Soluble Synthetic Multiporphyrin Arrays. 1. Modular Design and Synthesis

Richard W. Wagner, Thomas E. Johnson, and Jonathan S. Lindsey*

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

Received May 14, 1996[⊗]

Abstract: A set of porphyrin building blocks has been developed for the construction of light-harvesting model compounds and related molecular photonic devices. The porphyrins are facially encumbered to enhance solubility in organic solvents, are employed in a defined metalation state (free base (Fb) or zinc chelate), and bear peripheral functional groups such as iodo or ethyne for joining the porphyrins via covalent bonds. The coupling of an iodophenylporphyrin and an ethynylphenylporphyrin via mild Pd-mediated reactions (2−4 mM of each porphyrin in toluene/triethylamine (5:1) with $Pd_2(dba)_3$ and $AsPh_3$ at 35 °C for 2 h) yields the corresponding diphenylethyne-linked multiporphyrin array in 70−80% yield. The arrays are easily purified by a sequence of flash silica chromatography, preparative size exclusion chromatography, and gravity elution silica chromatography. The diphenylethyne linkers give a center-to-center separation of the porphyrins of ∼20 Å. Model light-harvesting compounds are easily prepared using Zn and Fb porphyrin building blocks. In order to investigate the role of the linker in through-bond electronic communication, and the effect of through-bond electronic communication on the rates and yields of photoinduced energy transfer in the arrays, four ZnFb dimers have been prepared that have a systematic increase in steric hindrance in the diphenylethyne unit. The presence of steric hindrance inhibits rotation of the phenyl group toward coplanarity with the porphyrin, thereby modulating the electronic communication. A linear ZnFbZn trimer and a right-angle ZnFbZn trimer have been prepared to probe the effects of geometry on electronic communication pathways. A linear ZnZnFb trimer has been synthesized to investigate the photodynamics of energy migration among isoenergetic zinc porphyrins. These multiporphyrin arrays have sufficient solubility (∼5 mM) for routine handling in organic solvents such as toluene, CH_2Cl_2, or $CHCl_3$, and can be examined spectroscopically (1−10 μM) in diverse solvents such as tetrahydrofuran, acetone, dimethyl sulfoxide, and castor oil. This building block approach should make diverse multiporphyrin arrays readily available.

Introduction

Natural photosynthetic systems employ elaborate light-harvesting antenna complexes, which absorb low intensity sunlight (∼280−900 nm) and funnel energy to the reaction centers. The light-harvesting complexes consist of large numbers of chlorophylls (or bacteriochlorophylls) and accessory pigments held in close proximity, usually in association with protein scaffoldings. The absorption of a photon by a pigment in the antenna complexes is followed by migration of the excited state among the pool of pigments until a reaction center is reached. Energy transfer can occur over long distances and involve large numbers of chromophores, yet is extraordinarily rapid (<100 ps) and has high quantum efficiency. An in-depth understanding of the molecular origins of light-harvesting phenomena has been difficult to acquire, mainly because the natural antenna complexes encapsulate large numbers of several types of pigments in self-assembling proteins that in turn are embedded in membranes.[1]

Many issues concerning the origins of efficient light-harvesting phenomena in natural systems remain unclear. Consideration of the *de novo* molecular design of light-harvesting systems highlights a broader range of unknowns: (1) What types of pigments are appropriate and how do their electronic, photophysical, and photochemical properties affect light-harvesting efficiency? (2) How does energy migration depend on the 3-dimensional organization (distance, orientation, and packing patterns) of the pigments? (3) What are the mechanisms of electronic communication among pigments, how is electronic communication affected by the local medium, and how is electronic communication altered in synthetic arrays that have covalent connections between pigments versus those with strictly non-covalent interactions? Most importantly, what types of interactions provide efficient excited-state energy transfer while simultaneously avoiding electron-transfer quenching processes? (4) How many pigments in an array can function as an antenna, and over what molecular distances can energy migration occur? (5) Can energy-migration efficiency be improved by structural alterations or energy gradients, and what are the design constraints for achieving vectorial energy migration? These questions are central to an understanding of light-harvesting processes in photosynthetic organisms and to realizing the objective of harnessing solar energy. Addressing these questions can best be accomplished with synthetic model systems. Furthermore, the ability to control and manipulate energy-transfer processes in synthetic systems may also form the basis for the design of a variety of molecular photonic devices whose properties transcend photosynthesis. The development of molecular-scale wires, gates, switches, sensors, energy funnels, and related devices utilizing energy transfer may lay the foundation for molecular-scale information-processing systems.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

(1) Larkum, A. W. D.; Barrett, J. *Adv. Bot. Res.* **1983**, *10*, 1−219. *Photosynthetic Light-Harvesting Systems*, Scheer, H., Siegried, S., Eds.; W. de Gruyter: Berlin 1988. Mauzerall, D. C.; Greenbaum, N. L. *Biochim. Biophys. Acta* **1989**, *974*, 119−140. Hunter, C. N.; van Grondelle, R.; Olsen, J. D. *Trends Biochem. Sci.* **1989**, *14*, 72−76. McDermott, G.; Prince, S. M.; Freer, A. A.; Hawethornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517−521. Karrasch, S.; Bullough, P. A.; Ghosh, R. *EMBO J.* **1995**, *14*, 631−638.

S0002-7863(96)01611-3 CCC: $12.00

The challenge of creating model systems for energy-transfer studies has led to many different approaches. Energy transfer in assemblies of porphyrins has been studied in lipid bilayers,[2] amorphous films,[3] monolayers,[4] coated microspheres,[5] and Langmuir−Blodgett multilayers.[6] These non-covalent assemblies are synthesized easily, involve large numbers of visible-absorbing chromophores, but often afford insufficient structural control. Energy-transfer processes among pendant chromophores in polymers have been characterized.[7] Covalently-linked systems for tests of the Forster theory of resonance energy transfer have been developed that involve two UV-absorbing chromophores held at defined distances.[8] A synthetic hemoglobin has been prepared containing four zinc−chlorophyllide molecules at defined locations in place of the hemes.[9] An ideal model system would afford the dual capabilities of incorporating a large and exact number of visible-absorbing pigments of known photophysical properties, and exercising precise structural control over the entire ensemble of pigments.

Two promising approaches for achieving this ideal and thereby addressing the issues outlined above are the self-assembly of pigments bearing molecular recognition units and the synthesis of covalent arrays of pigments. Balzani and coworkers have pioneered the self-assembly of visible-absorbing metal coordination compounds.[10] A few energy transfer model systems have been prepared involving the self-assembly of porphyrins[11] or porphyrins with other chromophores such as sapphyrins[12] or dansyl amides.[13] Far more covalent arrays containing two or more porphyrins have been prepared and their energy transfer properties characterized.[14−16] In addition, covalent systems have been prepared containing porphyrins and energy transfer donors such as anthracenyl polyenes,[17] boron−dipyrromethenes,[16,18] carbocyanines,[19] carotenoids,[20] polyynes,[21] and ruthenium coordination complexes (triplet transfer),[22] as have covalent systems containing porphyrins and energy transfer acceptors such as tricarbocyanines,[19] carotenoids (triplet transfer),[20] chlorins,[23] phthalocyanines,[24] and sapphyrins.[25] A recent system describes chlorin−chlorin energy transfer.[26] Moore has devised a dendritic antenna that is architecturally defined with a vectorial organization of numerous phenylethyne-based chromophores, though the absorption is predominantly in the ultraviolet.[27] In order to investigate visible light-harvesting phenomena in a systematic manner, we have developed a covalent building block approach for the synthesis of multiporphyrin arrays.

Molecular Design

Synthetic porphyrins share many of the general structural, chemical, redox, and photophysical features with the naturally-

(2) Clapp, P. J.; Armitage, B.; Roosa, P.; O'Brien, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 9166−9173. Nango, M.; Iida, K.; Kawakita, T.; Matsuura, M.; Harada, Y.; Yamashita, K.; Tsuda, K.; Kimura, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 545−547.

(3) Kampas, F. J.; Gouterman, M. *J. Luminescence* **1976**, *14*, 121−129.

(4) Tweet, A. G.; Bellamy, A. D.; Gaines, G. L., Jr. *J. Chem. Phys.* **1964**, *41*, 2068−2077. Shimomura, M.; Hamada, Y.; Onosato, T. *Thin Solid Films* **1988**, *160*, 287−297.

(5) Cellarius, R. A.; Mauzerall, D. *Biochim. Biophys. Acta* **1966**, *112*, 235−255.

(6) Langmuir, I.; Schaefer, V. J. *J. Am. Chem. Soc.* **1937**, *59*, 2075−2076. Schick, G. A.; Schreiman, I. C.; Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 1344−1350.

(7) Guillet, J. In *Polymer Photophysics and Photochemistry. An Introduction to the Study of Photoprocesses in Macromolecules*, Cambridge University Press: New York, 1985. Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469−1482. Strouse, G. F.; Worl, L. A.; Younathan, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 9101−9102. Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6441−6442.

(8) Haugland, R. P.; Yguerabide, J.; Stryer, L. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 23−30. Stryer, L.; Haugland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 719−726.

(9) Moog, R. S.; Kuki, A.; Fayer, M. D.; Boxer, S. G. *Biochemistry* **1984**, *23*, 1564−1571. Kuki, A.; Boxer, S. G. *Biochemistry* **1983**, *22*, 2923−2933.

(10) Balzani, V.; Ballardini, R. *Photochem. Photobiol.* **1990**, *52*, 409−416.

(11) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704−714. Hunter, C. A.; Sarson, L. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2313−2316.

(12) Král, V.; Springs, S. L.; Sessler, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 8881−8882.

(13) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408−9410.

(14) (a) Schwarz, F. P.; Gouterman, M.; Muljiani, Z.; Dolphin, D. H. *Bioinorg. Chem.* **1972**, *2*, 1−32. (b) Anton, J. A.; Loach, P. A.; Govindjee *Photochem. Photobiol.* **1978**, *28*, 235−242. (c) Selensky, R.; Holten, D.; Windsor, M. W.; Paine, J. B., III; Dolphin, D.; Gouterman, M.; Thomas, J. C. *Chem. Phys.* **1981**, *60*, 33−46. (d) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A. *Tetrahedron Lett.* **1982**, *23*, 3215−3218. (e) Mialocq, J. C.; Giannotti, C.; Maillard, P.; Momenteau, M. *Chem. Phys. Lett.* **1984**, *112*, 87−93. (f) Regev, A.; Galili, T.; Levanon, H.; Harriman, A. *Chem. Phys. Lett.* **1986**, *131*, 140−146. (g) Gonen, O.; Levanon, H. *J. Chem. Phys.* **1986**, *84*, 4132−4141. (h) Brookfield, R. L.; Ellul, H.; Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 219−233. (i) Davila, J.; Harriman, A.; Milgrom, L. R. *Chem. Phys. Lett.* **1987**, *136*, 427−430. (j) Noblat, S.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron Lett.* **1987**, *28*, 5829−5832. Chardon-Noblat, S.; Sauvage, J.-P.; Mathis, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 593−595. (k) Rempel, U.; Von Maltzan, B.; Von Borczyskowski, C. *Chem. Phys. Lett.* **1990**, *169*, 347−354. (l) Osuka, A.; Maruyama, K.; Yamazaki, I.; Tamai, N. *Chem. Phys. Lett.* **1990**, *165*, 392−396. (m) Osuka, A.; Nagata, T.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y. *Chem. Phys. Lett.* **1991**, *185*, 88−94. (n) Gust, D.; Moore, T. A.; Moore, A. L.; Gao, F.; Luttrull, D.; DeGraziano, J. M.; Ma, X. C.; Makings, L. R.; Lee, S-J.; Trier, T. T.; Bittersmann, E.; Seely, G. R.; Woodward, S.; Bensasson, R. V.; Rougée, M.; De Schryver, F. C.; Van der Auweraer, M. *J. Am. Chem. Soc.* **1991**, *113*, 3638−3649. (o) Gust, D.; Moore, T. A.; Moore, A. L.; Leggett, L.; Lin, S.; DeGraziano, J. M.; Hermant, R. M.; Nicodem, D.; Craig, P.; Seely, G. R.; Nemeth, R. A. *J. Phys. Chem.* **1993**, *97*, 7926−7931. (p) Tamiaki, H.; Nomura, K.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3062−3068. (q) Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, *115*, 4577−4589. (r) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618−4628. (s) DeGraziano, J. M.; Liddell, P. A.; Leggett, L.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1994**, *98*, 1758−1761. (t) Tamiaki, H.; Nomura, K.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1863−1871. (u) Harriman, A.; Heitz, V.; Ebersole, M.; van Willigen, H. *J. Phys. Chem.* **1994**, *98*, 4982−4989. (v) Iida, K.; Nango, M.; Okada, K.; Hikita, M.; Matsuura, M.; Kurihara, T.; Tajima, T.; Hattori, A.; Ishikawa, S.; Yamashita, K.; Tsuda, K.; Kurono, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1959−1968. (w) Osuka, A.; Tanabe, N.; Kawabata, S.; Yamazaki, I.; Nishimura, Y. *J. Org. Chem.* **1995**, *60*, 7177−7185.

(15) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519−7520.

(16) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760.

(17) Effenberger, F.; Schlosser, H.; Bauerle, P.; Maier, S.; Port, H.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 281−284. Wurthner, F.; Vollmer, M. S.; Effenberger, F.; Emele, P.; Meyer, D. U.; Port, H.; Wolf, H. C. *J. Am. Chem. Soc.* **1995**, *117*, 8090−8099. Bonfantini, E. E.; Officer, D. L. *J. Chem. Soc., Chem. Commun.* **1994**, 1445−1446.

(18) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996−3997.

(19) Lindsey, J. S.; Brown, P. A.; Siesel, D. A. *Tetrahedron* **1989**, *45*, 4845−4866.

(20) Gust, D.; Moore, T. A.; Moore, A. L.; Devadoss, C.; Liddell, P. A.; Hermant, R.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. *J. Am. Chem. Soc.* **1992**, *114*, 3590−3603. Moore, T. A.; Gust, D.; Moore, A. L. *Pure Appl. Chem.* **1994**, *66*, 1033−1040.

(21) Maruyama, K.; Kawabata, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3498−3507.

(22) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679−5690.

(23) Osuka, A.; Marumo, S.; Maruyama, K.; Mataga, N.; Tanaka, Y.; Taniguchi, S.; Okada, T.; Yamazaki, I.; Nishimura, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 262−276. Osuka, A.; Marumo, S.; Mataga, N.; Taniguchi, S.; Okada, T.; Yamazaki, Y.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1996**, *118*, 155−168.

(24) Tran-Thi, T. H.; Desforge, C.; Thiec, C.; Gaspard, S. *J. Phys. Chem.* **1989**, *93*, 1226−1233.

(25) Sessler, J. S.; Brucker, E. A.; Král, V.; Harriman, A. *Supramolecular Chemistry*; Gordon and Breach Science Publishers SA: New York, 1994; Vol. 4, pp 35−41.

(26) Osuka, A.; Marumo, S.; Wada, Y.; Yamazaki, I.; Yamazaki, T.; Shirakawa, Y.; Nishimura, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2909−2915.

(27) Xu, J.; Moore, J. S. *Acta Polym.* **1994**, *45*, 83−87.

occurring chlorophylls and bacteriochlorophylls. A chief difference, however, is that porphyrins absorb strongly only in the blue while chlorins and bacteriochlorins absorb strongly both in the blue and in the red regions of the solar spectrum. This distinction arises from the differing symmetries of the metalloporphyrin (D_{4h}), chlorin (C_{2v}), or bacteriochlorin (D_{2h}) macrocycles (considered for the unsubstituted planar chromophores). In addition to the enhanced absorption in the red, the symmetry of the hydroporphyrins also may facilitate vectorial energy transfer. Though hydroporphyrins ultimately are more desirable for incorporation in light-harvesting arrays, the more readily accessible synthetic porphyrins are suitable for beginning to investigate a number of issues concerning light-harvesting phenomena.

Our building block approach was designed with the goal of constructing arrays composed of large numbers of porphyrins in defined geometries.[28,29] Two anticipated problems that we sought to avoid included insolubility of the multiporphyrin arrays and photoinduced electron transfer quenching reactions among the porphyrins. The solubility problem can be acute; indeed, one early pentameric porphyrin array was practically insoluble,[30] and some architecturally elegant arrays made more recently also have been plagued by poor solubility.[31−33] Approaches to impart solubility to multiporphyrin arrays include incorporation of long alkyl groups at the β-pyrrole positions,[14v] incorporation of a variety of groups at the more accessible *meso*-positions including alkyl groups,[34] 3,5-di-*tert*-butylphenyl groups,[14j,35] 4-alkoxycarbonylphenyl groups with long-chain alkyl units at the ester,[31,33] and introduction of *ortho*-disubstituted phenyl groups.[15,16,28,36] A deep understanding of the factors that favor energy transfer over electron transfer is not available, however one approach for limiting electron transfer is to arrange the porphyrins at fixed, substantial distances where the electronic interactions are relatively weak. Gaining a deeper understanding of the design of energy transfer systems is a central goal of this work.

The porphyrin building blocks we have devised incorporate several distinctive features (Figure 1). Each porphyrin is in a defined metalation state (metal or free base), has *meso*-phenyl groups which can be substituted in the ortho positions, and bears one or more peripheral iodo or ethyne groups. The use of free base or metalloporphyrin building blocks enables the fabrication of arrays with predesignation of the metalation state of each porphyrin. The introduction of *ortho*-substituents such as methyl, methoxy or benzyloxy[36] is based on the notion that such facially-encumbered porphyrins are less able to undergo cofacial aggregation and hence should have greater solubility in organic solvents. Though it is often difficult to pinpoint the structural origins of why some compounds have high solubility and others do not, most of these facially encumbered porphyrins have

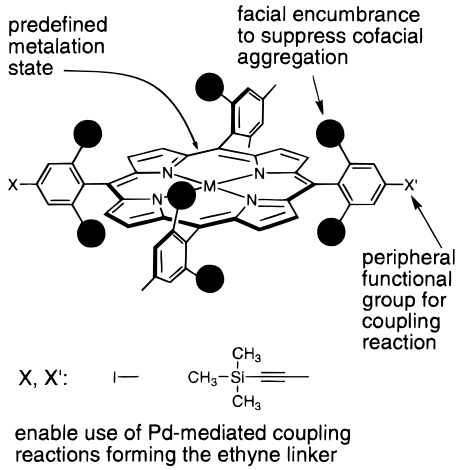


Figure 1. Schematic of a linear porphyrin building block.

sufficient solubility in a variety of organic solvents for routine synthesis, manipulation, and characterization. Using *ortho*-substituents leaves the *para*-positions unhindered, where the peripheral functional groups provide sites for joining the porphyrins in a covalent manner. The use of iodophenyl and ethynylphenyl groups yields a diphenylethyne linker when porphyrins are joined, causing the porphyrins to be separated by ~20 Å center-to-center. In principle, the synthesis of diverse arrays can be done by rational combination of a small set of different building blocks, in the same way that diverse proteins are available from a basis set of amino acids. The modular nature of this building block approach has been discussed in depth.[29]

The synthetic methods that make this building block approach possible include (1) a synthesis of *meso*-porphyrins that is compatible with a wide variety of precursor aldehydes,[37] including the *ortho*-disubstituted benzaldehydes that yield facially-encumbered porphyrins,[38] (2) a one-flask synthesis of *meso*-dipyrromethanes that enables a simple synthesis of *trans*-substituted porphyrins[39] and also boron−dipyrromethene dyes,[40] (3) general methods for preparing metalloporphyrins,[41] and (4) Pd-mediated coupling reactions that are optimized for joining the free base and metalloporphyrin building blocks under mild conditions in dilute solution without altering the metalation state of each porphyrin.[42] Powerful analytical methods that are invaluable for carrying out this synthesis program include the ability to separate the larger arrays by size exclusion chromatography (SEC) and to characterize them by laser desorption mass spectrometry. The mild, neutral to slightly basic nature of all experimental conditions in this approach ensures the integrity of each free base or metalloporphyrin in the array.

This modular approach has been used to construct a star-like array of five porphyrins (**1**)[15] as well as a linear array of four porphyrins and one accessory pigment (Figure 2). The latter functions as a molecular photonic wire (**2**).[16] A photon of light is absorbed at the input end and a photon of light is then emitted

(28) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941−8968.

(29) Lindsey, J. S. In *Modular Chemistry*; Michl, J., Ed.; NATO Series, Kluwer Academic Publishers: The Netherlands, in press.

(30) Wennerstrom, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129−1132.

(31) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972−981.

(32) Osuka, A.; Tanabe, N.; Zhang, R.-P.; Maruyama, K. *Chem. Lett.* **1993**, 1505−1508. Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054−3059.

(33) Anderson, H. L.; Walter, C. J.; Vidal-Ferran, A.; Hay, R. A.; Lowden, P. A.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2275−2279.

(34) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63−65.

(35) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569−1571.

(36) Wagner, R. W.; Breakwell, B. V.; Ruffing, J.; Lindsey, J. S. *Tetrahedron Lett.* **1991**, *32*, 1703−1706. Wagner, R. W.; Lindsey, J. S.; Turowska-Turk, I.; Scheidt, W. R. *Tetrahedron* **1994**, *50*, 11097−11112.

(37) Lindsey, J. S. In *Metalloporphyrin-Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer Academic Publishers: The Netherlands, 1994; pp 49−86. Lindsey, J. S.; MacCrum, K. A.; Tyhonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 579−587.

(38) Lindsey J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828−836.

(39) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427−11440.

(40) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1996**, *68*, 1373−1380.

(41) Buchler, J. W. In *Porphyrins and Metalloporphyrins;* Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 157−231. Buchler, J. W. In *The Porphyrins;* Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, pp 389−483.

(42) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266−5273.

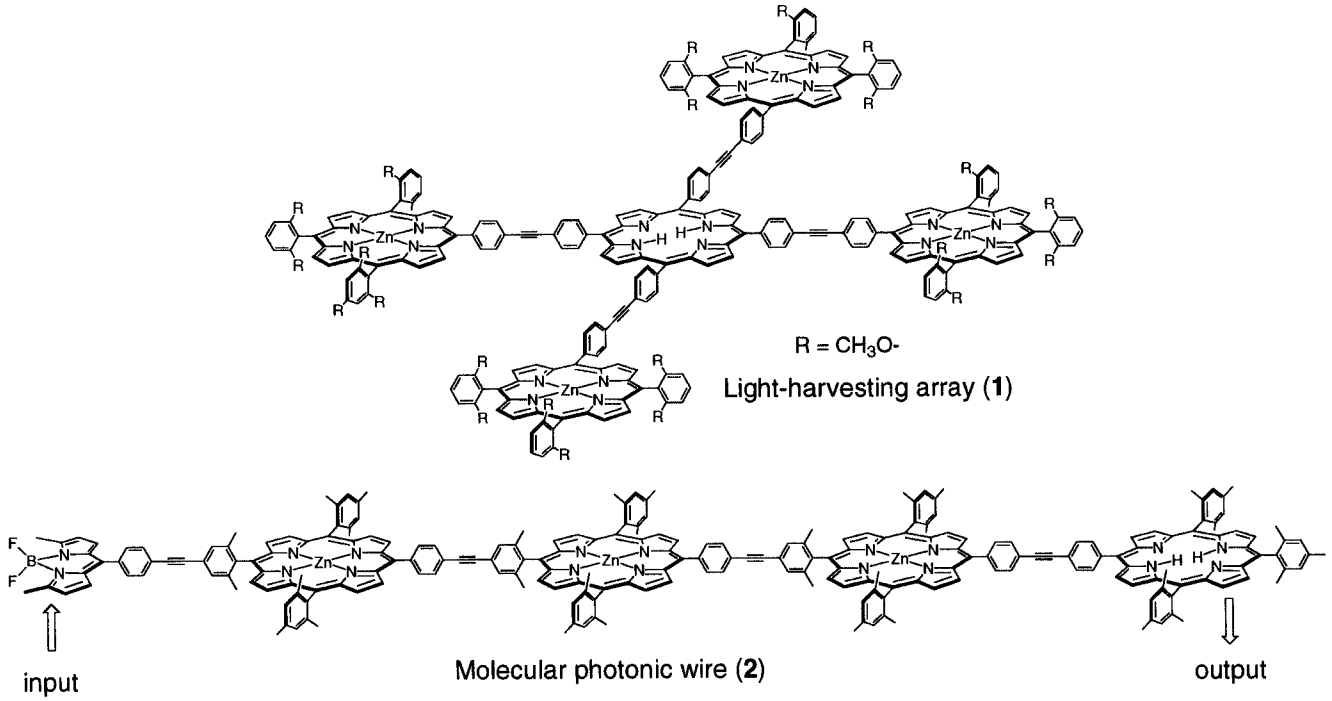


Figure 2. Light-harvesting array and a molecular photonic wire.

at the opposite (output) end of the same molecule. The quantum efficiency of energy migration from input to output is 76%. More recently two molecular optoelectronic gates have been devised based on the same general molecular architecture as the wire, and these also have been constructed using the same building block approach.[18] These porphyrin arrays have controlled inter-porphyrin distances yet exhibit high solubility in good organic solvents (5 mM in toluene or CH_2Cl_2). This building block approach is not restricted to the synthesis of hydrophobic compounds and has recently been applied to the synthesis of amphipathic dimeric and trimeric arrays for incorporation in lipid bilayer assemblies.[43]

We selected the diphenylethyne linker at the outset of this work because we felt it would provide ample distance of separation (20 Å center-to-center) to avoid competing electron transfer quenching reactions while still permitting energy transfer among the porphyrins. Indeed, the diphenylethyne linker affords a weakly coupled system where the absorption bands of the porphyrin arrays are only slightly perturbed from those of the component porphyrins, yet single-step energy-transfer efficiencies are ≥90% with no discernible electron-transfer quenching. More recently we have learned that in spite of the large distance and the relatively unchanged absorption spectra, the diphenylethyne linker provides some through-bond electronic communication between the attached porphyrins.[44] Other porphyrin arrays have been prepared with ethyne or butadiyne linkages attached directly to the porphyrins, and these show profound shifts in the optical spectra.[31,45]

In designing the diphenylethyne-linked multiporphyrin arrays we attempted to place methyl groups at all *ortho*-phenyl positions allowable by the available synthetic methods with the sole aim of increasing the solubility of the arrays. In resonance Raman experiments of various arrays, however, Seth *et al.* observed an enhanced band due to the ethyne unit in the linker.[44] Further studies showed that the enhanced band was present with those diphenylethyne linkers (or monomers bearing the ethyne substituent) lacking *ortho*-phenyl substitution (**3**), but was absent with those diphenylethyne linkers substituted with 2,6-dimethyl groups (**4**). These studies suggested that the diphenylethyne unit mediates electronic communication between the porphyrins, and that rotation toward a more coplanar geometry of the diphenylethyne with the porphyrin(s) would enhance the communication and thereby increase the energy-transfer rate (Figure 3). Conversely, phenyl rings that have constrained rotation due to *ortho*-dimethyl substitution would have diminished electronic communication and should exhibit slower rates of energy transfer.

To investigate this hypothesis concerning structural control of energy transfer, we have prepared a set of dimeric arrays with a progressive increase in the steric hindrance in the diphenylethyne linkers. This set of dimers allows systematic probing of the effects of linker structure on the rates and yields of energy transfer. Zinc and free base porphyrins are employed in the arrays. Zinc porphyrins are used as they exhibit photophysical properties similar to those of magnesium porphyrins but have been more easily synthesized than magnesium porphyrins. Free base porphyrins absorb and emit at longer wavelengths than zinc porphyrins and serve as a convenient low-energy trap to which excited-state energy flows. Two trimers have been prepared to examine the role of geometry (linear, right-angle) on electronic communication among porphyrins. An additional trimer has been designed to investigate the rate of energy transfer among isoenergetic zinc porphyrins in an array. Finally we summarize the solubility properties of this family of arrays and related compounds. This paper describes the synthesis of these arrays, and the two companion papers investigate the photophysical properties[46] and the modes

(43) Nishino, N.; Wagner, R. W.; Lindsey, J. S. *J. Org. Chem.* In press.
(44) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578−10592.
(45) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366−370. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron* **1992**, *48*, 8781−8792. Arnold, D. P.; Nitschinsk, L. J. *Tetrahedron Lett.* **1993**, *34*, 693−696. Arnold, D. P.; James, D. A.; Kennard, C. H. L.; Smith, G. *J. Chem. Soc., Chem. Commun.* **1994**, 2131−2132. Anderson, S.; Martin, S. J.; Bradley, D. D. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 655−657. Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972−981. Gosper, J. J.; Ali, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1707−1708. Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105−1111. Lin, V. S.-Y.; Therien, M. J. *Chem. Eur. J.* **1995**, *1*, 645−651.

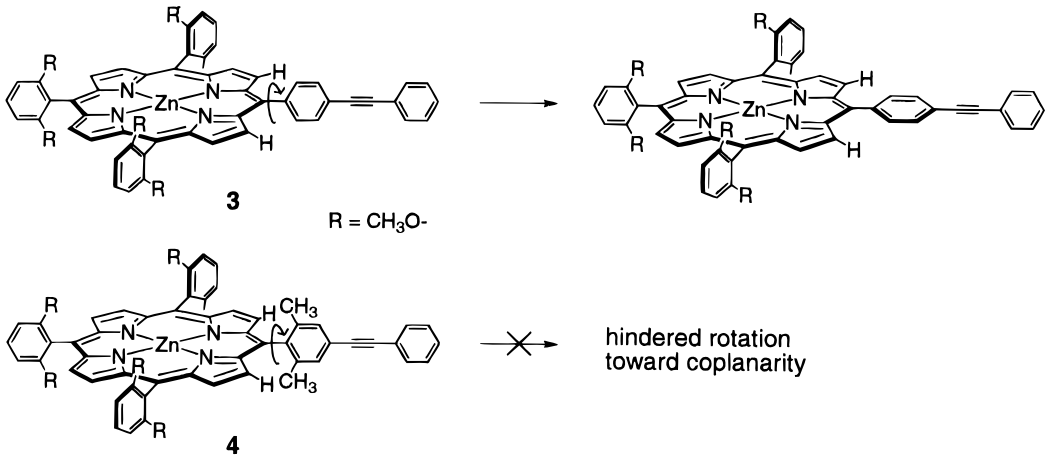
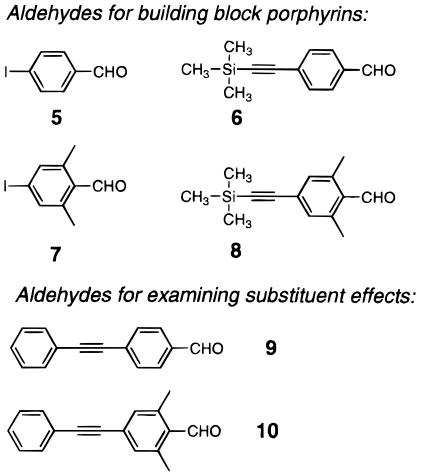


Figure 3. Effect of *ortho*-dimethyl groups on linker rotation.

Chart 1. Aldehyde Precursors to Porphyrins



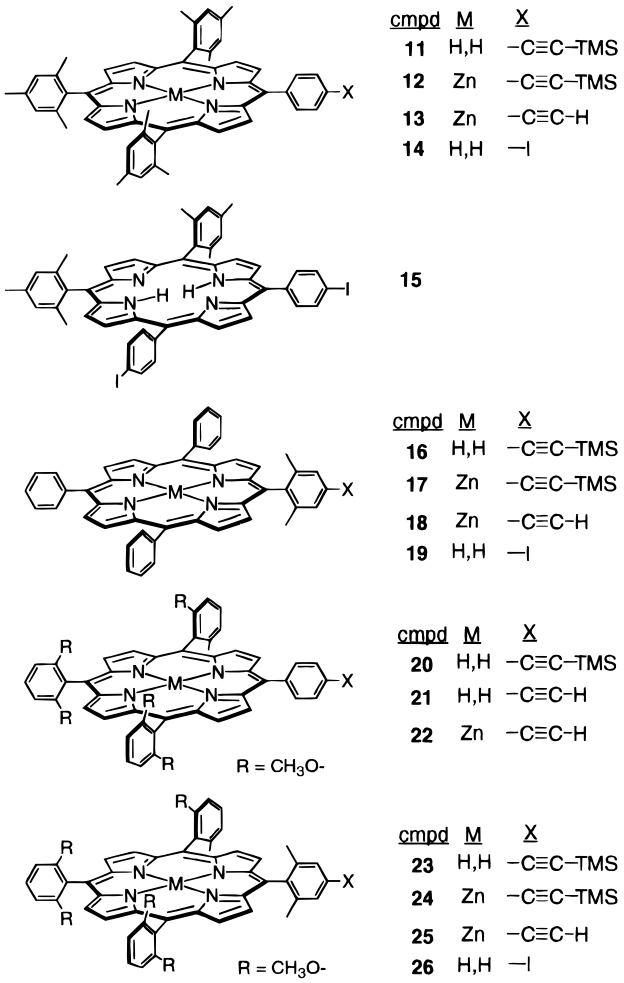
of electronic communication[47] in the same set of arrays. The results from these studies provide fundamental information for guiding the design of more sophisticated synthetic light-harvesting model compounds. This work is a prelude to addressing higher order organizational issues in light-harvesting systems, such as the 3-dimensional organization of pigments, channeling of energy migration, the role of energy gradations, and required photophysical properties of the pigments.

Results and Discussion

Synthesis of Porphyrin Building Blocks. The preparation of the porphyrin building blocks depends on the availability of the corresponding functionalized benzaldehydes. For preparing diphenylethyne linked arrays, the key benzaldehydes bear ethynes or iodo groups (Chart 1). 4-Iodobenzaldehyde (**5**) is commercially available, and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (**6**) is readily derived from **5** or from 4-bromobenzaldehyde. We have refined the syntheses of aldehydes **7** and **8**.[28] An improved diazotization of 2,6-dimethyl-4-iodoaniline afforded 2,6-dimethyl-4-iodobenzonitrile, the precursor to **7**, in 42% yield compared with 11% previously. Ethynylation of 2,6-dimethyl-4-bromobenzaldehyde via Pd-mediated coupling conditions under mild conditions (55 °C for 36 h) gave cleaner reaction mixtures with less higher-molecular weight material, affording **8** in 85% yield upon recrystallization from 2-propanol. These aldehydes enable the synthesis of a variety of porphyrin building blocks. In order to pinpoint the effects of substituents on the porphyrin ring, diphenylethyne carboxaldehydes (**9**, **10**) were prepared for the synthesis of the corresponding porphyrin model compounds.

Porphyrin building blocks bearing one functional group provide the basis for the synthesis of dimeric arrays. These types of porphyrins (Chart 2) can be obtained through mixed-aldehyde condensations using the two-step one-flask room

Chart 2. Porphyrin Bulding Blocks



(46) Paper 2 of this series: Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 11181−11193.

(47) Paper 3 of this series: Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194−11207.

(48) Little, R. G.; Anton, J. A.; Loach, P. A.; Ibers, J. A. *J. Heterocycl. Chem.* **1975**, *12*, 343−349.

temperature synthesis of porphyrins.[37,38] The method of mixed-aldehyde condensations with pyrrole affords a mixture of six porphyrins.[48] This approach is not elegant but is expedient if the desired porphyrin can be easily separated by chromatography. In general, the separability of these mixtures of porphyrins by adsorption chromatography depends on the different polarities of peripheral substituents, the different polarity of *ortho*-substituents, and the different amounts of facial encumbrance due to the presence of *ortho*-substituents.[28] In performing numerous mixed-aldehyde condensations, we have made the following observations:

(1) Condensation of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (**6**) and benzaldehyde with pyrrole affords a mixture of porphyrins that cannot be separated easily as the peripheral substituents (H, trimethylsilylethyne) have nearly identical polarities and neither aldehyde has *ortho*-substituents.

(2) Condensation of **6** and mesitaldehyde with pyrrole affords a mixture of porphyrins where each porphyrin (except the cis and trans) has different amounts of facial encumbrance; the components of this mixture closely chromatograph but separation can be achieved with repetitive column chromatography. The mono-ethynyl porphyrin **11** was obtained with some difficulty in this manner.[28]

(3) Condensation of 4-iodobenzaldehyde (**5**) and mesitaldehyde with pyrrole affords a mixture that is easily separable on a single adsorption column, due both to the differing degrees of facial encumbrance of the porphyrins and the slightly different polarities of the iodo and methyl groups. This approach readily afforded the mono-iodo porphyrin **14**, and other more highly iodinated porphyrins also can be obtained easily, such as the *cis*-diiodo-substituted porphyrin **15** (7% yield). The latter is the key building block for the synthesis of a right-angle trimeric array of porphyrins.

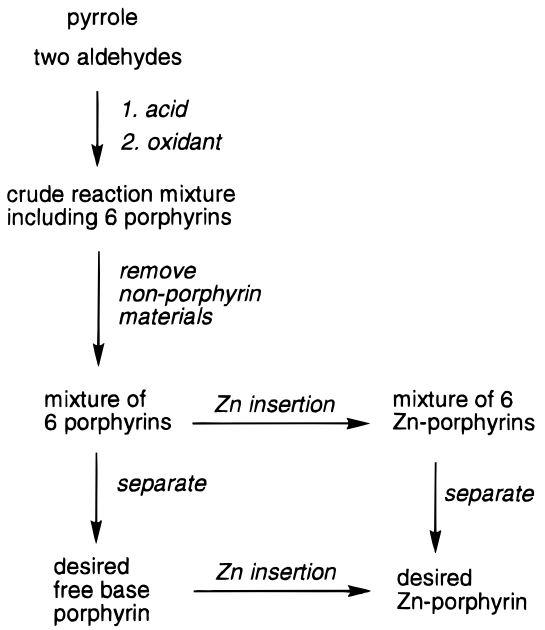
(4) Condensation of the *ortho*-dimethyl substituted benzaldehyde **7** (or **8**) and mesitaldehyde with pyrrole yields an inseparable mixture as each porphyrin has eight *ortho*-methyl groups. In contrast, condensation of **7** (or **8**) and benzaldehyde with pyrrole yields a separable mixture as each porphyrin (except the cis and trans) has different degrees of facial encumbrance. Thus condensation of benzaldehyde, **8**, and pyrrole gave **16** in 17% yield, while condensation of benzaldehyde, **7**, and pyrrole gave **19** in 13.5% yield. In each case one flash silica column was used to separate the porphyrins from unwanted side products, and a second flash silica column afforded separation of the various porphyrins. Porphyrins **16** and **19** each eluted as the fifth of the six porphyrin components in their respective mixtures.

(5) Condensation of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (**6**) and 2,6-dimethoxybenzaldehyde with pyrrole yields a crude reaction mixture from which the desired porphyrin (**20**) was isolated in 8% yield via a single flash silica chromatography column (similar results were obtained upon condensation with 4-iodobenzaldehyde and 2,6-dimethoxybenzaldehyde).[28] The polarity imparted by the *ortho*-methoxy groups dramatically eases the separation of this mixture of porphyrins.

(6) Condensation of the *ortho*-dimethyl substituted benzaldehyde **7** (or **8**) and 2,6-dimethoxybenzaldehyde with pyrrole yields a crude reaction mixture from which the desired porphyrin can be isolated via a single flash silica chromatography column. Although each porphyrin has substituents at all eight *ortho*-positions, the different polarity of the methoxy and methyl groups affords facile separation. Thus the mono-iodo porphyrin **26** and the mono-ethynyl porphyrin **23** were isolated in 4.8% and 4.4% yield, respectively.

In summary, it is not possible to easily obtain a mono- or trifunctionalized porphyrin building block via mixed condensations where both aldehydes have identical *ortho*-substituents (either all substituted or all unsubstituted) and nonpolar peripheral substituents (e.g., iodo or ethyne groups). Porphyrins that bear one iodo or ethyne group and three sites of facial encumbrance (**11** or **14**, derived from three mesitaldehyde molecules, and **6** or **5**) yet with similar polarity can be separated by repetitive chromatography. Porphyrins bearing only one site of facial encumbrance (**16** or **19**, derived from three benzaldehyde molecules and **8** or **7**) are more easily separated. Porphyrins that bear one ethyne (or iodo) group and three sites of facial encumbrance (**20**, derived from three 2,6-dimethoxybenzaldehyde molecules, and **6**) with polar groups can be separated easily by chromatography. Porphyrins with sets of *ortho*-substituents of considerably different polarity, as in the case of the methoxy-substituted porphyrins (**23**, **26**), also are separated with great ease.

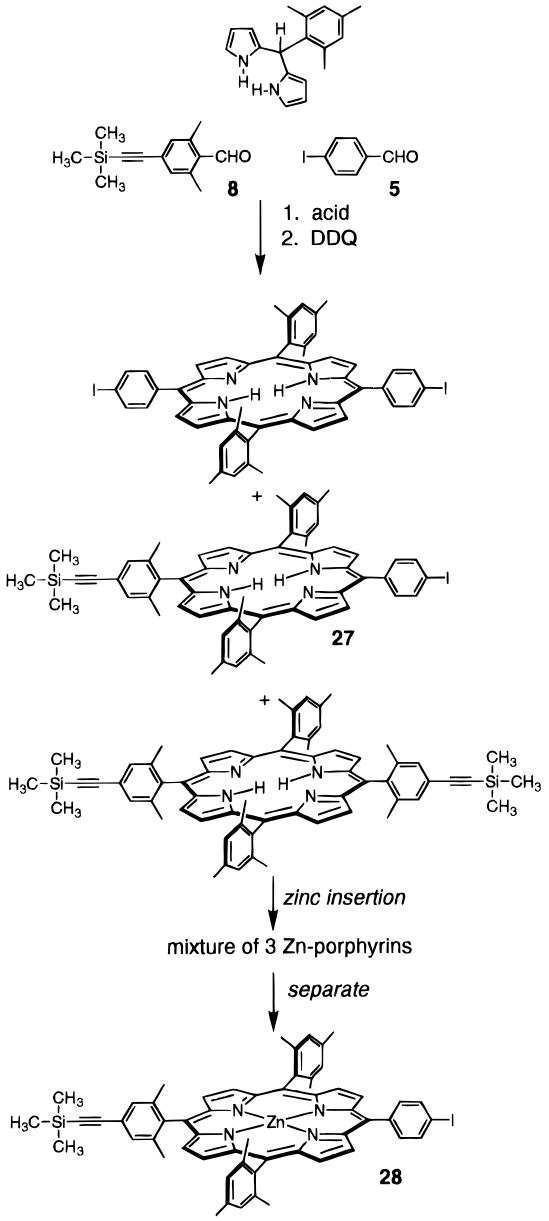
Scheme 1. Scheme for Preparing Porphyrin Building Blocks



The *ortho*-methoxy-substituted porphyrins were initially the most attractive as their separation is most straightforward. Though the ZnFb dimers exhibited good solubility in CH_2Cl_2 and other solvents, we subsequently found that the Zn_2 dimer having a hindered linker (prepared from **25** and **26**) had poor solubility in some electrochemical studies (*vide infra*). The family of *ortho*-methoxy-substituted porphyrins was abandoned for these studies and the more soluble mesityl-substituted porphyrin dimers were pursued. The desired mono-ethynyl porphyrin **11** is obtained with difficulty, however, and we sought a method to overcome this bottleneck.

To prepare the ZnFb dimers, one of the porphyrins is required as the zinc porphyrin. We found that metalation of the mixture of six porphyrins afforded the zinc porphyrins which could be easily separated via column chromatography (Scheme 1). Thus the crude mixture from a 2-L scale reaction of mesitaldehyde, aldehyde **6**, and pyrrole was concentrated and then passed over a flash silica column, yielding the mixture of free base porphyrins freed from reagents, byproducts, and open-chain oligopyrromethenes. This mixture was metalated with zinc. The resulting zinc porphyrins were separated on a single flash silica column, affording 280 mg of zinc mono-ethynyl porphyrin **12** in 12.4% overall yield. Given the two aldehydes the desired porphyrin can be obtained in ~2 days by this approach. The zinc mono-ethynyl porphyrin **12** can be demetalated to afford

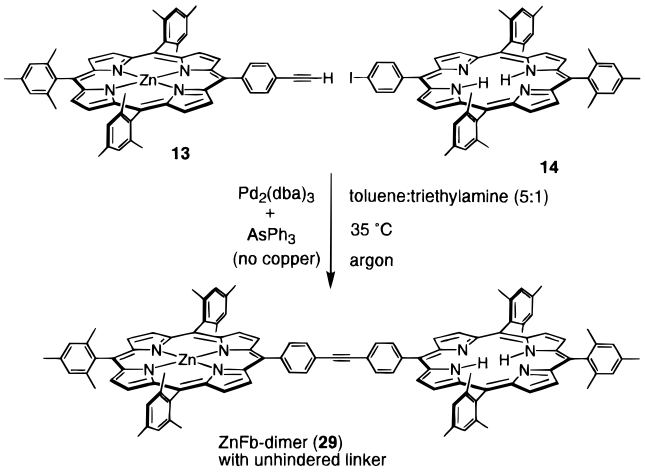
Scheme 2. Synthesis of a Porphyrin Building Block for Preparing Linear Arrays



the corresponding free base porphyrin **11** or can be deprotected forming **13** for use in the syntheses of arrays. In general, this approach is applicable for porphyrins that have peripheral and *ortho*-substituents that are nonpolar. The introduction of zinc imparts a polar site which enhances the affinity of the porphyrins for silica gel. The effects of facial encumbrance are accentuated as the interaction of the face of the zinc porphyrin with the chromatographic medium determines the affinity and the elution order of these otherwise nonpolar porphyrins. We find that even if the free base porphyrin **11** is desired, the separation of the zinc porphyrins and subsequent demetalation is the preferred route. The zinc porphyrins typically have the added advantage of higher solubility than the free base porphyrins.

In order to prepare linear arrays containing two or more porphyrins, as in the molecular wire **2**, a porphyrin building block with two different substituents in a *trans*-configuration is required. The iodo-ethynyl porphyrin **27**, which we previously synthesized,[39] meets these needs (Scheme 2). In the separation of the free base porphyrins on silica, the bis-ethyne and mono-ethyne porphyrins are not completely resolved and one or more alumina columns are required to isolate **27**. We

Scheme 3. Pd(0)-Catalyzed Synthesis of an Ethyne-Linked Porphyrin Dimer



have refined the synthesis of porphyrin **27** by separating the zinc porphyrins rather than the free base porphyrins. Thus the mixture of three porphyrins obtained from the 500-mL scale reaction of 2.5 mmol **8**, 2.5 mmol 4-iodobenzaldehyde (**5**), and 5 mmol *meso*-(mesityl)dipyrromethane was subjected to zinc insertion conditions and then chromatographed on flash silica gel. The three zinc porphyrins afforded distinct, non-overlapping chromatographic bands that were easily separated on a single flash silica column, and 280 mg (11%) of the zinc chelate **28** was obtained in a straightforward manner. Demetalation (0.03 M TFA in CH_2Cl_2) of **28** at room temperature afforded the free base porphyrin **27**.

In preparation for the coupling reactions the trimethylsilyl-protected porphyrins were deprotected at room temperature with tetrabutylammonium fluoride on silica, or with K_2CO_3 in THF/methanol. The use of K_2CO_3 is cleaner and generally gives higher yields than tetrabutylammonium fluoride on silica, though tetrabutylammonium fluoride on silica is used more frequently as most of these porphyrins lack adequate solubility in THF/methanol.

Synthesis of Dimeric Arrays. Porphyrin−porphyrin dimers are of interest for investigating the pairwise interactions of porphyrins in larger arrays. The preparation of the dimeric arrays relies on Pd-mediated coupling reactions of ethynyl porphyrins and iodo porphyrins (Scheme 3). Pd-mediated coupling reactions have often been performed at high concentrations and elevated temperatures with a copper reagent as a cocatalyst. To meet the constraints of porphyrin chemistry we refined this key Pd-mediated coupling reaction so that the porphyrins can be joined at modest temperature, in dilute solution of equimolar porphyrin reactants, in the absence of any copper reagents.[42] Thus the reaction of a free base iodoporphyrin (**14**, 5 mM) and a zinc ethynylporphyrin (**13**, 5 mM) with the Pd(0) reagent $Pd_2(dba)_3$ and $AsPh_3$ in toluene/triethylamine (5:1) at 35 °C under argon in standard glassware afforded the diphenylethyne-linked dimer **29** in 2 h in >70% yields. These conditions generate the Pd(0) reagent in situ and avoid the use of any copper cocatalysts. These conditions represent the outcome of a lengthy optimization study[42] and are superior to the more forcing conditions ($Pd(PPh_3)_4$ at ≥50 °C for 24 h) that we employed earlier.[28]

During the course of this work we sought to make sure that the Pd-coupling conditions were not inadvertently yielding any Pd porphyrins. Excess phenylacetylene and iodobenzene (0.01 M each) were subjected to these mild Pd-coupling conditions in the presence of *meso*-tetraphenylporphyrin (TPP, 0.001 M).

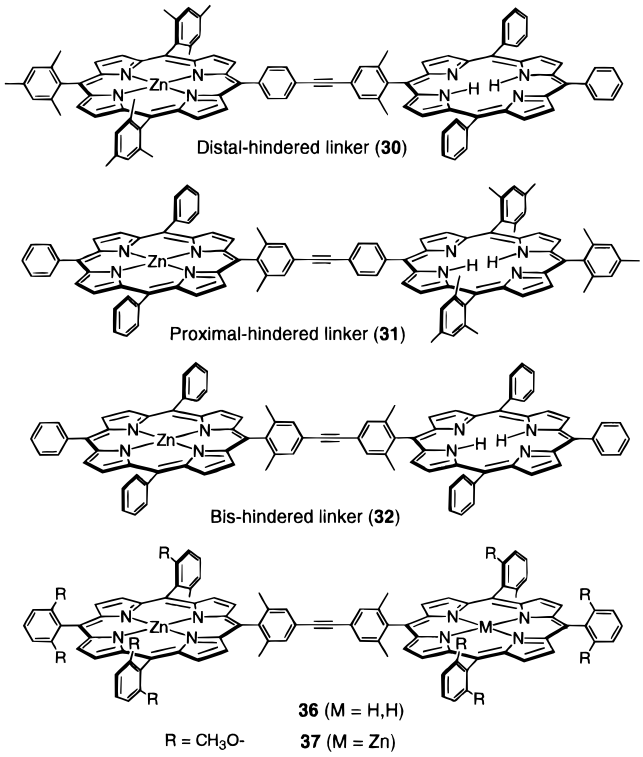
No PdTPP was observed by TLC analysis (silica, hexanes/CH_2Cl_2 (1:1), PdTPP R_f 0.7, TPP R_f 0.4) with calibrated standards of PdTPP; given the limits of detection the yield of PdTPP must be $\leq$0.05%. Preparative chromatography of this reaction mixture in an effort to isolate PdTPP (based on its known chromatographic retention factor) gave no PdTPP, indicating the yield of any Pd insertion into TPP is $\leq$0.0003%. Thus these Pd coupling conditions are compatible with free base porphyrins.

In the synthesis of ZnFb-dimer **29**, the milder coupling conditions give cleaner reaction mixtures with lesser amounts of high molecular weight materials and no detectable diphenylbutadiyne-linked dimer. The crude reaction mixture consists of small amounts of (uncharacterized) high molecular weight materials, desired diphenylethyne-linked ZnFb dimer (**29**), monomeric porphyrin starting materials or byproducts, reagents, and other byproducts. The progress of the reaction can be assessed by silica TLC or by analytical SEC. For preparative purification, initially we employed a single flash silica column with hexanes/CH_2Cl_2 (2:1). Upon performing time-resolved fluorescence measurements, we observed a multiphasic decay with a single component constituting 95% of the decay and two other components constituting the remaining 5%. The latter two components gave lifetimes characteristic of monomeric zinc and free base porphyrins.[46] Thus the single flash silica column afforded dimer having purity of 95%. To achieve higher levels of purity as required for photochemical studies, we devised a better purification scheme.

The improved purification scheme involves a sequence of three chromatography procedures. First, the concentrated crude reaction mixture is passed over a short flash silica column, eluting $AsPh_3$ first followed by the mixture of porphyrin components, leaving the Pd species bound to the top of the column. The porphyrin mixture then is passed over a preparative SEC column in toluene, which affords separation of higher molecular weight material, desired dimer, and most monomeric porphyrins. The fraction containing the desired dimer then is passed over a silica column using gravity elution with hexanes/CH_2Cl_2 (2:1), which removes a small amount of monomeric zinc porphyrin byproduct that co-chromatographed with the dimer fraction via preparative SEC. The purity of fractions can be assessed by analytical SEC at all stages of the purification. For example, the dimer fraction obtained from preparative SEC columns consists of dimer (99%) and residual monomeric zinc porphyrin (1%) based on integrated peak areas; upon the final silica column the dimer is the only integrated peak (100%) in the analytical SEC. The fluorescence lifetimes of these dimers were monophasic with amplitude $\geq$99%, reflecting the much cleaner samples which contained $\leq$1% zinc porphyrin monomer.[46]

The dimers **29**−**32** were obtained in 69−86% yields (Chart 3). This three-column chromatography sequence is applicable to all dimers (and the trimer) bearing mesityl substituents. The ZnFb diphenylethyne-linked dimers are easily identified because the visible absorption spectra (450−700 nm) of the dimers are the sum of the spectra of the component (zinc porphyrin, free base porphyrin) parts. No demetalation of the zinc porphyrin, transmetalation of the zinc porphyrin, or metalation of the free base porphyrin occurs during the synthetic reactions or the purification, as all the conditions to which the building block porphyrins and arrays are treated involve mild temperatures and neutral to slightly basic solvents. These coupling reactions are highly reproducible. The all-zinc dimers **33**−**35** were prepared by treatment of the appropriate ZnFb dimers with methanolic zinc acetate. Zinc insertions were generally quantitative. The methoxy-substituted bis-hindered dimer **36** also was obtained,

Chart 3. Zn−Fb Porphyrin Dimers with Different Sites of *o*-Methyl Substitution



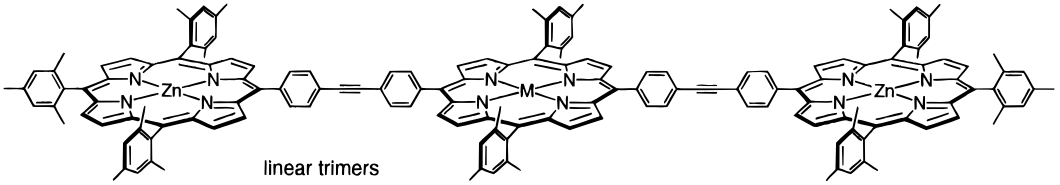
but upon attempted insertion of zinc into the free base porphyrin unit, a relatively insoluble Zn_2 dimer (**37**) was obtained. The insolubility of this dimer shows that extensive facial encumbrance alone, at least when groups of differing polarity are employed, is insufficient to ensure solubility in all cases.

Synthesis of Trimeric Arrays. A linear trimer and a right-angle trimer were prepared to investigate the influence of geometry on electronic communication among porphyrins. We have previously described the synthesis of the linear ZnFbZn-trimer **38** (Chart 4).[42] The corresponding right-angle trimer **40** was prepared in analogous fashion (Scheme 4). The reaction of the *cis*-diiodo free base porphyrin **15** and the zinc ethynyl porphyrin **13** under the Pd-mediated coupling reactions (Pd(0) reagent $Pd_2(dba)_3$ and $AsPh_3$ in toluene/triethylamine (5:1) at 35 °C under argon for 2 h) afforded a mixture consisting of higher molecular weight material, trimer **40**, dimer, and a monomeric zinc porphyrin, from which the desired right-angle trimer was obtained in 90% yield. Metalation of these trimers with zinc afforded the Zn_3 trimers **39** and **41**.

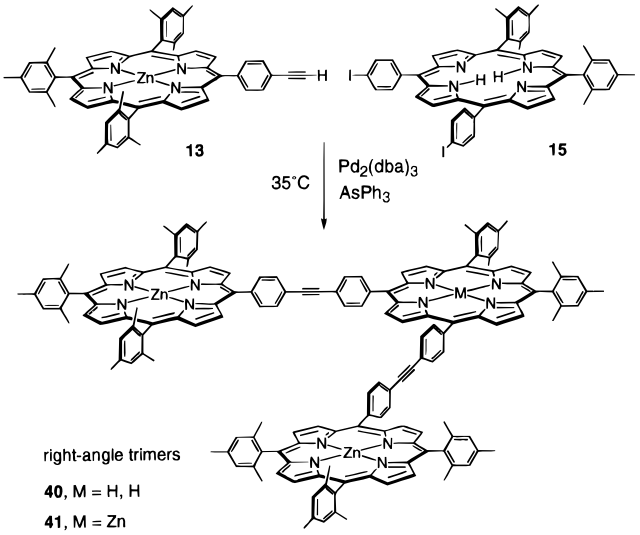
The natural light-harvesting complexes exhibit rapid energy migration among isoenergetic pigments. The molecular wire **2** includes an array of three zinc porphyrins, implying a minimum of two energy transfer steps between zinc porphyrins as energy flows from the boron-dipyrromethene dye to the free base porphyrin. In principle energy transfer can occur in either direction among the zinc porphyrins. To investigate the dynamics of energy migration, including the possibility of reversible energy transfer among zinc porphyrins, we prepared the linear ZnZnFb-trimer **44** shown in Scheme 5.

The reaction of the zinc ethynyl porphyrin **13** with the zinc iodo ethynyl porphyrin building block **28** via the Pd-coupling conditions afforded the porphyrin dimer **42** in 68% yield. This reaction proceeded like the previous syntheses of porphyrin dimers. Deprotection of **42** in $CHCl_3$ with tetrabutylammonium fluoride on silica gel afforded the monoethyne-substituted ZnFb-dimer **43** in 90% yield. Reaction of **43** with the free base iodo

Chart 4. Linear Porphyrin Trimers



Scheme 4. Synthesis of Right-Angle Porphyrin Trimers



porphyrin **14** via the same Pd-mediated coupling reactions afforded the ZnZnFb-trimer **44**. The formation of the trimer was easily detected by analytical SEC (but not by TLC). This compound could be purified exclusively by preparative SEC, but the improved chromatography procedures developed for the dimers **29**-**32** provided the highest quality purification. The ZnZnFb-trimer **44** was isolated in 80% yield. The identification of this trimer is facilitated as the visible absorption bands are the sum of the spectra of the component parts, showing two zinc porphyrins and one free base porphyrin. The yields in the synthesis of the trimer **44** (coupling 68%, deprotection 90%, coupling 80%) are consistently high, indicating the applicability of this approach for the synthesis of linear multiporphyrin arrays. This stepwise elongation process is the same strategy employed in the preparation of the molecular wire **2**.[16] The synthesis of the molecular wire will be described elsewhere.

Synthesis of a Pentameric Array. A pentamer was prepared by coupling tetrakis(4-iodophenyl)porphyrin[28] with the zinc monoethynyl porphyrin **22**. These methoxy-substituted porphyrins are not adequately soluble in toluene/triethylamine (5:1) thus pyridine/triethylamine (5:1) was employed as coupling solvent. We have not optimized the coupling conditions in this solvent, and use of $Pd(PPh_3)_4$ required reaction at 100 °C for 12 h to form the pentamer. The products of the reaction were easily separable by silica chromatography, however, and the Zn_4Fb pentamer was obtained in 50% yield. The architecture of the pentamer resembles a four-fold dimer as the core free base porphyrin is attached to four zinc porphyrins via diphenylethyne linkers. This pentamer was used in prior studies of electronic communication among the porphyrins.[44]

^{1}H NMR Features. The phenyl- or mesityl-substituted monomers and arrays were readily characterized by ^{1}H NMR spectroscopy in $CDCl_3$ or toluene-d_8, while the methoxy-substituted pentamer was examined in CD_2Cl_2. The resonances from the β-pyrrole protons, and from the protons flanking the ethyne unit, exhibit characteristic features in the covalently-linked arrays. For example, in monomer **13** (or **14**) the β-pyrrole protons that are flanked by the mesityl groups (distal from the *para*-substituted phenyl unit) give an unresolved singlet, while AB doublets are observed for the β-pyrrole protons that are situated between the mesityl group and the substituted phenylene unit. The protons on the phenylene group yield an AA′BB′ pattern. Upon coupling of **13** and **14** to form the ZnFb-dimer **29**, the observed splitting pattern due to the β-pyrrole protons is the sum of the splitting patterns of the component parts. The signals from the *meta*-phenylene protons of **13** and **14** shift downfield by ~0.2 ppm upon formation of the diphenylethyne linkage in **29**. This change in chemical shift is observed in all the arrays (dimers, trimers, pentamer) and is a diagnostic for the formation of the diphenylethyne linkage. Formation of the symmetric Zn_2-dimer **33** caused simplification of the ^{1}H NMR spectrum ($CDCl_3$), giving β-pyrrole and phenylene splitting patterns identical with zinc porphyrin monomer **13**.

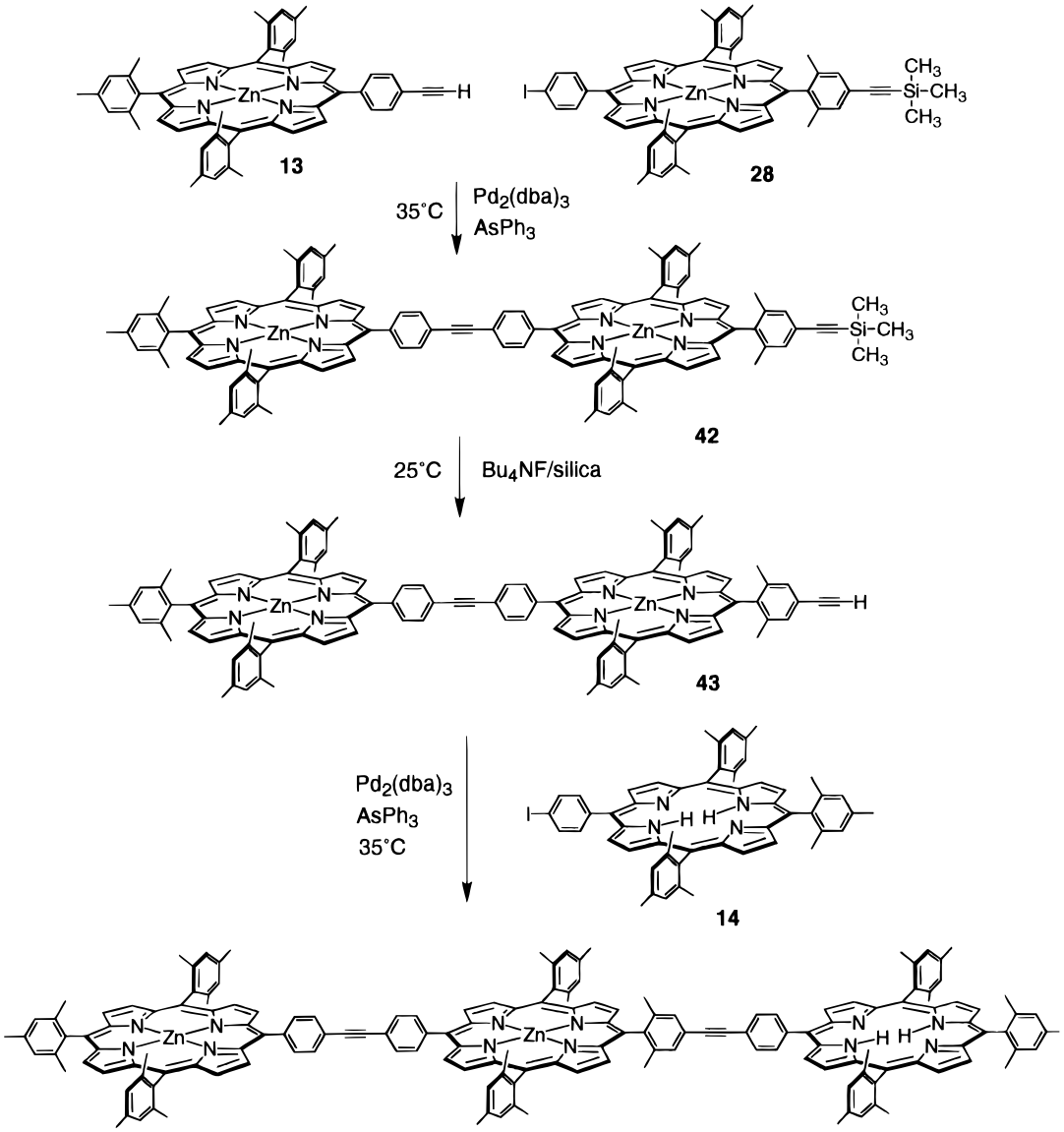
Similar features were observed in the larger arrays. The ZnFbZn-trimer **38** showed resonances from the β-pyrrole protons that are the sum of the spectra of the component parts, and the phenylene protons (8.33−8.06 ppm) exhibited, as expected, two sets of AA′BB′ patterns. In the pentamer **1**, the four-fold symmetric substitution causes the β-pyrrole protons of the core free base porphyrin to give a singlet (9.097 ppm). A detailed NMR study of the conformational mobility of these types of multiporphyrin arrays has been performed.[49]

Solubility. High solubility of the arrays in a variety of solvents is essential for synthesis, manipulation, chemical characterization, and spectroscopic analysis. Because of the high extinction coefficients of porphyrins, spectroscopic studies are usually performed at concentrations of 1−10 μM, but for synthesis, purification, and manipulation, higher solubility is a necessity. Here we delineate some of the operational solubilities we have observed. The ZnFb-dimers **29**-**32** are soluble in toluene/triethylamine (5:1) used in the Pd-coupling reactions (a convenient concentration of 1.8−4.3 mM), can be dissolved in hexanes/CH_2Cl_2 (1:1 or 2:1) for preparative chromatography (maximum solubility corresponds to ~4.7−7.8 mM), are soluble in $CHCl_3$ for conversion to the bis-zinc chelates (1.9−3.4 mM), and can be dissolved in a minimal amount of $CDCl_3$ for NMR spectroscopy (6.4−7.3 mM). For these dimers a concentration of 5 mM corresponds to ~8 mg/mL. Similar solubility properties also were observed for the larger arrays. Thus the ZnZnFb-trimer **44** was soluble at 2.4 mM in toluene/triethylamine (5:1) and at 4.2 mM in $CDCl_3$ (10 mg/mL). The molecular wire **2** was soluble at 1.5 mM in toluene/triethylamine (5:1) and at 2 mM in $CDCl_3$ (7 mg/mL).

In addition, the dimers and trimers have been examined for analytical and spectroscopic purposes in dilute solution in a variety of solvents, though the upper solubility limits in these solvents have not been established. The absorption bands hardly

(49) Bothner-By, A. A.; Dadok, J.; Johnson, T. E.; Lindsey, J. S. *J. Phys. Chem.* In press.

Scheme 5. Synthesis of the ZnZnFb Trimeric Porphyrin Array



shift across a change of solvent polarity from toluene to dimethyl sulfoxide (Table 1). Absorption and fluorescence spectroscopy of the dimers and trimers has been performed at 1−20 μM in solvents such as acetone, dimethyl sulfoxide, and the very viscous medium, castor oil. In addition, the purity of each of the arrays has been assessed by analytical SEC in THF (convenient concentration of 10^{-5} to 10^{-4} M).

The mesityl- or phenyl-substituted porphyrin arrays are soluble in a range of solvents, particularly toluene. The methoxy-substituted porphyrin arrays are soluble in CH_2Cl_2, $CHCl_3$, or pyridine, but are rather insoluble in toluene. The methoxy-substituted dimer **36** (Chart 3) was less soluble than the mesityl and phenyl arrays and surprisingly, the bis-zinc derivative **37** was found to be nearly insoluble. In general the highest solubilities of the methoxy-substituted arrays in the best solvents (CH_2Cl_2, $CHCl_3$, or pyridine) are less than that of the mesityl- or phenyl-substituted porphyrin arrays in toluene or CH_2Cl_2. Accordingly we shifted our focus toward the mesityl-substituted building block porphyrins and have used these in the preparation of the light harvesting model compounds described here, the molecular wire,[16] and molecular optoelectronic gates.[18]

Conclusions

Modular porphyrin building blocks can be used to construct a variety of synthetic multiporphyrin arrays. The multiporphyrin arrays are soluble in various organic solvents, have controlled interporphyrin distances, incorporate porphyrins in predetermined metalation states, and have visible absorption spectra that are nearly the sum of spectra of the component parts. The straightforward synthesis of these porphyrin building blocks and arrays should facilitate investigation of issues underlying light-harvesting phenomena and also allow the creation of a wide variety of molecular photonic devices.

Experimental Section

General. ^{1}H NMR spectra (300 MHz, IBM FT-300), absorption spectra (HP 8451A, Cary 3), and fluorescence spectra (Spex FluoroMax) were collected routinely. Porphyrins were analyzed by laser desorption (LD-MS) or plasma desorption mass spectrometry (PD-MS).[50] Pyrrole was distilled at atmospheric pressure from CaH_2. Commercial sources provided trimethylsilylacetylene (Janssen Chimica), pyridine (Fluka),

(50) Lindsey, J. S.; Chaudhary, T.; Chait, B. T. *Anal. Chem.* **1992**, *64*, 2804−2814.

Table 1. Absorption Maxima in Different Solvents[a]

sample	toluene	acetone	acetonitrile	DMSO	castor oil
monomers					
TPP	420	414	414	419	419
	548	545	546	549	549
FbU (**11**)	420	414	414	420	420
	548	545	547	549	549
FbH (**16**)	420	415	414	419	419
	551	545	546	548	548
ZnH (**17**)	424	422	423	428	427
	550	554	556	561	557
ZnTPP	423	422	422	427	426
	550	554	556	560	556
ZnU (**12**)	423	424	424	430	428
	550	556	558	562	558
dimers					
ZnFbU (**29**)	426	426	426	431	429
	550	555	556	562	556
ZnFbP (**31**)	426	424	424	429	429
	551	553	553	559	556
ZnFbD (**30**)	426	425	425	419, 431	429
	550	555	556	562	556
ZnFbB (**32**)	425	423	423	429	428
	550	553	554	559	556
Zn_2U (**33**)	427	428	429	433	428
	551	557	558	562	558
trimers					
ZnZnFb (**44**)	422, 430	423, 431	*b*	435	427, 434
	550	556		563	557
Zn_3L (**39**)	423, 431	424, 432	*b*	426, 436	426, 435
	550	558		563	558

[a] The compounds were dissolved in CH_2Cl_2 and 2−5 μL was added to 3 mL of solvent. The spectra were collected with 0.25 nm spectral resolution (slit width = 1 nm). The absorption maxima of the Soret band and the the principal visible band are shown. [b] The samples aggregated in this solvent.

4-iodobenzaldehyde (**5**, Karl Industries, Inc.), and all other reagents and starting materials (Aldrich).

Chromatography. Adsorption column chromatography was performed using flash silica (Baker) or alumina (Fisher A540, 80−200 mesh). Porphyrins were dissolved in CH_2Cl_2 (for silica) or toluene (for alumina) at high concentration and then hexanes was added to achieve a nonpolar loading solvent.

Preparative scale size exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1. A preparative scale glass column (4.8 × 60 cm) was packed using BioRad Bio-Beads SX-1 in toluene. The chromatography is performed with gravity flow (∼4 mL/min). A typical separation requires ∼3 h. Following purification, the SEC column is washed with two volume equivalents of toluene. Unlike adsorption columns, these SEC columns can be used repeatedly although with continued use for porphyrin separations the columns become uniformly slightly pink-brown. We have used some preparative SEC columns for more than 50 separations over as long as one year with no noticeable decline in fractionation capability.

Analytical scale SEC was performed to assess the purity of the array-forming reactions and to monitor the preparative purification of the arrays.[42] Analytical SEC columns (styrene−divinylbenzene copolymer) were purchased from Hewlett Packard and Phenomonex. Analytical SEC was performed with a Hewlett-Packard 1090 HPLC using 500 Å (300 × 7.8 mm), 500 Å (300 × 7.5 mm), and 100 Å (300 × 7.5 mm) columns (5 micron) in series eluting with THF (flow rate = 0.8 mL/min; void volume ∼ 18.0 min). Reaction monitoring was performed by removing aliquots from the reaction mixture and diluting with THF (Fisher, HPLC grade). Sample detection was achieved by absorption spectroscopy using a diode array detector with quantitation at 420 nm (±10 nm band width), which best captures the peaks of monomeric porphyrins and the multiporphyrin arrays. The dimers elute at 25.5 min and the trimer elutes at 23.9 min. Spectroscopic quantitation of the products of the reaction mixture is difficult because the monomers, dimers, trimers, and higher oligomers have different extinction coefficients, and the value of these often is not known. Furthermore, the dimer peak can consist of ethyne-linked dimer and butadiyne-linked dimer. In prior work we have determined the yield of particular components by injecting precise amounts of known concentrations of authentic samples. We also have obtained working curves that establish the linearity of Beers law for the concentrations of the samples investigated. We use analytical SEC primarily to monitor the progress of the reaction in a semiquantitative way, and then to check that the purified product is truly free of higher molecular weight material (which typically appears at the leading edge of the array), starting porphyrins, and intermediates.

Solvents. CH_2Cl_2 (Fisher, reagent grade) and $CHCl_3$ (Fisher certified A.C.S.) were subjected to simple distillation from K_2CO_3. The commercially-available $CHCl_3$ contained ethanol (0.75%) as a stabilizer. All references to $CHCl_3$ in this paper pertain to $CHCl_3$ containing 0.75% ethanol. Simple distillation does not significantly alter the ethanol content. THF (Fisher certified A.C.S.) and toluene (Fisher certified A.C.S.) were distilled from $LiAlH_4$ and triethylamine (Fluka puriss) was distilled from CaH_2. Other solvents were used as received.

Methoxy-Substituted Zn_4Fb-Pentamer 1.[15] A sample of tetrakis-(4-iodophenyl)-porphyrin[28] (25 mg, 22.4 μmol) was added to a solution of zinc ethynyl porphyrin (**22**, 80 mg, 90.8 μmol) in 15 mL of pyridine−triethylamine (5:1) and the mixture was deaerated with argon for 1 h. The Pd(0) catalyst ($Pd(PPh_3)_4$, 10 mg, 8.7 μmol) was added and deaeration was continued for 15 min. Then the flask was immersed in an oil bath at 100 °C. The reaction mixture became homogeneous within 30 min and remained homogeneous for the duration of the reaction. At 7.5 h the product distribution consisted of pentamer, zinc monomer, and several intermediates as determined by analytical SEC. Additional samples of **22** (20 mg) and $Pd(PPh_3)_4$ catalyst (2 mg) were added at this time and again at 10 h. At 12 h the product distribution consisted of lesser quantities of intermediates and increased amounts of pentamer and butadiyne-linked dimer. Solvent was removed under reduced pressure and the residue was treated with 1 mL of methanol and then dissolved in CH_2Cl_2. The solution was washed with H_2O and brine and then dried (Na_2SO_4). Column chromatography (2 cm diameter × 22 cm) over flash silica gel with CH_2Cl_2/ethyl acetate (96:4) yielded three major components (in order of elution): monomeric zinc porphyrin, butadiyne-linked dimer, and the pentamer **1**. The pentamer containing fractions were rechromatographed similarly, affording 45.6 mg (50%) of pure **1**. PD-MS $C_{252}H_{182}N_{20}O_{24}Zn_4$ calcd mass 4135.8, obsd 4136.0; λ_{abs} (CH_2Cl_2) 428, 519, 550, 590, 649 nm; ^{1}H NMR (300 MHz) (CD_2Cl_2) δ −2.7 (s, 2 H, NH), 3.548 (s, 24 H, OCH_3), 3.606 (s, 48 H, OCH_3), 7.060 (m, 8 H, J = 8.47, Hz, *o*-ArH), 7.095 (m, 16 H, J = 8.47 Hz, *o*-ArH), 7.767 (m, 4 H, J = 8.52 Hz, *p*-ArH), 7.795 (m, 8 H, J = 8.47 Hz, *p*-ArH), 8.101 (AA′BB′, 8 H, J = 8.30 Hz, ArH), 8.177 (AA′BB′, 8 H, J = 8.30 Hz, ArH), 8.316 (AA′BB′, 8 H, J = 8.30 Hz, ArH), 8.405 (AA′BB′, 8 H, J = 8.30 Hz, ArH), 8.763 (d, 8 H, J = 4.54 H, β-pyrrole peripheral porphyrins), 8.795 (d, 8 H, J = 4.54 H, β-pyrrole peripheral porphyrins), 8.884 (d, 8 H, J = 4.54 H, β-pyrrole peripheral porphyrins), 8.941 (d, 8 H, J = 4.54 H, β-pyrrole peripheral porphyrins), 9.097 (bs, 8 H, β-pyrrole core porphyrins).

Molecular Photonic Wire 2. See ref 16.

Zinc(II) 5,10,15-Tris[2,6-dimethoxyphenyl]-20-{4-(phenylethynyl)-phenyl}porphyrin (3). Samples of zinc porphyrin **22**[28] (50 mg, 57 μmol) and iodobenzene (6.5 μL, 57 μmol) were dissolved in 5.7 mL of toluene/triethylamine (5:1). The solution was purged with argon for 30 min, then $Pd(PPh_3)_4$ (2 mg, 1.4 μmol) was added and the solution was heated to reflux. After stirring for 4 h, the mixture was cooled, filtered, and concentrated to dryness. Chromatography on silica (CH_2Cl_2/hexanes, 10:1) yielded 37 mg (69%) of the desired porphyrin. ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 6 H, OCH_3), 3.55 (s, 12 H, OCH_3), 7.00 (d, J = 8.4 Hz, 6 H, ArH), 7.41, 7.45 (m, 3 H, ArH), 7.68, 7.73 (m, 5 H, ArH), 7.89 (AA′BB′, 2 H, ArH), 8.20 (AA′BB′, 2 H, ArH), 8.81 (s, 4 H, β-pyrrole), 8.84, 8.86 (m, 4 H, β-pyrrole); PD-MS $C_{58}H_{44}N_4O_6Zn$ calcd mass 956.3, obsd 957.6; λ_{abs} (CH_2Cl_2) 422, 548 nm.

Zinc(II) 5,10,15-Tris[2,6-dimethoxyphenyl]-20-{2,6-dimethyl-4-(phenylethynyl)phenyl}porphyrin (4). Samples of aldehyde **8** (468 mg, 2.0 mmol), 2,6-dimethoxybenzaldehyde (996 mg, 6 mmol), and pyrrole (555 μL, 8 mmol) were dissolved in 800 mL of $CHCl_3$, then 1.06 mL of $BF_3{\cdot}O(Et)_2$ (2.5 M in $CHCl_3$) was added and the mixture was stirred at room temperature. After 60 min the yield determined by spectroscopic monitoring was 24%. Then 1.36 g of DDQ was added

and the mixture was stirred at room temperature for a few minutes. The reaction mixture was concentrated to dryness, and the residue was chromatographed on flash silica gel, eluting with CH_2Cl_2/hexanes (10:1). The desired porphyrin was isolated in about 90% purity from the first column. The compound was rechromatographed on a second column in identical manner, affording 97 mg (5.0%) of the desired porphyrin. ^{1}H NMR ($CDCl_3$) δ −2.65 (br s, 2 H, NH), 1.90 (s, 6 H, $ArCH_3$), 3.55 (s, 6 H, OCH_3), 3.60 (s, 12 H, OCH_3), 7.05, 7.10 (m, 6 H, ArH), 7.40, 7.50 (m, 3 H, ArH), 7.65, 7.70 (m, 4 H, ArH), 7.73, 7.80 (m, 3 H, ArH), 8.60 (d, 2 H, β-pyrrole), 8.67−8.75 (m, 6 H, β-pyrrole); λ_{abs} (CH_2Cl_2) 418, 514, 544, 588, 644 nm. A sample of this porphyrin (20 mg, 0.021 mmol) was metalated using 1.5 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in CH_2Cl_2/methanol (9:1). Metal insertion was monitored spectroscopically and the reaction was complete in 2 h. The reaction mixture was poured into CH_2Cl_2 and extracted with 5% $NaHCO_3$ and water, and then the organic layer was dried (Na_2SO_4). Evaporation of the solvent afforded the zinc porphyrin in >95% yield. ^{1}H NMR (CD_2Cl_2) δ 1.81 (s, 6 H, $ArCH_3$), 3.48 (m, 18 H, OCH_3), 6.98 (m, 6 H, ArH), 7.35, 7.40 (m, 3 H, ArH), 7.57, 7.62 (m, 4 H, ArH), 7.66, 7.72 (m, 3 H, ArH), 8.62 (d, 2 H, β-pyrrole), 8.70, 8.78 (m, 6 H, β-pyrrole); PD-MS $C_{60}H_{48}N_4O_6Zn$ calcd mass 984.3, obsd 984.3; λ_{abs} (CH_2Cl_2) 420, 548 nm.

4-[2-(Trimethylsilyl)ethynyl]benzaldehyde (6). See ref 51.

2,6-Dimethyl-4-iodobenzaldehyde (7). A sample of 2,6-dimethyl-4-iodoaniline[52] (12.0 g, 48.6 mmol) was suspended in a mixture of 12 mL of concentrated HCl and 50 g of crushed ice. The mixture was cooled to 0 °C. A 10-mL aqueous solution of $NaNO_2$ (3.41 g, 49.4 mmol) was added over 10 min to the mixture, maintaining a temperature of 0−5 °C. After the addition the reaction was allowed to proceed for 30 min. When the presence of free nitrous acid was confirmed (starch−iodine paper), the diazonium salt mixture was carefully neutralized with anhydrous Na_2CO_3.

A cuprous cyanide mixture was prepared in the following manner. Cuprous cyanide (5.45 g, 60.9 mmol) was suspended in 25 mL of H_2O. Aqueous NaCN (12 mL, 7.6 g, 155 mmol) was added and the mixture was stirred at room temperature until the CuCN dissolved. Toluene (100 mL) was then added to the cuprous cyanide solution and the mixture was cooled to 0 °C.

The diazonium salt mixture was then added to the cuprous cyanide−toluene mixture with vigorous stirring, maintaining a reaction temperature of 0−5 °C. When the addition was complete, the mixture was stirred at 0 °C for 1 h and at room temperature for 4 h, then heated to 50 °C without stirring. The mixture was then allowed to cool to room temperature, the layers were separated, and the aqueous layer was extracted with toluene (2 × 100 mL). The organic layers were combined, washed with H_2O (1 × 50 mL), dried (Na_2SO_4), and concentrated to dryness, giving a dark green solid. The crude product was chromatographed on silica (4.8 × 18 cm, CH_2Cl_2/hexanes (1:1), 3 columns), affording 5.14 g (42%) of light yellow crystals. mp 113−114 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6 H, $ArCH_3$), 7.55 (s, 2 H, ArH). Anal. (C_9H_8IN) C, H, N.

A sample of 2,6-dimethyl-4-iodobenzonitrile (3.3 g, 12.8 mmol) was dissolved in 10 mL of CH_2Cl_2 (distilled from CaH_2) and the solution was cooled to 0 °C. A 15.4-mL solution of a diisobutylaluminum hydride (1 M in CH_2Cl_2, 15.4 mmol) was added dropwise. After the addition was complete, the reaction was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was then poured into a beaker containing 40 g of crushed ice and 50 mL of 6 N HCl. After stirring for 1 h, the aqueous phase was separated and extracted with CH_2Cl_2 (2 × 50 mL). The organic layers were combined, washed with 5% $NaHCO_3$ (25 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated to dryness affording 2.95 g (88%) of a white solid: mp 68−69 °C; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 6 H, $ArCH_3$), 7.48 (s, 2 H, ArH), 10.52 (s, 1 H, CHO). Anal. (C_9H_9IO) C, H.

2,6-Dimethyl-4-[2-(trimethylsilyl)ethynyl]benzaldehyde (8). Samples of 2,6-dimethyl-4-bromobenzaldehyde[52] (5.0 g, 23.5 mmol), trimethylsilylacetylene (4.0 mL, 28.2 mmol), and tri-2-furylphosphine (223 mg, 0.96 mmol) were dissolved in 50 mL of triethylamine. The solution was purged with argon for 30 min, then $Pd_2(dba)_3$ (107 mg, 0.12 mmol) was added and the flask was placed in an oil bath at 55 °C. After stirring for 24 h, trimethylsilylacetylene (2.0 mL, 14.1 mmol), tri-2-furylphosphine (223 mg, 0.96 mmol), and $Pd_2(dba)_3$ (107 mg, 0.12 mmol) were added. The reaction was judged to be complete at 36 h by GC-MS. At this point the mixture was cooled and filtered. The filtrate was concentrated to dryness, yielding a light brown solid. The residue was dissolved in diethyl ether, washed with brine, dried (Na_2SO_4), filtered, and concentrated to a light brown oil that solidified upon standing at 0 °C. Recrystallization from 2-propanol yielded 4.6 g (85%) of a light yellow powder: mp 62−63 °C; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9 H, $SiCH_3$), 2.45 (s, 6 H, $ArCH_3$), 7.05 (s, 2 H, ArH), 10.43 (s, 1 H, CHO). Anal. ($C_{14}H_{18}OSi$) C, H.

4-(Phenylethynyl)benzaldehyde (9). see ref 53.

2,6-Dimethyl-4-(phenylethynyl)benzaldehyde (10). Samples of 2,6-dimethyl-4-bromobenzaldehyde[52] (1 g, 4.7 mmol) and phenylacetylene (1.3 mL, 12 mmol) were dissolved in 10 mL of triethylamine at room temperature. The solution was deaerated with argon for 30 min. $Pd_2(dba)_3$ (43 mg, 47 μmol) and $AsPh_3$ (115 mg, 376 mmol) were added and the reaction vessel was placed in an oil bath at 90 °C. After refluxing for 4 h the reaction mixture was cooled to room temperature and then vacuum filtered. The remaining off-white precipitate was washed with hexanes. The filtrate was rotary evaporated to an oil. Flash column chromatography (silica, hexanes/CH_2Cl_2, 4:1) gave 760 mg (70%) of an off-white powder: mp 63−64 °C; ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 6 H, $ArCH_3$), 7.27 (s, 2 H, ArH), 7.37, 7.38 (m, 3H, ArH), 7.53, 7.55 (m, 2H, ArH), 10.60 (s, 1 H, CHO). Anal ($C_{17}H_{14}O$) C, H.

5,10,15-Trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}-porphyrin (FbU)[46] (11). A sample of zinc porphyrin **12** (200 mg, 0.22 mmol) was dissolved in 25 mL of CH_2Cl_2 and treated with TFA (68 μL, 0.88 mmol). The demetalation was complete after 10 min as evidenced by silica TLC, absorption, and fluorescence excitation spectroscopy. Triethylamine (184 μL, 1.32 mmol) was added and the reaction mixture was stirred for another 10 min. The solution was then washed three times with 10% $NaHCO_3$ and once with H_2O, dried (Na_2SO_4), filtered, and rotary evaporated to give 182 mg (100%) of a purple solid. The analytical data were consistent with an authentic sample.[28]

Zinc(II) 5,10,15-Trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}-porphyrin (ZnU)[46] (12). The crude reaction mixtures from several mixed aldehyde condensations (totaling 2 L) of 20 mmol of pyrrole, 15 mmol of mesitaldehyde, and 5 mmol of 4-[2-(trimethylsilyl)ethynyl]-benzaldehyde (**6**) were combined. This mixture was passed over a silica column (CH_2Cl_2/hexanes, 1:1) affording the six porphyrins (900 mg) free from dark pigments and quinone species. The mixture of six porphyrins (450 mg, half of the original mixture) was dissolved in 100 mL of $CHCl_3$, and metalated with $Zn(OAc)_2 \cdot 2H_2O$ (219 mg, 1 mmol, 10 mL methanol). After metalation was complete the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to a purple solid. The product mixture was dissolved in 10 mL of CH_2Cl_2 and then 20 mL of hexanes was added. The solution was loaded onto a silica column (6.8 × 12 cm, hexanes/CH_2Cl_2, 2:1). The six porphyrin products were clearly visible on the column as the separation proceeded. The title porphyrin comprised the second band, affording 280 mg (12.4%). ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 9 H), 1.83 (s, 12 H, $ArCH_3$), 1.84 (s, 6 H, $ArCH_3$), 2.63 (s, 9 H, $ArCH_3$), 7.27 (s, 6 H, ArH), 7.89 (AA′BB′, 2 H, ArH), 8.19 (AA′BB′, 2 H, ArH), 8.70 (s, 4 H, β-pyrrole), 8.77 (d, J = 4.5 Hz, 2 H, β-pyrrole), 8.83 (d, J = 4.5 Hz, 2 H, β-pyrrole); LD-MS $C_{58}H_{54}N_4SiZn$ calcd av mass 900.6, obsd 900.3; λ_{abs} (toluene) 423, 550 nm.

Zinc(II) 5,10,15-Trimesityl-20-(4-ethynylphenyl)porphyrin (13). See ref 42.

5,10,15-Trimesityl-20-(4-iodophenyl)porphyrin (14). See ref 28.

5,10-Dimesityl-15,20-bis{4-iodophenyl}porphyrin (15). Samples of mesitaldehyde (1.1 mL, 7.5 mmol), 4-iodobenzaldehyde (580 mg, 2.5 mmol), and pyrrole (694 μL, 10 mmol) were condensed in 1 L of $CHCl_3$ with $BF_3 \cdot O(Et)_2$ (1.32 mL of 2.5 M stock solution, 3.3 mM) at room temperature for 1 h. Then DDQ (1.7 g, 7.5 mmol) was added and after 1 h of stirring at room temperature the reaction mixture was

(51) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280−2286.

(52) Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600−602.

(53) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259−263.

worked up in the standard way.[28] One column (silica, CH_2Cl_2/hexanes, 2:1) was used to remove the non-porphyrinic components from the crude reaction mixture. The mixture of six porphyrins was chromatographed on neutral alumina (hexanes/toluene, 4:1) yielding 166 mg (7.0% yield) of the desired porphyrin, which eluted as the fourth porphyrin component. ^{1}H NMR ($CDCl_3$) δ −2.69 (bs, 2 H, NH), 1.84 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.27 (s, 4 H, ArH), 7.93 (AA′BB′, 4 H, ArH), 8.08 (AA′BB′, 4 H, ArH), 8.65 (s, 2 H, β-pyrrole), 8.70 (d, J = 5.1 Hz, 2 H, β-pyrrole), 8.76 (d, J = 5.1 Hz, 2 H, β-pyrrole), 8.81 (s, 2 H, β-pyrrole); PD-MS $C_{50}H_{40}I_2N4$ calcd av mass 950.1, obsd 950.3; λ_{abs} 420, 516, 552, 590, 648 nm.

5,10,15-Triphenyl-20-{2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]-phenyl}-porphyrin (FbH)[46] (16). Samples of benzaldehyde (514 μL, 5.06 mmol), aldehyde **8** (389 mg, 1.69 mmol), and pyrrole (468 μL, 6.75 mmol) were condensed in 675 mL of $CHCl_3$ with BF_3·O(Et)$_2$ (891 μL of 2.5 M stock solution, 3.3 mM) at room temperature for 1 h. Then DDQ (1.149 g, 5.06 mmol) was added and after 1 h of stirring at room temperature the reaction mixture was worked up in the standard way.[28] Chromatography on silica (CH_2Cl_2/hexanes (1:1), 6.8 × 7 cm) gave the six porphyrins eluting as one band. Subsequent chromatography on alumina (hexanes/toluene (2:1), 6.8 × 10 cm) yielded the desired porphyrin (217 mg, 17%) from the mixture as the fifth porphyrin band. ^{1}H NMR ($CDCl_3$) δ −2.72 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.85 (s, 6 H, $ArCH_3$), 7.63 (s, 2 H, ArH), 7.71, 7.80 (m, 9 H, PhH), 8.20, 8.23 (m, 6 H, PhH), 8.63 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.81, 8.83 (m, 6 H, β-pyrrole); LD-MS $C_{51}H_{42}N_4Si$ calcd av mass 739.0, obsd 739.9; λ_{abs} (toluene) 420, 514, 551, 592, 648 nm.

Zinc(II) 5,10,15-Triphenyl-20-{2,6-dimethyl-4-[2-(trimethylsilyl)-ethynyl]phenyl}porphyrin (ZnH)[46] (17). A sample of porphyrin **16** (150 mg, 0.20 mmol) was metalated in 50 mL of $CHCl_3$ with $Zn(OAc)_2$·$2H_2O$ (88 mg, 0.4 mmol, 5 mL methanol) over 2.5 h, affording 160 mg (100%) of the zinc chelate as a purple solid. ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H, $SiCH_3$), 1.84 (s, 6 H, $ArCH_3$), 7.63 (s, 2 H, ArH), 7.73, 7.76 (m, 9 H, PhH), 8.21, 8.24 (m, 6 H, PhH), 8.72 (d, 2 H, J = 4.8 Hz, β-pyrrole), 8.91 (d, 2 H, J = 4.8 Hz, β-pyrrole), 8.94 (s, 4 H, β-pyrrole); LD-MS $C_{51}H_{40}N_4SiZn$ calcd av mass 802.4, obsd 802.2; λ_{abs} (toluene) 424, 550 nm.

Zinc(II) 5,10,15-Triphenyl-20-{2,6-dimethyl-4-ethynylphenyl}-porphyrin (18). A sample of porphyrin **17** (150 mg, 0.11 mmol) was dissolved in 26.5 mL of THF/methanol (3:1). K_2CO_3 (53 mg, 0.39) was added and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated to dryness and then the purple solid was redissolved in 50 mL of $CHCl_3$. The organic solution was washed with H_2O, dried (Na_2SO_4), filtered, and concentrated to dryness. Column chromatography on silica (CH_2Cl_2/hexanes (1:1), 4.8 × 7 cm) afforded 130 mg (95%). ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6 H, $ArCH_3$), 3.25 (s, 1 H, CCH), 7.64 (s, 2 H, ArH), 7.74, 7.79 (m, 9 H, PhH), 8.21, 8.24 (m, 6 H, PhH), 8.73 (d, 2 H, J = 4.2 Hz, β-pyrrole), 8.91 (d, 2 H, J = 4.2 Hz, β-pyrrole), 8.94 (s, 4 H, β-pyrrole); LD-MS $C_{48}H_{32}N_4Zn$ calcd av mass 730.2, obsd 730.1; λ_{abs} (toluene) 423, 550 nm.

5,10,15-Triphenyl-20-{2,6-dimethyl-4-iodophenyl}porphyrin (19). Samples of benzaldehyde (1.45 mL, 14.25 mmol), aldehyde **7** (1.235 g, 4.75 mmol), and pyrrole (1.32 mL, 19 mmol) were condensed in 1.9 L of $CHCl_3$ with BF_3·O(Et)$_2$ (2.51 mL of 2.5 M stock solution, 3.3 mM) at room temperature for 1 h. Then DDQ (3.235 g, 14.25 mmol) was added and after 1 h of stirring at room temperature the reaction mixture was worked up in the standard way. Chromatography (silica, CH_2Cl_2/hexanes (1:1), 6.8 × 7 cm) gave the five porphyrins eluting as one band. The 5,10,15,20-tetrakis{2,6-dimethyl-4-iodophenyl}porphyrin did not elute because of limited solubility. Chromatography on alumina (hexanes/toluene (2:1), 6.8 × 10 cm) afforded the desired porphyrin (492 mg, 13.5%) as the last band in the porphyrin mixture. ^{1}H NMR ($CDCl_3$) δ −2.72 (s, 2 H, NH), 1.85 (s, 6 H, $ArCH_3$), 7.73, 7.79 (m, 9 H, PhH), 7.85 (s, 2 H, ArH), 8.19, 8.23 (m, 6 H, PhH), 8.66 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.82, 8.84 (m, 6 H, β-pyrrole); LD-MS $C_{46}H_{33}N_4I$ calcd av mass 768.7, obsd 770.0; λ_{abs} (toluene) 419, 514, 548, 592, 646 nm.

5,10,15-Tris(2,6-dimethoxyphenyl)-20-{4-[2-(trimethylsilyl)ethynyl]-phenyl}porphyrin (20). See ref 28.

5,10,15-Tris(2,6-dimethoxyphenyl)-20-{4-ethynylphenyl}-porphyrin (21). See ref 28.

Zinc(II) 5,10,15-Tris(2,6-dimethoxyphenyl)-20-{4-ethynylphenyl}-porphyrin (22). See ref 28.

5,10,15-Tris(2,6-dimethoxyphenyl)-20-{2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (23). Samples of 2,6-dimethoxybenzaldehyde (2.24 g, 13.5 mmol), aldehyde **8** (1.04 g, 4.5 mmol), and pyrrole (1.25 mL, 18 mmol) were condensed in 1.8 L of $CHCl_3$ with BF_3·O(Et)$_2$ (2.4 mL of 2.5 M stock solution, 3.3 mM) at room temperature for 1 h. Then DDQ (3.06 g, 13.5 mmol) was added and after 1 h of stirring at room temperature the reaction mixture was worked up in the standard way.[28] Chromatography (one column, silica, CH_2Cl_2) gave the first four porphyrins eluting as one band and the title porphyrin as the second porphyrin band, affording 180 mg (4.4%) of porphyrin. ^{1}H NMR ($CDCl_3$) δ −2.53 (s, 2 H, NH), 0.36 (s, 9 H, $SiCH_3$), 1.86 (s, 6 H, $ArCH_3$), 3.47 (s, 6 H, OCH_3), 3.48 (s, 12 H, OCH_3), 6.96 (d, 6 H, J = 6 Hz, ArH), 7.59 (s, 2 H, ArH), 7.67 (t, 3 H, J = 8.4 Hz, ArH), 8.50 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.65, 8.68 (m, 6 H, β-pyrrole); LD-MS $C_{57}H_{54}N_4O_6Si$ calcd av mass 919.2, obsd 920.9; λ_{abs} (toluene) 420, 514, 548, 592, 646 nm.

Zinc(II) 5,10,15-Tris(2,6-dimethoxyphenyl)-20-{2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (24). A sample of porphyrin **23** (155 mg, 0.17 mmol) was dissolved in 50 mL of $CHCl_3$, then a methanolic solution of $Zn(OAc)_2$·$2H_2O$ (75 mg, 0.34 mmol, 5 mL of methanol) was added. The reaction mixture was stirred at room temperature and was monitored by fluorescence excitation spectroscopy. After stirring overnight the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated affording 167 mg (100%) of the zinc chelate as a purple solid. ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9 H, $SiCH_3$), 1.84 (s, 6 H, $ArCH_3$), 3.49 (s, 6 H, OCH_3), 3.50 (s, 12 H, OCH_3), 6.98 (d, 6 H, J = 7.8 Hz, ArH), 7.58 (s, 2 H, ArH), 8.75 (t, 3 H, J = 9.6 Hz, ArH), 8.58 (d, 2 H, J = 4.2 Hz, β-pyrrole), 8.74 (d, 2 H, J = 4.2 Hz, β-pyrrole), 8.77 (m, 4 H, β-pyrrole); LD-MS $C_{57}H_{52}N_4O_6SiZn$ calcd av mass 982.5, obsd 983.3; λ_{abs} (toluene) 425, 549 nm.

Zinc(II) 5,10,15-Tris(2,6-dimethoxyphenyl)-20-{2,6-dimethyl-4-ethynylphenyl}porphyrin (25). A sample of zinc porphyrin **24** (167 mg, 0.17 mmol) was dissolved in 10 mL of anhydrous THF. Upon addition of 340 mg of tetrabutylammonium fluoride on silica (1.0−1.5 mmol F^-/g) a precipitate was observed. $CHCl_3$ (2 mL) was added to redissolve the starting porphyrin. After 30 min further aggregation was noted and 50 mL of $CHCl_3$ was added. After 1 h the deprotection was complete as evidenced by ^{1}H NMR spectroscopy. The reaction mixture was concentrated to dryness and then redissolved in 50 mL of $CHCl_3$. The organic layer was washed with 50 mL of 10% $NaHCO_3$ and 50 mL of H_2O, dried (Na_2SO_4), filtered, and concentrated to dryness. Column chromatography on silica (CH_2Cl_2, 4.8 × 7 cm) afforded 130 mg (82%) of porphyrin. ^{1}H NMR ($CDCl_3$) δ 1.86 (s, 6 H, $ArCH_3$), 3.22 (s, 1 H, CCH), 3.49 (s, 6 H, OCH_3), 3.50 (s, 12 H, OCH_3), 6.95, 6.99 (m, 6 H, ArH), 7.64 (s, 2 H, ArH), 7.64, 7.69 (m, 3 H, ArH), 8.60 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.76 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.78 (s, 4 H, β-pyrrole); LD-MS $C_{54}H_{44}N_4O_6Zn$ calcd av mass 910.3, obsd 911.0; λ_{abs} (toluene) 424, 550 nm.

5,10,15-Tris(2,6-dimethoxyphenyl)-20-{2,6-dimethyl-4-iodophenyl}-porphyrin (26). Samples of 2,6-dimethoxybenzaldehyde (1.246 g, 7.5 mmol), aldehyde **7** (650 mg, 2.5 mmol), and pyrrole (694 μL, 10 mmol) were condensed in 1 L of $CHCl_3$ with BF_3·O(Et)$_2$ (1.32 mL of 2.5 M stock solution, 3.3 mM) at room temperature for 1 h. Then DDQ (1.70 g, 7.5 mmol) was added and after 1 h of stirring at room temperature the reaction mixture was worked up in the standard way.[28] Chromatography (one column, silica, CH_2Cl_2) gave the first four porphyrins as one band and the desired product as the second band, yielding 110 mg (4.8%) of porphyrin. ^{1}H NMR ($CDCl_3$) δ −2.53 (s, 2 H, NH), 1.84 (s, 6 H, $ArCH_3$), 3.45 (s, 6 H, OCH_3), 3.49 (s, 12 H, OCH_3), 6.95, 6.99 (m, 6 H, ArH), 7.69 (t, 3 H, J = 8.4 Hz, ArH), 7.80 (s, 2 H, ArH), 8.52 (d, 2 H, J = 4.2 Hz, β-pyrrole), 8.66, 8.68 (m, 6 H, β-pyrrole); LD-MS $C_{52}H_{45}N_4IO_6$ calcd av mass 948.9, obsd 949.2; λ_{abs} (toluene) 420, 514, 550, 591, 651 nm.

5,15-Bis(mesityl)-10-(4-iodophenyl)-20-[2,6-dimethyl-4-(2-(trimethylsilyl)ethynyl)phenyl]porphyrin (27). A sample of zinc porphyrin **28** (200 mg, 0.20 mmol) was dissolved in 25 mL of CH_2Cl_2 and treated with TFA (62 μL, 0.80 mmol). The demetalation was complete after 10 min as evidenced by silica TLC, absorption, and fluorescence excitation spectroscopy. Triethylamine (167 μL, 1.20

mmol) was added and the reaction mixture was stirred for another 10 min. The solution was then washed three times with 10% $NaHCO_3$ and once with H_2O, dried (Na_2SO_4), filtered, and rotary evaporated to give 188 mg (100%) of a purple solid. The analytical data were consistent with an authentic sample.[39]

Zinc(II) 5,15-Bis(mesityl)-10-(4-iodophenyl)-20-[2,6-dimethyl-4-(2-(trimethylsilyl)ethynyl)phenyl]porphyrin (28). Samples of aldehyde **8** (576 mg, 2.5 mmol), 4-iodobenzaldehyde (580 mg, 2.5 mmol), and *meso*-(mesityl)dipyrromethane[39] (1.322 g, 5 mmol) were dissolved in 500 mL of $CHCl_3$. $BF_3{\cdot}O(Et)_2$ (660 μL of 2.5 M stock solution, 3.3 mM) was then added and the solution was stirred at room temperature for 45 min. Then DDQ (1.70 g, 7.5 mmol) was added and stirring was continued at room temperature for 1 h. Flash chromatography (silica, CH_2Cl_2/hexanes, 1:1) gave the mixture of three porphyrins (800 mg). To facilitate the purification, the mixture of three porphyrins was dissolved in 100 mL of $CHCl_3$ and metalated with $Zn(OAc)_2{\cdot}2H_2O$ (373 mg, 1.7 mmol, 10 mL methanol). After metalation was complete the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to a purple solid. The product mixture was dissolved in 15 mL of CH_2Cl_2 and then 30 mL of hexanes was added. The solution was loaded onto a silica column (6.8 × 12 cm, hexanes/CH_2Cl_2, 2:1). The three porphyrin products were clearly visible as distinct bands on the column as the separation proceeded. The desired zinc porphyrin was the second band off of the column, affording 280 mg (11%). ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H, $SiCH_3$), 1.84 (s, 12 H, $ArCH_3$), 1.85 (s, 6 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.29 (s, 4 H, ArH), 7.62 (s, 2 H, ArH), 7.94 (AA′BB′, 2 H, ArH), 8.08 (AA′BB′, 2 H, ArH), 8.58 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.65 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.70 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.77 (d, 2 H, J = 4.5 Hz, β-pyrrole); LD-MS $C_{57}H_{51}N_4$-ISiZn calcd av mass 1012.4, obsd 1011.1; λ_{abs} (toluene) 423, 550 nm.

Exemplary Procedure for Performing Pd-Coupling Reactions: 4-[Zinc(II) 5,10,15-trimesityl-20-porphinyl]-4′-[5,10,15-trimesityl-20-porphinyl]diphenylethyne (ZnFbU)[46] (29). Samples of free base iodo porphyrin **14** (82 mg, 95 μmol) and zinc ethynyl porphyrin **13** (84 mg, 100 μmol) were added to a 100-mL one-neck round-bottom flask containing 40 mL of toluene/triethylamine (5:1). The flask was heated to 35 °C and was fitted with a 15 cm reflux condenser through which a drawn glass pipet was mounted for deaeration with argon. The reaction vessel headspace including the condenser was deaerated with a high flow rate of argon for 5 min. The solution was then deaerated by immersing the pipet in the solution and gently bubbling argon for 30 min. The condenser was then elevated, leaving the pipet in the solution, and $Pd_2(dba)_3$ (12.8 mg, 14 μmol) and $AsPh_3$ (34 mg, 110 μmol) were added. The condenser was replaced and argon was bubbled through the solution for another 5 min. At this point the pipet was removed from the reaction mixture and positioned about 2 cm above the solution. The argon flow rate was turned up slightly and the reaction was allowed to proceed. After 2 h the reaction mixture was concentrated to dryness, redissolved in 9 mL of hexanes/CH_2Cl_2 (2:1), and poured on top of a flash silica chromatography column (4.8 × 5 cm; poured dry and then washed with hexanes/CH_2Cl_2, 2:1). Elution with ∼200 mL hexanes/CH_2Cl_2 (2:1) with gentle application of air pressure caused rapid elution of $AsPh_3$ with only slight movement of the porphyrin components which remained bound at the top of the column. TLC analysis (silica, hexanes/CH_2Cl_2, 2:1) of the eluant confirms the complete elution of $AsPh_3$. Then the column was washed with 300 mL of hexanes/CH_2Cl_2 (1:1), eluting zinc monomeric porphyrin, desired dimer, and higher molecular weight material. The Pd species remained bound to the top of the column, forming a black layer while the lower portion of the column was white. The mixture of porphyrins was then concentrated to dryness, dissolved in 2 mL of toluene, and then placed on top of a preparative SEC column (Bio-Beads SX-1 poured in toluene). Gravity elution afforded three major components (in order of elution): higher molecular weight material, desired dimer, and monomeric zinc porphyrin. The dimer-containing fraction was concentrated to dryness, dissolved in 15 mL of hexanes/CH_2Cl_2 (2:1), and chromatographed on silica (4.8 cm diameter × 10 cm, poured in hexanes/CH_2Cl_2, 2:1) with gravity elution. A small amount of monomeric zinc porphyrin eluted quickly, followed by the desired dimer. Concentration of the appropriate fractions gave 115 mg (77%). We previously prepared this dimer in 82% yield in a 24 h coupling reaction at half this scale.[28] The duration of these chromatographic procedures is as follows: flash silica column (30 min), preparative SEC (2 h), final silica column (2 h). ^{1}H NMR ($CDCl_3$) δ −2.73 (bs, 2 H, NH), 1.83 (s, 12 H, $ArCH_3$), 1.90 (s, 24 H, $ArCH_3$), 2.45 (s, 6 H, $ArCH_3$), 2.49 (s, 12 H, $ArCH_3$), 7.19 (s, 4 H, ArH), 7.29 (s, 8 H, ArH), 8.06 (AA′BB′, 4 H, ArH), 8.30 (AA′BB′, 4 H, ArH), 8.65, 8.94 (m, 16 H, β-pyrrole); LD-MS $C_{108}H_{92}N_8Zn$ calcd av mass 1567.4, obsd 1568.4; λ_{abs} (toluene) 426, 515, 550, 592, 650 nm.

Zinc(II) 5,10,15-Triphenyl-20-{4-[4-(5,10,15-triphenyl-20-porphinyl)phenylethynyl]-2,6-dimethylphenyl}porphyrin (ZnFbD)[46] (30). Samples of free base iodo porphyrin **19** (52 mg, 68 μmol) and zinc ethynyl porphyrin **13** (68 mg, 82 μmol) were coupled, affording 69 mg (69%) following chromatographic workup. ^{1}H NMR ($CDCl_3$) δ −2.67 (bs, 2 H, NH), 1.87 (s, 18 H, $ArCH_3$), 1.96 (s, 6 H, $ArCH_3$), 2.64 (s, 3 H, $ArCH_3$), 2.65 (s, 6 H, $ArCH_3$), 7.29 (s, 6 H, ArH), 7.76, 7.80 (m, 9 H, PhH), 7.84 (s, 2 H, ArH), 8.04 (AA′BB′, 2 H, ArH), 8.21, 8.24 (m, 6 H, PhH), 8.30 (AA′BB′, 2 H, ArH), 8.73 (s, 4 H, β-pyrrole), 8.76 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.81 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.86, 8.89 (m, 6 H, β-pyrrole), 8.94 (d, 2 H, J = 4.8 Hz, β-pyrrole); LD-MS $C_{101}H_{78}N_8Zn$ calcd av mass 1469.2, obsd 1472.1; λ_{abs} (toluene) 426, 515, 550, 591, 648 nm.

Zinc(II) 5,10,15-Triphenyl-20-{4-[4-(5,10,15-triphenyl-20-porphinyl)(2,6-dimethylphenyl)ethynyl]phenyl}porphyrin (ZnFbP)[46] (31). Samples of zinc ethynyl porphyrin **18** (60 mg, 82 μmol) and free base iodo porphyrin **14** (59 mg, 68 μmol) were coupled, affording 86 mg (86%) following chromatographic workup. ^{1}H NMR ($CDCl_3$) δ −2.55 (bs, 2 H, NH), 1.87 (s, 18 H, $ArCH_3$), 1.95 (s, 6 H, $ArCH_3$), 2.63 (s, 3 H, $ArCH_3$), 2.64 (s, 6 H, $ArCH_3$), 7.28 (s, 2 H, ArH), 7.30 (s, 4 H, ArH), 7.75, 7.78 (m, 9 H, PhH), 7.84 (s, 2 H, ArH), 8.05 (AA′BB′, 2 H, ArH), 8.22, 8.28 (m, 8 H, ArH), 8.65 (s, 4 H, β-pyrrole), 8.74 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.84, 8.87 (m, 4 H, β-pyrrole), 8.94, 8.98 (m, 6 H, β-pyrrole); LD-MS $C_{101}H_{78}N_8Zn$ calcd av mass 1469.2, obsd 1468.8; λ_{abs} (toluene) 426, 516, 551, 592, 650 nm.

4-[Zinc(II) 5,10,15-triphenyl-20-porphinyl]-4′-[5,10,15-triphenyl-20-porphinyl]di(2,6-dimethylphenyl)ethyne (ZnFbB)[46] (32). Samples of zinc ethynyl porphyrin **18** (58 mg, 79 μmol) and free base iodo porphyrin **19** (55 mg, 72 μmol) were coupled, affording 68 mg (69%) following chromatographic workup. ^{1}H NMR ($CDCl_3$) δ −2.67 (bs, 2 H, NH), 1.96 (s, 12 H, $ArCH_3$), 7.73, 7.79 (m, 18 H, PhH), 7.82 (s, 4 H, ArH), 8.20, 8.27 (m, 12 H, PhH), 8.76 (d, 4 H, J = 4.8 Hz, β-pyrrole), 8.86, 8.89 (m, 6 H, β-pyrrole), 8.96, 8.98 (m, 6 H, β-pyrrole); LD-MS $C_{94}H_{64}N_8Zn$ calcd av mass 1371.0, obsd 1372.5; λ_{abs} (toluene) 425, 515, 550, 590, 648 nm.

Zinc(II) 5,10,15-Trimesityl-20-{4-[4-(5,10,15-trimesityl-20-porphinyl)phenylethynyl]phenyl}zinc(II) Porphyrin (Zn_2U)[46,47] (33). See ref 28.

Zinc(II) 5,10,15-Triphenyl-20-{4-[4-(5,10,15-triphenyl-20-porphinyl)(2,6-dimethylphenyl)ethynyl]phenyl}zinc(II) Porphyrin (Zn_2M)[46,47] (34). A sample of ZnFb-dimer **31** (25 mg, 0.017 mmol) was dissolved in 5 mL of $CHCl_3$, then a methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (7.5 mg, 0.034 mmol, 500 μL methanol) was added. The reaction mixture was stirred at room temperature and was monitored by fluorescence excitation spectroscopy. After 1 h the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated affording 26 mg (100%) of the zinc chelate as a purple solid. ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 18 H, $ArCH_3$), 1.96 (s, 6 H, $ArCH_3$), 2.64 (s, 3 H, $ArCH_3$), 2.65 (s, 6 H, $ArCH_3$), 7.28 (s, 2 H, ArH), 7.30 (s, 4 H, ArH), 7.77, 7.89 (m, 9 H, PhH), 7.84 (s, 2 H, ArH), 8.05 (AA′BB′, 2 H, ArH), 8.25, 8.31 (m, 8 H, ArH), 8.73 (s, 4 H, β-pyrrole), 8.81 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.85 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.94, 8.97 (m, 8 H, β-pyrrole); LD-MS $C_{101}H_{76}N_8Zn_2$ calcd av mass 1532.5, obsd 1531.8; λ_{abs} (toluene) 427, 551 nm.

4,4′-Bis[zinc(II) 5,10,15-triphenyl-20-porphyrinyl]di(2,6-dimethylphenyl)ethyne (Zn_2B)[46,47] (35). A sample of ZnFb-dimer **32** (20 mg, 0.014 mmol) was metalated in 5 mL of $CHCl_3$ with a methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (7.9 mg, 0.036 mmol, 500 μL methanol) over 1 h, affording 20 mg (100%) of the zinc chelate as a purple solid. ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 12 H, $ArCH_3$), 7.76, 7.79 (m, 18 H, PhH), 7.82 (s, 4 H, ArH), 8.20, 8.27 (m, 12 H, PhH), 8.86 (d, 4 H, J = 4.5 Hz, β-pyrrole), 8.95, 8.98 (m, 12 H, β-pyrrole); LD-MS $C_{94}H_{62}N_8Zn_2$ calcd av mass 1434.3, obsd 1434.3; λ_{abs} (toluene) 427, 550 nm.

4-[Zinc(II) 5,10,15-tris(2,6-dimethoxyphenyl)-20-porphinyl]-4′-[5,10,15-tris(2,6-dimethoxyphenyl)-20-porphinyl]di(2,6-dimethylphenyl)ethyne (Methoxy-Based ZnFbB) (36). A deaerated solution of the zinc ethynyl porphyrin **25** (39 mg, 4.3 μmol), free base iodo porphyrin **26** (49 mg, 5.2 μmol), and tri-2-furylphosphine (5 mg, 2.1 μmol) in 12 mL of pyridine/triethylamine (5:1) was treated with 2.4 mg (2.6 μmol) of $Pd_2(dba)_3$ under argon in a one-neck round-bottom flask fitted with a reflux condenser. Deaeration was achieved by passing argon through a syringe needle immersed in the solution. The mixture was heated to 80 °C for 48 h. At this point the reaction mixture was cooled to room temperature and concentrated to dryness under reduced pressure. The crude material was dissolved in CH_2Cl_2 and purified on three consecutive chromatographic columns (first column, silica, CH_2Cl_2 enriched steadily with ethyl acetate; second column, silica, CH_2Cl_2 enriched steadily with ethyl acetate; third column, silica, CH_2Cl_2 enriched steadily with ethyl acetate), affording 16 mg (21%) of the dimer. ^{1}H NMR ($CDCl_3$ containing 5% pyridine-d_5) δ −2.47 (s, 2 H, NH), 2.07 (s, 12 H, $ArCH_3$), 3.50 (s, 18 H, OCH_3), 3.52 (s, 18 H, OCH_3), 6.94, 7.02 (m, 12 H, ArH), 7.63, 7.76 (m, 12 H, ArH), 8.54, 8.62 (m, 4 H, β-pyrrole), 8.69, 8.75 (m, 12 H, β-pyrrole); LD-MS $C_{106}H_{90}N_8O_{12}Zn$ calcd av mass 1733.3, obsd 1730.8; λ_{abs} (CH_2Cl_2) 422, 514, 548, 588, 642 nm.

Methoxy-Based Zn_2B 37. Attempts to prepare this dimer led to an insoluble porphyrin product.

ZnFbZn Linear Trimer (ZnFbZn-L)[47] 38. See ref 42.

Zn_3 Linear Trimer (Zn_3L)[46,47] 39. Zinc was inserted into 15 mg of **38** using the standard conditions of zinc acetate dihydrate and $CHCl_3$/methanol (10:1). The reaction mixture was stirred for 16 h at room temperature. ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 36 H, $ArCH_3$), 1.89 (s, 12 H, $ArCH_3$), 2.64 (s, 6 H, $ArCH_3$), 2.65 (s, 12 H, $ArCH_3$), 2.67 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.30 (s, 8 H, ArH), 7.33 (s, 4 H, ArH), 8.06, 8.10 (m, 8 H, ArH), 8.30, 8.35 (m, 8 H, ArH), 8.73 (s, 8 H, β-pyrrole), 8.82 (d, 4 H, J = 4.2 Hz, β-pyrrole), 8.86 (d, 4 H, J = 4.5 Hz, β-pyrrole), 8.95 (d, 4 H, J = 4.2 Hz, β-pyrrole), 8.99 (d, 4 H, J = 4.5 Hz, β-pyrrole); LD-MS $C_{160}H_{128}N_{12}Zn_3$ calcd av mass 2415.0, obsd 2407.9; λ_{abs} (toluene) 429, 550 nm.

ZnFbZn Right-Angle Trimer (ZnFbZn-R)[47] 40. Samples of free base diiodo porphyrin **15** (25 mg, 26.2 μmol) and zinc ethynyl porphyrin **13** (65 mg, 78.9 μmol) were coupled in 21 mL of toluene/triethylamine (5:1) using $AsPh_3$ (6.4 mg, 21.0 μmol) and $Pd_2(dba)_3$ (2.4 mg, 2.6 μmol) at 40 °C under anaerobic conditions (following the general conditions for ZnFbU dimer), affording 56 mg (90%) following chromatographic workup. ^{1}H NMR (toluene-d_8) δ −2.45 (s, 2 H, NH), 1.82 (s, 48 H, *o*-$ArCH_3$), 2.58 (s, 24 H, *p*-$ArCH_3$), 7.30 (s, 12 H, ArH), 7.35 (s, 4 H, ArH), 8.06 (AA′BB′, 4 H, ArH), 8.12 (AA′BB′, 4 H, ArH), 8.31 (AA′BB′, 4 H, ArH), 8.35 (AA′BB′, 4 H, ArH), 8.63, 8.71 (m, 12 H, β-pyrrole), 8.73 (d, 2 H, J = 4.7 Hz, β-pyrrole), 8.86 (m, 6 H, β-pyrrole), 8.91 (d, 2 H, J = 4.7 Hz, β-pyrrole), 8.98 (s, 2 H, β-pyrrole); LD-MS $C_{160}H_{130}N_{12}Zn_2$ calcd av mass 2351.6, obsd 2350.3; λ_{abs} (toluene) 424, 519, 550, 590, 648 nm.

Zn_3 Right-Angle Trimer (Zn_3R)[47] 41. 41 was prepared at the analytical scale by zinc insertion with **40** following the general metalation procedure described above. ^{1}H NMR (toluene-d_8) δ 1.86 (s, 12 H, *o*-$ArCH_3$), 1.88 (s, 24 H, *o*-$ArCH_3$), 1.89 (s, 12 H, *o*-$ArCH_3$), 2.60 (s, 6 H, *p*-$ArCH_3$), 2.62 (s, 12 H, *p*-$ArCH_3$), 2.60 (s, 6 H, *p*-$ArCH_3$), 7.29 (s, 8 H, ArH), 7.31 (s, 4 H, ArH), 7.33 (s, 4 H, ArH), 8.05, 8.10 (m, 8 H, ArH), 8.24, 8.34 (m, 8 H, ArH), 8.63 (m, 8 H, β-pyrrole), 8.66, 8.70 (m, 4 H, β-pyrrole), 8.74 (d, 4 H, J = 4.5 Hz, β-pyrrole), 8.86 (d, 4 H, J = 4.5 Hz, β-pyrrole), 8.90 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.97 (s, 2 H, β-pyrrole); LD-MS $C_{160}H_{128}N_{12}Zn_3$ calcd av mass 2415.0, obsd 2414.9; λ_{abs} (toluene) 428, 512, 550, 592 nm.

4-[Zinc(II) 5,10,15-trimesityl-20-porphyrinyl]-4′-[zinc(II) 5,15-dimesityl-10-{2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]phenyl}-20-porphinyl]diphenylethyne (Mono-Trimethylsilylethyne Dimer for ZnZnFb Trimer) (42). Samples of zinc iodo ethynyl porphyrin **28** (95 mg, 94 μmol) and zinc ethynyl porphyrin **13** (91 mg, 110 μmol) were coupled, affording 110 mg (68%) following chromatographic workup. ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H, $SiCH_3$), 1.86 (s, 36 H, $ArCH_3$), 2.63 (s, 3 H, $ArCH_3$), 2.64 (s, 12 H, $ArCH_3$), 7.30 (s, 10 H, ArH), 7.62 (s, 2 H, ArH), 8.06 (AA′BB′, 4 H, ArH), 8.30 (AA′BB′, 4 H, ArH), 8.66 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.72, 8.74 (m, 6 H, β-pyrrole), 8.80, 8.83 (m, 4 H, β-pyrrole), 8.93, 8.95 (m, 4 H, β-pyrrole); LD-MS $C_{112}H_{96}N_8SiZn_2$ calcd av mass 1712.9, obsd 1710.5; λ_{abs} (toluene) 427, 551 nm.

4-[Zinc(II) 5,10,15-trimesityl-20-porphyrinyl]-4′-[zinc(II) 5,15-dimesityl-10-{2,6-dimethyl-4-ethynylphenyl}-20-porphinyl]diphenylethyne (Mono-Ethyne Dimer for ZnZnFb Trimer) (43). A sample of **42** (100 mg, 0.058 mmol) was dissolved in 10 mL of $CHCl_3$. Tetrabutylammonium fluoride on silica gel (116 mg, 1.0−1.5 mmol F^-/g) was added and the reaction mixture was stirred at room temperature for 30 min. The organic layer was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated to dryness. Column chromatography on silica (CH_2Cl_2/hexanes (1:1), 4.8 × 7 cm) afforded 86 mg (90%). ^{1}H NMR ($CDCl_3$) δ 1.86 (s, 36 H, $ArCH_3$), 2.63 (s, 3 H, $ArCH_3$), 2.64 (s, 12 H, $ArCH_3$), 3.25 (s, 1 H, CCH), 7.28 (s, 4 H, ArH), 7.30 (s, 6 H, ArH), 7.63 (s, 2 H, ArH), 8.06 (AA′BB′, 4 H, ArH), 8.30 (AA′BB′, 4 H, ArH), 8.67 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.72, 8.75 (m, 6 H, β-pyrrole), 8.80, 8.83 (m, 4 H, β-pyrrole), 8.93 (d, 2 H, J = 3.3 Hz, β-pyrrole), 8.95 (d, 2 H, J = 3.3 Hz, β-pyrrole); LD-MS $C_{109}H_{88}N_8Zn_2$ calcd av mass 1640.7, obsd 1637.1; λ_{abs} (toluene) 427, 551 nm.

ZnZnFb Trimer (ZnZnFb)[46] 44. Samples of mono-ethynyl porphyrin dimer **43** (50 mg, 30 μmol) and free base iodo porphyrin **14** (29 mg, 33 μmol) were coupled in 12.6 mL of toluene/triethylamine (5:1) using $Pd_2(dba)_3$ (4.6 mg, 5 μmol) and $AsPh_3$ (12.2 mg, 40 μmol) in a 50-mL one-neck round-bottom flask at 35 °C for 2 h under anaerobic conditions (following the general conditions for ZnFbU dimer), affording 57 mg (80%) following chromatographic workup. ^{1}H NMR ($CDCl_3$) δ −2.55 (bs, 2 H, NH), 1.87 (s, 36 H, $ArCH_3$), 1.89 (s, 12 H, $ArCH_3$), 1.98 (s, 6 H, $ArCH_3$), 2.64 (s, 9 H, $ArCH_3$), 2.65 (s, 9 H, $ArCH_3$), 2.66 (s, 6 H, $ArCH_3$), 7.28 (s, 6 H, ArH), 7.30 (s, 6 H, ArH), 7.32 (s, 4 H, ArH), 7.84 (s, 2 H, ArH), 8.04, 8.09 (m, 6 H, ArH), 8.26, 8.32 (m, 6 H, ArH), 8.65 (s, 4 H, β-pyrrole), 8.75 (s, 8 H, β-pyrrole), 8.79, 8.89 (m, 8 H, β-pyrrole), 8.95 (d, 2 H, J = 4.5 Hz, β-pyrrole), 8.97 (d, 2 H, J = 4.5 Hz, β-pyrrole); LD-MS $C_{162}H_{134}N_{12}Zn_2$ calcd av mass 2379.7, obsd 2374.4; λ_{abs} (toluene) 425, 431, 516, 552, 593, 651 nm.

Acknowledgment. This work was supported by the NIH (GM36238). We thank Dr. Walter Svec at Argonne National Laboratory for performing laser desorption mass spectrometry, and Prof. Aksel A. Bothner-By for assistance with NMR spectroscopy.

JA961611N