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Trans-Substituted Porphyrin Building Blocks Bearing Iodo and Ethynyl Groups for Applications in Bioorganic and Materials Chemistry

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Abstract: The modular synthesis of linear or cyclic multiporphyrin arrays relies on the availability of *trans*-substituted porphyrin building blocks with high solubility in organic solvents. Eleven porphyrin building blocks were synthesized bearing iodo, ethynyl, and 2-(trimethylsilyl)ethynyl groups at the 4-, 3-, or 3,5-positions of two *meso*-aryl units, and mesityl groups at the other two *meso*-positions. The synthesis involves condensation of 5-mesityldipyrromethane with one or two aryl aldehydes. Combinations of functional groups include di-iodo, tetra-iodo, bis[(2-(trimethylsilyl)ethynyl], iodo and 2-(trimethylsilyl)ethynyl, and ethynyl and 2-(trimethylsilyl)ethynyl. In addition, a porphyrin bearing one 4-iodophenyl group and one 3,5-bis(boron-dipyrrin)phenyl group was synthesized for applications in molecular photonic devices. The iodo and ethynyl groups are ideally-suited for Pd-mediated coupling reactions, allowing the porphyrin building blocks to be joined in the systematic construction of soluble multiporphyrin arrays.

Porphyrin building blocks are important precursors for preparing models of naturally occurring porphyrinic systems and for creating porphyrin-based materials.[1,2] Of particular importance is the ability to construct arrays comprised of multiple porphyrins in well-defined architectures. In biology, non-covalent multiporphyrin arrays serve diverse purposes as in electron-transport chains,[3] enzymes such as hydroxylamine oxidase,[4] photosynthetic light harvesting antennae,[5] and photosynthetic reaction centers.[6] In bioorganic and materials chemistry, covalent multiporphyrin arrays have been constructed that function as multi-center redox catalysts,[7] light-harvesting arrays,[8] reaction centers,[9] photonic wires,[10] and optoelectronic gates.[11]

Porphyrins bearing ethyne and iodo groups have proved particularly useful in the construction of various molecular photonic devices containing porphyrins joined by diarylethyne linkers.[8,10,11] The key building block in the synthesis of a molecular photonic wire contained a *trans* arrangement of iodo and 2-(trimethylsilyl)ethynyl groups (Chart 1). The remaining *meso*-sites were occupied by mesityl groups, which provide enhanced solubility in organic solvents. The 2,6-dimethyl groups on the 4-ethynyl aryl unit facilitated separation of the porphyrin, which was prepared by condensation of 5-mesityldipyrromethane and the two respective aldehydes. Upon examining the photodynamics of various porphyrin dimers constructed using the same type of linking unit, we found that the torsional constraints due to the methyl groups on the diarylethyne linker suppressed through-bond electronic communication between the porphyrins. In particular, the rate of excited singlet-state energy transfer between the porphyrins decreased by 2-fold in the dimer having a dimethyl-substituted linker,

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and 3.5-fold in the dimer having a tetramethyl-substituted linker, compared with the dimer without any methyl groups on the diphenylethyne linker.[12] A 17-fold decrease in energy-transfer rate has been observed with porphyrins bearing two *meso*-substituents as well as eight β-alkyl groups, which has been attributed predominantly to the reversal of the a_{2u}/a_{1u} ordering of the porphyrin highest occupied molecular orbital.[13]

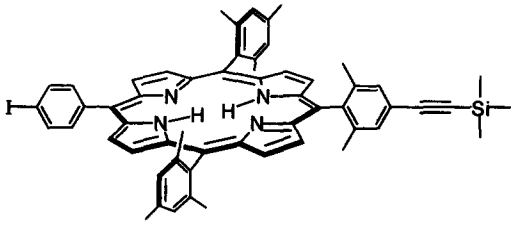


Chart 1. Porphyrin building block with 2,6-dimethyl groups on the ethynyl aryl unit.

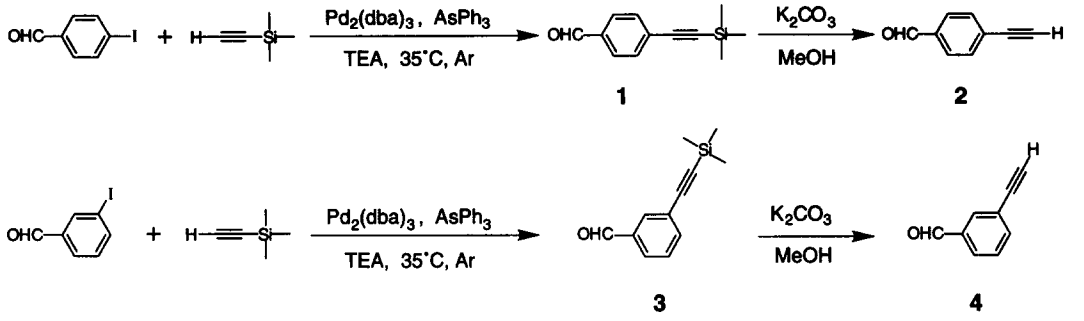
In this paper, we describe the synthesis of 12 new *meso*-substituted, β-unsubstituted porphyrin building blocks in order to meet the following objectives. (1) In order to achieve rapid excited-state energy transfer, each porphyrin building block lacks methyl groups on the ethynyl aryl unit. In addition, each porphyrin has *meso*-substituents but no β-alkyl substituents, thereby affording the a_{2u} highest occupied molecular orbital. (2) In order to prepare 3-dimensional multiporphyrin arrays, we have introduced one, two, or four iodo substituents at the *meta*-aryl positions. (3) In order to perform successive couplings on two ethynes in a given porphyrin, we have prepared porphyrins bearing one ethyne and one (trimethylsilyl)ethyne unit. (4) In order to create multiporphyrin arrays containing accessory pigments that can be selectively excited, we have prepared a porphyrin building block bearing two boron-dipyrrin chromophores and one iodo group. These objectives were met using refined procedures for preparing the requisite aryl aldehydes and for purifying porphyrins from mixed aldehyde condensations. These new porphyrin building blocks should enable the construction of various multiporphyrin arrays for applications in bioorganic and materials chemistry.

RESULTS AND DISCUSSION

Aldehyde Synthesis

Aldehydes **1-4** are useful precursors to various porphyrin building blocks (Scheme 1). Aldehyde **1** has been synthesized via several routes[14-16] and aldehydes **2-4** have also been synthesized previously.[14] We have used aldehyde **1** in the synthesis of porphyrin building blocks and multiporphyrin arrays.[1,8,10,11] We initially followed the first reported synthesis of **1**, which used 4-bromobenzaldehyde, (trimethylsilyl)acetylene, $Pd(OAc)_2$, and triphenylphosphine in triethylamine at reflux.[14] A preparative-scale purification procedure was not reported. In performing this reaction on numerous occasions using this and related Pd-mediated coupling conditions, we have observed an impurity peak (m/z = 300) upon GC-MS analysis that is consistent with the enyne product. It is known that Pd-mediated coupling reactions carried out at elevated temperature result in

enyne formation.[17] In order to minimize enyne formation, and to gain access to multi-gram quantities of pure ethynyl aldehyde, we have developed a refined synthetic procedure for the preparation of **1**.



Scheme 1. Syntheses of ethynyl-substituted aryl aldehydes.

The refined synthesis of **1** was performed with 4-iodobenzaldehyde and (trimethylsilyl)acetylene in triethylamine (TEA) at 35 °C in the presence of $Pd_2(dba)_3$ and $AsPh_3$ (Scheme 1). These conditions closely resemble those we have developed for preparing multiporphyrin arrays.[17] GC-MS analysis of the crude reaction mixture showed the putative enyne at the ~5% level. After filtration and flash column chromatography to remove the Pd species and $AsPh_3$, the resulting mixture was subjected to Kugelrohr distillation. Aldehyde **1**, free of any detectable enyne product, was isolated in 80% yield. Alternatively, the distillation could be replaced by recrystallization of the mixture with isopropanol, affording pure **1** in 64% yield. Desilylation afforded **2**. Aldehydes **3** and **4** were obtained in an identical manner. This refined process provides facile access to gram quantities of the aldehydes.

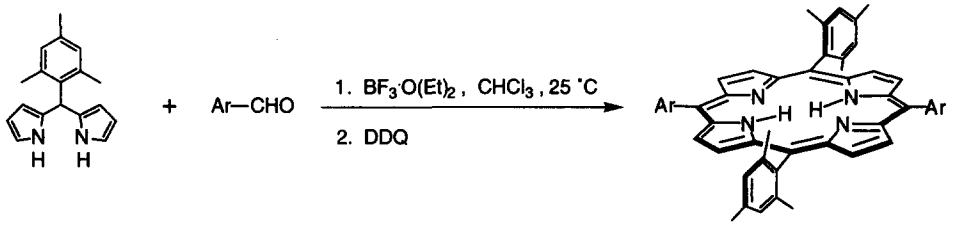
Porphyrin Synthesis

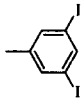
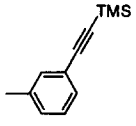
The *trans*-substituted porphyrin building blocks are readily formed via the two-step one-flask room temperature reaction of a dipyrromethane and one or two aldehydes.[18,19] Among the various possible 5-substituted dipyrromethanes, we have chosen 5-mesityldipyrromethane for all porphyrin condensations for two reasons. (1) Very little scrambling is observed when 5-mesityldipyrromethane is condensed with an aldehyde under the standard conditions for forming porphyrins.[19] Avoiding scrambling is essential for the integrity of the dipyrromethane and aldehyde condensations, affording the desired *trans*-substituted porphyrin without unexpected porphyrin by-products or isomers. (2) The mesityl group imparts enhanced solubility to the porphyrins. A different approach to achieve enhanced solubility is to incorporate β-alkyl substituents at the porphyrin periphery. Sanders *et al.* have synthesized iodophenyl-/ethynylphenyl-substituted porphyrin building blocks using a β-alkyl substituted 5-unsubstituted dipyrromethane. The resulting cyclic arrays have been investigated for their molecular recognition and catalytic properties.[20] For applications where through-bond electronic communication between porphyrins is important, and the porphyrins are to be joined at the *meso*-positions, soluble *meso*-substituted porphyrin building blocks are required that lack β-alkyl substituents.

Trans-A_2B_2-substituted porphyrins. The reaction of 5-mesityldipyrromethane and one aldehyde affords the corresponding *trans*-substituted porphyrin. The conditions for this reaction are identical to those of the two-step

one-flask reaction for forming porphyrins, involving $BF_3{\cdot}O(Et)_2$ catalysis at room temperature followed by oxidation with DDQ at room temperature. The reaction is rapid and the porphyrin is isolated by one flash-silica column chromatography procedure. Three *trans*-substituted porphyrins (**5-7**) bearing iodo or ethynyl groups were prepared in this manner (Table 1). The mass spectrum of each purified product was devoid of porphyrin molecular ion peaks expected upon scrambling. (Such peaks are readily observed by laser-desorption mass spectrometry when scrambling does occur.[21]) Porphyrin **6**, prepared from 3,5-diiodobenzaldehyde,[22] has four iodo groups and can be used to make cruciform structures in a four-fold coupling reaction. This route provides straightforward access to porphyrins bearing identical functional groups in a *trans*-architecture.

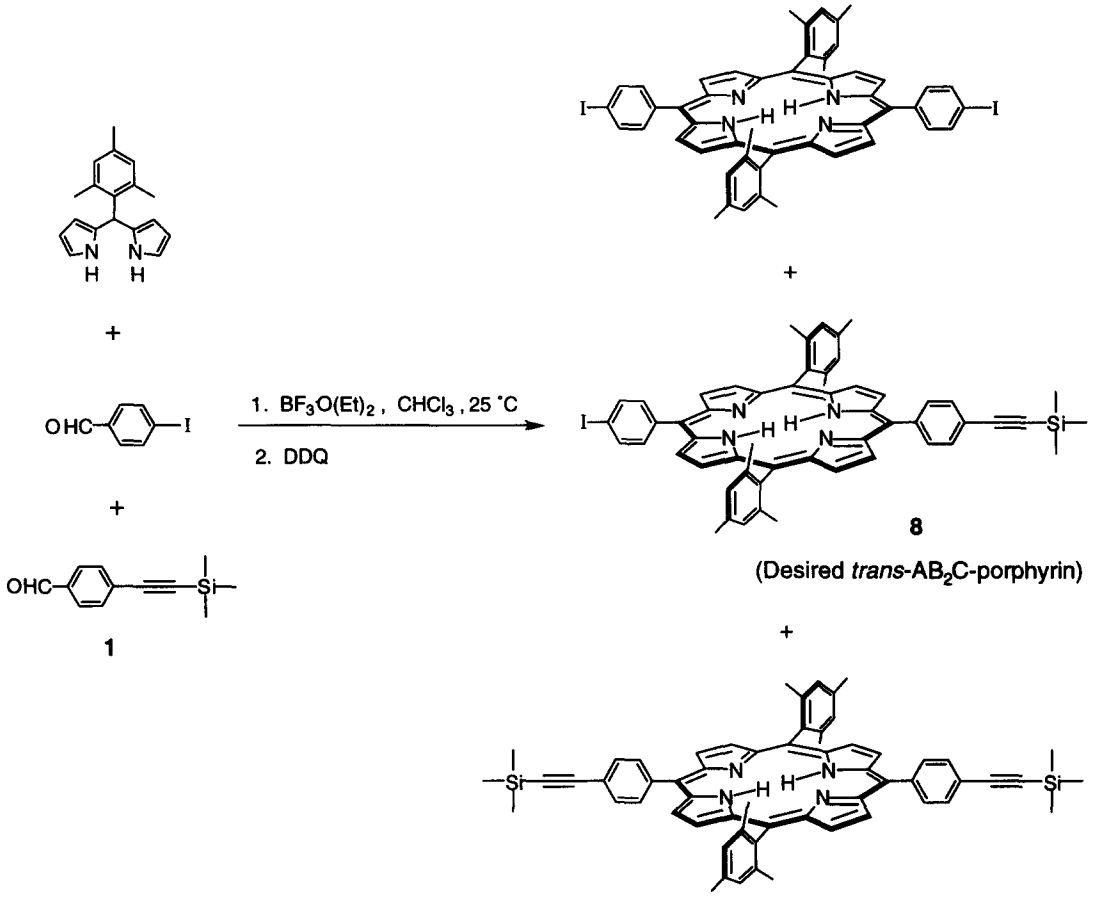
Table 1. Synthesis of A_2B_2-porphyrin building blocks.



Porphyrin	Ar	Yield (%)
5		27
6		27
7		27

Trans-AB_2C-substituted porphyrins. The condensation of 5-mesityldipyrromethane with two aldehydes affords, in principle, a mixture of three porphyrins. The desired "hybrid" AB_2C-porphyrin, derived from one of each of the aldehydes A and C and two equiv of the dipyrromethane (B), must be separated from the other two A_2B_2- and B_2C_2-porphyrins (Scheme 2). This is illustrated for the synthesis of porphyrin **8**, which was prepared via the condensation of 5-mesityldipyrromethane, 4-iodobenzaldehyde, and **1**. The mixture of three porphyrins could not be separated via flash silica column chromatography, as was the case with the related hybrid porphyrin

bearing the 2,6-dimethyl groups on the aryl ethyne unit (Chart 1). The desired porphyrin (**8**) was obtained in 14% yield using column chromatography on silica with very slow gravity elution [hexanes/$CHCl_3$ (4:1)]. The chromatography procedure is lengthy (6-8 mL per min for 8-10 h, or 3-4 mL per min for 35 h, with solvent recycling) but affords successful separation of the porphyrins.

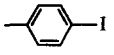
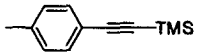
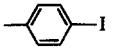
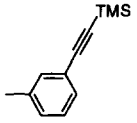
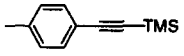
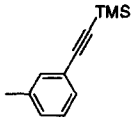
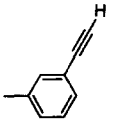
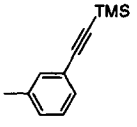
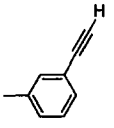
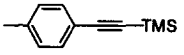
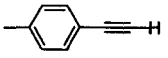
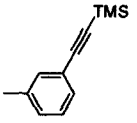
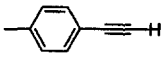
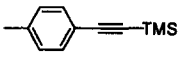


Scheme 2. Mixed-aldehyde condensation affording three porphyrins.

Porphyrin building blocks bearing iodo and (2-trimethylsilyl)ethynyl groups are highly desirable for preparing multiporphyrin arrays. Porphyrins with both functional groups at the *para*-position of the respective *meso*-aryl units are ideal for constructing linear multiporphyrin arrays, while porphyrins with one or both functional groups at the *meta*-positions provide a basis for constructing cyclic arrays. For stepwise sequential couplings, each building block requires two distinct sites that can be reacted successively. This requirement is met with both the iodo and 2-(trimethylsilyl)ethynyl groups, and the ethynyl and 2-(trimethylsilyl)ethynyl groups. The porphyrins **8-15** shown in Table 2 have been prepared using aldehydes with these substituents at

the *meta*- or *para*-positions. In each mixed aldehyde condensation, a mixture of three expected porphyrins was produced and the desired porphyrin was obtained by column chromatography following the general procedure employed for porphyrin **8**. In some cases, faint additional porphyrinic bands were observed, but these putative scrambled porphyrin products, derived from dipyrromethane acidolysis, did not interfere with the isolation of the desired AB_2C-porphyrin.

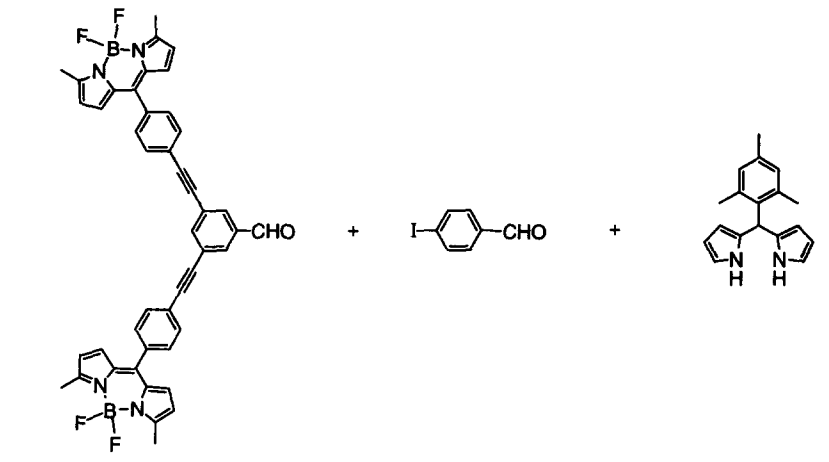
Table 2. AB_2C-porphyrin building blocks.

Porphyrin	Ar_1	Ar_2	Yield (%)
8			14
9			15
10			13
11			12
12			11
13			20
14			13
15			15

We focused on the issue of dipyrromethane acidolysis by examining the crude reaction mixture formed upon condensation of 3-iodobenzaldehyde, TMS-ethynylbenzaldehyde **1**, and 5-mesityldipyrromethane. LD-MS analysis of the crude reaction mixture (following removal of the quinone) showed dominant peaks at *m/z* 891.6 [porphyrin with substituents of $(TMS\text{-}CC)_2$, Ms_2], 921.3 [**10**], and 951.1 [**5**] due to the three expected porphyrins, much smaller peaks at *m/z* 836.7 [(TMS-CC), Ms_3] and 866.5 [I, Ms_3] attributed to porphyrins formed upon scrambling of 5-mesityldipyrromethane, weak peaks at *m/z* 794.8 (derived from **10**) and 825.6 (derived from **5**) characteristic of iodo-substituted porphyrins that have undergone iodide photolysis upon mass spectral analysis, and extremely weak peaks (slightly above the baseline noise) ranging from *m/z* 870-1030 of unknown identity. However, upon column chromatography the desired porphyrin **10** was obtained in pure form without the presence of any other porphyrins. Thus, the limited acidolysis that occurs with 5-mesityldipyrromethane was overcome upon purification. Furthermore, the mass spectrum of each purified porphyrin (**5**-**16**) was devoid of molecular ion peaks expected upon scrambling.

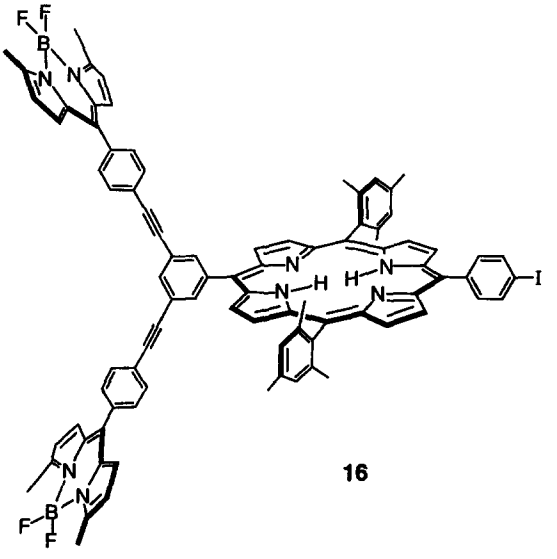
We sought to broaden the scope of the porphyrin building blocks by constructing a multipigment structure containing two accessory pigments, one porphyrin, and one reactive functional group. Such a building block is of interest as the input unit in various molecular photonic devices. We selected boron-dipyrrin dyes as the accessory pigments for the following reasons. (1) The strong absorption of boron-dipyrrin dyes in the green region complements the strong absorption of porphyrins in the blue, affording a combination with effective absorption across the solar spectrum. (2) Boron-dipyrrin dyes undergo efficient excited-state energy transfer with free base and zinc porphyrins. (3) The sharp absorption band of the boron-dipyrrin dyes enables their relatively selective excitation in the presence of porphyrins.[22,23] These attractive features have prompted us to use the boron-dipyrrin dye as the input unit of the molecular photonic wire,[10] in optoelectronic gates,[11] and in light-harvesting arrays.[23] In the molecular wire and gates, one boron-dipyrrin unit was positioned at the *p*-position of the *meso*-aryl ring and served as the sole input chromophore. In the light-harvesting arrays, as many as eight boron-dipyrrin units were positioned around the porphyrin by substitution at the *m*-position of the *meso*-aryl ring. In order to focus excitation predominantly at one site in a molecular photonic device, two boron-dipyrrin dyes can be positioned on one *meso*-aryl ring, with the remainder of the molecular device architecture elaborated from the opposing *meso*-aryl ring. The multipigment building block **16** is compatible with this design, using the iodo group as a handle for linking to the remainder of the molecular device (Scheme 3).

The multipigment building block (**16**) was synthesized by condensation of 5-mesityldipyrromethane, the appropriate $(boron\text{-}dipyrrin)_2$benzaldehyde,[23] and 4-iodobenzaldehyde in $CHCl_3$ at room temperature (Scheme 3). The crude reaction mixture was purified using two column chromatography procedures, affording the desired porphyrin **16** in 27% yield. The porphyrin Soret band and the boron-dipyrrin absorption band appear at 423 and 516 nm, respectively. The success of this reaction provides direct access to a useful component for building various molecular photonic devices, and augurs well for the use of dipyrromethane-aldehyde condensations in the construction of more elaborate porphyrin building blocks.



(Boron-dipyrrin)$_2$benzaldehyde

1. $BF_3O(Et)_2$, 25 °C
2. DDQ, 25 °C



16

Scheme 3. Direct formation of a multipigment building block.

EXPERIMENTAL

General. 3-Iodobenzaldehyde and 4-iodobenzaldehyde were obtained from Karl Industries. All other reagents were purchased from Aldrich. Solvents (A.C.S. grade) were obtained from Fisher. $CHCl_3$ (stabilized with EtOH) was distilled from K_2CO_3. Triethylamine was distilled from CaH_2. Column chromatography was performed using silica (Baker flash silica) or alumina (Fisher, 80-200 mesh). All reported NMR results were acquired at 300 MHz (General Electric GN300 or Varian Gemini 300). Mass spectra of porphyrins were obtained in neat form by laser desorption mass spectrometry (LD-MS) using a Bruker Proflex II, or fast atom bombardment (FAB-MS) using a JEOL HX110HF mass spectrometer. Porphyrins can be analyzed effectively with laser desorption mass spectrometry in the absence of any added matrix.[24] Gas chromatography was performed using an HP 6890, and GC-MS was performed using an HP 5890. GC or GC-MS conditions used were as follows: temp 1, 100 °C (3 min); temp 2, 270 °C (10 min); rate 10 °C/min, total runtime 30 min, column type HP-5. Absorption spectra were collected with an HP 8453 or Cary 3 UV-Vis absorption spectrometer.

Standard procedure for the formation and purification of porphyrins (except 6 and 16). Samples of 5-mesityldipyrromethane and the appropriate aldehyde(s) were dissolved in $CHCl_3$ under Ar in a one-neck round-bottom flask. $BF_3{\cdot}O(Et)_2$ (3.3 mM) was added to initiate the condensation. The reaction mixture was stirred for 1 h under Ar. Then DDQ was added to the reaction mixture and stirring was continued for another 1 h. The solvent was removed, the crude mixture was dissolved in $CHCl_3$ (10 mL), silica gel (1-2 g) was added, and the resulting slurry was concentrated to dryness. The dark powder was poured on top of a silica column (4.8 x 30 cm, slurry-packed with the eluant) and slow gravity elution with hexanes/$CHCl_3$ or hexanes/CH_2Cl_2 mixture was started. The typical elution rate was 6-8 mL/min and the total elution required 4-10 h. The eluant collected prior to the elution of any components was recycled. For the porphyrins prepared by reaction of 5-mesityldipyrromethane and one aldehyde (**5**, **7**), only one porphyrin was observed in each reaction mixture. For the porphyrins prepared by reaction of 5-mesityldipyrromethane and two aldehydes (**8**-**15**), the three expected porphyrins are observed as distinct bands after ~2 h. The desired porphyrin was the second band. Following the elution of the three bands, other more slowly eluting, rather faint porphyrinic bands also were observed. Dark materials were left on the top of the column. The solvent consumed in this chromatography procedure was ~1.5 L. The desired porphyrin was rechromatographed in an identical manner for final purification.

4-[2-(trimethylsilyl)ethynyl]benzaldehyde (1). 4-Iodobenzaldehyde (5.00 g, 21.4 mmol) and $AsPh_3$ (0.529 g, 1.73 mmol) were dissolved in 40 mL of TEA in a 100 mL one-neck round-bottom flask. The round-bottom flask was fitted with a rubber septum and two needles (Ar inlet and outlet). The solution was purged with Ar for 10 min. (Trimethylsilyl)acetylene (3.60 mL, 25.9 mmol) and $Pd_2(dba)_3$ (198 mg, 0.214 mmol) were added and the Ar flow was continued for an additional 30 min. The needles were removed and the rubber septum was sealed with Parafilm. [Note that the vessel must be sealed effectively due to the high volatility of trimethylsilylacetylene (bp 53 °C).] The reaction mixture was then placed in an oil bath at 35 °C and allowed to stir for 12 h. At this point a reaction aliquot was removed via a microliter syringe and analyzed by GC [t_R(4-iodobenzaldehyde) = 7.8 min, t_R(**1**) = 10.2 min, t_R(putative enyne product) = 15.3 min, $t_R(AsPh_3)$ = 18.2 min]. Upon completion of the reaction as judged by GC the reaction mixture was cooled to room temperature and gravity filtered. The solid filter cake was washed repeatedly with CH_2Cl_2 until the washings were colorless. The filtrate was concentrated by rotary evaporation to afford a dark brown oil which solidified upon standing overnight at 0 °C. The crude solid was dissolved in CH_2Cl_2 (10 mL) and silica gel (~2 g) was added to the solution. The resulting slurry was rotary evaporated to a fine powder. The powder was loaded on top of a flash silica column (4.8 x 10 cm) packed with hexanes. The residual $AsPh_3$ was eluted with hexanes, then the desired compound along with the putative enyne were eluted with hexanes/CH_2Cl_2 (1:1). Removal of

the solvent via rotary evaporation afforded a light yellow solid. A careful Kugelrohr distillation (75 - 80 °C/0.04 mmHg) of the yellow solid afforded a white solid (3.45 g, 80%). [Note that **1** was distilled leaving the putative enyne behind; the success of this purification step was confirmed by GC analysis.] Alternatively, the yellow solid was recrystallized from isopropanol (2.80 g, 64%). Analytical data were identical with the reported data.[14]

4-Ethynylbenzaldehyde (2). Following a known procedure,[14] anhydrous K_2CO_3 (90.0 mg, 0.651 mmol) was added to a solution of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (1.00 g, 4.94 mmol) in 15 mL of methanol. The mixture was stirred at room temperature under Ar for 3 h. The solvent was removed and the crude compound was dissolved in CH_2Cl_2. The organic layer was washed with $NaHCO_3$ (5%, 2 x 50 mL) and dried (Na_2SO_4). Removal of the solvent gave a light yellowish solid. Kugelrohr distillation (65 - 70 °C/0.05 mmHg) of the light yellow solid afforded a white solid (432 mg, 67%). Analytical data were identical with the reported data.[14]

3-[2-(trimethylsilyl)ethynyl]benzaldehyde (3). Following the procedure described for compound **1**, 3-iodobenzaldehyde (5.00 g, 21.4 mmol) was coupled with (trimethylsilyl)acetylene (3.60 mL, 25.9 mmol) in 40 mL of TEA in the presence of $Pd_2(dba)_3$ (198 mg, 0.214 mmol) and $AsPh_3$ (0.529 g, 1.73 mmol). The progress of the reaction was monitored by GC [t_R(3-iodobenzaldehyde) = 7.7 min, t_R(**3**) = 10.1 min]. Column chromatography (silica, hexanes/CH_2Cl_2, 1:1) of the crude reaction mixture gave a yellow oil which upon Kugelrohr distillation (90 °C/0.06 mmHg) afforded a colorless oil (3.52 g, 81%). Analytical data were identical with the reported data.[14]

3-Ethynylbenzaldehyde (4). Following a known procedure,[14] 3-[2-(trimethylsilyl)ethynyl]-benzaldehyde (1.00 g, 4.94 mmol) was treated with anhydrous K_2CO_3 (90.0 mg, 0.651 mmol) in 15 mL of methanol. The workup procedure was performed as described for compound **2**. Kugelrohr distillation (62 °C/0.05 mmHg) afforded a white flaky solid (415 mg, 65%). Analytical data were identical with the reported data.[14]

5,15-Dimesityl-10,20-bis(3-iodophenyl)porphyrin (5). A solution of 3-iodobenzaldehyde (878 mg, 3.78 mmol) and 5-mesityldipyrromethane[19] (1.00 g, 3.78 mmol) in 500 mL of $CHCl_3$ was treated with $BF_3{\cdot}O(Et)_2$ (660 μL of 2.5 M stock solution in $CHCl_3$, 3.3 mM). After 1 h, DDQ (860 mg, 3.78 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (1:1) afforded a purple solid (490 mg, 27%). ^{1}H NMR ($CDCl_3$) δ -2.70 (s, 2 H, NH), 1.83 (s, 12 H, $ArCH_3$), 2.62 (s, 6 H, $ArCH_3$), 7.27 (s, 4 H, ArH), 7.46 (t, 2 H, J = 8 Hz, ArH), 8.10 (d, 2 H, J = 9 Hz, ArH), 8.17 (d, 2 H, J = 9 Hz, ArH), 8.56 (s, 2 H, ArH), 8.70 (d, 4 H, J = 6 Hz, β-pyrrole), 8.76 (d, 4 H, J = 6 Hz, β-pyrrole); $C_{50}H_{40}N_4I_2$, calcd avg mass 950.1, obsd *m/z* 948.4 (LD-MS); calcd exact (M^+) 950.1343, obsd *m/z* 950.1347 (FAB-MS); λ_{abs} (CH_2Cl_2) 420, 516, 550, 591, 646 nm.

5,15-Dimesityl-10,20-bis(3,5-diiodophenyl)porphyrin (6). A solution of 3,5-diiodo-benzaldehyde[22] (17.9 mg, 0.05 mmol) and 5-mesityldipyrromethane[19] (13.2 mg, 0.05 mmol) in 5 mL of $CHCl_3$ was treated with $BF_3{\cdot}O(Et)_2$ (13.2 μL of 2.5 M stock solution in $CHCl_3$, 6.6 mM). After 75 min, DDQ (8.60 mg, 0.0376 mmol) was added and stirring was continued for 1 h. The solvent was removed and flash chromatography (silica, CH_2Cl_2/hexanes 1:1, 3.8 x 15 cm) gave a purple solid (8.00 mg, 27%). ^{1}H NMR ($CDCl_3$) δ -2.77 (s, 2 H, NH), 1.82 (s, 12 H, *o*-$ArCH_3$), 2.63 (s, 6 H, *p*-$ArCH_3$), 7.28 (s, 4 H, *m*-ArH), 8.47 (d, 2 H, J = 1.5 Hz, *p*-ArH), 8.50 (d, 4 H, J = 1.5 Hz, *o*-ArH), 8.73 (m, 8 H, β-pyrrole); $C_{50}H_{38}N_4I_4$, calcd avg mass 1202.5, obsd *m/z* 1201.2 (LD-MS); calcd exact (M^+) 1201.9276, obsd *m/z* 1202.0 (FAB-MS); λ_{abs} (ε in $M^{-1}cm^{-1}$) (toluene) 421 (395,000), 515 (18,900), 548 (6,900), 592 (5,600), 648 nm (3,400).

5,15-Dimesityl-10,20-bis{3-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (7). A solution of **3** (191 mg, 0.946 mmol) and 5-mesityldipyrromethane[19] (250 mg, 0.946 mmol) in 125 mL of $CHCl_3$ was treated with $BF_3{\cdot}O(Et)_2$ (165 μL of 2.5 M stock solution in $CHCl_3$, 3.3 mM). After 1 h, DDQ (215 mg, 0.946 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (1:1) gave a purple solid (232 mg, 27%). ^1H NMR ($CDCl_3$) δ -2.68 (s, 2 H, NH), 0.26 (s, 18 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.66 (t, 2 H, J = 8 Hz, ArH), 7.88 (d, 2 H, J = 9 Hz, ArH), 8.14 (d, 2 H, J = 9 Hz, ArH), 8.33 (s, 2 H, ArH), 8.69 (d, 4 H, J = 6 Hz, β-pyrrole), 8.73 (d, 4 H, J = 6 Hz, β-pyrrole); $C_{60}H_{58}N_4Si_2$, calcd avg mass 890.4, obsd *m/z* 891.6 (LD-MS); calcd exact (M^+) 890.4200, obsd *m/z* 890.4233 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 514, 548, 590, 646 nm.

5,15-Dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-iodophenyl)porphyrin (8). A solution of 4-iodobenzaldehyde (116 mg, 0.5 mmol), **1** (101 mg, 0.5 mmol), and 5-mesityldipyrromethane[19] (264 mg, 1 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3{\cdot}O(Et)_2$ (132 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (350 mg, 1.54 mmol) was added. Chromatography with hexanes/$CHCl_3$ (4:1) gave a purple solid (65.0 mg, 14%). ^1H NMR ($CDCl_3$) δ -2.66 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.85 (d, 2 H, J = 9 Hz, ArH), 7.94 (d, 2 H, J = 9 Hz, ArH), 8.07 (d, 2 H, J = 9 Hz, ArH), 8.16 (d, 2 H, J = 9 Hz, ArH) 8.70 (s, 4 H, β-pyrrole), 8.76 (s, 4 H, β-pyrrole); $C_{55}H_{49}N_4ISi$, calcd avg mass 920.3, obsd *m/z* 920.6 (LD-MS); calcd exact (M^+) 920.2771, obsd *m/z* 920.2772 (FAB-MS); λ_{abs} (CH_2Cl_2) 420, 515, 550, 591, 647 nm.

5,15-Dimesityl-10-{3-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-iodophenyl)porphyrin (9). A solution of 4-iodobenzaldehyde (116 mg, 0.5 mmol), **3** (101.2 mg, 0.5 mmol) and 5-mesityldipyrromethane[19] (264 mg, 1 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3{\cdot}O(Et)_2$ (132 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (350 mg, 1.54 mmol) was added. Chromatography with hexanes/$CHCl_3$ (4:1) gave a purple solid (70 mg, 15%). ^1H NMR ($CDCl_3$) δ -2.68 (s, 2 H, NH), 0.267 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.67 (t, 1 H, J = 8 Hz, ArH), 7.88 (d, 1 H, J = 6 Hz, ArH), 7.95 (d, 2 H, J = 6 Hz, ArH), 8.08 (d, 2 H, J = 6 Hz, ArH), 8.14 (d, 1 H, J = 6 Hz, ArH), 8.33 (s, 1 H, ArH), 8.69-8.75 (m, 8H, β-pyrrole); $C_{55}H_{49}N_4ISi$, calcd avg mass 920.3, obsd *m/z* 920.1 (LD-MS); calcd exact (M^+) 920.2771, obsd *m/z* 920.2776 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 515, 549, 590, 646 nm.

5,15-Dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(3-iodophenyl)porphyrin (10). A solution of 3-iodobenzaldehyde (116 mg, 0.5 mmol), **1** (101 mg, 0.5 mmol) and 5-mesityldipyrromethane[19] (264 mg, 1 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3{\cdot}O(Et)_2$ (132 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (350 mg, 1.54 mmol) was added. Chromatography with hexanes/$CHCl_3$ (4:1) gave a purple solid (60.0 mg, 13%). ^1H NMR ($CDCl_3$) δ -2.67 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.62 (s, 6 H, $ArCH_3$), 7.27 (s, 4 H, ArH), 7.45 (t, 1 H, J = 8 Hz, ArH), 7.86 (d, 2 H, J = 6 Hz, ArH), 8.10-8,17 (m, 4 H, ArH), 8.58 (s, 1 H, ArH), 8.71-8.77 (m, 8H, β-pyrrole); $C_{55}H_{49}N_4ISi$, calcd avg mass 920.3, obsd *m/z* 920.1 (LD-MS); calcd exact (M^+) 920.2771, obsd *m/z* 920.2794 (FAB-MS); λ_{abs} (CH_2Cl_2) 420, 515, 550, 590, 646 nm.

5,15-Dimesityl-10-{3-[2-(trimethylsilyl)ethynyl]phenyl}-20-(3-iodophenyl)porphyrin (11). A solution of 3-iodobenzaldehyde (116 mg, 0.5 mmol), **3** (101 mg, 0.5 mmol) and 5-mesityldipyrromethane[19] (264 mg, 1 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3{\cdot}O(Et)_2$ (132 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (350 mg, 1.54 mmol) was added. Chromatography with hexanes/$CHCl_3$ (4:1) gave a purple solid (55.0 mg, 12%). ^1H NMR ($CDCl_3$) δ -2.68 (s, 2 H, NH), 0.26 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 7.28 (s, 4 H, ArH), 7.46 (t, 1 H, J = 8 Hz, ArH), 7.67 (t, 1 H, J = 8 Hz, ArH), 7.88 (d, 1 H, J = 9 Hz, ArH), 8.11 (d, 1 H, J = 9 Hz, ArH), 8.18 (m, 2 H,

ArH), 8.33 (s, 1 H, ArH), 8.58 (s, 1 H, ArH), 8.70-8.76 (m, 8H, β-pyrrole); $C_{55}H_{49}N_4ISi$, calcd avg mass 920.3, obsd *m/z* 920.1 (LD-MS); calcd exact (M^+) 920.2771, obsd *m/z* 920.2833 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 514, 548, 590, 646 nm.

5,15-Dimesityl-10-{3-[2-(trimethylsilyl)ethynyl]phenyl}-20-(3-ethynylphenyl)-porphyrin (12). A solution of **3** (155 mg, 0.768 mmol), **4** (100 mg, 0.768 mmol) and 5-mesityldipyrromethane[19] (406 mg, 1.54 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3{\cdot}O(Et)_2$ (132 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (523 mg, 2.31 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (7:3) gave a purple solid (70.0 mg, 11%). ^1H NMR ($CDCl_3$) δ -2.67 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 3.16 (s, 1 H, CCH), 7.28 (s, 4 H, ArH), 7.68 (m, 2 H, ArH), 7.89 (m, 2 H, ArH), 8.17 (m, 2H, ArH), 8.34 (d, 2H, J = 6 Hz, ArH), 8.69-8.73 (m, 8 H, β-pyrrole); $C_{57}H_{50}N_4Si$, calcd avg mass 818.4, obsd *m/z* 818.4 (LD-MS); calcd exact (M^+) 818.3805, obsd *m/z* 818.3785 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 514, 548, 591, 646 nm.

5,15-Dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(3-ethynylphenyl)-porphyrin (13). A solution of **1** (38.9 mg, 0.192 mmol), **4** (25 mg, 0.193 mmol) and 5-mesityldipyrromethane[19] (102 mg, 0.386 mmol) in $CHCl_3$ (25 mL) was treated with $BF_3{\cdot}O(Et)_2$ (33 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (130 mg, 0.573 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (7:3) gave a purple solid (31.0 mg, 20%). ^1H NMR ($CDCl_3$) δ -2.66 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 3.12 (s, 1 H, CCH), 7.28 (s, 4 H, ArH), 7.70 (t, 1 H, J = 8 Hz, ArH), 7.88 (m, 3 H, ArH), 8.18 (m, 3H, ArH), 8.35 (s, 1H, ArH), 8.70-8.76 (m, 8 H, β-pyrrole); $C_{57}H_{50}N_4Si$, calcd avg mass 818.4, obsd *m/z* 818.9 (LD-MS); calcd exact (M^+) 818.3805, obsd *m/z* 818.3772 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 515, 550, 591, 646 nm.

5,15-Dimesityl-10-{3-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-ethynylphenyl)-porphyrin (14). A solution of **2** (25.0 mg, 0.192 mmol), **3** (38.9 mg, 0.192 mmol) and 5-mesityldipyrromethane[19] (102 mg, 0.386 mmol) in $CHCl_3$ (25 mL) was treated with $BF_3{\cdot}O(Et)_2$ (33 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (130 mg, 0.573 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (7:3) gave a purple solid (20.0 mg, 13%). ^1H NMR ($CDCl_3$) δ -2.66 (s, 2 H, NH), 0.26 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 3.30 (s, 1 H, CCH), 7.28 (s, 4 H, ArH), 7.67 (t, 1 H, J = 8 Hz, ArH), 7.88 (m, 3 H, ArH), 8.17 (m, 3H, ArH), 8.34 (s, 1H, ArH), 8.70-8.76 (m, 8 H, β-pyrrole); $C_{57}H_{50}N_4Si$, calcd avg mass 818.4, obsd *m/z* 818.7 (LD-MS); calcd exact (M^+) 818.3805, obsd *m/z* 818.3782 (FAB-MS); λ_{abs} (CH_2Cl_2) 419, 515, 549, 590, 646 nm.

5,15-Dimesityl-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-(4-ethynylphenyl)-porphyrin (15). A solution of **1** (77.7 mg, 0.384 mmol), **2** (50.0 mg, 0.384 mmol) and 5-mesityldipyrromethane[19] (203 mg, 0.768 mmol) in $CHCl_3$ (50 mL) was treated with $BF_3{\cdot}O(Et)_2$ (66 μL of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (265 mg, 1.17 mmol) was added. Chromatography with hexanes/CH_2Cl_2 (7:3) gave a purple solid (48.0 mg, 15%). ^1H NMR ($CDCl_3$) δ -2.65 (s, 2 H, NH), 0.37 (s, 9 H, $SiCH_3$), 1.83 (s, 12 H, $ArCH_3$), 2.63 (s, 6 H, $ArCH_3$), 3.31 (s, 1 H, CCH), 7.28 (s, 4 H, ArH), 7.86 (m, 4 H, ArH), 8.17 (m, 4 H, ArH), 8.70-8.76 (m, 8 H, β-pyrrole); $C_{57}H_{50}N_4Si$, calcd avg mass 818.4, obsd *m/z* 818.3 (LD-MS); calcd exact (M^+) 818.3805, obsd *m/z* 818.3781 (FAB-MS); λ_{abs} (CH_2Cl_2) 420, 515, 550, 591, 647 nm.

5,15-Dimesityl-10-[3,5-bis{2-[4-(N,N′-difluoroboryl-1,9-dimethyldipyrrin-5-yl)-phenyl]ethynyl}phenyl]-20-(4-iodophenyl)porphyrin (16). Samples of 3,5-bis{2-[4-(N,N′-difluoroboryl-1,9-dimethyldipyrrin-5-yl)phenyl]ethynyl}benzaldehyde[23] (60.0 mg, 0.081 mmol), 4-iodobenzaldehyde (19.0 mg, 0.081 mmol) and 5-mesityldipyrromethane[19] (43.0 mg, 0.162 mmol) were

dissolved in 8.1 mL of $CHCl_3$. $BF_3{\cdot}O(Et)_2$ (21.4 μL of 2.5 M stock solution, 6.6 mM) was added to initiate the reaction. The reaction mixture was stirred at room temperature for 1 h. DDQ (55.0 mg, 0.243 mmol) was added and the mixture was stirred for another 1 h at room temperature. Six colored components and some baseline materials were detected by TLC analysis (silica, CH_2Cl_2/hexane 2:1). The solvent was removed and the mixture was passed through a short column (silica, CH_2Cl_2, 3.8 x 15 cm) to remove the baseline materials, affording a mixture of six components. Chromatography (silica, CH_2Cl_2/hexane 2:1) removed the first three components. The last three components were then eluted upon enrichment with CH_2Cl_2. The mixture of the last three components was rechromatographed (silica, CH_2Cl_2/hexanes 5:2, 3.8 x 15 cm), yielding **16** as the second component (32.0 mg, 27%). ^1H NMR ($CDCl_3$) δ -2.66 (s, 2 H, NH), 1.85 (s, 12 H, $ArCH_3$), 2.64 [s, 18 H, pyrrole-CH_3 (12 H) and $ArCH_3$ (6 H)], 6.28 (m, 4 H, pyrrole-H), 6.71 (m, 4 H, pyrrole-H), 7.30 (s, 4 H, ArH), 7.49 (AA'BB', 4 H, ArH), 7.67 (AA'BB', 4 H, ArH), 7.96 (AA'BB', 2 H, ArH), 8.09 (AA'BB', 2 H, ArH), 8.19 (m, 1 H, ArH), 8.42 (m, 2 H, ArH), 8.72-8.86 (m, 8 H, β-pyrrole); $C_{88}H_{67}N_8B_2F_4I$, calcd avg mass 1461.1, obsd *m/z* 1462.0 (LD-MS); calcd exact (M^+) 1460.4656, obsd *m/z* 1460.5 (FAB-MS); λ_{abs} (ε in $M^{-1}cm^{-1}$) (toluene) 423 (464,000), 516 (154,000), 592 (6,200), 648 nm (4,100).

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