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Synthesis of *trans*-A_2B_2-Porphyrins Bearing Phenylethynyl Substituents

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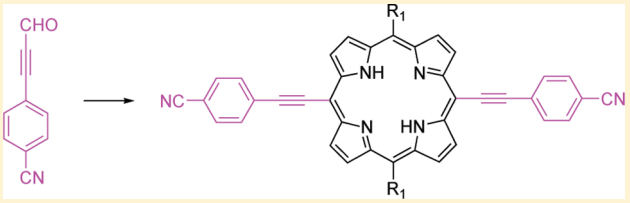
Supporting Information

ABSTRACT: Efficient and convenient conditions for the preparation of *trans*-A_2B_2-porphyrins bearing two phenylethynyl moieties directly from phenylpropargyl aldehydes and dipyrromethanes of diversified lipophilicity and reactivity have been developed. This new procedure allows the preparation of a library of porphyrins of this architecture with a wide range of substituents. Thanks to the identification of the reagent solubility as one of the key factors influencing the yield of the porphyrinogens, we were able to improve yields to ca. 30%. The scope and limitations of two sets of conditions have been explored. The methodological advantage of this approach is its straightforward access to building blocks and the formation of the porphyrin core in the last step without the need for deprotection of the triple bond or bromination and consecutive coupling reaction, which often demands copper salts to proceed smoothly, especially with electron-deficient alkyne partners. Therefore, it prevents undesired copper porphyrin formation, as well as the need for utilizing expensive alkynes. A two-step method for the preparation of phenylpropargyl aldehydes has also been refined.



INTRODUCTION

meso-Arylethynylporphyrins have received considerable attention in the field of materials chemistry due to their potential application in optoelectronic devices.[1] They have emerged as promising candidates for optical limiters,[2−4] two-photon absorption (2PA) sensitizers for near-infrared (NIR) photorefractive composites,[2] reverse saturable absorbers,[5] materials for second-harmonic generation,[1g] and dye-sensitized solar cells (DSSCs).[6] Arylethynylporphyrins have a significantly altered electronic structure. Incorporation of two ethynyl moieties elongates the π-conjugation pathway and improves the communication/electronic interactions between the phenyl substituents and the porphyrin core owing to the rigid two-dimensional structures, which results in enhancement of 2PA values[2] and bathochromatically shifted absorption.[1b,3,7] They also display large first-order hyperpolarizabilities[1g,8] and high thermal stability.[1g]

Several methods have been employed for the preparation of *meso*-arylethynyl *trans*-A_2B_2-porphyrins. Typically they are synthesized via preparation of *trans*-A_2-porphyrins unsubstituted at two meso-positions, followed by bromination and Sonogashira coupling.[1g,2,5a,9] This route was intensively explored by Anderson and co-workers.[10] An alternative route starts with the reaction of silyl-protected propargyl aldehydes with dipyrromethanes, followed by deprotection and Sonogashira coupling with various halogenoarenes.[11] These two methods are versatile, usually offer overall high yields, and have been employed to construct complex porphyrin structures. The third possible approach to such *trans*-A_2B_2-porphyrins starting from phenylpropargyl aldehydes is the least explored. To the best of our knowledge, there are only a few publications reporting this route. The first report presented the reaction of propargyl aldehydes with dipyrromethanes prepared from phenylpropargyl aldehyde.[12] There are also some interesting reports regarding the synthesis of *trans*-A_2B_2-porphyrins from trimethylsilylpropynal[7,11,13] and triisopropylsilylpropynal,[13] but the reaction outcomes were very sensitive to the applied conditions and the target porphyrins were usually accompanied by undesired rearrangement products (scrambling). In another case, the reaction of triisopropylsilylpropynal with a bulky dipyrromethane unexpectedly furnished [1.0.1.0.1.0]hexaphyrin, which significantly exceeded the amount of the target porphyrin.[14] When triisopropylsilylpropynal was replaced with phenylpropynal, the modified reaction conditions then suppressed the acid-catalyzed rearrangement process.[13]

Milgrom first reported the synthesis of A_4-porphyrins bearing four ethynyl linkages via direct condensation of substituted phenylpropargyl aldehydes with pyrrole, affording the final porphyrins in moderate yields.[1b] Higher yields (20−27%) were achieved when TIPS-propynal and 4-*n*-butylphenylpropynal were used as substrates.[5b,13] For other silyl-protected propynals, yields were rather moderate,[7,13] perhaps reflecting the occurrence of conjugate addition rather than attack at the carbonyl group. The elegant solution developed by Milgrom[15] was based on temporary masking of the

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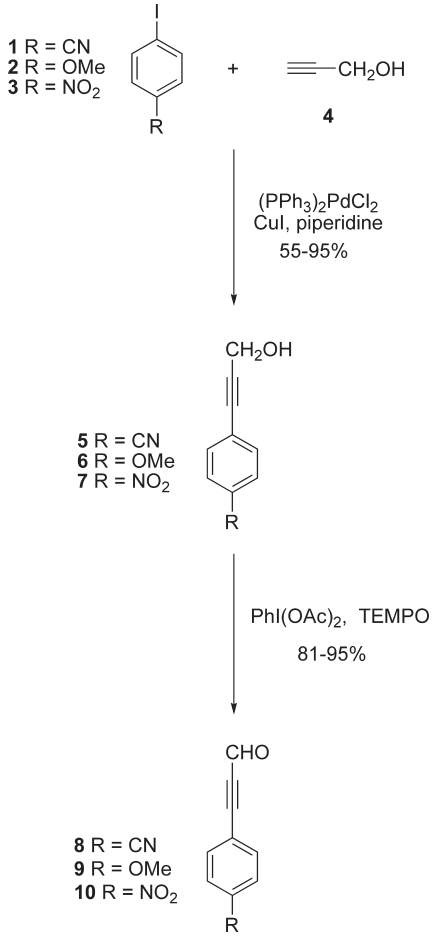
Scheme 1. Synthesis of Phenylpropargyl Aldehydes



triple bond by dicobalt octacarbonyl. This method improved the yields to 35%. Satisfactory yields of the desired A_4-porphyrins were also obtained in the reactions between 3,4-diethylpyrrole or isoindole derivatives and phenylpropargyl aldehyde.[16]

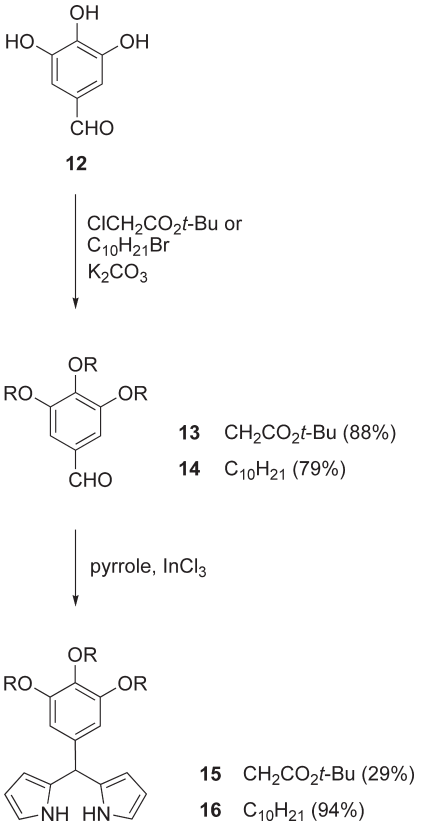
Although all the existing methodologies serve the synthetic community rather well, further development is still necessary. In this regard, the pathway based on direct condensation of dipyrromethanes and aldehydes has great potential in arylethynylporphyrins synthesis. Diminishing the occurrence of scrambling and of the Michael addition are obvious challenges in this regard. Thus, we were prompted to elaborate an efficient, nonscrambling, and straightforward route to porphyrins of the title architecture utilizing a [2 + 2] condensation approach.

RESULTS AND DISCUSSION

Preparation of Building Blocks. Since the aim of our investigation was to develop broadly applicable conditions for the preparation of *meso*-arylethynyl porphyrins, we designed three substituted derivatives **8**−**10** (Scheme 1) in addition to the parent phenylpropynal. Two of the phenylpropargyl aldehydes possessed electron-withdrawing substituents (CN, NO_2), while the third one contained an electron-donating substituent (OMe). As counterparts, we planned to use a diverse set of aryldipyrromethanes.

At the beginning of our survey, we faced a problem with the propynal synthesis. The most versatile pathway reported in the literature consists of two steps, which involve efficient Sonogashira coupling of propargyl alcohol with aryl iodides or bromides, followed by oxidation of the resulting phenylpropargyl alcohols to the corresponding aldehydes. The Sonogashira coupling of aryl iodides **1**−**3** was carried out under general and efficient conditions, affording alcohols **5**−**7** in 55−95% yields (Scheme 1). Subsequently, the propargyl alcohols were submitted to the oxidation reaction. Numerous conditions have been developed for the selective oxidation of primary alcohols to aldehydes, and we applied some of them to the preparation of phenylpropargyl aldehydes. Most of these methods, however, including those which utilized PCC[17] and $TiCl_4$,[18] did not provide satisfactory results (PCC) or afforded only traces of the desired products (PCC and $TiCl_4$). The only successful exception was the procedure employing Dess−Martin periodinate[19] as a mild and effective oxidizing agent. In this particular case, we obtained high yields of over 80% for aldehydes **8**−**10**. Unfortunately, this reagent is

Scheme 2. Synthesis of Trialkylated Dipyrromethanes 15 and 16



Scheme 3. Synthesis of 5-(4-Octadecyloxyphenyl)dipyrromethane (18)

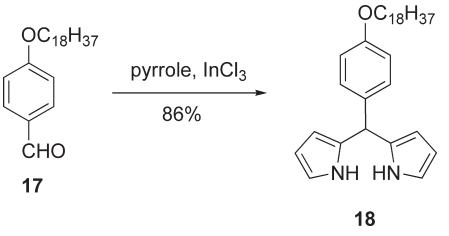


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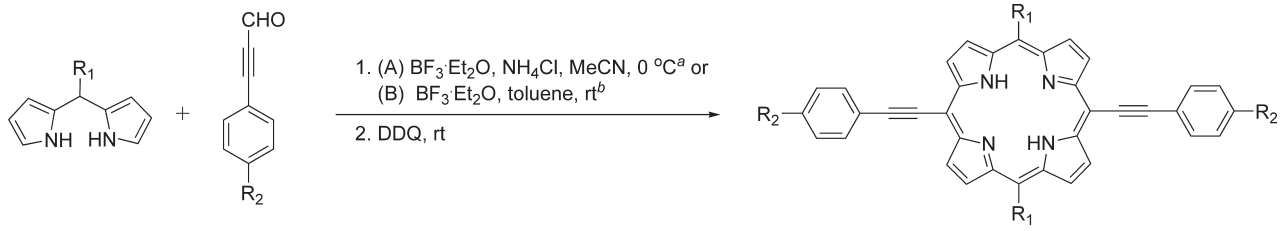
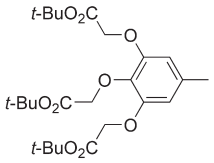
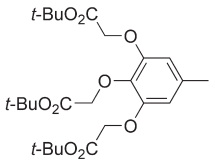
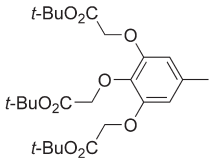
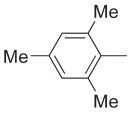
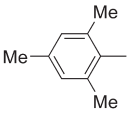
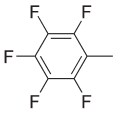
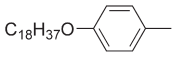
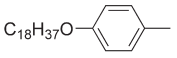
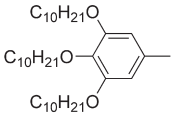
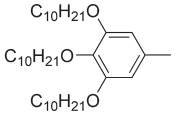
Table 1. The Synthesis of *trans*-A_2B_2-Porphyrins from Arylpropynals and Aryldipyrromethanes



aldehyde	R_2	dipyrromethane	R_1	porphyrin	method A	method B
8	CN	**15**		**21**	28%	-
10	NO_2	**15**		**22**	36%	-
11	H	**15**		**23**	21%	5%
8	CN	**19**		**24**	18%	-
9	OMe	**19**		**25**	9%	10%[c]
8	CN	**20**		**26**	4%	-
8	CN	**18**		**27**	0	14%
11	H	**18**		**28**	0	3%[d]
8	CN	**16**		**29**	7%	12%
10	NO_2	**16**		**30**	-	12%

[a] Method A: (1) aldehyde (0.01 M), dipyrromethane (0.01 M), $BF_3 \cdot Et_2O$ (0.001 M), NH_4Cl (0.1 M), MeCN, 0 °C, 4.5 h; (2) DDQ (0.02 mmol), rt, 1 h. [b] Method B: (1) aldehyde (0.01 M), dipyrromethane (0.01 M), $BF_3 \cdot Et_2O$ (0.002 M), toluene, rt, 3 h; (2) DDQ (0.02 mmol), rt, 1 h. [c] The time of first step was prolonged to 16.5 h. [d] $BF_3 \cdot Et_2O$ (0.004 M) and the time of the first step was prolonged to 22 h.

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not only very expensive but also difficult to handle due to its low stability upon exposure to air. Therefore, we sought alternative methods that would be easier to handle and would minimize the cost of the synthesis. We tested various conditions, including 2-iodoxybenzoic acid (IBX) in DMSO, IBX in DCM, [bis(acetoxy)-iodo]benzene (BAIB) with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO),[20] MnO_2,[21] and [bis(trifluoroacetoxy)iodo]benzene (PIFA) with TEMPO. All the methods afforded good to high yields of aldehydes **8**−**10**. In the selection of the oxidizing agent for preparative scale, we took into consideration various factors, such as stability, availability, and price of the oxidizing agent, as well as the time and the yield of the reaction. Finally, we decided on the clean and efficient method utilizing BAIB and TEMPO, which afforded aldehydes in very high yields ranging from 81% to 95% on ca. 18 mmol scale (Scheme 1).

For the purpose of this study, we also synthesized a set of dipyrromethanes **15**, **16**, **18**−**20**. The ester-functionalized benzaldehyde **13** was obtained in the reaction of 3,4,5-trihydroxybenzaldehyde (**12**) with *tert*-butyl chloroacetate, while related aldehyde **14** was prepared from **12** by a classical alkylation procedure (Scheme 2).[22]

Both unknown dipyrromethanes **15** and **16** (Scheme 2), as well as dipyrromethane **18** (Scheme 3), were prepared using Lindsey's general conditions.[23]

Synthesis of *trans*-A_2B_2-Porphyrin with Two Arylethynyl Moieties. Having in hand all necessary building blocks, we focused on the porphyrin-formation step. There are numerous methods for the preparation of *trans*-A_2B_2 porphyrins, but the vast majority of them apply to the sterically hindered dipyrromethanes,[24,25] which are less prone to acid-catalyzed scrambling. As a model system for optimization studies we chose the reaction of aldehyde **8** with dipyrromethane **15** leading to porphyrin **21** (Table 1). In the first phase of searching for suitable conditions, we observed that all the methods employing trifluoroacetic acid as a catalyst led to such extensive scrambling that in some cases the amount of rearrangement products exceeded the amount of target porphyrins.

Searching for a suitable alternative, we took advantage of the known procedure ($BF_3 \cdot Et_2O$, NH_4Cl, MeCN, 0 °C, 4.5 h) developed by Lindsey and co-workers for unhindered dipyrromethanes[25] and slightly modified it. We have noted that a prolonged time of degassing the solvent with a stream of argon by sonication significantly raised the yield of the porphyrin **22**. Additionally, we wanted to avoid residual chlorin, so instead of a two-step oxidation (as originally proposed by authors), we doubled the amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). In contrast to the report of Lindsey and co-workers, the increased amount of oxidant used to our specific case was sufficient to ensure complete oxidation of chlorin to porphyrin, which can be rationalized by lower steric hindrance and lower oxidation potential. The modified procedure was subsequently applied to a series of dipyrromethanes (both hindered and unhindered) and phenylpropargyl aldehydes **8**−**11**, affording *trans*-A_2B_2 porphyrins **21**−**26** and **29** in satisfactory yields reaching 30% in some cases (Table 1).

The biggest drawback of this method was performing the reaction in MeCN, a polar solvent that is inappropriate for more lipophilic building blocks, e.g., those possessing long alkyl chains like 5-(4-octadecyloxyphenyl)dipyrromethane (**18**). With this substrate, reactions with both 3-(4-cyanophenyl)propynal (**8**) and 3-phenylpropynal (**11**) gave no porphyrin. The predominant products after addition of DDQ were dipyrrines. This outcome could be explained by low solubility of the lipophilic substrate and intermediates formed during the course of the reaction in this reaction medium. Desiring to develop a more versatile methodology, we searched for alternative conditions that were suitable for these types of substrates. Initially, we changed the solvent as well as the salt, replacing polar MeCN with nonpolar toluene and NH_4Cl with polar but more lipophilic Ph_4BNH_4. We carried out the reaction of aldehyde **8** with dipyrromethane **18** at 0 °C for 3 h in dry and degassed toluene (entry 1, Table 2), followed by oxidation. These conditions resulted in a low (6%) yield of **27**, but the reaction was very clean and no scrambling was observed. Further variations in the concentration of the acid, the presence of Ph_4BNH_4, and the temperature (see Table 2) led to optimization of these conditions.

Table 2. Optimization of the Reaction of (4-Cyanophenyl)-propynal (8) with 5-(4-Octadecyloxyphenyl)dipyrromethane (18)[a]

	concn (M)			
entry	$BF_3 \cdot Et_2O$	Ph_4BNH_4	Temp. (°C)	yield of porphyrin **27**[b] (%)
1	0.001	0.1	0	6
2	0.001	0.1	20	6
3	0.002	0.1	20	12[c]
4	0.002	0	20	14[c]

[a] All reactions were performed under the following constant conditions: [aldehyde **8**] = 0.01 M, [dipyrromethane **18**] = 0.01 M, 3 h. [b] Isolated yields. [c] Minimal scrambling was observed.

Ultimately, we had to compromise between the yield and the formation of troublesome side products. Taking into account the time required for the preparation of some building blocks and the overall cost of their synthesis, as well as the price of borate salt, we decided on the method employing a higher concentration of acid, without an addition of salt, which provided high amounts of the final compounds, but with minimal scrambling.

From our study of the model condensation, we identified the following reaction conditions: (1) aldehyde (0.01 M), dipyrromethane (0.01 M) in dry toluene predegassed (Ar, 35 min, sonicator), $BF_3 \cdot Et_2O$ (0.002 M), rt, 3 h; (2) DDQ (0.02 mmol), rt, 1 h. The conditions optimized for lipophilic dipyrromethanes were subsequently applied to the preparation of porphyrins **29** and **30** from dipyrromethane **16** possessing three alkoxy groups and aldehydes **8** and **10** with satisfactory yields of 12% in each case (Table 1).

We also investigated whether the conditions optimized for the reaction between 5-(4-octadecyloxyphenyl)dipyrromethane (**18**) and 3-(4-cyanophenyl)propynal (**8**) could be applied to other building blocks. The system of our first choice was quite demanding and involved 5-[3,4,5-tris((*tert*-butoxycarbonyl)methyloxy)phenyl]dipyrromethane (**15**) and moderately reactive 3-phenylpropynal (**11**). The reaction in toluene afforded the corresponding porphyrin **23** in 5% yield (Table 1). These results were in line with our expectations, since for quite hydrophilic dipyrromethane the polar MeCN method seemed to be preferable. Subsequently, to compare the influence of reactivity and lipophilicity of dipyrromethanes on the reaction course, we performed the reaction between other aldehydes and dipyrromethanes (Table 1).

CONCLUSIONS

We have performed a detailed study of the direct [2 + 2] condensation of phenylpropargyl aldehydes with dipyrromethanes leading to *trans*-A_2B_2-porphyrins, and we have defined two sets of conditions that apply to reagents with greater or lesser lipophilicity. By identifying the issue of solubility of the substrates and

the intermediates in the reaction medium and by tailoring reaction conditions accordingly, we have achieved reasonable yields of a broad range of porphyrins. The most notable findings are as follows: (1) For less lipophilic reagents, the modified procedure in MeCN reported initially by Lindsey and co-workers is superior. We noticed that a prolonged time of degassing the solvent by sonication plays a crucial role and substantially increases the yield of the porphyrin formation. The reaction in MeCN does not work for highly lipophilic dipyrromethanes, probably due to the low solubility of substrates and intermediates formed during the course of the reaction. (2) For more lipophilic reagents, another set of conditions in toluene with no or minimal scrambling has been developed, providing satisfactory yields for reactive lipophilic dipyrromethanes and electron-deficient aldehydes. Addition of the lipophilic salt Ph_4BNH_4 limits the scrambling to some extent, probably due to decreasing the activation energies of the desired reactions through lowering the energies of the polar transition states. Decreasing the reaction temperature also reduced the amount of ring-rearrangement products, but it also lowers the yields significantly due to the extremely slow reaction rate.

These results are not only of theoretical significance in that they provide new insights into factors influencing the course of reactions of pyrrole derivatives with aldehydes leading to macrocyclic structures, but they also provide a complementary method to two established alternative approaches leading to this type of π-expanded porphyrins. The current methodology compares favorably with the existing procedures, especially for electron-deficient arylethynyl substituents where Sonogashira coupling of *meso*-Br-porphyrins with alkynes leads to inferior results.

EXPERIMENTAL SECTION

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All reported ^{1}H NMR and ^{13}C NMR spectra were collected using 600, 500, 400, or 200 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference or acetone as the external reference; *J* values are given in Hz. The UV/vis absorption spectra were recorded in CH_2Cl_2 or TFA. The absorption wavelengths are reported in nm with the extinction coefficient in M^{-1} cm^{-1} in brackets. Melting points of aldehydes were determined using a capillary type apparatus or a Boetius-type apparatus. Chromatography was performed on silica (230−400 mesh) or neutral alumina (activity I). Dry column vacuum chromatography (DCVC) was performed on preparative thin-layer chromatography silica. Preparative scale size exclusion chromatography (SEC) was carried out using BioRad Bio-Beads SX-1 with THF as an eluent. The mass spectra were obtained via field desorption MS (FD-MS), electrospray ionization (ESI-MS), and electron impact MS (EI-MS). Aldehydes **14** and **17** and dipyrromethanes **19** and **20** were prepared according to the literature procedures.[21,22,25]

3-(4-Cyanophenyl)prop-2-yn-1-ol (5). Bis(triphenylphosphine)-palladium(II) dichloride (60 mg, 0.085 mmol) was added to a stirred solution of propargyl alcohol (2.89 mL, 0.05 mol), 4-iodobenzonitrile (11.2 g, 49 mmol), piperidine (9.88 mL, 0.1 mol), and copper(I) iodide (30 mg, 0.16 mmol) in dry toluene (100 mL) under an argon atmosphere. The mixture was stirred at 35 °C for 2 h and then filtered through silica gel. The solvent was distilled off and the residue was chromatographed (silica, hexanes/CH_2Cl_2 1:1 then 2:3) followed by crystallization (AcOEt/hexanes) to afford pure product (7.43 g, 96%): mp = 85.7−86.3 °C (AcOEt/hexanes) (lit.[26] mp = 87.5−88 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88 (br s, 1H), 4.53 (s, 2H), 7.51 (m, 2H), 7.60 (m, 2H). Other spectral and physical properties concur with published data.[26]

3-(4-Methoxyphenyl)prop-2-yn-1-ol (6). Bis(triphenylphosphine)palladium(II) dichloride (60 mg, 0.085 mmol) was added to a stirred solution of propargyl alcohol (2.9 mL, 0.05 mol), 1-iodo-4-methoxybenzene (11.47 g, 49 mmol), piperidine (9.88 mL, 0.1 mol), and copper(I) iodide (30 mg, 0.16 mmol) in dry toluene (100 mL) under an argon atmosphere. The mixture was stirred at 35 °C for 24 h and then filtered through silica gel (silica, hexanes/CH_2Cl_2 2:3 then CH_2Cl_2). The solvent was distilled off and the residue was crystallized (AcOEt/hexanes) to afford pure product (4.37 g, 55%): mp = 63.1−63.5 °C (AcOEt/hexanes) (lit.[17] mp = 62.5−64.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77 (br s, 1H), 3.81 (s, 3H), 4.48 (s, 2H), 6.84 (m, 2H), 7.37 (m, 2H). Other spectral and physical properties concur with published data.[17]

3-(4-Nitrophenyl)prop-2-yn-1-ol (7). Bis(triphenylphosphine)palladium(II) dichloride (120 mg, 0.171 mmol) was added to a stirred solution of propargyl alcohol (5.77 mL, 0.1 mol), 1-iodo-4-nitrobenzene (24.5 g, 98 mmol), piperidine (19.76 mL, 0.2 mol), and copper(I) iodide (60 mg, 0.32 mmol) in dry toluene (100 mL) under an argon atmosphere. The mixture was stirred at 35 °C for 2 h and then filtered through silica gel. The solvent was distilled off and the residue was chromatographed (silica, toluene/CH_2Cl_2 1:1) followed by crystallization ($CHCl_3$) to afford pure solid (5.5 g). The filtrate containing the contaminated product was rechromatographed (silica, CH_2Cl_2) and crystallized, yielding an additional 7.1 g of the pure compound **7** (12.6 g, total yield, 73%): mp = 98.7−99.9 °C ($CHCl_3$) (lit.[26] mp = 97−98 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.84 (br s, 1H), 4.55 (s, 2H), 7.58 (m, 2H), 8.19 (m, 2H). Other spectral and physical properties concur with published data.[26]

General Procedure for the Oxidation of Propargyl Alcohols to Propargyl Aldehydes. To the solution of TEMPO (269 mg, 1.7 mmol) and alcohol (17.6 mmol) in DCM (17.7 mL) was added bisacetoxyiodobenzene (6.28 g, 19.5 mmol). The reaction mixture was stirred for 1.5 h. Then the organic layer was washed with aqueous solution of $Na_2S_2O_3$. The water layer was extracted with methylene chloride, and then combined organic extracts were washed with aqueous solution of $NaHCO_3$ to pH 7, dried (Na_2SO_4), filtered, and evaporated. Further purification details are described for each case as follows.

(4-Cyanophenyl)propynal (8). The crude product was chromatographed (silica, hexanes/CH_2Cl_2 3:2) followed by crystallization (CH_2Cl_2/hexanes) to afford pure aldehyde **8** as colorless crystals. The filtrate was rechromatographed (silica, hexanes/CH_2Cl_2 3:2) and crystallized, providing additional portion of pure product **8** (2.31 g, total yield 84%): mp = 100.9−101.7 °C (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (m, 4H), 9.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 90.3, 91.2, 114.6, 117.7, 124.2, 132.3, 133.4, 176.1; HR MS (EI) calcd for $C_{10}H_5NO$ 155.0371, found 155.0374. Anal. Calcd for $C_{10}H_5NO$: C, 77.41; H, 3.25; N, 9.03. Found: C, 77.17; H, 3.23; N, 9.12.

(4-Methoxyphenyl)propynal (9). The crude product was chromatographed (silica, hexanes/CH_2Cl_2 3:2) followed by crystallization (CH_2Cl_2/hexanes) to afford pure aldehyde **9** as colorless crystals (2.69 g, 95%): mp = 45.4−45.8 °C (CH_2Cl_2/hexane) (lit.[17] mp = 47−48.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.91 (m, 2H), 7.56 (m, 2H), 9.40 (s, 1H). Other spectral and physical properties concur with published data.[17]

(4-Nitrophenyl)propynal (10). The crude product was chromatographed (silica, hexanes/CH_2Cl_2 2:3) and crystallized (CH_2Cl_2/hexane) to afford the title compound (2.16 g, 81%) as colorless crystals: mp = 120.2−120.7 °C (CH_2Cl_2/hexane) [lit.[27] mp = 123.0−123.5 °C (petroleum ether)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (m, 2H), 8.28 (m, 2H), 9.47 (s, 1H). Other spectral and physical properties concur with published data.[27]

3,4,5-Tris[(*tert*-butoxycarbonyl)methyloxy)]benzaldehyde-(13). 3,4,5-Trihydroxybenzaldehyde (**12**) (1.50 g, 8.7 mmol) was dissolved in MeCN (100 mL), and *tert*-butyl chloroacetate (5 mL, 35 mmol), K_2CO_3 (3.3 g, 24 mmol) were added, followed by KI (3.32 g, 20 mmol). The reaction mixture was refluxed for 8 h. In the meantime, an additional portion of K_2CO_3 (3.0 g, 22 mmol) was added. Then the

mixture was cooled down and filtered. The filtrate was evaporated and chromatographed (silica, hexanes/CH_2Cl_2 3:2 to give oil, which slowly solidified. The solid was recrystallized (hexane/AcOEt) to obtain colorless crystals (3.83 g, 88%): mp = 76.9−77.3 °C (hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 9H), 1.48 (s, 18H), 4.64 (s, 4H), 4.82 (s, 2H), 7.07 (s, 2H), 9.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.1, 66.9, 69.8, 81.8, 82.6, 109.6, 131.1, 143.2, 151.4, 167.4, 168.0, 190.3; HR MS (ESI) calcd for $C_{25}H_{36}O_{10}Na$ 519.2201, found 519.2224. Anal. Calcd for $C_{25}H_{36}O_{10}$: C, 60.47; H, 7.31. Found: C, 60.43; H, 7.55.

5-[3,4,5-Tris((*tert*-butoxycarbonyl)methyloxy)phenyl]dipyrromethane (15). The solution of aldehyde **13** (622 mg, 1.25 mmol) and pyrrole (4.34 mL, 63 mmol) was degassed with a stream of argon for 10 min. $InCl_3$ (27.8 mg, 0.13 mmol) was added, and the mixture was stirred under argon at room temperature for 2 h. The pyrrole was recovered and the crude product obtained upon removal of pyrrole was chromatographed (silica, CH_2Cl_2 then CH_2Cl_2/acetone 50:1). Crystallization from cyclohexane afforded the title compound (223 mg, 29%): mp = 112.3−113.4 °C (cyclohexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 18H), 1.48 (s, 9H), 4.50 (s, 4H), 4.62 (s, 2H), 5.33 (s, 1H), 5.88 (m, 2H), 6.11 (m, 2H), 6.65 (m, 2H), 7.97 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.1, 43.8, 66.8, 70.1, 81.4, 82.2, 107.2, 108.4, 108.8, 117.2, 131.8, 136.7, 137.5, 151.3, 167.9, 168.4; HR MS (ESI) calcd for $C_{33}H_{44}N_2O_9Na$ 635.2939, found 635.2962. Anal. Calcd for $C_{33}H_{44}N_2O_9$: C, 64.69; H, 7.24; N, 4.57. Found: C, 64.54; H, 7.15; N, 4.61.

5-(3,4,5-Trisdecyloxyphenyl)dipyrromethane (16). The solution of aldehyde **14** (2.56 g, 4.45 mmol) and pyrrole (16 mL, 231 mmol) was degassed with a stream of argon for 15 min. $InCl_3$ (130 mg, 0.59 mmol) was added, and the mixture was stirred under argon at room temperature for 3 h. Then ground NaOH (583 mg, 14.58 mmol) was added, the reaction mixture was stirred for a further 0.5 h and filtered through a pad of Celite. The pyrrole was recovered and the crude solid obtained upon removal of pyrrole was chromatographed (silica, hexanes/CH_2Cl_2 1:1). Then the solid was rechromatographed in order to remove N-confused dipyrromethane (silica, CH_2Cl_2/AcOEt/hexanes 3:1:16) to afford pure product **16** (2.899 g, 94%): mp = 31.5−32.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (m, 9H), 1.17−1.45 (m, 42 H), 1.64−1.77 (m, 6H), 3.84−3.96 (m, 6H), 5.38 (s, 1H), 5.96 (m, 2H), 6.16 (m, 2H), 6.40 (s, 2H), 6.70 (m, 2H), 7.92 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 26.1, 29.4, 29.4, 29.4, 29.6, 29.7, 29.8, 30.3, 31.9, 44.1, 69.0, 73.4, 106.9, 107.1, 108.4, 117.0, 132.4, 136.9, 137.0, 153.1; HR MS (ESI) calcd for $C_{45}H_{74}N_2O_3Na$ 713.5592, found 713.5619. Anal. Calcd for $C_{45}H_{74}N_2O_3$: C, 78.21; H, 10.79; N, 4.05. Found: C, 78.19; H, 10.48; N, 3.89.

5-(4-Octadecyloxyphenyl)dipyrromethane (18). The mixture of aldehyde **17** (1.87 g, 4.99 mmol) and pyrrole (35 mL, 506 mmol) was heated to 50 °C in order to dissolve aldehyde. To the homogeneous solution was added a portion of $InCl_3$ (111 mg, 0.50 mmol) and the reaction mixture was stirred at rt for 2 h. Then an additional portion of $InCl_3$ (111 mg, 0.50 mmol) was added due to the incomplete conversion of the aldehyde, and stirring was continued for the next 2 h. When the conversion was full, ground NaOH (1.2 g, 30 mmol) was added. After 1 h the suspension was filtered through a pad of Celite and evaporated to dryness, providing a brownish residue, which was crystallized from hot MeOH to afford **18** as off-white crystals (2.109 g, 86%): mp = 75.7−77.8 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (m, 3H), 1.20−1.35 (m, 28H), 1.44 (m, 2H), 1.76 (m, 2H), 3.92 (t, J = 6.5 Hz, 2H), 5.42 (s, 1H), 5.91 (m, 2H), 6.15 (m, 2H), 6.68 (m, 2H), 6.84 (m, 2H), 7.11 (m, 2H), 7.90 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.3, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 43.1, 68.0, 107.0, 108.4, 114.6, 117.0, 129.3, 132.9, 133.9, 158.1; HR MS (EI) calcd for $C_{33}H_{50}N_2O$ 490.3923, found 490.3918. Anal. Calcd for $C_{33}H_{50}N_2O$: C, 80.76; H, 10.27; N, 5.71. Found: C, 80.89; H, 10.21; N, 5.56.

General Procedure for the Preparation of *trans*-A_2B_2-Porphyrins in MeCN. NH_4Cl (214 mg, 4 mmol) was added to MeCN (40 mL) degassed with a stream of Ar by sonication for 20 min. Then the suspension was cooled down under Ar to 0 °C, and samples of aldehyde (0.4 mmol) and dipyrromethane (0.4 mmol) were added, followed by $BF_3 \cdot Et_2O$ (5 μL, 0.04 mmol). After 4.5 h, DDQ (180 mg, 0.8 mmol) was added, and the reaction mixture was stirred at rt for an additional 1 h. The purification details are described for each case as follows.

5,15-Bis(4-cyanophenylethynyl)-10,20-bis[tris((*tert*-butoxycarbonyl)methyloxy)phenyl]porphyrin (21). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2), and all fractions containing porphyrin **21** were combined, evaporated to dryness, and chromatographed (silica, hexanes/acetone 4:1) to obtain pure porphyrin **21** (83.5 mg, 28%) which was crystallized (acetone/hexane), affording green crystals: R_f = 0.53 (hexane/acetone 1:1); UV/vis (CH_2Cl_2) λ (ε) = 446 (433 000), 603 (58 900), 691 (32 700), 293 (19 300), 559 (8800), 520 nm (5200); ^{1}H NMR (500 MHz, $CDCl_3$) δ −2.08 (s, 2H), 1.39 (s, 36 H), 1.63 (s, 18 H), 4.75 (s, 8H), 5.02 (s, 4H), 7.36 (s, 4H), 7.88 (d, J = 8.2 Hz, 4H), 8.10 (d, J = 8.2 Hz, 4H), 8.91 (d, J = 4.7 Hz, 4H), 9.60 (d, J = 4.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.3, 66.9, 70.5, 81.7, 82.3, 95.7, 96.1, 100.1, 111.9, 115.4, 118.6, 121.6, 128.5, 132.1, 132.5, 135.9, 138.1, 149.7, 167.7, 168.6; HR MS (ESI) calcd for $C_{86}H_{88}N_6O_{18}Na_2$ 769.2970, found 769.2957; isotope profiles match.

5,15-Bis(4-nitrophenylethynyl)-10,20-bis[tris((*tert*-butoxycarbonyl)methyloxy)phenyl]porphyrin (22). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2) to give almost pure product. Subsequent crystallization (CH_2Cl_2/hexane) afforded porphyrin **22** (110 mg, 36%) in the form of green crystals: R_f = 0.58 (hexane/acetone 1:1); UV/vis (CH_2Cl_2) λ (ε) = 453 (405 000), 608 (93 900), 694 nm (68 800); ^{1}H NMR (600 MHz, $CDCl_3$) δ −2.08 (s, 2H), 1.40 (s, 36H), 1.64 (s, 18H), 4.78 (s, 8H), 5.04 (s, 4H), 7.39 (s, 4H), 8.04 (m, 4H), 8.33 (m, 4H), 8.94 (d, J = 4.6 Hz, 4H), 9.61 (d, J = 4.6 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.0, 28.3, 66.9, 70.5, 81.7, 82.3, 95.6, 97.1, 100.1, 115.4, 121.7, 124.0, 130.4, 132.1, 135.9, 138.1, 147.1, 149.8, 167.7, 168.6; HR MS (ESI) calcd for $C_{84}H_{89}N_6O_{22}$ 1533.6025, found 1533.6042; isotope profiles match.

5,15-Bis(phenylethynyl)-10,20-bis[tris((*tert*-butoxycarbonyl)methyloxy)phenyl]porphyrin (23). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2), and all fractions containing porphyrin **23** were combined, evaporated to dryness, and chromatographed (silica, $CHCl_3$/MeOH 189:1 to 49:1) to obtain pure porphyrin **23** (60 mg, 21%) which was crystallized (acetone/hexane), affording green crystals: R_f = 0.55 (hexane/acetone 1:1); UV/vis (CH_2Cl_2) λ (ε) = 443 (394 000), 599 (52 400), 689 (24 400), 298 (22 700), 555 (10 000), 517 nm (6000); ^{1}H NMR (500 MHz, $CDCl_3$) δ −2.04 (s, 2H), 1.38 (s, 36H), 1.62 (s, 18H), 4.74 (s, 8H), 5.02 (s, 4H), 7.36 (s, 4H), 7.53 (m, 2H), 7.60 (m, 4H), 8.04 (m, 4H), 8.87 (d, J = 4.5 Hz, 4H), 9.65 (d, J = 4.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.3, 66.8, 70.5, 81.6, 82.3, 91.7, 97.4, 101.3, 115.1, 120.9, 123.8, 128.8, 128.8, 131.7, 136.3, 137.9, 149.7, 167.7, 168.6; HR MS (FD) calcd for $C_{84}H_{90}N_4O_{18}$ 1442.6250, found 1442.6232; isotope profiles match.

5,15-Dimesityl-10,20-bis(4-cyanophenylethynyl)porphyrin (24). The reaction mixture was passed through a short pad of alumina (alumina, hexane/acetone 4:1) to give pure product and a contaminated fraction, which was rechromatographed (silica, $CHCl_3$/toluene 1:3) to give pure porphyrin **24**. Both fractions were combined (28 mg, 18%) and crystallized from hot $CHCl_3$/hexanes to afford green crystals, which were washed with hexanes, followed by CH_2Cl_2: R_f = 0.37 ($CHCl_3$/toluene 1:1); UV/vis (CH_2Cl_2) λ (ε) = 445 (461 000), 602 (63 600), 692 (42 300), 257 (29 200), 294 (22 500), 558 (9800), 519 nm (6900); ^{1}H NMR (500 MHz, TFA−$CDCl_3$) δ 1.90 (s, 12H), 2.69 (s, 6H), 7.43 (s, 4H), 8.00 (d, J = 8.2 Hz, 4H), 8.20 (d, J = 8.5 Hz, 4H), 8.76 (d, J = 4.7 Hz, 4H), 9.52 (d, J = 4.7 Hz, 4H); ^{13}C NMR (125 MHz, TFA−$CDCl_3$) δ 20.6, 21.2, 91.5, 102.5, 112.0, 123.8, 127.4, 128.9, 129.2, 129.9, 132.8, 132.9, 134.1, 139.8, 141.5, 145.3, 145.8; HR MS (FD) calcd for $C_{56}H_{40}N_6$ 796.3314, found 796.3324; isotope profiles match.

5,15-Dimesityl-10,20-bis(4-methoxyphenylethynyl)porphyrin (25). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2). Subsequent chromatography (silica, hexanes/CH_2Cl_2 1:1) afforded pure porphyrin **25** (14 mg, 9%): R_f = 0.46 (CH_2Cl_2/hexane 3:2); UV/vis (CH_2Cl_2) λ (ε) = 447 (387 000), 605 (53 900), 696 (30 800), 311 (23 300), 366 (16 600), 521 nm (5800); ^{1}H NMR (500 MHz, $CDCl_3$) δ −1.76 (s, 2H), 1.87 (s, 12H), 2.65 (s, 6H), 3.94 (s, 6H), 7.09 (m, 4H), 7.30 (s, 4H), 7.93 (m, 4H), 8.65 (d, J = 4.7 Hz, 4H), 9.59 (d, J = 4.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 21.5, 55.5, 90.5, 97.2, 101.0, 114.4, 116.0, 120.0, 127.8, 133.2, 137.7, 137.9, 139.2, 160.1; HR MS (FD) calcd for $C_{56}H_{46}N_4O_2$ 806.3621, found 806.3594; isotope profiles match.

5,15-Bis(4-cyanophenylethynyl)-10,20-bis(pentafluorophenyl)-porphyrin (26). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2/hexanes 1:1). All fractions containing porphyrin were not evaporated due to the poor solubility of the product. The porphyrin slowly crystallized from the solution. Then the crystals were centrifuged, the supernatant was removed, and the solid was washed with hexanes to give pure product **26** as green crystals (14.3 mg, 4%): R_f = 0.53 (DMF/CCl_4 1:12); UV/vis (TFA) λ (ε) = 457 (265 000), 344 (21 400), 671 nm (1800); ^{1}H NMR (500 MHz, TFA) δ 7.47 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 8.2 Hz, 4H), 8.43 (d, J = 4.9 Hz, 4H), 9.15 (d, J = 4.9 Hz, 4H); ^{13}C NMR (125 MHz, TFA) δ 89.3, 103.6, 104.2, 107.1, 111.4, 126.5, 128.7, 129.3, 132.0, 132.0, 144.0, 146.6; HR MS (FD) calcd for $C_{50}H_{19}F_{10}N_6$ 892.1433, found 892.1450; isotope profiles match.

5,15-Bis(4-cyanophenylethynyl)-10,20-bis(3,4,5-trisdecyloxyphenyl)porphyrin (29). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2). All fractions containing porphyrin were combined, evaporated, and rechromatographed (silica, hexanes/CH_2Cl_2 3:1 to 2:3). Then the solid was suspended in hexanes and filtered to give the title porphyrin (23 mg, 7%) as green crystals: R_f = 0.59 (CH_2Cl_2/hexane 7:3); UV/vis (CH_2Cl_2) λ (ε) = 448 (429 000), 604 (62 100), 693 (37 400), 560 (10 500), 521 nm (6400); ^{1}H NMR (500 MHz, $CDCl_3$) δ −2.00 (s, 2H), 0.83 (m, 12H), 0.92 (m, 6H), 1.22−1.54 (m, 80H), 1.69 (m, 4H), 1.89 (m, 8H), 1.99 (m, 4H), 4.13 (t, J = 6.4 Hz, 8H), 4.32 (m, 4H), 7.41 (s, 4H), 7.86 (d, J = 8.2 Hz, 4H), 8.10 (d, J = 8.2 Hz, 4H), 8.98 (d, J = 4.6 Hz, 4H), 9.63 (d, J = 4.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.2, 22.7, 22.8, 26.2, 26.3, 29.3, 29.5, 29.5, 29.5, 29.6, 29.6, 29.8, 29.8, 29.9, 30.6, 31.9, 32.0, 69.5, 73.8, 95.6, 96.3, 100.0, 111.9, 114.4, 122.8, 128.6, 132.1, 132.5, 135.9, 138.4, 151.5; HR MS (FD) calcd for $C_{110}H_{148}N_6O_6$ 1649.1460, found 1649.1483; isotope profiles match.

General Procedure for the Preparation of *trans*-A_2B_2-Porphyrins in Toluene. Samples of aldehyde (0.4 mmol) and dipyrromethane (0.4 mmol) were added to dry toluene (40 mL) degassed with a stream of Ar by sonication for 35 min. Then $BF_3 \cdot Et_2O$ (10 μL, 0.08 mmol) was added and the reaction mixture was stirred at rt for 3 h. After this time, DDQ (180 mg, 0.8 mmol) was added, and the reaction mixture was stirred at rt for an additional 1 h. The purification details are described for each case as follows.

5,15-Bis(phenylethynyl)-10,20-bis[tris((*tert*-butoxycarbonyl)-methyloxy)phenyl]porphyrin (23). The reaction mixture was passed through a short pad of alumina (alumina, acetone/hexanes 1:4). All fractions containing porphyrin were combined and rechromatographed (silica, AcOEt/hexanes 1:3) to give pure porphyrin **23**, which was suspended in hexanes and centrifuged, affording green crystals (14 mg, 5%). Spectroscopic data were identical to those reported for the method in MeCN.

5,15-Bis(4-cyanophenylethynyl)-10,20-bis(4-octadecyloxyphenyl)porphyrin (27). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2). Subsequent chromatography (silica, CH_2Cl_2/hexanes 1:4 to 2:3) afforded pure porphyrin **27** (35 mg, 14%), which was crystallized from CH_2Cl_2/hexane to give **27** in the form of green crystals: R_f = 0.30 (CH_2Cl_2/hexane 3:2); UV/vis (CH_2Cl_2) λ (ε) = 445 (442 000), 604 (62 800), 694 (40 500), 384 (26 900), 562 (10 800), 521 nm (6800); ^{1}H NMR (500 MHz, $CDCl_3$) δ −2.02 (s, 2H), 0.88 (m, 6H), 1.27−1.54 (m, 56H), 1.65 (m, 4H), 2.01 (m, 4H), 4.28 (t, J = 6.5 Hz, 4H), 7.32 (d, J = 8.6 Hz, 4H), 7.80 (d, J = 8.4 Hz, 4H), 7.99 (d, J = 8.4 Hz, 4H), 8.08 (d, J = 8.4 Hz, 4H), 8.88 (d, J = 4.7 Hz, 4H), 9.55 (d, J = 4.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 26.3, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 29.7, 29.7, 29.8, 31.9, 68.4, 95.4, 96.3, 99.8, 111.6, 113.1, 118.6, 122.5, 128.5, 131.9, 132.3, 133.1, 135.6, 159.4; HR MS (FD) calcd for $C_{86}H_{100}N_6O_2$ 1248.7908, found 1248.7883; isotope profiles match.

5,15-Bis(4-cyanophenylethynyl)-10,20-bis(3,4,5-trisdecyloxyphenyl)porphyrin (29). The reaction mixture was passed through a short pad of alumina (alumina, CH_2Cl_2). Subsequent chromatography (silica, CH_2Cl_2/hexanes 1:3 to 3:2) afforded pure product which was crystallized from hot acetone to give **29** (36 mg) as green crystals. The filtrate containing contaminated product was rechromatographed (DCVC, AcOEt/hexanes 3:7 to 1:1) and the solid was crystallized, yielding additional 4.5 mg of the pure compound **29** (40.5 mg, total yield, 12%). Spectroscopic data were identical to those reported for the method in MeCN.

5,15-Bis(3,4,5-trisdecyloxyphenyl)-10,20-bis(4-nitrophenylethynyl)porphyrin (30). The reaction mixture was passed through a short pad of silica (silica, CH_2Cl_2/hexanes 1:3 to 3:2), followed by DCVC (CH_2Cl_2/hexanes 1:3 to 2:3). SEC (THF) afforded pure solid which was crystallized from hot acetone to give pure porphyrin **30** (41 mg, 12%) as green crystals: R_f = 0.37 (CH_2Cl_2/hexane 1:1); UV/vis (CH_2Cl_2) λ (ε) = 455 (332 000), 609 (61 600), 696 (42 200), 384 (28 300), 523 nm (6700); ^{1}H NMR (500 MHz, $CHCl_3$) δ −1.98 (s, 2H), 0.83 (m, 12H), 0.92 (m, 6H), 1.22−1.54 (m, 80H), 1.69 (m, 4H), 1.90 (m, 8H), 2.00 (m, 4H), 4.13 (t, J = 6.4 Hz, 8H), 4.33 (t, J = 6.4 Hz, 4H), 7.42 (s, 4H), 8.12 (d, J = 8.9 Hz, 4H), 8.42 (d, J = 8.5 Hz, 4H), 9.00 (d, J = 4.6 Hz, 4H), 9.65 (d, J = 4.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.2, 22.7, 22.8, 26.2, 26.3, 29.3, 29.5, 29.5, 29.6, 29.6, 29.8, 29.9, 30.6, 31.9, 32.0, 69.5, 73.8, 95.5, 97.3, 99.9, 114.4, 122.9, 124.1, 130.6, 132.2, 135.8, 138.4, 147.2, 151.5; HR MS (FD) calcd for $C_{108}H_{148}N_6O_{10}$ 1689.1257, found 1689.1228; isotope profiles match.

Procedures for the Preparation of 25 and 28. *5,15-Dimesityl-10,20-bis(4-methoxyphenylethynyl)porphyrin (**25**).* Aldehyde **9** (64 mg, 0.4 mmol) and dipyrromethane **19** (106 mg, 0.4 mmol) were added to dry toluene (40 mL) degassed with a stream of Ar by sonication for 35 min. Then $BF_3 \cdot Et_2O$ (10 μL, 0.08 mmol) was added and the reaction mixture was stirred at rt for 16.5 h. After this time, DDQ (140 mg, 0.62 mmol) was added, and the reaction mixture was stirred at rt for an additional 1 h. Then the reaction mixture was passed through a short pad of silica (silica, CH_2Cl_2/hexanes 7:13 to 1:1). The solid was suspended in hexanes and centrifuged to give pure porphyrin **25** (16 mg, 10%). Spectroscopic data were identical to those reported for the method in MeCN.

*5,15-Bis(4-octadecyloxyphenyl)-10,20-bis(phenylethynyl)porphyrin (**28**).* Aldehyde **11** (50 μL, 0.4 mmol) and dipyrromethane **18** (200 mg, 0.4 mmol) were added to dry toluene (40 mL) degassed with a stream of Ar by sonication for 35 min. Then $BF_3 \cdot Et_2O$ (20 μL, 0.16 mmol) was added and the reaction mixture was stirred at rt for 22 h. After this time, DDQ (180 mg, 0.8 mmol) was added, and the reaction mixture was stirred at rt for an additional 1 h. Then the reaction mixture was passed through a short pad of silica (silica, CH_2Cl_2/hexanes 1:1). Subsequent chromatography (silica, CH_2Cl_2/hexanes 1:1 to 3:2) afforded pure porphyrin **28** (7 mg, 3%), which was suspended in acetone and centrifuged to give **28** in form of green crystals: R_f = 0.49 (hexane/CH_2Cl_2 3:2); UV/vis (CH_2Cl_2) λ (ε) = 442 (364 000), 601 (50 500), 692 (27 200), 556 (9800), 517 nm (6100); ^{1}H NMR (500 MHz, $CDCl_3$) δ −1.95 (s, 2H), 0.88 (m, 6H), 1.26−1.53 (m, 56H), 1.64 (m, 4H), 2.00 (m, 4H), 4.27 (t, J = 6.4 Hz, 4H), 7.31 (d, J = 8.5 Hz, 4H), 7.49−7.52 (m, 2H), 7.56−7.59 (m, 4H), 8.02−8.03 (m, 4H), 8.09 (d, J = 8.5 Hz, 4H), 8.87 (d, J = 4.6 Hz, 4H), 9.67 (d, J = 4.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 26.3, 29.4, 29.5, 29.6, 29.7, 29.7,

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29.7, 29.7, 31.9, 68.4, 92.0, 97.2, 101.0, 113.0, 121.8, 123.9, 128.7, 131.7, 133.5, 135.6, 159.2; HR MS (FD) calcd for $C_{84}H_{102}N_4O_2$ 1198.8003, found 1198.7974; isotope profiles match.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra of compounds **5**−**10**, **13**, **15**, **16**, **18**, **21**−**30** and ^{13}C NMR spectra of compounds **8**, **13**, **15**, **16**, **18**, **21**−**30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

This paper is dedicated to Prof. Janusz Jurczak on occasion of his 70th birthday.

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