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Synthesis of a New *trans*-A_2B_2 Phthalocyanine Motif as a Building Block for Rodlike Phthalocyanine Polymers

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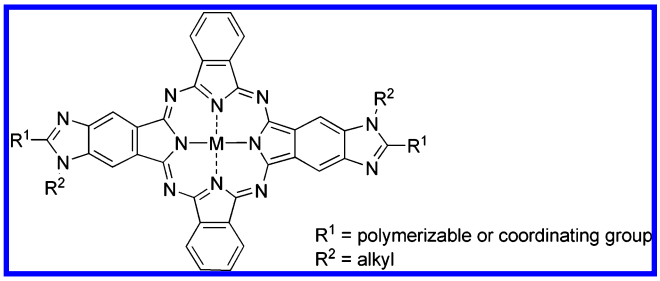
Received October 10, 2005



Polyphthalocyanines have potential application in the development of electronic materials. One-dimensional polyphthalocyanines are accessible through monomers having a *trans*-A_2B_2 structure, but the preparation of a truly linear polyphthalocyanine is challenging because of limitations imposed by the geometry of phthalocyanines and the methodology for their synthesis. Benzimidazoporphyrazines are a known class of extra-annulated phthalocyanines. A *trans*-A_2B_2 benzimidazoporphyrazine is geometrically suitable for the preparation of rodlike polymers. A new synthesis of benzimidazoporphyrazines is presented as a stepping stone to the synthesis of *trans*-A_2B_2 benzimidazoporphyrazines.

Introduction

Phthalocyanine dyes are explored for use in diverse applications such as textile colorants,[1] nonlinear optical generation and limiting,[2,3] photodynamic therapy,[4] photovoltaics,[5,6] sensors,[7] electrochromic displays,[8] and information storage.[9] In the field of molecular electronics, ordered phthalocyanine (Pc) materials are generally preferred over disordered Pc materials, and the routes to ordered Pc materials can vary widely. These routes include sublimation of phthalocyanines into crystalline layers,[10−12] Langmuir−Blodgett film formation,[13,14] mesomorphism,[15,16] and backbone polymerization.[17−22]

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(1) Christie, R. M. *Colour Chemistry*; Royal Society of Chemistry: Cambridge, UK, 2001.

(2) de la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671−1683.

(3) Calvete, M.; Yang, G. Y.; Hanack, M. *Synth. Met.* **2004**, *141*, 231−243.

(4) Allen, C. M.; Sharman, W. M.; Van Lier, J. E. *J. Porphyrins Phthalocyanines* **2001**, *5*, 161−169.

(5) Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M.; Wörhle, D.; Schnurpfeil, G.; Hirth, A.; Trombach, N. *J. Porphyrins Phthalocyanines* **1999**, *3*, 230−237.

(6) Petritsch, K.; Friend, R. H.; Lux, A.; Rozenberg, G.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1999**, *102*, 1776−1777.

(7) Zhou, R.; Josse, F.; Gopel, W.; Ozturk, Z. Z.; Bekaroglu, O. *Appl. Organomet. Chem.* **1996**, *10*, 557−577.

(8) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: San Diego, CA, 2001, 188−189 and references therein.

(9) (a) Li, J.; Gryko, D.; Dabke, R. B.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7379−7390. (b) Gryko, D.; Li, J.; Diers, J. R.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Mater. Chem.* **2001**, *11*, 1162−1180. (c) Gross, T.; Chevalier, F.; Lindsey, J. S. *Inorg. Chem.* **2001**, *40*, 4762−4774. (d) Schweikart, K.-H.; Malinovskii, V. L.; Diers, J. R.; Yasseri, A. A.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 808−828. (e) Schweikart, K.-H.; Malinovskii, V. L.; Yasseri, A. A.; Li, J.; Lysenko, A. B.; Bocian, D. F.; Lindsey, J. S. *Inorg. Chem.* **2003**, *42*, 7431−7446. (f) Wei, L.; Padmaja, K.; Youngblood, W. J.; Lysenko, A. B.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2004**, *69*, 1461−1469.

(10) Hassan, A. K.; Gould, R. D. *Phys. Stat. Sol. A* **1992**, *132*, 91−101.

(11) Nespurek, S.; Podlesak, H.; Hamann, C. *Thin Solid Films* **1994**, *249*, 230−235.

(12) Rajesh, K. R.; Menon, C. S. *Mater. Lett.* **2002**, *53*, 329−332.

(13) Xia W.; Minch, B. A.; Carducci, M. D.; Armstrong, N. R. *Langmuir* **2004**, *20*, 7998−8005.

(14) Oshiro, T.; Backstrom, A.; Cumberlidge, A. M.; Hipps, K. W.; Mazur, U.; Pevovar, S. P.; Bahr, D. F.; Smieja, J. *J. Mater. Res.* **2004**, *19*, 1461−1470.

(15) Piechocki, C.; Simon, J. *J. Am. Chem. Soc.* **1982**, *104*, 5245−5247.

(16) McKeown, N. B.; Painter, J. *J. Mater. Chem.* **1994**, *4*, 1153−6.

(17) (a) Gürek, A. G.; Bekaroglu, O. *J. Porphyrins Phthalocyanines* **1997**, *1*, 67−76. (b) Gürek, A. G.; Bekaroglu, O. *J. Porphyrins Phthalocyanines* **1997**, *1*, 227−237.

10.1021/jo052122l CCC: $33.50
Published on Web 03/30/2006

Backbone polymerized phthalocyanines are distinguished from axially connected or "shish-kebab" phthalocyanines.[23] The advantages of backbone polymerized phthalocyanines relative to noncovalently assembled phthalocyanines are (1) improved thermal and chemical stability of the short and long-range structure, (2) reproducible preparation of materials without expensive or delicate instrumentation, and sometimes (3) the addition of through-bond electronic communication between the component monomers as a complement to through-space transfer mechanisms for energy and/or electrons. Backbone polymerization of phthalocyanines is difficult because typical methods of Pc synthesis allow little control over the number and geometry of substituents and because the poor solubility of most phthalocyanines hinders their use in polymerization chemistries.

Backbone Pc polymers exist as either two-dimensional or one-dimensional materials. Most efforts at preparing two-dimensional backbone polyphthalocyanines have utilized the Pc macrocyclization reaction as the material-forming step, with bilateral or bridged building blocks such as 1,2,4,5-tetracyanobenzene or bis-dicyanobenzenes linked by alkyl chains or other intermediary groups.[17,18] Polyphthalocyanine sheets have also been prepared by the polymerization of square oligomers of four fused phthalocyanines, each bearing polymerizable end groups.[19,20] One-dimensional polymers are prepared from *trans*-A_2B_2 Pc monomers. Hanack and co-workers have prepared one-dimensional ladder oligomers and polymers based on phthalocyanines and hemiporphyrazines.[21] However, the stepwise synthesis used for such oligomers is not well suited to the preparation of polymers bearing many phthalocyanine macrocycles. Kingsborough and Swager prepared a thiophene-linked metallophthalocyanine polymer by electropolymerization of thiophene end groups.[22] The resulting polymer chains are described as "nearly linear"; however, they are unlikely to hold a rodlike shape due to the natural substituent geometry of phthalocyanines (vide infra).

The optoelectronic properties of a polyphthalocyanine material may differ from monomeric phthalocyanine properties according to the nature of the linking groups. The electroactive thiophene linking groups in Kingsborough's polyphthalocyanine play a large role in the electronic character of the resulting polymer,[22] such that it is not the equivalent of an all-phthalocyanine polymer. The fused linkages in the ladder oligomers and phthalocyanine sheets have a significant effect on the photochemical and electrochemical properties of the individual chromophores of the resulting material, resulting in broadening and red-shifting of the native Pc UV−vis absorption spectra.[17−20] In some cases, the perturbations that are caused by the nature of the linkages between phthalocyanines may be beneficial and intentional. Theoretical study of fused polyphthalocyanines using molecular orbital theory has led to the prediction that such materials should exhibit intrinsic metallic conductivities.[24] As a complement to this type of beneficial perturbation, researchers may also seek access to polyphthalocyanines that exhibit properties very similar to the constituent monomer precursors.

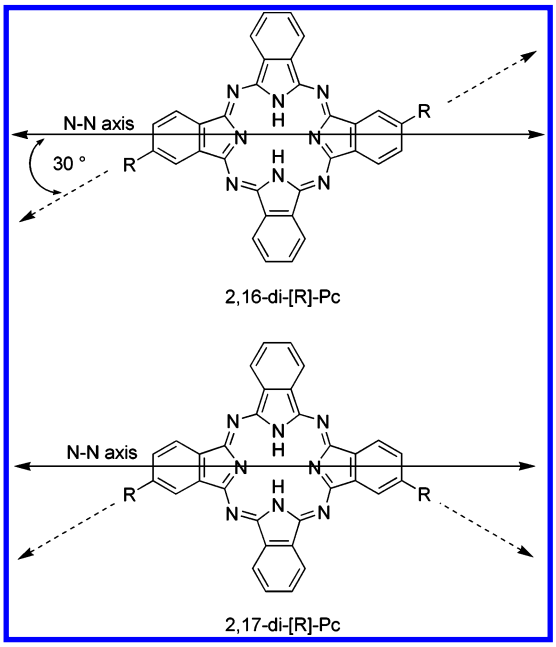


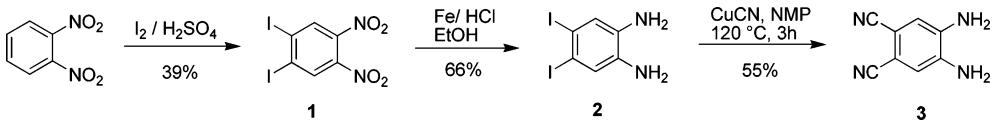
FIGURE 1. Structures of two disubstituted phthalocyanines. The N−N axis bisects two inner nitrogen atoms and two opposing benzo rings. The axis equally can be displayed bisecting the NH−NH atoms.

Backbone polymerization of porphyrins has been achieved without perturbation of the monomeric pigment properties. Lindsey and co-workers have prepared backbone polymers of diethynylporphyrins by chemical as well as thermal polymerization of ethyne end groups.[25,26] The chemically polymerized porphyrin "light-harvesting rods" are of interest in the capture of solar energy,[25] whereas the thermally polymerized porphyrins have been examined as electroactive films for information storage.[26] In the light-harvesting rods the linkages between porphyrins are made by Glaser coupling and are phenylbutadiynylphenyl groups, which allow for through-bond communication (excited-state energy, ground-state hole/electron transfer) without perturbing the electronic properties of the linked porphyrins.[25,27] A one-dimensional Pc polymer that could retain the native electronic properties of the Pc subunits while engaging in through-bond communication would be a useful counterpart to the porphyrin-based rods.

The inherent geometry of phthalocyanines plays a major role in the design of a linear phthalocyanine polymer. In Figure 1, two possible ABAB phthalocyanines are shown, having 2,16- and 2,17-substitution patterns. The substituents of the 2,16-isomer are parallel but not collinear, while the substituents of the 2,17-isomer are at a 120° angle with respect to each other. These geometries result from the fact that each of the peripheral

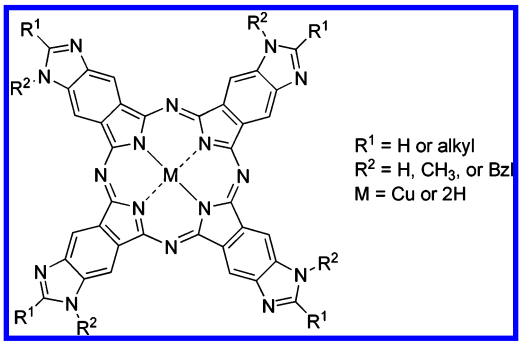
(18) Wörhle, D.; Benters, R.; Suvorova, O.; Schurpfeil, G.; Trombach, N.; Bogdahn-Rai, T. *J. Porphyrins Phthalocyanines* **2000**, *4*, 491−497.
(19) Achar, B. N.; Fohlen, F. M.; Parker, J. A. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1785−1790.
(20) Venkatachalam, S.; Rao, K. V. C.; Manoharan, P. T. *J. Polym. Sci. Part B* **1994**, *32*, 37−52.
(21) (a) Hauschel, B.; Ruff, D.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2449−2451. (b) Hanack, M.; Stihler, P. *Eur. J. Org. Chem.* **2000**, 303−311. (c) Rack, M.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1646−1648.
(22) Kingsborough, R. P.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2897−2900.
(23) Hanack, M.; Hees, M.; Stihler, P.; Winter, G.; Subramanian, L. R. In *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p 381.
(24) Gomez-Romero, P.; Lee, Y.-S.; Kertesz, M. *Inorg. Chem.* **1988**, *27*, 3672−3675.
(25) Loewe, R. S.; Tomizaki, K.; Youngblood, W. J.; Bo, Z.; Lindsey, J. S. *J. Mater. Chem.* **2002**, *12*, 3438−3451.
(26) Liu, Z.; Schmidt, I.; Thamyongkit, P.; Loewe, R. S.; Syomin, D.; Diers, J. R.; Zhao, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. *Chem. Mater.* **2005**, *17*, 3728−3742.
(27) Youngblood, W. J.; Gryko, D. T.; Lammi, R. K.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2002**, *67*, 2111−2117.

SCHEME 1



substituents is offset with respect to one of the central N−N axes by a 30° angle (see Figure 1 for definition of the N−N axis). A polymer prepared from a mixture of these isomers could not be expected to afford a linear alignment. Even a polymer produced solely from the 2,16-isomer would be unlikely to hold a 180° alignment over long range due to rotation about the bonds between the phthalocyanines and their linkages.

To produce rodlike phthalocyanine polymers, the core pigment scaffold must be modified such that substituents are collinear with the N−N axes of the macrocycles. Such architecture can be achieved with phthalocyanines bearing five-membered outer rings, either in place of the standard benzo rings, or by extra-annulation. A five-membered all-carbon ring would break the aromaticity of the macrocycle, so the outermost ring must be heterocyclic. There are reported syntheses for phthalocyanines bearing diverse five-membered heterocyclic outer rings.[28] Some are prepared from heterocyclic building blocks, whereas others are achieved by peripheral modification of phthalocyanines. Examples that permit substitution at the outermost position include pyrrole, indole, imidazole, and thiophene. From this list, the extra-annulated imidazole is the most accessible in terms of numbers and types of synthetic steps. Phthalocyanines bearing this motif have been previously termed imidazophthalocyanines,[28] as well as benzimidazoloporphyrazines (note that a tetrabenzoporphyrazine is synonymous with a phthalocyanine.).[29] The general form of this compound class is shown below, with regard to the examples known in the literature (note that up to four regioisomers are possible based on the placement of the $N_{imidazo}$ substituents).



This report uses the term benzimidazoporphyrazines, a slight abbreviation of a previous name, and still unambiguous with respect to the motif. The work described herein has produced a linear, *trans*-substituted phthalocyanine analogue, based on the benzimidazoporphyrazine scaffold. The development of new synthetic methodology for benzimidazoporphyrazines (BzImPAs) is presented as a stepping-stone toward the desired *trans*-BzImPA(s). The structural properties and photochemical behavior are compared with those of well-known phthalocyanines.

Results and Discussion

Synthesis. All of the published reports of benzimidazoporphyrazines have employed 5,6-dicyanobenzimidazoles as the key building blocks.[29,30] Kudrik and co-workers showed the utility of dicyanophenylenediamine **3** (Scheme 1) as a precursor to 2-alkyl-5,6-dicyanobenzimidazoles.[30] Their synthesis of **3** required seven steps, with an overall yield of ∼7%.[31] The best reported route to **3** is the preparation by Mitzel and co-workers, with a 14% yield over four steps.[32,33] Scheme 1 shows a new synthesis of **3**, with a 14% yield over three steps.

The iodination of dinitrobenzene uses I_3^+, formed by mixing iodine with oleum.[34] The reconstitution of I_2 as a product of the ensuing iodination reaction allows the I_3^+ intermediate to reform continuously and, thus, makes atom-economic use of the halogen starting material. However, the previously reported yield of 56% for diiodination when using only 0.5 equiv of I_2 seems unreasonable in view of the reaction stoichiometry. Attempts to repeat the reaction as reported consistently gave yields of 19−20%. The yield was improved to 39% by lowering the temperature of the reaction from 170 to 120 °C, shortening the time from 105 to 75 min, and increasing the iodine to the stoichiometric requirement (1 equiv of I_2 for diiodination). The reduction of **1** to the corresponding diamino compound **2** using Sn/HCl has been reported by Whitesides and co-workers, although no specific procedure or yield was provided.[35] The use of Fe/HCl gave the compound in 66% yield and avoids the voluminous tin salts which are typical of Sn reductions. Compared to the cyanation of the corresponding dibromophenylenediamine,[32] the cyanation of **2** proceeds at lower temperature (120 vs 140 °C) more quickly (3 vs 15 h) and in greater yield (55 vs 25%). Complexation of products **2** and **3** with the metal salts left over at the end of each reaction is avoided by treatment of the hot crude mixtures with aqueous EDTA.

Dicyanobenzimidazoles have previously been prepared by dehydrative cyclization of **3** with low molecular weight carboxylic acids (e.g., formic to hexanoic acid).[30] The reactions were conducted neat, with the carboxylic acids serving as reagent, solvent, and Bronsted acid catalyst. Scheme 2 shows

(28) Stuzhin, P. A.; Ercolani, C. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2003; Vol. 15, pp 263−364.

(29) Pardo, C.; Yuste, M.; Elguero, J. *J. Porphyrins Phthalocyanines* **2000**, *4*, 505−509.

(30) (a) Kudrik, E. V.; Shaposhnikov, G. P. *Mendeleev Commun.* **1999**, 85−86. (b) Kudrik, E. V.; Shaposhnikov, G. P.; Balakirev, A. E. *Russ. J. Gen. Chem.* **1999**, *69*, 1321−1324. (c) Balakirev, A. E.; Kudrik, E. V.; Shaposhnikov, G. P. *Russ. J. Gen. Chem.* **2002**, *72*, 1616−1619.

(31) For syntheses leading to the starting material **3** used in ref 29, see: (a) Zharnikova, M. A.; Balakirev, A. E.; Maizlish, V. E.; Kudrik, E. V.; Shaposhnikov, G. P. *Russ. J. Gen. Chem.* **1999**, *69*, 1870−1871. (b) Shishkina, O. V.; Maizlish, V. E.; Shaposhnikov, G. P.; Lyubimtsev, A. V.; Smirnov, R. P.; Baran'ski, A. *Russ. J. Gen. Chem.* **1997**, *67*, 842−845. (c) Elvidge, J. A.; Golden, J. H.; Linstead, R. P. *J. Chem. Soc.* **1957**, 2466−2469; Levy, L. F.; Stephen, H. *J. Chem. Soc.* **1931**, 79−82.

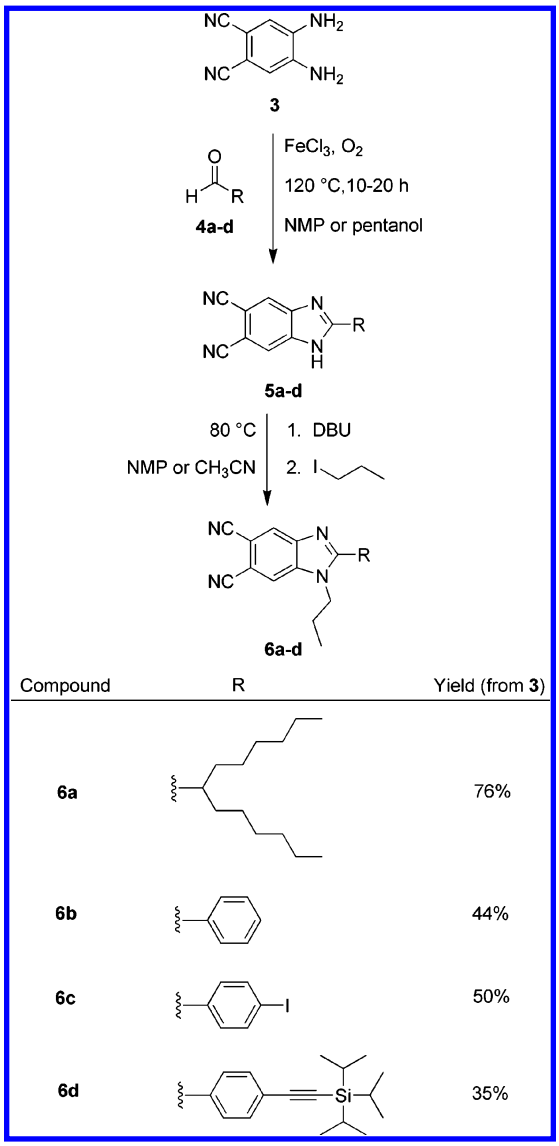
(32) Mitzel, F.; Fitzgerald, S.; Beeby, A.; Faust, R. *Chem. Eur. J.* **2003**, *9*, 1233−1241.

(33) For syntheses leading to the starting material used in ref 31, see: (a) Cheeseman, G. W. H. *J. Chem. Soc.* **1962**, 1170−1176. (b) Acheson, R. M. *J. Chem. Soc.* **1956**, 4731−4735. Elderfield, R. C.; Meyer, V. B. *J. Am. Chem. Soc.* **1954**, 1887−1891. (c) Mørkved, E. H.; Neset, S. M.; Bjørlo, O.; Kjøsen, H.; Hvistendahl, G.; Mo, F. *Acta Chem. Scand.* **1995**, *49*, 658−662.

(34) Arotsky, J.; Butler, R.; Darby, A. C. *J. Chem. Soc. C* **1970**, 1480−1485.

(35) Schwiebert, K. E.; Chin, D. N.; MacDonald, J. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 4018−4029.

SCHEME 2



the conversion of **3** to various benzimidazoles via oxidative cyclization with selected aldehydes **4a**−**d**. Originally developed by Weidenhagen using $Cu(OAc)_2$ as the oxidant,[36] this method has evolved in recent years to the more environmentally benign use of O_2, with $FeCl_3$ as a catalytic oxidant.[37,38] The oxidative cyclization is a comparatively mild alternative to the dehydrative condensation of phenylenediamines with substituted benzoic acids, which typically requires strong hygroscopic acids such as concd HCl and polyphosphoric acid.[39] Yields of 58% and 81% were obtained for benzimidazoles **5a** and **5d**, respectively. Benzimidazole **5d** was also prepared directly from **2**, taking advantage of the copper salts left over from the cyanation reaction (Scheme 1), by adding aldehyde **4d** and bubbling O_2 through the crude reaction mixture containing **3**. This procedure was considerably faster than the $FeCl_3$ method, due to the large quantity of copper salts present, and gave **5d** in 41% yield (see the Experimental Section). Due to the poor solubility of compounds **5b** and **5c**, the cyclization reaction mixture was carried forward directly to alkylation at the 1-position, giving **6b** and **6c**.

Alkylation of the 1-position of these dicyanobenzimidazoles with the relatively small propyl group was predicated on the intent to use the resulting benzimidazoporphyrazines as components in materials where the macrocycles would be closely packed. Larger alkyl groups, although perhaps helpful for the solubility of the benzimidazoporphyrazines, would prohibit the close packing of the macrocycles. Benzimidazoles **5a** and **5d** proved unreactive to iodopropane in the absence of a base, even at elevated temperature. Deprotonation could be effected with DBU, and subsequent alkylation with iodopropane (bp 101 °C) succeeds at 80 °C in acetonitrile or NMP (*N*-methyl pyrrolidinone). Propyldicyanobenzimidazoles **6a**−**d** were obtained in 35−76% yield from diamine **3**. The swallowtail benzimidazole **5a** gave better results in the alkylation reaction (94%) compared to the 2-arylbenzimidazoles, suggesting some influence of the 2-substituent on the basicity/nucleophilicity of the benzimidazole.

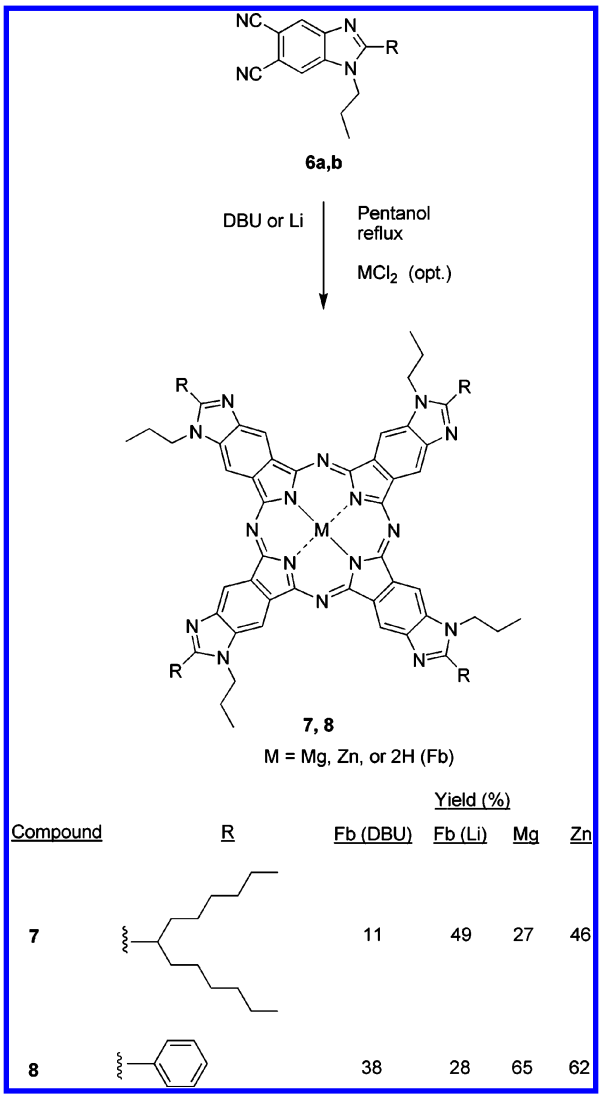
The swallowtail- and phenylbenzimidazoles **6a** and **6b** were chosen as benchmark motifs for tetrasubstituted (A_4) 2-alkyl- and 2-aryl-5,6-benzimidazoporphyrazines, respectively (Scheme 3). In principle, a wide variety of aldehyde-bearing groups can be installed at the 2-position. This versatility is limited by the stability of a given aldehyde-bearing group under the conditions of the oxidative cyclization and alkylation reactions. Groups that might interfere with or be affected by these two steps, such as ferrocenyl or pyridyl, can be transformed to dicyanobenzimidazoles by cross-coupling to the *p*-iodophenyl-benzimidazole **6c**. The protected ethynylphenylbenzimidazole **6d** was prepared as a building block for *trans*-diethynylbenzimidazoporphyrazines.

The previous reports of A_4-type benzimidazoporphyrazines report UV−vis absorption spectra in DMF and sulfuric acid.[29,30] **Fb-7** and **Fb-8** (Scheme 3), as well as the their zinc and magnesium chelates, were prepared to investigate the photochemical properties of these macrocycles (ϵ, λ_{abs}, λ_{em}, Φ_f) in common organic solvents. Such photochemical studies provide a comparison of the extra-annular imidazole ring with the corresponding benzo rings of naphthalocyanine (see the Supporting Information for a discussion of the photochemistry of BzImPAs). The yields of the DBU-mediated reactions of **6a** increase according to the presence and type of metal salt in the order Fb < Mg < Zn, in accord with known results for phthalocyanine formation using DBU with and without metal salts.[40] The corresponding reactions with **6b** do show an improvement in the yields for the metallo-derivatives compared to the free base, but the yields of **Mg-8** and **Zn-8** are essentially equivalent within experimental variation. Surprisingly, the yield of **Fb-8** in the DBU-mediated reaction was slightly better than that using lithium pentoxide.

The ^{1}H NMR spectrum of **Fb-8** shows the usual evidence of the aromatic ring current, with the core protons found at −3.13 ppm. The ^{1}H NMR spectrum of **Fb-7** shows no signal for the core protons in the negative ppm region, even as far as −8 ppm. The core protons of **Fb-7** were assigned to an otherwise unaccountable broad signal at 0.30−0.50 ppm that bears a correct integration for the two NH protons and is absent from

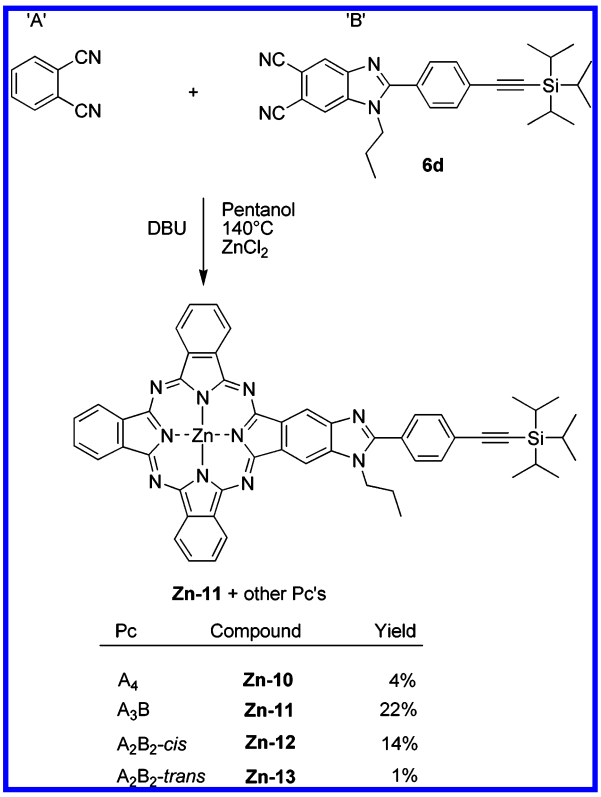
(36) (a) Weidenhagen, R. *Chem. Ber.* **1936**, *69*, 2263−2272. (b) Weidenhagen, R.; Weedon, U. *Chem. Ber.* **1938**, *71*, 2347−2360.
(37) Coville, N. J.; Neuse, E. W. *J. Org. Chem.* **1977**, *42*, 3485−491.
(38) Singh, M. P.; Sasmal, S.; Lu, W.; Chatterjee, M. N. *Synthesis* **2000**, 1380−1390.
(39) Grimmett, M. R. *Imidazole and Benzimidazole Synthesis*; Academic Press: New York, 1997; pp 71−94.
(40) (a) Tomoda, H.; Saito, S.; Ogawa, S.; Shiraishi, S. *Chem. Lett.* **1980**, 1277−1280. (b) Tomoda, H.; Saito, S.; Shiraishi, S. *Chem. Lett.* **1983**, 313−316.

SCHEME 3



Compound	R	Yield (%) Fb (DBU)	Fb (Li)	Mg	Zn
7		11	49	27	46
8		38	28	65	62

SCHEME 4



Pc	Compound	Yield
A_4	**Zn-10**	4%
A_3B	**Zn-11**	22%
A_2B_2-*cis*	**Zn-12**	14%
A_2B_2-*trans*	**Zn-13**	1%

the ^{1}H NMR spectra in the metalated analogues **Mg-7** and **Zn-7**. It is not known whether the appearance of the core protons of **Fb-7** at relatively higher ppm could be due to a steric or electronic effect. The general structure shown in Scheme 3 depicts a macrocycle having C_{4h} symmetry, but the A_4 benzimidazoporphyrazines can have up to four regioisomers resulting from the placement of the propyl groups. As a result, the ^{1}H NMR spectra of the zinc and free base forms of **7** and **8** exhibited broad signals for most of the expected resonances. The ^{1}H NMR signatures for **Mg-7** and **Mg-8**, however, were far less complex, indicating a possibly monodisperse product. The effect of metal templating on the distribution of regioisomers in phthalocyanine-forming reactions has been previously detailed.[41] All of the A_4 benzimidazoporphyrazines are green in solid form as well as in solution.

The initial attempt to prepare a *trans*-diethynylbenzimidazoporphyrazine used a mixture of **6a** and **6b** in a macrocyclization reaction. This reaction gave an inseparable product mixture. The same problem was encountered for the reaction between **6d** and diheptylphthalonitrile (**10**).[42] The reaction of **6d** with dicyanobenzene (Scheme 4) gave a separable mixture of products. The smaller macrocyclic products (A_4, A_3B, and A_2B_2) were separated from the larger ones (AB_3 and B_4) by size-exclusion chromatography. The smaller macrocycles were then separated from one another by adsorption chromatography. The larger macrocycles were not individually isolated. Compound **6d** appeared to be slightly more reactive than 1,2-dicyanobenzene, and a 1:1 ratio of the two reactants, respectively, gave a product mixture favoring the AB_3 and B_4 products. A corresponding ratio of 1:1.5 (**6d**/dicyanobenzene) gave a more even distribution of the possible products. The recovered samples of the *trans*-diethynylbenzimidazoporphyrazine **Zn-13** and the *cis*-isomer **Zn-12** displayed similar ^{1}H NMR and LD-MS spectra, but were easily distinguished by their respective UV−vis absorption spectra (see the Supporting Information). **Zn-11** was easily separated in the initial size-exclusion column. **Zn-11** is a blue solid, but takes on a blue-green color in solution. The A_2B_2 compounds are also blue solids, but appear green in solution.

Dicyanobenzimidazole **6d** was transformed into the corresponding diiminoisoindoline **14** in 76% yield using a well-known procedure (Scheme 5).[43] The product did not fully crystallize from the reaction, but the quantity of recovered solid could be amplified by concentrating the mixture using a stream of argon. The crystals obtained were greenish-white needles that turned deep green upon melting. The melted sample was recovered from the capillary and was found to exhibit a UV−vis absorption profile analogous to that of **Fb-8** (see the Supporting Information).

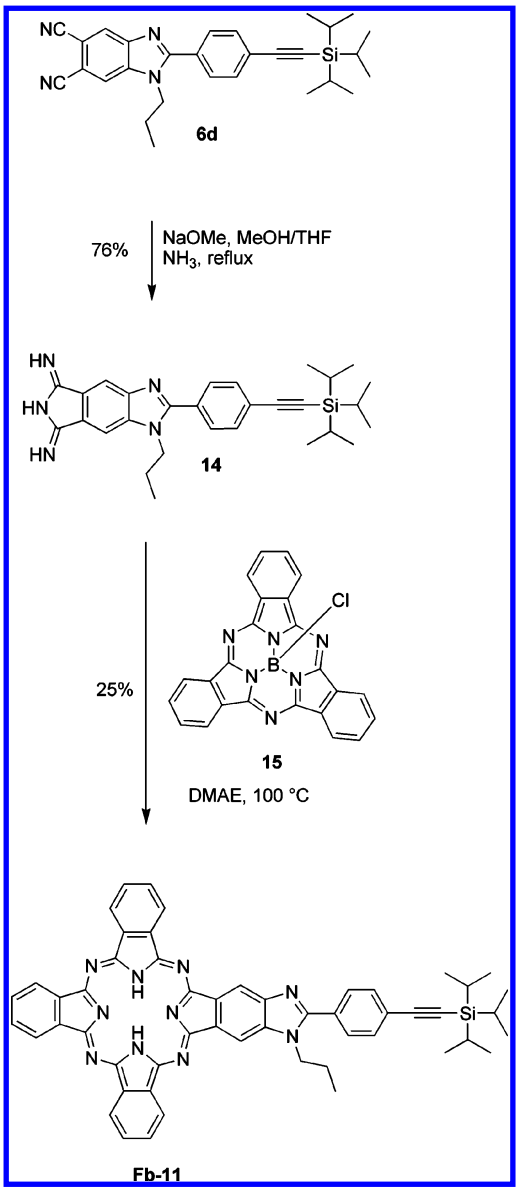
Diiminoisoindoline **14** was reacted with boron subphthalocyanine (**15**) to prepare the A_3B compound **Fb-11** (Scheme 5).

(41) Rager, C.; Schmid, G.; Hanack, M. *Chem. Eur. J.* **1999**, *5*, 280−288.

(42) (a) Nishi, H.; Azuma, N.; Kitahara, K. *J. Heterocycl. Chem.* **1992**, *29*, 475−477. (b) Hanack, M.; Haisch, P.; Lehmann, H.; Subramanian, L. R. *Synthesis* **1993**, 387−390.

(43) Brach, P. J.; Grammatica, S. J.; Ossanna, O. A.; Weinberger, L. *J. Heterocycl. Chem.* **1970**, *7*, 1403−1405.

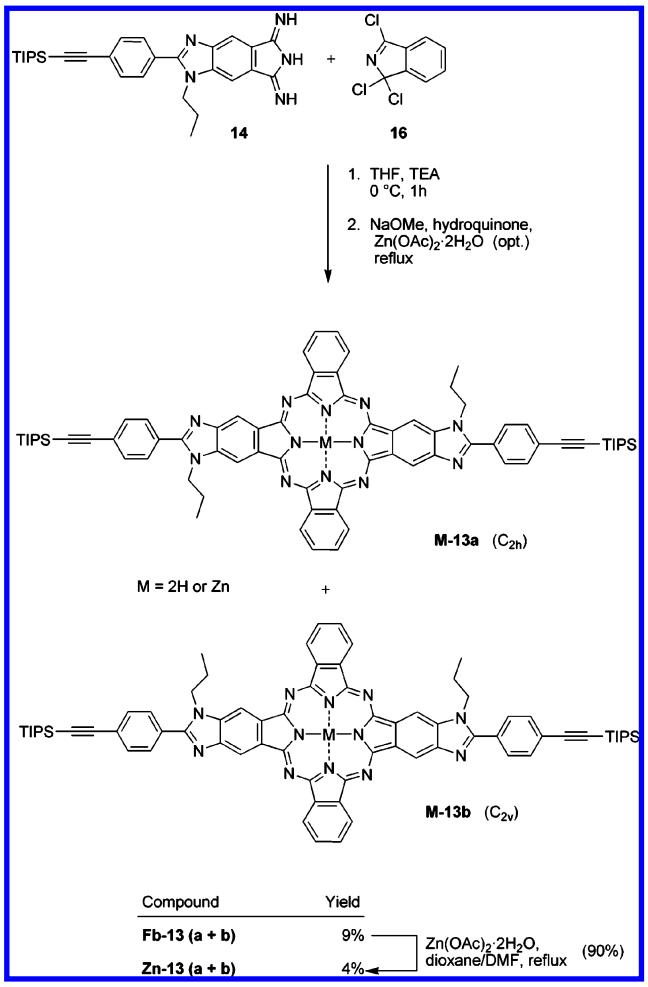
SCHEME 5



The subPc **15** had to be employed at four times the stoichiometric ratio in order to suppress the formation of products having more than one benzimidazole moiety. **Fb-11** exhibits poor solubility but is marginally more soluble than the large quantity of unsubstituted phthalocyanine that is also formed. **Fb-11** could be largely separated from the unsubstituted phthalocyanine by Soxhlet extraction of the product mixture using chloroform, followed by size-exclusion chromatography. The yield is modest (25%), but the alternative route to **Fb-11** would be the demetalation of **Zn-11**, which is not possible under mild conditions. (Zinc porphyrins can be demetalated in the presence of TFA at room temperature, but this is ineffective for zinc phthalocyanines.) There is no published report of the demetalation of a zinc phthalocyanine. **Fb-11** is blue in solid form and greenish-blue in solution.

The *trans*-diethynylbenzimidazoporphyrazine **Fb-13** was prepared in 9% yield by cross-condensation of diiminoisoindoline **14** with trichloroisoindolenine **16** (Scheme 6), following the procedure reported by Young and Onyebuagu.[44] A trace quantity of an AB_3 byproduct was formed in the reaction, as previously observed.[45] The yield of the *trans*-A_2B_2 product

SCHEME 6



dropped to 4% when $ZnCl_2$ was used as a templating agent in the reaction. The compound **Zn-13** was more accessible by metalation of **Fb-13** using $Zn(OAc)_2 \cdot 2H_2O$. There are two possible regioisomers of the *trans*-A_2B_2 structure, of C_{2v} and C_{2h} symmetries, because of the position of the respective $N_{imidazo}$ substituents. For **Fb-13** these regioisomers were not separable by chromatography on silica gel.

The ^{1}H NMR spectra of the isolated sample of **Fb-13** had duplicate signals for each expected resonance, including the protons within the macrocycle (see the Supporting Information). Compounds **Fb-8** and **Fb-11** have slightly broadened signals for the inner protons, but not the twinned peaks that are seen for **Fb-13**. Hanack and co-workers attributed the split appearance of the inner proton resonance of their *trans*-A_2B_2 phthalocyanine to the different environments encountered by the NH protons in the tautomers of the structure.[45] A variable-temperature ^{1}H NMR experiment in THF-d_8 showed that the signals for the various duplicated resonances of **Fb-13** did approach one another at high temperatures (up to 55 °C), but the signals never merged, and the usual broadening associated with exchange-equilibrium behavior was not observed. Given the rather low-temperature limit of the solvent, this result is not conclusive as to the origin of the twinned resonances.

The ^{1}H NMR spectrum of a sample of **Zn-13** having both regioisomers was far less complex than the corresponding

(44) Young, J. G.; Onyebuagu, W. *J. Org. Chem.* **1990**, *55*, 2155−2159.
(45) Stihler, P.; Hauschel, B.; Hanack, M. *Chem. Ber.* **1997**, *130*, 801−806.

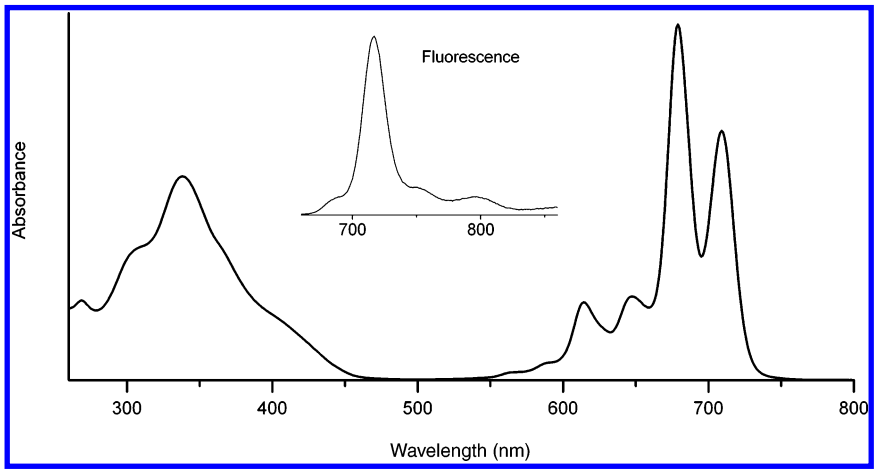
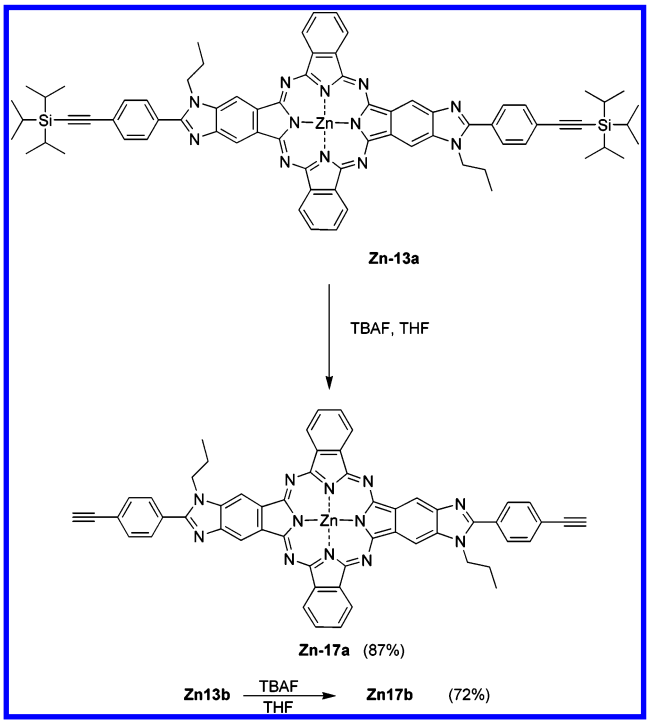


FIGURE 2. Absorption and emission spectra for **Zn-13a** in THF.

signature of the free base compound. Only the aromatic region showed more complexity than would be expected for a monodisperse sample. The regioisomers of **Zn-13** were separable by chromatography on silica gel and exhibited distinct patterns in the aromatic region of the ^{1}H NMR spectrum, enabling assignment. The first eluting species, **Zn-13a**, exhibits an ABCD splitting pattern for the protons on the benzo rings, consistent with the assignment of C_{2h} symmetry. The second eluting species, **Zn-13b**, shows multiplets that resemble typical AA′BB′ splitting patterns, corresponding to the structure assigned to C_{2v} symmetry. COSY NMR analyses were performed to confirm the coupling patterns that support these assignments of the regioisomers (see Supporting Information). As with the A_2B_2 products from the reaction of **6d** with dicyanobenzene, all of the *trans*-A_2B_2 compounds are blue in solid form but deeply green in solution. The UV−vis spectrum of compound **Zn-13a** is shown in Figure 2. The lowered symmetry of the macrocycle results in a split Q-band structure, but the photochemical behavior of the sample is otherwise similar to typical zinc-phthalocyanines. A detailed presentation of the photochemistry of the benzimidazoporphyrazines prepared for this report can be found in the Supporting Information.

The deprotection of **Zn-13a** and **Zn-13b** proceeded smoothly using TBAF in dichloromethane, but the compounds proved to be surprisingly polar during chromatography (Scheme 7). Loss of the triisopropylsilyl groups also adversely affected the solubility of the resulting diethynyl compounds. **Zn-13a** and **Zn-13b** are soluble in chlorinated solvents and very soluble in THF, whereas **Zn-17a** and **Zn-17b** slowly precipitated after chromatographic purification. Pure samples of **Zn-17a** and **Zn-17b** are weakly soluble in chlorinated solvents and moderately soluble in THF.

SCHEME 7



Conclusion

The substituent geometry of benzimidazoporphyrazines makes them useful for constructs that require a controlled alignment of phthalocyanine macrocycles. A new basic route to 2-substituted dicyanobenzimidazoles via the oxidative cyclization of **3** with various aldehydes gives access to benzimidazoporphyrazines bearing useful substituents for elucidation into supramolecular complexes and/or materials. Free base and metallobenzimidazoporphyrazines of A_4, A_3B and *trans*-A_2B_2 substitution patterns can be prepared in useful quantities. Linear, *trans*-diethynylbenzimidazoporphyrazines (**Zn-17a** and **Zn-17b**) have been prepared as precursors to rodlike phthalocyanine polymers. The quantities of the isolated diethynyl-*trans*-benzimidazoporphyrazines were small (<10 mg), but sufficient for their full characterization and testing in exploratory polymerizations. The procedures developed for this route typically gave moderate to low yields but are each amenable to higher scale.

Experimental Section

Noncommercial Compounds. Compounds **4a**,[46] **4d**,[47] **9**,[42] **15**,[48] and **16**[49] were prepared according to the literature.

(46) Kato, M.; Komoda, K.; Namera, A.; Sakai, Y.; Okada, S.; Yamada, A.; Yokoyama, K.; Migita, E.; Minobe, Y.; Tani, T. *Chem. Pharm. Bull.* **1997**, *45*, 1767−1776.

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

(48) Claessens, C. G.; Gonzalez-Rodriguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H. P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, *14*, 2547−2551.

(49) Farbenfabriken Bayer, U. S. Patent 2,701,252; Feb. 1, 1955.

1,2-Diiodo-4,5-dinitrobenzene (1). A three-necked, 100 mL round-bottom flask was charged with oleum (38 mL of a 20% solution, 0.18 mol SO_3) and a magnetic stirring bar. The flask was fitted with a condenser and a bubbler, and the spare necks were closed with glass stoppers. The flask was placed in an oil bath heated to 120 °C. Iodine (6.86 g, 27.0 mmol) was added, after 20 min, *o*-dinitrobenzene (4.54 g, 27.0 mmol) was added, and the reaction was heated for 75 min and then removed from heat and immediately poured into a 1 L conical flask filled with ice. The crude mixture was quenched with NaOH pellets until it was slightly alkaline to pH paper, with more ice added to keep the mixture cold. The mixture was then filtered through filter paper, and the filtrate was extracted with $CHCl_3$. The organic layer of the extraction was washed with aqueous $Na_2S_2O_5$, water, and brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The dark brown filter cake was stirred with 200 mL of hot water to which $Na_2S_2O_5$ was added until no further bubbling was observed. The mixture was then filtered and the filtrate was discarded. The filter cake and the residue from the extraction were recrystallized (EtOH/water) yielding dark brown crystals (4.47 g, 39%): mp 183−184 °C (lit.[34] mp 184 °C); ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 2H); ^{13}C NMR δ 114.6, 134.8. Anal. Calcd for $C_6H_2I_2N_2O_4$: C, 17.16; H, 0.48; N, 6.67; Found: C, 17.44; H, 0.41, 6.61.

Scale-up. The above procedure was followed with the following quantities of reagents: oleum (200 mL), iodine (37.80 g), *o*-dinitrobenzene (25.0 g). To quench the large volume of SO_2 produced by the reaction, the evolved gas was bubbled through a solution of aqueous NaOH (5 M, 1 L), which was later used to quench the acidic crude reaction mixture over ice, along with an additional 125 g of NaOH, followed by $Na_2S_2O_5$ (18.5 g). The $CHCl_3$ extraction of the initial crude filtrate was omitted. Yield: 32%. Characterization data were consistent with the smaller scale reaction.

1,2-Diamino-4,5-diiodobenzene (2). Following a literature procedure, a sample of **1** (17.42 g, 41.5 mmol) and a magnetic stirring bar were added to a 500 mL conical flask fitted with a jacketed condenser. EtOH (95%, 150 mL) and concd aqueous HCl (68.6 mL, 0.83 mol) were added, and the mixture was stirred and heated to boiling. Fe powder (18.59 g, 0.332 mol) was added in portions, resulting in foaming of the mixture and accelerated refluxing of the EtOH, which subsided within a few minutes of each addition. The reaction was heated for 45 min beyond the final addition of Fe. A hot solution of EDTA (156 g, 0.411 mol, in 300 mL H_2O) was added to the mixture, and KOH pellets were added until the solution was alkaline to pH paper. The hot mixture was extracted twice with ethyl acetate, and the extracts were combined, washed with water and then with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue was recrystallized (EtOH/water), giving tan needles (9.92 g, 66%): mp 135−136 °C; ^{1}H NMR (THF-d_8) δ 4.21 (br s, 4H), 7.03 (s, 2H); ^{13}C NMR (THF-d_8) δ 91.1, 124.5, 137.6. Anal. Calcd for $C_6H_6I_2N_2$: C, 20.02; H, 1.68; N, 7.78; Found: C, 20.19; H, 1.59, 7.71.

1,2-Diamino-4,5-dicyanobenzene (3). A 50 mL round-bottom flask was charged with **2** (6.94 g, 19.3 mmol), CuCN (6.91 g, 77.2 mmol, 4 equiv), and a magnetic stirring bar. The vessel was capped with a septum and flushed with Ar for 10 min, and NMP (20 mL) was added. The vessel was heated to 120 °C for 3 h, then diluted with DMF (20 mL) and added to a hot aqueous solution of EDTA (88 g, 232 mmol, in 500 mL H_2O) in a 1 L conical flask. Oxygen was bubbled through the mixture as it was stirred and heated for 2 h. After 2 h, the dark heterogeneous mixture turned to a homogeneous green solution. The hot green solution was extracted twice with ethyl acetate, and the extracts were washed with water, then with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue was recrystallized (EtOH/water), giving tiny tan needles (1.66 g, 55%): mp 262−264 °C (lit.[30b,32] mp 193−195 or 272−275 °C); ^{1}H NMR (acetone-d_6) δ 5.40 (br s, 4H), 7.04 (s, 2H); ^{13}C NMR (acetone-d_6) δ 103.8, 117.1, 117.4, 139.4; FAB-MS obsd 158.0591, calcd 158.0592 ($C_6H_6N_4$).

5,6-Dicyano-2-(undec-7-yl)benzimidazole (5a). A 100 mL round-bottom flask was charged with **3** (1.32 g, 8.37 mmol), pentanol (42 mL), 2-hexyl-1-octanal[46] (1.77 g, 8.37 mmol), and a magnetic stirring bar. The flask was fitted with a Hickman still and placed in an oil bath heated to 120 °C. NMP (4.0 mL) was added to fully dissolve the solid material. The mixture was heated and stirred for 2 h. Then $FeCl_3 \cdot 6H_2O$ (113 mg, 0.42 mmol) was added to the reaction vessel, and oxygen was bubbled through the mixture as it was heated and stirred for an additional 12 h. The reaction mixture was then removed from heat and added to 200 mL of diethyl ether. The ether solution was washed three times with water, then washed with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue was chromatographed (silica, $CHCl_3$), yielding a tan solid (2.37 g, 81%): mp 148−149 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.6 Hz, 6H), 1.10−1.30 (m, 16H), 1.77−1.87 (m, 2H), 2.90−3.04 (m, 1H), 8.07 (br s, 2H), 10.36 (br s, 1H); ^{13}C NMR δ 14.2, 22.8, 27.7, 29.4, 31.8, 34.9, 41.3, 108.4, 117.0, 165.3; FAB-MS obsd 351.2551, calcd 351.2549 ($C_{22}H_{30}N_4$).

5,6-Dicyano-2-(4-(triisopropylsilylethynyl)phenyl)benzimidazole (5d). The same procedure was followed as for **5a**, with the following quantities: **3** (468 mg, 2.96 mmol), NMP (15 mL), **4d** (847 mg, 2.96 mmol), and $FeCl_3 \cdot 6H_2O$ (296 μL of a 100 mM solution, 30 μmol). The product was isolated by chromatography (silica, $CHCl_3$, 2% ethyl acetate) as a colorless solid (732 mg, 58%): mp 347−348 °C; ^{1}H NMR (acetone-d_6) δ 1.15−1.18 (m, 21H), 7.05 (d, J = 8.4 Hz, 2H), 8.24−8.28 (m, 4H); ^{13}C NMR (acetone-d_6) δ 11.5, 18.5, 93.5, 106.7, 108.4, 116.7, 118.4, 122.1 (br), 126.3, 127.6, 128.7, 132.7, 142.0 (br), 156.4; FAB-MS obsd 425.2161, calcd 425.2083 [(M + H), M = $C_{26}H_{28}N_4Si$].

Synthesis of 5d Directly from 2.: A two-necked 25 mL flask was charged with **2** (577 mg, 1.60 mmol), CuCN (573 mg, 6.40 mmol), and NMP (2 mL). The vessel was fitted with a bubbler, and the second neck was capped with a septum. The mixture was heated at 120 °C for 2 h, and then more NMP (8 mL) and **4d** (458 mg, 1.60 mmol) were added and O_2 was bubbled through the mixture. After 40 min, TLC (silica, $CHCl_3$, 4% 2-propanol) showed the desired product and no remaining **3** or **4d**, so the mixture was transferred to a 500 mL conical flask containing a hot solution of aqueous EDTA (4.87 g, 12.8 mmol, in 200 mL), and the mixture was heated and stirred for 30 min and then filtered. The filter cake was dried in vacuo and chromatographed (silica, CH_2Cl_2, 2% ethyl acetate), giving a colorless solid (280 mg, 41%). Characterization data were identical with the preparation from **3** above.

5,6-Dicyano-1-propyl-2-(undec-7-yl)benzimidazole (6a). A 10 mL round-bottom flask was charged with **5a** (743 mg, 2.12 mmol) and CH_3CN (2.0 mL). The flask was capped with a septum and placed in an oil bath heated to 80 °C. DBU (317 μL, 2.12 mmol) was added, and the mixture was stirred for 2 min. Then iodopropane (207 μL, 2.12 mmol) was added, and the mixture was stirred for 20 min. A second dose of DBU (317 μL, 2.12 mmol), followed by iodopropane (207 μL, 2.12 mmol), was added, and 20 min later, a third round of DBU and iodopropane was added. HPLC analysis of the reaction mixture (C-18 reverse phase, CH_3CN as eluent) indicated that the yields of the reaction after the first, second, and third round of reagents were 60%, 78%, and 97%, respectively. After the third round of reagents was added, and the mixture was stirred for 20 min, the reaction mixture was removed from heat and added to 200 mL diethyl ether. The ether solution was washed three times with water, then washed with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue was chromatographed (silica, hexanes/ethyl acetate 7:1, then hexanes/ethyl acetate 6:1), yielding a tan solid (786 mg, 94%): mp 52−53 °C; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 6.8 Hz, 6H), 1.02 (t, J = 7.2 Hz, 3H), 1.05−1.13 (m, 16H), 1.72−1.82 (m, 6H), 2.88−2.98 (m, 1H), 4.15 (t, J = 7.6 Hz, 2H); ^{13}C NMR δ 11.6, 14.2, 14.2, 22.8, 23.8, 27.8, 29.5, 31.8, 35.2, 38.3, 45.9, 107.8, 108.4, 116.2, 116.9, 117.0, 125.8, 137.0, 145.3, 165.5. Anal. Calcd for $C_{25}H_{36}N_4$: C, 76.49; H, 9.24; N, 14.27. Found: C, 76.38; H, 9.36; N, 14.18.

5,6-Dicyano-2-phenyl-1-propylbenzimidazole (6b). A 25 mL round-bottom flask was charged with **3** (316 mg, 2.00 mmol), NMP (10 mL), benzaldehyde, (202 μL, 2.00 mmol), and a magnetic stirring bar. The flask was fitted with a Hickman still, placed in an oil bath heated to 120 °C, and stirred for 1 h. Then $FeCl_3 \cdot 6H_2O$ (27 mg, 0.10 mmol) was added to the reaction vessel, and oxygen was bubbled through the mixture as it was heated and stirred for an additional 20 h. The reaction mixture was then removed from heat and added to ethyl acetate. The mixture was washed three times with water, then with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue (458 mg, 1.88 mmol) was dissolved in NMP (2 mL) and heated to 80 °C. Then DBU (280 μL, 1.88 μmol) was added, the mixture was stirred for 2 min, and iodopropane (183 μL, 1.88 mmol) was added. After 20 min, the mixture was treated with a second round of DBU and iodopropane, and after an additional 20 min, a third round of reagents was added. After a final 20 min of heating, the mixture was transferred to ethyl acetate and washed three times with water, then with brine, dried over Na_2SO_4, filtered, concentrated to dryness, and chromatographed (silica, CH_2Cl_2, 3% ethyl acetate, 1% 2-propanol), yielding an off-white solid (253 mg, 44%): mp 183−185 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.6 Hz, 2H), 1.81−1.92 (m, 2H), 4.29 (t, J = 7.6 Hz, 2H), 7.56−7.62 (m, 3H), 7.70−7.73 (m, 2H), 7.89 (s, 1H), 8.20 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 11.4, 23.5, 47.3, 108.7, 109.0, 116.7, 116.8, 116.9, 126.6, 128.8, 129.5, 129.5, 131.4, 137.8, 145.4, 159.5; FAB-MS obsd 287.1302, calcd 287.1297 [$(M + H)^+$; M = $C_{18}H_{14}N_4$].

5,6-Dicyano-2-(4-iodophenyl)-1-propylbenzimidazole (6c). A 25 mL round-bottom flask was charged with **3** (340 mg, 2.15 mmol), NMP (10 mL), 4-iodobenzaldehyde, (499 mg, 2.15 mmol), and a magnetic stirring bar. The flask was fitted with a Hickman still, placed in an oil bath heated to 120 °C, and stirred for 1 h. Then $FeCl_3 \cdot 6H_2O$ (29 mg, 0.11 mmol) was added to the reaction vessel, and oxygen was bubbled through the mixture as it was heated and stirred for an additional 24 h. The reaction mixture was then removed from heat and added to ethyl acetate. The ethyl acetate solution was washed three times with water, then washed with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. The residue (603 mg, 1.63 mmol) was suspended in CH_3CN and heated to 80 °C. Then DBU (243 μL, 1.63 μmol) was added, the mixture was stirred for 2 min, and iodopropane (159 μL, 1.63 mmol) was added. After 20 min, the mixture was treated with a second round of DBU and iodopropane, and after an additional 20 min, a third round of reagents was added. After a final 20 min of heating, the mixture was transferred to ethyl acetate and washed three times with water, followed by brine. After the organic layer was dried over Na_2SO_4, the mixture was filtered, concentrated to dryness, and chromatographed (silica, $CHCl_3$, 5% ethyl acetate), giving a white solid (440 mg, 50%): mp 208−209 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.6 Hz, 3H), 1.80−1.91 (m, 2H) 4.26 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.87 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 11.4, 23.6, 47.4, 98.4, 109.0, 109.3, 116.55, 116.62, 116.9, 126.7, 128.2, 130.9, 137.8, 138.7, 145.3, 158.4. Anal. Calcd for $C_{18}H_{13}IN_4$: C, 52.45; H, 3.18; N, 13.59. Found: C, 52.40; H, 3.06; N, 13.40.

5,6-Dicyano-2-(4-(triisopropylsilylethynyl)phenyl)-1-propylbenzimidazole (6d). The same procedure was followed as for **6a**, with the following quantities: **5d** (763 mg, 1.79 mmol), NMP (10 mL), DBU (267 μL, 1.79 mmol per dose), and iodopropane (175 μL, 1.79 mmol per dose). The product was isolated by chromatography (silica, $CHCl_3$) as a colorless solid (506 mg, 61%): mp 242−243 °C; ^{1}H NMR (acetone-d_6) δ 0.89 (t, J = 7.2 Hz, 3H), 1.17−1.19 (m, 21H), 1.86−1.96 (m, 2H), 4.53 (t, J = 7.6 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 8.36 (s, 1H), 8.50 (s, 1H); ^{13}C NMR (acetone-d_6) δ 10.5, 11.3, 18.4, 23.2, 47.1, 93.1, 106.6, 108.1, 108.3, 116.8, 116.9, 118.3, 125.8, 126.3, 129.6, 129.9, 132.5, 138.5, 145.4, 158.4. Anal. Calcd for $C_{29}H_{34}N_4Si$: C, 74.63; H, 7.34; N, 12.01. Found: C, 74.75; H, 7.32; N, 12.01.

Tetrakis(2-tridec-7-yl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazine (Fb-7). A 5 mL reaction vial was charged with **6a** (150 mg, 382 μmol), pentanol (1.90 mL), and a magnetic stirring bar. The vial was capped and heated in a heating block set at 145 °C, and then DBU (57 μL, 382 μmol) was added. Heating and stirring continued for 18 h. The vial was then removed from heat, and upon cooling to room temperature, the mixture was diluted with 18 mL of MeOH, and then centrifuged. The supernatant was removed, and the pellet was resuspended in MeOH and centrifuged again. After the supernatant was removed a second time, the pellet was redissolved in THF (2 mL) and precipitated by addition of MeOH (18 mL). The mixture was centrifuged, and upon removal of the supernatant, the pellet was dried in vacuo, revealing a green solid (17 mg, 11%): ^{1}H NMR (THF-d_8) δ 0.30−0.50 (br s, 2H), 0.80−1.00 (m, 24H), 1.17−1.60 (m, 76H), 1.80−2.10 (m, 8H), 2.10−2.42 (m, 16H), 3.10−3.25 (m, 2H), 3.30−3.40 (m, 2H), 4.30−4.50 (m, 4H), 4.70−4.84 (m, 4H), 9.30−9.70 (m, 8H); LD-MS obsd 1570.8; FAB-MS obsd 1571.2178, calcd 1571.1916 ($C_{100}H_{146}N_{16}$); λ_{abs} (nm) 309, 342, 376, 640, 676, 713, 737; λ_{em} 742 nm; Φ_f = 0.59.

Preparation of Fb-7 Using Lithium Pentoxide. A 5 mL reaction vial was charged with a magnetic stirring bar, pentanol (1.0 mL), and Li ribbon (23 mg, 3.3 mmol). The vial was capped, vented, and warmed to 90 °C. After all of the Li was consumed (40 min), the vial was removed from heat and allowed to cool to room temperature. Then a sample of **6a** (150 mg, 0.382 mmol) in pentanol (1.0 mL) was added, and the vial was capped and heated to 140 °C for 4 h. The vial was then removed from heat, and upon cooling to room temperature, the mixture was diluted with 18 mL of MeOH (2% CH_3CO_2H) and centrifuged, and the supernatant was removed. The pellet was resuspended in MeOH and centrifuged again. After the supernatant was removed a second time, the pellet was redissolved in THF (2 mL) and precipitated by addition of MeOH (18 mL). The mixture was centrifuged, and upon removal of the supernatant, the pellet was dried in vacuo, giving a green solid (74 mg, 49%). Characterization data were consistent with the material produced from the DBU-mediated reaction (vide supra).

Tetrakis(2-tridec-7-yl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazinatomagnesium(II) (Mg-7). A 5 mL reaction vial was charged with **6a** (150 mg, 382 μmol), $MgCl_2$ (13 mg, 96 μmol), pentanol (1.90 mL), and a magnetic stirring bar. The vial was capped and heated in a heating block set at 145 °C, and then DBU (57 μL, 382 μmol) was added. Heating and stirring continued for 18 h. The vial was then removed from heat, and upon cooling to room temperature, the mixture was diluted with 16 mL of MeOH and 2 mL of water and then centrifuged. The supernatant was removed, and the pellet was resuspended in MeOH/water (8:1) and centrifuged again. After the supernatant was removed a second time, the pellet was redissolved in THF (2 mL) and precipitated by addition of MeOH (16 mL) and water (2 mL). The mixture was centrifuged, and upon removal of the supernatant, the pellet was dried in vacuo, giving a green solid (41 mg, 27%): ^{1}H NMR (THF-d_8) δ 0.82−0.96 (m, 24H), 1.16−1.58 (m, 76H), 1.87−2.02 (m, 8H), 2.18−2.36 (m, 16H), 3.24−3.34 (m, 4H), 4.66−4.74 (m, 8H), 9.40 (s, 2H), 9.47 (s, 2H), 9.65 (s, 2H), 9.68 (s, 2H); LD-MS obsd 1592.7; FAB-MS obsd 1593.1650, calcd 1593.1610 ($C_{100}H_{144}MgN_{16}$); λ_{abs} (nm) 310, 363, 640, 680, 713; λ_{em} 720 nm; Φ_f = 0.69.

Tetrakis(2-tridec-7-yl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazinatozinc(II) (Zn-7). A 5 mL reaction vial was charged with **6a** (150 mg, 382 μmol) and a magnetic stirring bar. The vial was then introduced into a glovebox under argon atmosphere, and $ZnCl_2$ (13 mg, 96 μmol) was added. The vial was capped and removed from the glovebox, and pentanol (1.90 mL) was added. The vial was heated to 140 °C in a heating block, and then DBU (57 μL, 382 μmol) was added. The temperature of the heating block was raised to 145 °C and continued for 18 h. The vial was then removed from heat, and upon cooling to room temperature, the mixture was diluted with 16 mL of MeOH and 2

mL of water and then centrifuged. The supernatant was removed, and the pellet was resuspended in MeOH and centrifuged again. After the supernatant was removed a second time, the pellet was redissolved in THF (2 mL) and precipitated by addition of MeOH (16 mL) and water (2 mL). The mixture was centrifuged, and upon removal of the supernatant, the pellet was dried in vacuo, giving a green solid (72 mg, 46%): ^{1}H NMR (THF-d_8) δ 0.82−0.95 (m, 24H), 1.20−1.60 (m, 76H), 1.88−2.05 (m, 8H), 2.17−2.35 (m, 16H), 3.20−3.35 (m, 4H), 4.60−4.80 (m, 8H), 9.45 (s, 2H), 9.50 (s, 2H), 9.64−9.74 (m, 4H); LD-MS obsd 1633.0; FAB-MS obsd 1633.1111, calcd 1633.1051 ($C_{100}H_{144}N_{16}Zn$); λ_{abs} (nm) 309, 357, 640, 681, 713; λ_{em} 724 nm; $\Phi_f = 0.47$.

Tetrakis(2-phenyl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazine (Fb-8). The same procedure was followed as for **Fb-7** using DBU, with the following quantities: **6b** (50.0 mg, 0.175 μmol), pentanol (875 μL), and DBU (26 μL, 175 μmol). The product was a green solid (19 mg, 38%). Due to the presence of regioisomers, some ^{1}H NMR resonances have noninteger integrations: ^{1}H NMR (THF-d_8) δ −3.13 (br s, 2H), 1.02−1.25 (m, 12H), 2.04−2.34 (m, 8H), 4.18−4.56 (m, 8H), 7.50−7.70 (m 12H), 7.90−8.08 (m, 8H), 8.12−8.22 (br s, 1H), 8.28−8.77 (m, 5H), 8.90−8.96 (m, 0.5H), 9.00−9.12 (m, 1.5H); LD-MS obsd 1146.7; FAB-MS obsd 1147.5127, calcd 1147.5109 [$(M + H)^+$; $M = C_{72}H_{58}N_{16}$]; λ_{abs} (nm) 316, 382, 648, 679, 718, 740; λ_{em} 744 nm; $\Phi_f = 0.70$.

Preparation of Fb-8 Using Lithium Pentoxide. The same procedure was followed as for **Fb-7** using Li, with the following quantities: pentanol (875 μL), Li ribbon (10.0 mg, 1.44 mmol), and **6b** (50 mg, 175 μmol). The product was isolated as a green solid (14 mg, 28%). Characterization data were consistent with the material produced from the DBU-mediated preparation of **Fb-8** (vide supra).

Tetrakis(2-phenyl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazinatomagnesium(II) (Mg-8). The same procedure was followed as for **Mg-7**, with the following quantities: **6b** (50.0 mg, 0.175 μmol), $MgCl_2$ (4.2 mg, 44 μmol), pentanol (875 μL), and DBU (26 μL, 175 μmol). The product was isolated as a green solid (33 mg, 65%): ^{1}H NMR (THF-d_8) δ 1.12−1.22 (m, 12H), 2.22−2.34 (m, 8H), 4.83−4.92 (m, 8H), 7.59−7.72 (m, 12H), 8.06−8.12 (m, 8H), 9.55 (br s, 2H), 9.63 (br s, 2H), 9.76−9.84 (m, 4H); LD-MS obsd, 1168.8; FAB-MS obsd 1168.4695, calcd 1168.4724 ($C_{72}H_{56}MgN_{16}$); λ_{abs} (nm) 314, 364, 643, 684, 717; λ_{em} 724 nm; $\Phi_f = 0.84$.

Tetrakis(2-phenyl-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*:5″,6″-*l*:5‴,6‴-*q*])porphyrazinatozinc(II) (Zn-8). The same procedure was followed as for **Zn-7**, with the following quantities: **6b** (50.0 mg, 0.175 μmol), $ZnCl_2$ (6.0 mg, 44 μmol), pentanol (875 μL), and DBU (26 μL, 175 μmol). The product was isolated as a green solid (33 mg, 62%). The sample was found to be a regioisomeric mixture of products, which resulted in some ^{1}H NMR resonances having noninteger integrations: ^{1}H NMR (THF-d_8) δ 1.11−1.21 (m, 12H), 2.20−2.33 (m, 8H), 4.72−4.86 (m, 8H), 7.60−7.71 (m, 12H), 8.05−8.12 (m, 8H), 9.30−9.43 (m, 4H), 9.49 (s, 0.5H), 9.59, (br s, 1.5H), 9.66 (s, 0.5H), 9.71−9.74 (m, 1.5H); LD-MS obsd, 1208.6; FAB-MS obsd 1208.4205, calcd 1208.4165 ($C_{72}H_{56}N_{16}Zn$); λ_{abs} (nm) 315, 357, 643, 685, 717; λ_{em} 724 nm; $\Phi_f = 0.43$.

Preparative-Scale Macrocyclization Reaction Using 6d and 1,2-Dicyanobenzene. A two-necked, 25 mL round-bottom flask was charged with **6d** (317 mg, 0.679 mmol), dicyanobenzene (130 mg, 1.02 mmol, 1.5 equiv), and a magnetic stirring bar. The flask was fitted with a condenser and a bubbler and a septum for the second neck. The apparatus was flushed for 20 min with a stream of argon and then briefly opened to add $ZnCl_2$ (58 mg, 0.43 mmol). Then pentanol (8.5 mL) was added, and the mixture was gradually heated to reflux. When the mixture was homogeneous, DBU (254 μL, 1.70 mmol) was added. The mixture was refluxed overnight (12 h). The mixture was then cooled to room temperature and diluted into MeOH (300 mL) and water (50 mL). The resulting precipitate was filtered, rinsed with EtOH, and dried in vacuo. The residue was then dissolved in THF, eluted through a short plug of silica gel in THF, and chromatographed over a column of Bio-Beads SX-3 in THF. The mixture separated into three bands. The first band (green) appeared (by HPLC-SEC analysis) to contain compounds containing two or more benzimidazoles. The second band (blue) contained **Zn-11**. The third band (blue) contained **Zn-10**. The fractions containing **Zn-10** and **Zn-11** were set aside, and the first band of green material was reconcentrated and chromatographed over a column of Bio-Beads SX-1 in THF. The mixture separated into two broad green bands. The first band, containing pigments having three and four benzimidazoles, could not be further purified by any chromatographic method and was therefore discarded. The second green band contained a mixture of **Zn-12** and **Zn-13**. The mixture was separated by chromatography (silica, $CHCl_3$, 2% 2-propanol).

Zinc Phthalocyanine (Zn-10, A_4). The compound was isolated as a blue band from chromatography on Bio-Beads SX-3 (vide supra). The THF solution was concentrated, and the residue was chromatographed over a short column (silica, $CHCl_3$, 2% 2-propanol). Fractions containing the product were concentrated, giving a blue solid (10 mg, 4%): ^{1}H NMR (THF-d_8) δ 8.17−8.23 (m, 8H), 9.45−9.50 (m, 8H); LD-MS obsd, 576.3; FABMS obsd 576.0813, calcd 576.0789 ($C_{32}H_{16}N_8Zn$); λ_{abs} 666 nm.

Tribenzo[*g*,*l*,*q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*])porphyrazinatozinc(II) (Zn-11, A_3B). The compound was isolated as a blue band from chromatography on Bio-Beads SX-3 (vide supra). The THF solution was concentrated, and the residue was chromatographed over a short column (silica, $CHCl_3$, 2% 2-propanol). Fractions containing the product were concentrated, giving a blue solid (86 mg, 22%): ^{1}H NMR (THF-d_8) δ 1.14 (t, $J = 7.2$ Hz, 3H), 1.27 (s, 21H), 2.16−2.26 (m, 2H), 4.75 (t, $J = 7.6$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 8.00−8.15 (m, 8H), 9.09 (s, 1H), 9.13 (d, $J = 7.6$ Hz, 1H), 9.22−9.34 (m, 5H), 9.37 (s, 1H); LD-MS obsd, 914.7; FAB-MS obsd 914.2986, calcd 914.2968 ($C_{53}H_{46}N_{10}SiZn$); λ_{abs} (nm) 340, 611, 674; λ_{em} 692 nm; $\Phi_f = 0.47$.

Dibenzo[*l*,*q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*:5′,6′-*g*])porphyrazinatozinc(II) (Zn-12, *cis*-A_2B_2). The compound was isolated from silica gel chromatography as the first green band and concentrated to give a green solid (74 mg, 14%): ^{1}H NMR (THF-d_8) δ 1.09−1.20 (m, 6H), 2.15−2.30 (m, 4H), 4.81 (t, $J = 7.6$ Hz, 4H), 7.76−7.84 (m, 4H), 8.06−8.19 (m, 8H), 9.12−9.50 (m, 5H), 9.63 (s, 1H), 9.70 (s, 1H); LD-MS obsd 1252.6; FAB-MS obsd 1252.5148, calcd 1252.5146 ($C_{74}H_{76}N_{12}Si_2Zn$); λ_{abs} (nm) 340, 623, 693; λ_{em} 701 nm; $\Phi_f = 0.44$.

Dibenzo[*g*,*q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*:5′,6′-*l*])porphyrazinatozinc(II)-C_{2v} (Zn-13b, *trans*-A_2B_2). The compound was isolated from chromatography as the second green band and concentrated to give a green solid (4 mg, 1%). Characterization data were consistent with the compound **Zn-13b** isolated from the metalation of **Fb-13** (vide infra): ^{1}H NMR (THF-d_8) δ 1.15 (t, $J = 7.2$ Hz, 6H), 1.25 (s, 42H), 2.20−2.28 (m, 4H), 4.81 (t, $J = 7.2$ Hz, 4H), 7.79 (d, $J = 8.4$ Hz, 4H), 8.09 (d, $J = 8.4$ Hz, 4H), 8.12−8.17 (m, 2H), 8.17−8.22 (m, 2H), 9.37 (s, 2H), 9.37−9.42 (m, 2H), 9.43−9.48 (m, 2H), 9.60 (s, 2H); LD-MS obsd 1252.6, calcd 1252.5 ($C_{74}H_{76}N_{12}Si_2Zn$); λ_{abs} (nm) 335, 679, 708; FAB-MS and fluorescence data were not separately obtained for this sample, but were obtained for the sample reported from the metalation of **Fb-13**.

Tribenzo[*g*,*l*,*q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*])porphyrazine (Fb-11, A_3B). A 20 mL reaction vial was charged with **14a** (40.0 mg, 83 μmol), boron subphthalocyanine **15**[48] (143 mg, 332 μmol, 4 equiv), DMAE (4 mL), and a magnetic stirring bar. The vial was capped and heated in an oil bath at 100 °C. Periodically, a few microliters of the reaction mixture were removed, diluted into THF, and analyzed by UV−vis spectroscopy. After the reaction had proceeded for 10 h, **15** could not be observed in the UV−vis spectrum. The reaction was then cooled to room temperature and diluted with MeOH (50

mL) and water (30 mL). The mixture was filtered through paper, and the solid residue was rinsed with MeOH and air-dried. The filter paper containing the solid residue was then loaded into a Soxhlet thimble, and the thimble was extracted with $CHCl_3$ for 20 h. Upon the apparatus was cooled, most of the extracted pigment precipitated out of the filtrate. The solvent was removed from the filtrate under reduced pressure and the solid material was resuspended in THF (20 mL) with sonication. The mixture was filtered through a cotton-plugged pipet and chromatographed over a column of Bio-Beads SX-3 in THF. The desired compound was recovered from the column as a dark blue-green band that eluted just after a faint green band and before a purple band. The faint green band was identified by UV−vis as a mixture of benzimidazoporphyrazines having more than one benzimidazole, and was discarded. The purple band was identified by UV−vis as a mixture of remaining subPc **15** and unsubstituted phthalocyanine and was discarded. The fractions containing the desired compound were concentrated and chromatographed over silica gel (CH_2Cl_2, 2% 2-propanol, 2.5% THF, 2.5% ethyl acetate). Fractions containing the desired compound were concentrated, giving a blue solid (18 mg, 25%): ^{1}H NMR (THF-d_8) δ −3.29 (br s, 2H), 1.17 (t, J = 7.6 Hz, 3H), 1.32 (s, 21H), 2.10−2.25 (m, 2H), 4.45−4.60 (m, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.75−7.94 (m, 4H), 7.87 (d, J = 8.0 Hz, 4H), 8.11 (d, J = 8.0 Hz, 4H), 8.24−8.32 (m, 1H), 8.52−8.66 (m, 3H), 8.68−8.82 (m, 4H); LD-MS obsd 852.5; FAB-MS obsd 853.3945, calcd 853.3911 [$(M + H)^+$; $M = C_{53}H_{48}N_{10}Si$]; λ_{abs} (nm) 337, 622, 649, 669, 695; λ_{em} (nm) 700, 714; Φ_f = 0.68.

Dibenzo[*g,q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*:5′,6′-*l*])porphyrazine (Fb-13, *trans*-A_2B_2). An oven-dried, three-necked, 300 mL round-bottom flask was charged with **14** (465 mg, 0.96 mmol) and a magnetic stirring bar. The vessel was flushed with argon for 10 min and immersed in an ice bath. Freshly dried THF (70 mL) and freshly dried TEA (269 μL, 1.92 mmol, 2 equiv) were added to the flask. A sample of **16**[49] (212 mg, 0.96 mmol) was dissolved in dry THF (10 mL) and slowly added to the reaction vessel. The mixture was kept at 0−5 °C for 1 h and then allowed to warm to room temperature overnight. Then the triethylammonium salt that had formed was removed by filtration of the mixture into an oven-dried, two-necked, 250 mL round-bottom flask. The vessel was flushed with argon for 5 min, and a sample of hydroquinone (106 mg, 0.96 mmol) in THF (10 mL) was added, followed by NaOMe (658 μL of a 25 wt % solution in MeOH, 2.88 mmol, 3 equiv). The mixture was refluxed for 6 h, then cooled to room temperature and poured into MeOH (20 mL), to which water (100 mL) was added. After standing for 1 h, the mixture was filtered and the solid residue was air-dried, dissolved in CH_2Cl_2, and chromatographed (silica, CH_2Cl_2, 1% 2-propanol, 5% ethyl acetate, 5% THF). The first green band (faint) was identified by LD-MS as the AB_3 macrocycle (LD-MS *m*/*z* 1526.0). The product was collected as the second (dark) green band (49 mg, 9%): ^{1}H NMR (THF-d_8) δ −4.32 (br s, 1H), −4.22 (br s, 1H), 1.02 (t, J = 6.8 Hz, 3H), 1.10 (t, J = 6.8 Hz, 3H), 1.34 (s, 42H), 1.82−2.10 (m, 4H), 4.10−4.38 (m, 4H), 7.29−7.37 (m, 1H), 7.47−7.64 (m, 4H), 7.74−7.83 (m, 4H), 7.83−7.90 (m, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.99−8.15 (m, 4H), 8.17−8.24 (m, 1H), 8.29−8.47 (m, 1H); LDMS obsd 1190.7; FABMS obsd 1190.6040, calcd 1190.6011 ($C_{74}H_{78}N_{12}Si_2$); λ_{abs} (nm) 340, 610, 631, 662, 681, 703, 732; λ_{em} (nm) 711, 739; Φ_f = 0.66.

Dibenzo[*g,q*]-(2-{4-(2-triisopropylsilylethynyl)phenyl}-1-propylbenzimidazo[5,6-*b*:5′,6′-*l*])porphyrazinatozinc(II) (Zn-13, *trans*-A_2B_2). From Cross-Condensation Reaction. An oven-dried 20 mL reaction vial was charged with **14** (48 mg, 99 μmol) and a magnetic stirring bar. The vial was capped with a septum flushed with argon for 10 min and immersed in an ice bath. Freshly dried THF (8 mL) and freshly dried TEA (28 μL, 0.20 mmol, 2 equiv) were added to the vial. A sample of **16**[49] (22 mg, 99 μmol) was dissolved in dry THF (2 mL) and slowly added to the reaction vial. The mixture was kept at 0−5 °C for 1 h and then allowed to warm to room temperature overnight. The triethylammonium salt that had formed was removed by filtration of the mixture into an oven-dried, 25 mL round-bottom flask. Hydroquinone (11 mg) was added, and the vessel was flushed with argon for 5 min, and NaOMe (69 μL of a 25 wt % solution in MeOH, 0.30 mmol, 3 equiv) was added. The mixture was refluxed for 6 h, then cooled to room temperature and poured into MeOH (50 mL), to which water (2 mL) was added. After standing for 1 h, the mixture was filtered, and the solid residue was air-dried, dissolved in CH_2Cl_2, and chromatographed (silica, CH_2Cl_2, 1% 2-propanol, 2.5% ethyl acetate, 2.5% THF). The first green band (faint) was identified by LD-MS as the $ZnAB_3$ macrocycle (LD-MS *m*/*e* 1591.0). The product was collected as the second (dark) green band (5.0 mg, 4%): ^{1}H NMR (THF-d_8) δ 1.15 (t, J = 7.6 Hz, 6H), 1.28 (s, 42H), 2.13−2.25 (m, 4H), 4.69 (t, J = 7.6 Hz, 4H), 7.80 (d, J = 8.0 Hz, 4H), 8.02−8.20 (m, 4H), 8.09 (d, J = 8.0 Hz, 4H), 9.06−9.13 (m, 1H), 9.18−9.24 (m, 2H), 9.29−9.43 (m, 5H); LD-MS obsd 1252.8; FAB-MS obsd 1252.5242, calcd 1252.5146 ($C_{74}H_{76}N_{12}Si_2Zn$); λ_{abs} (nm) 338, 614, 648, 679, 709. Fluorescence data were not collected from this sample but were collected for the separated regioisomers (vide infra).

From Zinc Metalation of Fb-13. A 20 mL reaction vial was charged with **Fb-13** (20 mg, 17 μmol), $Zn(OAc)_2 \cdot 2H_2O$ (7.4 mg, 34 μmol, 2 equiv), dioxane (2.0 mL), DMF (0.5 mL), and a magnetic stirring bar. The vial was kept in an oil bath heated to 100 °C for 2 h, upon which the UV−vis absorbance analysis of a removed sample showed a spectrum for **Zn-13** with no evidence of remaining starting material. The reaction mixture was cooled and diluted to 20 mL with MeOH. The mixture was filtered, and the solid was air-dried, then dissolved through the filter with THF, and concentrated to dryness. The residue was chromatographed (silica, toluene, 10% THF) to separate a trace of remaining **Fb-13** that was too small to be detected in the mixture by UV−vis analysis. The product eluted as the first (dark) green band (19 mg, 90%). A second chromatography (silica, CH_2Cl_2, 1% 2-propanol, 5% ethyl acetate, 5% THF) separated the two regioisomeric products. The first green band was assigned as **Zn-13a**. Fractions containing the second green band were rechromatographed twice to separate all trace of the first eluting isomer. The second eluting species was assigned as **Zn-13b**. These two isomers, **Zn-13a** and **Zn-13b**, were determined by their COSY NMR data to be the C_{2h} and C_{2v} symmetric structures, respectively (see the Results and Discussion). Data for **Zn-13a** (C_{2h}): yield = 10.0 mg (47%); ^{1}H NMR (THF-d_8) δ 1.16 (t, J = 8.0 Hz, 6H), 1.28 (s, 42H), 2.14−2.26 (m, 4H), 4.71 (t, J = 8.0 Hz, 4H), 7.81 (d, J = 8.0 Hz, 4H), 8.02−8.14 (m, 4H), 8.08 (d, J = 8.0 Hz, 4H), 8.88 (s, 2H), 9.13 (d, J = 7.2 Hz, 2H), 9.22 (s, 2H), 9.23 (d, J = 7.2 Hz, 2H); LD-MS obsd 1253.0; FAB-MS obsd 1252.5214, calcd 1252.5146 ($C_{74}H_{76}N_{12}Si_2Zn$); λ_{abs} (nm) 338, 614, 648, 679, 709; λ_{em} 717 nm; Φ_f = 0.32.

Data for **Zn-13b** (C_{2v}): yield = 9.0 mg (43%); ^{1}H NMR (THF-d_8) δ 1.15 (t, J = 7.6 Hz, 6H), 1.28 (s, 42H), 2.13−2.25 (m, 4H), 4.69 (t, J = 7.6 Hz, 4H), 7.79 (d, J = 7.6 Hz, 4H), 8.13 (d, J = 7.6 Hz, 6H), 8.10−8.19 (m, 2H), 8.95 (s, 2H), 9.09−9.20 (m, 2H), 9.21−9.35 (m, 4H); LD-MS obsd 1252.4; FAB-MS 1252.5172, calcd 1252.5146 ($C_{74}H_{76}N_{12}Si_2Zn$); λ_{abs} (nm) 338, 614, 648, 679, 709; λ_{em} 717 nm; Φ_f = 0.26.

2-(4-(2-(Triisopropylsilyl)ethynyl)phenyl)-1-propylimidazo-[4,5-*f*]isoindole-1,3-diimine (14). Following a literature procedure,[43] a 25 mL round-bottom flask was charged with **6d** (606 mg, 1.30 mmol) and a magnetic stirring bar. The vessel was sealed with a condenser, a bubbler, and a septum for the second neck. The apparatus was flushed with argon for 15 min, and then anhydrous MeOH (14 mL), freshly dried THF (7 mL), and NaOMe (30 μL of a 25 wt % solution in MeOH, 130 μmol) were added. The reaction flask was heated in an oil bath at 70 °C, and the mixture became homogeneous. The argon line was removed, and ammonia gas was bubbled through the mixture as it refluxed for 6 h. The flask was then removed from heat and allowed to cool under ammonia atmosphere. When the mixture reached room temperature, the ammonia gas flow was stopped and the mixture was allowed to stand overnight under a slowly flowing stream of argon, during

which time some greenish-white crystals formed in the vessel. The supernatant was drained off with a pipet, and the crystals were washed with a few milliliters of anhydrous MeOH and then dried in vacuo, yield 479 mg, 76%; mp 248−250 °C, upon which the sample melted and turned deep green. The melting capillary was broken and the residue taken up in THF and analyzed by UV−vis spectroscopy, which showed a spectrum similar to that of **Fb-8**. Due to the presence of tautomeric forms of the product, the NH signals do not all integrate to integers: ^{1}H NMR (THF-d_8) δ 0.86 (t, J = 7.2 Hz, 3H), 1.19 (s, 21H), 1.80−1.92 (m, 2H), 3.14 (br s, 0.5H), 4.30−4.44 (m, 2H), 7.48 (br s, 0.5H), 7.65 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.80−8.60 (m, 4H); due to poor solubility, ^{13}C NMR spectroscopy was not performed; IR (film) 3260, 3201, 2941, 2861, 2161, 1666, 1547, 1460, 1410, 1345, 1144, 1109, 1081, 1054, 994, 916, 882; FAB-MS obsd 484.2876, calcd 484.2896 [(M + H)$^+$; M = $C_{29}H_{37}N_5Si$] Anal. Calcd for $C_{29}H_{37}N_5$-Si: C, 72.01; H, 7.71; N, 14.48. Found: C, 69.90; H, 7.86; N, 13.91 (consistent with crystal inclusion of one molecule MeOH per molecule compound..

Dibenzo[*g,q*]-(2-{4-ethynylphenyl}-1-propylbenzimidazo[5,6-*b*:5′,6′-*l*])porphyrazinatozinc(II)-C_{2h} (Zn-17a, *trans*-A_2B_2). A 20 mL vial was charged with **Zn-13a** (9.5 mg, 7.6 μmol), CH_2Cl_2 (4 mL), and a magnetic stirring bar. Then TBAF (17 μL of a 1 M solution in THF, 17 μmol) was added, and the mixture was stirred at room temperature for 1.5 h. TLC analysis (silica, CH_2Cl_2, 1% 2-propanol, 5% ethyl acetate, 5% THF) indicated that neither starting material nor intermediate remained, so the mixture was directly added to a short (15 cm) silica gel column packed in CH_2-Cl_2. The product proved to be very polar, and the eluent (CH_2Cl_2, 1% 2-propanol, 5% ethyl acetate, 5% THF) was changed to increasing amounts of THF (final eluent: CH_2Cl_2/THF, 1:4) to elute the product as a dark blue-green band (6.2 mg, 87%): ^{1}H NMR (THF-d_8) δ 1.17 (t, J = 7.2 Hz, 6H), 2.18−2.28 (m, 4H), 3.84 (s, 2H), 4.74 (t, J = 8.0 Hz, 4H), 7.70 (d, J = 8.4 Hz, 4H), 8.02−8.12 (m, 4H), 8.05 (d, J = 8.4 Hz, 2H), 9.04 (br s, 2H), 9.21 (d, J = 6.4 Hz, 2H), 9.26−9.32 (m, 4H); LD-MS obsd 940.6; FAB-MS obsd 940.2510, calcd 940.2477 ($C_{56}H_{36}N_{12}Zn$).

Dibenzo[*g,q*]-(2-{4-ethynylphenyl}-1-propylbenzimidazo[5,6-b:5′,6′-*l*])porphyrazinatozinc(II)-C_{2v} (Zn-17b, *trans*-A_2B_2). The same procedure was followed as for **Zn-17a**, with the following quantities: **Zn-13b** (8.2 mg, 6.5 μmol), CH_2Cl_2 (4 mL), and TBAF (14 μL of a 1 M solution in THF, 14 μmol). The chromatography procedure was followed similarly (final eluent: CH_2Cl_2, 30% THF), and the product eluted as a dark blue-green band (4.4 mg, 72%): ^{1}H NMR (d_8-THF) δ 1.15 (t, J = 6.8 Hz, 6H), 2.16−2.27 (m, 4H), 3.85 (s, 2H), 4.72 (t, J = 7.6 Hz, 4H), 7.77 (d, J = 7.6 Hz, 4H), 8.04 (d, J = 7.6 Hz, 6H), 8.12−8.17 (m, 2H), 9.04 (s, 2H), 9.16−9.22 (m, 2H), 9.29−9.35 (m, 4H); LD-MS obsd 940.9; FAB-MS obsd 940.2490, calcd 940.2477 ($C_{56}H_{36}N_{12}Zn$).

Acknowledgment. I thank Prof. Jonathan S. Lindsey for helpful advice on this work. This research was supported by a grant to Prof. Jonathan S. Lindsey from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. W.J.Y. was also supported by a GAANN-ELMAT fellowship from the Department of Education. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the NCSU Facility was obtained from the North Carolina Biotechnology Center and the NSF.

Supporting Information Available: A detailed presentation of the photochemical behavior of the benzimidazoporphyrazines prepared for this report, as well as general experimental information and characterization data (NMR, LD-MS, UV−vis, fluorescence) for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO052122L