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Efficient Synthesis of Porphyrin-Containing, Benzoquinone-Terminated, Rigid Polyphenylene Dendrimers

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A series of rigid polyphenylene, free-base porphyrin-containing dendrimers terminated with either dimethoxybenzene or benzoquinone end-groups were prepared by a combined divergent and convergent synthesis. Unlike previous routes for preparing polyphenylene dendrimers that are incompatible with end-groups bearing certain functional moieties, the synthetic methodology chosen for this work enables incorporation of functional groups on the dendrimer end-groups during preparation of the dendrimer wedges and during synthesis of the final dendrimer. The basic strategy utilized a convergent preparation of dendrimer wedges using Suzuki coupling conditions, which were then either attached to a porphyrin core in a divergent coupling step or cyclized to form the porphyrin dendrimer in a convergent step. The latter approach was found to be more general and resulted in higher yields and more readily separated products. Steady-state absorption measurements for these dendrimers showed Soret and Q-band absorptions typical of free-base porphyrins. Preliminary steady-state fluorescence measurements of these dendrimers indicate quenching of the S_1 state of the free-base porphyrin in all benzoquinone-containing dendrimers that is attributed to efficient electron-transfer from the excited porphyrin to the benzoquinone end-groups. The amount of fluorescence quenching was in good agreement with the number of benzoquinone groups at the dendrimer periphery and the distance between the porphyrin and benzoquinone groups as calculated by semiempirical (AM1) molecular orbital calculations.

Introduction

The photosynthetic reaction center has evolved over time to facilitate photoinduced electron-transfer from an electronically excited "special pair" of chlorophylls to a quinone acceptor.[1] Artificial mimics that duplicate the electron-transfer relay in photosynthesis are interesting for a variety of reasons, including understanding the factors that influence photosynthesis[1−4] and for use as potential alternative fuel sources.[5] A primary goal of such research is separation of the electronic charges for sufficiently long time periods that the resulting chemical potential can be realized. Research in this area has involved multicomponent molecules,[6−10] supramolecular assemblies,[11] polymers,[12] and, most recently, dendrimers.[13−16] These systems share a common theme in that they generally contain two or more electron donor and acceptor groups covalently attached to one another by either flexible[10] or rigid[6,7] bridging groups (i.e., donor−

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(1) For recent reviews of the events occurring in the photosynthetic reaction center and light-harvesting complex, see: (a) Arnett, D. C.; Moser, C. C.; Dutton, P. L.; Scherer, N. F. *J. Phys. Chem. B* **1999**, *103*, 2014−2032. (b) Pullerits, T.; Sundström, V. *Acc. Chem. Res.* **1996**, *29*, 381−389.

(2) See, for example: (a) Yachandra, V. K.; Sauer, K.; Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927−2950. (b) Rüttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1−24. (c) Debus, R. J. *Biochim. Biophys. Acta* **1992**, *1102*, 269−352.

(3) See, for example: (a) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461. (b) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35−41. (c) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (c) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Parts A−D.

(4) For recent reviews of electron transfer in related systems, see: Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148−13168. Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; Decola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019.

(5) O'Regan, B.; Graetzel, M. *Nature* **1991**, *353*, 737. Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34.

(6) (a) Levanon, H.; Galili, T.; Regev, A.; Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 6366−6373. (b) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719−721. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562−5563. (d) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080−1082. (e) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043−5045.

(7) (a) Gust, D.; Moore, T. A. In *The Porphyrin Handbook: Electron Transfer*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego: 2000; Vol. 8. (b) Kuciauskaas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604−8614. (c) Steinberg-Yfrach, G.; Rigaud, J.-L.; Durantini, E. N.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature (London)* **1998**, *392*, 479−482 (d) Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S.-C.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature (London)* **1997**, *385*, 239−241. (e) Gust, D.; Moore, T. A.; Moore, A. L. *Pure Appl. Chem.* **1998**, *70*, 2189−2200. (f) Maniga, N. I.; Sumida, J. P.; Stone, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Porphyrins Phthalocyanines* **1999**, *3*, 32−44. (g) Sumida, J. P.; Liddell, P. A.; Lin, S.; Macpherson, A. N.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. A* **1998**, *102*, 5512−5519.

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bridge−acceptor). Photoinduced electron-transfer reactions in these molecules occur through either a superexchange (through-bond) or through-space mechanism.

The chemistry of dendrimers has expanded dramatically in recent years.[17] This research is driven in part by the desire to utilize the inherent structural properties of these unique macromolecules for use in energy transfer,[18] catalysis,[19] sensor applications,[20] and as drug delivery agents.[21] Not surprisingly, the composition of end-groups in the dendrimer can influence solubility,[22] conformation,[23] and further synthetic transformations. It is clear that the ability to perform transformations on terminal functional groups is quite important. Our group[13] and others[14−16] have used the dendritic architecture as a bridging group in intramolecular photoinduced electron-transfer. We have chosen to use a core electron-donor group and electron-acceptor end-groups for two reasons. First, this arrangement of donor and acceptor groups should result in an increased yield of charge-separation relative to monomeric analogues.[7d] Second, the reduction of one or more of the electron-acceptor groups on the dendrimer surface makes an *intermolecular* electron-transfer to a secondary acceptor group, also present in solution, competitive with charge recombination. In this way, the dendrimer might act similar to the photosynthetic reaction center, where the reduced ubiquinone is removed through a transmembrane process, by removing the electron from the porphyrin for potentially lengthy periods of time.

We recently described photoinduced electron-transfer reactions in flexible Newkome-type dendrimers that contained tetraphenylporphyrin cores and anthraquinone peripheral groups.[13] Photoexcitation of the porphyrin core resulted in efficient electron-transfer to the anthraquinone groups. The electron-transfer rate constants in these dendrimers were found to be largely independent of the generation number, indicating a through-space electron-transfer mechanism. These results were explained in terms of the substitution pattern and flexible nature of these dendrimers that resulted in extensive backfolding of the dendrimer branches. Such backfolding allowed both π-stacking of the terminal anthraquinone

(8) (a) Lammi, R. K.; Ambroise, A.; Balasubramian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579−7591. (b) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323−7344. (c) Li, J.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927−8940. (d) Li, J.; Diers, J. R.; Seth, J.; Yang, S. I.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 9090−9100. (e) Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1999**, *121*, 4008−4018. (f) Shediac, R.; Gray, M. H. B.; Uyeda, H. T.; Johnson, R. C.; Hupp, J. T.; Angiolillo, P. J.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 7017−7033. (g) Iovine, P. M.; Kellett, M. A.; Redmore, N. P.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 8717−8727. (h) Kumble, R.; Palese, S.; Lin, V. S.-Y.; Therien, M. J.; Hochstrasser, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11489−11498. (i) Hyslop, A. G.; Therien, M. J. *Inorg. Chim. Acta* **1998**, *275−276*, 427−434. (j) Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1497−503.

(9) (a) Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 2516−2525. (b) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461−9472. (c) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679−5690. (d) Brun, A. M.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657−8663. (e) Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1292−1295. (f) Andersson, M.; Linke, M.; Chambron, J.-C.; Davidsson, J.; Heitz, V.; Sauvage, J.-P.; Hammarstroem, L. *J. Am. Chem. Soc.* **2000**, *122*, 3526−3527.

(10) (a) Connolly, J. S.; Hurley, J. K.; Bell, W. L.; Marsh, K. L. In *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Reidel Publishing Company: Boston, 1987. (b) Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733−1740. (c) Kong, J. L. Y.; Spears, K. G.; Loach, P. A. *Photochem. Photobiol.* **1982**, *35*, 545−553. (d) McIntosh, A. R.; Siemiarczuk, A.; Bolton, J. R.; Stillman, M. J.; Ho, T.-F.; Weedon, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 7215−7223. (e) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224−7230.

(11) (a) Turró, C.; Chang, C. K.; Leroi, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 4013−4015. (b) Roberts, J. A.; Kirby, J. P.; Nocera, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 8051−8052. (c) Flamigni, L.; Armaroli, N.; Barigelletti, F.; Chambron, J.-C.; Sauvage, J.-P.; Solladie, N. *New J. Chem.* **1999**, *23*, 1151−1158. (d) Heleg-Shabtai, V.; Gabriel, T.; Willner, I. *J. Am. Chem. Soc.* **1999**, *121*, 3220−3221. (e) Willner, I.; Joselevich, E. *J. Phys. Chem. B* **1999**, *103*, 9262−9268. (f) Willner, I.; Kaganer, E.; Joselevich, E.; Durr, H.; David, E.; Gunter, M. J.; Johnston, M. R. *Coord. Chem. Rev.* **1998**, *171*, 261−285. (g) Kaganer, E.; Joselevich, E.; Willner, I.; Chen, Z.; Gunter, M. J.; Gayness, T. P.; Johnson, M. R. *J. Phys. Chem. B* **1998**, *102*, 1159−1165.

(12) (a) Fox, M. A. *Acc. Chem. Res.* **1999**, *32*, 201−207. (b) Kaschak, D. M.; Johnson, S. A.; Waraksa, C. C.; Pogue, J.; Mallouk, T. E. *Coord. Chem. Rev.* **1999**, *185−186*, 403−416. (c) Jiang, B.; Yang, S. W.; Bailey, S. L.; Hermans, L. G.; Niver, R. A.; Bolcar, M. A.; Jones, W. E., Jr. *Coord. Chem. Rev.* **1998**, *171*, 365−386. (d) Fossum, R. D.; Fox, M. A. *J. Phys. Chem. B* **1997**, *101*, 6384−6393. (e) Fossum, R. D.; Fox, M. A. *Polym. Mater. Sci. Eng.* **1997**, *76*, 389−390. (f) Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6441−6442. (g) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.

(13) (a) Rajesh, C. S.; Capitosti, G. J.; Cramer, S. C.; Modarelli, D. A. *J. Phys. Chem. B* **2001**, *105*, 10175−10188. (b) Capitosti, G. J.; Cramer, S. C.; Rajesh, C. S.; Modarelli, D. A. *Org. Lett.* **2001**, *3* (11), 1645−1648.

(14) Ghaddar, T. H.; Wishart, J. F.; Kirby, J. P.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 12832−12836.

(15) Segura, J. L.; Gómez, R.; Martín, N.; Luo, C.; Swartz, A.; Guldi, D. M. *Chem. Commun.* **2001**, 707−708.

(16) Toba, R.; Quintela, J. M.; Peinador, C.; Román, E.; Kaifer, A. E. *Chem. Commun.* **2001**, 857−858. Ceroni, P.; Vicinelli, V.; Maestri, M.; Balzani, V.; Müller, W. M.; Müller, U.; Hahn, U.; Osswald, F.; Vögtle, F. *New J. Chem.* **2001**, *25*, 989−993.

(17) (a) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819−3868. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665−1688. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689−1746. (d) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.

(18) (a) Matos, M. S.; Hofkens, J.; Verheijen, W.; De Schryver, F. C.; Hecht, S.; Pollak, K. W.; Fréchet, J. M. J.; Forier, B.; Dehaen, W. *Macromolecules* **2000**, *33*, 2967−2973. (b) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175−1185. (c) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701−1710. (d) Xu, Z.; Moore, J. S. *Acta Polym.* **1994**, *45*, 83−87. (e) Devadoss, C.; Bharati, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635−9644. (f) Shortreed, M. R.; Swallen, S. F.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318−6322. (g) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34. (h) Zhou, X.; Tyson, D. S.; Castellano, F. N. *Angew. Chem., Int. Ed.* **2000**, *39*, 4301−4305.

(19) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5708−5711.

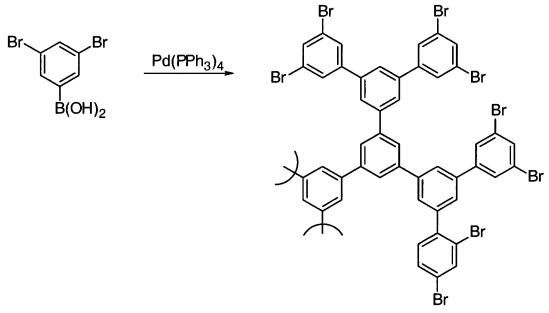
(20) Snejdarkova, M.; Svobodova, L.; Gajdos, V.; Hianik, T. *J. Mater. Sci.* **2001**, *12*, 1079−1082. Krasteva, N.; Besnard, I.; Guse, B.; Bauer, R. E.; Muellen, K.; Yasuda, A.; Vossmeyer, T. *Nano Lett.* **2002**, *2*, 551−555. Vossmeyer, T.; Guse, B.; Besnard, I.; Bauer, R. E.; Mullen, K.; Yasuda, A. *Adv. Mater.* **2002**, *14*, 238−242. Schlupp, M.; Weil, T.; Berresheim, A. J.; Wiesler, U. M.; Bargon, J.; Mullen, K. *Angew. Chem, Int. Ed.* **2001**, *40*, 4011−4015.

(21) Esfand, R.; Tomalia, D. A. *Drug Delivery Today* **2001**, *6*, 427−436. Liu, M.; Kono, K.; Frechét, J. M. J. *J. Controlled Release* **2000**, *65*, 121−131. Liu, M.; Kono, K.; Frechét, J. M. J. *J. Polym. Chem. A* **1999**, *37*, 3492−3503. Balogh, L.; Swanson, D. R.; Tomalia, D. A.; Hagnauer, G. L.; McManus, A. T. *Nano Lett.* **2001**, *1*, 18−21.

(22) Newkome, G.; Moorefield, C. N.; Baker, G. R.; Saunders: M. J.; Grossman, S. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1178−1180. Tomalia, D. A., Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polymer J.* **1985**, *17*, 117−132.

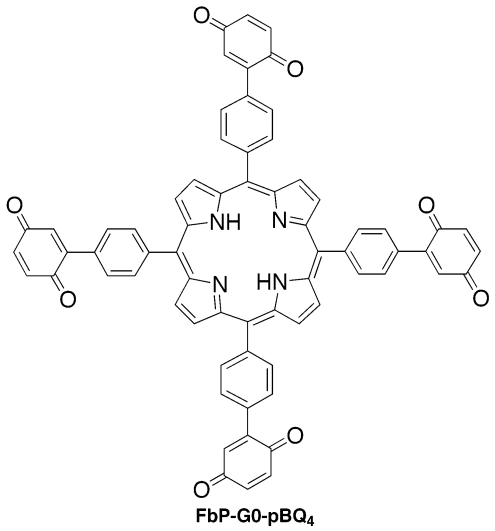
(23) Chai, M. H.; Niu, Y. H.; Youngs, W. J.; Rinaldi, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 4670−4678. Recker, J.; Tomcik, D. J.; Parquette, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 10298−10307. Huang, B.; Parquette, J. R. *Org. Lett.* **2000**, *2*, 239−242.

SCHEME 1

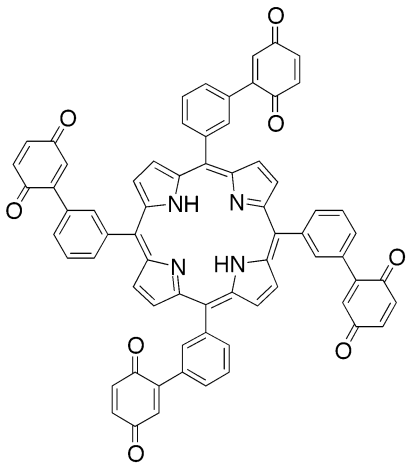


groups with the porphyrin cores, and in the case of the zinc-metalated analogues, ligation of the end-group with the zinc porphyrin.[13] Preliminary Monte Carlo stochastic dynamics calculations on the G1 dendrimer indicate that backfolding of the dendrimer branches place the anthraquinone groups very close to the porphyrin core. Because of the close proximity of the oxidized porphyrin and reduced anthraquinone units, however, charge recombination is suspected to be quite rapid in these dendrimers. Experiments to verify this prediction are ongoing. In an effort to better control the charge-separation and charge-recombination steps occurring upon irradiation of porphyrin-containing dendrimers, we have begun to examine the photoinduced electron-transfer chemistry in rigid dendrimers and starburst macromolecules. The branches in these dendrimers are composed of polyphenylene linkages and cannot backfold. The electron-transfer rate constants in these dendrimers are therefore expected to be highly dependent upon the generation number, and electron transfer will likely proceed by a superexchange mechanism.

The synthesis of polyphenylene dendrimers was first reported by Miller[24] and Kimura.[25] These syntheses were modeled after the work of Kim et al.,[26] who reacted an aryl boronic acid under Suzuki coupling conditions (Scheme 1) to yield hyperbranched polymers. Miller et al. modified this procedure to yield dendrimers by sequentially reacting 3,5-dibromo-1-(trimethylsilyl)benzene with aryl boronic acids, also under Suzuki coupling conditions. Conversion of the trimethylsilyl group to the boronic acid was accomplished in one step with boron tribromide. Repetition of this sequence resulted in the controlled synthesis of dendrimers with well-defined structures. Kimura and co-workers[25] modified this procedure to make porphyrin-containing dendrimers **FbTBP-G**n ($n = 0-2$) as shown in Scheme 2. While this synthesis is efficient for the synthesis of unsubstituted polyphenylene dendrimers, the necessity of the boron tribromide addition to form boronic acids is incompatible with many functional groups. The synthesis of porphyrin-containing polyphenylene dendrimers requiring dimethoxybenzene groups at the peripheral positions on the dendrimer by a convergent route is, unfortunately, unsuitable with the previously published approaches to polyphenylene dendrimers, as phenyl methyl ethers are readily cleaved with boron tribromide, the step necessary to convert the trimethylsilyl groups to the boronic acid groups in the syntheses used by Miller and Kimura. Thus, we sought an alternate procedure for preparing these dendrimers.



FbP-G0-pBQ$_4$



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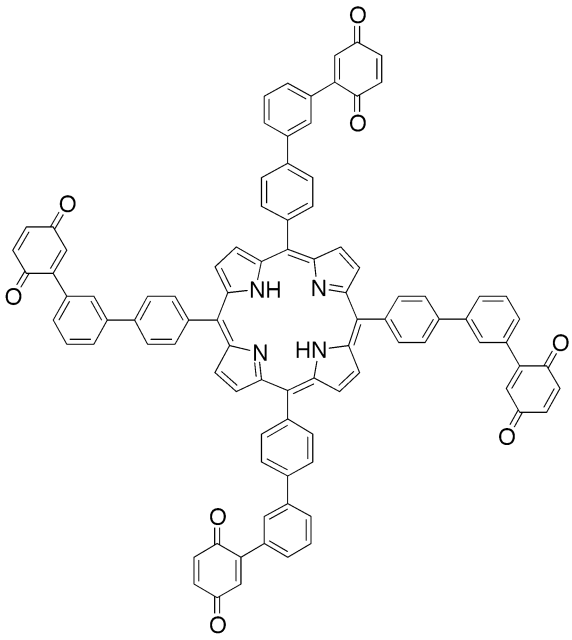
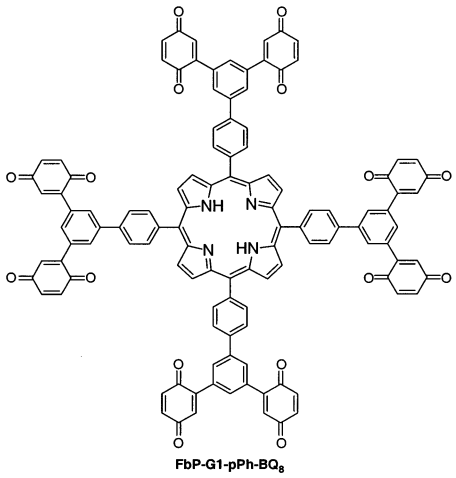
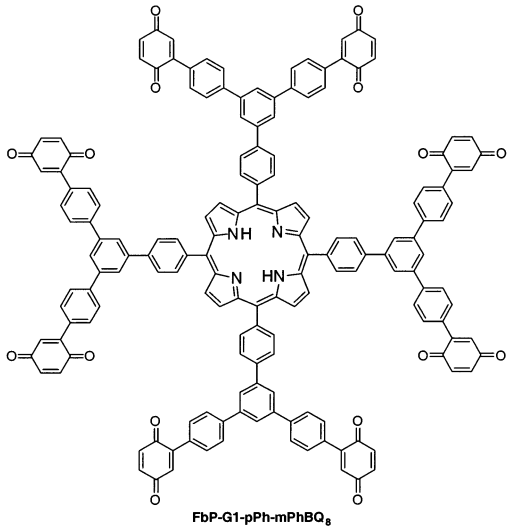
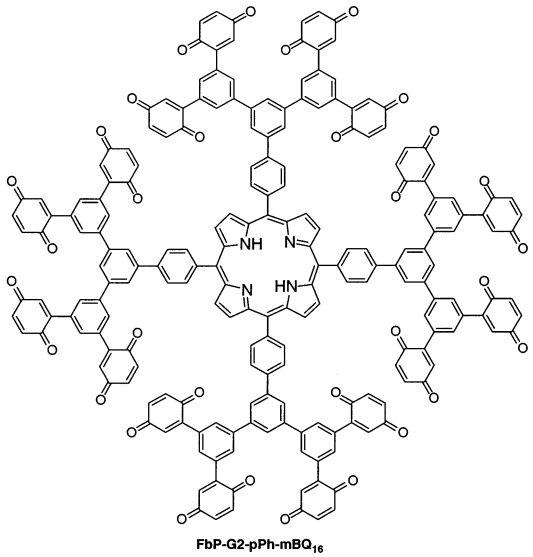


FbP-G0-pPh-mBQ$_4$

(24) Miller, T. M.; Neeman, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.
(25) Kimura, M.; Shiba, T.; Yamazaki, M.; Haqnabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc.* **2001**, *123*, 5636−5642.
(26) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.







Herein, we report the facile synthesis of polyphenylene, porphyrin-containing dendrimers, and starburst polymers having dimethoxybenzene end-groups that are then readily converted into the corresponding benzoquinone end-groups. The preparation of these dendrimers ultimately involved either Suzuki coupling of large polyphenylene boronic acid dendrons to *meso*-tetrakis(4-tetrabromophenyl)porphyrin or the cyclization of large polyphenylene aldehydes with pyrrole. Both of these syntheses proceed in relatively high yields to generate porphyrin-containing dendrimers of high purity. These synthetic methods should be generally applicable to a wide variety of dendrimer end-groups. In this work, we also describe preliminary fluorescence quenching data for both dimethoxybenzene and benzoquinone containing dendrimers, as well as semiempirical calculations of the dendrimer structures.

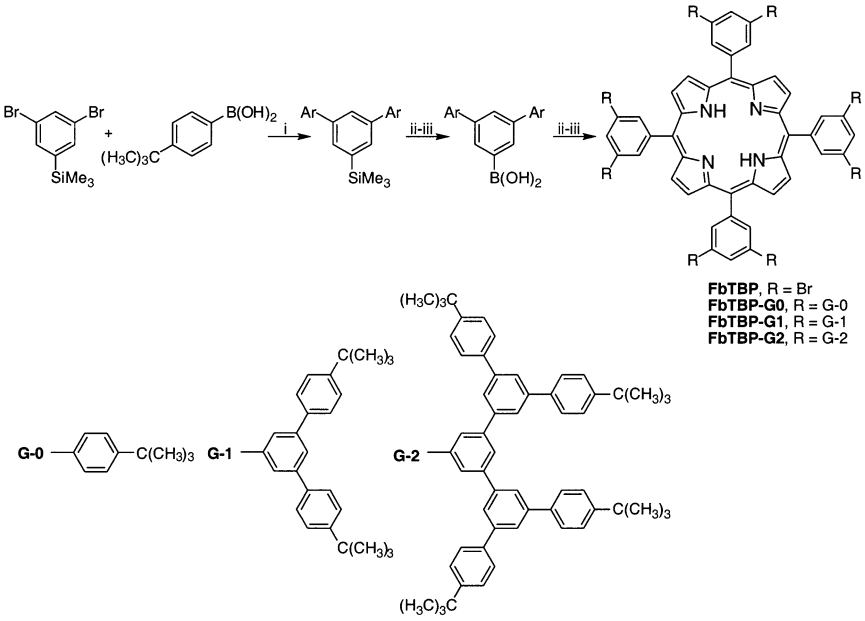
Results and Discussion

Synthesis. Although the syntheses of both **FbP-G0-pBQ$_4$** and **FbP-G0-mBQ$_4$** have been previously reported,[27] we employed a different synthetic approach because of problems with purification using the literature methods. Thus, *meso*-tetrakis(4-bromophenyl)porphyrin (**1**) was first synthesized under Lindsey[28] conditions from *p*-bromobenzaldehyde[29] and pyrrole. Coupling 4 equiv of 2,5-dimethoxyphenylboronic acid (**2**) to tetrabromophenylporphyrin **1** under Suzuki conditions[30] ($Pd(PPh_3)_4$, K_2CO_3, 3:1 toluene/ethanol, reflux) yielded *meso*-tetrakis-((2′,5′-dimethoxyphenyl)-4-phenyl)porphyrin **FbP-G0-pDMB$_4$** (Scheme 3) as a purple solid. Chan and coworkers[27] reported the purification of **FbP-G0-pDMB$_4$** using column chromatography on silica gel (3:1 CH_2Cl_2/hexanes). Under these conditions, **FbP-G0-pDMB$_4$** could not be removed from the silica column; successive changes of the eluant to increasingly polar solvents were unsuccessful in moving the product off the column as well. The chromatographic conditions were therefore modified, and successful purification was carried out on alumina (95:5 CH_2Cl_2/ethyl acetate). The dimethoxybenzene-terminated porphyrin (**FbP-G0-pDMB$_4$**) was subsequently converted to the hydroquinone with boron tribromide and oxidized to the benzoquinone-containing porphyrin (**FbP-G0-pBQ$_4$**) with 2,3-dichloro-4,5-dicyanoquinone (DDQ) in 43% yield. Porphyrin **FbP-G0-pBQ$_4$** was readily purified by washing with methanol, which was found to remove the excess DDQ, the reduced DDQ byproduct, and any porphyrin still containing unoxidized hydroquinone moieties.

Dendrimer **FbP-G0-mBQ$_4$** is also a G0 dendrimer but has the benzoquinone groups positioned meta to the porphyrin ring on the *meso* phenyl groups. This dendrimer was prepared to examine the effects of regiochemistry on electron-transfer rate constants through a phenyl bridging group (i.e., para vs meta). Two routes were considered for the synthesis of **FbP-G0-mBQ$_4$**: (a) a divergent approach analogous to that used to prepare **FbP-G0-pBQ$_4$**, wherein 2,5-dimethoxyphenylboronic acid would be added using Suzuki coupling conditions to *meso*-tetrakis(3-bromophenyl)porphyrin, and (b) a convergent approach where the dendrimer is assembled in one step

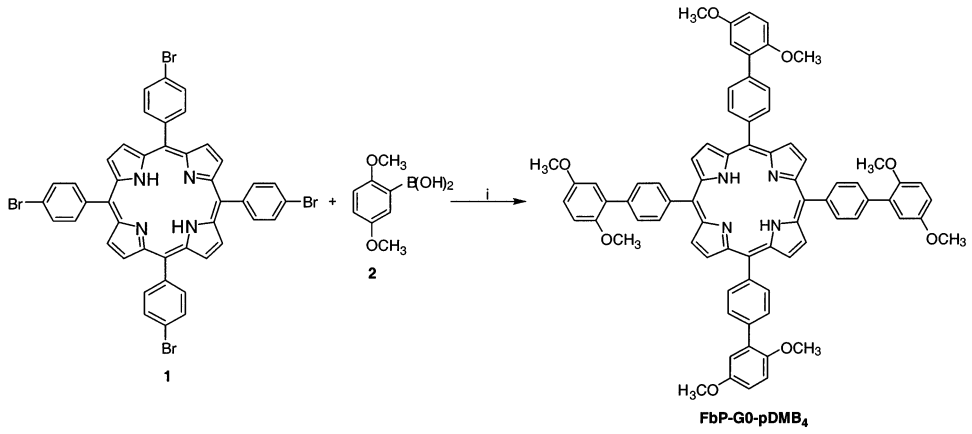
(27) Chan, C.-S.; Tse, A. K.-S.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 6084−6089.
(28) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987**, *28*, 3069−3070.
(29) Gradyushko, A. T.; Kozhich, D. T.; Solov'ev, K. N.; Tsvirko, M. P. *Dokl. Akad. Nauk Beloruss. SSR* **1972**, *16*, 534−7. Kim, J. B.; Leonard, J. J.; Longo, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 3986−92.
(30) Bobe, F.; Tunoori, A. R.; Niestroj, A. J.; Gronwald, O.; Maier, M. E. *Tetrahedron* **1996**, *52*, 9485.

SCHEME 2[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3, Δ; (ii) BBr_3; (ii) KOH; (iv) **1**, $Pd(PPh_3)_4$, Na_2CO_3, Δ.

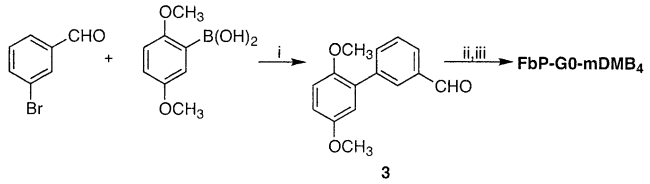
SCHEME 3[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ.

from a prefabricated wedge, having a benzaldehyde group as the foci. Fréchet and co-workers[31] have demonstrated the feasibility of both approaches in the synthesis of porphyrin-containing Frechét dendrimers. For reasons related to ease of purification, the convergent approach is generally considered a more convenient route for the synthesis of pure dendrimers and was therefore chosen for the preparation of **FbP-G0-mBQ$_4$**. In addition, a convergent synthetic approach appeared to be more general for the preparation of the larger dendrimers in this series (i.e., **FbP-G1-pPh-mBQ$_4$**, **FbP-G1-pPh-mPhBQ$_8$**, and **FbP-G2-pPh-mBQ$_{16}$**). The synthesis of the dimethoxybenzene-containing precursor (**FbP-G0-mDMB$_4$**) of **FbP-G0-mBQ$_4$** required the preparation of 2′,5′-dimethoxyphenyl-3-benzaldehyde (**3**), which was synthesized from 2,5-dimethoxyphenylboronic acid and 3-bromobenzaldehyde using Suzuki coupling conditions

SCHEME 4[a]

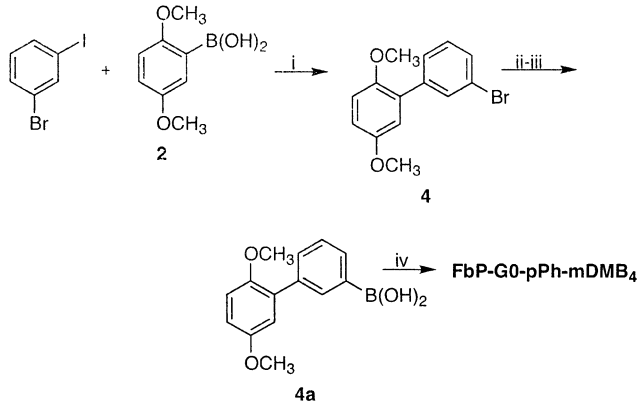


[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) BF_3·OEt_2, pyrrole, CH_2Cl_2; (iii) DDQ.

(Scheme 4) as a pale yellow oil in 93% after column chromatography (silica, 9:1 CH_2Cl_2/hexanes). Cyclization of **3** with pyrrole under Lindsey conditions[28] gave porphyrin **FbP-G0-mDMB$_4$** as a purple solid in 36% yield after chromatography (alumina, 95:5 CH_2Cl_2/hexanes). The dimethoxybenzene-terminated porphyrin (**FbP-G0-mDMB$_4$**) was subsequently converted to the hydroquinone with boron tribromide and oxidized to the benzoquinone-containing porphyrin (**FbP-G0-mBQ$_4$**) with

(31) Pollak, K. W.; Sanford, E. M.; Fréchet, J. M. J. *J. Mater. Chem.* **1998**, *8*, 519−527.

SCHEME 5[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) *t*-BuLi, −78 °C; (iii) $B(OiPr)_3$; (iv) **1**, $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ.

DDQ. Porphyrin **FbP-G0-mBQ$_4$** was readily purified in the usual fashion by washing with methanol and isolated in 75% yield as a purple solid.

Dendrimer **FbP-G0-pPh-mBQ$_4$** is a G0 dendrimer analogous to **FbP-G0-mBQ$_4$** but has a biphenyl linkage between the porphyrin and benzoquinone groups. Initially a divergent approach (Scheme 5) was used to synthesize the dimethoxybenzene-containing precursor, **FbP-G0-pPh-mDMB$_4$**. This reaction sequence required the coupling of (2′,5′-dimethoxyphenyl)-3-phenylboronic acid (**4a**) with tetrabromophenylporphyrin **1** using Suzuki coupling conditions (as per the successful synthesis of **FbP-G0-pDMB$_4$**). The synthesis of boronic acid **4a** was accomplished by first coupling 2,5-dimethoxyphenylboronic acid (**2**) to 1-bromo-3-iodobenzene to give 3-(2′,5′-dimethoxyphenyl) bromobenzene **4** in 85% yield as a white solid (column chromatography on silica, 10% ethyl acetate/hexanes). Subsequent treatment of this bromide with *tert*-butyllithium followed by triisopropylborate ((*i*PrO)$_3$B) yielded the corresponding boronic acid. While preparation of this boronic acid was successful, all attempts (i.e., crystallization, column chromatography, and extraction) to isolate it in high purity were unsuccessful. TLC data for all purification attempts showed the presence of two different products. Impurities in Suzuki couplings can lead to problems with preparation and isolation of the final pure product. Because of the problems isolating the pure boronic acid, this route was abandoned.

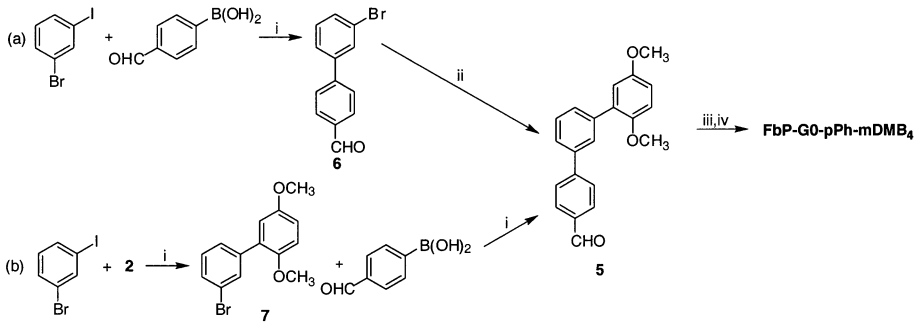
The successful synthesis of porphyrin **FbP-G0-mBQ$_4$** by a convergent approach, wherein aldehyde **3** was cyclized under Lindsey conditions, suggested that **FbP-G0-pPh-mDMB$_4$** might also be successfully synthesized in a similar fashion (Scheme 6). Thus, [1,1′:3′,1″-(2″,5″-dimethoxy)-terphenyl]-4-carboxyaldehyde (**5**) was prepared by two separate routes (Scheme 6). The first route (Scheme 6a) involved the Suzuki coupling reaction of 4-formylphenylboronic acid to 1-bromo-3-iodobenzene to give aldehyde **6** in 61% yield as a pale yellow solid after column chromatography (60:40 CH_2Cl_2/hexanes on silica). The subsequent reaction of aldehyde **6** with boronic acid **2** under Suzuki reaction conditions gave aldehyde **5** as a pale yellow oil in 70% yield (1:3 ethyl acetate/hexanes on silica). A second, higher-yield reaction sequence was also employed to synthesize **5** (Scheme 6b). This sequence utilized the Suzuki coupling reaction of bromide **7** to 4-formylphenylboronic acid to give **5** after chromatography (25% ethyl acetate/hexanes on silica) in 94% yield. Condensation of aldehyde **5** under Lindsey conditions resulted in formation of dendrimer **FbP-G0-pPh-mDMB$_4$** as a purple solid in 46% yield (95:5 CH_2Cl_2/hexanes on alumina). Porphyrin dendrimer **FbP-G0-pPh-mDMB$_4$** was subsequently converted to the hydroquinone with boron tribromide, oxidized to the benzoquinone-containing porphyrin (**FbP-G0-pPh-mBQ$_4$**) with DDQ in 78% yield, and purified in the normal manner.

The next higher homologue in this rigid polyphenylene series of dendrimers, **FbP-G1-mBQ$_8$**, is a G1 dendrimer similar to **FbP-G0-pPh-mBQ$_4$** but has bis(3′,5′-benzoquinone)-4-phenyl substitution at the *meso* phenyl (para) positions on the porphyrin. Preparation of this dendrimer (Scheme 7) used a (divergent) synthetic approach similar to that used to synthesize dendrimer **FbP-G0-pBQ$_4$**. For the synthesis of dimethoxybenzene-containing precursor **FbP-G1-pPh-mDMB$_8$**, 3,5-bis(2′,5′-dimethoxyphenyl)-phenyl boronic acid **8** functioned as the reactive dendritic wedge and was to be coupled to tetrabromophenylporphyrin **1** using Suzuki coupling conditions. The preparation of boronic acid wedge **8** involved the reaction of 1,3,5-tribromobenzene with 2 equiv of 2,5-dimethoxyphenyl boronic acid under Suzuki coupling conditions (Scheme 7). Purification by column chromatography on silica with a gradient of CH_2Cl_2/hexanes (from 1:1 to 3:1) resulted in the isolation of 1-bromo-3,5-(2′,5′-dimethoxyphenyl)-benzene **9** in 68% yield as a white solid. The synthesis of **9** proved to be problematic because of formation of a low-melting impurity suspected to be 1,3-(2′,5′-dimethoxyphenyl)benzene, the product obtained from replacement of bromine with hydrogen during the coupling step. The synthesis was initially carried out using 0.03 equiv of $Pd(PPh_3)_4$ per coupling site and a 24 h reaction time. Upon reducing the time of the reaction to 3 h and the amount of catalyst to a total amount of 0.01 equiv, **9** was isolated without the low-melting impurity.

Reaction of bromide **9** with *tert*-butyllithium at −78 °C, followed by addition of triisopropyl borate, resulted in the formation of 3,5-(2′,5′-dimethoxyphenyl)phenylboronic acid (**8**) as a colorless oil (Scheme 7). Extraction into aqueous base, followed by re-acidification and re-extraction into ether gave the boronic acid as a white solid (84% yield). Porphyrin-dendrimer **FbP-G1-pPh-mDMB$_8$** was synthesized by reaction of **9** with tetrabromophenylporphyrin **1** using Suzuki coupling conditions. Purification of the crude product by column chromatography on alumina (95:5 CH_2Cl_2/ethyl acetate) resulted in the isolation of porphyrin **FbP-G1-pPh-mDMB$_8$** as a purple solid in 75% yield. Porphyrin **FbP-G1-pPh-mDMB$_8$** was subsequently converted to the hydroquinone with boron tribromide and oxidized to the benzoquinone-containing porphyrin (**FbP-G1-pPh-mBQ$_8$**) with DDQ in 79% yield. Porphyrin **FbP-G1-pPh-mBQ$_8$** was readily purified by washing with methanol in the usual fashion.

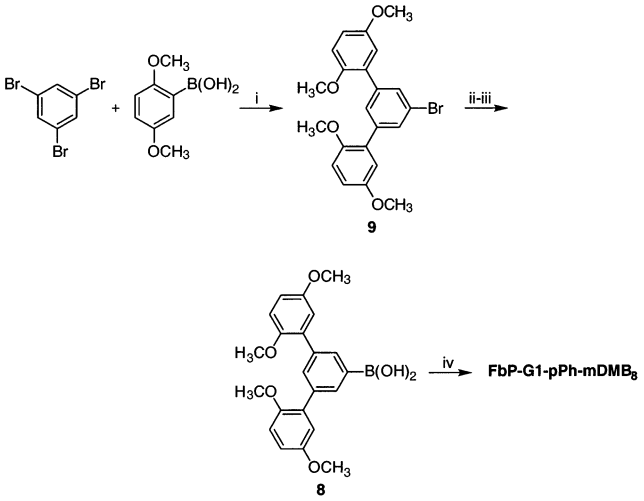
The final two dendrimers in this rigid polyphenylene porphyrin-containing dendrimer series, **FbP-G1-pPh-mPhBQ$_8$** and **FbP-G2-pPh-mBQ$_{16}$**, were assembled by a convergent synthetic approach. The dendritic wedges were prepared as aldehydes and then reacted under

SCHEME 6[a]



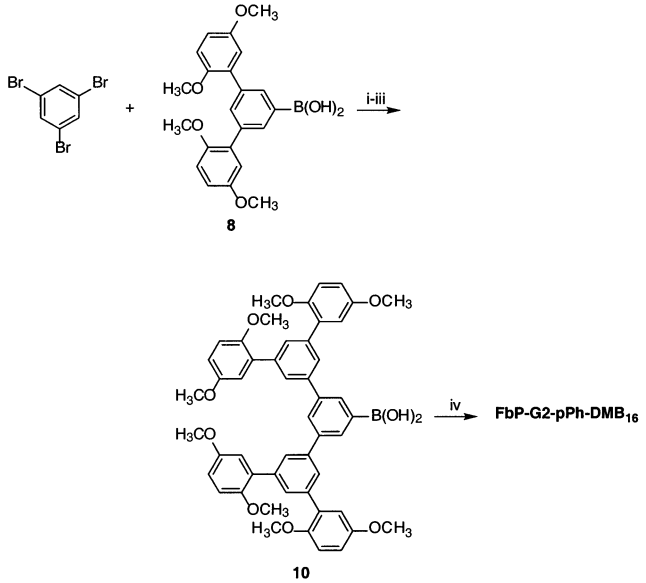
[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) **2**, $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (iii) $BF_3{\cdot}OEt_2$, pyrrole, CH_2Cl_2; (iv) DDQ.

SCHEME 7[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) *t*-BuLi, −78 °C; (iii) $(i\text{-}PrO)_3B$; (iv) **1**, $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ.

SCHEME 8[a]



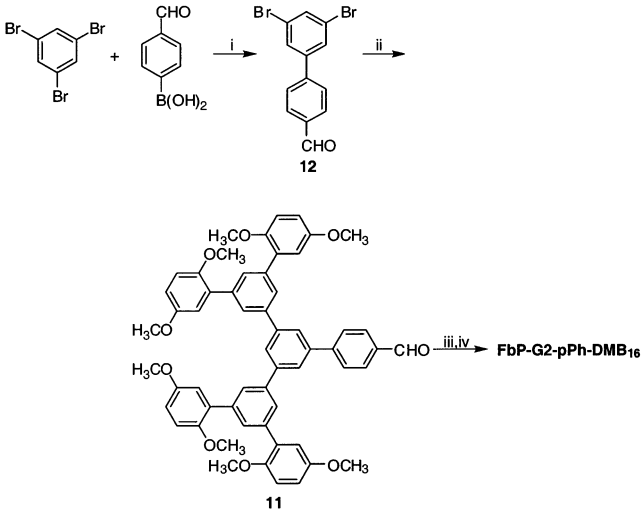
[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) *t*-BuLi, −78 °C; (iii) $(i\text{-}PrO)_3B$; (iv) **1**, $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ.

Lindsey conditions to directly provide the porphyrin dendrimer. Dendrimer **FbP-G1-pPh-mPhBQ$_8$** is a first generation dendrimer with eight 1,1′:3′,1″-bis(4,4″-benzoquinone)-terphenyl peripheral groups substituted at the para carbons on the *meso* phenyl rings of tetraphenylporphyrin. Dendrimer **FbP-G2-pPh-BQ$_{16}$** is the second generation analogue of **FbP-G1-pPh-mBQ$_8$** and contains sixteen peripheral benzoquinone groups.

Initially, a divergent approach was used to synthesize **FbP-G2-pPh-DMB$_{16}$**. In this synthesis (Scheme 8), boronic acid wedge **10** was targeted to be coupled in a final step with tetrabromophenylporphyrin **1**. The Suzuki coupling reaction of boronic acid **8** with 1,3,5-tribromobenzene, the critical step necessary to prepare the bromide precursor to **10**, was unsuccessful, and only the monosubstituted product was isolated, indicating unfavorable steric interactions in the Suzuki coupling step with 1,3,5-tribromobenzene.

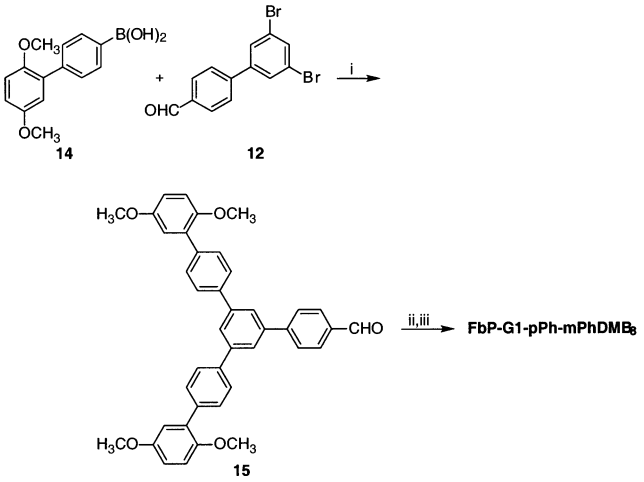
As a result of this problem, a convergent route was designed to synthesize the dimethoxybenzene-containing dendrimer, **FbP-G2-pPh-mDMB$_{16}$**, by the cyclization reaction of aldehyde **11** with pyrrole (Scheme 9). Aldehyde **12** was first synthesized as a precursor to **11** through the carefully controlled coupling reaction of 1,3,5-tribromobenzene with 4-formylphenylboronic acid (Scheme 9). The best results were achieved when 1,3,5-tribromobenzene was in a 2.5 molar excess and the reaction concentration was 0.033 M in the aldehyde. Under these conditions, **12** was obtained as a white solid in 63% yield after column chromatography employing 2:1 CH_2Cl_2/hexanes followed by 95:5 CH_2Cl_2/ethyl acetate on silica. The subsequent reaction of **12** with 2.2 equiv of **8** followed by column chromatography resulted in formation of aldehyde **11** in 65% yield (Scheme 9). Condensation of **11** with pyrrole under Lindsey conditions[28] followed by oxidation with DDQ resulted in the formation of porphyrin dendrimer **FbP-G2-pPh-mDMB$_{16}$**. Isolation of porphyrin **FbP-G2-pPh-mDMB$_{16}$** as a purple solid in 54% yield was achieved by column chromatography on alumina (95:5 CH_2Cl_2/ethyl acetate). Porphyrin dendrimer **FbP-G2-pPh-mDMB$_{16}$** was subsequently converted to the benzoquinone-containing dendrimer **FbP-G2-pPh-mBQ$_{16}$** after treatment with boron tribromide and oxidation with DDQ. Porphyrin **FbP-G2-pPh-mBQ$_{16}$** was readily purified in the usual fashion and isolated in 79% yield as a purple solid. This dendrimer has only limited

SCHEME 9[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) **8**, $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (iii) $BF_3{\cdot}OEt_2$, pyrrole, CH_2Cl_2; (iv) DDQ.

SCHEME 10[a]



[a] Reaction conditions: (i) $Pd(PPh_3)_4$, K_2CO_3, 3:1 $PhCH_3$/EtOH, Δ; (ii) $BF_3{\cdot}OEt_2$, pyrrole, CH_2Cl_2; (iii) DDQ.

solubility and was difficult to characterize except through absorption spectroscopy.

The final dendrimer (**FbP-G1-pPh-mPhBQ$_8$**) in this series was synthesized by the same convergent strategy successfully used in the synthesis of **FbP-G2-pPh-mBQ$_{16}$**. The initial boronic acid (**13**) used in the preparation of **FbP-G1-pPh-mPhDMB$_8$** was synthesized by the Suzuki coupling reaction of **2** with 1-bromo-4-iodobenzene followed by conversion of the resulting bromide (**13**) to 4-(2′,5′-dimethoxyphenyl)-phenylboronic acid (**14**) using *tert*-butyllithium followed by triisopropyl borate. Boronic acid **14** was then reacted with aldehyde **12** (Scheme 10) in a Suzuki coupling reaction to give the doubly branched aldehyde **15** as a white solid in 64% yield (8:2 CH_2Cl_2/hexanes on silica). Condensation of **15** with pyrrole under Lindsey conditions yielded porphyrin **FbP-G1-pPh-mPhDMB$_8$** as a purple solid in 64% yield after column chromatography on alumina (95:5 CH_2Cl_2/ethyl acetate). Porphyrin dendrimer **FbP-G1-pPh-mPhDMB$_8$** was subsequently converted to the benzoquinone-containing dendrimer **FbP-G1-pPh-mPhBQ$_8$** after treatment with boron tribromide and oxidation with DDQ. Porphyrin **FbP-G1-pPh-mPhBQ$_8$** was readily purified in the usual fashion and isolated in 80% yield as a purple solid.

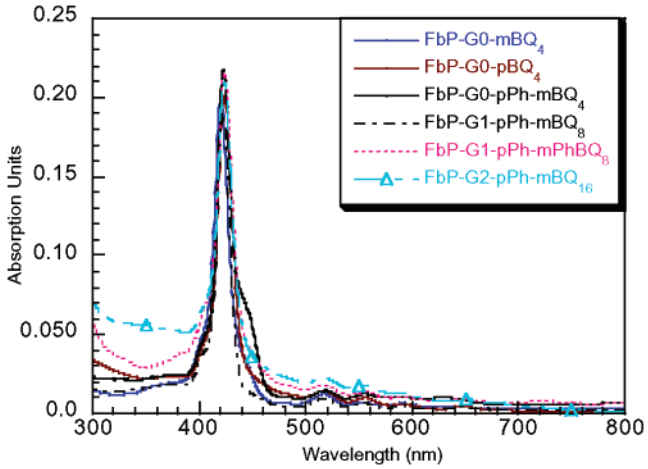


FIGURE 1. Absorption spectra in CH_2Cl_2 measured for dendrimers **FbP-G0-pBQ$_4$**, **FbP-G0-mBQ$_4$**, **FbP-G0-pPh-mBQ$_4$**, **FbP-G1-pPh-mBQ$_8$**, **FbP-G1-pPh-mPhBQ$_8$**, and **FbP-G2-pPh-mBQ$_{16}$**.

TABLE 1. Absorption Maxima of Free Base Porphyrin Dendrimers FbP-G0-pBQ$_4$, FbP-G0-mBQ$_4$, FbP-G0-pPh-mBQ$_4$, FbP-G1-pPh-mBQ$_8$, FbP-G1-pPh-mPhBQ$_8$, and FbP-G2-pPh-mBQ$_{16}$ and the Respective Dimethoxybenzene (DMB)-Containing Reference Compounds

dendrimer	solvent	absorption maxima (nm)
FbP-G0-pDMB$_4$	CH_2Cl_2	422 518 554 591 648
FbP-G0-pBQ$_4$	CH_2Cl_2	419 517 556 591 648
FbP-G0-mDMB$_4$	CH_2Cl_2	421 518 554 592 647
FbP-G0-mBQ$_4$	CH_2Cl_2	420 517 553 590 623, 646
FbP-G0-pPh-mDMB$_4$	CH_2Cl_2	423 519 555 593 648
FbP-G0-pPh-mBQ$_4$	CH_2Cl_2	423 518 554 593 648
FbP-G1-pPh-mDMB$_8$	CH_2Cl_2	423 519 555 593 648
FbP-G1-pPh-mBQ$_8$	CH_2Cl_2	423 518 555 590 628, 644
FbP-G1-pPh-mPhDMB$_8$	CH_2Cl_2	424 519 555 593 649
FbP-G1-pPh-mPhBQ$_8$	CH_2Cl_2	424 518 555 594 648
FbP-G2-pPh-mDMB$_{16}$	CH_2Cl_2	423 518 555 594 649
FbP-G2-pPh-mBQ$_{16}$[a]	CH_2Cl_2	424 518 556 593 650

[a] This dendrimer was only moderately soluble in CH_2Cl_2.

Steady-State Absorption Spectroscopy. The absorption spectra (Figure 1, Table 1) of the rigid dendrimers synthesized in this work are largely typical of free base porphyrins. In CH_2Cl_2, the Soret bands for these dendrimers were observed at ~420 nm, similar to the Soret band observed for H_2TPP (λ_{max} ~419 nm in CH_2Cl_2). Neither the position nor the shape of the Soret transition is substantially affected by increasing dendrimer generation or substitution pattern.

Computational Results

Flexible dendrimers have been shown computationally[32] and experimentally[13,33] to undergo extensive backfolding with the end-groups positioned throughout the structure of the dendrimer and not at the dendrimer surface. The primary purpose of synthesizing the rigid dendrimers presented in this work was to prevent this

backfolding from occurring. Photoinduced electron-transfer would then occur from a relatively fixed geometry in these dendrimers, rather than one of a variety of conformations.[13] In this manner we had hoped to better control electron-transfer rate constants in porphyrin- and quinone-containing dendrimers. A second aspect of dendrimer chemistry we seek to exploit in future work relates to the accessibility of substrate molecules to the core porphyrin. Large-generation flexible dendrimers have been reported[13,19] to isolate the core group from the surrounding environment. We anticipated that the larger rigid dendrimer(s) reported here might behave similarly. To probe these structural issues we performed semiempirical calculations on the porphyrin dendrimers reported. The following structural details were particularly interesting for these dendrimers: (a) the porphyrin−benzoquinone center-to-center distance, (b) the total size of the dendrimer (outer diameter), and (c) the size of the opening in the dendrimer above and below the porphyrin core (inner diameter). Calculations were performed at the semiempirical (AM1) level as implemented by PCSpartan Plus.[34] The results of these calculations are shown in Figure 2 and summarized in Table 2.

Monosubstituted dendrimers, **FbP-G0-pBQ$_4$** and **FbP-G0-mBQ$_4$**, are found to be the smallest dendrimers synthesized in this work, with **FbP-G0-mBQ$_4$** (the smallest dendrimer) having a porphyrin−benzoquinone center-to-center distance of 9.7 Å and outer diameter distances of ∼2.2 nm (cis conformation) and ∼2.3 nm (trans conformation). The para-substituted dendrimer **FbP-G0-pBQ$_4$** is slightly larger in terms of both the porphyrin−benzoquinone distance (11.4 Å) and the outer diameter (∼2.6 nm). The additional phenyl spacer between the porphyrin and benzoquinone groups in dendrimer **FbP-G0-pPh-mBQ$_4$** increases the porphyrin−benzoquinone distance to 13.6 Å and increases the outer diameter of the dendrimer to 3.0 nm. The doubly substituted first-generation analogue of this dendrimer, **FbP-G1-mBQ$_8$**, has a porphyrin−benzoquinone distance of 13.8 Å that is approximately the same size as that in **FbP-G0-pPh-mBQ$_4$**. The outer diameter of this dendrimer is ∼3.0 nm.

More interesting in terms of their structural characteristics are the larger dendrimers **FbP-G1-pPh-mPhBQ$_8$** and **FbP-G2-pPh-mBQ$_{16}$**. The porphyrin−benzoquinone distance in G1 dendrimer **FbP-G1-pPh-mPhBQ$_8$** is 17.5 Å. Two orientations of the benzoquinone groups exist in the G2 dendrimer **FbP-G2-pPh-mBQ$_{16}$**, with the shorter porphyrin−benzoquinone distance (13.8 Å) resulting from the benzoquinone groups positioned above or below the plane of the porphyrin core and the longer distance (17.9 Å) resulting from the benzoquinone groups positioned in more equatorial orientations (i.e., in-plane) with the porphyrin ring. Both dendrimers are substantially larger than any of the other dendrimers and have outer diameters of ∼3.4 nm (**FbP-G1-pPh-mPhBQ$_8$**) and ∼3.7 nm (**FbP-G2-pPh-mBQ$_{16}$**). Only the largest G2 dendrimer, **FbP-G2-pPh-mBQ$_{16}$**, has structural characteristics that suggest potential sequestration of the porphyrin core. The inner diameter in this dendrimer is ∼2.4 nm. It would therefore appear from the computational data that, while these dendrimers represent a potential method of providing protection to the porphyrin core, the critical size necessary for more complete isolation has not been synthesized. An AM1 calculation on **FbP-G2-mBQ$_{16}$** (not synthesized), an analogue of **FbP-G2-pPh-mBQ$_{16}$** where the phenyl group between the initial branching point of the dendrimer and the porphyrin core has been removed, indicates an inner diameter of ∼1.5 nm and may be better suited for this purpose. The computational results on the dendrimers prepared

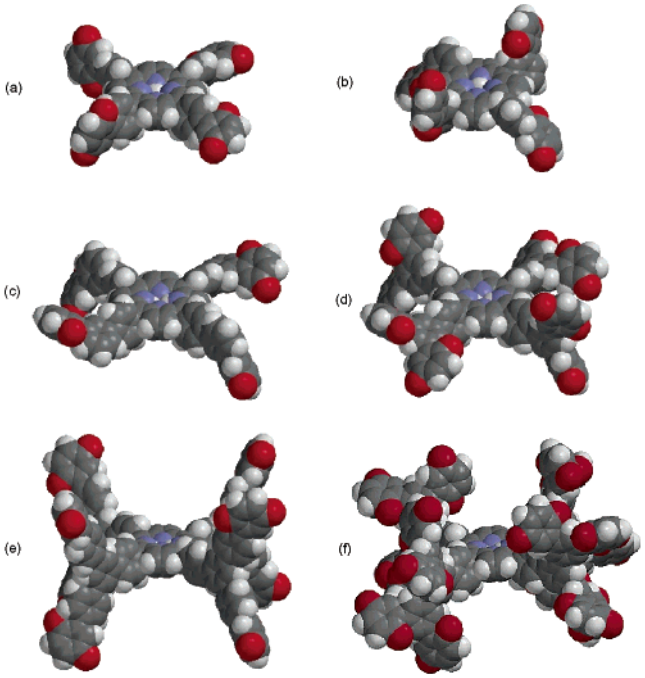


FIGURE 2. Space-filling models of the rigid polyphenylene porphyrin-containing dendrimers synthesized in this work. Optimized geometries are shown for all dendrimers: (a) **FbP-G0-pBQ$_4$**, (b) **FbP-G0-mBQ$_4$**, (c) **FbP-G0-pPh-mBQ$_4$**, (d) **FbP-G1-mBQ$_8$**, (e) **FbP-G1-pPh-mPhBQ$_8$**, and (f) **FbP-G2-pPh-mBQ$_{16}$**.

TABLE 2. Summary of Computational Data for Dendrimers FbP-G0-pBQ$_4$, FbP-G0-mBQ$_4$, FbP-G0-pPh-mBQ$_4$, FbP-G1-pPh-mBQ$_8$, FbP-G1-pPh-mPhBQ$_8$, and FbP-G2-pPh-mBQ$_{16}$

dendrimer	porphyrin−benzoquinone distance (Å)	outer diameter (nm)	inner diameter (nm)
FbP-G0-pBQ$_4$	11.4	2.6	
FbP-G0-mBQ$_4$	9.7	2.2 (cis), 2.3 (trans)	
FbP-G0-pPh-mBQ$_4$	13.6	3.0	
FbP-G1-pPh-mBQ$_8$	13.8	3.0	
FbP-G1-pPh-mPhBQ$_8$	17.5	3.4	
FbP-G2-pPh-mBQ$_{16}$	13.8, 17.9	3.7	2.4

(32) (a) Mansfield, M. L. *Macromolecules* **2000**, *33*, 8043−8049. (b) Bhalgat, M. K.; Roberts, J. C. *Eur. Polym. J.* **2000**, *36*, 647−651. (c) Cavallo, L.; Fraternali, F. *Chem. Eur. J.* **1998**, *4*, 927−934. (d) Boris, D.; Rubinstein, M. *Macromolecules* **1996**, *29*, 7251−7260. (e) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278. (f) Mansfield, M. *Polymer* **1994**, *35*, 1827. (g) Lescanec, R. L.; Muthukumar, M. *Macromolecules* **1990**, *23*, 2280.

(33) (a) Kao, H.-M.; Stefanescu, A. D.; Wooley, K. L.; Schaefer, J. *Macromolecules* **2000**, *33*, 6214−6216. (b) Baugher, A. H.; Goetz, J. M.; McDowell, L. M.; Huang, H.; Wooley, K. L.; Schaefer, J. *Biophys. J.* **1998**, *75*, 2574−2576. (c) Tasaki, K.; Klug, C. A.; Wooley, K. L.; Schaefer, J. *Annu. Technol. Conf. − Soc. Plast. Eng.* **1997**, *2* , 2249−2252. (d) Wooley, K. L.; Klug, C. A.; Tasaki, K.; Schaefer, J. *J. Am. Chem. Soc.* **1997**, *119*, 53−58.

(34) *MacSpartan 4.0*; Wavefunction, Inc.: Irvine, CA.

TABLE 3. Fluorescence Quantum Yields (ϕ) and Relative Fluorescence Quantum Yields (ϕ_{BQ}/ϕ_{DMB}) of Free Base Porphyrin Dendrimers FbP-G0-pBQ$_4$, FbP-G0-mBQ$_4$, FbP-G0-pPh-mBQ$_4$, FbP-G1-pPh-mBQ$_8$, FbP-G1-pPh-mPhBQ$_8$, and FbP-G2-pPh-mBQ$_{16}$ and the Respective Dimethoxybenzene (DMB)-Containing Reference Compounds

dendrimer	solvent	$\Phi^{a,b}$	$\phi_{BQ}/\phi_{DMB}{}^{c}$
FbP-G0-pDMB$_4$	CH_2Cl_2	0.149	
FbP-G0-pBQ$_4$	CH_2Cl_2	0.00032	0.0073
FbP-G0-mDMB$_4$	CH_2Cl_2	0.153	
FbP-G0-mBQ$_4$	CH_2Cl_2	0.00009	0.00057
FbP-G0-pPh-mDMB$_4$	CH_2Cl_2	0.168	
FbP-G0-pPh-mBQ$_4$	CH_2Cl_2	0.0073	0.0433
FbP-G1-pPh-DMB$_8$	CH_2Cl_2	0.187	
FbP-G1-pPh-BQ$_8$	CH_2Cl_2	0.00176	0.0094
FbP-G1-pPh-pPhmDMB$_8$	CH_2Cl_2	0.187	
FbP-G1-pPh-pPhmBQ$_8$	CH_2Cl_2	0.0354	0.1891
FbP-G2-pPh-mDMB$_{16}$	CH_2Cl_2	0.180	
FbP-G2-pPh-mBQ$_{16}$[d]	CH_2Cl_2	0.00883	0.04913
H$_2$TPP	CH_2Cl_2	0.11	

[a] Excited at the Soret bands to avoid aggregation due to concentration effects. [b] Absolute fluorescence quantum yields determined by ratio comparisons to the known yield of H_2TPP.[35] Quantum yields were calculated using standard methods. [c] Relative to the fluorescence of the corresponding dimethoxybenzene (DMB)-containing dendrimer. [d] Relatively higher error expected due to poor solubility.

here indicate sequestration will occur only at larger generations, although we expect that the synthesis of these dendrimers will be difficult. Experimental work to determine whether **FbP-G2-pPh-mBQ$_{16}$** can isolate the porphyrin core from external substrates is underway.

Steady-State Fluorescence Spectroscopy. Preliminary steady-state fluorescence spectra for the dimethoxybenzene-containing reference dendrimers show fluorescence quantum yields (ϕ_{FL}, Table 3) that are slightly higher than that observed for H_2TPP in CH_2Cl_2. These data are consistent with the data reported by Kimura et al.[25] for porphyrin-containing polyphenylene dendrimers **FbTBP-Gn** (Scheme 2). Examination of the fluorescence spectra of the benzoquinone-terminated dendrimers reveals a substantial decrease in the intensity of fluorescence relative to that of the dimethoxybenzene-terminated dendrimers that is dependent upon both dendrimer generation and substitution pattern. Because the sole difference between these dendrimers is the replacement of the dimethoxybenzene group with the benzoquinone group, the decrease in the fluorescence of the benzoquinone-containing dendrimers relative to their dimethoxybenzene-terminated analogues can be attributed to electron-transfer from the porphyrin core to the peripheral benzoquinone groups. Steady-state fluorescence measurements at a variety of dendrimer concentrations indicate that interdendrimer electron-transfer is not responsible for the fluorescence quenching, and fluorescence quenching thus occurs via intramolecular ET. To compare the fluorescence quantum yield data from the various dendrimers without biasing in generation-dependent effects, the relative quantum yields (ϕ_{BQ}/ϕ_{DMB}) were calculated as described in the Experimental Section. The relative quantum yields of G0 dendrimers **FbP-G0-pBQ$_4$** and **FbP-G0-mBQ$_4$** are the smallest of the dendrimers reported here and have ϕ_{BQ}/ϕ_{DMB} values of 0.0073 and 0.00057, respectively. Excited state quenching in these molecules presumably arises from a through-bond (superexchange) electron-transfer mechanism having strong electronic coupling between the donor and acceptor groups. The center-to-center distance (see Computational Results) between the porphyrin and benzoquinone groups for **FbP-G0-mBQ$_4$** (9.7 Å) is shorter by ~1.7 Å than that calculated for **FbP-G0-pBQ$_4$** (11.4 Å), consistent with the more pronounced amount of fluorescence quenching in this dendrimer. An increase in the distance between the donor and acceptor groups to 13.6 Å in **FbP-G0-pPh-mBQ$_4$** leads to a large increase in the relative fluorescence quantum yield (ϕ_{BQ}/ϕ_{DMB} ~0.0433). However, increasing the number of electron-acceptor end-groups by a factor of 2 leads to a 5-fold decrease in the relative quantum yield of the analogous G1 dendrimer **FbP-G1-BQ$_8$** (0.0094). These results are consistent with those of Gust, Moore, and Moore,[7d] who demonstrated that an increase in the number of acceptor groups attached to a given donor has a scaling effect on electron transfer. The porphyrin−benzoquinone distance in **FbP-G1-pPh-pPhmBQ$_8$** is found to be ~17.5 Å, while the shorter distance in **FbP-G2-pPh-mBQ$_{16}$** is ~13.8 Å. The shorter distance and greater number of acceptor groups suggest that **FbP-G2-pPh-mBQ$_{16}$** should have a greater amount of fluorescence quenching resulting from electron transfer than **FbP-G1-pPh-pPhmBQ$_8$**. The relative quantum yields obtained from the fluorescence spectra of **FbP-G1-pPh-pPhmBQ$_8$** ($\phi_{BQ}/\phi_{DMB} \approx 0.1891$) and **FbP-G2-pPh-mBQ$_{16}$** ($\phi_{BQ}/\phi_{DMB} \approx 0.04913$) confirm this prediction and indicate more substantial quenching of the singlet excited state in the latter dendrimer. Electron transfer in the larger dendrimers likely occurs through a combination of through-bond and through-space mechanisms, the exact mechanism of which is probably highly dependent upon the specific dendrimer. These results, together with picosecond time-resolved fluorescence and femtosecond time-resolved absorption measurements, will be reported in greater detail in due course.

Conclusions

In conclusion, a rigid series of free-base porphyrin- and benzoquinone-containing polyphenylene dendrimers have been prepared by a combination of divergent and convergent synthetic approaches. Unlike previous routes for preparing polyphenylene dendrimers that are incompatible with end-groups bearing certain functional moieties, the synthetic methodology presented here enables incorporation of functional groups on the dendrimer end-groups during preparation of the dendrimer wedges. These syntheses have been performed in a manner that enables further manipulation of the functionalized end-groups. Yields in all steps of the syntheses were relatively high. Steady-state absorption measurements for all dendrimers are typical for free-base porphyrins. Steady-state fluorescence measurements indicate efficient quenching of the S_1 state of the free-base porphyrin in all dendrimers. This quenching is attributed to efficient electron-transfer from the singlet excited state of the porphyrin core to the benzoquinone end-groups. The electron transfer likely occurs through a through-bond (superexchange), a through-space mechanism, or a combination of both mechanisms, the exact mechanism of which is probably highly dependent upon the specific dendrimer. Future work on this project includes time-resolved fluorescence

and absorption measurements of electron-transfer on the picosecond and femtosecond time scales, the results of which will be reported in due course.

Experimental Section

General Methods. All reactions were run under a nitrogen atmosphere unless indicated otherwise. THF was distilled from the sodium benzophenone ketyl, while all other solvents were used as received. All starting materials were used as received. Flash chromatography was carried out on silica gel (230−400 mesh) or neutral alumina (60−325 mesh). All melting points were taken using a capillary melting point apparatus and are uncorrected. Proton NMR spectra were acquired at either 300 or 750 MHz. Proton-decoupled ^{13}C NMR spectra were acquired at 75 MHz and referenced to chloroform. MALDI-TOF-MS were obtained using α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Samples were prepared by mixing 1.0 mL of a solution of the dendrimer in CH_2Cl_2 with 1 mL of a solution of the matrix in 50:45:5 MeCN/EtOH/H_2O. Steady-state fluorescence measurements were run on an ISA Jobin Yvon-SPEX Fluorolog 3-22 fluorometer having dual input and output monochromators. Fluorescence spectra were collected using argon-saturated solutions by exciting at the Soret maxima of optically matched samples (OD = 0.20) in the S/R mode to correct for changes in the lamp output intensity. Quantum yield measurements were made relative to H_2TPP. Relative quantum yields (ϕ_{BQ}/ϕ_{DMB}) were calculated in order to compare the fluorescence quantum yield data from the various dendrimers without biasing in generation-dependent effects and were calculated as defined in eq 1,[13] where *I*(**DMB**) and *I*(**BQ**)

$$\frac{\phi_{BQ}}{\phi_{DMB}} = \frac{I(\mathbf{BQ})}{I(\mathbf{DMB})}\frac{A(\mathbf{DMB})}{A(\mathbf{BQ})} \qquad (1)$$

represent the fluorescence intensity of the appropriate dendrimer, and *A*(**DMB**) and *A*(**BQ**) represent the optical density of the sample used in the measurement. Slits were set to 0.75 mm each for the entrance, exit, and intermediate excitation slits and 4.00 mm each for the emission slits. All dendrimers synthesized in this work were fully characterized by NMR (^{1}H and ^{13}C) and MALDI-TOF MS, except **FbP-G2-pPh-mBQ$_{16}$**, which was not sufficiently soluble for any characterization except UV−vis.

Preparation of *meso*-Tetrakis-(4-bromophenyl)porphyrin (1).[29] Into a 2000 mL round-bottom flask containing *p*-brombenzaldehyde (3.000 g, 16.21 mmol) in 1621 mL of $CHCl_3$ was added pyrrole (1.088 g, 16.21 mmol). After the solution was purged with argon for 5 min, $BF_3{\cdot}OEt_2$ (0.6721 mL, 5.351 mmol) was added, and the resulting solution was stirred under argon for 1 h. After 1 h, DDQ (2.761 g, 12.16 mmol) was added rapidly as a solid. The solution was stirred for an additional 1 h, at which time the solvent was evaporated. The crude solid was placed on a filter and washed with methanol until the filtrate became colorless, which resulted in the isolation of **1** as a bright purple solid (2.033 g, 58%): ^{1}H NMR ($CDCl_3$, δ) −2.86 (s, 1H), 7.92 (d, 4H, J = 8 Hz), 8.08 (d, 4H, J = 8 Hz), 8.85 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 119.20, 122.86, 130.21, 136.04, 141.04; UV/vis (λ_{max}, nm, CH_2Cl_2) 420.0, 515.5, 551.0, 589.5, 646.5.

Preparation of 3-(2,5-Dimethoxyphenyl)benzaldehyde (3).[36] 3-Bromobenzaldehyde (1.000 g, 5.405 mmol), 2,5-dimethoxyphenylboronic acid (1.180 g, 6.486 mmol), and anhydrous potassium carbonate (0.9929 g, 7.188 mmol) were added to a 100 mL round-bottom flask. Toluene (30 mL) and ethanol (10 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.06260 g, 0.05405 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 3 h. The solution was cooled to room temperature and diluted with chloroform and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was separated and dried over Na_2SO_4. Concentration of the solvent resulted in the crude product. Purification by column chromatography on silica using 9:1 CH_2Cl_2/hexanes yielded **3** as a pale yellow oil (1.2187 g, 93%): ^{1}H NMR ($CDCl_3$, δ) 3.78 (s, 3H), 3.83 (s, 3H), 6.93 (m, 3 H), 7.58 (t, 1H, J = 7.6 Hz), 7.84 (m, 2H), 8.06 (t, 1H, J = 1.5 Hz) 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.02, 56.43, 112.82, 114.03, 116.77, 128.35, 128.90, 130.18, 131.22, 135.77, 136.53, 139.57, 150.85, 154.04, 192.64; IR (neat) 1692 cm^{-1} (C═O).

Preparation of 3-(2,5-Dimethoxyphenyl)bromobenzene (4). 1-Bromo-3-iodobenzene (1.500 g, 5.304 mmol), 2,5-dimethoxyphenylboronic acid (0.9653 g, 5.304 mmol), and anhydrous potassium carbonate (0.9744 g, 7.054 mmol) were placed in a 250 mL round-bottom flask. Toluene (75 mL) and ethanol (25 mL) were then added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.06144 g, 0.05304 mmol) was added, and the mixture was brought to reflux where it was allowed to stir under argon for 3 h. The solution was then cooled to room temperature and diluted with chloroform and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica using 10% ethyl acetate/hexanes, yielding **4** as a white solid (1.3276 g, 85%): mp 72−74 °C; ^{1}H NMR ($CDCl_3$, δ) 3.78 (s, 3H), 3.82 (s, 3H), 6.91 (m, 3H), 7.29, (t, 1H, J = 8 Hz), 7.47 (d, 2H, J = 8 Hz), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.04, 56.49, 112.85, 113.94, 116.74, 122.27, 128.33, 129.72, 130.22, 132.60, 140.67, 150.83, 153.96. Anal. Calcd for $C_{14}H_{13}O_2Br$ (293.17): C, 57.35; H, 4.48. Found: C, 57.40; H, 4.65.

Preparation of [1,1′:3′,1″-(2″,5″-dimethoxy)-terphenyl)-4-carboxyaldehyde (5). Bromide **4** (1.500 g, 5.116 mmol), 4-formylphenylboronic acid (0.9207 g, 6.140 mmol), and anhydrous potassium carbonate (0.9399 g, 6.805 mmol) were placed in a 250 mL round-bottom flask. Toluene (105 mL) and ethanol (35 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, the $Pd(PPh_3)_4$ (0.0593 g, 0.05116 mmol) was added, and the resulting solution was brought to reflux where it was allowed to stir under argon for 3 h. The solution was cooled to room-temperature diluted with $CHCl_3$ and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by column chromatography on silica using 25% ethyl acetate/hexanes yielded **5** as a pale yellow oil (1.533 g, 94%): ^{1}H NMR ($CDCl_3$, δ) 3.80 (s, 3H), 3.84 (s, 3H), 6.95 (m, 3H), 7.58 (m, 3H), 7.81 (d, 3H, J = 8 Hz), 7.98 (d, 2H, J = 8 Hz), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.01, 56.51, 112.82, 113.53, 117.01, 126.27, 127.98, 128.75, 128.90, 129.82, 130.45, 131.28, 135.38, 139.39, 139.69, 147.47, 150.93, 154.00, 192.12; IR (neat) 1693 cm^{-1} (C═O). Anal. Calcd for $C_{21}H_{18}O_3$ (318.39): C, 79.21; H, 5.71. Found: C, 78.86; H, 5.81.

Preparation of 3′-Bromo-4-formylbiphenyl (6). 1-Bromo-3-Iodobenzene (2.166 g, 7.659 mmol), 4-formylphenylboronic acid (1.148 g, 7.659 mmol), and anhydrous potassium carbonate (1.407 g, 10.19 mmol) were placed in a 250 mL round-bottom flask. Toluene (105 mL) and ethanol (35 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.0887 g, 0.07659 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 3 h. The solution was cooled to room temperature and diluted with $CHCl_3$ and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by column chromatography using 60:40 CH_2Cl_2/hexanes resulted in the isolation of **7** as a pale yellow solid (1.213 g, 61%): ^{1}H NMR ($CDCl_3$, δ) 7.36 (t,

(35) Strachan, J. P.; Gentemann, J. S.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191.
(36) Malesani, G.; Galiano, F.; Pietrogrande, A.; Rodighiero, G. *Tetrahedron* **1978**, *34*, 2355−2359.

1H, $J = 8$ Hz), 7.55 (t, 1H, $J = 2$ Hz), 7.58 (s,1H), 7.73 (d, 2H, $J = 8$ Hz), 7.79 (t, 1H, $J = 2$ Hz), 7.98 (d, 2H, $J = 8$ Hz), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 123.35, 126.19, 127.94, 130.53, 130.63, 130.73, 131.59, 135.84, 142.03, 145.77, 191.97; IR (Nujol) 1692 cm^{-1} (C═O). Anal. Calcd for $C_{15}H_{14}O_3$ (242.28): C, 74.36; H, 5.82. Found: C, 74.59; H, 6.11.

Preparation of 3-(2′,5′-Dimethoxyphenyl)bromobenzene (7). 1-Bromo-3-iodobenzene (1.500 g, 5.304 mmol), 2,5-dimethoxyphenylboronic acid (0.9653 g, 5.304 mmol), and anhydrous potassium carbonate (0.9744 g, 7.054 mmol) were placed in a 250 mL round-bottom flask. Toluene (75 mL) and ethanol (25 mL) were then added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.06144 g, 0.05304 mmol) was added, and the mixture was brought to reflux where it was stirred under argon for 3 h. The solution was then cooled to room temperature and diluted with chloroform and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica using 10% ethyl acetate/hexanes, yielding **7** as a white solid (1.3276 g, 85%): mp 72−74 °C; ^{1}H NMR ($CDCl_3$, δ) 3.78 (s, 3H), 3.82 (s, 3H), 6.91 (m, 3H), 7.29, (t, 1H, $J = 8$ Hz), 7.47 (d, 2H, $J = 8$ Hz), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.04, 56.49, 112.85, 113.94, 116.74, 122.27, 128.33, 129.72, 130.22, 132.60, 140.67, 150.83, 153.96. Anal. Cald for $C_{14}H_{13}O_2Br$ (293.17): C, 57.35; H, 4.48. Found: C, 57.40; H, 4.65.

Preparation of 3,5-Bis(2′,5′-dimethoxyphenyl)phenyl Boronic Acid (8). A 250 mL round-bottom flask containing **9** (3.5000 g, 8.152 mmol) in 40 mL of THF was cooled to −78 °C. *tert*-Butyllithium (1.7 M in pentane, 9.60 mL, 16.30 mmol) was added by cannula, turning the mixture a blue-green color. This solution was allowed to stir at −78 °C for 30 min. Triisopropyl borate (7.666 g, 40.76 mmol) was added, and the mixture turned cloudy and pale yellow. The solution was allowed to warm slowly to room temperature over the course of 3 h. After 3 h, 3 M HCl was added until two clear layers formed. The biphasic solution was washed with ether (3 × 50 mL). The combined ether layers were then extracted with 10% NaOH. The base layer was re-acidified with 10% HCl to a pH of ∼5 and extracted with ether. The ether layer was dried over Na_2SO_4 and evaporated to yield **8** as a white solid (2.723 g, 85%). ^{1}H NMR (acetone-d_6, δ) 3.74 (s, 6H), 3.80 (s, 6H), 5.80 (s, 2H), 6.97 (m, 6H), 7.79 (t, 1H, $J = 1.8$ Hz), 7.97 (d, 2H, $J = 1.7$ Hz); ^{13}C NMR (acetone-d_6, δ) 56.00, 56.68, 113.89, 113.93, 117.52, 132.87, 133.61, 134.69, 135.66, 138.36, 151.89, 154.95.

Preparation of 1-Bromo-3,5-(2′,5′-dimethoxyphenyl)-benzene (9). 1,3,5-Tribromobenzene (4.000 g, 12.70 mmol), 2,5-dimethoxyphenylboronic acid (4.625 g, 25.40 mmol), and anhydrous potassium carbonate (4.668 g, 33.80 mmol) were placed in a 500 mL round-bottom flask. Toluene (216 mL) and ethanol (72 mL) were added, and the mixture was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.05887 g, 0.05083 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 3 h. The solution was cooled to room temperature and diluted with chloroform and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was separated and dried over Na_2SO_4. Evaporation of the solvent resulted in the crude product, which was purified by column chromatography on silica with a CH_2Cl_2/hexane gradient from 1:1 to 3:1. The purification resulted in isolation of **9** as a white solid (3.693 g, 68%): mp 134−136 °C; ^{1}H NMR ($CDCl_3$, δ) 3.79 (s, 3H), 3.82 (s, 3H), 6.91 (m, 3H), 7.64 (d, 1H, $J = 12.6$ Hz); ^{13}C NMR ($CDCl_3$, δ) 55.80, 56.27, 112.57, 113.74, 116.55, 121.53, 129.35, 130.09, 130.96, 139.87, 150.67, 153.72. Anal. Calcd for $C_{22}H_{21}O_4$-Br (429.33): C, 61.54; H, 4.94. Found: C, 61.30; H, 5.13.

Preparation of 4-Formyl-3′,5′-(3,5-(2,5-dimethoxyphenyl)phenyl)biphenyl (11). Aldehyde **12** (2.000 g, 5.882 mmol), **8** (5.102 g, 12.94 mmol), and anhydrous potassium carbonate (2.161 g, 15.65 mmol) were placed in a 250 mL round-bottom flask. Toluene (120 mL) and ethanol (40 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.6813 g, 0.05882 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 24 h. The solution was cooled to room temperature, diluted with $CHCl_3$, and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by column chromatography on silica initially using 9:1 CH_2Cl_2/hexanes and changing to 95:5 CH_2Cl_2/ethyl acetate resulted in **11** as a white solid (3.3642 g, 65%): mp 114−117 °C; ^{1}H NMR ($CDCl_3$, δ) 3.80 (s,12H), 3.82 (s, 12H), 6.96 (m, 12H), 7.76 (s, 2H), 7.89 (m, 8H), 8.01, (d, 3H, $J = 8$ Hz), 10.10 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.04, 56.54, 112.77, 113.62, 117.02, 125.67, 127.00, 127.58, 128.11, 130.33, 130.58, 131.56, 135.58, 138.99, 140.54, 140.92, 143.03, 147.40, 151.06, 153.98, 192.17; IR (Nujol) 1693 cm^{-1} (C═O); FAB-MS 881.00 (calculated for $C_{57}H_{50}O_9$: 879.07). Anal. Calcd for $C_{57}H_{50}O_9$ (879.07): C, 77.87; H, 5.74. Found: C, 76.37; H, 5.70.

Preparation of 4-Formyl-3′,5′-dibromobiphenyl (12). 1,3,5-Tribromobenzene (4.200 g, 13.34 mmol), 4-formylphenylboronic acid (0.8000 g, 5.335 mmol), and anhydrous potassium carbonate (0.9801 g, 7.096 mmol) were placed in a 250 mL round-bottom flask. Toluene (120 mL) and ethanol (40 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.0618 g, 0.05335 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 3 h. The solution was cooled to room temperature, diluted with $CHCl_3$, and then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated. Purification of the crude product by column chromatography on silica using a hexane/CH_2Cl_2 gradient from 2:1 to 1:1 resulted in **12** as a white solid (1.1369 g, 63%): mp 117−120 °C; ^{1}H NMR ($CDCl_3$, δ) 7.70 (m, 5H), 7.98, (d, 2H, $J = 8$ Hz), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 123.75, 127.97, 129.40, 130.58, 133.94, 136.24, 143.44, 144.25, 191.79; IR (Nujol) 1697 cm^{-1} (C═O). Anal. Calcd for $C_{13}H_8OBr_2$ (340.02): C, 45.92; H, 2.38. Found: C, 43.92; H, 2.37.

Preparation of (4′-Bromo)-2,5-dimethoxybiphenyl (13). 1-Bromo-4-iodobenzene (1.682 g, 5.950 mmol), 2,5-dimethoxyphenylboronic acid (0.9836 g, 5.404 mmol), and potassium carbonate (1.093 g, 7.906 mmol) were all placed in a 100 mL round-bottom flask. Toluene (30 mL) and ethanol (10 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.2066 g, 0.1783 mmol) was added, and the solution was brought to reflux where it was stirred under argon for 3 h. After 3 h, the solution was diluted with $CHCl_3$, washed with 20% NaOH (4 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated to dryness. The crude residue was purified by column chromatography on silica using 10% ethyl acetate/hexanes, which resulted in isolation of (4′-bromo)-2,5-dimethoxybiphenyl as a white solid (1.318 g, 83%): mp 59−60 °C; ^{1}H NMR ($CDCl_3$, δ) 3.77 (s, 3H), 3.82 (s, 3H), 6.90 (m, 3H), 7.42 (d, 2H, $J = 7$ Hz), 7.54 (d, 2H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$, δ) 55.3, 55.8, 112.2, 113.9, 117.0, 120.7, 130.0, 131.6, 131.2, 137.9, 150.1, 153.2. Anal. Calcd for $C_{14}H_{13}O_2Br$ (293.17): C, 57.35; H, 4.48. Found: C, 57.32; H, 4.63.

Preparation of 4-(2′,5′-Dimethoxyphenyl)-phenylboronic Acid (14). A 50 mL round-bottom flask containing (4′-bromo)-2,5-dimethoxybiphenyl (1.3000 g, 4.4343 mmol) in 13.5 mL of THF was cooled to −78 °C. *tert*-Butyllithium (1.7 M in pentane, 5.22 mL, 8.869 mmol) was added by cannula, turning the mixture a deep blue color. This solution was allowed to stir at −78 °C for 30 min. Triisopropyl borate (2.500 g, 13.30 mmol) was added, and the mixture turned cloudy and pale yellow. The solution was allowed to warm slowly to room temperature over the course of 3 h. After 3 h, 3 M HCl was added until two clear layers had formed. The biphasic solution was washed with ether (3 × 50 mL). The combined ether layers were then washed with 3 M HCl, dried over Na_2SO_4, filtered,

and concentrated under vacuum. The crude product was recrystallized from 50% CH_2Cl_2/hexane and then again from hexane, which resulted in **14** as a white solid (0.9270 g, 81%): mp 165−172 °C; ^{1}H NMR ($CDCl_3$, δ) 3.80 (s, 3H), 3.85 (s, 3H), 6.95 (m, 3H), 7.71 (d, 2H, J = 8 Hz), 8.33 (d, 2H, J = 8 Hz); ^{13}C NMR ($CDCl_3$, δ) 56.05, 56.60, 113.06, 113.76, 116.92, 129.31, 131.67, 135.62, 142.97, 151.09, 154.02.

Preparation of 4-Formyl-3′,5′-(4-(2,5-dimethoxyphenyl)-phenyl)biphenyl (15). Aldehyde **12** (0.4217 g, 1.240 mmol), **14** (0.7402 g, 2.728 mmol), and anhydrous potassium carbonate (0.4557 g, 3.299 mmol) were placed in a 40 mL round-bottom flask. Toluene (30 mL) and ethanol (10 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.1436 g, 0.1240 mmol) was added. The resulting solution was brought to reflux, where it was allowed to stir under argon for 24 h. The solution was cooled to room temperature and diluted with $CHCl_3$. The solution was then washed with 10% NaOH (3 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and evaporated under vacuum. Purification of the crude product by column chromatography on silica initially using 8:2 CH_2Cl_2/hexanes resulted in **15** as a white solid (0.4858 g, 65%): mp 94−98 °C; ^{1}H NMR ($CDCl_3$, δ) 3.82 (s, 6H), 3.85 (s, 6H), 6.95 (m, 6H), 7.70 (d, 4H, J = 8 Hz), 7.78 (d, 4H, J = 8 Hz), 7.88 (s, 2H), 7.90 (d, 2H, J = 8 Hz), 7.96 (t, 1H, J = 2 Hz), 8.03 (d, 2H J = 8 Hz), 10.11 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) 56.04, 56.54, 112.85, 113.47, 116.91, 125.41, 126.41, 127.22, 128.14, 130.24, 130.58, 131.22, 135.63, 138.15, 139.66, 141.06, 142.65, 147.40, 151.05, 154.03, 192.14; IR (Nujol) 1692 cm^{-1} (C═O); FAB-MS 606.00 (calcd for $C_{41}H_{34}O_5$, 606.75). Anal. Calcd for $C_{41}H_{34}O_5$ (606.75): C, 81.16; H, 5.66. Found: C, 79.64; H, 5.69.

Preparation of *meso*-Tetrakis-[4-(2,5-dimethoxyphenyl)-phenyl]porphyrin (FbP-G0-pDMB$_4$). Porphyrin **1** (0.5000 g, 0.5732 mmol), 2,5-dimethoxyphenyl boronic acid (0.6259 g, 3.439 mmol), and anhydrous K_2CO_3 (0.6338 g, 4.586 mmol) were added to a 200 mL round-bottom flask. Toluene (48 mL) and ethanol (16 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.0738 g, 0.06368 mmol) was added. The mixture was brought to reflux where it was stirred for 2 days. The reaction mixture was diluted with chloroform and washed with 20% NaOH (4 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on alumina (95:5 CH_2Cl_2/ethyl acetate). The first purple band was collected and evaporated to dryness to yield **FbP-G0-pDMB$_4$** as a purple solid (0.4886 g, 74%): ^{1}H NMR ($CDCl_3$, δ) −2.65 (s, 1H), 3.96 (s, 6H), 3.98 (s, 6H), 7.00 (m, 2H), 7.09 (d, 2H, J = 9 Hz), 7.30 (d, 2H, J = 3 Hz), 8.00 (d, 4H, J = 8 Hz), 8.32 (d, 4H, J = 8 Hz), 9.05 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 55.93, 56.47, 112.92, 113.51, 116.96, 120.09, 127.76, 131.24, 134.53, 137.67, 140.89, 151.06, 153.99; UV/vis (λ_{max}, nm, CH_2Cl_2) 306.5, 422.5, 518.0, 554.5, 591.5, 648.0.

Preparation of *meso*-Tetrakis[3-(2,5-dimethoxyphenyl)-phenyl]porphyrin (FbP-G0-mDMB$_4$). To a 500 mL round-bottom flask containing **3** (0.5000 g, 2.064 mmol) in 206 mL of $CHCl_3$ was added pyrrole (0.1384 g, 2.064 mmol). After purging the solution with argon for 5 min, BF_3·OEt_2 (0.0860 mL, 0.0681 mmol) was added, and the resulting solution was stirred under argon for 1 h. After 1 h, DDQ (0.3514 g, 1.548 mmol) was added rapidly as a solid. The solution was stirred for an additional 1 h, at which time the solvent was evaporated. The crude solid was placed on a filter and washed with methanol until the filtrate became colorless. The resulting purple product was purified by column chromatography on alumina (95:5 CH_2Cl_2/ethyl acetate). The first purple band was collected and evaporated to dryness to yield **FbP-G0-mDMB$_4$** as a purple solid (0.2183 g, 36%): ^{1}H NMR ($CDCl_3$, δ) −2.68 (s, 1H), 3.83 (s, 6H), 3.89 (s, 6H), 6.90 (d, 2H, J = 8.8 Hz), 6.99 (d, 2H, J = 8.8 Hz), 7.23 (s, 2H), 7.83 (t, 2H, J = 7.6 Hz), 7.98 (d, 2H, J = 7.7 Hz), 8.22 (s, 2H), 8.52 (s, 2H), 9.07 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 56.06, 56.72, 113.06, 113.58, 117.18, 120.40, 126.69, 128.73, 131.63, 133.93, 136.40, 136.94, 141.96, 151.36, 154.12; MALDI-TOF-MS 1158.21 (calcd for $C_{76}H_{62}O_8N_4$, 1159.42); UV/vis (λ_{max}, nm, CH_2Cl_2) 306.5, 421.5, 517.0, 553.0, 590.5, 647.0.

Preparation of *meso*-Tetrakis-[4-(3-(2,5-dimethoxyphenyl)phenyl)phenyl]porphyrin (FbP-G0-pPh-mDMB$_4$). To a 1000 mL round-bottom flask containing **5** (1.5000 g, 4.713 mmol) in 471 mL of $CHCl_3$ was added pyrrole (0.3162 g, 4.713 mmol). After purging the solution with argon for 5 min, BF_3·OEt_2 (0.1954 mL, 1.555 mmol) was added, and the resulting solution was stirred under argon for 1 h. After 1 h, DDQ (0.8024 g, 3.535 mmol) was added rapidly as a solid. The solution was stirred for an additional 1 h, at which time the solvent was evaporated. The crude solid was placed on a filter and washed with methanol until the filtrate became colorless. The resulting purple product was purified by column chromatography on alumina using 95:5 CH_2Cl_2/ethyl acetate. The first purple band was collected and evaporated to dryness to yield **FbP-G0-pPh-mDMB$_4$** as a purple solid (0.7997 g, 46%): ^{1}H NMR ($CDCl_3$, δ) −2.63 (s, 1H), 3.88 (s, 6H), 3.89 (s, 6H), 7.02 (m, 6H), 7.68 (s, 4H), 7.92 (s, 2H), 8.07 (d, 4H, J = 8 Hz), 8.13 (s, 2H), 8.35 (d, 4H, J = 8 Hz), 9.01 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 56.11, 56.71, 113.00, 113.56, 117.10, 120.18, 125.75, 126.35, 128.81, 128.93, 129.01, 131.86, 135.35, 139.38, 140.71, 140.84, 141.39, 151.14, 154.09; MALDI-TOF-MS 1463.38 (calcd for $C_{100}H_{78}O_8N_4$, 1463.82); UV/vis (λ_{max}, nm, CH_2Cl_2) 305.0, 424.0, 518.5, 556.0, 592.0, 648.5.

Preparation of *meso*-Tetrakis[4-(3,5-(2,5dimethoxyphenyl)phenyl)phenyl]porphyrin (FbP-G1-pPh-mDMB$_8$). Porphyrin **1** (0.1020 g, 0.1096 mmol), **8** (0.2593 g, 0.6578 mmol), and anhydrous potassium carbonate (0.1211 g, 0.8768 mmol) were added to a 25 mL round-bottom flask. Toluene (9 mL) and ethanol (3 mL) were added, and the resulting solution was purged with argon for 10 min. After 10 min, $Pd(PPh_3)_4$ (0.0140 g, 0.01206 mmol) was added. The mixture was brought to reflux where it was stirred for 48 h. The reaction mixture was diluted with chloroform and washed with 20% NaOH (4 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on alumina using 95:5 CH_2Cl_2/ethyl acetate. The first purple band was collected and evaporated to dryness to yield **FbP-G1-pPh-mDMB$_8$** as a purple solid (0.1720 g, 78%): mp 294−297 °C; ^{1}H NMR ($CDCl_3$, δ) −2.63 (s, 1H), 3.89 (s, 12H), 3.90 (s, 12H), 7.05 (m, 12H), 7.85 (s, 2H), 8.10 (t, 8H, J = 3 Hz), 8.36 (d, 4H, J = 8 Hz), 9.02 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 56.11, 56.72, 112.96, 113.65, 117.12, 120.23, 125.88, 127.69, 130.18, 131.88, 135.38, 139.05, 140.57, 140.82, 141.36, 151.21, 154.08; MALDI-TOF-MS 2008.79 (calcd for $C_{132}H_{110}O_{16}N_4$: 2008.46); UV/vis (λ_{max}, nm, CH_2Cl_2) 309.0, 424.5, 519.5, 556.5, 592.0, 649.0.

Preparation of *meso*-Tetrakis-[4-(3,5-(4-(2,5-dimethoxyphenyl)phenyl)phenyl)phenyl]porphyrin (FbP-G1-pPh-mPhDMB$_8$). To a 250 mL round-bottom flask containing **15** (0.5000 g, 0.8241 mmol) in 82 mL of $CHCl_3$ was added pyrrole (0.05528 g, 0.8241 mmol). After the solution was purged with argon for 5 min, BF_3·OEt_2 (0.03416 mL, 0.2719 mmol) was added, and the resulting solution was stirred under argon for 1 h. After 1 h, DDQ (0.1403 g, 0.6180 mmol) was added rapidly as a solid. The solution was stirred for an additional 1 h, at which time the solvent was evaporated. The crude solid was placed on a filter and washed with methanol until the filtrate became colorless. The resulting purple product was purified by column chromatography on alumina using 95:5 CH_2Cl_2/ethyl acetate. The first purple band was collected and evaporated to dryness to yield **FbP-G1-pPh-mPhDMB$_8$** as a purple solid (0.3470 g, 64%): ^{1}H NMR ($CDCl_3$, δ) −2.56 (s, 1H), 3.86 (s, 12H), 3.88 (s, 12H), 6.99 (m, 12H), 7.78 (d, 8H, J = 8 Hz), 7.95 (d, 8H, J = 8 Hz), 8.07 (s, 2H), 8.20 (d, 4H, J = 8 Hz), 8.25 (s, 4H), 8.45 (d, 4H, J = 8 Hz), 9.09 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 56.05, 56.57, 112.94, 113.54, 116.96, 120.23, 125.64, 125.96, 127.42, 130.32, 131.43, 135.55, 138.07, 140.19, 140.74, 141.79, 142.24, 142.66, 151.16, 154.10; MALDI-TOF-MS 2614.96

(calcd for $C_{180}H_{142}O_{16}N_4$, 2617.26); UV/vis (λ_{max}, nm, CH_2Cl_2) 311.0, 423.5, 517.5, 554.5, 592.0, 647.5.

Preparation of *meso*-Tetrakis-[4-(3,5-(3,5-(2,5-dimethoxyphenyl)phenyl)phenyl)phenyl]porphyrin (FbP-G2-pPh-mDMB$_{16}$). To a 250 mL round-bottom flask containing **11** (0.5000 g, 0.5688 mmol) in 57 mL of $CHCl_3$ was added pyrrole (0.03816 g, 0.5688 mmol). After the solution was purged with argon for 5 min, $BF_3{\cdot}OEt_2$ (0.02358 mL, 0.1877 mmol) was added, and the resulting solution was stirred under argon for 1 h. After 1 h, DDQ (0.09684 g, 0.4266 mmol) was added rapidly as a solid. The solution was stirred for an additional 1 h, at which time the solvent was evaporated. The crude solid was placed on a filter and washed with methanol until the filtrate became colorless. The resulting purple product was purified by column chromatography on alumina using 95:5 CH_2Cl_2/ethyl acetate. The first purple band was collected and evaporated to dryness to yield **FbP-G2-pPh-mDMB$_{16}$** as a purple solid (0.2828 g, 54%): ^{1}H NMR ($CDCl_3$, δ) −2.63 (s, 1H), 3.85 (s, 48H), 7.00 (m, 25H), 7.81 (s, 4H), 8.00 (s, 8H), 8.10 (s, 2H), 8.15 (d, 4H, J = 8 Hz), 8.24 (s, 4H), 8.38 (d, 4H, J = 8 Hz), 9.02 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 56.06, 56.10, 56.62, 56.67, 112.89, 113.66, 117.04, 117.10, 120.13, 125.82, 126.22, 127.72, 130.22, 131.78, 135.48, 138.99, 140.60, 141.00, 141.71, 142.06, 142.97, 151.17, 154.04; MALDI-TOF-MS 3705.15 (calcd for $C_{244}H_{206}O_{32}N_4$, 3706.54); UV/vis (λ_{max}, nm, CH_2Cl_2) 307.5, 423.5, 518.5, 554.5, 593.5, 647.5.

Preparation of *meso*-Tetrakis-[4-(2,5-benzoquinonyl)-phenyl]porphyrin (FbP-G0-pBQ$_4$). Dendrimer **FbP-G0-pDMB$_4$** (0.0740 g, 0.06728 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (0.6728 mL, 0.6728 mmol) in CH_2Cl_2 (15 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness. The remaining residue was dissolved in methanol, and DDQ (0.2795 g, 1.231 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of **FbP-G0-pBQ$_4$** as a purple solid (0.0297 g, 43%): ^{1}H NMR ($CDCl_3$, δ) −2.80 (s, 1H), 6.94 (m, 2H), 7.00 (d, 2H, J = 10 Hz), 7.21 (s, 2H), 7.90 (d, 4H, J = 8 Hz), 8.31 (d, 4H, J = 8 Hz), 8.89 (s, 4H); IR (Nujol) 1653, 1590 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2) 419.0, 517.0, 556.5, 591.0, 648.5.

Preparation of *meso*-Tetrakis-[3-(2,5-benzoquinonyl)-phenyl]porphyrin (FbP-G0-mBQ$_4$). Dendrimer **FbP-G0-mDMB$_4$** (0.1400 g, 0.1208 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (1.45 mL, 1.45 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The remaining residue was dissolved in methanol, and DDQ (0.5486 g, 2.416 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of the product as a purple solid (0.0937 g, 75%): ^{1}H NMR ($CDCl_3$, δ) −2.78 (s, 1H), 6.82 (d, 2H, J = 9.7 Hz), 6.89 (d, 2H, J = 9.7 Hz), 7.13 (s, 2H), 7.87 (d, 4H, J = 6.8 Hz), 8.36 (d, 4H, J = 7.3 Hz), 8.97 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 119.63, 127.31, 128.91, 131.54, 133.43, 135.43, 136.40, 136.56, 137.28, 142.48, 146.01, 186.86, 187.67; UV/vis (λ_{max}, nm, CH_2Cl_2) 420.5, 516.5, 553.0, 588.0, 645.5.

Preparation of *meso*-Tetrakis-[4-(3-(2,5-benzoquinonyl)-phenyl)phenyl]porphyrin (FbP-G0-pPh-mBQ$_4$). Dendrimer **FbP-G0-pPh-mDMB$_4$** (0.1500 g, 0.1025 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (1.25 mL, 1.25 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The remaining residue was dissolved in methanol, and DDQ (0.4652 g, 2.049 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of the product as a purple solid (0.1076 g, 78%): ^{1}H NMR ($CDCl_3$, δ) −2.79 (s, 1H), 6.89 (d, 2H, J = 9.9 Hz), 6.94 (d, 2H, J = 9.9 Hz), 7.06 (s, 2H), 7.59 (d, 2H, J = 7.8 Hz), 7.70 (t, 2H, J = 7.8 Hz), 8.03 (d, 8H, J = 7.5 Hz), 8.35 (d, 4H, J = 7.9 Hz), 8.98 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 120.05, 124.88, 126.72, 127.67, 128.45, 129.60, 130.31, 132.59, 133.84, 134.63, 136.27, 137.88, 138.80, 139.93, 141.58, 141.88, 146.21, 186.88, 187.81; UV/vis (λ_{max}, nm, CH_2Cl_2) 422.5, 517.5, 554.5, 588.0, 628.0.

Preparation of *meso*-Tetrakis[4-(3,5-(2,5-benzoquinonyl)phenyl)phenyl]porphyrin (FbP-G1-pPh-mBQ$_8$). Dendrimer **FbP-G1-pPh-mDMB$_8$** (0.1500 g, 0.07468 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (1.80 mL, 1.80 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The remaining residue was dissolved in methanol, and DDQ (0.6782 g, 2.987 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of the product as a purple solid (0.1046 g, 79%): ^{1}H NMR ($CDCl_3$, δ) −2.80 (s, 1H), 6.69 (d, 8H, J = 9.2 Hz), 6.94 (s, 4H), 7.57 (s, 2H), 8.03 (s, 8H), 8.33 (d, 4H, J = 5.9 Hz), 8.94 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 119.94, 125.96, 129.26, 130.12, 133.44, 133.92, 135.44, 136.51, 137.08, 139.28, 141.96, 141.19, 145.21, 186.48, 187.37; UV/vis (λ_{max}, nm, CH_2Cl_2) 422.5, 517.5, 554.0, 590.5, 647.0.

Preparation of *meso*-Tetrakis-[4-(3,5-(4-(2,5-benzoquinonyl)phenyl)phenyl)phenyl]porphyrin (FbP-G1-pPh-mPhBQ$_8$). Dendrimer **FbP-G1-pPh-mPhDMB$_8$** (0.1554 g, 0.05938 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (1.40 mL, 1.40 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The remaining residue was dissolved in methanol, and DDQ (0.5392 g, 2.375 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of the product as a purple solid (0.1123 g, 80%): ^{1}H NMR ($CDCl_3$, δ) −2.68 (s, 1H), 6.90 (m, 12H), 7.66 (d, 8H, J = 7.1 Hz), 7.91 (d, 8H, J = 7.5 Hz), 7.96 (s, 2H), 8.12 (d, 4H, J = 7.1 Hz), 8.19 (s, 4H), 8.36 (d, 4H, J = 6.6 Hz), 8.99 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 120.02, 125.66, 125.87, 126.16, 127.77, 130.17, 132.25, 132.69, 135.50, 136.56, 137.27, 140.22, 141.94, 142.56, 142.92, 145.57, 186.89, 187.72; UV/vis (λ_{max}, nm, CH_2Cl_2) 423.5, 517.5, 554.5, 592.5, 647.5.

Preparation of *meso*-Tetrakis-[4-(3,5-(3,5-(2,5-benzoquinonyl)phenyl)phenyl)phenyl]porphyrin (FbP-G2-pPh-mBQ$_{16}$). Dendrimer **FbP-G2-pPh-mDMB$_{16}$** (0.1500 g, 0.04876 mmol) dissolved in the minimum amount of CH_2Cl_2 was added via a dropping funnel into BBr_3 (2.35 mL, 2.35 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The solution was stirred at −78 °C for 1 h. After 1 h, the solution was warmed to room temperature where it was stirred overnight. The solution was cooled to 0 °C, and water was added to hydrolyze the excess BBr_3. The mixture was then washed with triethylamine to neutralize the porphyrin dication. The purple organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The remaining residue was dissolved in methanol, and DDQ (0.8854 g, 3.900 mmol) was added. The mixture was then refluxed for 30 min. After 30 min, the mixture was filtered and the solid was washed with methanol, resulting in the isolation of the product as a purple solid (0.0995 g, 79%). ^{1}H NMR, ^{13}C NMR: the dendrimer was not sufficiently soluble to obtain NMR spectra; UV/vis (λ_{max}, nm, CH_2Cl_2) 421.5, 517.0, 570.5, 659.5.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of aldehydes **11** and **12** and all dendrimers synthesized in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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