

Efficient Synthesis of Light-Harvesting Arrays Composed of Eight Porphyrins and One Phthalocyanine

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Effective light-harvesting arrays require multiple photoactive energy donors that funnel energy to an energy acceptor. Porphyrins and phthalocyanines are attractive components for light-harvesting arrays due to their strong absorption in the blue and red regions, respectively, and because energy transfer can occur from porphyrin to phthalocyanine regardless of their respective metalation states. Star-shaped light-harvesting arrays comprised of eight peripheral porphyrins and one core phthalocyanine have been prepared by a streamlined synthesis involving minimal reliance on protecting groups, a high degree of convergence, and facile chromatographic purification. The synthesis involves three distinct stages of complementary chemistries (porphyrin formation, Pd-mediated porphyrin dimer formation, phthalocyanine formation). Statistical reaction of *p*-iodobenzaldehyde, a phthalonitrile-linked benzaldehyde, and 5-mesityldipyrromethane afforded the desired *trans*-iodo/phthalonitrile-substituted porphyrin, which underwent Pd-mediated coupling with a monoethynyl porphyrin to give the porphyrin dimer bearing a phthalonitrile unit. Reaction of the dimer in 1-pentanol in the presence of MgCl₂ and DBU for 48 h at 145 °C afforded the all-magnesium (porphyrin)₈-phthalocyanine nonamer (MgP)₈MgPc in 5.0% yield. The same reaction with lithium pentoxide in 1-pentanol for 2 h at 145 °C gave the all-free base nonamer (H₂P)₈H₂Pc in 34% yield. The all-zinc nonamer (ZnP)₈ZnPc was prepared by addition of zinc acetate at the end of the reaction. Similar treatment of a monomeric porphyrin-phthalonitrile afforded the pentameric (ZnP)₄ZnPc in 58% yield. The (MgP)₈MgPc was also obtained by magnesium insertion of (H₂P)₈H₂Pc. The three nonamers were readily purified and are soluble in solvents such as toluene, THF, and CH₂Cl₂. Each nonamer absorbs strongly across the solar spectrum and exhibits efficient energy transfer from the porphyrins to the phthalocyanine.

Introduction

A major objective in the field of artificial photosynthesis is to create synthetic light-harvesting complexes. Such constructs must incorporate a large number (ultimately hundreds) of closely related pigments in a well-defined 3-dimensional architecture, absorb strongly across the solar spectrum, and funnel energy efficiently to a designated site (the reaction center). Porphyrins are attractive pigments for incorporation in light-harvesting arrays, but only a few synthetic approaches have provided access to covalently linked arrays comprised of more than six porphyrins.^{1–3} Gaining access to large light-harvesting arrays requires new synthetic approaches that are rapid and efficient. While porphyrin building blocks offer versatility in design,^{4–6} a major challenge remains to find efficient methods for assembling these modular components in architecturally defined target molecules that can be readily purified.

We have used Pd-mediated reactions to join iodo/ethynyl-substituted porphyrin building blocks in the

synthesis of a variety of multiporphyrin arrays.^{7,8} The repetitive use of one type of chemistry in the synthesis of an array requires protected building blocks and one deprotection step prior to each coupling operation.^{9,10} The exclusive reliance on one type of chemistry and a set of closely related building blocks often suffers from the accumulation of byproducts that differ only slightly from the target molecule, making purification difficult and extensive chromatography essential. This problem is an inherent feature of even the most well-developed applications of modular building blocks, including the chemical synthesis of biopolymers.

One approach that largely avoids these problems involves use of complementary chemistries in successive stages of the synthesis. By the appropriate choice of reactions, the reactivity of a given site is only manifest on one occasion during the entire synthesis. Thus, a protecting group is not required for that site, affording a highly streamlined synthesis. The use of a distinct type of reaction in each stage also provides an opportunity to make significant changes to the polarity of the desired product with each new reaction, and to design purifica-

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tion schemes accordingly. Because the types of impurities are generally different in each reaction, and a given reaction is not used repetitively, this approach can significantly mitigate purification problems.

Recently, several elegant routes to large multiporphyrin arrays have been reported that exploit use of complementary chemistries. Osuka employed successive acid-catalyzed condensations to form a linear porphyrin oligomer (albeit using protecting groups), followed by oxidative dimerization of the porphyrin oligomers, yielding *meso,meso*-linked windmill architectures comprised of 12 Ni porphyrins and 2 Zn porphyrins.³ Officer employed Wittig reactions to prepare porphyrin dimers derivatized with an aldehyde, which upon condensation with pyrrole afford the corresponding star-shaped arrays comprised of eight Ni porphyrins and one free base porphyrin.^{1,11} Sanders alternated 2-fold Pd-mediated ethyne coupling and 4-fold Mitsunobu coupling in the synthesis of an array comprised of nine Zn porphyrins.² No protecting groups were required, and in the Mitsunobu coupling the desired 4-fold-coupled product was the only nonpolar array, affording facile separation via adsorption chromatography. These pioneering approaches provide efficient access to arrays comprised of multiple porphyrins. A further objective is to meet an essential requirement of a light-harvesting array, that multiple photoactive energy donors funnel energy to one lower lying energy acceptor.¹²

We recently investigated the synthesis of arrays containing four porphyrins and one phthalocyanine.¹³ The porphyrin–phthalocyanine motif is very attractive for light-harvesting, because the pigments absorb strongly in the blue and red regions, respectively, and energy transfer can occur from porphyrins to phthalocyanines regardless of metalation state.¹⁴ A major challenge to the incorporation of phthalocyanines into light-harvesting arrays involves the preparation and handling of phthalocyanines bearing reactive handles (i.e., phthalocyanine building blocks). Indeed, only a few porphyrin–phthalocyanine dimers¹⁵ and pentamers^{13,16} have been prepared. We found that a phthalonitrile moiety was compatible with the acidic and oxidative conditions involved in porphyrin formation,¹⁷ enabling synthesis of porphyrin–

phthalonitrile (**1**) (Scheme 1). Treatment of **1** to the basic reductive conditions involved in forming phthalocyanines¹⁷ afforded the star-shaped array comprised of a core phthalocyanine and four peripheral porphyrins.¹³ This reaction was performed using Shiraishi conditions (DBU and a metal salt in 1-pentanol),¹⁸ affording the all-magnesium pentamer (MgP)₄MgPc and all-zinc pentamer (ZnP)₄ZnPc in 45% and 15% yield with MgCl₂ and zinc acetate, respectively. While phthalocyanine monomers are often quite insoluble, the pentamers exhibited good solubility in a variety of organic solvents. The desired pentamer was the only chromatographically mobile species, making purification very straightforward. Thus, the formation of the phthalocyanine in the last step avoided handling phthalocyanine monomers, provided a simple purification, and introduced a single energy acceptor at the core of the porphyrin antenna. Moreover, the complementary nature of porphyrin and phthalocyanine formation¹⁷ enabled the synthesis to be performed without protecting groups in these transformations.

The success of this approach prompted us to investigate the preparation of larger light-harvesting arrays. In this paper we describe the synthesis of arrays with twice the antenna size, where eight porphyrins funnel energy to one phthalocyanine. The route we describe has been used to prepare milligram quantities of pure arrays in a very simple manner; such amounts are sufficient for thorough spectroscopic study and characterization of the dynamics of energy transfer. The unidirectional flow of energy from porphyrin to phthalocyanine opens up design possibilities that do not exist with arrays composed of porphyrins alone. One example involves use of free base porphyrins as antenna pigments, where energy transfer among free base porphyrins is followed by transfer to the phthalocyanine. Accordingly, the nonamers we have prepared are composed of the all-free base, all-magnesium, or all-zinc constituents. Static absorption and fluorescence measurements were used to assess the efficiency of energy transfer from the porphyrins to the phthalocyanine.

Results and Discussion

Synthesis of Porphyrin–Phthalocyanine Nonamers. To prepare nonamers, we elected to examine the cyclotetramerization of a phthalonitrile-derivatized porphyrin dimer in phthalocyanine formation. Porphyrin dimers with a diphenylethyne linker undergo efficient energy transfer,¹⁹ and can be prepared via Pd-mediated coupling of an iodoporphyrin and an ethynylporphyrin.²⁰ The Pd-mediated coupling reactions afford a variety of byproducts,²¹ and are best used to prepare porphyrin precursors and small multiporphyrin arrays where purification can be readily performed. The route to nonamers involved three stages of chemistry (porphyrin forma-

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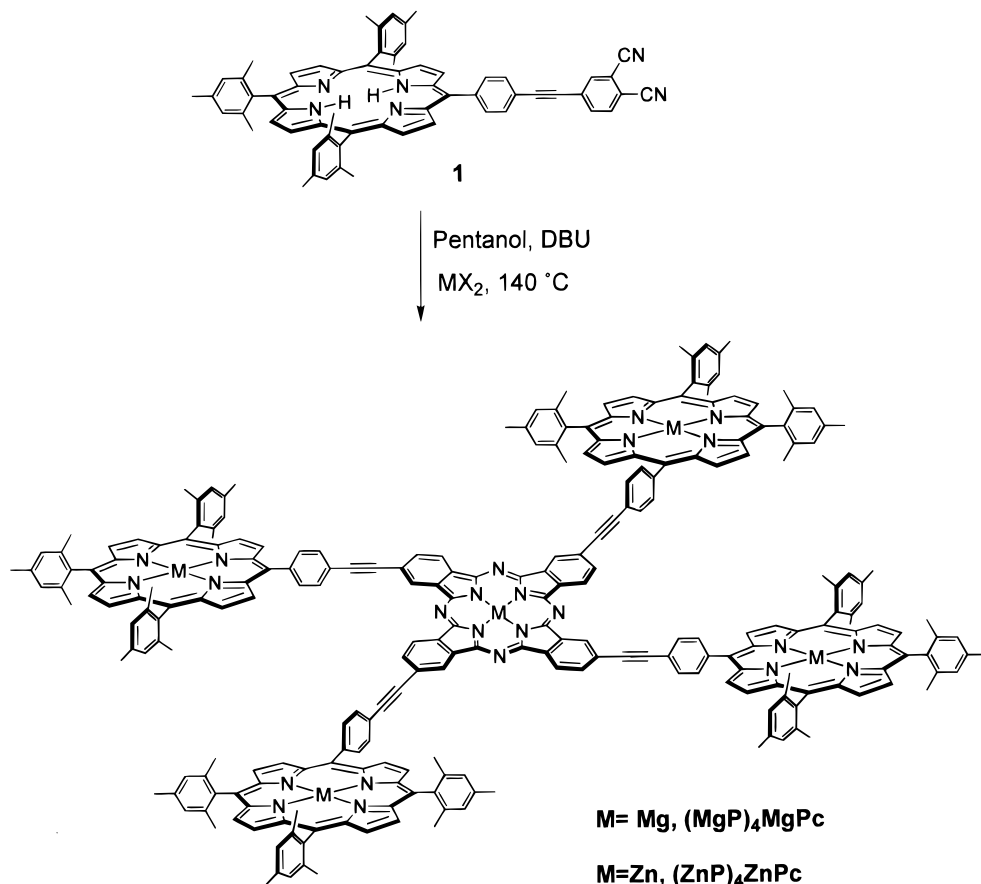
(17) Though porphyrins and phthalocyanines are members of the porphyrinic family, their chemistry is fundamentally different. Synthesis of a porphyrin involves a two-step process of acid-catalyzed pyrrole–aldehyde condensation yielding a porphyrinogen and 4H₂O; the addition of an oxidant removes 6 e⁻ and 6 H⁺ from the porphyrinogen in forming the porphyrin. Synthesis of a phthalocyanine involves a reductive cyclotetramerization of a phthalonitrile, where a reducing agent is required to add 2 e⁻ and 2 H⁺ (or 2 e⁻ + M²⁺) in forming the free base (or metallo) phthalocyanine. See: Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K., Guilard, R., Eds.; Academic Press: San Diego, CA, 1999; Vol. 1, pp 45–118.

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Scheme 1. One-Flask Syntheses of Porphyrin–Phthalocyanine Pentamers^a

^a Each pentamer is composed of a mixture of regioisomers.

tion, Pd-mediated porphyrin dimer formation, and phthalocyanine formation), which we sought to perform with minimal use of protecting groups.

The phthalonitrile–benzaldehyde (**2**)¹³ allowed the phthalonitrile moiety to be introduced at the porphyrin synthesis stage where the inherent polarity of the phthalonitrile could be exploited in the isolation of porphyrin **3**. The *trans*-substituted porphyrin **3** was prepared using new nonscrambling conditions for the acid-catalyzed condensation of sterically hindered dipyrromethanes and aldehydes.²² Thus, the statistical condensation of 5-mesityldipyrromethane,²³ 4-iodobenzaldehyde, and **2** followed by oxidation with DDQ gave the diiodoporphyrin, the diphtalonitrile–porphyrin, and the desired *trans*-iodophthalonitrile–porphyrin (**3**). The polar phthalonitrile group enabled facile separation of the mixture of three porphyrins by flash column chromatography, affording **3** in 11% yield (Scheme 2).

The reaction of **3** and trimesitylmonoethynylporphyrin (**4**) was performed using refined Pd-mediated coupling conditions (Scheme 3).²¹ These conditions employ Pd₂(dba)₃ and tri-*o*-tolylphosphine in the absence of copper reagents, and enable reaction under mild conditions with dilute solutions (2.5 mM) of free base porphyrins. The desired all-free base porphyrin dimer **5** was obtained in

51% yield. The phthalonitrile unit was compatible with these reaction conditions.

The cyclotetramerization of (porphyrin)₂–phthalonitrile (**5**) to form the desired nonameric array was examined first under Shiraishi conditions (Scheme 4).¹⁸ These conditions have become prevalent for the preparation of phthalocyanines bearing large substituents.²⁴ However, the reaction with MgCl₂ and DBU in 1-pentanol produced no phthalocyanine (entry 1, Table 1). This failure appeared to stem from the poor solubility of **5** in 1-pentanol (insoluble at room temperature), because porphyrin–phthalonitrile **1** is soluble in 1-pentanol at the concentration used for cyclotetramerization and readily gave the corresponding pentamer.¹³ Upon dissolving **5** in hot

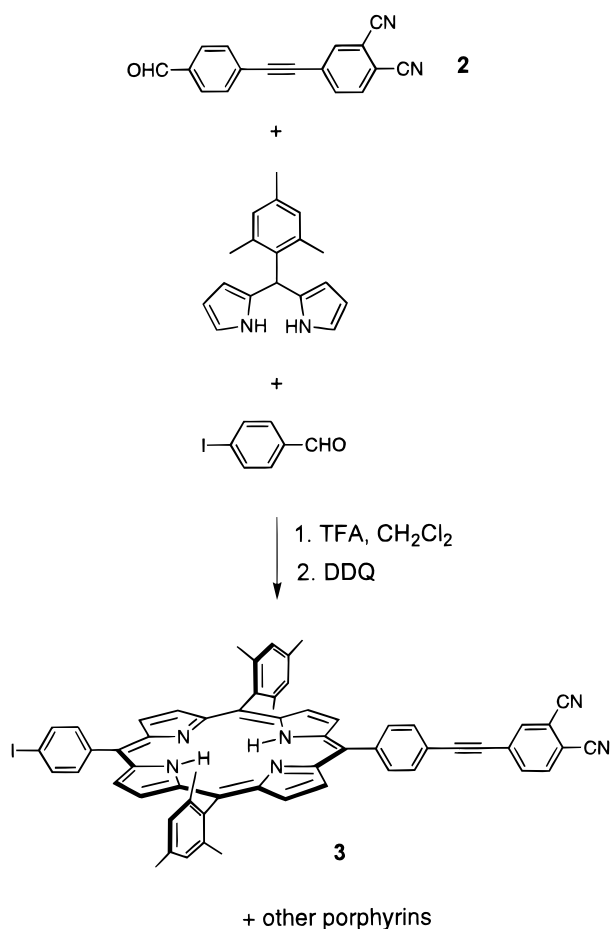
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Scheme 2



o-dichlorobenzene followed by addition of 1-pentanol to give a 1:1 solvent mixture, the desired all-magnesium porphyrin–phthalocyanine nonamer [(MgP)₈MgPc] was obtained in 3.1% yield (entry 2). To further increase the solubility, the all-magnesium chelate (**Mg₂-5**) was prepared by reaction of **5** with MgI₂ and DIEA at room temperature.²⁵ Examination of **Mg₂-5** (slightly soluble in 1-pentanol at room temperature) under the same conditions in 1-pentanol/*o*-dichlorobenzene (1:1) gave (MgP)₈MgPc in 5.0% yield (entry 3). Attempts to use higher reaction temperatures with quinoline as solvent gave no product (entry 4).

Though changes in solvent in the Shiraishi method provided the desired nonamer, the low yields prompted us to examine other methods for forming phthalocyanines. The lithium pentoxide method (involving the reaction of a phthalonitrile in 1-pentanol containing lithium pentoxide) is one of the oldest methods for preparing phthalocyanines²⁶ but has been largely supplanted by the Shiraishi method for reactions of phthalonitriles bearing large substituents.²⁴ However, phthalonitriles bearing short alkylethynyl²⁷ or tetrathiafulvalene-linked²⁸ substituents were recently converted to the corresponding phthalocyanines using the lithium pentoxide method. To our delight, the reaction of **5** via the lithium pentoxide method (2 h at 145 °C) afforded

the all-free base array (H₂P)₈H₂Pc in 34% yield (entry 5, Table 1). Such direct access to the all-free base array is attractive for light-harvesting purposes. In contrast, the Shiraishi method generally affords quite low yields of free base phthalocyanines.

The initial product of the lithium pentoxide method is the dilithium phthalocyanine (Li₂Pc), and the subsequent addition of metal salts conveniently affords the corresponding metallophthalocyanine.²⁷ Thus, the same cyclotetramerization of **5** with addition of zinc acetate after the 2 h heating period afforded the all-zinc chelate (ZnP)₈ZnPc in 28% yield (entry 6). This yield is nearly twice that obtained for the all-zinc pentamer (ZnP)₄ZnPc using the Shiraishi method.¹³ The same reaction with addition of MgCl₂ at the end of the reaction gave the partially magnesiated nonamer. Chromatographic work-up and subsequent metalation with MgI₂ and DIEA in CH₂Cl₂ gave (MgP)₈MgPc in 30% yield (entry 7). Alternatively, (MgP)₈MgPc was prepared in 96% yield by metalation of (H₂P)₈H₂Pc with MgI₂ and DIEA in CH₂Cl₂ at room temperature.

The striking success of the phthalocyanine-forming reactions via the lithium pentoxide method prompted us to reexamine the synthesis of the pentameric arrays. The (ZnP)₄ZnPc array was prepared previously by reaction of **1** under Shiraishi conditions in 15% yield (entry 8, Table 1).¹³ The reaction of **1** via the lithium pentoxide method afforded (ZnP)₄ZnPc in 58% yield (entry 9). The shorter reaction time (2 h vs 24 h) and higher yield make the latter reaction conditions far more attractive for this class of porphyrin–phthalocyanine arrays.

The phthalocyanine-forming reaction mixtures were readily purified. In the case of (H₂P)₈H₂Pc and (ZnP)₈ZnPc, the crude reaction mixture following phthalocyanine formation exhibited only one mobile species, the porphyrin–phthalocyanine nonamer, and all other materials remained bound at the top of the column. These nonamers were much less polar than the starting phthalonitrile-substituted dimer (**5**), and were each easily purified by chromatography with a single silica column. Arrays containing magnesium porphyrins are demetalated on silica.²⁹ The reaction mixture containing partially metalated nonamer was chromatographed on alumina (the (MgP)₈MgPc was more polar than **Mg₂-5**) followed by one SEC column, affording the purified (but incompletely magnesiated) nonameric product, which was then metalated exhaustively. The simple purification of these porphyrin–phthalocyanine arrays is in contrast to the multiple size exclusion chromatography and adsorption chromatography operations required for multiporphyrin arrays of similar or even smaller size.^{8,9,20}

The nonamers are soluble in organic solvents such as THF, CHCl₃, and toluene. In each case the ¹H NMR spectrum showed the presence of four possible regioisomers of the phthalocyanine, as expected.³⁰

Absorption and Fluorescence Properties. The absorption spectrum in toluene of each nonamer resembles, but does not equal, the sum of the spectra of the corresponding monomeric components. A representative example is shown for (H₂P)₈H₂Pc (Figure 1). The absorption spectrum is dominated by the intense Soret

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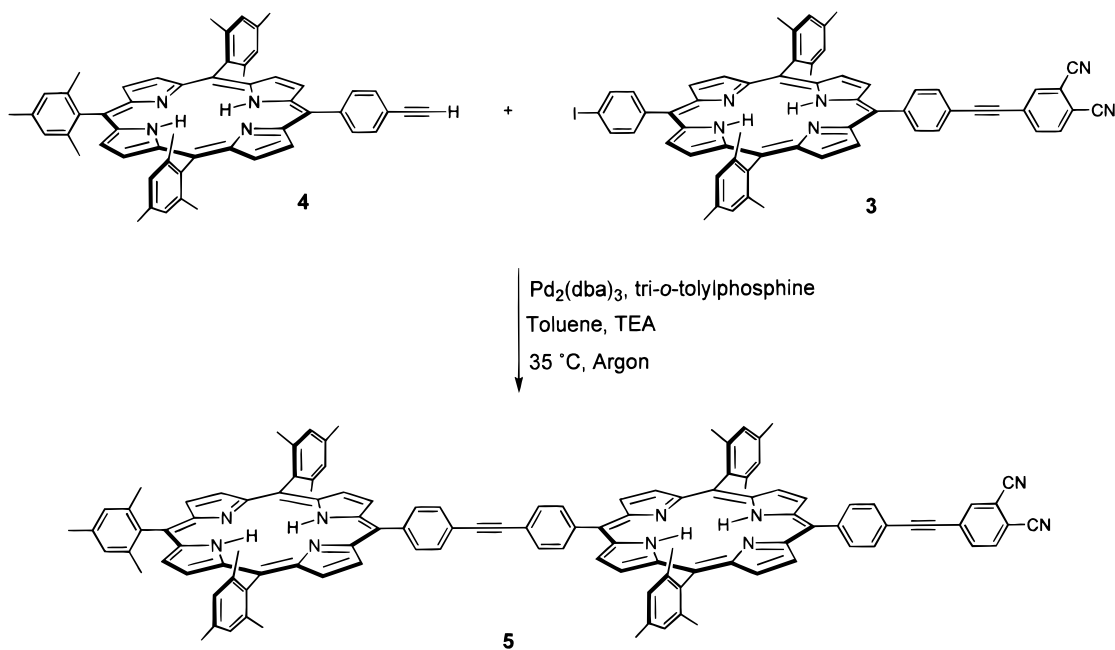
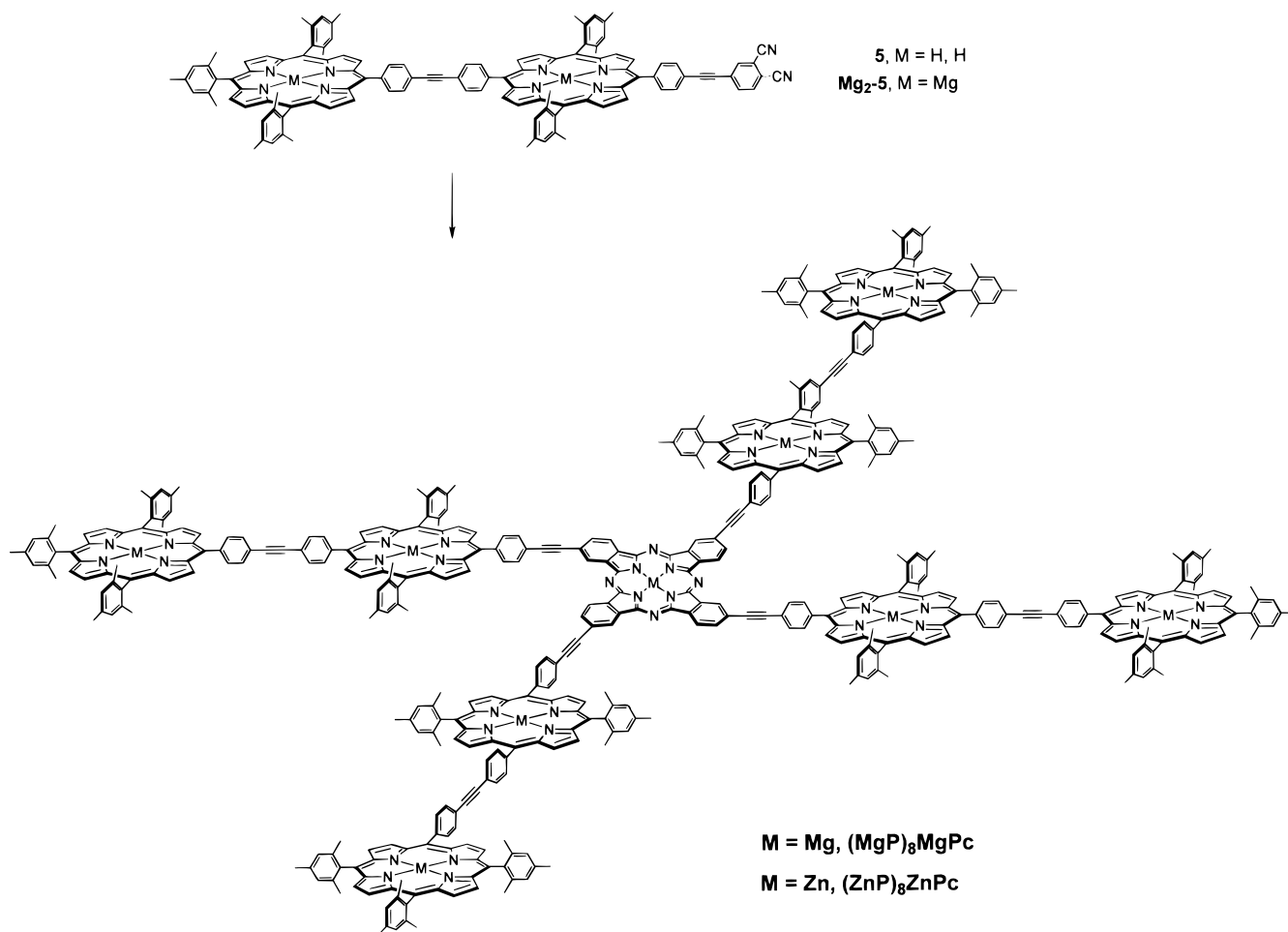
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Scheme 3

Scheme 4. Convergent Synthesis of Multiporphyrin–Phthalocyanine Nonamers^a

^a Each nonamer is composed of a mixture of regioisomers.

band of the eight porphyrin constituents at 425 nm ($\epsilon = 2.8 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$). The Soret band is slightly broadened (19 nm), a characteristic of diphenylethyne-linked porphyrin dimers.¹⁹ The weaker Q-bands of the porphyrins

lie between 500 and 660 nm. The Soret band of the phthalocyanine core component lies near 370 nm, and the Q-bands of the phthalocyanine give rise to the relatively strong absorption at 723 nm ($\epsilon = 2.5 \times 10^5 \text{ M}^{-1}$

Table 1. Investigation of Conditions for Forming the Multiporphyrin–Phthalocyanine Arrays

entry	starting material	base	metal	solvent	<i>T</i> (°C)	time (h)	product	yield (%)
1	5	DBU	MgCl ₂	pentanol	145	48		0
2	5	DBU	MgCl ₂	pentanol/DCB	145	48	(MgP) ₈ MgPc	3.1
3	Mg₂-5	DBU	MgCl ₂	pentanol/DCB	145	48	(MgP) ₈ MgPc	5.0
4	5	quinoline	MgCl ₂	quinoline	180	6, 12		0 ^a
5	5	C ₅ H ₁₁ OLi	Li	pentanol	145	2	(H ₂ P) ₈ H ₂ Pc	34
6	5	C ₅ H ₁₁ OLi	Li/Zn(OAc) ₂ ^b	pentanol	145	2	(ZnP) ₈ ZnPc	28
7	5	C ₅ H ₁₁ OLi	Li/MgCl ₂ ^b	pentanol	145	2	(MgP) ₈ MgPc ^c	<i>c</i>
8	1	DBU	Zn(OAc) ₂	pentanol	145	24	(ZnP) ₄ ZnPc	15 ^d
9	1	C ₅ H ₁₁ OLi	Li/Zn(OAc) ₂ ^b	pentanol	145	2	(ZnP) ₄ ZnPc	58

^a The reaction mixture partially turned green when the temperature reached 180 °C; however, no phthalocyanine species were detected upon workup. ^b The metal salt was added after 2 h at 145 °C when phthalocyanine formation was finished. Note that zinc acetate was used as the dihydrate. ^c The isolated compound contained partially magnesiated species. Subsequent metalation with MgI₂ gave (MgP)₈MgPc in 30% overall yield. ^d Prior results.¹³

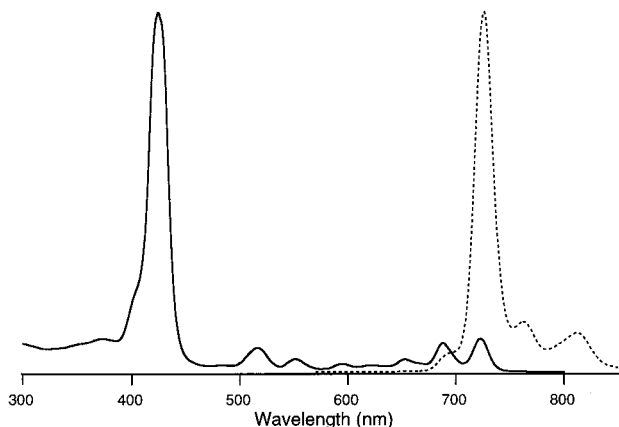


Figure 1. Absorption (solid line) and fluorescence emission (dashed line, $\lambda_{\text{exc}} = 515$ nm) spectra of (H₂P)₈H₂Pc in toluene at room temperature.

cm⁻¹) and 688 nm. Similar features were observed for (ZnP)₈ZnPc and (MgP)₈MgPc. The phthalocyanine Q(0,0) bands in each of these three arrays are red shifted ~20 nm relative to those in tetra-*tert*-butylphthalocyanine [(*t*-Bu)₄H₂Pc]³¹ and its Mg and Zn chelates, (*t*-Bu)₄MgPc³¹ and (*t*-Bu)₄ZnPc.¹⁴ This red shift is attributed to conjugation of the phthalocyanine with the four phenylethynyl linkers from the attached porphyrins. Each of the nonamers provided strong absorption in the blue and red, as expected for arrays comprised of porphyrins and phthalocyanines.

Upon excitation of (H₂P)₈H₂Pc at 515 nm, where the porphyrin is the dominant absorber, fluorescence was observed exclusively from the phthalocyanine moiety with $\Phi_f = 0.89$ (Figure 1). The fluorescence intensity of the free base porphyrin was decreased by at least 60-fold compared with that of H₂TPP. The phthalocyanine Φ_f measured upon excitation at 670 nm was 0.93, compared with $\Phi_f = 0.77$ for (*t*-Bu)₄H₂Pc.³¹ These results indicate that very efficient energy transfer occurs from the porphyrins to the phthalocyanine, and that the excited-state properties of the phthalocyanine are not altered in a deleterious manner by the presence of the adjacent porphyrins.

Similar fluorescence results were observed for (ZnP)₈ZnPc. Excitation at 550 nm resulted in strong fluorescence from the phthalocyanine and a small amount of

emission from the porphyrin (diminished 8.3-fold compared with that of ZnTPP), with the total $\Phi_f = 0.34$. The phthalocyanine Φ_f measured upon excitation at 670 nm was 0.39, compared with $\Phi_f = 0.23$ for (*t*-Bu)₄ZnPc.¹⁴ These results indicate efficient intramolecular singlet excited-state energy transfer from the porphyrins to the phthalocyanine.

Excitation of (MgP)₈MgPc at 564 nm resulted in emission from both the phthalocyanine and the porphyrin, with total $\Phi_f = 0.20$. The fluorescence emission of the porphyrin was diminished 8.3-fold compared with MgTPP. The phthalocyanine Φ_f measured upon excitation at 670 nm was 0.19, compared with $\Phi_f = 0.84$ for (*t*-Bu)₄MgPc.³¹ These results are consistent with efficient energy transfer from porphyrin to phthalocyanine followed by quenching of the excited-state phthalocyanine. The all-magnesium pentamer (MgP)₄MgPc exhibited similar behavior.¹³ More precise estimates of the energy-transfer yields and examination of the dynamics of energy migration in each of the arrays require time-resolved measurements.

Conclusions. The synthetic route employed here affords arrays composed of eight porphyrins that funnel energy to the core phthalocyanine. The synthesis involves three distinct stages: (1) formation of the porphyrin building blocks, (2) joining the porphyrin building blocks into a dimer, and (3) construction of the phthalocyanine macrocycle. The overall route could be implemented with minimal use of protecting groups due to the complementary nature of the chemistry in these three stages,¹⁷ and the general robustness of the phthalonitrile unit toward acidic, oxidative, and Pd-mediated reactions. Indeed, the use of protecting groups in the overall synthesis occurred solely in the preparation of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde, a precursor to **2** (and **4**). The only significant limitations to this route stem from the chromatography procedures required by the statistical reaction affording the monoethynylporphyrin and the statistical reaction affording the *trans*-porphyrin bearing one iodo group and one phthalonitrile unit. Recent methodology for the rational synthesis of such porphyrins should alleviate these bottlenecks.³² The Pd-mediated coupling reactions were restricted to the synthesis of small molecules such as the aldehyde precursors to the porphyrin monomers (the TMS-ethynylbenzaldehyde used in preparing **4**, the phthalonitrile-linked benzaldehyde **2**) and the ethyne-linked porphyrin dimer **5** where purification could be easily achieved. The phthalonitrile bearing a porphyrin monomer or dimer reacted smoothly

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under the lithium pentoxide method, affording the corresponding all-free base nonamer, which could subsequently be metalated. The porphyrin–phthalocyanine nonamers were readily purified by adsorption chromatography. This route highlights the utility of complementary chemistries in gaining access to multiporphyrin arrays with a high degree of 3-dimensional organization. The further development of complementary chemistries in successive synthesis stages should provide an effective means of creating architectures comprised of large numbers of pigments for studies of light-harvesting phenomena.

Experimental Section

General Procedures. ^1H NMR spectra were collected at 300 MHz. Mass spectra of porphyrins and multiporphyrin–phthalocyanine arrays were obtained via laser desorption mass spectrometry (LD-MS) or by high-resolution fast atom bombardment (FAB). Porphyrins and phthalocyanines can be analyzed effectively by LD-MS without the use of matrices.³³ Tri-*o*-tolylphosphine, tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-pentanol, and lithium ribbon were used as received from Aldrich. 4-Iodobenzaldehyde was obtained from Karl Industries, Ltd.

Chromatography. Adsorption column chromatography was performed using alumina (Fisher A-540, 80–200 mesh) converted to grade V alumina,⁸ or flash silica gel (Baker, 60–200 mesh). Preparative scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1. A preparative scale glass column was packed using Bio-Beads SX-1 in tetrahydrofuran (for $(\text{MgP})_3\text{MgPc}$) or toluene (for **5**), and eluted with gravity flow. Analytical scale SEC was performed as previously to assess the purity of **5** and to monitor the progress of the coupling reaction.^{9,20}

Absorption and Emission. Static absorption and fluorescence measurements were performed on nonde-aerated samples in toluene at room temperature as described previously.¹⁹ Total integrated emission yields of the nonamers were measured by comparison of integrated corrected spectra over the range of 570–850 nm with the appropriate porphyrin as a standard [H_2TPP ($\Phi_f = 0.11$),³⁴ MgTPP ($\Phi_f = 0.16$),^{8,35} or ZnTPP ($\Phi_f = 0.033$)³⁴], with excitation at 515 (free base), 564 (Mg), or 550 (Zn) nm. Emission quantum yields of the porphyrins in the nonamers were estimated by comparing the intensity of the Q(0,0) band with that of the appropriate porphyrin monomer. The integrated intensities could not be used due to overlap of the Q(0,1) band with the absorption of the phthalocyanine. Emission quantum yields of the phthalocyanines were measured by comparison of integrated corrected spectra over the range of 680–850 nm using (*t*-Bu)₄H₂Pc ($\Phi_f = 0.77$)³¹ as the standard and excitation at 670 nm.

5,15-Dimesityl-10-[4-[2-(3,4-dicyanophenyl)ethynyl]phenyl]-20-(4-iodophenyl)porphyrin (3). Following a known method,²² samples of 5-mesityldipyrrromethane²³ (528 mg, 2.0 mmol), 4-iodobenzaldehyde (232 mg, 1.0 mmol), and **2**¹³ (256 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (200 mL) in a 250 mL round-bottom flask, and then TFA (274 μL , 3.6 mmol) was added slowly over 30 s. The solution was stirred at room temperature for 1 h, then DDQ (0.45 g, 2.0 mmol) was added, and the reaction mixture was stirred at room temperature for another 1 h. The resulting green solution was then passed over a short alumina column and eluted with CH_2Cl_2 until the eluant was pale brown. The fractions were combined and

concentrated under reduced pressure to give a black solid, which was dissolved in toluene (40 mL) and heated under reflux for 1 h in the presence of DDQ (0.45 g, 1.98 mmol) to oxidize any remaining chlorin. The reaction mixture was allowed to cool to room temperature, then passed through an identical alumina column, and eluted with CH_2Cl_2 until all purple material eluted. The solvent was then removed under reduced pressure, and the solid dissolved in CH_2Cl_2 /hexanes (3:2) and loaded onto a flash silica gel column (3.5 \times 20). Elution with the same solvent system afforded three porphyrin bands. The second band was the desired compound, which was collected and concentrated, affording 110 mg (11.3%) of purple solid: ^1H NMR (CDCl_3) δ -2.66 (s, 2 H), 1.83 (s, 12 H), 2.63 (s, 6 H), 7.29 (s, 4 H), 7.83–7.97 (m, 7 H), 8.07 (d, $J = 8.1$ Hz, 2 H), 8.26 (d, $J = 8.1$ Hz, 2 H), 8.70–8.73 (m, 4 H), 8.76–8.79 (m, 4 H); LD-MS calcd av mass 974.9, obsd 970.1; HRMS (FAB) calcd for $\text{C}_{60}\text{H}_{43}\text{IN}_6$ 974.2594, obsd 974.2601; λ_{abs} (toluene) 422, 516, 550, 593, 649 nm.

5-(4-[2-[4-(5,10,15-Trimesityl-20-porphinyl)phenyl]ethynyl]phenyl)-10,20-dimesityl-15-[4-[2-(3,4-dicyanophenyl)ethynyl]phenyl]porphyrin (5). Following a known method,²¹ samples of **3** (128 mg, 0.13 mmol), **4**⁵ (100 mg, 0.13 mmol), $\text{Pd}_2(\text{dba})_3$ (18 mg, 0.020 mmol), and tri-*o*-tolylphosphine (48 mg, 0.16 mmol) were added to a 100 mL flask, and the flask was degassed/argon-purged three times on a Schlenk line. Then a de-aerated solution of toluene/triethylamine (5:1, 54 mL) was added via syringe, and the flask was placed in an oil bath at 35 °C. The reaction was allowed to proceed at 35 °C with magnetic stirring, and the reaction progress was checked by analytical SEC. Upon completion (3.5 h) of the reaction, the mixture was concentrated to dryness, redissolved in toluene, and loaded onto a flash silica gel column (3.5 \times 24 cm). Elution with toluene afforded the porphyrin dimers together with higher molecular weight material as the third band. The fractions were collected, concentrated to ca. 5 mL, and loaded onto a preparative SEC column packed with toluene. Gravity elution afforded the desired dimer as the second band, affording 108 mg (51.4%) of purple solid: ^1H NMR (CDCl_3) δ -2.59 (s, 2 H), -2.53 (s, 2 H), 1.87 (s, 30 H), 2.65 (s, 15 H), 7.28–7.31 (m, 10 H), 7.86–8.09 (m, 9 H), 8.27–8.32 (m, 6 H), 8.65–8.90 (m, 16 H); LD-MS calcd av mass 1612.0, obsd 1605.2; HRMS (FAB) calcd for $\text{C}_{115}\text{H}_{90}\text{N}_{10}$ 1610.74, obsd 1610.75; λ_{abs} (toluene) 424, 516, 551, 593, 650 nm.

All-Free Base Nonamer [(H₂P)₈H₂Pc]. To 2.5 mL of 1-pentanol was added 12 mg of lithium ribbon. The mixture was stirred under argon at 90 °C until all of the lithium was consumed. The resulting alkoxide solution was cooled to room temperature, and 25 mg of **5** was added. The reaction mixture was then heated to 145 °C and stirred under argon for 2 h. After being cooled to room temperature, the green mixture was poured into a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ (5:1:0.1, 20 mL), and the precipitate formed was collected by centrifugation and washed with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1). The crude compound obtained was then dissolved in toluene, and loaded onto a silica gel column (3.5 \times 25 cm). Elution with toluene afforded a green-brown band, which upon removal of the solvent and washing with methanol gave 8.5 mg (34%) of purple solid: ^1H NMR (CDCl_3) δ -2.72 ~ -2.56 (m, 18 H), 1.54–1.85 (m, 120 H), 2.40–2.61 (m, 60 H), 7.03–7.26 (m, 40 H), 7.97–8.38 (m, 48 H), 8.63–8.82 (m, 64 H), 9.46 (br, 12 H); LD-MS calcd av mass for $\text{C}_{460}\text{H}_{362}\text{N}_{40}$ 6450.1, obsd 6459.4; λ_{abs} (log ϵ) (toluene) 424 (6.4, fwhm = 19 nm), 516 (5.3), 595 (4.8), 652 (5.0), 688 (5.3), 723 (5.4) nm.

All-Zinc Nonamer [(ZnP)₈ZnPc]. To 2.5 mL of 1-pentanol was added 12 mg of lithium ribbon. The mixture was stirred at 90 °C until all of the lithium was consumed. At this point the alkoxide solution was cooled to room temperature, and 25 mg of **5** was added. The reaction mixture was then heated to 145 °C and stirred under argon for 2 h. Then the temperature was lowered to 80 °C, and 50 mg of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was added. The reaction mixture was allowed to stir for an additional 2 h at 80 °C. The reaction mixture was then cooled to room temperature and poured into a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1, 20 mL), and the precipitate formed was collected by centrifugation and washed with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1). The crude com-

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pound obtained was then dissolved in toluene/ethyl acetate (20:1) and loaded onto a silica gel column (3.5 × 25 cm). Elution with toluene/ethyl acetate (20:1) afforded a green-brown band, which upon removal of the solvent gave 7.5 mg (28%) of purple solid: $^1\text{H NMR}$ (THF- d_6) δ 1.77, 1.86 (m, 120 H), 2.45, 2.60 (m, 60 H), 7.20–7.29 (m, 40 H), 7.80–8.34 (m, 48 H), 8.62–9.00 (m, 64 H), 9.40–9.75 (m, 12 H); LD-MS calcd av mass for $\text{C}_{460}\text{H}_{344}\text{N}_{40}\text{Zn}_9$ 7020.5, obsd 7022.7; λ_{abs} (log ϵ) (toluene) 429 (6.4, fwhm = 20 nm), 551 (5.3), 591 (4.6), 631 (4.7), 701 (5.5) nm.

All-Magnesium Nonamer [(MgP) $_8$ MgPc]. (1) Cyclotetramerization in the Presence of DBU. Samples of **5** (25 mg), MgCl_2 (25 mg), and DBU (two drops) were added to a 5 mL flask containing *o*-dichlorobenzene (1 mL), the mixture was stirred for 2 min, and then 1-pentanol (1 mL) was added. The resulting mixture was heated at reflux with stirring under an argon atmosphere for 48 h. After being cooled to room temperature, the green reaction mixture was poured into a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1, 15 mL), and the precipitate formed was collected by centrifugation and washed with methanol. The crude compound obtained was then dissolved in toluene/ethyl acetate (20:1), and loaded onto an alumina column (grade V, 3 × 20 cm). Elution with toluene/ethyl acetate (20:1) first removed a red band, and elution with toluene/ethyl acetate (10:1) afforded the desired compound as a green band. Further purification was achieved by chromatography of a sample in THF on a preparative SEC column (3 × 45 cm). Gravity elution afforded the desired compound as the first (green) band, which upon removal of the solvent gave 0.8 mg (3.1%) of a purple solid. The same procedure with **Mg₂-5** (25 mg, prepared by treatment with MgI_2 in CH_2Cl_2 in the presence of DIEA)²⁵ afforded 1.3 mg (5.0%) of purple solid.

(2) Cyclotetramerization in the Presence of Lithium Pentoxide. To 2.5 mL of 1-pentanol was added 12 mg of lithium ribbon. The mixture was stirred at 90 °C until all of the lithium was consumed. The resulting alkoxide solution was cooled to room temperature, and 25 mg of **5** was added. The reaction mixture was then heated to 145 °C and stirred under argon for 2 h. Then the temperature was lowered to 80 °C, and 30 mg of MgCl_2 was added. The reaction mixture was allowed to stir for an additional 2 h at 80 °C. The reaction mixture was then cooled to room temperature and poured into a solution of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1, 20 mL), and the precipitate formed was collected by centrifugation and washed with $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (5:1). The crude compound obtained was then dissolved in toluene/ethyl acetate (10:1), and loaded onto an alumina column (grade V, 3.5 × 25 cm). Elution with toluene/

ethyl acetate (10:1) afforded a green band. Further purification was achieved by chromatography in THF on a preparative SEC column (3 × 45 cm). Gravity elution afforded the desired compound as the first (green) band, which upon removal of the solvent gave a purple solid (8.1 mg). The solid was a partially magnesiated nonamer as evidenced by absorption spectroscopy. Treatment of this material with MgI_2 in CH_2Cl_2 in the presence of DIEA²⁵ gave 7.6 mg (30% overall yield) of purple solid.

(3) Metalation of (H₂P) $_8$ H₂Pc. To a solution of (H₂P) $_8$ H₂Pc (6.9 mg) in CH_2Cl_2 (2 mL) were added MgI_2 (240 mg) and DIEA (300 μL).²⁵ The reaction mixture was stirred magnetically at room temperature overnight under an argon atmosphere. The dark green mixture was then diluted with CH_2Cl_2 (25 mL), washed with NaHCO_3 (5%, 3 × 25 mL), dried (Na_2SO_4), and filtered and the solvent removed under reduced pressure. Column chromatography on alumina (grade V) eluting with toluene/ethyl acetate (10:1) gave the product as a purple solid. The solid was suspended in methanol, centrifuged, and dried under vacuum, affording 6.8 mg (96%): $^1\text{H NMR}$ (THF- d_6) δ 1.88, 1.93 (m, 120 H), 2.60 (m, 60 H), 7.25–7.34 (m, 40 H), 7.03–8.34 (m, 48 H), 8.54–8.89 (m, 64 H), 9.64–9.96 (m, 12 H); LD-MS calcd av mass for $\text{C}_{460}\text{H}_{344}\text{N}_{40}\text{Mg}_9$ 6650.8, obsd 6650.8; λ_{abs} (log ϵ) (toluene) 429 (6.2, fwhm = 22 nm), 566 (5.1), 610 (4.9), 636 (4.6), 706 (5.1) nm.

All-Zinc Pentamer [(ZnP) $_4$ ZnPc]. A sample of 32.0 mg of **1** in 2.5 mL of 1-pentanol was treated in a fashion identical with that for **5** in the synthesis of (ZnP) $_8$ ZnPc, affording 19.8 mg (58.0%) of purple solid. The analytical data were identical to those reported previously.¹³

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Supporting Information Available: $^1\text{H NMR}$ and LD-MS spectra for all porphyrins and porphyrin–phthalocyanine arrays, and absorption and fluorescence spectra for all porphyrin–phthalocyanine arrays. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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