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Synthesis of β-Substituted Porphyrin Building Blocks and Conversion to Diphenylethyne-Linked Porphyrin Dimers

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Abstract: A recent hypothesis concerning effects of orbital ordering on electronic communication (excited-state energy transfer, ground-state hole-hopping) in covalently linked porphyrin arrays prompted the development and application of methodology for the synthesis of β-linked porphyrin dimers. Reaction of a β-substituted pyrrole with 2-hydroxymethylpyrrole led to the dipyrromethane bearing a single β-substituent and no *meso*- nor α-substituents. Condensation of the β-substituted dipyrromethane with an aldehyde and a *meso*-substituted dipyrromethane gave the desired β-substituted porphyrin building block, albeit in low yield. Four building blocks were prepared with a *p*-iodophenyl or *p*-ethynylphenyl group at one β-position, no substituent at the flanking *meso*-position, and mesityl or pentafluorophenyl groups at the three non-flanking *meso*-positions. The porphyrin building blocks were coupled via Pd-mediated reactions, affording diphenylethyne-linked dimers with the linker attached at β-positions. This approach provided access to zinc-free base porphyrin dimers and bis-zinc dimers bearing mesityl or pentafluorophenyl groups at the three non-linking *meso*-positions. The availability of these dimers and monomeric benchmarks enabled a critical test of the orbital ordering hypothesis. This methodology for preparing porphyrin building blocks bearing a lone, non-hindered β-substituent complements existing methods for preparing *meso*-substituted porphyrin building blocks. The ability to position the linker at the *meso*- or β-positions provides a desirable level of versatility for incorporating porphyrinic molecules with an a_{2u} or a_{1u} HOMO in various molecular devices.

Keywords: alkynes; orbital effects; porphyrins; pyrroles.

As part of a program aimed at the rational design and synthesis of molecular photonic devices, we recently prepared a set of porphyrin dimers containing a Zn porphyrin and a free base (Fb) porphyrin joined by a diarylethyne linker at the *meso*-positions (Chart 1).[1] One dimer has mesityl groups at all non-linking *meso*-positions (ZnFbU), while the other has pentafluorophenyl groups at all non-linking *meso*-positions (F_{30}ZnFbU). Excited-state energy-transfer occurred with a rate of $(24\ ps)^{-1}$ in the former and $(240\ ps)^{-1}$ in the latter. In both cases the energy-transfer process is dominated by a through-bond mechanism mediated by the diphenylethyne linker. We attributed this 10-fold rate difference to the reversal of orbital ordering in the two dimers, as the Zn porphyrin in ZnFbU has an $a_{2u}(\pi)$ HOMO while F_{30}ZnFbU has an $a_{1u}(\pi)$ HOMO. The $a_{2u}(\pi)$ and $a_{1u}(\pi)$ orbitals, which constitute the two nearly degenerate HOMOs of porphyrins,[2] have significantly different electron-density distributions. The $a_{2u}(\pi)$ orbital has electron density at the *meso*-positions and the central nitrogens, whereas the $a_{1u}(\pi)$ orbital has nodes at these positions but exhibits considerable electron density at the pyrrole carbons (Chart 1). The ordering of the two orbitals is altered by energetic stabilization/destabilization caused by electron-withdrawing/releasing groups arranged around the periphery of the porphyrin.[3] The extent of through-bond electronic communication between the porphyrins is proportional to the electron density at the site of attachment of the linker joining the porphyrins.[4-10] Thus, the presence of electron density at the *meso*-carbons in the HOMO of ZnFbU, and the presence of a node at the *meso*-carbons in the HOMO of F_{30}ZnFbU, provides an explanation of the observed rates.

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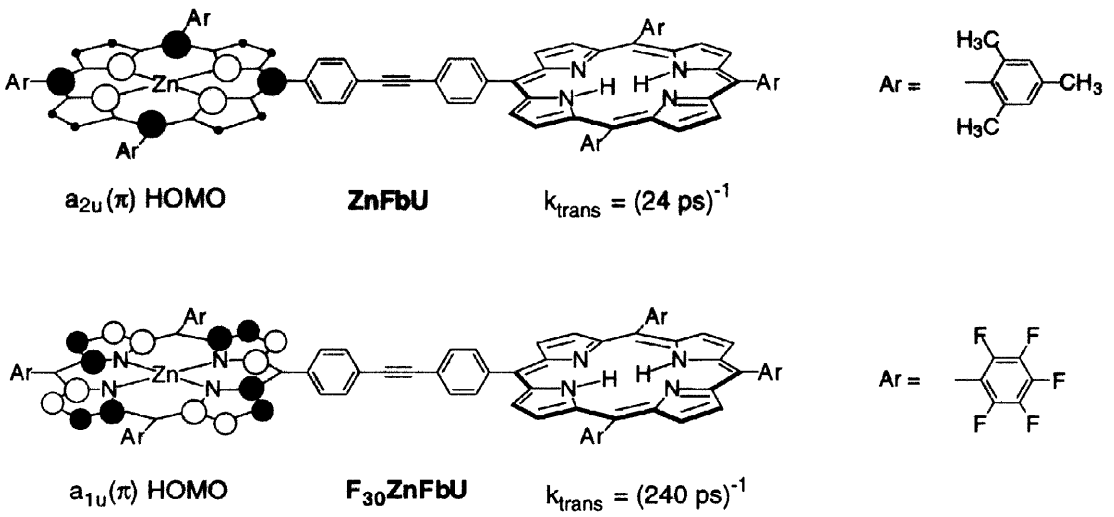


Chart 1. *Meso*-linked dimers.

This orbital-ordering hypothesis[1] led to the prediction that a β-linked ZnFb dimer with an a_{1u} HOMO (obtained with pentafluorophenyl groups at the non-linking *meso*-positions) should give a faster rate of energy transfer than the β-linked ZnFb dimer with an a_{2u} HOMO (obtained with mesityl groups at the non-linking *meso*-positions). In this paper, we describe the synthesis of the β-linked dimers (ZnFbU-β, F_{30}ZnFbU-β) and appropriate monomeric porphyrin benchmarks required to test this hypothesis (Chart 2). The design of these dimers required the development of methodology for the synthesis of dipyrromethanes bearing a single β-substituent and no other substituents.

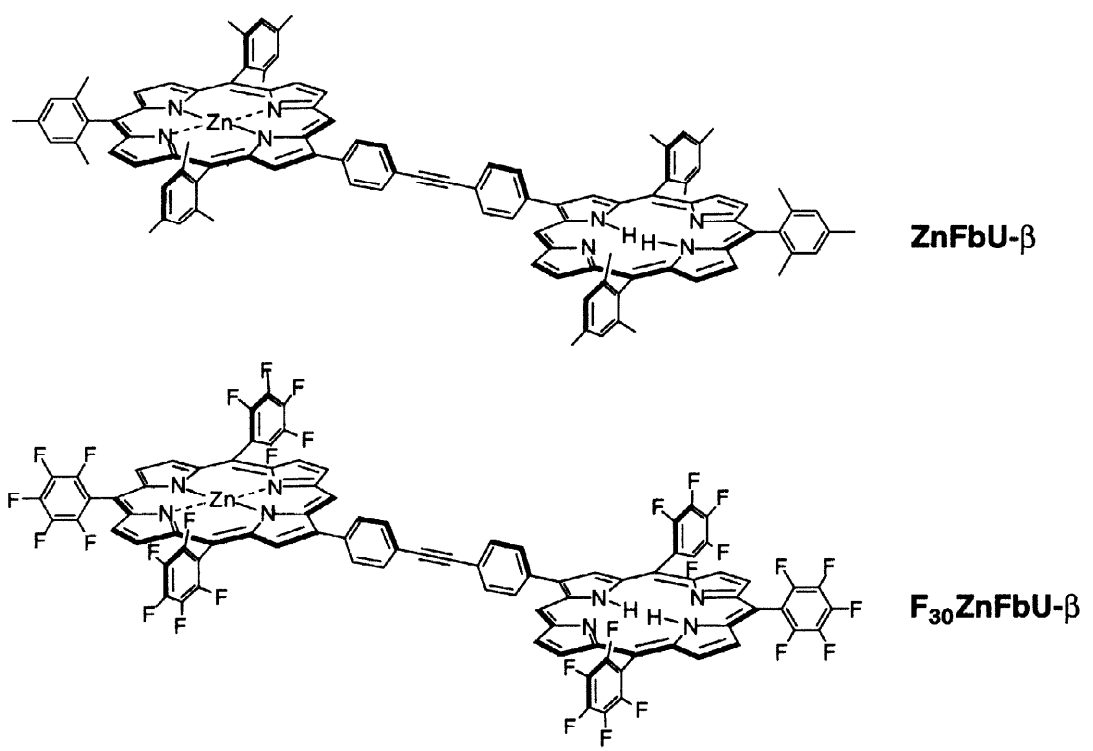
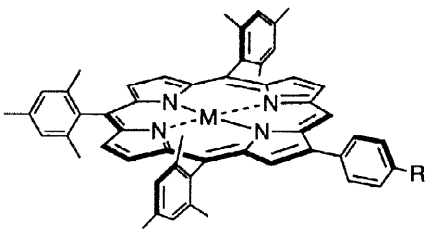
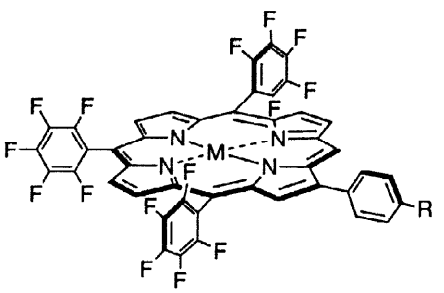


Chart 2. β-Linked dimers.

In testing the orbital-ordering hypothesis, the rate of excited-state energy transfer was found to be (56 ps)$^{-1}$ for ZnFbU-β and (24 ps)$^{-1}$ for F_{30}ZnFbU-β.[11] Thus, the presence of pentafluorophenyl groups causes *enhancement* of electronic communication in the β-linked dimers but *attenuation* in the *meso*-linked dimers. In other words, the combination of an a_{1u} HOMO with a β-linker or an a_{2u} HOMO with a *meso*-linker results in optimal electronic communication. More generally, the design of molecular photonic devices must take into account the nature of the frontier orbitals when considering the position of connection of a covalent linker. The ability to position the linker at the *meso*- or β-positions provides versatility in incorporating porphyrinic molecules with an a_{2u} or a_{1u} HOMO in various molecular devices.



M	R	Compd
H,H	I	**FbI-β**
Zn	I	**ZnI-β**
H,H	CCTMS	**FbU-β**
Zn	CCTMS	**ZnU-β**
Zn	CCH	**ZnU'-β**



M	R	Compd
H,H	I	**F_{15}FbI-β**
H,H	CCTBDMS	**F_{15}FbU-β**
Zn	CCTBDMS	**F_{15}ZnU-β**

Chart 3. Monomeric porphyrin intermediates and benchmarks.

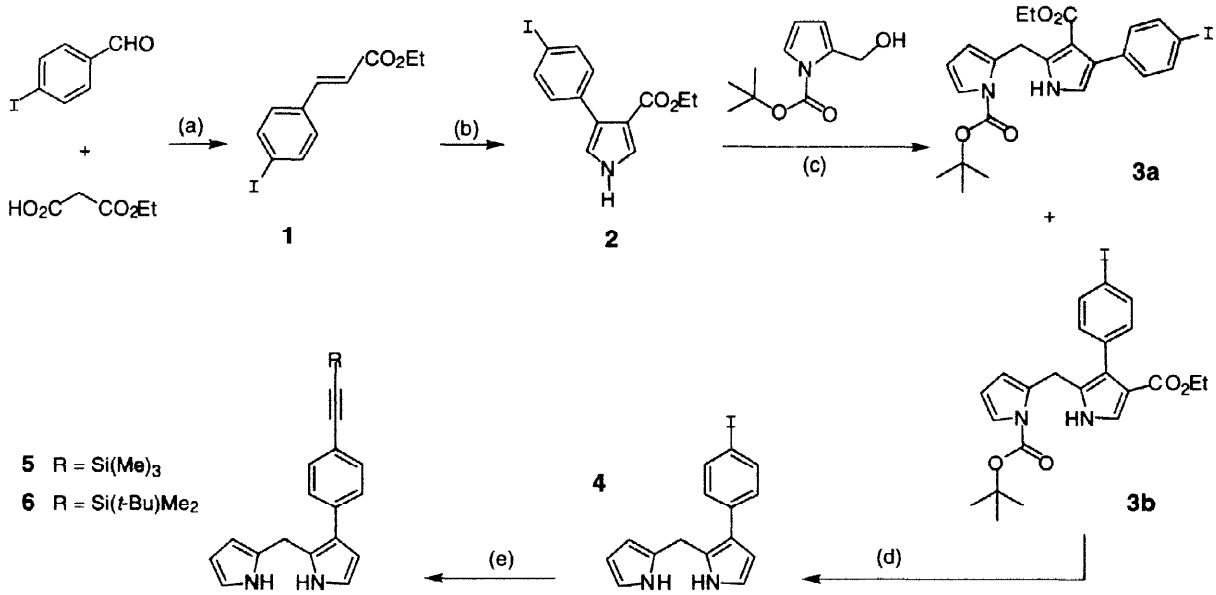
RESULTS AND DISCUSSION

The synthesis of β-linked dimers with each porphyrin in a defined metalation state required the development of methodology to fulfill the following requirements. (1) Access to monomeric porphyrin building blocks bearing *p*-iodophenyl or *p*-ethynylphenyl groups at the β-positions. Porphyrins with these types of synthetic handles can be linked via Pd-mediated coupling methods without alteration of the porphyrin metalation state.[12] (2) Absence of substitution at the *meso*-position flanking the β-substituent. The steric interactions of substituents at adjacent *meso*- and β-positions cause conformational deformation of the porphyrin,[13] which must be avoided for valid comparison of the β-linked and *meso*-linked dimers. (3) The ability to place a variety of groups at the three non-flanking *meso*-positions, which enables the ordering of the a_{2u} and a_{1u} orbitals to be tuned in a systematic manner. The methodology that meets these criteria extends established approaches using dipyrromethanes as precursors in the synthesis of *meso*-substituted porphyrin building blocks,[14] and complements approaches pioneered by Therien[15] and by Chan[16] for the synthesis of β-linked porphyrin dimers with flanking *meso*-substituents.

Synthesis of Dipyrromethanes

Reaction of 4-iodobenzaldehyde with monoethyl malonate under Knoevenagel conditions gave ethyl 4-iodocinnamate (**1**) in 88% yield. Treatment of **1** and tosylmethylisocyanide (TosMIC) with NaH using van Leusen's methodology[17] afforded 3-ethoxycarbonyl-4-(4-iodophenyl)pyrrole (**2**) in 65% yield. A major issue was whether to remove the ethoxycarbonyl group at this stage or after completing the synthesis of the

dipyrromethane. The latter course was selected for two reasons: (1) The ethoxycarbonyl pyrrole is expected to be more stable than the decarboxylated pyrrole. (2) Two regioisomers can be formed in the condensation with 2-hydroxymethyl-*N*-Boc-pyrrole and we felt that the electron withdrawing effect of the ester group might preferentially direct substitution to the 5-position.[18] The reaction of **2** and 2-hydroxymethyl-*N*-Boc-pyrrole under acidic conditions[19] afforded two regioisomers in a 2:1 ratio, in favor of the desired 5-substituted product (Scheme 1). The two isomers were easily separated by flash column chromatography. Removal of the ethoxycarbonyl and Boc groups was achieved in a one-flask reaction by treatment with powdered NaOH in ethylene glycol at 195-200 °C for 1 h, giving **4** in 69% yield.



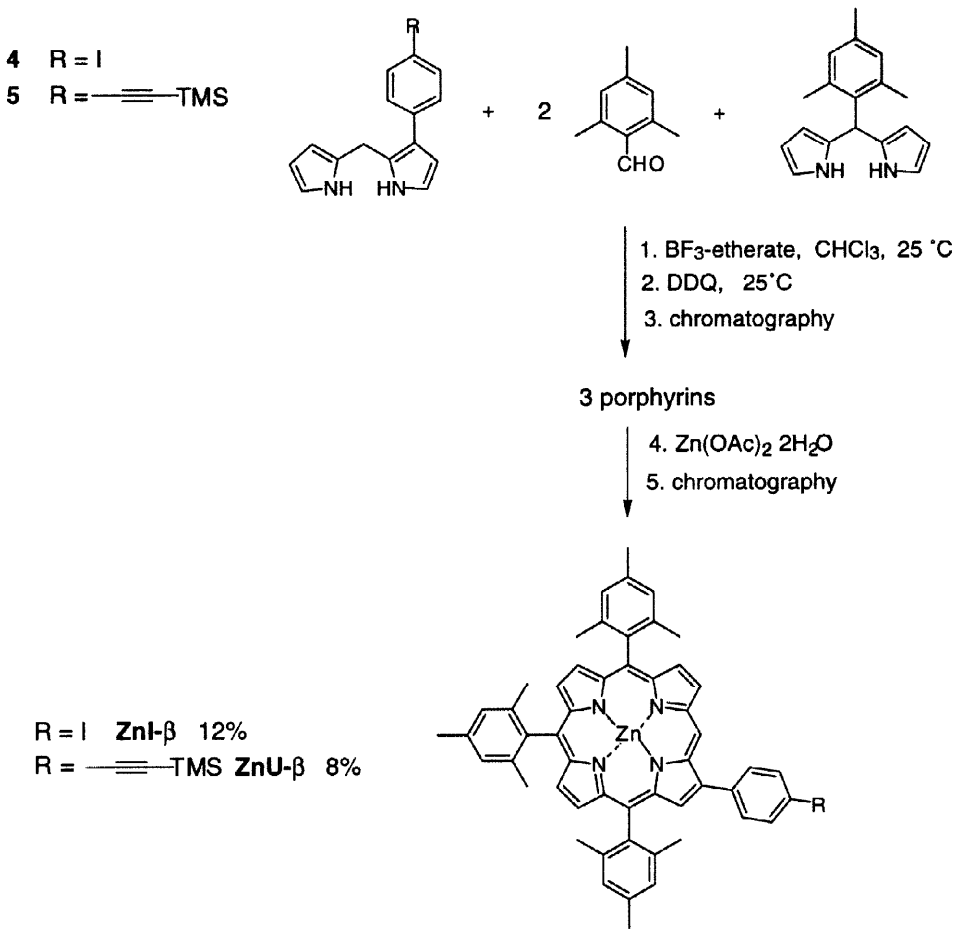
Scheme 1. Synthesis of dipyrromethanes. (a) Piperidine, pyridine, reflux 7 h, 83% yield. (b) Tosylmethylisocyanide (TosMIC), NaH, Et_2O/DMSO (2:1), room temperature, 1 h, Ar, 65% yield. (c) 1,4-Dioxane, 10% aq HCl, room temperature, 18 h, 68% yield (**3a** and **3b**, 1:2). (d) Ethylene glycol, NaOH, 195-200 °C, 1 h, Ar, 69% yield. (e) Trimethylsilylacetylene or *tert*-butyldimethylsilylacetylene, $Pd_2(dba)_3$, Ph_3As, THF/Et_3N (1:1). 30-36 h, Ar, 60% yield (**5**); 55% yield (**6**).

Attempted preparation of 3-(4-(2-trimethylsilyl)ethynyl)phenyldipyrromethane via the same strategy from the trimethylsilylethynyl cinnamic acid derivative failed due to loss of the protecting group. Accordingly, we incorporated the ethynyl group by Pd-mediated coupling ($AsPh_3$, $Pd_2(dba)_3$, THF/Et_3N (1:1), 35 °C)[20] of trimethylsilylacetylene and **4**, which afforded the ethynyldipyrromethane **5** in a rather sluggish reaction (Scheme 1). **5** was obtained in 60% yield (95% purity based on ^1H NMR spectroscopy) after lengthy purification involving chromatography followed by Kugelrohr distillation. Use of *tert*-butyldimethylsilylacetylene also proceeded slowly (24-36 h), but the purification was simplified and **6** was obtained after a single flash column in 55% yield. Dipyrromethanes **5** and **6** required storage at 0 °C and were used in subsequent chemistry within a few days of preparation.

Synthesis of β-substituted porphyrins

Under porphyrin-forming conditions,[21] 5-mesityldipyrromethane,[14] 3-(4-iodophenyl)dipyrromethane (**4**) and mesitaldehyde were condensed in $CHCl_3$ in the presence of BF_3-etherate for 1 h, then treated with DDQ. Analysis of the crude porphyrin mixture by ^1H NMR spectroscopy and LD-MS showed the presence of the three

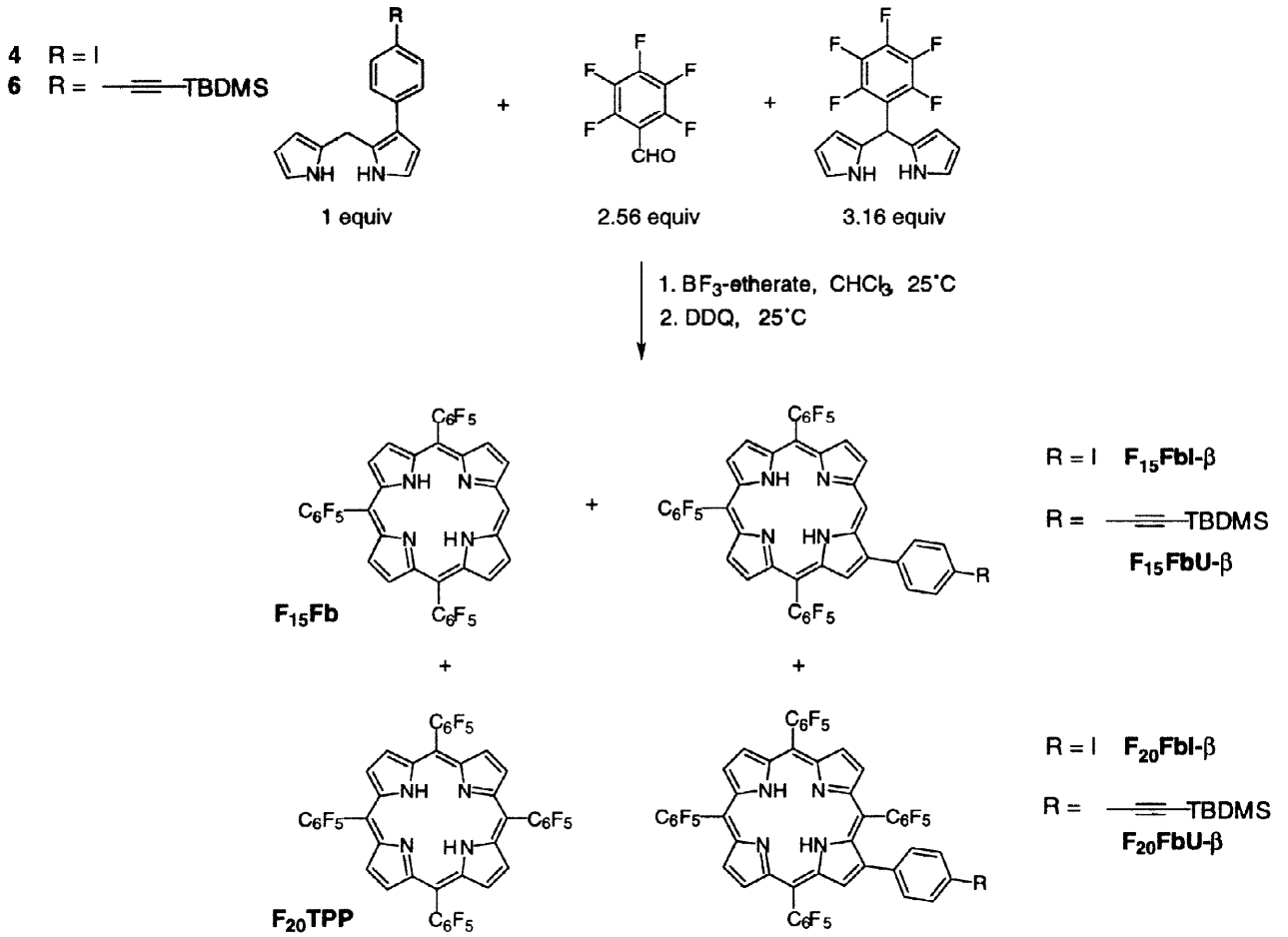
expected porphyrins as the principal products (or four given the possibility of structural isomers). Separation of the porphyrins by chromatography proved to be very difficult; therefore, the mixture was treated with methanolic $Zn(OAc)_2 2H_2O$ to afford the Zn-porphyrins which were more readily separated by column chromatography on silica. The desired porphyrin ZnI-β was obtained in 12% yield (Scheme 2). Demetalation of ZnI-β with TFA gave the free base porphyrin FbI-β in quantitative yield. A similar condensation of **5**, 5-mesityldipyrromethane, and mesitaldehyde, followed by metalation and chromatography afforded ZnU-β in 8% yield. Demetalation with TFA then gave FbU-β in 80% yield.



Scheme 2. Synthesis of porphyrin monomers ZnI-β and ZnU-β.

The preparation of the analogous F_{15}-porphyrins (F_{15}FbI-β, F_{15}FbU-β) via the same strategy presented a number of problems. The reaction of 5-pentafluorophenyldipyrromethane[14] (1.0 equiv), 3-(4-iodophenyl)dipyrromethane (**4**) (1.0 equiv) and pentafluorobenzaldehyde (2.0 equiv) with BF_3-etherate gave mainly the porphyrin derived from 2 + 2 condensation of **4** and pentafluorobenzaldehyde (not shown), with trace amounts of other porphyrins including the desired F_{15}FbI-β porphyrin. With a 10-fold excess of 5-pentafluorophenyldipyrromethane, the major product was F_{20}TPP and only a small amount of the desired porphyrin was obtained. The reaction of 5-pentafluorophenyldipyrromethane (3.16 equiv), dipyrromethane **4** (1.0 equiv), and pentafluorobenzaldehyde (2.56 equiv) in CH_2Cl_2 with BF_3-etherate gave F_{15}FbI-β in 5% yield, with the other major porphyrin products consisting of F_{20}TPP (9-10%), F_{20}FbI-β (6%) and F_{15}Fb (4%) (Scheme 3). The porphyrin byproducts were isolated by column chromatography and characterized by ^{1}H NMR spectroscopy and LD-MS. Under similar conditions, reaction of 5-pentafluorophenyldipyrromethane,

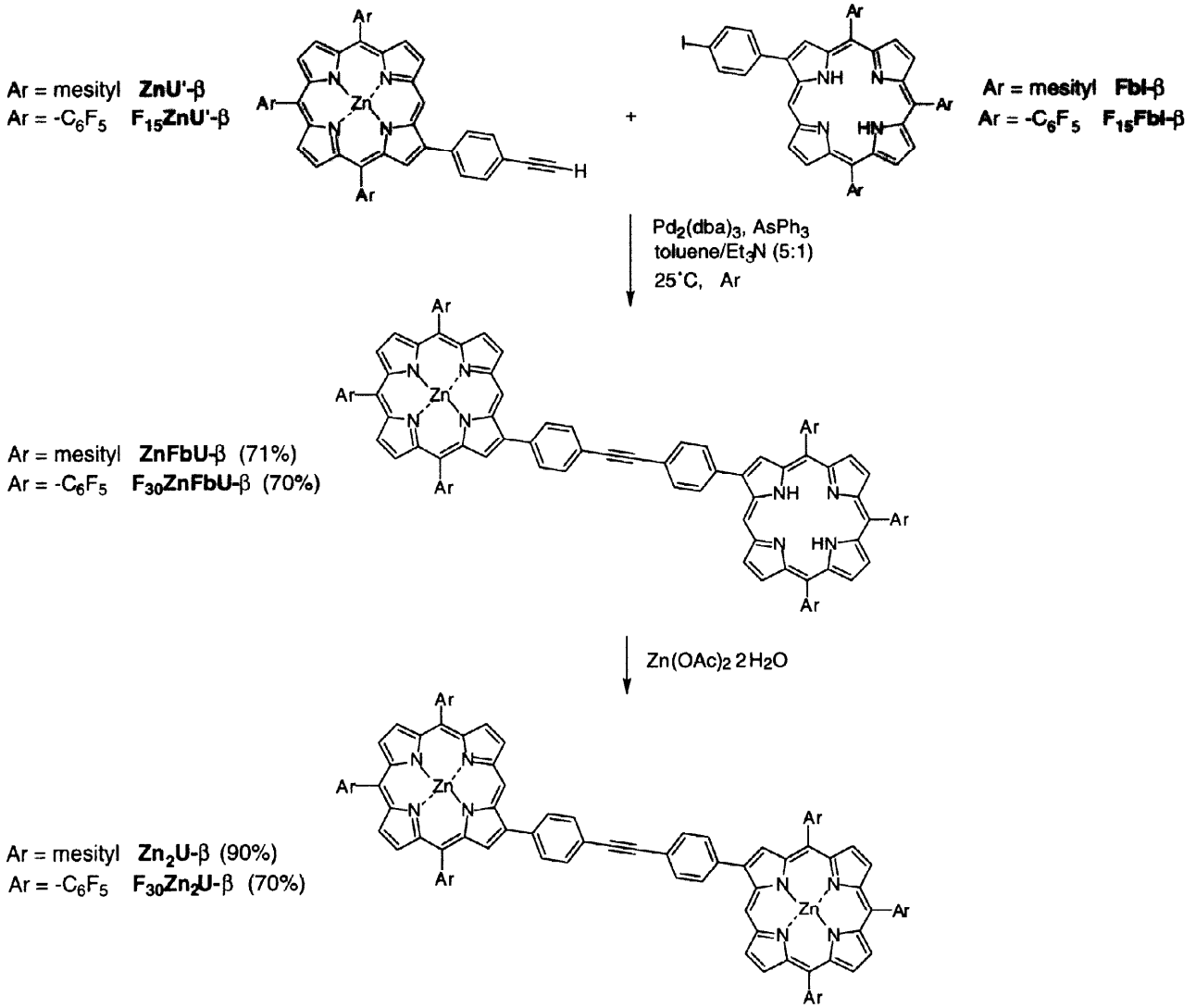
ethynyldipyrromethane **6**, and pentafluorobenzaldehyde afforded F_{15}FbU-β (3%), F_{20}TPP (8-9%), F_{20}FbU-β (5%), and F_{15}Fb (3-4%). In spite of the scrambling observed in this condensation, the porphyrins could be isolated by column chromatography, and were characterized by ^{1}H NMR spectroscopy and LD-MS analysis. Treatment of F_{15}FbU-β with excess methanolic $Zn(OAc)_2 2H_2O$ at reflux in CH_2Cl_2 for 5-6 h afforded F_{15}ZnU-β in 80% yield. Deprotection of ZnU-β and F_{15}ZnU-β with TBAF on silica afforded the Zn–ethynylporphyrins ZnU′-β and F_{15}ZnU′-β, respectively.



Scheme 3. Synthesis of porphyrin monomers F_{15}FbI-β and F_{15}FbU-β, plus scrambled byproducts.

Synthesis of Dimers

The Pd-mediated coupling[12] of FbI-β and ZnU′-β with $Pd_2(dba)_3$ and $AsPh_3$ in toluene/triethylamine (5:1) at 35°C under argon for 2 h afforded the β-linked dimer ZnFbU-β (Scheme 4). Purification by chromatography was achieved with a sequence of one silica column to remove $AsPh_3$ and Pd-species, one SEC column in THF to fractionate high molecular weight material, the desired dimer, and porphyrin monomers, and one final silica column. The dimer ZnFbU-β was obtained in 71% yield. Similarly, Pd-mediated coupling of F_{15}FbI-β and F_{15}ZnU′-β afforded F_{30}ZnFbU-β in 70% yield (Scheme 4). Treatment of ZnFbU-β or $F_{30}Zn_2$U-β with methanolic $Zn(OAc)_2 2H_2O$ in CH_2Cl_2 afforded the all-zinc complex Zn_2U-β or $F_{30}Zn_2$U-β in 90% or 70% yield, respectively.



Scheme 4. Synthesis of porphyrin dimers.

CONCLUSION

The methodology described here provided access to porphyrin building blocks that have a synthetic handle at one β-position, no sterically-hindering substituent at the flanking *meso*-position, and identical aryl groups at the three non-flanking *meso*-positions. Small quantities (15-25 mg) of β-linked porphyrin dimers were prepared with each porphyrin in a defined metalation state. The ZnFb dimers and Zn_2 dimers enabled a critical test of the effects of orbital ordering on excited-state energy transfer and ground state hole-hopping processes, respectively, by comparison with a corresponding set of *meso*-linked ZnFb and Zn_2 dimers.[11] Given the interplay of position of connection and the nature of the frontier molecular orbitals, the ability to connect the linker at either the *meso*- or β-positions provides versatility for working with diverse porphyrinic pigments. Hydroporphyrins such as chlorins, for example, are extremely attractive due to their strong absorption in the near-infrared spectral region. Chlorins have an a_{1u} HOMO. This methodology for preparing β-substituted dipyrromethanes may prove useful in the synthesis of β-substituted chlorin building blocks, thereby enabling maximal through-bond electronic communication in covalently-linked chlorin-containing arrays.

EXPERIMENTAL

General. ^1H and ^{13}C NMR spectra (300 MHz, 75 MHz, General Electric GN 300NB), absorption spectra (HP 8453, Cary 3), and fluorescence spectra (Spex FluoroMax) were collected routinely. Fluorescence quantum yields of monomeric porphyrins (except those containing iodo substituents) were determined at room temperature in toluene by ratioing corrected integrated spectral intensities with that of ZnTPP (Φ_f = 0.033).[11] Fluorescence emission and excitation spectroscopy was used to ensure quantitative metalation reactions. Porphyrins were analyzed by laser desorption ionization mass spectrometry (LD-MS) without a matrix[22] using a Bruker Proflex II spectrometer. Pyrrole was distilled at atmospheric pressure from CaH_2. Stock solutions of BF_3-etherate were prepared by diluting BF_3-etherate (Aldrich, 8.1 M) to 2.5 M in $CHCl_3$ or CH_2Cl_2. Melting points are uncorrected. Unless otherwise indicated, all reagents were obtained from Aldrich Chemical Co. and all solvents were obtained from Fisher Scientific. 4-Iodobenzaldehyde was obtained from Karl Industries, Inc.

Chromatography. Preparative adsorption chromatography was performed using flash silica gel (Baker, 40 μm). Porphyrins were pre-adsorbed onto the silica, then loaded onto the column while keeping the eluent level in the column a few millimeters above the silica. Analytical SEC (HP 1090 HPLC, 5 μm column (1000 Å, 30 cm), λ_{abs} 420 nm, THF elution at 0.8 mL/min) and preparative SEC were performed as previously described.[7,12,23,24] GC analysis was performed using an HP6890 Series GC with an oven temp ramp of 100 °C (3) to 295 °C (14), (15 °C/min) and a runtime of 30 min.

Solvents. THF was distilled from sodium benzophenone ketyl as required. Dry diethyl ether was prepared by distilling from sodium. Dry DMSO was prepared by storing over CaH_2 overnight, distilling from CaH_2 under reduced pressure, and storage over 4 Å molecular sieves. Toluene, triethylamine and CH_2Cl_2 were distilled from CaH_2. $CHCl_3$ was distilled from K_2CO_3. All other solvents and reagents were used as received.

Ethyl 4-iodocinnamate (1). A solution of 4-iodobenzaldehyde (11.7 g, 50.4 mmol), monoethyl malonate (10.0 g, 75.7 mmol), piperidine (0.6 mL) and pyridine (25 mL) was heated at reflux for 7 h in a 100-mL round-bottom flask. The reaction mixture was cooled to room temperature, poured into 2N aqueous HCl (200 mL) and extracted with ether (3 x 60 mL). The combined ethereal portions were successively washed with H_2O (2 x 60 mL), saturated aqueous $NaHCO_3$ (2 x 60 mL), water (2 x 60 mL), and 60 mL brine. The ether portion was dried (Na_2SO_4) and evaporated to give a brown solid. Recrystallization from absolute ethanol gave 13.5 g (88%) of a colorless solid. mp 38-39 °C; ^1H NMR ($CDCl_3$) δ 1.33 (t, J = 7.5 Hz, 3H), 4.26 (q, J = 7.5 Hz, 2H), 6.43 (d, J = 16.2 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 16.2 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 60.6, 96.4, 118.9, 129.4, 133.8, 138.0, 143.2, 166.6; HRMS (EI^+) for $C_{11}H_{11}O_2I$ calcd 301.9804, found 301.9793; Anal. Calcd for $C_{11}H_{11}O_2I$: C, 43.71; H, 3.67, Found: C, 43.79; H, 3.69.

3-Ethoxycarbonyl-4-(4-iodophenyl)pyrrole (2). To a suspension of NaH (1.2 g, 60% dispersion in mineral oil, 1.2 equiv) in 50 mL dry ether under argon was added dropwise over 30 min a solution of ethyl 4-iodocinnamate (**1**) (7.55 g, 25.0 mmol) and tosylmethylisocyanide (TosMIC) (5.00 g, 25.6 mmol) in 120 mL of dry ether/DMSO (2:1). Care must be exercised during addition as an exothermic reaction ensues. The resulting reaction mixture was stirred for 30 min, carefully quenched with 100 mL of ice-cold water, and extracted with ether (3 x 100 mL). The ethereal portion was dried (Na_2SO_4), filtered, and evaporated under reduced pressure to give a brown solid. Recrystallization from absolute ethanol gave 5.5 g (65%) of a light brown solid. mp 183-184 °C; ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.76 (s, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.48 (s, 1H), 7.66 (d, J = 8.1 Hz, 2H), 8.62 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.3, 59.7, 92.0, 113.7, 118.2, 125.4, 125.6, 131.3, 134.3, 136.7, 164.6; MS (EI^+) 341 (M^+,100%), 313(M-(C_2H_4),10), 296 (M-(CH_3CH_2O),20), 169 (M-(CH_3CH_2O+I), 20); HRMS (EI^+) for $C_{13}H_{12}NO_2I$ calcd

340.9913, found 340.9900; Anal. Calcd for $C_{13}H_{12}NO_2I$: C, 45.75; H, 3.55; N, 4.11. Found: C, 45.92; H, 3.70; N, 4.11.

2-Ethoxycarbonyl-3-(4-iodophenyl)-11-*N*-(*tert*-butoxycarbonyl)dipyrromethane (3b). To a solution of 2-hydroxymethyl *N*-(*tert*-butoxycarbonyl)pyrrole[19] (0.90 g, 4.57 mmol) and 4-(4-iodophenyl)-3-ethylcarboxypyrrole (**2**) (1.53 g, 4.49 mmol) in 45 mL of 1,4-dioxane was added aqueous HCl (10%, 9 mL). The reaction mixture was stirred at room temperature for 6 h. Another portion of 2-hydroxymethyl *N*-(*tert*-butoxycarbonyl)pyrrole (0.30 g, 1.52 mmol) was added and the reaction mixture was left to stir for an additional 12 h. Upon completion of the reaction as judged by TLC (hexane/ethyl acetate, 4:1), saturated aqueous $NaHCO_3$ (25 mL) and H_2O (50 mL) were carefully added to quench the reaction. The aqueous phase was extracted with ether (4 x 50 mL). The combined ethereal fraction was successively washed with water (3 x 100 mL), 100 mL of brine, dried (Na_2SO_4), filtered, and evaporated. TLC analysis (silica, hexane/ethyl acetate, 4:1) showed the minor and major products to have R_f values of 0.42 and 0.20, respectively. Purification by flash column chromatography (silica, hexane/ethyl acetate, 3:1) separated the two compounds, with regioisomer **3a** eluting first as a colorless solid (0.55 g, 23%) and **3b** eluting second as a colorless solid (1.05 g, 45%). Data for **3a**: mp 135-136 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.56 (s, 9H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.56 (s, 2H), 6.11 (t, *J* = 3.0 Hz, 1H), 6.24 (brs, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.18 (m, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 9.09 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 25.9, 27.9, 59.4, 84.4, 91.5, 109.4, 110.7, 114.1, 115.6, 121.4, 125.9, 131.3, 131.5, 135.6, 136.5, 138.3, 150.3, 165.3; HRMS (EI^+) for $C_{23}H_{25}N_2O_4I$ calcd 520.0859, found 520.0871. Data for **3b**: mp 70-71 °C; ^{1}H NMR ($CDCl_3$) δ 1.15 (t, *J* = 7.2 Hz, 3H), 1.59 (s, 9H), 4.02 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 5.73 (s, 1H), 6.03 (t, *J* = 2.7 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.12 (m, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 9.21 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 14.2, 24.7, 28.0, 59.3, 84.3, 92.1, 110.5, 113.1, 114.4, 121.2, 121.8, 122.9, 128.8, 132.7, 132.8, 134.7, 136.6, 150.3, 164.7; MS (EI^+) 521.1 (MH^+, 100%), 520.1 (M^+, 66%), 464.0 (M-(t-bu), 32%); HRMS (EI^+) for $C_{23}H_{25}N_2O_4I$ calcd 520.0859, found 520.0884; Anal. Calcd for $C_{23}H_{25}N_2O_4I$: C, 53.07; H, 4.84; N, 5.38. Found: C, 52.86; H, 4.85; N, 5.27.

3-(4-Iodophenyl)dipyrromethane (4). A 25-mL round-bottom flask was charged with **3b** (1.00 g 1.92 mmol) and 8 mL of ethylene glycol. The system was flushed with argon for 10 min then powdered NaOH (0.20 g, 5.0 mmol) was added and the flask was immersed in an oil bath at 180 °C. The oil bath temperature was increased to 195-200 °C and held there (total time, 1 h). Then the reaction flask was cooled to room temperature and 30 mL of 10% aq NaCl was added. The aqueous portion was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic layers were washed with 50 mL of brine, dried (Na_2SO_4), filtered, and evaporated. Purification by flash column chromatography (silica, hexane/ethyl acetate 3:1 containing 1-2 % Et_3N) afforded a light-brown solid (0.48 g, 69%): mp 124-125 °C; ^{1}H NMR ($CDCl_3$) δ 4.07 (s, 2H), 6.06 (brs, 1H), 6.17 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.32 (t, *J* = 3.0 Hz, 1H), 6.63 (brs, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.75 (brs, 1H), 7.86 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 25.2, 90.4, 107.0, 108.6, 117.0, 117.6, 120.5, 125.3, 128.3, 129.5, 135.9, 137.5; MS (EI^+) 348 (M^+, 100%), 269 (20); HRMS (EI^+) calcd for $C_{15}H_{13}N_2I$ 348.0124, found 348.0115; Anal. Calcd for $C_{15}H_{13}N_2I$: C, 51.72; H, 3.76; N, 8.05. Found: C, 51.73; H, 3.78; N, 7.95.

3-[4-(Trimethylsilylethynyl)phenyl]dipyrromethane (5). Samples of **4** (0.35 g, 1.0 mmol), trimethylsilylacetylene (0.20 mL, 1.42 mmol), and triphenylarsine (0.078 g, 0.25 mmol) were suspended in 3 mL of dry THF/Et_3N (1:1) in an oven dried 10-mL round-bottom flask fitted with a reflux condenser. The solution was purged with argon for 20 min. $Pd_2(dba)_3$ (0.030 g, 0.03 mmol) was added to the flask and then the flask was lowered into an oil bath at 35-40 °C. GC analysis after 12 h showed that dipyrromethane **4** remained unreacted. Additional trimethylsilylacetylene (0.10 mL each) was added at 12 h and 24 h. GC analysis at 30 h showed the complete disappearance of dipyrromethane **4**. Ether (25 mL) was added and the reaction mixture

was filtered through a bed of alumina. The alumina was repeatedly washed with ether until the filtrate was colorless. The filtrate was concentrated and purified by flash column chromatography (silica, hexane/ether from 4:1 to 3:1). The product was further purified by Kugelrohr distillation (ot 185-190 °C, 0.05 mm Hg) affording 190 mg (>95% purity, 60% yield): ^{1}H NMR ($CDCl_3$-CD_2Cl_2) δ 0.25 (s, 9H), 4.09 (s, 2H), 6.08 (brs, 1H), 6.18 (q, J = 2.7 Hz, 1H), 6.35 (t, J = 2.7 Hz, 1H), 6.63 (m, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.77 (brs, 1H), 7.85 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 0.0, 25.4, 93.9, 105.4, 107.1, 108.6, 108.7, 117.0, 117.6, 119.9, 120.9, 125.6, 127.2, 128.3, 132.2, 136.7; HRMS (FAB) for $C_{20}H_{22}N_2Si$ calcd 318.1552, found 318.1559.

3-[4-(*tert*-Butyldimethylsilylethynyl)phenyl]dipyrromethane (6). Following the procedure for preparation of **5**, samples of **4** (0.35 g, 1.0 mmol), *t*-butyldimethylsilylacetylene (0.17 g, 1.21 mmol) and $AsPh_3$ (0.126 g, 0.41 mmol) were suspended in 3 mL of dry THF/Et_3N (1:1) and purged with argon for 20 min. $Pd_2(dba)_3$ (0.048 g, 0.052 mmol) was added and the mixture was heated at 35-40 °C for 12 h. At this point, additional *t*-butyldimethylsilylacetylene (0.070 g) was added and the reaction was continued for another 24 h. Workup proceeded as described with purification by flash column chromatography (silica, hexane/ether, from 4:1 to 3:1), affording a gum (200 mg, 55%): ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 6H), 1.00 (s, 9H), 4.13 (s, 2H), 6.08 (brs, 1H), 6.17 (q, J = 3.0 Hz, 1H), 6.36 (t, J = 3.0 Hz, 1H), 6.68 (t, J = 3.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.87 (brs, 1H), 7.96 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ -4.6, 0.0, 25.5, 26.1, 92.0, 106.0, 107.0, 108.6, 108.8, 117.0, 117.6, 120.1, 120.9, 125.6, 127.2, 128.3, 132.2, 136.8; HRMS (FAB) for $C_{23}H_{28}N_2Si$ calcd 360.2022, found 360.2015.

Zn(II)-5,10,15-Trimesityl-2-(4-iodophenyl)porphyrin (ZnI-β). To a solution of 5-mesityldipyrromethane[14] (0.14 g, 0.54 mmol), **4** (0.19 g, 0.54 mmol), and mesitaldehyde (0.16 g, 1.08 mmol) in 100 mL of $CHCl_3$ under argon was added BF_3-etherate (132 μL of a 2.5 M stock solution in $CHCl_3$, 3.3 mM). The reaction mixture was stirred at room temperature for 45 min. DDQ (0.37 g, 1.63 mmol, 3 equiv) was added and stirring was continued for an additional 1 h. The solvent was evaporated under reduced pressure and the residue was filtered through a silica gel column (hexane/CH_2Cl_2 1:1) to remove quinone species and dark pigments. The porphyrin band that eluted first from the column was collected and concentrated. Analysis by ^{1}H NMR spectroscopy and LD-MS showed the presence of TMP, FbI-β and FbI_2-β (this latter porphyrin is derived from 2 + 2 condensation of **4** and mesitaldehyde). The porphyrin mixture (0.15-0.2 g) was dissolved in 50 mL of CH_2Cl_2 and treated with methanolic $Zn(OAc)_2{\cdot}2H_2O$ (0.12 g in 2 mL methanol). The mixture was heated at reflux for 1 h and worked up by dilution with 100 mL of CH_2Cl_2, then the organic portion was successively washed with saturated aqueous $NaHCO_3$ (2 x 60 mL), H_2O (2 x 60 mL), 60 mL of brine, then dried (Na_2SO_4), filtered, and concentrated. The crude porphyrin mixture was purified by gravity chromatography (silica, $CHCl_3$/hexane, 7:3). There were three dominant bands (and a few minor bands) visible on the column, with order of elution ZnTMP, ZnI-β, and finally ZnI_2-β. The yield of ZnI-β was 12% (50 mg): λ_{abs} (log ε) in toluene, 422 (5.59), 548 (4.32), 581 nm; λ_{em} (toluene) 586, 641 nm; ^{1}H NMR ($CDCl_3$) δ 1.84 (m, 18H), 2.64 (s, 9H), 7.28 (m, 6H), 8.05 (AA'BB', J = 6.3 Hz, 4H), 8.73 (s, 4H), 8.86 (m, 2H), 9.29 (d, J = 4.2 Hz, 1H), 10.16 (s, 1H); LD-MS for $C_{53}H_{45}N_4ZnI$ calcd avg mass 928.2, obsd 927.5; HRMS (FAB) calcd 928.1980, found 928.2001.

Zn(II)-5,10,15-Trimesityl-2-[4-(trimethylsilylethynyl)phenyl]porphyrin (ZnU-β). Following the procedure outlined above, 5-mesityldipyrromethane[14] (0.13 g, 0.50 mmol), **5** (0.16 g, 0.50 mmol), and mesitaldehyde (0.15 g, 1.0 mmol) were condensed in 100 mL $CHCl_3$, affording 35 mg (8%): λ_{abs} (log ε) in toluene, 423 (5.68), 548 (4.49), 581 (3.74) nm; λ_{em} (toluene) 586, 641 nm (Φ_f = 0.033); ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H), 1.85 (m, 18H), 2.62 (m, 9H), 7.27 (m, 6H), 7.87 (d, J = 8.1 Hz, 2H), 8.23 (d, J = 7.8 Hz, 2H), 8.73 (m, 4H), 8.87 (d, J = 4.5 Hz, 1H), 8.88 (s, 1H), 9.27 (d, J = 4.5 Hz, 1H), 10.17 (s, 1H); LD-MS for $C_{58}H_{54}N_4SiZn$ calcd avg mass 898.3, obsd 897.0; HRMS (FAB) calcd 898.3409, found 898.3403.

5,10,15-Trimesityl-2-(4-iodophenyl)porphyrin (FbI-β). A solution of ZnI-β (54.0 mg, 58.0 μmol) in 15 mL of CH_2Cl_2 was treated with TFA (30 μL, >5 equiv.). The reaction was found to be complete after 1 h as judged by silica TLC, absorption spectroscopy, and fluorescence excitation spectroscopy. Triethylamine (100 μL) was added and the reaction mixture was stirred for another 10 min, then diluted with 50 mL CH_2Cl_2, washed with 10% aqueous $NaHCO_3$ (2 x 50 mL), 50 mL of H_2O, 50 mL of brine, then dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure to give a purple solid (48 mg, 100%). λ_{abs} (log ε) in toluene, 420 (5.66), 512 (4.47), 544 (3.69), 589 (3.90), 646 nm; λ_{em} (toluene) 646, 714 nm; ^{1}H NMR ($CDCl_3$) δ -2.72 (brs, 2H), 1.86 (m, 18H), 2.62 (m, 9H), 7.28 (m, 6H), 7.99 (d, *J* = 8.1 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 8.64 (s, 2H), 8.68 (s, 2H), 8.77 (s, 1H), 8.81 (d, *J* = 4.5 Hz, 1H), 9.23 (d, *J* = 4.5 Hz, 1H), 10.10 (s, 1H); LD-MS for $C_{53}H_{47}N_4I$ calcd avg mass 866.3, obsd 867.2; HRMS (FAB) calcd 866.2845, found 866.2888.

5,10,15-Trimesityl-2-[4-(trimethylsilylethynyl)phenyl]porphyrin (FbU-β). Under similar conditions as described above, a solution of ZnU-β (10.0 mg, 11.0 μmol) in 10 mL of CH_2Cl_2 was treated with 7 μL TFA at room temperature to afford 8 mg (81%). λ_{abs} (toluene) 423, 514, 548, 591, 647 nm; λ_{em} (toluene) 646, 715 nm (Φ_f = 0.071); ^{1}H NMR ($CDCl_3$) δ -2.71 (brs, 2H), 0.35 (s, 9H), 1.85 (m, 18H), 2.62 (m, 9H), 7.28 (m, 6H), 7.87 (d, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 2H), 8.64 (s, 2H), 8.67 (s, 2H), 8.80 (m, 2H), 9.22 (d, *J* = 4.5 Hz, 1H), 10.12 (s, 1H); LD-MS for $C_{58}H_{56}N_4Si$ calcd avg mass 836.4, obsd 835.1; HRMS (FAB) calcd 836.4274; obsd 836.4283.

Zn(II)-5,10,15-Trimesityl-2-(4-ethynylphenyl) porphyrin (ZnU′-β). A solution of ZnU-β (36.0 mg, 40.0 μmol) in 12 mL of dry THF under argon was treated with tetrabutylammonium fluoride on silica (1.0 – 1.5 mmol F/g, 80.0 mg). The reaction mixture was stirred for 1 h at room temperature. The reaction mixture was concentrated under reduced pressure and dissolved in 50 mL of $CHCl_3$. The organic layer was washed with 10% aqueous $NaHCO_3$ (2 x 50 mL), H_2O (2 x 50 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Column chromatography (silica, hexane/CH_2Cl_2 1:1) afforded a purple solid (34 mg, 90%). λ_{abs} (log ε) in toluene, 420 (5.77), 548 (4.53), 581 (3.76) nm; λ_{em} (toluene) 587, 641 nm (Φ_f = 0.035); ^{1}H NMR ($CDCl_3$) δ 1.84, 1.85 (m, 18H), 2.63 (m, 9H), 3.26 (s, 1H), 7.27 (m, 6H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.26 (d, *J* = 8.1 Hz, 2H), 8.73 (s, 4H), 8.87 (d, *J* = 5.1 Hz, 1H), 8.89 (s, 1H), 9.28 (d, *J* = 4.2 Hz, 1H), 10.19 (s, 1H); LD-MS for $C_{55}H_{46}N_4Zn$ calcd avg mass 826.3, obsd 827.8; HRMS (FAB) calcd 826.3014, found 826.3044.

5,10,15-Tris(pentafluorophenyl)-2-(4-iodophenyl)porphyrin (F_{15}FbI-β). A solution of 5-(pentafluorophenyl)dipyrromethane[14] (0.49 g, 1.58 mmol), **4** (0.18 g, 0.50 mmol) and pentafluorobenzaldehyde (0.25 g, 1.28 mmol) in 300 mL of CH_2Cl_2 under argon was treated with BF_3-etherate (396 μL of 2.5 M stock solution, 3.3 mM). The reaction mixture was stirred for 80 min at room temperature. DDQ (0.70 g, 3.08 mmol) was added and stirring was continued for an additional 1 h. The solvent was removed under reduced pressure followed by chromatography (silica, hexane/CH_2Cl_2 1:1) to free the porphyrins from black byproducts. LD-MS of the porphyrin fractions indicated the presence of at least four porphyrins including the desired F_{15}FbI-β. Further flash column chromatography (silica, slow elution, hexane/$CHCl_3$ 82:18) gave the desired porphyrin as the third band (25 mg, 5%): λ_{abs} (log ε) in toluene, 416 (5.39), 508 (4.34), 539 (3.69), 585 (3.83), 639 nm; λ_{em} (toluene) 641, 708 nm; ^{1}H NMR ($CDCl_3$) δ -3.04 (brs, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.1 Hz, 2H), 8.95 (m, 6H), 9.44 (d, *J* = 5.1 Hz, 1H), 10.35 (s, 1H); LD-MS for $C_{44}H_{14}F_{15}IN_4$ calcd avg mass 1010.0, found 1011.5; HRMS (FAB) calcd 1010.0024, found 1010.0006. Data for F_{15}Fb: λ_{abs} (toluene) 412, 504, 537, 580, 634 nm; λ_{em} (toluene) 636, 703 nm; ^{1}H NMR ($CDCl_3$) δ -3.13 (brs, 2H), 8.93 (m, 4H), 8.98 (d, *J* = 4.2 Hz, 2H), 9.46 (d, *J* = 4.2 Hz, 2H), 10.37 (s, 1H); HRMS (FAB) for $C_{38}H_{11}F_{15}N_4$ calcd 808.0744, found 808.0762. Data for F_{20}FbI-β: λ_{abs} (toluene) 419, 510, 587, 640 nm; λ_{em} (toluene) 645, 714 nm; ^{1}H NMR ($CDCl_3$) δ -2.84 (brs, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1

Hz, 2H), 8.75 (s, 1H), 8.80 (d, J = 5.1Hz, 1H), 8.86 (d, J = 5.1Hz, 1H), 8.91 (s, 4H); HRMS (FAB) for $C_{50}H_{13}F_{20}IN_4$ calcd 1175.99, found 1175.98.

5,10,15-Tris(pentafluorophenyl)-2-[4-(*tert*-butyldimethylsilylethynyl)phenyl]-porphyrin (F_{15}FbU-β). 5-(Pentafluorophenyl)dipyrromethane[14] (0.49 g, 1.58 mmol), **6** (0.18 g, 0.50 mmol) and pentafluorobenzaldehyde (0.25 g, 1.28 mmol) were condensed in 300 mL of CH_2Cl_2 following the procedure outlined above. Chromatography (silica, gravity column, hexane/CH_2Cl_2 1:1) gave a mixture of porphyrins, which were further purified (silica, gravity column, 3% ethyl acetate in hexane). The first band contained a mixture of the desired F_{15}FbU-β and F_{20}FbU-β. These two porphyrins were separated on silica (gravity or low pressure, hexane/$CHCl_3$ 82:18). The first band corresponded to F_{20}FbU-β (30 mg, 5%) and the second band corresponded to the desired F_{15}FbU-β (15 mg, 3%). λ_{abs} (log ε) in toluene, 417 (5.42), 509 (4.41), 541 (3.85), 586 (3.92), 639 (3.60) nm; λ_{em} (toluene) 642, 709 nm (Φ_f = 0.086); ^{1}H NMR ($CDCl_3$) δ -3.03 (brs, 2H), 0.30 (s, 6H), 1.1 (s, 9H), 7.94 (d, J = 8.1 Hz, 2H), 8.23 (d, J = 7.8 Hz, 2H), 8.93 (m, 6H), 9.43 (d, J = 4.5 Hz, 1H), 10.37 (s, 1H); LD-MS for $C_{52}H_{29}F_{15}N_4Si$ calcd avg mass 1022.2, obsd 1020.2; HRMS (FAB) calcd 1022.1922, found 1022.1957. Data for F_{20}FbU-β: λ_{abs} (toluene) 420, 511, 588, 641 nm; λ_{em} (toluene) 645, 713 nm; ^{1}H NMR ($CDCl_3$) δ –2.83 (brs, 2H), 0.28 (s, 6H), 1.09 (s, 9H), 7.55 (s, 4H), 8.84 (m, 7H); HRMS (FAB) for $C_{58}H_{28}F_{20}N_4Si$ calcd 1188.18, found 1188.18.

Zn(II)-5,10,15-Tris(pentafluorophenyl)-2-[4-(*tert*-butyldimethylsilylethynyl)-phenyl]porphyrin (F_{15}ZnU-β). A solution of F_{15}FbU-β (25.0 mg, 24 μmol) in 10 mL of CH_2Cl_2 under argon was treated with a methanolic solution of $Zn(OAc)_2 2H_2O$ (440 mg, in 1-2 mL methanol) and the resulting reaction mixture was heated at reflux for 5-6 h under argon. The reaction was monitored by silica TLC for the disappearance of Fb-porphyrin and worked up by diluting with 50 mL of CH_2Cl_2. The organic portion was successively washed with 10% aqueous $NaHCO_3$ (2 x 50 mL), water (2 x 50 mL), dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure. Chromatography (silica, short column, hexane/CH_2Cl_2 1:1) afforded 20 mg (80%): λ_{abs} (log ε) in toluene, 422 (5.19), 546 (4.05), 583 (3.80) nm; λ_{em} (toluene) 587, 640 nm (Φ_f = 0.036); ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 6H), 1.11 (s, 9H), 7.94 (d, J = 8.1 Hz, 2H), 8.26 (d, J = 8.1 Hz, 2H), 9.00 (m, 6H), 9.47 (d, J = 4.5 Hz, 1H), 10.43 (s, 1H); LD-MS for $C_{52}H_{27}F_{15}N_4SiZn$ calcd avg mass 1086.2, found 1086.0; HRMS (FAB) calcd 1084.1057, found 1084.1034.

Zn(II)-5,10,15-Tris(pentafluorophenyl)-2-(4-ethynylphenyl)porphyrin (F_{15}ZnU′-β). A solution of F_{15}ZnU-β (18.0 mg, 17 μmol) in 7 mL of dry THF under argon was treated with TBAF on silica gel (36.0 mg). The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the resulting residue was dissolved in 30 mL of $CHCl_3$. The organic portion was washed with 10% aqueous $NaHCO_3$ (2 x 25 mL), water (2 x 25 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Chromatography (silica, short column, hexane/$CHCl_3$ 1:1) afforded 12 mg (70%): ^{1}H NMR ($CDCl_3$) δ 3.32 (s, 1H), 7.97 (d, J = 8.1 Hz, 2H), 8.29 (d, J = 7.8 Hz, 2H), 9.01 (m, 6H), 9.50 (d, J = 4.5 Hz, 1H), 10.45 (s, 1H); LD-MS for $C_{46}H_{13}F_{15}N_4Zn$ calcd avg mass 970.0, found 969.2.

ZnFbU-β. Under typical Pd-mediated coupling conditions, samples of FbI-β (25.0 mg, 29 μmol) and ZnU′-β (26.0 mg, 31 μmol) were placed in a 25-mL single-neck round-bottom flask containing 12 mL of toluene and Et_3N (5:1). The flask was fitted with a reflux condenser through which a drawn glass pipette was mounted for deaeration with argon. The reaction vessel head space was purged with argon for 10 min and then the solution was deaerated by bubbling argon into the solution for 15 min. Then the pipette was removed and the whole system was purged with argon for an additional 10 min. $AsPh_3$ (10.0 mg, 33 μmol) and $Pd_2(dba)_3$ (4.0 mg, 4.4 μmol) were added and the flask was placed in a preheated oil bath at 35 °C. The reaction mixture was stirred at 35 °C and the reaction was monitored by analytical SEC. After 2 h, the reaction mixture was concentrated, redissolved in 5 mL of hexane/CH_2Cl_2 (2:1), then chromatographed (silica, hexane/CH_2Cl_2 2:1)

under moderate pressure. $AsPh_3$ eluted first followed by the monomers, desired dimer and higher molecular weight material. The dimer containing fractions were further purified by preparative SEC with THF as the eluent. The second band on the SEC column was further purified (silica, hexane/CH_2Cl_2, 2:1), affording 34 mg (71%): λ_{abs} (log ε) in toluene, 423 (5.60), 513 (4.31), 548 (4.35), 587 (3.91), 645 (3.10) nm; λ_{em} (toluene) 647, 715 nm; ^{1}H NMR ($CDCl_3$) δ -2.66 (brs, 2H), 1.87 (m, 24H), 1.91 (m, 12H), 2.64, 2.66 (m, 18H), 7.31 (m, 12H), 8.06 (m, 4H), 8.36 (m, 4H), 8.66 (s, 2H), 8.70 (s, 2H), 8.75 (m, 4H), 8.84 (d, J = 4.5 Hz, 1H), 8.87 (s, 1H), 8.91 (d, J = 4.2 Hz, 1H), 8.96 (s, 1H), 9.29 (d, J = 4.5 Hz, 1H), 9.33 (d, J = 4.2 Hz, 1H), 10.23 (s, 1H), 10.28 (s, 1H); LD-MS for $C_{108}H_{92}N_8Zn$ calcd avg mass 1567.4, found 1568.8; HRMS (FAB) calcd 1564.6736, found 1564.6763.

F_{30}ZnFbU-β. Employing similar Pd-coupling conditions as described above, a solution of F_{15}FbI-β (12.5 mg, 12 μmol) and F_{15}ZnU′-β (12.0 mg, 12 μmol) in 6 mL of toluene/Et_3N (5:1) was treated with $AsPh_3$ (4.5 mg, 14 μmol) and $Pd_2(dba)_3$ (1.7 mg, 1.8 μmol). Purification via the sequence of silica (hexane/$CHCl_3$ 1:1), SEC (toluene), and silica afforded 16 mg (70%): λ_{abs} (log ε) in toluene, 422 (5.91), 509 (4.67), 545 (4.74), 584 (4.61), 640 (3.82) nm; λ_{em} (toluene) 642, 709 nm; ^{1}H NMR ($CDCl_3$) δ -2.98 (brs, 2 H), 8.16 (d, J = 8.1 Hz, 4H), 8.40 (m, 4H), 9.00 (m, 12H), 9.50 (d, J = 4.2 Hz, 1H), 9.55 (d, J = 5.1 Hz, 1H), 10.48 (s, 1H), 10.53 (s, 1H); LD-MS for $C_{90}H_{26}F_{30}N_8Zn$ calcd avg mass 1852.1, found 1847.1; HRMS (FAB) calcd 1852.11, found 1852.09.

Zn_2U-β. A solution of ZnFbU-β (14.0 mg, 9 μmol) in 7 mL of CH_2Cl_2 was treated with a methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (5.0 mg, 0.5 mL of methanol) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 (25 mL), washed with saturated aqueous $NaHCO_3$ (2 x 20 mL), H_2O (2 x 20 mL), 25 mL of brine, then dried (Na_2SO_4), filtered, and concentrated. Chromatography (silica, short column hexane/CH_2Cl_2 1:1) afforded 12 mg (90%): λ_{abs} (toluene) 424, 548, 582 nm; λ_{em} (toluene) 587, 643 nm; ^{1}H NMR ($CDCl_3$) δ 1.88 (m, 36H), 2.64, 2.65 (m, 18H), 7.30 (m, 12H), 8.07 (d, J = 8.1 Hz, 4H), 8.37 (d, J = 8.1 Hz, 4H), 8.75 (m, 8H), 8.90 (d, J = 4.5 Hz, 2H), 8.96 (s, 2H), 9.33 (d, J = 4.5 Hz, 2H), 10.28 (s, 2H); LD-MS for $C_{108}H_{90}N_8Zn_2$ calcd avg mass 1630.7, obsd 1633.7; HRMS (FAB) calcd 1626.5871, found 1626.5854.

$F_{30}Zn_2$U-β. A solution of F_{30}ZnFbU-β (7.0 mg, 3.7 μmol) in 5 mL of CH_2Cl_2 was treated with methanolic $Zn(OAc)_2{\cdot}2H_2O$ (80.0 mg, 1 mL methanol) and the reaction mixture was heated to reflux for 5-6 h under an argon atmosphere. The reaction was monitored for the disappearance of F_{30}ZnFbU-β by TLC and worked up by diluting with 25 mL of CH_2Cl_2. The organic portion was successively washed with 10% aqueous $NaHCO_3$ (2 x 20 mL), H_2O (2 x 20 mL), and 25 mL of brine, then dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Chromatography (silica, short column, hexane/$CHCl_3$ 2:3) afforded 5 mg (70%): λ_{abs} (toluene) 422, 546, 584 nm; λ_{em} (toluene) 588, 641 nm; ^{1}H NMR ($CDCl_3$) δ 8.03 (m, 12H), 8.16 (d, J = 8.1 Hz, 4H), 8.41 (d, J = 7.8 Hz, 4H), 9.55 (d, J = 4.5 Hz, 2H), 10.53 (s, 2H); LD-MS for $C_{90}H_{24}F_{30}N_8Zn_2$ calcd avg mass 1914.0; obsd 1909.7; HRMS (FAB) calcd 1914.02, found 1914.02.

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