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Tetrahedron 60 (2004) 2011–2023
Tetrahedron

Synthesis of phenylethyne-linked porphyrin dyads

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Received 8 December 2003; revised 6 January 2004; accepted 6 January 2004

Abstract—Four new porphyrin dyads have been prepared for studies in artificial photosynthesis. The two porphyrins are joined at the *meso* positions via a phenylethyne linker and are present in zinc/zinc or zinc/free base metalation states. The porphyrin bearing the ethynyl unit incorporates zero, one, or two pentafluorophenyl groups at non-linking *meso* positions for tuning the porphyrin redox potentials. The synthetic approach entailed Pd-mediated coupling of porphyrin building blocks that bear a single ethynylphenyl or bromo/iodo substituent.

1. Introduction

Molecular architectures that incorporate multiple porphyrinic pigments can serve as prototype light-harvesting antennas and charge-separation devices for studies in artificial photosynthesis.[1–8] In covalently linked architectures, the chief function of the linker is to anchor the porphyrinic units in a defined location. In addition to this mechanical role, the linker can interact electronically with the porphyrin (altering redox potentials, absorption/emission spectra, and excited-state lifetimes) and also provide a conduit for electronic communication between the porphyrins.

In studies of multiporphyrin light-harvesting arrays, we found that the use of aryl linkers with *meso*-substituted porphyrins resulted in multiporphyrin arrays with visible absorption spectra that were essentially unchanged from those of benchmark reference porphyrins. However, excited-state energy transfer between a zinc porphyrin and a free base porphyrin occurred with high efficiency: the rate was found to be $(38\ \text{ps})^{-1}$, $(24\ \text{ps})^{-1}$, or $(3.5\ \text{ps})^{-1}$ for the porphyrin dyad joined by a 4,4′-diphenylbutadiyne,[9] 4,4′-diphenylethyne,[10] or 1,4-phenylene linker,[11] respectively (Chart 1). The mechanism of energy transfer was found to be dominated by a through-bond contribution (mediated by the linker) rather than a through-space contribution (which would be independent of linker).[12] To investigate the effects of a slightly stronger coupling, we considered the use of a linker that contains an ethynyl unit attached directly to the porphyrin macrocycle.

The study of ethynyl-porphyrins originated with the work of Arnold, who synthesized a nickel(II)octaethylporphyrin bearing an ethynyl group at the *meso* position.[13] Further work by the group of Hevesi[14] and by Anderson[15] led to tetraalkynyl-substituted porphyrins. Ethynyl- or butadiynyl-linked multiporphyrin arrays have been synthesized and characterized by the groups of Arnold,[16–22] Anderson,[23–27] and Therien.[28,29] The general features of alkynyl porphyrins are as follows: (i) significantly red-shifted absorption spectra, (ii) intensified Q-bands relative to the Soret bands, and (iii) less negative reduction potentials.

Milgrom extended this work to porphyrins bearing arylethynyl substituents at the four *meso* positions.[30–35] The

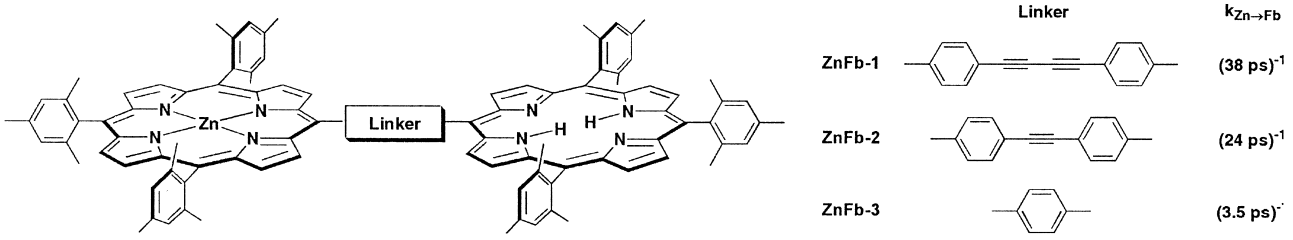

Chart 1.

Keywords: Porphyrin; Dipyrromethane; Ethyne; Phenylethyne; Energy transfer.
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doi:10.1016/j.tet.2004.01.003

arylethynyl units enable incorporation of a variety of substituents on the aryl unit for electronic modulation or increased solubility of the porphyrin,[30–44] and cause a greater red shift and intensification of the Q bands versus that of ethynyl groups alone. Indeed, the spectral perturbation is so pronounced for *meso*-tetrakis(phenylethynyl)-porphyrin versus *meso*-tetraphenylporphyrin that the former afford green solutions, prompting Milgrom to term the former 'chlorphyrins'.[30] Nakano et al. reported the synthesis and energy-transfer properties of all-zinc porphyrin triads wherein the linker was a phenylethynyl unit, or the central porphyrin was substituted with two non-linking phenylethynyl groups.[45] The phenylethynyl-substituted porphyrin exhibits red-shifted spectral features and functions as the low energy-trapping component in the light-harvesting array. In general, in a phenylethyne-linked dyad composed of identical porphyrin components, the ethyne-substituted porphyrin is shifted to lower energy and serves as the acceptor while the phenyl-substituted porphyrin is energetically unperturbed and serves as the donor.

In this paper, we describe the synthesis of porphyrin dyads where the porphyrins are joined by a phenylethyne linker and the two porphyrins are in zinc/free base or zinc/zinc metalation states (Chart 2). The dyads enable the role of the phenylethyne linker in mediating excited-state energy transfer to be probed, particularly by comparison with the dyads described in Chart 1. In addition, we prepared a set of dyads wherein one porphyrin contains one or two pentafluorophenyl groups at non-linking *meso* positions. The pentafluorophenyl groups enable tuning of the energy levels of the porphyrin, thereby opening the possibility of employing the dyads as charge-separation units. For comparison purposes, we have also prepared and characterized a set of benchmark porphyrins containing one or two *meso*-phenylethynyl groups. The electronic and

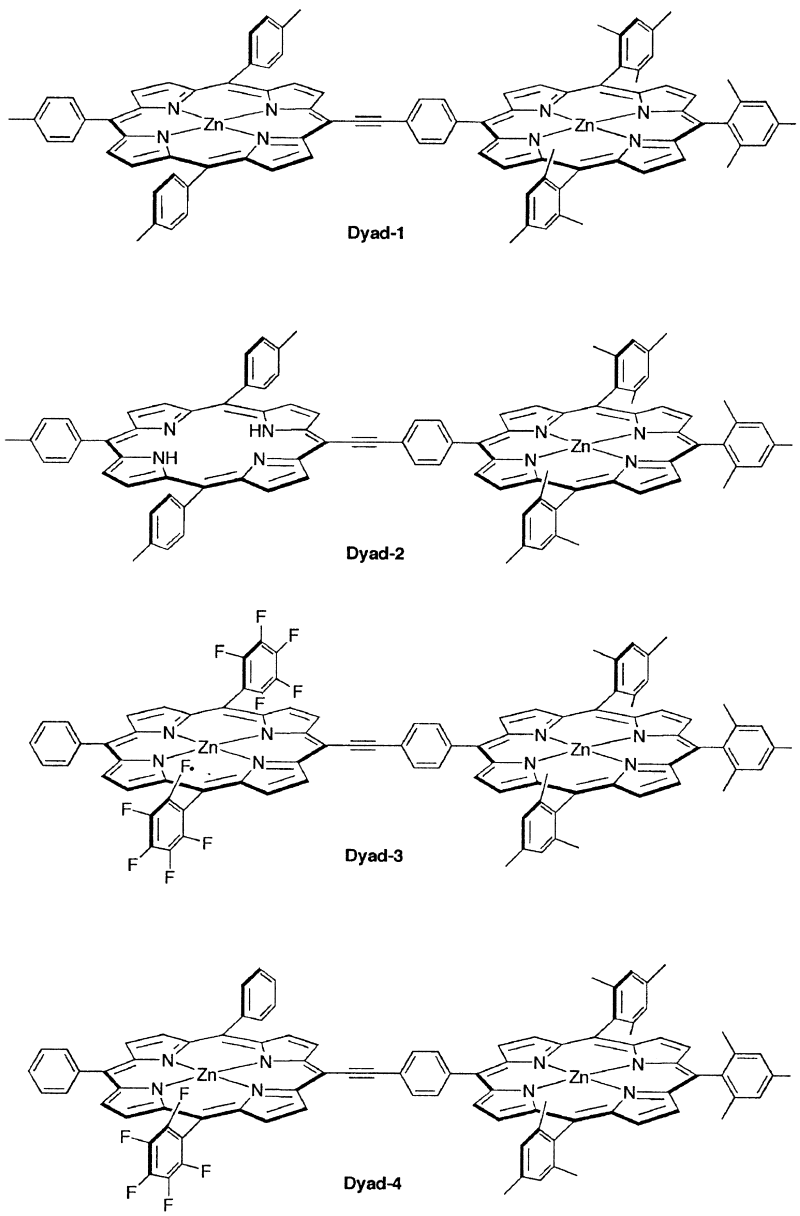


Chart 2.

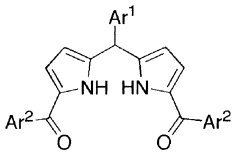
photochemical properties of the dyads and benchmarks are reported elsewhere.[46]

2. Results and discussion

The synthetic route to the phenylethyne-linked porphyrin dyads relies on three methods: (1) the rational synthesis of porphyrin building blocks that bear distinct patterns of substituents,[47,48] including a single ethynylphenyl group or one free *meso* position, (2) halogenation of the lone *meso* position,[49,50] and (3) Pd-mediated coupling of an ethynylphenyl-porphyrin and a halo-porphyrin.[51,52] This route affords control over the metalation state and substituent pattern in each porphyrin in the dyad. While each method is well established, this approach to phenylethyne-linked dyads composed of zinc and free base porphyrins has not been investigated previously.

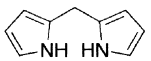
2.1. Synthesis of building blocks

The *meso*-halo-substituted porphyrin building blocks incorporate zero, one, or two pentafluorophenyl substituents to systematically increase the oxidation potential of the porphyrin. The porphyrins with zero or two pentafluorophenyl groups are *trans*-AB_2-porphyrins while those with one pentafluorophenyl group are *cis*-AB_2-porphyrins. The



1a-c

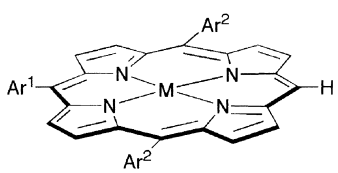
(1) $NaBH_4$, THF, MeOH (10:1)
(2)



2a

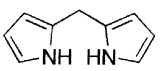
$Yb(OTf)_3$ or $InCl_3$, CH_2Cl_2, rt
20-30 min
(3) DDQ, rt, 1 h

and (optional)
(4) $Zn(OAc)_2 \cdot 2H_2O$
$CHCl_3$, MeOH, rt



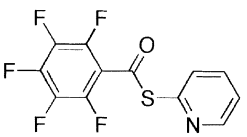
Reactant	Porphyrin	Ar^1	Ar^2	M	Yield (%)
1a ⟶	**Fb3a**	*p*-Tol	*p*-Tol	H,H	14
1b ⟶	**Zn3b**	Ph	Ph	Zn	12
1c ⟶	**Zn3c**	Ph	C_6F_5	Zn	14

Scheme 1.



2a

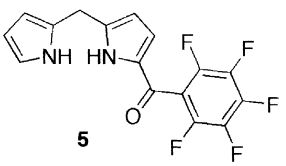
(1) EtMgBr, THF, -78 °C
(2)



4

59%

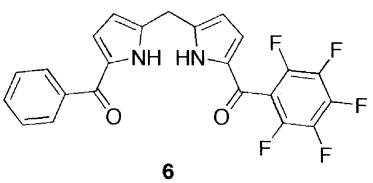
-78 °C



5

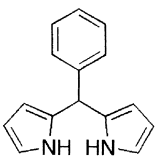
81%

(1) EtMgBr, toluene, rt
(2) benzoyl chloride
toluene



6

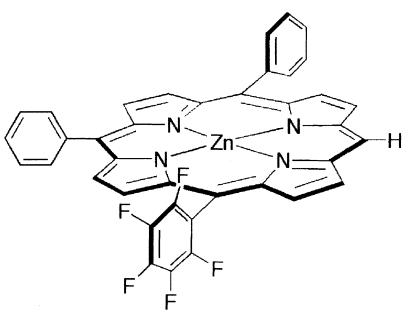
(1) $NaBH_4$, THF, MeOH (10:1)
30 min
(2)



2b

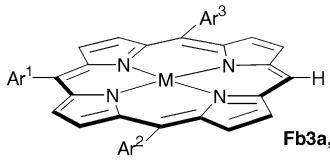
18%

$InCl_3$, CH_2Cl_2
rt, 30 min
(3) DDQ, rt, 1 h
(4) $Zn(OAc)_2 \cdot 2H_2O$
$CHCl_3$, MeOH, rt, 16 h



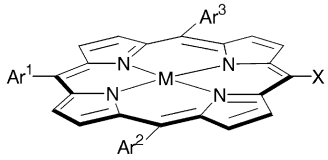
Zn3d

Scheme 2.



Fb3a, Zn3a-d

NBS, pyridine, $CHCl_3$
0 °C, 30 min
or
I_2, [Bis(trifluoroacetoxy)iodo]benzene
$CHCl_3$, pyridine, rt, 1h



Reactant		Porphyrin	Ar^1	Ar^2	Ar^3	M	X	Yield (%)
Fb3a	→	**Fb7a**	*p*-Tol	*p*-Tol	*p*-Tol	H,H	Br	98
Zn3b	→	**Zn7b**	Ph	Ph	Ph	Zn	Br	77
Zn3c	→	**Zn7c**	Ph	C_6F_5	C_6F_5	Zn	Br	96
Zn3d	→	**Zn7d**	Ph	Ph	C_6F_5	Zn	Br	91
Fb3a	→	**Fb8a**	*p*-Tol	*p*-Tol	*p*-Tol	H,H	I	82

Scheme 3.

synthesis of both types of porphyrins proceeds by condensation of a dipyrromethane-dicarbinol and a dipyrromethane followed by oxidation.[47]

The synthesis of the *trans*-AB_2-porphyrins begins with known diacyldipyrromethanes. Thus, reduction of a diacyldipyrromethane (**1a**–**c**)[47,53] with $NaBH_4$ in dry THF/methanol at room temperature gave the corresponding dipyrromethane-dicarbinol. Condensation of the latter with dipyrromethane (**2a**) under new catalysis conditions[54] that employ a mild Lewis acid ($InCl_3$ or $Yb(OTf)_3$ in CH_2Cl_2 at room temperature) followed by oxidation with DDQ afforded the free base porphyrin. In one case, the free base porphyrin was purified (**Fb3a**) while in others, the crude product was treated with zinc acetate and the corresponding zinc porphyrin was obtained (**Zn3b** and **Zn3c**) (Scheme 1). It is noteworthy that earlier synthetic procedures were developed for preparing the triphenylporphyrin **Fb3a** and its zinc chelate **Zn3a**, including (1) mixed-aldehyde condensation of benzaldehyde, paraformaldehyde, and pyrrole,[55] (2) reaction of 5,15-diphenylporphyrin with a phenyl lithium reagent;[56] and (3) Suzuki coupling of phenylboronic acid and Zn(II)-5-bromo-10,20-diphenylporphyrin.[57]

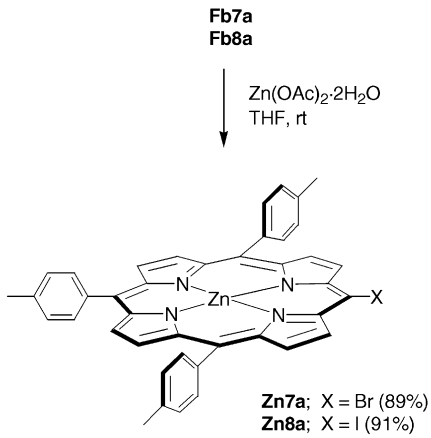
The synthesis of the *cis*-AB_2-porphyrin requires access to an appropriate 1,9-diacyldipyrromethane, which was prepared following the general procedures for the synthesis of ABCD-porphyrins.[47] Thus, dipyrromethane (**2a**)[58,59] was treated with *S*-2-pyridyl pentafluorobenzothioate (**4**)[48] in the presence of EtMgBr in THF, affording the 1-acyl-dipyrromethane **5** in 59% yield. The reaction of **5** with the more potent acylating agent benzoyl chloride in the presence of EtMgBr in toluene gave the 1,9-diacyldipyrromethane **6** in 81% yield. Reduction of **6** with $NaBH_4$ in dry THF/methanol at room temperature gave the corresponding dipyrromethane-dicarbinol, which was condensed with 5-phenyldipyrromethane (**2b**) in the presence of $InCl_3$ in CH_2Cl_2. Subsequent oxidation with DDQ and metalation with $Zn(OAc)_2{\cdot}2H_2O$ afforded the pentafluorophenyl-substituted porphyrin **Zn3d** in 18% yield (Scheme 2).

The availability of porphyrins with a single free *meso* position facilitated preparation of the mono-halo-substituted porphyrins. We prepared both *meso*-bromo and *meso*-iodo porphyrins. Bromination was carried out with either zinc or free base porphyrins (**Fb3a**, **Zn3b**–**d**) using NBS in $CHCl_3$/pyridine for 30 min at 0 °C,[49] in each case affording the mono-brominated porphyrin in high yield. The presence of one or two pentafluorophenyl groups had no adverse effect on the yield of halogenation. Iodination was carried out in one case on a free base porphyrin (**Fb3a**) using [bis(trifluoroacetoxy)iodo]benzene in $CHCl_3$/pyridine for 1 h at room temperature,[50] affording **Fb8a** in 82% yield (Scheme 3). Both procedures are straightforward and the mono-halo-porphyrins are obtained without apparent formation of poly-halogenated products.

The mono-halo-porphyrins are stable to routine handling and manipulation. The free base bromo-porphyrin **Fb7a** was metalated with zinc acetate to give **Zn7a** in 89% yield. The zinc iodo-porphyrin **Zn8a**, prepared by iodination of the zinc porphyrin, also could be prepared by zincation of the free base iodo-porphyrin **Fb8a** in 91% yield (Scheme 4).

2.2. Synthesis of phenylethyne-linked porphyrin dyads

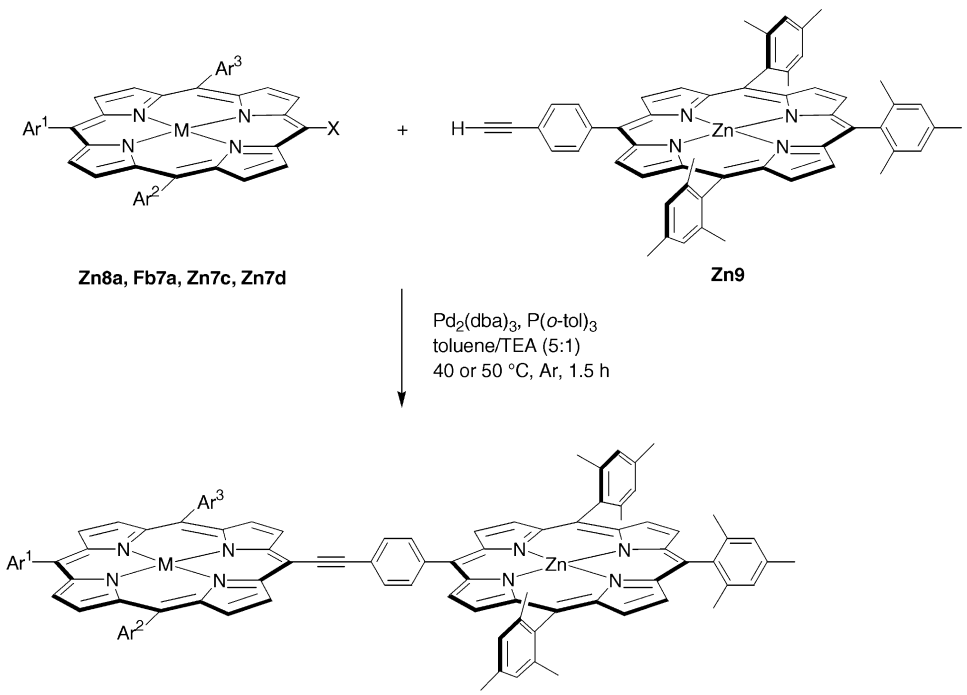
We previously developed conditions for the Sonogashira



Scheme 4.

coupling of an ethynylphenyl-porphyrin and an iodophenyl-porphyrin to give the diphenylethyne-linked porphyrin dyad.[51,52] The key features of the reaction conditions developed for this Pd-mediated coupling reaction were (1) the use of equimolar quantities of the two porphyrins, (2) the reaction in dilute solution, typically 2.5 mM for each porphyrin, (3) the use of low temperatures (e.g., 35 °C), and (4) the absence of copper, which can readily metalate free base porphyrins. We also extended this method to include bromoaryl-porphyrins.[60] The coupling reactions typically afford the desired diphenylethyne-linked porphyrin array in ~60% yield in addition to a sizable quantity of high molecular weight material (HMWM). The purification protocol entails removal of palladium reagents by silica-pad filtration, separation of the target array and HMWM by gravity-flow size exclusion chromatography (SEC), and final silica-gel chromatography to remove residual impurities (including those introduced from the SEC column).

The coupling of ethynylphenyl-porphyrin **Zn9**[51] and iodoporphyrin **Zn8a** under the standard conditions (0.38 mM $Pd_2(dba)_3$ and 3.0 mM P(*o*-tol)$_3$ in toluene/TEA (5:1) at 40 °C with 2.5 mM of each porphyrin) afforded **Dyad-1** in 56% yield accompanied by HMWM as judged by analytical SEC. Several modifications to the reaction conditions were investigated with yields estimated by analytical SEC. Reaction under continuous sonication, replacement of P(*o*-tol)$_3$ with $AsPh_3$, or an increased concentration of the porphyrin building blocks (10 mM) each gave **Dyad-1** in lower yield (~40–45%). On the other hand, reaction with a decreased concentration of the porphyrin building blocks (1.25 or 0.63 mM) gave **Dyad-1** in 60 or 65%. Alternatively, addition of samples of **Zn9** in four portions at 20 min intervals to the reaction mixture gave **Dyad-1** in 65% yield. On the basis of these results, the dyad-forming reactions were performed under Pd-coupling conditions with equimolar quantities of the two porphyrins at 0.63 mM.



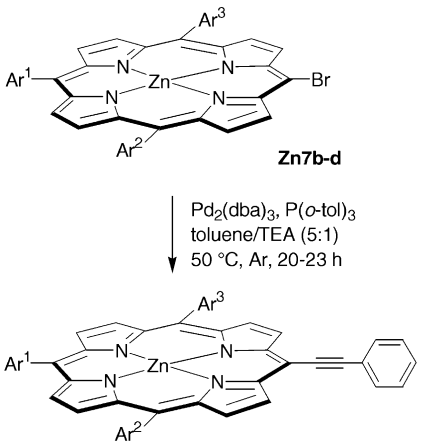
Porphyrins	Ar^1	Ar^2	Ar^3	M	X	Product	Yield (%)
Zn8a + Zn9	*p*-Tol	*p*-Tol	*p*-Tol	Zn	I	**Dyad-1**	41
Fb7a + Zn9	*p*-Tol	*p*-Tol	*p*-Tol	H, H	Br	**Dyad-2**	47
Zn7c + Zn9	Ph	C_6F_5	C_6F_5	Zn	Br	**Dyad-3**	62
Zn7d + Zn9	Ph	Ph	C_6F_5	Zn	Br	**Dyad-4**	48

Scheme 5.

The dilute-solution Pd-coupling conditions were applied to prepare **Dyad-1** as shown in Scheme 5. The same coupling conditions were employed with bromo-porphyrins to give **Dyads-2–4**, although the temperature was increased from 40 to 50 °C due to the use of a *meso*-bromo-porphyrin in place of a *meso*-iodo-porphyrin. After chromatographic workup (three column procedure: silica, SEC, silica), **Dyads-1–4** were obtained in 41–62% yield. The dyads were stable to routine handling.

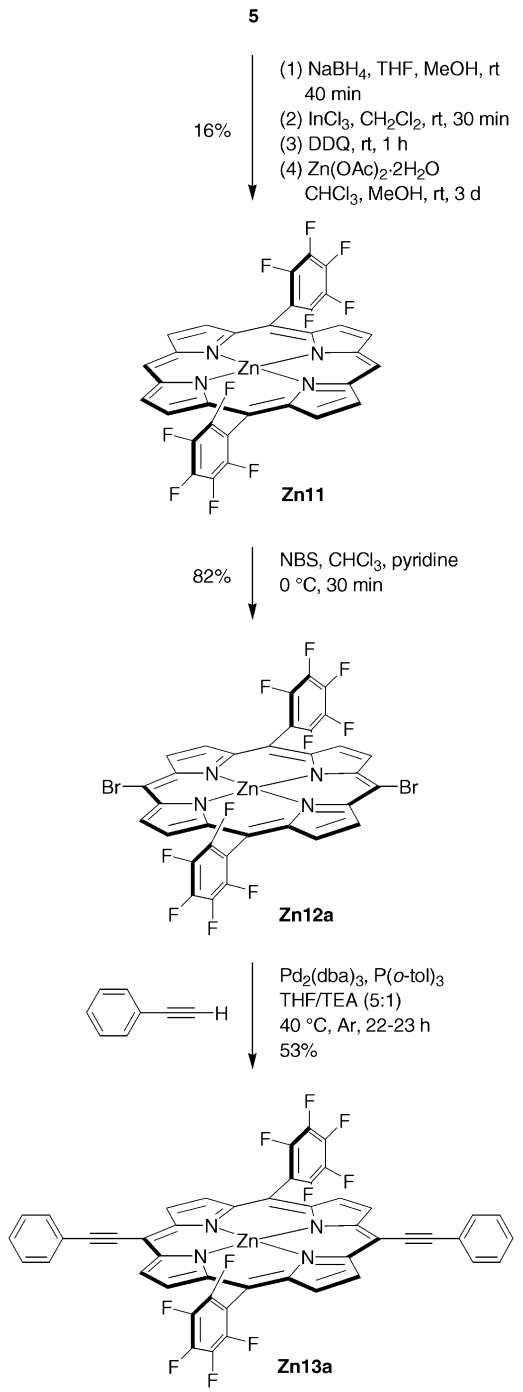
2.3. Synthesis of benchmark porphyrins

For comparison purposes, a series of porphyrins was prepared wherein each porphyrin contains one phenylethynyl group. Thus, the coupling reaction of phenylacetylene and a bromo-porphyrin (**Zn7b–d**) was performed under a slight modification to the standard conditions for bromoaryl-porphyrins [$Pd_2(dba)_3$ and P(*o*-tol)$_3$ in toluene/TEA (5:1) at 50 °C];[60] the modification entailed (1) initial reaction of 2.5 mM porphyrin and 10 mM phenylacetylene, and (2) later addition of an equal quantity of phenylacetylene. After chromatographic workup, phenylethynyl-substituted porphyrins **Zn10b–d** were obtained in 52–74% yield (Scheme 6).



Porphyrin	Ar^1	Ar^2	Ar^3	Yield (%)
Zn10b	Ph	Ph	Ph	52
Zn10c	Ph	C_6F_5	C_6F_5	74
Zn10d	Ph	Ph	C_6F_5	73

Scheme 6.

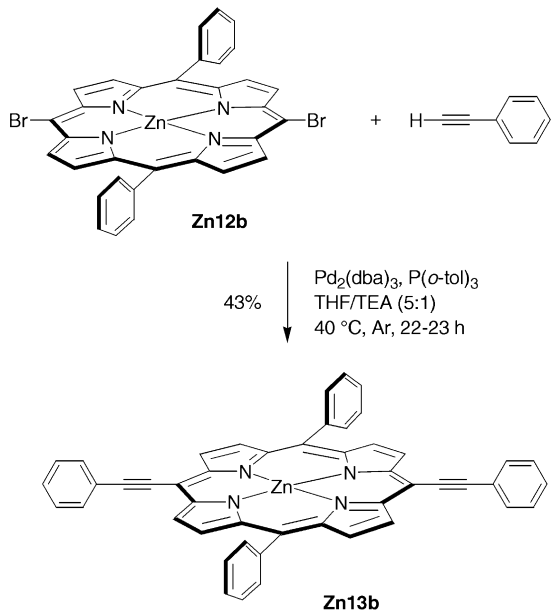


Scheme 7.

2.4. Synthesis of bis(phenylethynyl)porphyrins

Porphyrins bearing two phenylethynyl groups in a *trans*-configuration at the *meso* positions were prepared following a general procedure for the synthesis of *trans*-A_2B_2-porphyrins (Scheme 7).[48] Reduction of 1-acyldipyrromethane **5** with $NaBH_4$ in dry THF/methanol at room temperature afforded the corresponding dipyrromethane-monocarbinol, which underwent self-condensation in CH_2Cl_2 containing $InCl_3$. Subsequent oxidation with DDQ and metalation with zinc acetate afforded porphyrin **Zn11** in 16% yield. Treatment of **Zn11** with NBS afforded dibromo-porphyrin **Zn12a** in 82% yield. **Zn12a** is a known compound but the synthetic procedure has not been described.[61]

Porphyrins **Zn12a** and **Zn12b**[49] were each coupled with excess phenylacetylene in the presence of $Pd_2(dba)_3$ and P(*o*-tol)$_3$ in THF/TEA (5:1) at 40 °C. The solvent THF was employed owing to the limited solubility of the dibromo-porphyrins in toluene (Scheme 8). Upon chromatographic workup, **Zn13a** and **Zn13b** were obtained in 53 and 43% yields, respectively.



Scheme 8.

2.5. Characterization

Each porphyrin was characterized by absorption spectroscopy, laser-desorption mass spectrometry, FAB-MS, ^{1}H NMR spectroscopy, and ^{13}C NMR spectroscopy. Each dyad was examined for purity by analytical SEC and characterized by absorption spectroscopy, fluorescence spectroscopy, laser-desorption mass spectrometry, FAB-MS, ^{1}H NMR spectroscopy, and ^{13}C NMR spectroscopy (except for **Dyad-2**). It is noteworthy that the ^{13}C NMR spectra showed chemical shifts typical of porphyrins bearing four identical *meso* substituents,[62] with multiple resonances consistent with the expected pattern of substituents about the porphyrin perimeter. In the case of zinc porphyrins, characteristic signals of the α-,β-, and *meso*-carbons were easily observed. The signals of the pyrrole α-carbons were observed at 149–153 ppm, while the pyrrole β-carbons gave signals at 130–134 ppm. The chemical shifts of the *meso*-carbons depend on the adjacent substituents: *meso*-H (106 ppm), *meso*-aryl (120 ppm), *meso*-Br (103–104 ppm), *meso*-I (77 ppm), and *meso*-ethyne (100 ppm). In phenylethyne-substituted porphyrins, characteristic signals (93 and 96 ppm) of the ethyne moiety were observed.

3. Conclusions

The synthetic route employed herein relies on the rational synthesis of porphyrin building blocks followed by joining of an ethynylphenyl-porphyrin and a bromo/iodo-porphyrin in a Pd-mediated coupling reaction. The resulting phenylethyne-linked dyads contain porphyrins with defined metalation states and substitution patterns. The phenylethynyl group perturbs the optical and electronic properties of the attached porphyrin. In multiporphyrin arrays, the phenylethyne linker provides a conduit for excited-state energy transfer. The availability of rational synthetic routes to phenylethyne-linked porphyrins enables the phenylethynyl motif to be employed where appropriate in artificial photosynthetic systems.

4. Experimental

4.1. General

^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded in $CDCl_3$ or THF-d_8. Mass spectra of porphyrins were obtained by high-resolution fast atom bombardment (FAB-MS), by laser desorption mass spectrometry (LD-MS) with neat samples,[63] and/or by matrix assisted laser desorption mass spectrometry (MALDI-MS). Absorption and emission spectra were collected in toluene unless noted otherwise. Elemental analyses were performed by Atlantic Microlab, Inc. Melting points are uncorrected. Silica gel (Baker 40 μm average particle size) was used for column chromatography. Preparative SEC was performed using BioRad Bio-Beads SX-1 (200–400 mesh) beads. Analytical SEC was performed using an HP 1100 Series Liquid Chromatograph (column size=300 mm, 1000 Å; flow rate=0.800 mL/min; solvent=THF; quantitation at 420 and 450 nm; reference at 680 nm; oven temperature=25 °C).[64] All Pd-mediated reactions were performed using a Schlenk line. The conditions for Sonogashira reactions with porphyrins use tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and the ligand P(*o*-tol)$_3$ in the absence of any copper reagents.[51,52] Palladium insertion and transmetalation have not been observed with these conditions. Toluene and triethylamine (TEA) were freshly distilled from CaH_2 and sparged of oxygen prior to use. Chloroform contained 0.8% ethanol as a stabilizer.

4.2. Non-commercial compounds

Compounds **1a**,[53] **1b**,[47] **1c**,[53] **2a**,[58,59] **2b**,[59] **4**,[48] **Zn9**,[51] and **Zn12b**[49] were prepared according to the literature.

4.3. Pd-coupling conditions

The standard Pd-coupling conditions[51,52,60] for use with metalloporphyrins and free base porphyrins were modified slightly for the reactions performed herein. The following dilute-solution coupling method was identified for use with an ethynylphenyl-porphyrin and a *meso*-iodo-porphyrin: [ethynylphenyl-porphyrin]=[iodo-porphyrin]=0.63 mM, [$Pd_2(dba)_3$]=0.38 mM, [P(*o*-tol)$_3$]=3.0 mM in toluene/TEA (5:1) at 40 °C. The dyad-forming reactions with a bromo-porphyrin were performed at 50 °C. The reaction of phenylacetylene and a bromo-porphyrin was carried out in a similar manner but with 2.5 mM porphyrin and a 5 or 6-fold molar excess of phenylacetylene (with accompanying Pd-coupling reagents) added in two batches.

4.4. Porphyrin building blocks

4.4.1. 5,10,15-Tris(4-methylphenyl)porphyrin (Fb3a). Following a standard procedure,[47,54]a solution of diacyldipyrromethane **1a** (1.00 g, 2.12 mmol) in dry THF/methanol (50 mL, 10:1) was treated with $NaBH_4$ (1.59 g, 42.4 mmol) at room temperature for 55 min. The reaction was quenched with aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated to dryness. The resulting dipyrromethane-dicarbinol and dipyrromethane **2a** (310 mg, 2.12 mmol) were dissolved in CH_2Cl_2 (848 mL) and treated

with $InCl_3$ (60 mg, 0.32 mmol) at room temperature for 20 min. DDQ (1.44 g, 6.36 mmol) was added and the mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized with TEA and concentrated to dryness. Chromatography [silica, CH_2Cl_2/hexanes (2:1)] afforded a purple solid (177 mg, 14%): ^{1}H NMR ($CDCl_3$) δ −2.97 (s, 2H), 2.70–2.75 (br s, 9H), 7.56 (d, J=7.6 Hz, 2H), 8.11 (d, J=7.6 Hz, 2H), 7.60 (d, J=7.6 Hz, 4H), 8.14 (d, J=7.6 Hz, 4H), 8.89–8.95 (m, 4H), 9.05 (d, J=4.4 Hz, 2H), 9.33 (d, J=4.4 Hz, 2H), 10.20 (s, 1H); ^{13}C NMR (THF-d_8) δ 20.77 (two peaks have overlapped), 104.68, 119.60, 120.54, 127.33, 127.62, 130.2–130.5 (broadening due to NH tautomerism), 131.0–131.6 (broadening due to NH tautomerism), 134.43, 134.66, 137.46 (two peaks have overlapped), 139.22, 140.07, 145.2–145.6 (broadening due to NH tautomerism); LD-MS obsd 580.4; FAB-MS obsd 580.2635, calcd 580.2627 ($C_{41}H_{32}N_4$); λ_{abs} 414, 509, 544, 585, 641 nm.

4.4.2. Zn(II)-5,10,15-triphenylporphyrin (Zn3b). Following a standard procedure[47,54] a solution of **1b** (300 mg, 0.700 mmol) in dry THF/methanol [30 mL (10:1)] was treated with $NaBH_4$ (526 mg, 14.0 mmol) at room temperature for 40 min. The resulting dipyrromethane-dicarbinol and **2a** (102 mg, 0.700 mmol) were dissolved in CH_2Cl_2 (280 mL) and treated with $Yb(OTf)_3$ (555 mg, 0.896 mmol) at room temperature for 20 min. DDQ (477 mg, 2.10 mmol) was added and the mixture was stirred at room temperature for 1 h. After standard workup, chromatography [silica, CH_2Cl_2/hexanes (2:1)] afforded the free base porphyrin. The resulting porphyrin was treated with $Zn(OAc)_2{\cdot}2H_2O$ (154 mg, 0.700 mmol) in $CHCl_3$ (10 mL) and methanol (3 mL) at room temperature for 15 h. Standard workup, chromatography [silica, $CHCl_3$/hexanes (2:1)], and trituration (hexanes) afforded a purple solid (49 mg, 12%): ^{1}H NMR ($CDCl_3$) δ 7.72–7.80 (m, 9H), 8.21–8.25 (m, 6H), 8.97 (d, J=4.4 Hz, 2H), 8.99 (d, J=5.1 Hz, 2H), 9.09 (d, J=4.4 Hz, 2H), 9.39 (d, J=4.4 Hz, 2H), 10.24 (s, 1H); ^{13}C NMR (THF-d_8) δ 105.43, 120.10, 120.96, 126.32, 126.43, 127.29 (two peaks have overlapped), 131.27, 131.39, 131.49, 132.01, 134.59, 134.71, 143.72, 143.92, 149.78, 150.10, 150.18, 150.23; LD-MS obsd 598.56 [M^+]; FAB-MS obsd 600.1307, calcd 600.1292 ($C_{38}H_{24}N_4Zn$); λ_{abs} 418, 543 nm; λ_{em} (λ_{ex}=540 nm) 590, 637 nm.

4.4.3. Zn(II)-5,15-bis(pentafluorophenyl)-10-phenylporphyrin (Zn3c). Following a standard procedure,[47,54] a solution of **1c** (750 mg, 1.23 mmol) in dry THF/methanol [40 mL (10:1)] was treated with $NaBH_4$ (924 mg, 24.6 mmol, 20 M equiv.) at room temperature for 40 min. The resulting dipyrromethane-dicarbinol and **2a** (180 mg, 1.23 mmol) were dissolved in CH_2Cl_2 (492 mL) and treated with $InCl_3$ (35.0 mg, 0.157 mmol) at room temperature for 30 min. DDQ (838 mg, 3.69 mmol) was added and the mixture was stirred at room temperature for 1 h. After standard workup, chromatography [silica CH_2Cl_2/hexanes (3:1)] afforded the free base porphyrin. The resulting porphyrin was treated with $Zn(OAc)_2{\cdot}2H_2O$ (360 mg, 1.64 mmol) in $CHCl_3$ (40 mL) and methanol (10 mL) at room temperature for 4 h. Standard workup, chromatography [silica, $CHCl_3$/hexanes (2:1) then $CHCl_3$/hexanes (3:2)], and trituration (hexanes) afforded a purple solid (132 mg, 14%): ^{1}H NMR ($CDCl_3$) δ 7.77–7.82 (m, 3H), 8.20–8.23 (m, 2H), 8.93 (d, J=5.1 Hz, 2H), 9.05–9.08 (m, 4H), 9.52 (d, J=5.1 Hz, 2H), 10.36 (s, 1H); ^{13}C NMR (THF-d_8) δ 101.63, 106.47, 117.6–118.1 (m), 122.19, 126.48, 127.65, 129.90, 130.68, 133.04, 133.22, 134.61, 135.9–136.3 (m), 139.2–139.6 (m), 143.22, 143.4–143.8 (m), 145.1–145.5 (m), 147.3–147.6 (m), 148.3–148.7 (m), 149.46, 149.68, 150.49, 150.97; MALDI-MS (dithranol) obsd 776.60 [M^+]; FAB-MS obsd 780.0391, calcd 780.0350 ($C_{38}H_{14}F_{10}N_4Zn$); λ_{abs} 416, 542, 576 nm; λ_{em} (λ_{ex}= 540 nm) 583, 637 nm.

4.4.4. 1-(Pentafluorobenzoyl)dipyrromethane (5). Following a standard procedure,[48] a solution of dipyrromethane **2a** (731 mg, 5.00 mmol) in THF (5.0 mL) was treated with EtMgBr (12.5 mL, 12.5 mmol, 1.0 M solution in THF) under argon at −78 °C for 10 min. A solution of **4** (1.53 g, 5.00 mmol) in THF (5.0 mL) was added over 1 min. The reaction mixture was stirred at −78 °C for 10 min, then at room temperature for 30 min. Standard workup and chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] afforded a colorless solid (826 mg, 59%): mp 125–127 °C; ^{1}H NMR ($CDCl_3$) δ 4.06 (s, 2H), 6.04–6.07 (m, 1H), 6.11–6.14 (m, 1H), 6.18–6.20 (m, 1H), 6.66–6.68 (m, 1H), 6.69–6.72 (m, 1H), 8.80 (s, 1H), 11.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.8, 107.2, 108.7, 111.9, 118.1, 125.0, 126.8, 131.0, 136.1–136.3 (m), 139.2–139.7 (m), 140.6–140.9 (m), 142.2–142.5 (m), 143.9–144.3 (m), 144.5, 145.5–145.8 (m), 172.0; FAB-MS obsd 340.0632, calcd 340.0635 ($C_{16}H_9F_5N_2O$). Anal. Calcd: C, 56.48; H, 2.67; N, 8.23. Found: C, 56.44; H, 2.71; N, 8.22.

4.4.5. 1-Benzoyl-9-pentafluorophenyldipyrromethane (6). Following a standard procedure,[48] a solution of **5** (830 mg, 2.44 mmol) in toluene (5 mL) was treated with EtMgBr (4.88 mL, 4.88 mmol, 1.0 M solution in THF) at room temperature under argon. After 5 min, a solution of benzoyl chloride (343 mg, 2.44 mmol) in toluene (5 mL) was added and the mixture was stirred at room temperature for 10 min. A subsequent addition of EtMgBr (2.44 mL, 2.44 mmol, 1.0 M solution in THF) and a solution of benzoyl chloride (343 mg, 2.44 mmol) in toluene (5 mL) was performed. Standard workup, chromatography [silica, CH_2Cl_2/ethyl acetate (97:3→95:5)], and precipitation (CH_2Cl_2/hexanes) afforded colorless crystals (882 mg, 81%): mp 166–168 °C; ^{1}H NMR (THF-d_8) δ 4.15 (s, 2H), 5.50–5.51 (m, 1H), 6.05–6.11 (m, 1H), 6.62–6.67 (m, 1H), 6.74–6.75 (m, 1H), 7.42–7.54 (m, 3H), 7.84–7.86 (m, 2H), 11.34 (s, 1H), 11.69 (s, 1H); ^{13}C NMR (THF-d_8) δ 27.2, 110.3, 111.4, 120.2, 122.9, 129.0, 129.7, 132.2, 132.5, 136.8–137.2 (m), 137.4, 140.1–140.5 (m), 141.0–141.4 (m), 142.0, 143.1–143.3 (m), 144.5–144.6 (m), 146.3–146.6 (m), 171.4, 184.2; FAB-MS obsd 444.0892, calcd 444.0897 ($C_{23}H_{13}F_5N_2O_2$). Anal. Calcd: C, 62.17; H, 2.95; N, 6.30. Found: C, 60.36; H, 2.96; N, 6.04.

4.4.6. Zn(II)-5-pentafluorophenyl-10,15-diphenylporphyrin (Zn3d). Following a standard procedure,[47,54] a solution of **6** (420 mg, 0.945 mmol) in dry THF/methanol [25 mL (10:1)] was treated with $NaBH_4$ (712 mg, 18.9 mmol, 20 M equiv.) at room temperature for 30 min. The resulting dipyrromethane-dicarbinol and **2b** (210 mg, 0.945 mmol) were dissolved in CH_2Cl_2 (378 mL) and treated with $InCl_3$ (26.0 mg, 0.118 mmol, 0.32 mM) at

room temperature for 30 min. DDQ (645 mg, 2.84 mmol) was added and the mixture was stirred at room temperature for 1 h. After standard workup, chromatography [silica CH_2Cl_2/hexanes (3:1)] afforded the free base porphyrin. The resulting porphyrin was treated with $Zn(OAc)_2{\cdot}2H_2O$ (170 mg, 0.780 mmol) in CH_2Cl_2 (20 mL) and methanol (5.0 mL) at room temperature for 16 h. Standard workup, chromatography [silica, CH_2Cl_2/hexanes (2:1)], and trituration (hexanes) afforded a purple solid (120 mg, 18%): ^{1}H NMR ($CDCl_3$) δ 7.74–7.83 (m, 6H), 8.20–8.22 (m, 4H), 8.90–8.91 (m, 1H), 8.96–8.98 (m, 2H), 9.00–9.02 (m, 1H), 9.06 (d, J=4.4 Hz, 1H), 9.35 (d, J=4.4 Hz, 1H), 9.48 (d, J=5.1 Hz, 1H), 10.25 (s, 1H); ^{13}C NMR (THF-d_8) δ 99.82, 106.06, 118.1–118.4 (m), 121.68, 121.98, 126.42, 126.48, 127.59 (two peaks have overlapped), 129.38, 130.13, 131.57, 131.68, 131.80, 132.66, 132.99, 133.07, 134.59, 134.70, 136.3–136.9 (m), 138.8–139.4 (m), 140.4–140.8 (m), 143.0–143.4 (m), 143.41, 143.56, 145.4–146.0 (m), 147.8–148.4 (m), 149.56, 149.78, 149.90, 150.06, 150.17, 150.31, 150.43, 150.66; MALDI-MS (dithranol) obsd 692.87 [M^+], 679.76 [$(M-F)^+$]; FAB-MS obsd 690.0850, calcd 690.0821 ($C_{38}H_{19}F_5N_4Zn$); λ_{abs} 417, 543 nm; λ_{em} (λ_{ex}=540 nm) 585, 636 nm.

4.4.7. 5-Bromo-10,15,20-tris(4-methylphenyl)porphyrin (Fb7a). Following a standard procedure,[49] a solution of **Fb3a** (581 mg, 1.00 mmol) in $CHCl_3$ (250 mL) was treated with NBS (178 mg, 1.00 mmol) and pyridine (1.0 mL) at 0 °C for 15 min. Acetone (20 mL) was added. The reaction mixture was concentrated to dryness. Chromatography [silica, $CHCl_3$/hexanes (3:1)] and recrystallization ($CHCl_3$/methanol) afforded a purple solid (645 mg, 98%): ^{1}H NMR ($CDCl_3$) δ −2.72 (s, 2H), 2.70–2.74 (br s, 9H), 7.54–7.60 (m, 6H), 8.05–8.11 (m, 6H), 8.80–8.83 (m, 4H), 8.93 (d, J=4.8 Hz, 2H), 9.67 (d, J=4.8 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.76 (two peaks have overlapped), 102.09, 121.01, 121.30, 127.57 (two peaks have overlapped), 134.38, 134.54, 137.70, 137.74, 139.15, 139.26, resonances from the α- and β-carbons of the porphyrin were not observed due to NH tautomerism; LD-MS obsd 659.3; FAB-MS obsd 658.1749, calcd 658.1732 ($C_{41}H_{31}BrN_4$); λ_{abs} 423, 486, 520, 554, 597, 655 nm.

4.4.8. Zn(II)-5-bromo-10,15,20-triphenylporphyrin (Zn7b). Following a standard procedure,[49] a solution of **Zn3b** (44 mg, 73 μmol) in $CHCl_3$ (15 mL) was treated with NBS (13 mg, 73 μmol) and pyridine (21 μL) at 0 °C for 30 min. Standard workup, chromatography [silica, $CHCl_3$/hexanes (2:1)], and trituration (hexanes) afforded a purple solid (38.0 mg, 77%): ^{1}H NMR ($CDCl_3$) δ 7.77–7.78 (m, 9H), 8.11–8.27 (m, 6H), 8.85–8.92 (m, 4H), 8.98–8.99 (m, 2H), 9.68–9.80 (m, 2H); ^{13}C NMR (THF-d_8) δ 103.54, 121.45, 121.63, 126.48, 126.59, 127.47, 127.50, 131.828, 121.832, 132.26, 132.74, 134.46, 134.62, 143.33, 143.41, 149.68, 150.55, 150.62, 150.69; LD-MS obsd 678.45 [M^+]; FAB-MS obsd 678.0397, calcd 678.0398 ($C_{38}H_{23}BrN_4Zn$); λ_{abs} 426, 555 nm. **Zn7b** is a known compound but the synthetic procedure has not been described.[61]

4.4.9. Zn(II)-5-bromo-10,20-bis(pentafluorophenyl)-15-phenylporphyrin (Zn7c). Following a standard procedure,[49] a solution of **Zn3c** (110 mg, 0.141 mmol) in $CHCl_3$ (30 mL) was treated with NBS (25 mg, 0.14 mmol) and pyridine (41 μL) at 0 °C for 30 min. Standard workup, chromatography [silica, $CHCl_3$/hexanes (2:1)⟶(3:1)], and trituration (hexanes) afforded a purple solid (116 mg, 96%): ^{1}H NMR ($CDCl_3$) δ 7.74–7.82 (m, 3H), 8.16–8.19 (m, 2H), 8.84 (d, J=5.1 Hz, 2H), 8.95 (d, J=4.4 Hz, 2H), 8.99 (d, J=5.1 Hz, 2H), 9.86 (d, J=5.1 Hz, 2H); ^{13}C NMR (THF-d_8) δ 103.00, 104.62, 117.4–117.7 (m), 122.63, 126.62, 127.81, 130.53, 131.39, 133.50, 133.93, 134.52, 135.9–136.5 (m), 139.2–139.7 (m), 140.4–140.7 (m), 142.77, 143.6–144.1 (m), 144.9–145.7 (m), 148.1–148.6 (m), 149.95, 150.00, 150.40, 151.53;- MALDI-MS (dithranol) obsd 855.46 [M^+]; FAB-MS obsd 857.9459, calcd 857.9455 ($C_{38}H_{13}BrF_{10}N_4$-Zn); λ_{abs} 425, 552 nm.

4.4.10. Zinc(II)-5-bromo-20-pentafluorophenyl-10,15-diphenylporphyrin (Zn7d). Following a standard procedure,[49] a solution of **Zn3d** (100 mg, 0.145 mmol) in $CHCl_3$ (30 mL) was treated with NBS (26 mg, 0.15 mmol) and pyridine (42 μL) at 0 °C for 30 min. Standard workup, chromatography [silica, $CHCl_3$/hexanes (3:1)], and trituration (hexanes) afforded a purple solid (102 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 7.74–7.78 (m, 6H), 8.17–8.18 (m, 4H), 8.81–8.82 (m, 1H), 8.90–8.93 (m, 3H), 8.98–9.01 (m, 2H), 9.76 (d, J=4.4 Hz, 1H), 9.85 (d, J=4.4 Hz, 1H); ^{13}C NMR (THF-d_8) δ 101.15, 104.23, 117.6–118.1 (m), 122.26, 123.39, 126.56, 126.59, 127.67, 127.72, 130.02, 130.95, 132.05, 132.42, 132.46, 133.24, 133.41, 133.85, 134.52, 134.66, 136.3–136.9 (m), 138.8–139.4 (m), 140.5–141.1 (m), 143.08, 143.1–143.6 (m), 143.12, 145.4–146.0 (m), 147.8–148.4 (m), 149.92, 150.12, 150.18 (two peaks have overlapped), 150.51, 150.61, 150.91, 151.32; MALDI-MS (dithranol) obsd 770.67 [M^+], 753.64 [$(M-F)^+$], 694.55 [$(M-Br)^+$]; FAB-MS obsd 767.9951, calcd 767.9926 ($C_{38}H_{18}BrF_5N_4Zn$); λ_{abs} 426, 553, 594 nm.

4.4.11. 5-Iodo-10,15,20-tris(4-methylphenyl)porphyrin (Fb8a). Following a standard procedure,[50] a solution of porphyrin **Fb3a** (871 mg, 1.50 mmol) and I_2 (267 mg, 1.05 mmol) in $CHCl_3$ (210 mL) was treated with a solution of [bis(trifluoroacetoxy)iodo]benzene (478 mg, 1.20 mmol) and pyridine (1.3 mL) in $CHCl_3$ (30 mL). The mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2, washed with aqueous $Na_2S_2O_3$, and dried (Na_2SO_4). The solution was concentrated to ~100 mL, then 30 mL of hexanes was added. The resulting purple precipitate was filtered, washed (CH_2Cl_2, hexanes) and dried to give a purple powder (618 mg). The filtrate was concentrated and chromatographed [silica, warm toluene/hexanes (7:3)] affording an additional amount of the title compound (253 mg). The total yield is 871 mg (82%): ^{1}H NMR ($CDCl_3$) δ −2.70 (s, 2H), 2.69–2.74 (br s, 9H), 7.53–7.59 (m, 6H), 8.04–8.09 (m, 6H), 8.78–8.83 (m, 4H), 8.89 (d, J=4.8 Hz, 2H), 9.67 (d, J=4.8 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.77 (two peaks have overlapped), 77.92, 121.04, 121.45, 127.53, 127.59, 134.41, 134.53, 137.72 (two peaks have overlapped), 139.71, 139.28, resonances from the α-and β-carbons of the porphyrin were not observed due to NH tautomerism; LD-MS obsd 706.9; FAB-MS obsd 706.1613, calcd 706.1593 ($C_{41}H_{31}IN_4$); λ_{abs} 424, 520, 557, 598, 656 nm.

4.4.12. Zn(II)-5-bromo-10,15,20-tris(4-methylphenyl)-porphyrin (Zn7a). A solution of porphyrin **Fb7a**

(594 mg, 0.900 mmol) in THF (60 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (988 mg, 4.50 mmol). The mixture was heated (~50 °C) for a few minutes and then stirred at room temperature for 11 h. Standard workup, chromatography [silica, $CHCl_3$/hexanes (3:2)] and recrystallization (hexanes/CH_2Cl_2) afforded a purple solid (582 mg, 89%): ^{1}H NMR ($CDCl_3$) δ 2.67 (s, 3H), 2.70 (s, 6H), 7.52–7.60 (m, 6H), 8.00–8.08 (m, 6H), 8.78–8.82 (m, 4H), 8.91 (d, J=4.8 Hz, 2H), 9.68 (d, J=4.8 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.78, 20.80, a resonance from the C–Br carbon was not observed, 119.88, 120.03, 127.02, 127.07, 128.44, 131.11, 131.28, 131.80, 134.44, 134.47, 136.73, 136.77, 140.97, 141.07, 149.86, 149.96, 150.23, 150.42; LD-MS obsd 723.8; FAB-MS obsd 720.0901, calcd 720.0867 ($C_{41}H_{29}BrN_4Zn$); λ_{abs} 427, 555, 595 nm.

4.4.13. Zn(II)-5-iodo-10,15,20-tris(4-methylphenyl)porphyrin (Zn8a). A solution of **Fb8a** (353 mg, 0.500 mmol) in THF (60 mL) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (1.10 g, 5.00 mmol). The mixture was heated (~50 °C) for a few minutes and then stirred at room temperature for 8 h. Standard workup, chromatography [silica, $CHCl_3$/hexanes (1:1)], and recrystallization (hexanes/CH_2Cl_2) afforded a purple solid (349 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 2.67–2.70 (br s, 9H), 7.53–7.59 (m, 6H), 8.01–8.06 (m, 6H), 8.76–8.80 (m, 4H), 8.86–8.91 (m, 2H), 9.72 (d, J=4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.79, 20.80, 79.54, 121.51, 121.92, 127.16 (two peaks have overlapped), 131.16, 131.70, 131.83, 132.98, 134.55 (two peaks have overlapped), 137.07, 137.10, 140.47, 140.56, 150.70 (two peaks have overlapped), 151.29, 152.13; LD-MS obsd 770.5; FAB-MS obsd 768.0760, calcd 768.0728 ($C_{41}H_{29}IN_4Zn$); λ_{abs} 429, 519, 556, 596 nm.

4.5. Porphyrin dyads

4.5.1. Dyad-1. Samples of **Zn9** (11 mg, 13 μmol), **Zn8a** (10 mg, 13 μmol), $Pd_2(dba)_3$ (7.1 mg, 7.7 μmol), and P(o-tol)$_3$ (19 mg, 62 μmol) were placed into a 100 mL Schlenk flask which was then pump-purged three times with argon. Toluene/TEA [20.6 mL (5:1)] was added, and the reaction mixture was stirred at 40 °C for 1.5 h. The reaction mixture was concentrated to dryness. The resulting residue was passed through a pad of silica ($CHCl_3$). The eluant was concentrated and then further purified by preparative SEC (THF) and adsorption chromatography [silica, $CHCl_3$/hexanes (2:1)]. The desired fraction was concentrated to dryness and then triturated with methanol. Filtration afforded the title compound as a purple solid (7.3 mg, 41%): ^{1}H NMR ($CDCl_3$) δ 1.86–1.88 (m, 18H), 2.63–2.64 (m, 9H), 2.72 (s, 3H), 2.74 (s, 6H), 7.29 (s, 2H), 7.30 (s, 4H), 7.56 (d, J=8.1 Hz, 2H), 7.60 (d, J=8.1 Hz, 4H), 8.09 (d, J=8.1 Hz, 2H), 8.14 (d, J=8.1 Hz, 4H), 8.41–8.46 (m, 4H), 8.71–8.74 (m, 4H), 8.84 (d, J=5.1 Hz, 2H), 8.90–8.93 (m, 4H), 9.05 (d, J=4.4 Hz, 2H), 9.12 (d, J=4.4 Hz, 2H), 10.03 (d, J=4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.80 (two peaks have overlapped), 20.82 (two peaks have overlapped), 21.27, 21.33, 94.40, 95.89, 99.10, 118.18, 118.33, 119.31, 121.89, 122.78, 123.78, 127.15, 127.22, 127.71 (two peaks have overlapped), 129.50, 130.16, 130.43, 130.46, 130.57, 131.32, 131.66, 131.75, 132.44, 132.47, 134.37, 134.54, 135.03 (two peaks have overlapped), 137.08, 137.30, 139.14 (two peaks have overlapped), 139.85, 139.95, 140.52, 140.62, 143.91, 149.74, 149.78, 149.86, 149.88, 150.04, 150.16, 150.80, 152.47; MALDI-MS (dithranol) obsd 1465.84 [M^+]; FAB-MS obsd 1466.4607, calcd 1466.4619 ($C_{96}H_{74}N_8Zn_2$); λ_{abs} 442, 445, 553, 618 nm; λ_{em} (λ_{ex}=550 nm) 627, 681 nm.

4.5.2. Dyad-2. A mixture of **Zn9** (25 mg, 30 μmol), **Fb7a** (20 mg, 30 μmol), $Pd_2(dba)_3$ (17 mg, 18 μmol), and P(o-tol)$_3$ (44 mg, 0.14 mmol) in toluene/TEA [48 mL (5:1)] was stirred at 50 °C for 1.5 h under argon. Standard workup, preparative SEC (THF), chromatography [silica, $CHCl_3$/hexanes (2:1)], and trituration (THF/hexanes) afforded a purple solid (19 mg, 47%): ^{1}H NMR ($CDCl_3$) δ −2.23 (s, 2H), 1.86–1.89 (m, 18H), 2.63–2.65 (m, 9H), 2.71 (s, 3H), 2.73 (s, 6H), 7.28–7.30 (m, 6H), 7.56 (d, J=7.3 Hz, 2H), 7.60 (d, J=8.1 Hz, 4H), 8.08 (d, J=8.1 Hz, 2H), 8.13 (d, J=8.1 Hz, 4H), 8.40 (d, J=8.1 Hz, 2H), 8.45 (d, J=8.1 Hz, 2H), 8.72–8.73 (m, 4H), 8.80–8.81 (m, 4H), 8.83 (d, J=4.4 Hz, 2H), 9.01–9.04 (m, 4H), 9.93 (d, J=5.1 Hz, 2H); MALDI-MS (dithranol) obsd 1409.27 [$(M+H)^+$]; FAB-MS obsd 1404.5476, calcd 1404.5484 ($C_{96}H_{76}N_8Zn$); λ_{abs} 422, 439, 550, 578, 672 nm; λ_{em} (λ_{ex}=550 nm) 675, 747 nm.

4.5.3. Dyad-3. A mixture of **Zn9** (20 mg, 24 μmol), **Zn7c** (21 mg, 24 μmol), $Pd_2(dba)_3$ (13 mg, 14 μmol), and P(o-tol)$_3$ (35 mg, 0.11 mmol) in toluene/TEA [38 mL (5:1)] was stirred at 50 °C for 1.5 h under argon. Standard workup, preparative SEC (THF), chromatography [silica, $CHCl_3$/hexanes (2:1→3:1)], and trituration (hexanes) afforded a purple solid (24 mg, 62%): ^{1}H NMR ($CDCl_3$) δ 1.87–1.89 (m, 18H), 2.63–2.66 (m, 9H), 7.28–7.29 (m, 2H), 7.30–7.32 (m, 4H), 7.75–7.82 (m, 3H), 8.21 (d, J=7.3 Hz, 2H), 8.42 (d, J=7.3 Hz, 2H), 8.47 (d, J=8.1 Hz, 2H), 8.73–8.75 (m, 4H), 8.84–8.86 (m, 4H), 9.00 (d, J=5.1 Hz, 2H), 9.03–9.05 (m, 4H), 10.12 (d, J=4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 20.83 (two peaks have overlapped), 21.30, 21.35, 93.37, 96.74, 100.86, 103.43, 117.5–117.8 (m), 118.25, 118.38, 119.14, 123.25, 123.58, 126.62, 127.71, 127.74, 127.82, 129.70, 130.08, 130.20, 130.52, 130.63, 131.09, 131.70, 132.30, 133.32, 134.52, 135.11, 136.4–137.0 (m), 137.32 (two peaks have overlapped), 139.0–139.6 (m), 139.14 (two peaks have overlapped), 139.84, 139.94, 140.5–141.0 (m), 142.85, 143.1–143.6 (m), 144.42, 145.3–145.9 (m), 147.8–148.4 (m), 149.46, 149.77, 149.78, 149.82, 149.87, 149.89, 150.88, 153.13; MALDI-MS (dithranol) obsd 1604.77 [M^+]; FAB-MS obsd 1604.3187, calcd 1604.3208 ($C_{93}H_{58}F_{10}N_8Zn_2$); λ_{abs} 422, 445, 553, 607 nm; λ_{em} (λ_{ex}=550 nm) 616, 678 nm.

4.5.4. Dyad-4. A mixture of **Zn9** (12 mg, 15 μmol), **Zn7d** (12 mg, 15 μmol), $Pd_2(dba)_3$ (9.0 mg, 9.0 μmol), and P(o-tol)$_3$ (22 mg, 0.072 mmol) in toluene/TEA [24 mL (5:1)] was stirred at 50 °C for 1.5 h under argon. Standard workup, preparative SEC (THF), and chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a purple solid (11 mg, 48%): ^{1}H NMR ($CDCl_3$) δ 1.86–1.89 (m, 18H), 2.62–2.65 (m, 9H), 7.29–7.30 (m, 6H), 7.74–7.83 (m, 6H), 8.19–8.22 (m, 2H), 8.24–8.26 (m, 2H), 8.41–8.47 (m, 4H), 8.71–8.74 (m, 4H), 8.81–8.85 (m, 3H), 8.89–8.93 (m, 2H), 8.99 (d, J=4.4 Hz, 1H), 9.02 (d, J=5.1 Hz, 1H), 9.04 (d, J=5.1 Hz, 2H), 9.12 (d, J=4.4 Hz, 1H), 10.05 (d, J=4.4 Hz,

1H), 10.13 (d, J=5.1 Hz, 1H); ^{13}C NMR (THF-d_8) δ 20.82 (two peaks have overlapped), 21.28, 21.33, 93.79, 96.40, 100.21, the *meso*-carbon adjacent to the pentafluorophenyl group was not observed, 118.20, 118.35, 119.20, 123.23, 123.46, 123.64, 126.55, 126.57, 127.66 (two peaks have overlapped), 127.72 (two peaks have overlapped), 129.52, 129.60, 129.52, 129.60, 130.17, 130.48, 130.59 (two peaks have overlapped), 131.71, 131.93, 132.14 (two peaks have overlapped), 132.94, 133.16, 134.47, 134.63, 135.07 (two peaks have overlapped), 137.30 (two peaks have overlapped), 139.14 (two peaks have overlapped), 139.84, 139.94, 143.13, 143.15, 144.20, 149.75, 149.78, 149.84, 149.87, 150.59, 152.75, resonances from some of the α-carbons of the porphyrin were not observed clearly, and resonances from the carbons of the pentafluorophenyl group were not observed; MALDI-MS (dithranol) obsd 1518.39 [M$^+$]; FAB-MS obsd 1514.3712, calcd 1514.3679 ($C_{93}H_{63}F_5N_8Zn_2$); λ_{abs} 422, 446, 553, 611 nm; λ_{em} (λ_{ex}= 550 nm) 618, 675 nm.

4.6. Benchmark phenylethynyl-porphyrins

4.6.1. Zn(II)-5-(phenylethynyl)-10,15,20-triphenylporphyrin (Zn10b). A mixture of **Zn7b** (30 mg, 44 μmol), phenylacetylene (24 μL, 0.22 mmol), $Pd_2(dba)_3$ (6.1 mg, 6.7 μmol), and P(*o*-tol)$_3$ (16 mg, 53 μmol) in toluene/TEA [18 mL (5:1)] was stirred at 50 °C under argon. After 6 h, phenylacetylene (24 μL, 0.22 mmol), $Pd_2(dba)_3$ (6.1 mg, 6.7 μmol), and P(*o*-tol)$_3$ (16 mg, 53 μmol) were added. After 14 h, the reaction mixture was concentrated to dryness. Chromatography [silica, CH_2Cl_2/hexanes (3:2)] and trituration (hexanes) afforded a blue-purple solid (16 mg, 52%): ^{1}H NMR ($CDCl_3$) δ 7.46–7.51 (m, 1H), 7.54–7.59 (m, 2H), 7.70–7.82 (m, 9H), 8.03 (d, J=7.3 Hz, 2H), 8.17–8.22 (m, 6H), 8.86–8.87 (m, 4H), 9.01 (d, J=4.4 Hz, 2H), 9.84 (d, J=4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 92.95, 96.48, 100.49, 122.27, 122.99, 124.45, 126.82, 126.88, 127.86 (two peaks have overlapped), 128.65, 128.91, 131.15, 131.85, 132.16, 132.46, 133.13, 134.52, 134.64, 142.66, 142.77, 150.12, 150.27, 150.77, 152.53; LD-MS obsd 700.15 [M$^+$]; FAB-MS obsd 700.1610, calcd 700.1605 ($C_{46}H_{28}N_4Zn$); λ_{abs} 440, 567, 611 nm; λ_{em} (λ_{ex}= 560 nm) 618, 673 nm.

4.6.2. Zn(II)-5-pentafluorophenyl-10,15-diphenyl-20-(phenylethynyl)porphyrin (Zn10c). A mixture of **Zn7c** (20 mg, 26 μmol), phenylacetylene (14 μL, 0.13 mmol), $Pd_2(dba)_3$ (3.7 mg, 4.0 μmol), and P(*o*-tol)$_3$ (9.9 mg, 32 μmol) in toluene/TEA [10.4 mL (5:1)] was stirred at 50 °C under argon. After 5 h, phenylacetylene (14 μL, 0.13 mmol), $Pd_2(dba)_3$ (3.7 mg, 4.0 μmol), and P(*o*-tol)$_3$ (9.9 mg, 32 μmol) were added. After 15 h, the reaction mixture was concentrated to dryness. Chromatography [silica, CH_2Cl_2/hexanes (3:2)] and trituration (hexanes) afforded a purple solid (15 mg, 73%): ^{1}H NMR ($CDCl_3$) δ 7.49–7.58 (m, 3H), 7.72–7.81 (m, 6H), 8.00–8.03 (m, 2H), 8.16–8.22 (m, 4H), 8.79 (d, J=5.1 Hz, 1H), 8.86–8.89 (m, 2H), 8.93 (d, J=4.4 Hz, 1H), 8.96 (d, J=5.1 Hz, 1H), 9.02 (d, J=4.4 Hz, 1H), 9.83 (d, J=5.1 Hz, 1H), 9.92 (d, J= 4.4 Hz, 1H); ^{13}C NMR (THF-d_8) δ 92.35, 96.26, 100.68, 103.33, 117.5–117.8 (m), 123.52, 124.33, 126.59, 127.79, 128.67, 128.85, 130.03, 130.95, 131.69, 132.13, 133.28, 134.48, 136.5–137.1 (m), 138.8–139.4 (m), 140.6–1401.1 (m), 142.81, 143.0–143.5 (m), 145.2–145.8 (m), 147.8–148.3 (m), 149.37, 149.81, 150.82, 152.96; MALDI-MS (dithranol) obsd 793.71 [(M+H)$^+$], 775.58 [(M−F)$^+$]; FAB-MS obsd 790.1099, calcd 790.1134 ($C_{46}H_{23}F_5N_4Zn$); λ_{abs} 442, 567, 606 nm; λ_{em} (λ_{ex}=560 nm) 612, 671 nm.

4.6.3. Zn(II)-5,15-bis(pentafluorophenyl)-10-phenyl-20-(phenylethynyl)porphyrin (Zn10d). A mixture of **Zn7d** (40 mg, 46 μmol), phenylacetylene (25 μL, 0.23 mmol), $Pd_2(dba)_3$ (6.4 mg, 7.0 μmol), and P(*o*-tol)$_3$ (17 mg, 55 μmol) in toluene/TEA [18 mL (5:1)] was stirred at 50 °C under argon. After 5 h, phenylacetylene (25 μL, 0.23 mmol), $Pd_2(dba)_3$ (6.4 mg, 7.0 μmol), and P(*o*-tol)$_3$ (17 mg, 55 μmol) were added. After 18 h, the reaction mixture was concentrated to dryness. Chromatography [silica, CH_2Cl_2/hexanes (3:2)] and trituration (hexanes) afforded a purple solid (30 mg, 74%): ^{1}H NMR (THF-d_8) δ 7.50–7.54 (m, 1H), 7.57–7.62 (m, 2H), 7.72–7.79 (m, 3H), 8.08 (d, J=6.6 Hz, 2H), 8.16–8.19 (m, 2H), 8.85 (d, J= 5.1 Hz, 2H), 8.88 (d, J=5.1 Hz, 2H), 9.03 (d, J=5.1 Hz, 2H), 9.88 (d, J=4.4 Hz, 2H); ^{13}C NMR (THF-d_8) δ 92.79, 95.95, 100.05, 101.58, 117.9–118.1 (m), 123.17, 123.55, 124.54, 126.53, 126.55, 127.65 (two peaks have overlapped), 128.48, 128.81, 129.49, 130.47, 130.62, 131.61, 131.84, 131.89, 131.99, 132.82, 133.12, 134.45, 134.59, 136.5–137.0 (m), 138.8–139.3 (m), 140.3–140.8 (m), 143.10, 143.13, 143.2–143.4 (m), 145.4–1445.8 (m), 147.8–148.4 (m), 149.47, 149.84, 149.90, 150.22, 150.53, 150.58, 152.67, 152.69; MALDI-MS (dithranol) obsd 882.07 [M$^+$]; FAB-MS obsd 880.0638, calcd 880.0663 ($C_{46}H_{18}F_{10}N_4Zn$); λ_{abs} 443, 566, 602 nm; λ_{em} (λ_{ex}= 565 nm) 616, 674 nm.

4.6.4. Zn(II)-5,15-bis(pentafluorophenyl)porphyrin (Zn11). Following a standard procedure,[48,54] a solution of **5** (681 mg, 2.00 mmol) in dry THF/methanol [66 mL, (10:1)] was treated with $NaBH_4$ (1.50 g, 40.0 mmol) at room temperature for 40 min. The resulting dipyrromethane-monocarbinol was dissolved in CH_2Cl_2 (400 mL) and treated with $InCl_3$ (28 mg, 0.13 mmol, 0.32 mM) at room temperature for 30 min. DDQ (681 mg, 3.00 mmol) was added and the mixture was stirred at room temperature for 1 h. Standard workup and chromatography [silica, CH_2Cl_2/hexanes (3:1)] afforded a mixture of free base porphyrin and chlorin. The mixture was dissolved in toluene (100 mL) and reoxidized with DDQ (681 mg, 3.00 mmol) under reflux for 1 h. The reaction mixture was cooled, diluted with hexanes (100 mL), and filtered. The resulting porphyrin was treated with $Zn(OAc)_2{\cdot}2H_2O$ (3.29 g, 15.0 mmol) in $CHCl_3$ (800 mL) and methanol (30 mL) at room temperature for 3 days. Standard workup and trituration (methanol) afforded a purple solid (114 mg, 16%): ^{1}H NMR (THF-d_8) δ 9.12 (d, J=4.4 Hz, 4H), 9.52 (d, J=4.4 Hz, 4H), 10.39 (s, 2H); ^{13}C NMR (THF-d_8) δ 100.08, 106.75, 130.52, 133.13, 149.50, 150.45, resonances from the C–F carbons of the pentafluorophenyl group were not observed; MALDI-MS (dithranol) obsd 704.23 [M$^+$], 686.20 [(M−F)$^+$]; FAB-MS obsd 704.0049, calcd 704.0037 ($C_{32}H_{10}F_{10}N_4Zn$); λ_{abs} (THF) 409, 541, 575 nm; λ_{em} (λ_{ex}=540 nm, THF) 581, 633 nm.

4.6.5. Zn(II)-5,15-dibromo-10,20-bis(pentafluorophenyl)porphyrin (Zn12a). Following a standard procedure,[49]

a solution of **Zn11** (100 mg, 0.142 mmol) in $CHCl_3$ (30 mL) was treated with NBS (50 mg, 0.28 mmol) and pyridine (0.1 mL) at 0 °C for 30 min. Standard workup, chromatography [silica, THF/hexanes (3:17)], and trituration (methanol) afforded a purple solid (101 mg, 82%): ^{1}H NMR (THF-d_8) δ 9.00 (d, J=5.1 Hz, 4H), 9.75 (d, J=5.1 Hz, 4H); ^{13}C NMR (THF-d_8) δ 103.69, 105.33, 116.8–117.5 (m), 131.85, 134.32, 136.3–136.9 (m), 138.8–139.4 (m), 140.7–141.3 (m), 143.2–143.7 (m), 145.3–145.9 (m), 147.7–148.4 (m), 150.31, 150.98; MALDI-MS (dithranol) obsd 862.16 [M^+], 844.27 [$(M-F)^+$], 782.45 [$(M-Br)^+$]; FAB-MS obsd 859.8242, calcd 859.8247 ($C_{32}H_8Br_2F_{10}N_4Zn$); λ_{abs} (THF) 427, 562, 608 nm.

4.6.6. Zn(II)-5,15-bis(pentafluorophenyl)-10,20-bis-(phenylethynyl)porphyrin (Zn13a). A mixture of **Zn12a** (90 mg, 0.10 mmol), phenylacetylene (69 μL, 0.62 mmol), $Pd_2(dba)_3$ (29 mg, 32 μmol), and P(o-tol)$_3$ (76 mg, 0.13 mmol) in THF/TEA [42 mL (5:1)] was stirred at 40 °C under argon. After 4 h, phenylacetylene (69 μL, 0.22 mmol), $Pd_2(dba)_3$ (29 mg, 32 μmol), and P(o-tol)$_3$ (76 mg, 0.13 mmol) were added. After 18 h, the mixture was concentrated to dryness. Chromatography [silica, THF/hexanes (3:17)] and trituration [$CHCl_3$/hexanes (1:1), then methanol] afforded a blue-purple solid (50 mg, 53%): ^{1}H NMR (THF-d_8) δ 7.63–7.68 (m, 2H), 7.71–7.75 (m, 4H), 8.19–8.22 (m, 4H), 9.10 (d, J=5.1 Hz, 4H), 9.95 (d, J=5.1 Hz, 4H); ^{13}C NMR (THF-d_8) δ 92.24, 96.86, 102.26, 104.27, 117.1–117.9 (m), 124.14, 128.83, 128.86, 130.92, 131.73, 132.27, 136.4–137.0 (m), 138.9–139.5 (m), 140.6–141.2 (m), 143.1–143.7 (m), 145.3–145.9 (m), 147.7–148.3 (m), 149.55, 152.76; MALDI-MS (dithranol) obsd 904.35 [M^+], 885.40 [$(M-F)^+$]; FAB-MS obsd 904.0646, calcd 904.0663 ($C_{48}H_{18}F_{10}N_4Zn$); λ_{abs} 454, 585, 627 nm; λ_{em} (λ_{ex}=585 nm) 633, 697 nm.

4.6.7. Zn(II)-5,15-diphenyl-10,20-bis(phenylethynyl)porphyrin (Zn13b). A mixture of **Zn12b** (100 mg, 0.146 mmol), phenylacetylene (96 μL, 0.88 mmol), $Pd_2(dba)_3$ (40 mg, 44 μmol), and P(o-tol)$_3$ (107 mg, 350 μmol) in THF/TEA [58 mL (5:1)] was stirred at 40 °C under argon. After 6 h, phenylacetylene (96 μL, 0.88 mmol), $Pd_2(dba)_3$ (40 mg, 44 μmol), and P(o-tol)$_3$ (107 mg, 350 μmol) were added. After 17 h, the mixture was concentrated to dryness. Chromatography [silica, THF/hexanes (3:17), then CH_2Cl_2/hexanes (2:1)] and trituration (hexanes) afforded a blue-purple solid (46 mg, 43%). Analytical data were identical to those described in the literature for the synthesis using copper as a cocatalyst.[37]

Acknowledgements

This research was supported by a grant from the NSF (CHE-9988142). Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the NSF.

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