Synthesis of Bis(phenylethynyl)arylene-Linked Diporphyrins Designed for Studies of Intramolecular Energy Transfer

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Abstract: A series of donor-bridge-acceptor systems has been designed to give information on how the medium between the donor and the acceptor influences the excitation energy transfer process. The donor and the acceptor are zinc and free base porphyrins, respectively. The systems were obtained by a synthetic strategy that guarantees a precise state of metalation, i.e. by a building block approach in which a third chromophore is formed as the two porphyrins are covalently linked together in a geometrically well defined structure. The porphyrins are linked by one of the three different bridge chromophores; 9,10-bis(phenylethynyl)anthracene, or 1,4-bis(phenylethynyl)-substituted benzene or naphthalene. The different units were assembled using copper-free, palladium-catalyzed cross-coupling of aryl iodides with terminal alkynes. Reference compounds that correspond to different parts of the systems have also been prepared.

Key words: porphyrin; molecular design; palladium; cross-coupling; donor-bridge-acceptor systems

The preparation of porphyrin arrays is an important area of research, not only for mimicry of different biological processes and elucidation of their mechanisms, but also for the development of molecular electronic devices. In recent years, one of the major tasks has been to prepare arrays of chromophores to probe the electronic communication, i.e. electronic coupling, between the chromophores. Electronic coupling between chromophores is the basis of electron and excitation energy transfer from a donor to an acceptor,[1] two important transfer reactions crucial to natural photosynthesis[2] and molecular devices.[3] The electronic coupling between a donor and an acceptor has been shown to be enhanced by π-conjugated bridges linking donor and acceptor together.[4] However, a systematic study has not yet been reported on how the magnitude of the coupling depends on the energies of the lowest excited states of such a bridge in comparison with corresponding energies of the donor and acceptor. Diporphyrin donor-acceptor systems with large π-conjugated bridges have been prepared and studied with respect to the geometry and distance dependence of the excitation energy or electron transfer.[5]

In this paper, we report the synthesis of a series of diporphyrin donor-bridge-acceptor (**D-B-A**) systems designed to give information on how the energetics of the bridge, i.e. the medium between the donor and acceptor, influences excitation energy transfer. In addition to this primary purpose our design of the **D-B-A** systems was based on two general considerations: ease of preparation and ease of interpretation of photophysical data[6] obtained from the systems. The **D-B-A** systems were thus given the following features (Figure): The medium between donor (zinc porphyrin) and acceptor (free base porphyrin) was varied by covalently linking the porphyrins together with different bridge chromophores. The *tert*-butyl groups (**I**) provide the facial encumbrance necessary for good solubility. The methyl groups in the β position (**II**) force the planes of the porphyrin and the phenyl ring to be nearly perpendicular and interchromophore conjugation is thereby minimized to preserve the identity of the three chromophores. Triple bonds (**III**) give geometrically well defined systems, which simplifies the interpretation of photophysical data, and provide established coupling methods by which the **D-B-A** systems were assembled. Finally the donor-acceptor distance was kept the same throughout the series in order to facilitate immediate comparisons.

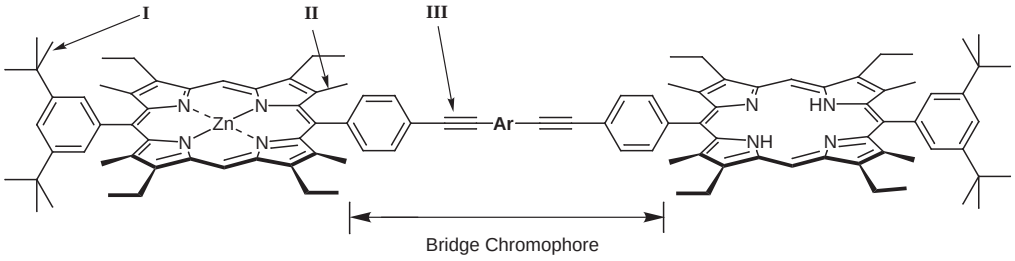
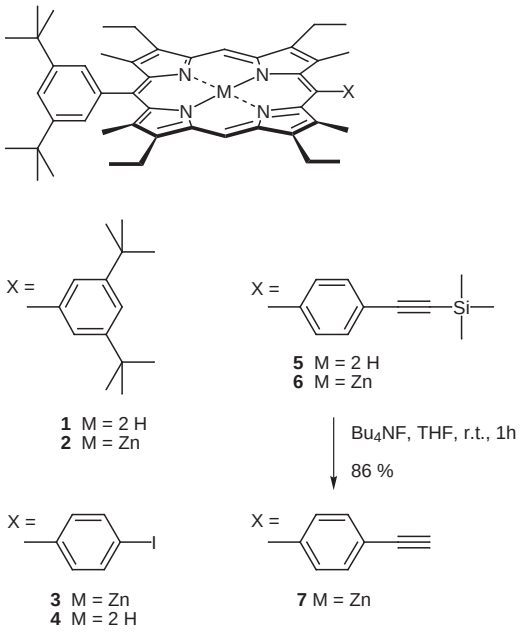


Figure Structure of the synthesized **D-B-A** systems consisting of a donor (zinc porphyrin), a bridged chromophore, and an acceptor (free base porphyrin). **ZnP-BB-H_2P** (Ar = 1,4-phenylene), **ZnP-NB-H_2P** (Ar = 1,4-naphthylene), **ZnP-AB-H_2P** (Ar = 9,10-anthrylene)

The phenylene system, **ZnP-BB-H_2P**, was prepared in a straightforward synthesis from the mono-protected *p*-di(ethynyl)benzene **9**, zinc iodoporphyrin **3** and free base iodoporphyrin **4** (see Scheme 2). Unfortunately, the other two systems could not be prepared using the same synthetic protocol. Attempts were made to prepare trimethylsilyl-protected naphthalene and anthracene analogs of **9,** but this failed due to polymerization. It is known that 1,4-diethynylnaphthalene readily polymerizes in the presence of light,[7] even in the solid state, and also the mono-silylated form appears to be highly light and heat sensitive. Thus, the ethynyl group had to be on the porphyrin in the preparation of the naphthylene and anthrylene systems, **ZnP-NB-H_2P** and **ZnP-AB-H_2P**. These systems were prepared from zinc ethynylporphyrin **7** and 1,4-diiodonaphthalene, and 9,10-diiodoanthracene, respectively (see Scheme 3).

A similar approach has been used by Kawabata et al. to prepare a derivative of the phenylene linked diporphyrin **ZnP-BB-H_2P** from an ethynylporphyrin and 1,4-diiodobenzene.[5a] A disadvantage of this protocol is that when ethynylporphyrins participate in palladium-catalyzed cross-coupling reactions they can form butadiyne-linked dimers via homocoupling. The butadiyne-linked dimers can be troublesome byproducts as they may be difficult to remove from the desired products. However, this side reaction is suppressed by using proper reaction conditions in the assembling of the **D-B-A** systems.[8] In the course of this work we have observed that the palladium-catalyzed cross-coupling of zinc porphyrins work better compared to when the same reaction is performed with the corresponding free base porphyrin. For example, zinc porphyrin **12N** could be prepared from zinc ethynylporphyrin **7** and 1,4-diiodonaphthalene in 27% yield. However, in an attempt to prepare free base porphyrin **13N** directly from the free base ethynylporphyrin and 1,4-diiodonaphthalene, using the same conditions as in the preparation of **12N**, only ca 5% of **13N** could be isolated. Zinc porphyrins seem to have a small co-catalytic effect that is observable when the cross-coupling is performed under mild conditions. Therefore, a zinc porphyrin was introduced in the first step in the preparation of the **D-B-A** systems. In this way a zinc porphyrin is present in both of the palladium-catalyzed steps. A possible explanation to this observation is that Ph_3P or Ph_3As coordinates to the zinc porphyrin which acts as a scavenger for free ligands. This has been shown to be the co-catalytic effect of copper in the Stille coupling.[9]

The synthesis of the different systems started with the preparation of the appropriate building blocks. The porphyrins were prepared by acid-catalyzed condensation of 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane[10] and functionalized benzaldehydes,[11] followed by oxidation.[12] The free base porphyrin **5** was converted to zinc porphyrin **6** and then deprotected with tetrabutylammonium fluoride to zinc ethynylporphyrin **7** (Scheme 1).

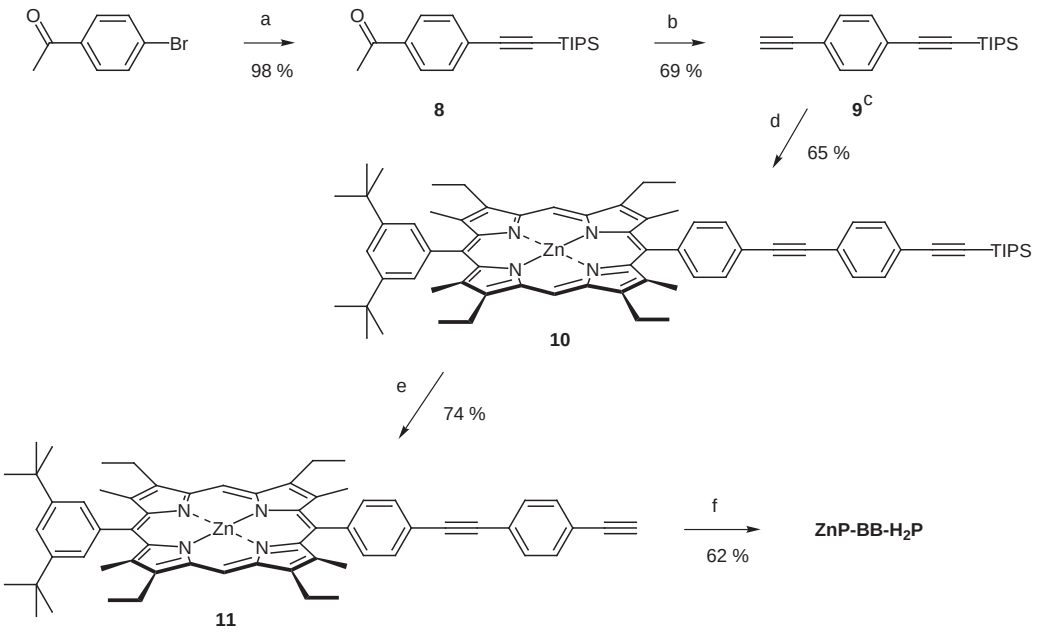


Scheme 1

1-Ethynyl-4-[(triisopropylsilyl)ethynyl]benzene[13] (**9**) was prepared in two steps from 4-bromoacetophenone (Scheme 2). In the first step, 4-bromoacetophenone was converted to 4-[(triisopropylsilyl)ethynyl]acetophenone (**8**) by cross-coupling with (triisopropylsilyl)acetylene following a procedure similar to that used by Takahashi et al. in the preparation of the trimethylsilyl-protected analogue.[14] Then, the methyl ketone was converted to a terminal alkyne using the procedure of Negishi et al.[15] affording **9**. When trimethylsilyl was used as a protecting group, the acetylide ion formed by treating the ketone with lithium diisopropylamide and diethyl chlorophosphate attacked the trimethylsilyl group and a mixture of non-, mono-, and disilylated dialkyne was obtained. 9,10-Diiodoanthracene was prepared from 9,10-dibromoanthracene by lithiation followed by iodinolysis.[16] 1,4-Diiodonaphthalene was obtained from 1,4-dibromonaphthalene using the same procedure but in this case, the use of more than 4 equivalents of *tert*-butyllithium was necessary to drive the formation of the intermediate dilithio compound to completion.

The **D-B-A** systems were then assembled using the reaction conditions developed by Wagner et al.,[8] i.e. treatment with $Pd_2(dba)_3{\cdot}CHCl_3/Ph_3As$ (dba = dibenzylideneacetone) in a mixture of toluene and triethylamine at 40°C (Schemes 2 and 3). The bridge building block **9** was reacted with zinc iodoporphyrin **3**, the resulting porphyrin was deprotected and zinc ethynylporphyrin **11** was coupled with free base iodoporphyrin **4** affording **ZnP-BB-H_2P**.

The coupling products were obtained in decent yields (65 and 62%) using a reaction time of 4 hours. The coupling reactions of the naphthyl and anthryl iodides were slower. In the first step in the preparation of **ZnP-NB-H_2P** and **ZnP-AB-H_2P**, zinc ethynylporphyrin **7** was treated with a

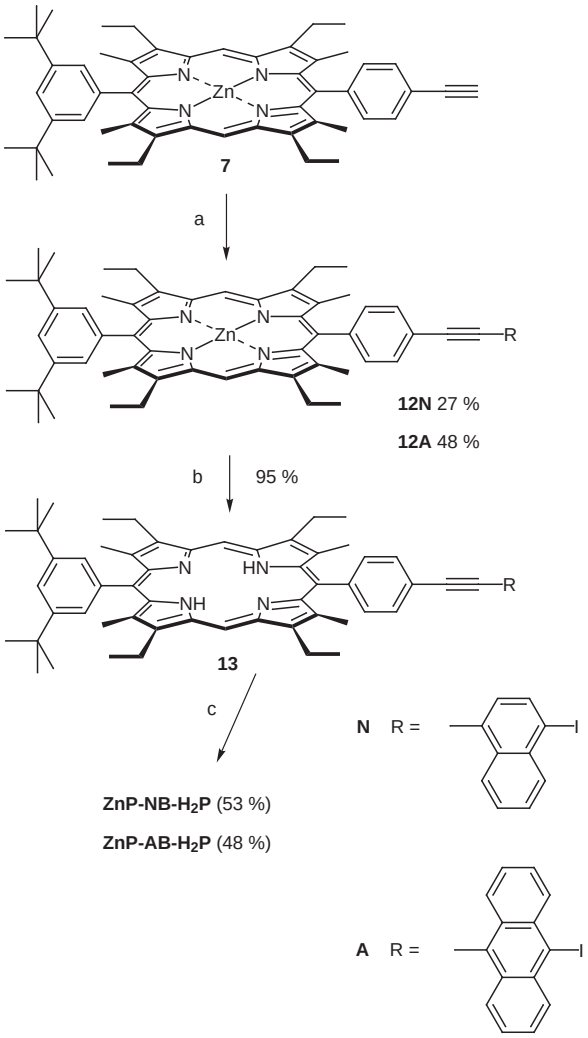


Scheme 2 Reagents and conditions: (a) (triisopropylsilyl)acetylene, $(Ph_3P)_4Pd$ (5 mol%), CuI (10 mol%), Et_3N, reflux, 2 h;[14] (b) LDA, THF, –78°C, 1 h; $(EtO)_2P(O)Cl$, –78°C to r. t., 3 h; LDA, –78°C to r.t., 2.5 h;[15] (c) Ref. 13; (d) **3**, $Pd_2(dba)_3{\cdot}CHCl_3$, Ph_3As, toluene/Et_3N (3:1), 40°C, 4 h; (e) Bu_4NF, THF, r.t.; 1 h; (f) **4**, $Pd_2(dba)_3{\cdot}CHCl_3$, Ph_3As, toluene/Et_3N (3:1), 40°C, 4 h

five-fold excess of 1,4-diiodonaphthalene and 9,10-diiodoanthracene, respectively (Scheme 3). The building blocks **12** were obtained in low but synthetically useful yields (27 and 48%) by heating the reaction mixture to 40°C for 4 days. Attempts were also made to prepare the building blocks **12** at reflux temperature but this led to a complex mixture of compounds both when Ph_3P and Ph_3As were employed as a ligand. The zinc iodoporphyrins **12** were demetalated to the corresponding free base iodoporphyrins **13**. These were then coupled with zinc ethynylporphyrin **7** (Scheme 3). This route was chosen in order to facilitate the purification of the final products, **ZnP-NB-H_2P** and **ZnP-AB-H_2P**, because it was easy to remove di(zinc porhyrin) dimers from the **D-B-A** systems using CH_2Cl_2 on silica gel, whereas di(free base porphyrin) dimers had a chromatographic mobility comparable to that of the **D-B-A** systems. This means, that any butadiyne linked dimer formed as a byproduct in the cross-coupling reaction of **13** and zinc ethynylporphyrin **7**, was a di(zinc porphyrin) which was easy to separate from the **D-B-A** systems **ZnP-NB-H_2P** and **ZnP-AB-H_2P**.

The compounds **1**, **2**, **14**, **16**, and **17** (Schemes 1 and 4) correspond to different parts of the **D-B-A** systems. These compounds have been used as references in the photophysical investigations.[6] The bis(di-*tert*-butylphenyl)-substituted porphyrins **1** (free base porphyrin) and **2** (zinc porphyrin) have been used as model compounds for the separate acceptor and donor, respectively. These porphyrins were isolated in the preparation of porphyrins **3** and **5**. The bridge chromophores **14**[17] were prepared by Pd/Cu catalyzed cross-coupling of phenylacetylene and 1,4-diiodobenzene, 1,4-diiodonaphthalene, and 9,10-diiodoanthracene, respectively. Following flash chromatography (silica gel, pentane/toluene 10:1) the bridge chromophores were isolated in 63–92% yield. The building blocks **15** were prepared by the same procedure using a three-fold excess of the diiodoaryls; **15** were then coupled with zinc ethynylporphyrin **7** affording reference porphyrins **16**. The zinc reference porphyrins were demetalated to the corresponding free base porphyrins **17**.

Et_2O, toluene and THF were dried by distillation from sodium/benzophenone under N_2. CH_2Cl_2, Et_3N and MeCN were dried by distillation from CaH_2 under N_2. Dried solvents were used immediately after distillation. Commercially available reagents were used without further purification. Column chromatography of zinc porphyrins and porphyrin dimers was performed using silica gel (Merck, grade 60, 70–230 mesh). Flash chromatography was performed using silica gel (Matrex LC 60 Å / 35–70 micron). Size exclusion chromatography (SEC) was performed using BioRad Bio-Beads S-X3 in toluene. ^1H (400 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded at r.t. with $CDCl_3$ as solvent, using a Varian UNITY-400 NMR spectrometer. Chemical shifts are reported relative to TMS (δ_H 0) and $CDCl_3$ (δ_C 77.0). Mass spectra were recorded using a VG ZabSpec instrument. Porphyrin containing substances were analyzed by positive FAB-MS (matrix 3-nitrobenzyl alcohol), other substances were analyzed by EI-MS (70 eV). Deaeration of reaction mixtures was performed by bubbling argon through the solution for 30 min. All palladium-catalyzed reactions were performed under argon atmosphere, palladium-catalyzed reactions involving porphyrins were performed in the dark. 3,3'-Diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane,[10] 3,5-di-*tert*-butylbenzaldehyde,[11a] 4-[(trimethylsilyl)ethynyl]benzaldehyde,[11b] 9,10-diiodoanthracene,[16] 1,4-dibromonaphthalene,[18] and $Pd_2(dba)_3{\cdot}CHCl_3$[19] were prepared according to the literature procedures.



Scheme 3 Reagents and conditions: (a) diiodoaryl (5 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$, Ph_3As, toluene/Et_3N (3:1), 40°C, 96 h; (b) TFA, CH_2Cl_2, r.t., 1 h; (c) **7**, $Pd_2(dba)_3{\cdot}CHCl_3$, Ph_3As, toluene/Et_3N (3:1), 40°C, 48 h

Demetalation of Zinc Porphyrins; General Procedure

Zinc porphyrins were demetalated with trifluoroacetic acid (TFA) using the method of Lindsey et al.[20] The zinc porphyrin was dissolved in 10% TFA in CH_2Cl_2 (ca 0.5 mL/μmol) and the solution immediately turned dark green. The mixture was stirred at r.t. for 1 h in the dark and poured into EtOAc. The solution was washed with 5% aq $NaHCO_3$ solution until the reddish porphyrin color returned, washed with H_2O, and dried (Na_2SO_4). The free base porphyrins were purified by chromatography on silica gel. Traces of zinc porphyrin were removed using CH_2Cl_2 and the free base porphyrin was then eluted by adding MeOH to the eluent. Removal of the solvents and drying in vacuo gave the free base porphyrins as brown solids in 90–95% yield.

1,4-Diiodonaphthalene

A solution of 1,4-dibromonaphthalene (3.00 g, 10.5 mmol) in anhyd Et_2O (40 mL) was treated with *t*-BuLi in pentane (53 mmol, 33 mL of a 1.60 M solution) and iodine crystals (8.90 g, 35 mmol) using the procedure of Duerr et al.[16] The mixture was then diluted with Et_2O (100 mL) and transferred to a separatory funnel and washed with 10% aq $Na_2S_2O_3$ solution (5 × 30 mL) and H_2O (30 mL). The organic phase was dried (Na_2SO_4), filtered, and evaporated. The crude product was redissolved in CH_2Cl_2 (100 mL) and filtered through a pad of silica. Removal of the solvent and recrystallization from EtOH gave 2.42 g (61%) of pale yellow needles, mp 110–111°C (Lit.[21] mp 110–111°C).

^{1}H NMR: δ = 7.60 (AA'BB', 2 H, ArH), 7.51 (s, 2 H, ArH), 8.04 (AA'BB', 2 H, ArH).

^{13}C NMR: δ = 100.7, 128.6, 133.0, 134.7, 138.1.

5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[(trimethylsilyl)ethynyl]phenyl}porphyrin (5)

3,5-Di-*tert*-butylbenzaldehyde (1.10 g, 4.8 mmol), 4-[(trimethylsilyl)ethynyl]benzaldehyde (0.97 g, 4.8 mmol) and 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane (2.10 g, 9.6 mmol) were dissolved in anhyd MeCN (100 mL). Trichloroacetic acid (0.27 g, 1.6 mmol) was added and the solution was stirred under argon at r.t. for 18 h in the dark. A solution of DDQ (3.50 g, 15.4 mmol) in anhyd THF (100 mL) was added, and the mixture was stirred for another 3 h. It was then poured into H_2O (200 mL) and extracted with $CHCl_3$ (4 × 150 mL) until the extract was colorless. The combined $CHCl_3$ layers were washed with 5% aq $NaHCO_3$ solution (5 × 150 mL) and H_2O (150 mL), and dried (Na_2SO_4). Silica gel (20 g) was added to the solution, the solvent was removed under reduced pressure, and the sample was added to a chromatographic column. The porphyrins were separated by flash chromatography (silica gel, pentane/Et_2O, 40:1 to pentane/Et_2O, 20:1). Recrystallization from CH_2Cl_2/MeOH gave 1.32 g (33% yield; purple crystals) of **5** and 0.55 g (13% yield; purple crystals) of **1**.[22] The disilylated porphyrin was not isolated.

^{1}H NMR: δ = −2.44 (br s, 2 H, NH), 0.40 [s, 9 H, $Si(CH_3)_3$], 1.50 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.51 (s, 6 H, pyrrole-CH_3), 4.02 (m, 8 H, CH_2CH_3), 7.80 (t, 1 H, *J* = 1.8 Hz, ArH), 7.88 (dm, 2 H, *J* = 8 Hz, ArH), 7.91 (d, 2 H, *J* = 1.8 Hz, ArH), 8.05 (dm, 2 H, *J* = 8 Hz, ArH), 10.23 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{57}H_{70}N_4Si$ 838.537, found 838.536. *m*/*z* Calcd for $C_{57}H_{70}N_4Si + H^+$ 839.545, found 839.545.

Zinc(II) 5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-{4-[(trimethylsilyl)ethynyl]phenyl}porphyrin (6)

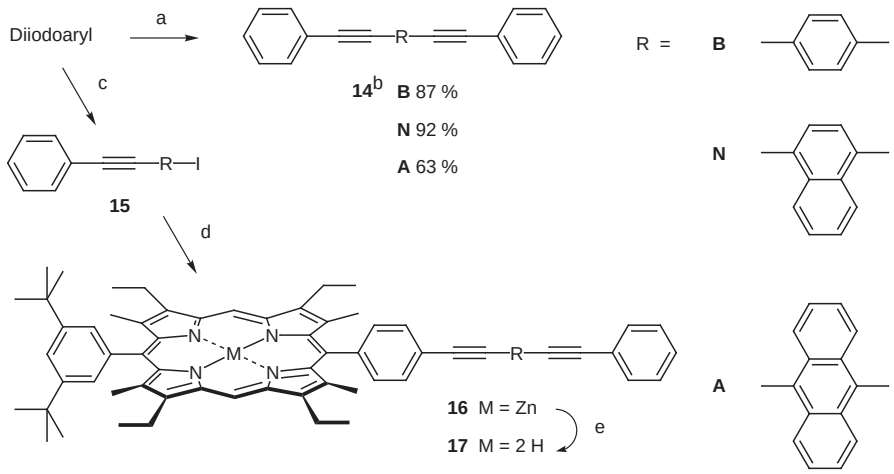
Free base porphyrin **5** (0.88 g, 1.05 mmol) was dissolved in CH_2Cl_2 (250 mL), then $Zn(OAc)_2{\cdot}2H_20$ (0.44 g, 2.0 mmol) dissolved in MeOH (30 mL) was added. The mixture was stirred at r.t. for 3 h and poured into EtOAc (200 mL). The solution was washed with 5% aq $NaHCO_3$ solution (2 × 150 mL) and H_2O (2 × 100 mL). The organic phase was dried (Na_2SO_4), and evaporated. The residue was redissolved in CH_2Cl_2 and chromatographed through a short column of silica gel to remove free base porphyrin which was stuck on the top of the column. Removal of the solvent gave 0.93 g (98%) of a red powder.

^{1}H NMR: δ = 0.41 [s, 9 H, $Si(CH_3)_3$], 1.51 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.44 (s, 6 H, pyrrole-CH_3), 2.49 (s, 6 H, pyrrole-CH_3), 4.01 (m, 8 H, CH_2CH_3), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.87 (dm, 2 H, *J* = 8 Hz, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 8.05 (dm, 2 H, *J* = 8 Hz, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{57}H_{68}N_4SiZn$ 900.450, found 900.445.

Zinc(II) 5-(3,5-Di-*tert*-butylphenyl)-15-(4-ethynylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (7)

A sample of **6** (0.66 mmol, 0.60 g) was dissolved in anhyd THF (100 mL) under argon. Bu_4NF (1.3 mmol, 1.2 ml of a 1.1 M solution in THF) was added, and the mixture was stirred at r.t. for 1 h. The solvent was removed and the solid residue was dissolved in $CHCl_3$



Scheme 4 Reagents and conditions: (a) phenylacetylene, $(Ph_3)_4Pd$ (5 mol%), CuI (10 mol%), Et_3N, reflux, 2 h; (b) Ref. 17; (c) phenylacetylene, $(Ph_3P)_4Pd$ (5 mol%), CuI (10 mol%), Et_3N; (d) **7**, $Pd_2(dba)_3{\cdot}CHCl_3$, Ph_3As, toluene/Et_3N (3:1), reflux, 2 h; (e) TFA, CH_2Cl_2, r.t., 1 h

(150 mL). The organic phase was washed with 5% aq $NaHCO_3$ solution (2 ↔ 50 mL), dried (Na_2SO_4), and filtered. Silica gel (15 g) was added to the solution, the solvent was removed under reduced pressure, and the sample was added to a chromatographic column. Chromatography (silica gel , pentane/Et_2O, 20:1) gave 0.47 g (86%) of purple crystals.

^{1}H NMR: δ = 1.51 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.44 (s, 6 H, pyrrole-CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 3.33 (s, 1 H, CCH), 4.00 (m, 8 H, CH_2CH_3), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.89 (dm, 2 H, *J* = 8 Hz, ArH), 7.94 (d, 2 H, *J* = 1.8 Hz, ArH), 8.06 (dm, 2 H, *J* = 8 Hz, ArH), 10.18 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{54}H_{60}N_4Zn$ 828.411, found 828.409.

Zinc(II) 5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-iodophenylporphyrin (3)

Prepared from 4-iodobenzaldehyde (1.61 g, 6.94 mmol) as described for **5**. The crude porphyrin mixture was metalated as described for **6** before separation on silica gel. Chromatography (silica gel, pentane/CH_2Cl_2, 7:3) gave 1.62 g (25%) of **5** and 0.78 g (12%) of **2**.[22]

^{1}H NMR: δ = 1.51 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.44 (s, 6 H, pyrrole-CH_3), 2.50 (s, 6 H, pyrrole-CH_3), 4.00 (m, 8 H, CH_2CH_3), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.84 (dm, 2 H, *J* = 8 Hz, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 8.08 (dm, 2 H, *J* = 8 Hz, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{52}H_{59}N_4IZn$ 930.308, found 930.305.

5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-iodophenylporphyrin (4)

Zinc porphyrin **3** was demetalated as described above in the general procedure.

^{1}H NMR: δ = –2.44 (br s, 2 H, NH), 1.50 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.53 (s, 6 H, pyrrole-CH_3), 4.02 (m, 8 H, CH_2CH_3), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.84 (dm, 2 H, *J* = 8 Hz, ArH), 7.91 (d, 2 H, *J* = 1.8 Hz, ArH), 8.09 (dm, 2 H, *J* = 8 Hz, ArH), 10.23 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{52}H_{61}N_4I$ 868.394, found 868.394. *m*/*z* Calcd for $C_{52}H_{61}N_4I + H^+$ 869.402, found 869.402.

1-[(Triisopropylsilyl)ethynyl]-4-{[zinc(II) 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}benzene (10)

Ph_3As (20 mg, 65 μmol) and $Pd_2(dba_3){\bullet}CHCl_3$ (8 mg, 8 μmol) were added to a deaerated solution of **3** (50 mg, 54 μmol) and the monoprotected dialkyne **9** (23 mg, 81 μmol) in toluene/Et_3N (3:1, 16 mL). The mixture was stirred at 40°C for 4 h and concentrated. Chromatography (silica gel, pentane/CH_2Cl_2, 3:1) and SEC gave 38 mg (65%) of a red solid.

^{1}H NMR: δ = 1.17 [s, 21 H, $CH(CH_3)_2$], 1.51 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.45 (s, 6 H, pyrrole-CH_3), 2.51 (s, 6 H, pyrrole-CH_3), 4.01 (m, 8 H, CH_2CH_3), 7.56 (dm, 2 H, *J* = 8 Hz, ArH), 7.64 (dm, 2 H, *J* = 8 Hz, ArH), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.94 (m, 4 H, ArH), 8.10 (dm, 2 H, *J* = 8 Hz, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{71}H_{84}N_4SiZn$ 1084.594, found 1084.576.

1-Ethynyl-4-{[zinc(II) porphyrinyl]phenylethynyl}benzene 11

The silylated ethynylporphyrin **10** (38 mg, 35 μmol) was deprotected with Bu_4NF (105 μmol, 95 mL of a 1.1 M solution) using the same procedure as in the preparation of **7**. The crude product was purified by SEC to remove residues of the protecting group. Removal of the solvent and drying in vacuo afforded 24 mg (74%) of **11**.

^{1}H NMR: δ = 1.51 (s, 18 H, *t*-C_4H_9), 1.77 (m, 12 H, CH_2CH_3), 2.44 (s, 6 H, pyrrole-CH_3), 2.52 (s, 6 H, pyrrole-CH_3), 3.22 (s, 1 H, CCH), 4.01 (m, 8 H, CH_2CH_3), 7.57 (dm, 2 H, *J* = 8 Hz, ArH), 7.66 (dm, 2 H, *J* = 8 Hz, ArH), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.93 (m, 4 H, ArH), 8.10 (dm, 2 H, *J* = 8 Hz, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{62}H_{64}N_4Zn$ 928.442, found 928.445.

1-{[5-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}-4-{[zinc(II) 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}benzene (ZnP-BB-H_2P)

Ph_3As (10 mg, 33 μmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mg, 4 μmol) were added to a deaerated solution of **4** (34 mg, 39 μmol) and zinc ethynylporphyrin **11** (24 mg, 26 μmol) in toluene/Et_3N (3:1, 12 mL). The mixture was stirred at 40°C for 4 h and concentrated. Chromatography (silica gel, CH_2Cl_2 to CH_2Cl_2/MeOH, 50:1), and SEC gave 27 mg (62%) of a red solid.

^{1}H NMR: δ = –2.41 (br s, 2 H, NH), 1.52 (s, 36 H, *t*-C_4H_9), 1.79 (m, 24 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 2.56 (s, 6 H, pyrrole-CH_3), 2.59 (s, 6 H, pyrrole-CH_3), 4.03

(m, 16 H, CH_2CH_3), 7.79 (s, 4 H, ArH), 7.82 (m, 2 H, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 7.95 (d, 2 H, *J* = 1.8 Hz, ArH), 7.98 (dm, 4 H, *J* = 8 Hz, ArH), 8.14 (m, 4 H, ArH), 10.22 (s, 2 H, *meso*), 10.26 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{114}H_{124}N_8Zn$ 1668.924, found 1668.936.

1-Iodo-4-{[zinc(II) 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}naphthalene (12N)

Ph_3As (32 mg, 106 μmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (13 mg, 13 μmol) were added to a deaerated solution of **7** (73 mg, 88 μmol) and 1,4-diiodonaphthalene (167 mg, 440 μmol) in toluene/Et_3N (3:1, 28 mL). The mixture was stirred at 40°C for 4 days and concentrated. Chromatography (silica gel, pentane/CH_2Cl_2, 3:1) gave 26 mg (27%) of a red solid.

^{1}H NMR: δ = 1.52 (s, 18 H, *t*-C_4H_9), 1.78 (m, 12 H, CH_2CH_3), 2.45 (s, 6 H, pyrrole-CH_3), 2.56 (s, 6 H, pyrrole-CH_3), 4.02 (m, 8 H, CH_2CH_3), 7.61 (d, 1 H, *J* = 7.6 Hz, ArH), 7.66 (AA'BB', 1 H, ArH), 7.73 (AA'BB', 1 H, ArH), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.94 (d, 2 H, *J* = 1.8 Hz, ArH), 8.05 (dm, 2 H, *J* = 8.0 Hz, ArH), 8.16 (m, 4 H, ArH), 8.62 (AA'BB', 1 H, ArH), 10.20 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{64}H_{65}IN_4Zn$ 1080.355, found 1080.367.

9-Iodo-10-{[zinc(II) porphyrinyl]phenylethynyl}anthracene 12A

Prepared from zinc ethynylporphyrin **7** (95 mg, 0.11 mmol) and 9,10-diiodoanthracene (237 mg, 0.55 mmol) as described for **12N**. Following purification by column chromatography (silica gel, pentane/CH_2Cl_2, 4:1 to pentane/CH_2Cl_2, 2:1) and SEC, **12A** was isolated in 48% yield.

^{1}H NMR: δ = 1.52 (s, 18 H, *t*-C_4H_9), 1.78 (m, 12 H, CH_2CH_3), 2.45 (s, 6 H, pyrrole-CH_3), 2.61 (s, 6 H, pyrrole-CH_3), 4.02 (m, 8 H, CH_2CH_3), 7.63 (AA'BB', 2 H, ArH), 7.69 (AA'BB', 2 H, ArH), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.94 (d, 2 H, *J* = 1.8 Hz, ArH), 8.21 (m, 4 H, ArH), 8.54 (AA'BB', 2 H, ArH), 8.88 (AA'BB', 2 H, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{68}H_{67}IN_4Zn$ 1130.370, found 1130.365.

Free Base Iodoporphyrins 13

The zinc iodoporphyrins **12** were demetalated as described above in the general procedure.

Compound **13N**

^{1}H NMR: δ = –2.41 (br s, 2 H, NH), 1.51 (s, 18 H, *t*-C_4H_9), 1.79 (m, 12 H, CH_2CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 2.59 (s, 6 H, pyrrole-CH_3), 4.03 (m, 8 H, CH_2CH_3), 7.63 (d, 1 H, *J* = 7.6 Hz, ArH), 7.70 (AA'BB', 1 H, ArH), 7.78 (AA'BB', 1 H, ArH), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.92 (d, 2 H, *J* = 1.8 Hz, ArH), 8.05 (dm, 2 H, *J* = 8.0 Hz, ArH), 8.14–8.22 (m, 4 H, ArH), 8.63 (AA'BB', 1 H, ArH), 10.25 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{64}H_{67}IN_4$ 1018.441, found 1018.440. Calcd for $C_{64}H_{67}IN_4$+H^+1019.449, found 1019.446.

Compound **13A**

^{1}H NMR: δ = –2.40 (br s, 2 H, NH), 1.51 (s, 18 H, *t*-C_4H_9), 1.80 (m, 12 H, CH_2CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 2.64 (s, 6 H, pyrrole-CH_3), 4.04 (m, 8 H, CH_2CH_3), 7.72 (AA'BB', 4 H, ArH), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 8.20 (m, 4 H, ArH), 8.60 (AA'BB', 2 H, ArH), 8.91 (AA'BB', 2 H, ArH), 10.26 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{68}H_{69}IN_4$ 1068.457, found 1068.463. *m*/*z* Calcd for $C_{68}H_{69}IN_4$ + H^+1069.465, found 1069.474.

1-{[Free Base Porphyrinyl]phenylethynyl}-4-{[zinc(II) porphyrinyl]phenylethynyl}naphthalene ZnP-NB-H_2P

Ph_3As (9 mg, 29 μmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (4 mg, 4 μmol) were added to a deaerated solution of **13N** (24 mg, 24 μmol) and **7** (30 mg, 36 μmol) in toluene/Et_3N (3:1, 12 mL). The mixture was stirred at 40°C for 4 d and concentrated. Chromatography (silica gel, CH_2Cl_2 to CH_2Cl_2/MeOH, 50:1), and SEC gave 22 mg (53%) of a red solid.

^{1}H NMR: δ = –2.38 (br s, 2 H, NH), 1.52 (s, 36 H, *t*-C_4H_9), 1.81 (m, 24 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.48 (s, 6 H, pyrrole-CH_3), 2.61 (s, 6 H, pyrrole-CH_3), 2.63 (s, 6 H, pyrrole-CH_3), 4.05 (m, 16 H, CH_2CH_3), 7.82–7.88 (m, 4 H, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 7.95 (d, 2 H, *J* = 1.8 Hz, ArH), 8.03 (s, 2 H, ArH), 8.11 (dm, 4 H, *J* = 8 Hz, ArH), 8.20 (m, 4 H, ArH), 8.79 (AA'BB', 2 H, ArH), 10.23 (s, 2 H, *meso*), 10.27 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{118}H_{126}N_8Zn$ 1718.940, found 1718.849.

9-{[Free Base Porphyrinyl]phenylethynyl}-10-{[zinc(II) porphyrinyl]phenylethynyl}anthracene ZnP-AB-H_2P

Prepared from **13A** (35 mg, 33 μmol) and **7** (39 mg, 47 μmol) as described for **ZnP-NB-H_2P**. Chromatography (silica gel, CH_2Cl_2 to CH_2Cl_2/MeOH, 50:1), and SEC gave 28 mg (48%) of a red solid.

^{1}H NMR: δ = –2.38 (br s, 2 H, NH), 1.52 (s, 36 H, *t*-C_4H_9), 1.81 (m, 24 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.48 (s, 6 H, pyrrole-CH_3), 2.65 (s, 6 H, pyrrole-CH_3), 2.67 (s, 6 H, pyrrole-CH_3), 4.05 (m, 16 H, CH_2CH_3), 7.83 (m, 6 H, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 7.95 (d, 2 H, *J* = 1.8 Hz, ArH), 8.25 (s, 8 H, ArH), 9.02 (AA'BB', 4 H, ArH), 10.24 (s, 2 H, *meso*), 10.28 (s, 2 H, *meso*).

HRMS: *m*/*z* Calcd for $C_{122}H_{128}N_8Zn$ 1768.955, found 1768.930.

1-Phenylethynyl-4-iodobenzene (15B)

Phenylacetylene (0.22 mL, 2.0 mmol) was added to a deaerated solution of 1,4-diiodobenzene (2.0 g, 6.1 mmol), $(Ph_3P)_4Pd$ (48 mg, 41 μmol) and CuI (16 mg, 84 μmol) in Et_3N (40 mL). The mixture was stirred at r.t. for 1.5 h, filtered, and evaporated. Flash chromatography (silica gel, pentane/toluene, 100:1) gave 0.48 g (78%) of a white powder. Recrystallization from EtOH gave white flakes, mp 105–106 °C (Lit.[17a] mp 103–105 °C).

^{1}H NMR: δ = 7.25 (dm, 2 H, *J* = 8 Hz, ArH), 7.35 (m, 3 H, ArH), 7.52 (m, 2 H, ArH), 7.69 (dm, 2 H, *J* = 8 Hz, ArH).

1-Phenylethynyl-4-iodonaphthalene (15N)

Prepared from 1,4-diiodonaphthalene (0.95 g, 2.5 mmol) as described for **15B**. The mixture was stirred at r.t. for 30 min and then heated to reflux for another 30 min. The mixture was cooled, filtered, and evaporated. Column chromatography (silica gel, pentane/toluene, 40:1) gave 211 mg (72%) of a colorless oil which solidified. Recrystallization from EtOH gave white needles, mp 90–91°C.

^{1}H NMR: δ = 7.40 (m, 3 H, ArH), 7.45 (d, 1 H, *J* = 8 Hz, ArH), 7.64 (m, 4 H, ArH), 8.08 (d, 1 H, *J* = 8 Hz, ArH), 8.12 (AA'BB', 1 H, ArH), 8.40 (AA'BB', 1 H, ArH).

HRMS: *m*/*z* Calcd for $C_{18}H_{11}I$ 353.991, found 353.995.

Anal. Calcd for $C_{18}H_{11}I$: C, 61.04; H, 3.13. Found C, 60.97; H, 3.04.

9-Phenylethynyl-10-iodoanthracene (15A)

Prepared from 9,10-diiodoanthracene (0.86 g, 2.0 mmol) using the same procedure as for the preparation of **13A**. The mixture was filtered and the solids were washed with a small amount of toluene, leaving most of the unreacted diiodoanthracene on the filter. The filtrate was evoporated. The residue was dissolved in toluene, silica gel (5 g) was added, the solvent removed under reduced pressure, and the sample added to a chromatographic column. Column chromatography (silica gel, pentane/toluene, 40:1) gave 90 mg (33% yield) of a yellow solid, mp 165–166°C.

^{1}H NMR: δ = 7.45 (m, 3 H, ArH) 7.62 (AA'BB', 4 H, ArH), 7.78 (m, 2 H, ArH), 8.52 (AA'BB', 2 H, ArH), 8.66 (AA'BB', 2 H, ArH).

HRMS: *m/z* Calcd for $C_{22}H_{13}I$ 404.006, found 404.008.

Anal. Calcd for $C_{22}H_{13}I$: C, 65.37; H, 3.24. Found C, 65.49; H, 3.22.

1-Phenylethynyl-4-{[zinc(II) 5-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-porphyrinyl]phenylethynyl}benzene (ZnP-phenylene-Bridged 16B)

To a deaerated solution of **7** (58 mg, 70 μmol) and **15B** (43 mg, 141 μmol) in toluene/Et_3N (3:1, 12 mL) were added $Pd_2(dba)_3$·$CHCl_3$ (11 mg, 11 μmol) and Ph_3P (22 mg, 84 μmol) under argon flushing. The mixture was refluxed for 2 h, cooled and concentrated. Chromatography (silica gel, hexane/CH_2Cl_2, 2:1), and SEC gave 42 mg (60%) of a red solid.

^{1}H NMR: δ = 1.51 (s, 18 H, *t*-C_4H_9), 1.78 (m, 12 H, CH_2CH_3), 2.45 (s, 6 H, pyrrole-CH_3), 2.52 (s, 6 H, pyrrole-CH_3), 4.01 (m, 8 H, CH_2CH_3), 7.38 (m, 3 H, ArH), 7.58 (m, 2 H, ArH), 7.61 (dm, 2 H, *J* = 8 Hz, ArH), 7.69 (dm, 2 H, *J* = 8 Hz, ArH), 7.82 (t, 1 H, *J* = 1.8 Hz, ArH), 7.94 (m, 4 H, ArH), 8.11 (dm, 2 H, *J* = 8 Hz, ArH), 10.20 (s, 2 H, *meso*).

HRMS: *m/z* Calcd for $C_{68}H_{68}N_4Zn$ 1004.474, found 1004.473.

1-Phenylethynyl-4-{[zinc(II) porphyrinyl]phenylethynyl}naphthalene, ZnP-naphthylene-Bridged 16N

Prepared from **7** (73 mg, 88 μmol) and **15N** (62 mg, 176 μmol) as described for **16B**. Chromatography (silica gel, hexane/CH_2Cl_2, 2:1) and SEC gave 63 mg (68% yield) of a red solid.

^{1}H NMR: δ = 1.52 (s, 18 H, *t*-C_4H_9), 1.78 (m, 12 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.55 (s, 6 H, pyrrole-CH_3), 4.01 (m, 8 H, CH_2CH_3), 7.42 (m, 3 H, ArH), 7.68–7.84 (m, 6 H, ArH), 7.91 (d, 1 H, *J* = 8 Hz, ArH), 7.95 (d, 2 H, *J* = 1.8 Hz, ArH), 8.06 (dm, 2 H, *J* = 8 Hz, ArH), 8.15 (dm, 2 H, *J* = 8 Hz, ArH), 8.53 (AA'BB', 1 H, ArH), 8.70 (AA'BB', 1 H, ArH), 10.19 (s, 2 H, *meso*).

HRMS: *m/z* Calcd for $C_{72}H_{70}N_4Zn$ 1054.489, found 1054.508.

9-Phenylethynyl-10-{[zinc(II) porphyrinyl]phenylethynyl}anthracene, ZnP-anthrylene-Bridged 16A

Prepared from **7** (30 mg, 36 μmol) and **15A** (32 mg, 79 μmol) as described for **16B**. Chromatography (silica gel, hexane/CH_2Cl_2, 2:1) and SEC gave 26 mg (65%) of a red solid.

^{1}H NMR: δ = 1.52 (s, 18 H, *t*-C_4H_9), 1.79 (m, 12 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.62 (s, 6 H, pyrrole-CH_3), 4.03 (m, 8 H, CH_2CH_3), 7.49 (m, 3 H, ArH), 7.75 (AA'BB', 4 H, ArH), 7.82 (m, 3 H, ArH), 7.95 (d, 1 H, *J* = 8 Hz, ArH), 8.21 (m, 4 H, ArH), 8.77 (AA'BB', 2 H, ArH), 8.94 (AA'BB', 2 H, ArH), 10.22 (s, 2 H, *meso*).

HRMS: *m/z* Calcd for $C_{76}H_{72}N_4Zn$ 1104.505, found 1104.509.

H_2P-Arylene-Bridged 17

The zinc porphyrins **16** were demetalated as described above.

Compound **17B**

^{1}H NMR: δ = –2.43 (br s, 2 H, NH), 1.51 (s, 18 H, *t*-C_4H_9), 1.78 (m, 12 H, CH_2CH_3), 2.46 (s, 6 H, pyrrole-CH_3), 2.56 (s, 6 H, pyrrole-CH_3), 4.03 (m, 8 H, CH_2CH_3), 7.38 (m, 3 H, ArH), 7.58 (m, 2 H, ArH), 7.61 (dm, 2 H, *J* = 8 Hz, ArH), 7.69 (dm, 2 H, *J* = 8 Hz, ArH), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.92 (d, 2 H, *J* = 1.8 Hz, ArH), 7.94 (dm, 2 H, *J* = 8 Hz, ArH), 8.11 (dm, 2 H, *J* = 8 Hz, ArH), 10.24 (s, 2 H, *meso*).

FAB-MS: *m/z* Calcd for $C_{68}H_{70}N_4 + H^+$ 943.6, found 943.2.

Compound **17N**

^{1}H NMR: δ = –2.41 (br s, 2 H, NH), 1.51 (s, 18 H, *t*-C_4H_9), 1.79 (m, 12 H, CH_2CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 2.60 (s, 6 H, pyrrole-CH_3), 4.04 (m, 8 H, CH_2CH_3), 7.43 (m, 3 H, ArH), 7.68–7.80 (m, 4 H, ArH), 7.81 (t, 1 H, *J* = 1.8 Hz, ArH), 7.84 (d, 1 H, *J* = 8 Hz, ArH), 7.92 (m, 3 H, ArH), 8.07 (dm, 2 H, *J* = 8 Hz, ArH), 8.16 (dm, 2 H, *J* = 8 Hz, ArH), 8.56 (AA'BB', 1 H, ArH), 8.71 (AA'BB', 1 H, ArH), 10.25 (s, 2 H, *meso*).

FAB-MS: *m/z* Calcd for $C_{72}H_{72}N_4 + H^+$ 993.6, found 993.2.

Compound **17A**

^{1}H NMR: δ = –2.40 (br s, 2 H, NH), 1.51 (s, 18 H, *t*-C_4H_9), 1.79 (m, 12 H, CH_2CH_3), 2.47 (s, 6 H, pyrrole-CH_3), 2.64 (s, 6 H, pyrrole-CH_3), 4.05 (m, 8 H, CH_2CH_3), 7.49 (m, 3 H, ArH), 7.68–7.85 (m, 7 H, ArH), 7.93 (d, 2 H, *J* = 1.8 Hz, ArH), 8.21 (m, 4 H, ArH), 8.78 (AA'BB', 2 H, ArH), 8.94 (AA'BB', 2 H, ArH), 10.26 (s, 2 H, *meso*).

FAB-MS: *m/z* Calcd for $C_{76}H_{74}N_4 + H^+$ 1043.6, found 1043.3.

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