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A Modified Procedure for Sonogashira Couplings: Synthesis and Characterization of a Bisporphyrin, 1,1-Bis[zinc(II) 5′-ethynyl-10′,15′,20′-trimesitylporphyrinyl]methylenecyclohexane

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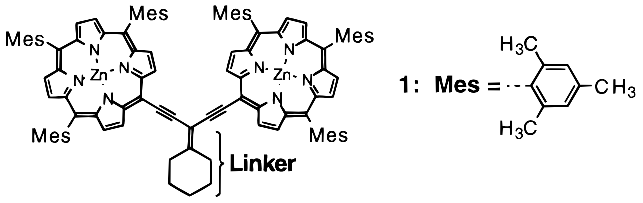
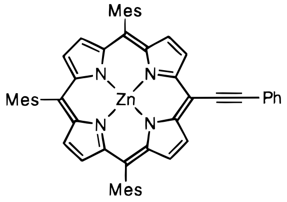
The preparation of a bisporphyrin, 1,1-bis[zinc(II) 5′-ethynyl-10′,15′,20′-trimesitylporphyrinyl]-methylenecyclohexane (**1**), is described. The new molecule was prepared by two routes employing modified palladium-mediated coupling methodology. Our modification consists of *in situ* liberation of alkyne from the corresponding TMS-protected compound. This variation decreases yields of undesired products presumably by keeping the unprotected alkyne concentration low during the reaction. In addition, our method obviates TMS-alkyne deprotection and subsequent purification steps. The electronic absorption spectrum of **1** is compared to two model compounds.

To enhance interactions in porphyrinic magnetic materials,[1−7] we are preparing radical-substituted porphyrins[8,9] and novel porphyrin arrays. Properly designed bisporphyrins, connected by certain linkers, can be oxidized[10] to yield high-spin biradical dications and can be used to create extended solids. Efficient spin−spin coupling in such materials requires that the bisporphyrin linker group be of sufficient size to allow coplanarity of the porphyrins, but not so large as to dilute spin density. To this end, we designed bisporphyrin **1**, in which aryl groups are omitted at *meso*-positions that lead to the linker fragment. Instead, ethyne groups directly connect the *meso*-positions with methylenecyclohexane in a geminal fashion, creating a trimethylenemethane-type coupling fragment.[2,11,12] Herein, we describe the preparation of **1** using modified Pd-mediated coupling methodology, and we compare **1** to model compounds **2** and **3**.





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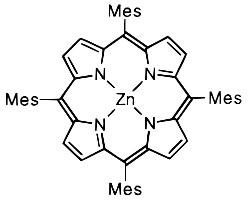
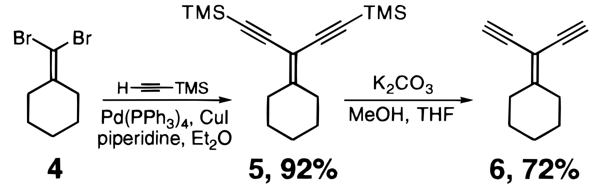


3

The linker components **4**−**6** were prepared as shown below. Condensation of cyclohexanone with carbon tetrabromide/triphenylphosphine reagent according to the conditions of Posner[13] provided dibromide **4**[14] in nearly quantitative yield. Coupling of **4** with 2 equiv (trimethylsilyl)acetylene in the presence of piperidine[15] gave **5** in excellent yield, followed by deprotection,[16] to give **6** as a volatile liquid.



Zinc porphyrin **7** was prepared as described previously,[8] while porphyrins **8** and **9** were prepared from **7** as shown below.[17] Ethynylporphyrin, **9**, prepared by deprotection of **8** with methanolic K_2CO_3,[16] was rather unstable and was used immediately following isolation. Attempts at purifying **9** by silica gel chromatography resulted in substantial decomposition.

Tetramesitylporphyrin was obtained as a byproduct in the synthesis of **7**,[8] and metalated using zinc acetate in

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[1] Conklin, B. J.; Sellers, S. P.; Fitzgerald, J. P.; Yee, G. T. *Adv. Mater.* **1994**, *6*, 836.

[2] Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

[3] Kamachi, M. *Nihon Butsuri Gakkaishi* **1987**, *42*, 351.

[4] Kitano, M.; Koga, N.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1994**, 447.

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[9] Shultz, D. A.; Knox, D. A.; Morgan, L. W.; Sandberg, K.; Tew, G. N. *Tetrahedron Lett.* **1993**, *34*, 3975.

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[14] Entmayr, P.; Köbrich, G. *Chem. Ber.* **1976**, *109*, 2175.

[15] Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.

[16] Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.

[17] Unlike reactions to produce the bisporphyrin, the yield of monoporphyrin **8** was high. However, *10* equiv of (trimethylsilyl)-acetylene was used. This large excess is not economically feasible for reactions using **9** and is precluded by stoichiometry requirements in reactions using **6**.

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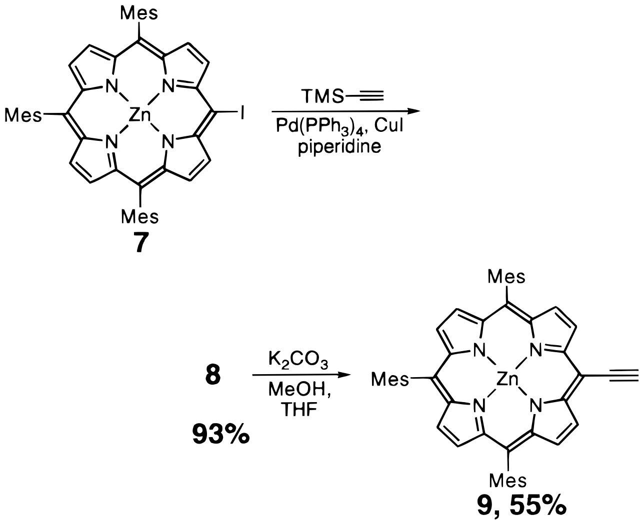
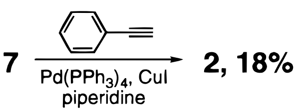


7

8 **93%**

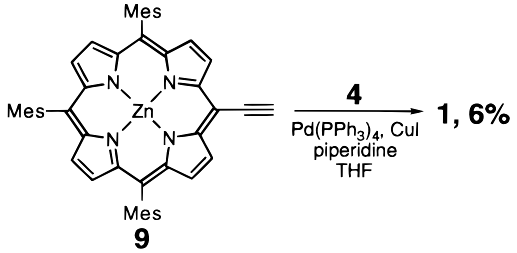
9, 55%

chloroform,[18] to yield **3**.[19] The synthesis of model compound **2** was achieved by coupling of phenylacetylene to iodoporphyrin **7**.[20]



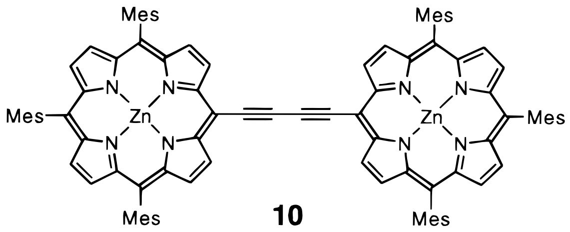
7 → **2, 18%**

Bisporphyrin **1** was prepared by Sonogashira couplings[21−23] using four different combinations of coupling partners.[24] The first route involves coupling of 2 equiv of **9** to **4**, to provide bisporphyrin **1** in nearly 24% yield (determined by NMR). However, this reaction resulted in substantial amounts of butadiyne bisporphyrin **10** which was extremely difficult to separate from **1**. Consequently, the isolated yield was only 6%.



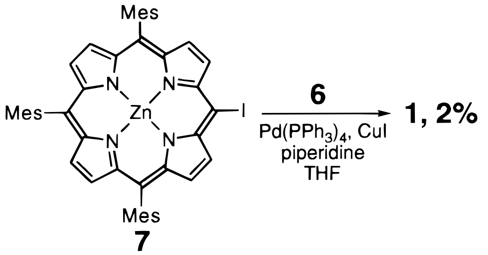
9

1, 6%



10

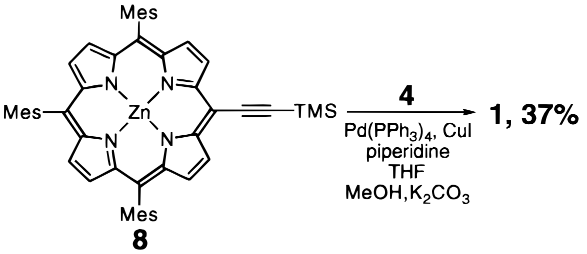
The second route, coupling of 2 equiv of iodoporphyrin **7** with dialkyne **6**, produced **1** (24% yield by NMR) and undesired alkyne dimers, again resulting in a difficult-to-separate mixture and a very low isolated yield.[24] Several attempts using these two procedures resulted in undesired porphyrins despite measures to exclude oxygen.[27]



7

1, 2%

We avoided undesired butadiynes by liberating the alkyne or dialkyne in situ from the corresponding TMS-protected compound. This *in situ* deprotection was effected by adding methanolic K_2CO_3 to the reaction mixture. We reasoned that this procedure would keep the concentration of alkyne low during the course of the reaction and result in a decrease in butadiyne formation. In our experience the time required for deprotection and coupling are comparable. In fact, examination of TLC during the course of a reaction shows only small amounts of deprotected alkyne (compared to desired product), suggesting a low concentration of the free alkyne, as expected. This approach also avoids the TMS-alkyne deprotection and purification steps. Thus, TMS-protected ethynylporphyrin **8** was reacted with dibromide **4** in the presence of methanolic K_2CO_3 to give **1** in 45% yield. No butadiyne **10** was visible in the ^1H NMR spectrum of the crude reaction mixture. The yield of **1** after chromatographic purification was 37%—6 times the isolated yield employing unprotected ethynylporphyrin **9** as a coupling partner.



8

1, 37%

Alternatively, iodoporphyrin **7** was reacted with **5** under normal conditions, except for addition of methanolic K_2CO_3. This procedure gave bisporphyrin **1** in 69% isolated yield and only a small amount of undesired coupling products.

$$\mathbf{7} \xrightarrow[\substack{\text{Pd(PPh}_3)_4\text{, CuI}\\ \text{piperidine}\\ \text{THF}\\ \text{MeOH, K}_2\text{CO}_3}]{\mathbf{5}} \mathbf{1}\text{, 69\%}$$

To further illustrate the success of this variation, we prepared **2** from **7** and 2-phenyl-1-(trimethylsilyl)acety-

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[18] Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941.

[19] Hoffmann, P.; Robert, A.; Meunier, B. *Bull. Soc. Chim. Fr.* **1992**, *129*, 85.

[20] This reaction produced reduced **7** which is difficult to separate from the desired porphyrin.

[21] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

[22] Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259.

[23] Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253.

[24] Therien reported[25,26] excellent yields for double couplings but uses excess alkyne. Because of our different stoichiometry requirements, and our more elaborate coupling partners, we cannot use an excess of alkyne.

[25] LeCours, S. M.; DeMagno, S. G.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11854.

[26] LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497.

[27] Procedures in which solvent and reagents were added to the reaction flask in a glovebox also failed to give clean reactions.

Table 1. Electronic Absorption Spectroscopic Data for 1 and Model Compounds 2 and 3[a]

porphyrin	λ_{max}/nm (log ϵ)[b]	λ_{max}/nm (log ϵ)[c]
1	433 (5.56)	530 (4.03)
	446 (5.77)	567 (4.55)
		617 (4.65)
2	438 (5.61)	527 (3.71)
		565 (4.37)
		610 (4.42)
3	421 (5.70)	512 (3.39)
		550 (4.27)
		586 (3.31)

[a] CH_2Cl_2 solutions. [b] Soret region. [c] Q-band region.

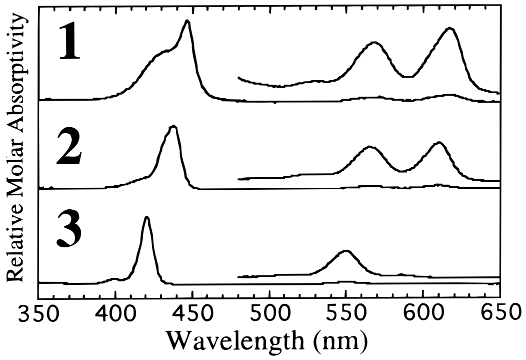
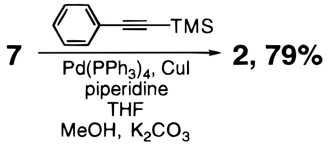


Figure 1. Electronic absorption spectra for **1**−**3** as solutions in CH_2Cl_2.

lene in the presence of methanolic K_2CO_3. The yield of desired product was 79%, compared to 18% yield using phenylacetylene as the alkyne source—representing over a 4-fold increase in yield.



Electronic absorption spectroscopic data for **1**−**3** are listed in Table 1 and spectra are shown in Figure 1. As expected, ethynylporphyrins **1** and **2** have absorption maxima that are red-shifted and broadened Soret bands with respect to those of **3**.[25] The molar absorptivities of **1** are nearly twice those of **2**, consistent with two porphyrin chromophores in **1**. Bisporphyrin **1** exhibits a split Soret, similar to *gable* bisporphyrins.[28,29] The split peaks have different shapes, comparable to some D_{2h} 5,15-dialkynylporphyrins.[30]

In summary, we prepared a new bisporphyrin using modified Sonogashira couplings. Our modification consists of *in situ* liberation of alkyne from the corresponding TMS-protected compound. This variation avoids undesired dimerization products presumably by keeping the unprotected alkyne concentration low during the reaction. In addition, our method avoids TMS-alkyne deprotection and subsequent purification steps.[31] Bisporphyrin **1** exhibits a split Soret, and red-shifted absorption bands compared to model compound **2**. Further characterization and chemistry of **1** and related compounds is underway.

Experimental Section

Chemicals were purchased from Aldrich Chemical Co. unless noted otherwise. Solvent distillations and synthetic procedures were carried out under an argon atmosphere. THF was distilled from sodium benzophenone-ketyl prior to use. Methylene chloride was distilled from calcium hydride. The Chromatotron is a product of Harrison Research, Palo Alto, CA. NMR spectra were recorded on a Varian 300 MHz spectrometer using either deuteriochloroform as solvent and referenced to protiochloroform at 7.26 ppm for ^{1}H spectra and 77.0 ppm for ^{13}C spectra, or deuteriomethylene chloride as solvent and referenced to protiomethylene chloride at 5.32 ppm for ^{1}H spectra and 54.0 ppm for ^{13}C spectra. Elemental analysis was performed by Atlantic Microlab, Inc, Norcross, GA.

1,1-Bis[Zinc(II) 5′-ethynyl-10′,15′,20′-trimesitylporphyrin]methylenecyclohexane (1): Standard Procedure from 9 and 4. A 25 mL Schlenk flask containing **4** (0.013 g, 0.052 mmol), $Pd(PPh_3)_4$ (0.024 g, 0.021 mmol), CuI (0.0002 g, 0.0013 mmol), and piperidine (0.018 mL, 0.259 mmol) in THF (5 mL) was sparged with argon for 5 min and pumped/purged 10 times. The reaction mixture was heated to reflux. After 30 min, 1 equiv of **9** (0.039 g, 0.052 mmol) was added by cannulation followed by an additional 1 equiv of **9** every 4 h thereafter until a total of 4 equiv had been added. After an additional 4 h of reflux, the mixture was allowed to cool, and *n*-pentane and saturated aqueous NH_4Cl were added. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was run through a short flash chromatography column (SiO_2, ether). Crude ^{1}H NMR was consistent with a 24% yield of **1** and a 14% yield of **10**. Partial purification was achieved by successive separations on a Chromatotron (SiO_2, 20−25% CH_2Cl_2/petroleum ether), an alumina column (80% CH_2Cl_2/petroleum ether), and again using a Chromatotron (10−30% CH_2Cl_2/petroleum ether), to give **1** (5 mg, 6% yield). The remainder of the material was a mixture of **1** and **10**.

Compound 1. ^{1}H NMR (CD_2Cl_2) δ 10.04 (d, 4H, $J = 4.5$ Hz), 8.86 (d, 4H, $J = 4.5$ Hz), 8.67 (bs), 7.33 (s, 8H), 7.31 (s, 4H), 3.44 (t, 4H, $J = 5.4$ Hz), 2.64 (s, 12H), 2.62 (s, 6H), 2.13 (m, 6H), 1.89 (bs, 36H); ^{13}C NMR (CD_2Cl_2) δ 161.9, 152.9, 150.9, 150.5, 150.2, 139.8, 139.6, 138.3, 132.2, 131.9, 131.6, 128.3, 121.1, 120.6, 100.9, 100.4, 95.5, 94.1, 34.8, 29.1, 27.2, 22.0, 21.9; IR (film) ν_{max} 2921, 2859, 2161, 1609, 1476, 1440, 1378, 1338, 1205, 1060, 999, 797 cm^{-1}; UV−Vis ($CHCl_3$) λ_{max}/nm (log ϵ) 313 (4.58), 433 (5.56), 446 (5.77), 530 (4.03), 567 (4.55), 617 (4.65). MS−FAB $C_{105}H_{92}N_8Zn_2$ calcd exact mass: 1592.6028, obsd: 1592.5970.

1,4-Bis[Zinc(II) 10′,15′,20′-trimesitylporphyrin-5′-yl]-buta-1,3-diyne (10). ^{1}H NMR (CD_2Cl_2) δ 9.94 (d, 4H, $J = 4.1$ Hz), 8.89 (d, 4H, $J = 4.1$ Hz), 8.64 (br s, 8H), 7.31 (m, 18H), 2.65 (s, 12H), 2.62 (s, 6H), 1.89 (s, 24H), 1.86 (s, 12H); IR (film) ν_{max} 2912, 2851, 2116, 1478, 1444, 1376, 1336, 1206, 1058, 996, 798 cm^{-1}. Maldi-TOF *m/z* (M^+) for $C_{98}H_{82}N_8Zn_2$, calcd: 1498.5244, obsd: 1498.5.

Compound 1 from 7 and 6. A 25 mL Schlenk flask containing **7** (0.267 g, 0.313 mmol), $Pd(PPh_3)_4$ (0.120 g, 0.104 mmol), CuI (0.0005 g, 0.0026 mmol), and piperidine (0.051 mL, 0.521 mmol) in THF (8 mL) was sparged with argon for 5 min and pump/purged 10 times. The reaction mixture was refluxed for 30 min. One-sixth equivalent of **6** (0.008 g, 0.052 mmol) was added by cannulation, and the reaction mixture was heated to reflux for 4 h. After this time, an additional one-sixth equivalent of **6** (0.008 g, 0.052 mmol) was added by cannulation followed by an additional 4 h reflux. Once cool,

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[28] Tabushi, I.; Sasaki, T. *Tetrahedron Lett.* **1982**, *23*, 1913.

[29] Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem.* **1986**, *51*, 2838.

[30] Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.

[31] Negishi recently reported Pd-mediated synthesis of terminal alkynes, obviating TMS protection altogether: Negishi, E.; Kotora, M.; Xu, C. *J. Org. Chem.* **1997**, *62*, 8957.

ether and saturated NH_4Cl were added. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed *in vacuo*. The residue was run through a short flash chromatography column (SiO_2, ether). Crude ^1H NMR of the collected material was consistent with a 24% yield of **1.** Partial purification was achieved by flash column chromatography (SiO_2, 10−30% CH_2Cl_2/petroleum ether), followed by separation using a Chromatotron (20−25% CH_2Cl_2/petroleum ether), an alumina column (80% CH_2Cl_2/petroleum ether), and finally again on a Chromatotron (10−30% CH_2Cl_2/petroleum ether), to give **1** (4.1 mg, 2.4% yield). The remainder of the material was a mixture of **1** and unidentified porphyrins.

Compound 1: Modified Method A (from 8 and 4). A 50 mL Schlenk flask containing **8** (0.1415 g, 0.172 mmol), K_2CO_3 (0.052 g, 0.378 mmol), piperidine (0.34 mL, 3.43 mmol), $Pd(PPh_3)_4$ (0.040 g, 0.034 mmol), and CuI (0.0016 g, 0.0086 mmol) was sparged with argon for 5 min. Dibromide **4** (0.024 g, 0.094 mmol) in THF (20 mL) was cannulated into the reaction mixture, followed by distilled methanol (2.7 mL), and the reaction mixture was pump/purged 10 times and then refluxed for 16 h. Once cool, ether and saturated NH_4Cl were added. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was run through a short flash chromatography column (SiO_2, ether), and the ^1H NMR spectrum of the collected material showed only **1**, *i.e.*, no butadiyne, **10**, was visible. The mixture was purified by flash chromatography (SiO_2, 10−30% CH_2Cl_2/petroleum ether), giving **1** (0.050 g, 37% yield).

Compound 1: Modified Method B (from 7 and 5). A 50 mL Schlenk flask containing **5** (0.045 g, 0.176 mmol), **7** (0.300 g, 0.351 mmol), and K_2CO_3 (0.107 g, 0.773 mmol) in THF (30 mL) was sparged with argon for 5 min. Piperidine (0.34 mL, 3.51 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.018 mmol), CuI (0.0017 g, 0.0087 mmol), and distilled methanol (4 mL) were added, and the reaction mixture was pump/purged 10 times with argon and then refluxed for 19 h. Once cool, ether and saturated aqueous NH_4Cl were added. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed *in vacuo*. The residue was run through a short flash chromatography column (SiO_2, ether), and the ^1H NMR spectrum of the collected material showed only **1**, *i.e.*, no butadiyne, **10**, was visible. The mixture was purified by flash chromatography (SiO_2, 10−30% CH_2Cl_2/petroleum ether), giving **1** (0.193 g, 69% yield).

1,1-Bis[(trimethylsilyl)ethynyl]methylenecyclohexane (5). A 25 mL Schlenk flask containing **4** (0.05 g, 0.197 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.039 mmol), CuI (0.002 g, 0.01 mmol), and piperidine (0.097 mL, 0.984 mmol) in diethyl ether (10 mL) was sparged with argon for 5 min and pump/purged 10 times. The reaction mixture was heated to reflux. After 15 min, 1 equiv of (trimethylsilyl)acetylene (0.028 mL, 0.084 g, 0.197 mmol) was added quickly with argon purging followed by an additional 3 equiv of (trimethylsilyl)acetylene every 3 h thereafter until a total of 10 equiv had been added. After an additional 4 h of reflux, the mixture was allowed to cool, and *n*-pentane and saturated aqueous NH_4Cl were added. The layers were separated, the organic layer was dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was run through a short column flash chromatography column (SiO_2, CH_2Cl_2), followed by separation on a Chromatotron (SiO_2, pentane), giving **5** as a white solid (52.3 mg, 92% yield). ^1H NMR (CD_2Cl_2) δ 2.49 (m, 4H), 1.58 (m, 6H), 0.20 (s, 18H); ^{13}C NMR (CD_2Cl_2) δ 164.8, 101.7, 98.8, 96.7, 33.4, 28.2, 26.7, 0.3; IR (film) ν_{max} 2932, 2857, 2151, 1584, 1446, 1250, 1189, 1008 cm^{-1}. Anal. Calcd for $C_{17}H_{28}Si_2$: C, 70.75; H 9.77, Found: C, 70.75; H, 9.84.

(1,1-Diethynylmethylene)cyclohexane (6). Trimethylsilyl-protected diyne **5** (0.047 g, 0.163 mmol) was stirred with K_2CO_3 (0.095 g, 0.685 mmol) in THF/MeOH (3:1, 5.3 mL) for 16 h. Petroleum ether was added, and the solution was washed with saturated aqueous NH_4Cl followed by drying with Na_2SO_4 and concentration under reduced pressure. The remaining material was purified using a Chromatotron (SiO_2, pentane), giving **6** (0.017 g, 72%) as a colorless, volatile liquid. ^1H NMR (CD_2Cl_2) δ 3.12 (s, 2H), 2.51 (m, 4H), 1.59 (m, 6H); ^{13}C NMR (CD_2Cl_2) δ 165.5, 96.3, 80.4, 79.8, 33.3, 28.2, 26.6; IR (film) ν_{max} 3291, 2933, 2857, 2101, 1592, 1447, 1349, 1281, 1231, 1005, 855, 631 cm^{-1}. MS−FAB $C_{11}H_{12}$ calcd exact mass: 144.0939, obsd: 144.0934.

5-[(Trimethylsilyl)ethynyl]-10,15,20-trimesityl-(Zn)-porphyrin (8). A 25 mL round-bottom flask containing **7** (0.153 g, 0.179 mmol) and piperidine (10 mL) was sparged with argon for 5 min. $Pd(PPh_3)_4$ (0.0166 g, 0.014 mmol) and CuI (0.0054 g, 0.028 mmol) were added, and the mixture was sparged with argon and then pump/purged 10 times. (Trimethylsilyl)acetylene (0.253 mL, 1.79 mmol) was added, and the reaction mixture was heated to 80 °C for 18 h. Once cool, ether and saturated NH_4Cl were added. The layers were separated, the organic layer was dried over Na_2SO_4, and the solvent removed in vacuo. The residue was purified by short column flash chromatography (SiO_2, CH_2Cl_2), followed by separation on a Chromatotron (SiO_2, 5% ether, 5% CH_2Cl_2 in pentane), giving **8** (0.138 mg, 93% yield). ^1H NMR (CD_2Cl_2) δ 9.68 (d, 2H, $J = 4.6$ Hz), 8.77 (d, 2H, $J = 4.6$ Hz), 8.63 (d, 2H, $J = 4.7$ Hz), 8.60 (d, 2H, $J = 4.6$ Hz), 7.32 (s, 4H), 7.29 (s, 2H), 2.64 (s, 6H), 2.61 (s, 3H), 1.86 (bs, 18H), 0.63 (s, 9H); ^{13}C NMR (CD_2Cl_2) δ 152.9, 150.8, 150.1, 139.7, 139.6, 138.1, 131.8, 131.7, 131.5, 131.2, 128.2, 122.6, 121.1, 120.2, 108.8, 100.8, 98.5, 22.0, 21.8, 0.7; IR (film) ν_{max} 2964, 2923, 2853, 2144, 1657, 1602, 1460, 1379, 1338, 1260, 1090, 1020, 799 cm^{-1}. MS−FAB $C_{52}H_{50}N_4SiZn$ calcd exact mass: 822.3085, obsd: 822.3100.

Zinc(II) 5-Ethynyl-10,15,20-trimesitylporphyrin (9). Trimethylsilyl-protected porphyrin **8** (0.183 g, 0.221 mmol) was stirred with K_2CO_3 (0.067 g, 0.487 mmol) in THF−MeOH (3:1, 17.5 mL) for 20 h, after which saturated NH_4Cl and CH_2Cl_2 were added. The organic layer was washed twice with saturated NH_4Cl and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by short flash chromatography (SiO_2, CH_2Cl_2) and Chromatotron with 2% THF/petroleum ether, giving **9** (0.092 g, 55%). ^1H NMR ($CDCl_3$) δ 9.67 (d, 2H, $J = 4.7$ Hz), 8.78 (d, 2H, $J = 4.7$ Hz), 8.61 (bs, 4H), 7.26 (bs, 4H) 7.25 (bs, 2H), 4.13 (s, 1H), 2.63 (s, 6H), 2.61 (s, 3H), 1.83 (bs, 18H); IR (film) ν_{max} 3293, 2920, 2855, 2098, 1610, 1442, 1206, 1062, 999, 798 cm^{-1}. Maldi-TOF *m/z* (M^+) for $C_{49}H_{42}N_4Zn$, calcd: 750.3, obsd: 749.0.

Zinc(II) 5-(Phenylethynyl)-10,15,20-trimesitylporphyrin (2). A 25 mL Schlenk flask containing **7** (0.100 g, 0.117 mmol) and piperidine (15 mL) was purged with argon. $Pd(PPh_3)_4$ (0.0095 g, 0.0082 mmol), CuI (0.0011 g, 0.0058 mmol), and phenylacetylene (0.130 mL, 1.171 mmol) were added, the reaction mixture was pump/purged 10 times and heated at 80 °C for 15 h. Once cool, ether and saturated NH_4Cl were added. The organic layer was separated, washed twice with saturated NH_4Cl, and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by flash chromatography (SiO_2, 5−10% CH_2Cl_2/petroleum ether), giving **2** and a slightly higher R_f byproduct. Further purification using two consecutive passes on the Chromatotron (SiO_2, 5−10% CH_2Cl_2/pentane followed by 3% THF/petroleum ether) gave pure **2** (0.017 g, 18% yield). ^1H NMR (CD_2Cl_2) δ 9.84 (d, 2H, $J = 4.5$ Hz), 8.88 (d, 2H, $J = 4.7$ Hz), 8.69 (bs, 4H), 7.99 (d, 2H, $J = 7.1$ Hz), 7.48 (t, 2H, $J = 7.4$ Hz), 7.38 (m, 1H), 7.35 (s, 4H), 7.31 (s, 2H), 2.65 (s, 6H), 2.63 (s, 3H), 1.90 (bs, 18H); ^{13}C NMR (CD_2Cl_2) δ 152.7, 150.9, 150.4, 150.1, 139.7, 139.3, 138.3, 132.0, 131.9, 131.6, 131.5, 129.2, 128.8, 128.3, 124.8, 121.2, 120.6, 99.7, 96.4, 93.1, 21.9, 21.8; IR (film) ν_{max} 2922, 2860, 2191, 1600, 1496, 1447, 1336, 1206, 1060, 999, 796 cm^{-1}; UV−Vis (CH_2Cl_2) λ_{max}/nm (log ϵ) 307 (4.363), 350 (shoulder) (4.165), 415 (shoulder) (4.929), 438 (5.614), 498 (3.389), 527 (3.711), 565 (4.368), 610 (4.415). MS−FAB $C_{55}H_{46}N_4Zn$ calcd exact mass: 826.3014, obsd: 826.3045.

Compound 2: Modified Method (from 7 and 2-phenyl-1-(trimethylsilyl)acetylene). A 50 mL Schlenk flask containing **7** (0.100 g, 0.117 mmol), 2-phenyl-1-(trimethylsilyl)acetylene (0.061 g, 0.351 mmol), piperidine (0.23 mL, 2.34 mmol), $Pd(PPh_3)_4$ (0.019 g, 0.0164 mmol), CuI (0.0007 g, 0.0035 mmol), and K_2CO_3 (0.036 g, 0.258 mmol) in THF (20 mL) was sparged with argon for 5 min. Distilled methanol (2.7 mL) was added, and the reaction mixture was pump/purged 10 times and then refluxed for 15 h. Once cool, ether and saturated NH_4Cl were added. The organic layer was separated, washed twice with saturated NH_4Cl, and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by flash chromatography (SiO_2, 20% CH_2Cl_2/petroleum ether), giving **2** (0.0763 g, 79% yield).

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Supporting Information Available: Spectral data (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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