn$_3$Fb$_3$-1d** and **Zn$_6$-1d**,**g**] or $CDCl_3$ [**Zn$_3$Fb$_3$-1b**,**e**−**h** and **Zn$_6$-1b**,**f**] to obtain well-resolved ^{1}H NMR spectra. It was difficult to obtain a clear ^{1}H NMR spectrum of putative hexamer **Zn$_3$Fb$_3$-1c** due to the small amount obtained (~1.0 mg). While analytical SEC of the purified product showed a single sharp peak at t_R = 9.29 min, no firm evidence is in hand to confirm the expected structure.

It is noteworthy that no significant change in yield (5.9% versus 5.3%) was observed for the formation of the cyclic hexamer in the synthesis of the less sterically hindered cyclic hexamer **Zn$_3$Fb$_3$-1d** versus **Zn$_3$Fb$_3$-1a**. The former bears a *meso*-H while the latter bears a *meso*-mesityl group at the nonlinking position of the Zn porphyrin. The template-directed formation of the cyclic hexamer entails binding of tripyridyl template **4** at the apical position of the Zn porphyrin. Thus, an enhanced template effect was not observed upon removal of the *meso*-mesityl groups.

(4) Electrochemical Studies. The electrochemical behavior of **Zn$_3$Fb$_3$-1g** was first investigated for a sample in solution. As expected, the voltammogram of **Zn$_3$Fb$_3$-1g** (not shown) exhibits wave characteristics of both Zn and Fb tetraarylporphyrins. These waves are similar to those observed for other tetraarylporphyrins.[37] In particular, **Zn$_3$Fb$_3$-1g** exhibits two distinct oxidation waves at potentials of ~0.58 and ~1.10 V, and a broad wave centered near ~0.87 V (versus Ag/Ag$^+$; Fc/Fc$^+$ = 0.19 V). The lowest potential wave corresponds to the first oxidation of the three (equivalent) Zn porphyrins in the hexamer. The broad wave corresponds to the second oxidation of the three Zn porphyrins overlapped with the first oxidation of three (equivalent) Fb porphyrins. The highest potential wave corresponds to the second oxidation of the three Fb porphyrins. The values of these potentials are similar to those of monomeric Zn and Fb porphyrins, indicative of the weak interactions between the constituents of the hexamer.[10]

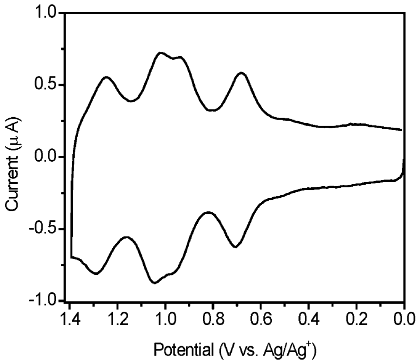

FIGURE 2. Voltammetry of **Zn$_3$Fb$_3$-1g** in a SAM on Au. The solvent was CH_2Cl_2 containing 1.0 M Bu_4NPF_6; the scan rate was 100 V s^{-1}.

The electrochemical behavior of **Zn$_3$Fb$_3$-1g** self-assembled on gold was also investigated by using methods employed previously (see Supporting Information). The fast-scan voltammogram (100 V/s) of the **Zn$_3$Fb$_3$-1g** SAM is shown in Figure 2. The general appearance of the voltammogram of the SAM is similar to that observed in solution. Two distinct waves are observed at ~0.68 and ~1.27 V. These waves straddle a broader wave centered at ~1.0 V. The waves contributing to the broad wave are modestly resolved and occur at ~0.98 and ~1.03 V. The waves at ~0.68 and 1.27 V are attributed to the first oxidation of the three Zn porphyrins and the second oxidation of the three Fb porphyrins. The wave at 1.03 V is attributed to the second oxidation of the three Zn porphyrins, whereas the wave at 0.98 V is attributed to the first oxidation of the three Fb porphyrins. The assignment of these waves to the Zn and Fb porphyrins, respectively, is consistent with the trends observed for monomeric Zn and Fb tetraarylporphyrins in solution (the second oxidation of a Zn porphyrin is at a higher potential than the first oxidation of the analogous Fb porphyrin[37]). In addition, our previous studies of monomeric Zn porphyrin SAMs (in which the porphyrin is similar to that of the constituent porphyrin in the hexamer) have shown that the first and second waves occur near ~0.70 and ~1.05 V.[19]

The fact that the oxidation potentials of the Zn and Fb porphyrins in the **Zn$_3$Fb$_3$-1g** SAM occur at more positive values than in solution is consistent with our previous studies of a number of different types of porphyrin SAMs, including monomers and more complex architectures.[19−21] The key observation of the present study is that the redox potentials of the three Zn porphyrins in the **Zn$_3$Fb$_3$-1g** SAM are identical with one another, as is also the case for the three Fb porphyrins. The equivalent electrochemical behavior of the Zn (and Fb) porphyrins in the hexamer is consistent with an architecture in which all six porphyrins are in the same proximity to the surface. Such a structure could result if each of the six porphryins is attached to the surface via its thiol linker. However, we have no experimental evidence that all six of the thiols do in fact attach. Regardless, in other architectures (for example, in which one porphyrin is lying flat on the surface) the porphyrin

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[37] Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 53−125.

constituents would become electrochemically inequivalent (because the various constituents would exhibit different interactions with the surface). The relatively simple pattern of redox waves for the **Zn_3Fb_3-1g** SAM argues against the existence of any appreciable concentration of architectures in which the porphyrins are electrochemically inequivalent.

Finally, we note that the surface coverage of the **Zn_3Fb_3-1g** SAM is $\sim 4.3 \times 10^{-12}$ mol cm^{-2} (as determined by integrating the first redox wave). This coverage corresponds to a molecular area of ~4000 Å^2 per hexamer. This area is considerably larger than the molecular footprint of the hexamer attached in a corral-like geometry (at most 1000 Å^2 per hexamer). Accordingly, the coverage of the arrays on the surface is relatively sparse.

Conclusions

The template-directed one-flask synthesis of the cyclic hexameric porphyrin array was applied in the preparation of six new derivatives. The one-flask synthesis is compatible with sensitive groups, including protected carboxyl groups, protected thiol groups, and protected amidino groups. The cyclic hexamers have an alternating pattern of porphyrins where the nonlinking meso-positions bear 6−12 carboxyl groups, 12 amidino groups, 6 thiol groups, or 6 thiol groups and 6 carboxyl groups. The low yield of cyclic hexamer formation (3.6−9.6%) is offset by the expediency of the synthesis and the availability of gram quantities of the starting *trans*-A_2B_2- or *trans*-AB_2C-porphyrin building blocks.

The chemistry of cyclic hexamers has entailed multiple types of self-assembly processes: (1) the template-directed one-flask synthesis of the cyclic hexameric array forming six covalent diphenylene linkers, (2) the noncovalent assembly of the wheel-and-spoke architecture upon binding the tripyridyl template or the dipyridyl porphyrin, and (3) the formation of a self-assembled monolayer on an electroactive surface. The cyclic hexamers with functional groups arrayed along the wheel perimeter now enable investigation of additional supramolecular properties of these shape-persistent macrocycles, including intermolecular interactions leading to columnar structures.

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Supporting Information Available: Complete experimental procedures and spectral data (absorption, fluorescence, ^1H NMR, LDMS) for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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