Pergamon

Tetrahedron 57 (2001) 9285–9298

TETRAHEDRON

Investigation of two rational routes for preparing *p*-phenylene-linked porphyrin trimers

Lianhe Yu and Jonathan S. Lindsey*

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Received 8 August 2001; accepted 10 September 2001

Abstract—Multiporphyrin arrays with *p*-phenylene linkers, aryl groups at the non-linking *meso* positions, and no β-substituents are attractive constructs for light-harvesting applications. Condensation of a free base porphyrin-benzaldehyde and 5-mesityldipyrromethane (10 mM each) in CH_2Cl_2 containing 100 mM TFA at room temperature for 30–40 min followed by oxidation with DDQ afforded a *p*-phenylene-linked porphyrin trimer in 36% yield. Suzuki coupling of an iodo-porphyrin and a bis(dioxaborolane)-porphyrin (20 and 10 mM, respectively) in toluene/DMF (2:1) containing K_2CO_3 (8 equiv.) at 90–95°C for ~20 h afforded the same trimer in 66% yield. The former route was used to prepare a diethynyl substituted *p*-phenylene-linked porphyrin trimer. While the two routes are somewhat complementary in scope, both are convergent and proceed in a rational manner.

1. Introduction

As part of a program in artificial photosynthesis, we have been working to construct multiporphyrin light-harvesting arrays in which the porphyrins are weakly coupled electronically.[1] Weakly coupled arrays exhibit absorption spectra and electrochemical potentials that are essentially the sum of the features observed for the corresponding monomers, thereby facilitating molecular design. Studies of *meso*-substituted (β-unsubstituted) porphyrin dyads have shown that *p*-phenylene,[2] diphenylethyne[3] and diphenylbutadiyne[4] linkers afford differing extents of interporphyrin communication, though each remains within the weak coupling regime. A particularly attractive construct is a linear trimeric porphyrin building block with the following features: (1) *p*-phenylene linkers across the *meso*-positions to join the porphyrins, (2) electron-rich substituents at the non-linking *meso*-positions, (3) no substituents at the β-positions of the porphyrins, and (4) iodophenyl or ethynylphenyl substituents at the termini of the trimer for extension to larger multiporphyrin constructs via Sonogashira or Glaser coupling (affording diphenylethyne or diphenylbutadiyne linkers, respectively).

The motivation for this molecular design stems from synthetic, biomimetic, and photophysical considerations. *Synthesis*: the use of multimeric building blocks provides greater efficiency in the construction of large arrays compared with monomeric building blocks. Moreover, attachment of linkers at the porphyrin *meso*-positions (i.e. 5,15-positions) takes advantage of methodology for the synthesis of *meso*-substituted porphyrin building blocks.[5] *Biomimicry*: the photosynthetic antenna complexes are composed of domains of pigments, with stronger interactions within domains and weaker interactions between domains.[6] An architecture with domains of *p*-phenylene-linked trimers interspersed by diphenylbutadiyne or diphenylethyne linkers would provide a primitive model for the flow of energy in photosynthetic antenna complexes. *Photophysics*: excited-state energy transfer in covalently linked porphyrin arrays occurs predominantly via a linker-mediated through-bond mechanism.[1] The rate of energy transfer ($k_{Zn\rightarrow Fb}$) depends both on the distance of separation of the porphyrins and the electron density of the porphyrin frontier molecular orbitals at the position of linker attachment. Dyads comprised of a zinc tetraarylporphyrin and a free base tetraarylporphyrin (Chart 1) exhibit an energy-transfer rate that depends on the nature of the linker in the following way: $(38\ ps)^{-1}$, 4,4′-diphenylbutadiyne linker;[4] $(24\ ps)^{-1}$, 4,4′-diphenylethyne linker;[3] $(3.5\ ps)^{-1}$, *p*-phenylene linker.[2] The porphyrins in these dyads are linked at the *meso*-positions, bear mesityl groups at the non-linking *meso*-positions, and have no β-substituents. Analogous dyads with a full complement of substituents at the eight β-positions on each porphyrin exhibit rates of $(417\ ps)^{-1}$ (4,4′-diphenylethyne)[7,8] or $(10\ ps)^{-1}$ (*p*-phenylene linker).[8] The difference in rate is attributed to the characteristics of the porphyrin frontier molecular orbitals in the different systems. A tetraarylporphyrin with electron-rich substituents[†] at the *meso*-positions has an $a_{2u}(\pi)$ HOMO,

Keywords: porphyrins and analogues; pyrroles; Suzuki reactions; alkynes.

* Corresponding author. Tel.: +1-919-515-6406; fax: +1-919-513-2830; e-mail: jlindsey@ncsu.edu

† The presence of strongly electron-withdrawing groups (e.g. pentafluorophenyl) at the *meso*-positions results in the a_{1u} HOMO, hence the requirement for electron-rich groups at the non-linking *meso*-positions.[1,7]

0040–4020/01/$ - see front matter
PII: S0040-4020(01)00928-0

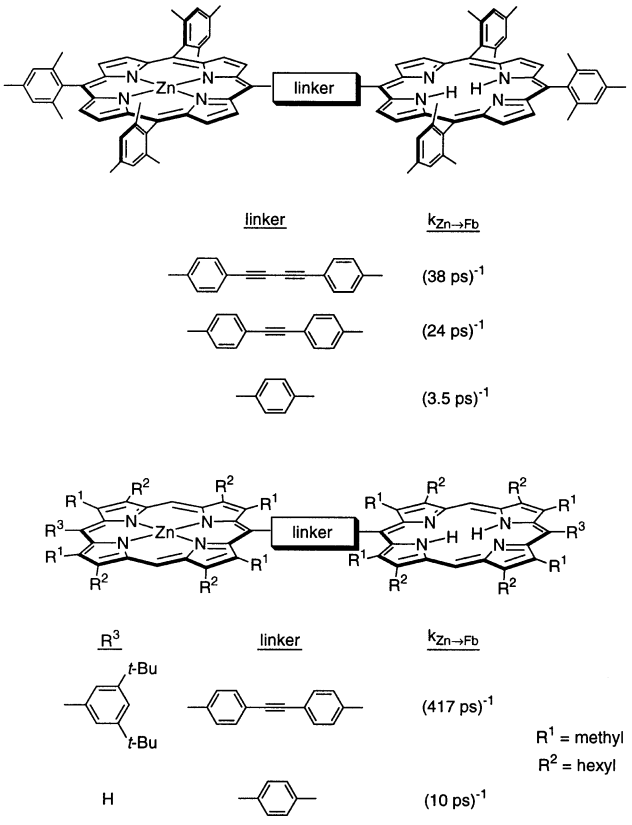
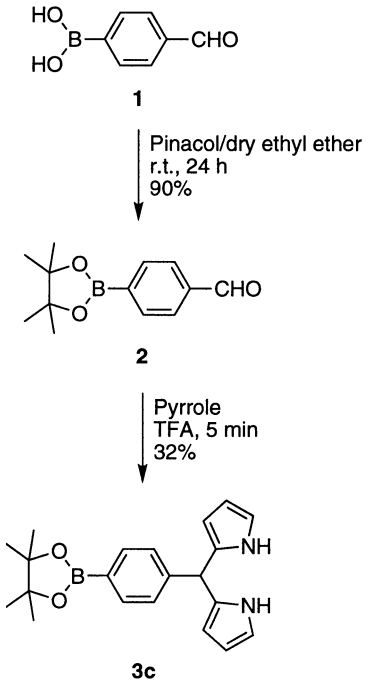
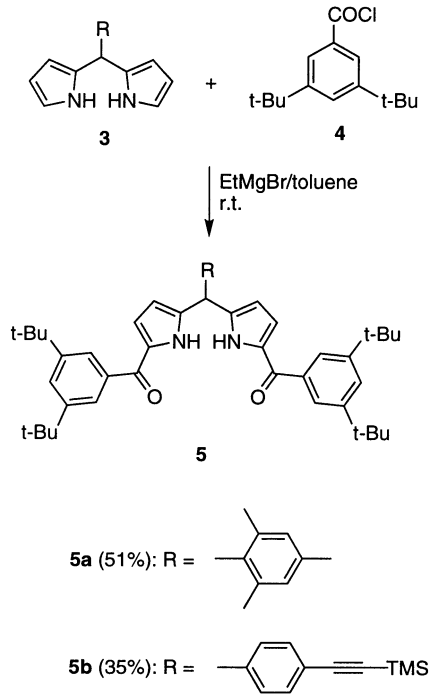


Chart 1.

which has electron density at the *meso*-position (thereby enhancing through-bond energy transfer); a β-substituted octaalkylporphyrin has an $a_{1u}(\pi)$ HOMO, which has a node at the *meso*-position. Thus, achieving the fastest possible rate of energy transfer requires the avoidance of β-alkyl groups in arrays with linkers attached to the *meso*-positions.



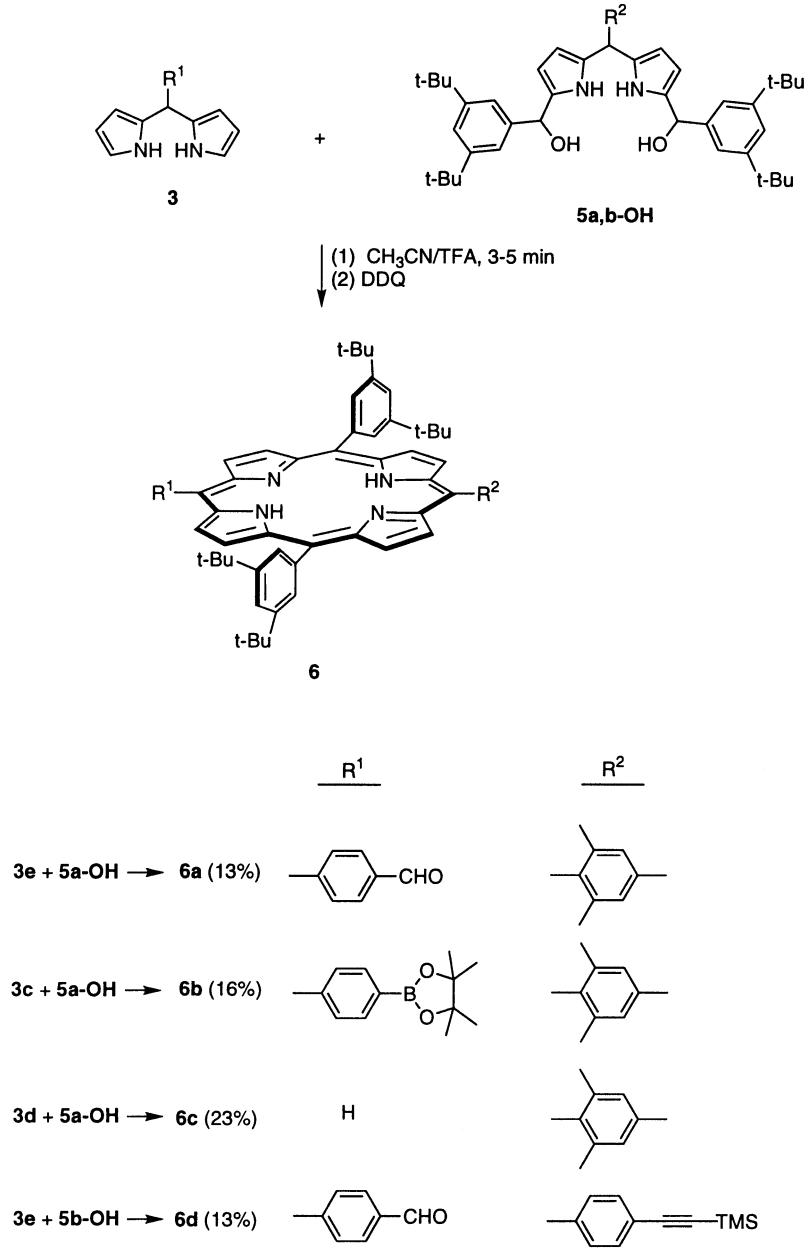
Scheme 1.



Scheme 2.

With one exception,[9] all *p*-phenylene-linked porphyrin trimers synthesized to date have incorporated the linker across the *meso*-positions of porphyrins bearing alkyl groups at all eight β-positions.[10–15] No trimers have included synthetic handles at the termini of the trimer. The syntheses of *p*-phenylene linked trimers generally have employed reaction of a porphyrin-benzaldehyde with a β-substituted dipyrromethane thereby creating the inner porphyrin macrocycle. The reaction proceeds via acid-catalyzed condensation followed by quinone-mediated oxidation. In any acid-catalyzed reaction with a dipyrromethane, acidolysis can occur yielding fragments that upon undesired recombination afford a mixture of porphyrin species (i.e. scrambling).[16] While β-substituted (*meso*-unsubstituted) dipyrromethanes are quite stable toward acidolysis,[17] the stability of *meso*-substituted (β-unsubstituted) dipyrromethanes depends on the nature of the group attached to the *meso*-position: a sterically hindered group (e.g. mesityl) provides resistance while an unhindered group (e.g. phenyl) results in susceptibility to acidolysis.[16] Indeed, in the only prior example of the synthesis of a *p*-phenylene-linked porphyrin trimer lacking β-substituents, a complex mixture of porphyrins was obtained upon reaction of a porphyrin-benzaldehyde with 5-(*p*-tolyl)dipyrromethane, while with 5-pentyldipyrromethane the desired trimer was obtained in 12% yield.[9] Accordingly, the acid-catalyzed condensations studied herein have employed 5-mesityl-dipyrromethane to minimize scrambling processes.

An alternative approach for preparing *p*-phenylene-linked trimers employs the Suzuki coupling of a dialkoxyboryl-porphyrin and a halo-porphyrin. Suzuki coupling has been employed for (1) attaching diverse groups to porphyrins,[18–21] and (2) preparing porphyrin dimers with a phenylene unit across the β,*meso*-positions,[21,22] a direct C–C bond across the β,β-positions,[23] and a carbazole unit across the



Scheme 3.

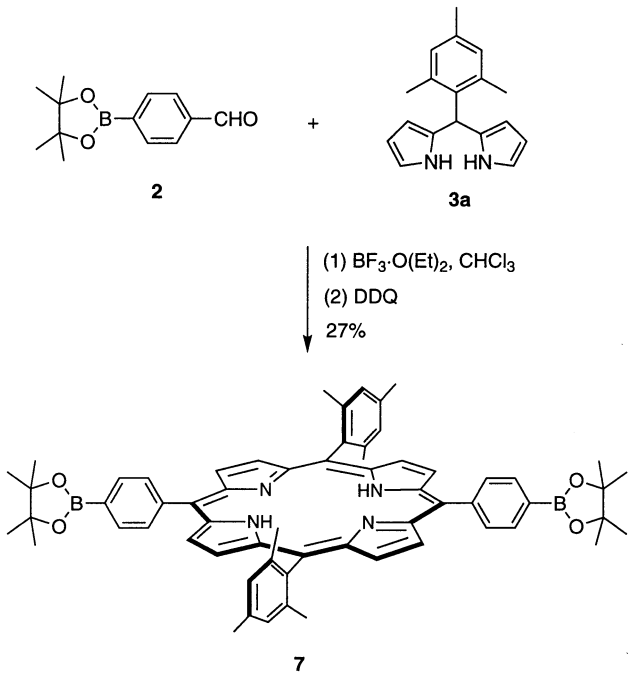
meso,*meso*-positions.[20] However, to our knowledge Suzuki coupling has not been employed previously to prepare trimers or larger multiporphyrin arrays.

In this paper, we report a comparison of two routes for preparing β-unsubstituted *p*-phenylene-linked porphyrin trimers. We first synthesized several porphyrin building blocks in a rational manner. With these building blocks, the condensation of a porphyrin-benzaldehyde and 5-mesityldipyrromethane was investigated to identify optimal acid-catalysis conditions. Suitable conditions were also examined for the Suzuki coupling of a *meso*-iodo-substituted porphyrin and a *meso*-substituted porphyrin bearing two dioxaborolane groups in a *trans* architecture (porphyrin 5,15-positions). In all cases, free base porphyrins were employed, no statistical reactions were performed, and potential scrambling processes were investigated.

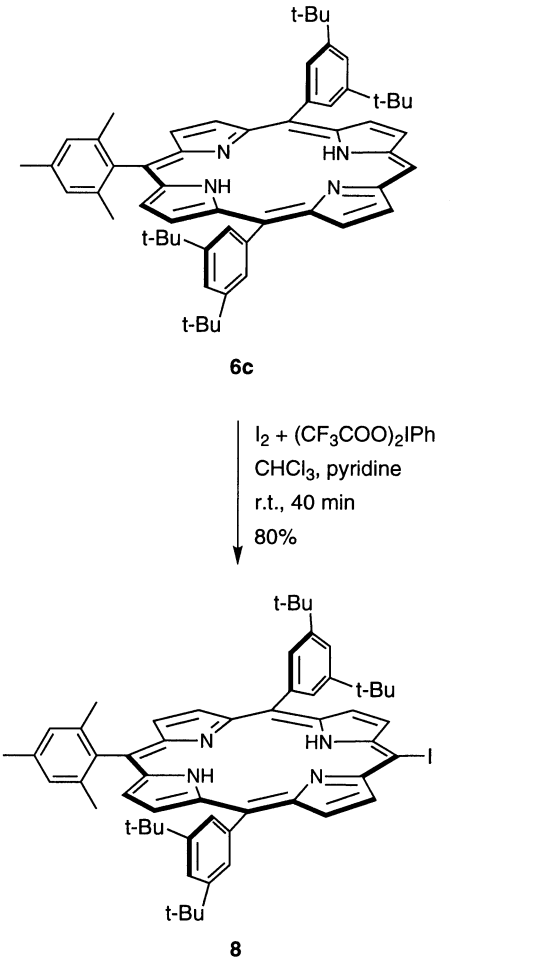
2. Results and discussion

2.1. 5-Substituted dipyrromethanes

Dipyrromethanes bearing a wide variety of substituents at the 5-position are readily available, including mesityl (**3a**),[24] 4-[2-(trimethylsilyl)ethynyl]phenyl (**3b**),[25] no substituent (**3d**),[24] and 4-formylphenyl (**3e**).[5] The synthesis of the dioxaborolane-dipyrromethane **3c** is shown in Scheme 1. The synthesis of aldehyde **2** has been reported but without a detailed procedure or characterization data.[26] To facilitate eventual purification of the porphyrin, the boronic acid group was employed as the dioxaborolane derivative. Aldehyde **2** was obtained in 90% yield by treatment of **1** with pinacol in dry ethyl ether followed by column chromatography. The reaction of aldehyde **2** with pyrrole under TFA catalysis in a one-flask process[24] afforded the desired dipyrromethane **3c** in 32% yield.



Scheme 4.



Scheme 5.

2.2. Porphyrin building blocks

To pursue the two routes for forming *p*-phenylene-linked porphyrin trimers, porphyrins bearing 4-formylphenyl, 4-[2-(trimethylsilyl)ethynyl]phenyl or 4-(1,3,2-dioxaborolan-2-yl)phenyl substituents were prepared via rational procedures. The method of synthesis depends on the pattern of substituents at the perimeter of the porphyrin. For these applications, AB_2C-porphyrins[5] and *trans*-A_2B_2-porphyrins[16] were prepared bearing 3,5-di-*tert*-butylphenyl or mesityl (rather than phenyl) groups at non-linking positions to enhance the solubility of the corresponding porphyrin trimers.

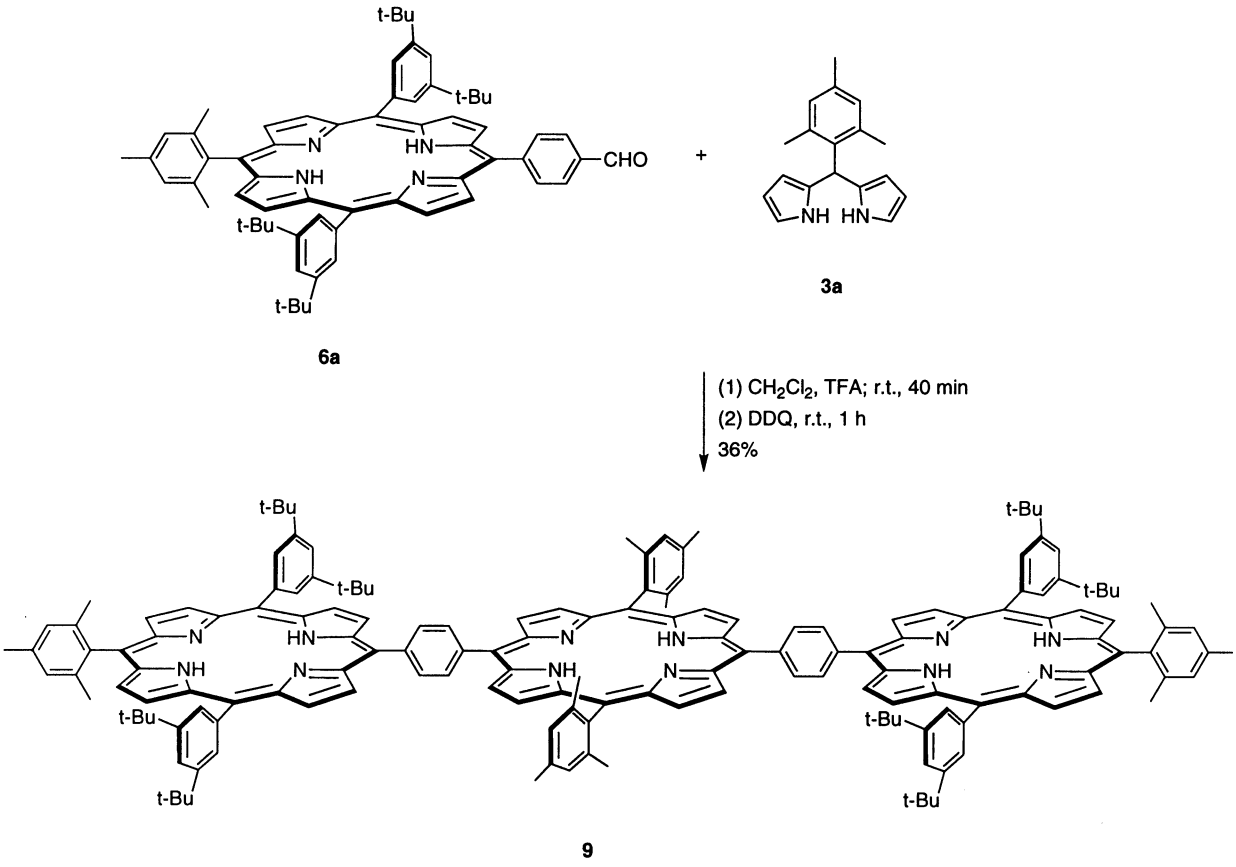
For the synthesis of AB_2C-type porphyrins (**6a**–**d**), treatment of dipyrromethane **3** (A component) with 5 equiv. of EtMgBr followed by 2.5 equiv. of acid chloride **4** (B component) in toluene (Scheme 2) afforded diacyldipyrromethane **5a** or **5b** (BAB component) in 51 or 35% yield, respectively. Reduction of diacyldipyrromethane **5** with $NaBH_4$ in THF/methanol afforded the corresponding dipyrromethane-dicarbinol (**5-OH**), which was condensed directly with another dipyrromethane **3** (C component) in acetonitrile containing TFA followed by oxidation with DDQ (Scheme 3). The dipyrromethane+dipyrromethane-dicarbinol reaction gave yields ranging from 13 to 23%. Several observations are noteworthy: (1) the dipyrromethane with a free formyl group (**3e**) gave a somewhat low yield (13%) in two cases examined; (2) purification of dioxaborolane-porphyrin **6b** could not be achieved by chromatography on alumina due to the significant loss of product incurred.

The *trans*-A_2B_2-type porphyrin **7** was prepared by the condensation of 5-mesityldipyrromethane (**3a**) and the dioxaborolane-benzaldehyde **2** as shown in Scheme 4. The acid catalysis conditions ($BF_3{\cdot}O(Et)_2$ in $CHCl_3$)[27] employed in this reaction are now known to afford a small amount of scrambling.[16] However, porphyrin **7** was readily isolated in pure form (27% yield) after silica column chromatography.

Iodo-porphyrin **8** was prepared as shown in Scheme 5. Treatment of porphyrin **6c** with bis(trifluoroacetoxy)iodobenzene and iodine in $CHCl_3$/pyridine[19,28] at room temperature afforded **8** in 80% yield after column chromatography. No β-iodinated products were observed upon ^1H NMR analysis.

2.3. Synthesis of *p*-phenylene-linked porphyrin trimers by condensation/oxidation of a porphyrin-benzaldehyde+dipyrromethane

We previously studied the reaction of an aldehyde and a dipyrromethane leading to a *trans*-A_2B_2-porphyrin.[16] We found that the condensation of sterically hindered dipyrromethanes and an aryl aldehyde catalyzed by TFA gave no scrambling for all reactions examined, regardless of the acid catalyst concentration, reaction solvent, reagent concentration, reaction temperature, presence of catalytic salts or reagent ratio. The optimum conditions that emerged from this study were as follows: 5-mesityldipyrromethane (10 mM) and aryl aldehyde (10 mM) in reagent-grade CH_2Cl_2 containing TFA (17.8 mM) at room temperature



Scheme 6.

followed by oxidation with DDQ. Under these conditions, seven porphyrins were prepared in 28–48% yield.[16]

Two issues arise for the reaction of a porphyrin-benzaldehyde and a dipyrromethane. First, the porphyrin can buffer the acid employed for catalysis of the condensation.

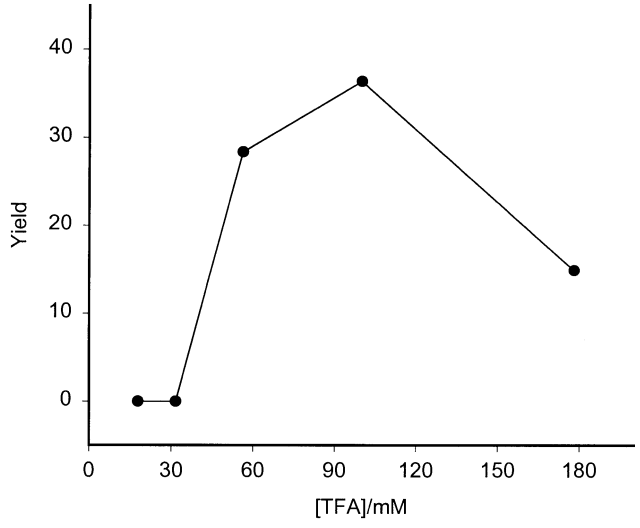
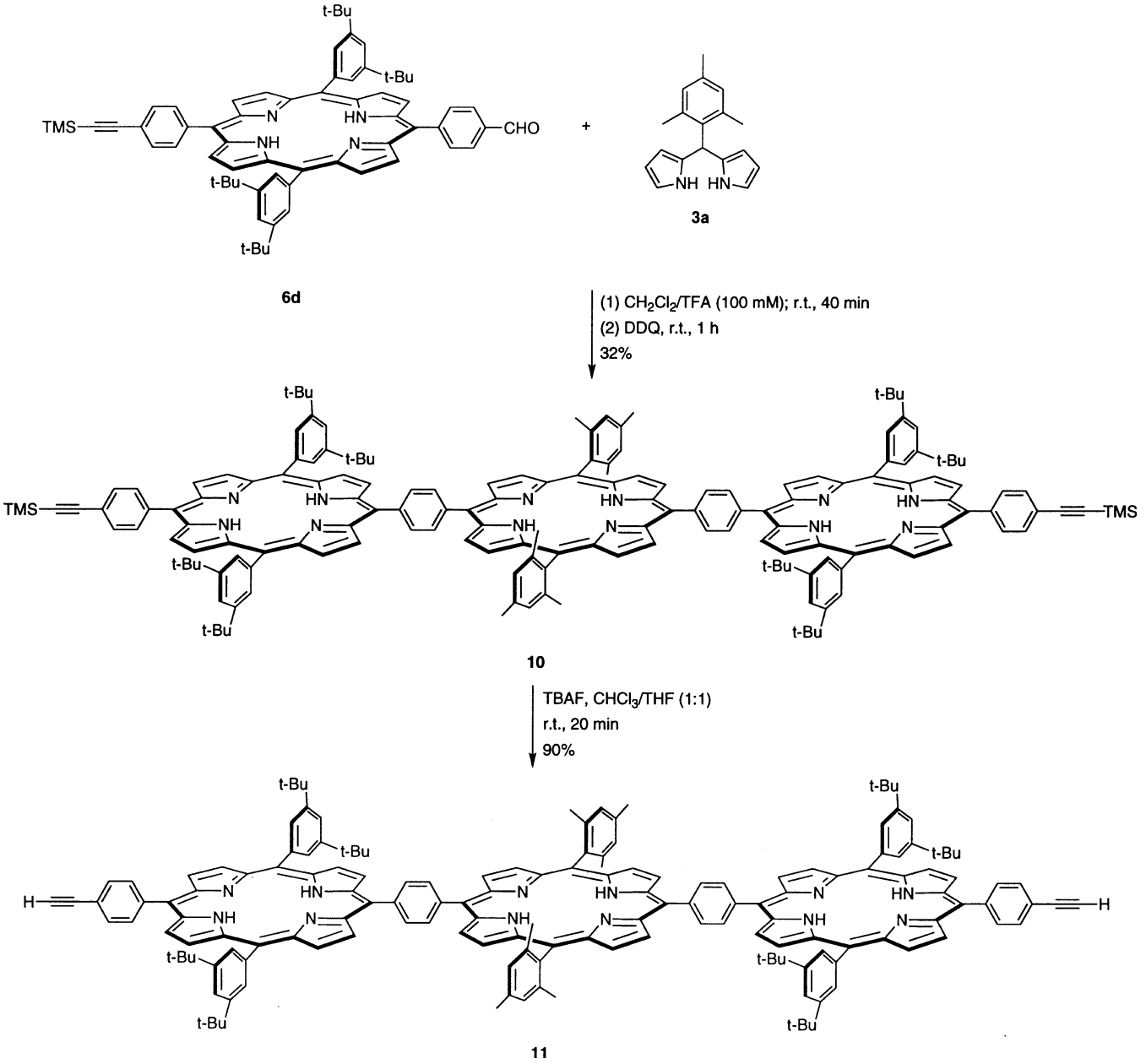


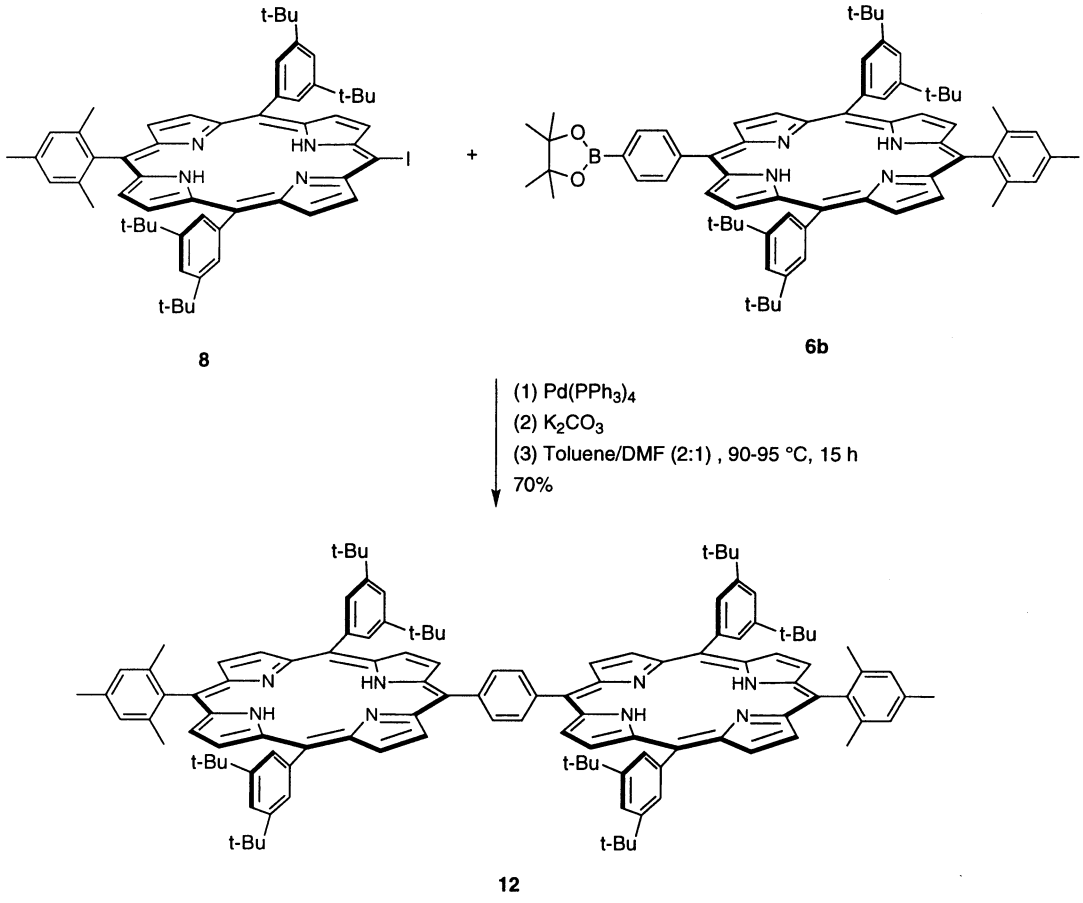
Figure 1. Isolated yield of trimer **9** as a function of the concentration of TFA. The condensation was performed in CH_2Cl_2 at room temperature for 40 min with constant amounts of porphyrin-benzaldehyde **6a** and 5-mesityldipyrromethane (**3a**) (10 mM each). Oxidation was performed with DDQ and the product isolated for yield determination.

Second, because the benzaldehyde bears a porphyrin, the inevitable polypyrrolic byproducts each incorporate one or more porphyrins, which can complicate identification and isolation of the desired trimer.

The trimer-forming reaction (Scheme 6) was performed under the standard conditions for an aldehyde+dipyrromethane condensation (10 mM reactants and 17.8 mM TFA in CH_2Cl_2 at room temperature) followed by oxidation with DDQ.[16] However, analysis of the crude reaction mixture by TLC or LD-MS showed no detectable trimer (**9**) was observed, even with reaction times of up to 2.5 h. We therefore investigated the condensations at different TFA concentrations as shown in Fig. 1. The data show the isolated yield obtained upon workup of the reaction mixture after 40 min. The yield peaked with reactions at 100 mM TFA. The reactions performed with the higher TFA concentrations (56.2, 100, 178 mM) were rapid. Indeed, after 40 min no starting porphyrin was detected upon TLC or LD-MS analysis. In addition, LD-MS analysis of oxidized reaction aliquots showed no peaks due to the formation of scrambled porphyrin products. Thus, suitable conditions for the trimer-forming reaction are as follows: porphyrin-benzaldehyde (10 mM), 5-mesityldipyrromethane (10 mM), and TFA (100 mM) in CH_2Cl_2 at room temperature for 30–40 min followed by oxidation with DDQ. Under these conditions, the desired trimer **9** was obtained in 36% yield. The crude product contained a chlorin contaminant, which upon oxidation with DDQ in refluxing toluene[29] yielded the desired porphyrin trimer.


t-Bu
TMS
CHO
NH
HN
N
6d
3a
(1) CH_2Cl_2/TFA (100 mM); r.t., 40 min
(2) DDQ, r.t., 1 h
32%
10
TBAF, $CHCl_3$/THF (1:1)
r.t., 20 min
90%
H
11

Scheme 7.



Scheme 8.

The concentration of acid is substantially higher than that for the normal synthesis of *trans*-A_2B_2-porphyrins, but the data show that 100 mM TFA with a porphyrin-benzaldehyde and 5-mesityldipyrromethane does not result in a mixture of scrambled products.

Prior studies of the reaction of a porphyrin-benzaldehyde and a β-substituted dipyrromethane have led to different findings concerning the amount of acid required for reaction. Nagata et al. found an increased concentration of trichloroacetic acid in acetonitrile was required compared with that for a reaction with an aldehyde without an attached porphyrin (37 mM trichloroacetic acid; 9 mM reactants),[12] giving yields of 35–47%.[12–15] On the other hand, Sessler et al. employed a slightly lower concentration of TFA (10 mM; 10 mM reactants) in dichloromethane than would be used for the reaction of an aryl aldehyde and pyrrole (20–50 mM TFA), obtaining yields of 60.4[10,11] and 81.6%.[11] Comparative studies of acid catalysis indicate that β-substituted dipyrromethanes and *meso*-substituted dipyrromethanes have quite different reactivity.[17]

We applied the refined acid-catalysis conditions employed for the synthesis of **9** to prepare a *p*-phenylene-linked porphyrin trimer bearing two TMS-protected ethynyl groups as shown in Scheme 7. The purification of the trimer from this method involved: (1) filtration of the crude reaction mixture through alumina; (2) silica gel chromatography; (3) re-oxidation with DDQ in toluene (refluxing for 1 h) to convert trace amounts of chlorin to the porphyrin; (4) filtration through a silica pad; (5) size exclusion chromatography (SEC)[30] and (6) a final silica gel chromatography. Trimer **10** was obtained in 32% yield. A final oxidation was a necessary step because of the presence of chlorin contamination; chlorin formation is a common byproduct in the synthesis of *trans*-porphyrins by the reaction of a dipyrromethane and an aldehyde.[16] Deprotection of the TMS groups with tetra-*n*-butylammonium fluoride (TBAF) in $CHCl_3$/THF gave the diethynyl substituted trimer **11** in 90% yield.

2.4. Synthesis of *p*-phenylene-linked porphyrin dimers and trimers via Suzuki coupling

The use of Pd-coupling methods for joining porphyrins often requires conditions that are substantially different from those employed in mainstream organic chemistry for coupling small molecules.[30] The chief difference stems from the fact that porphyrins typically have low solubility and require reactions to be performed with 1–10 mM porphyrin concentrations. Consequently, many coupling methods that work very well under mild conditions with small molecules at high concentration (0.1 to 1 M) give poor results or fail altogether in more dilute solution. One objective of our study of the Suzuki coupling was whether the milder conditions[31] reported quite recently could be applied to the synthesis of trimeric porphyrin building blocks.

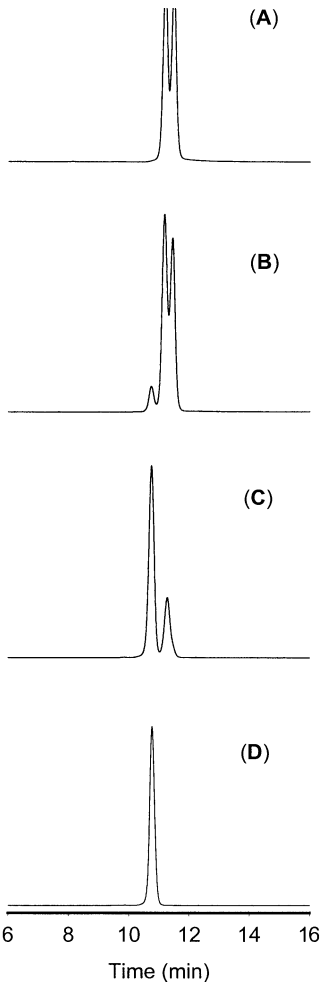


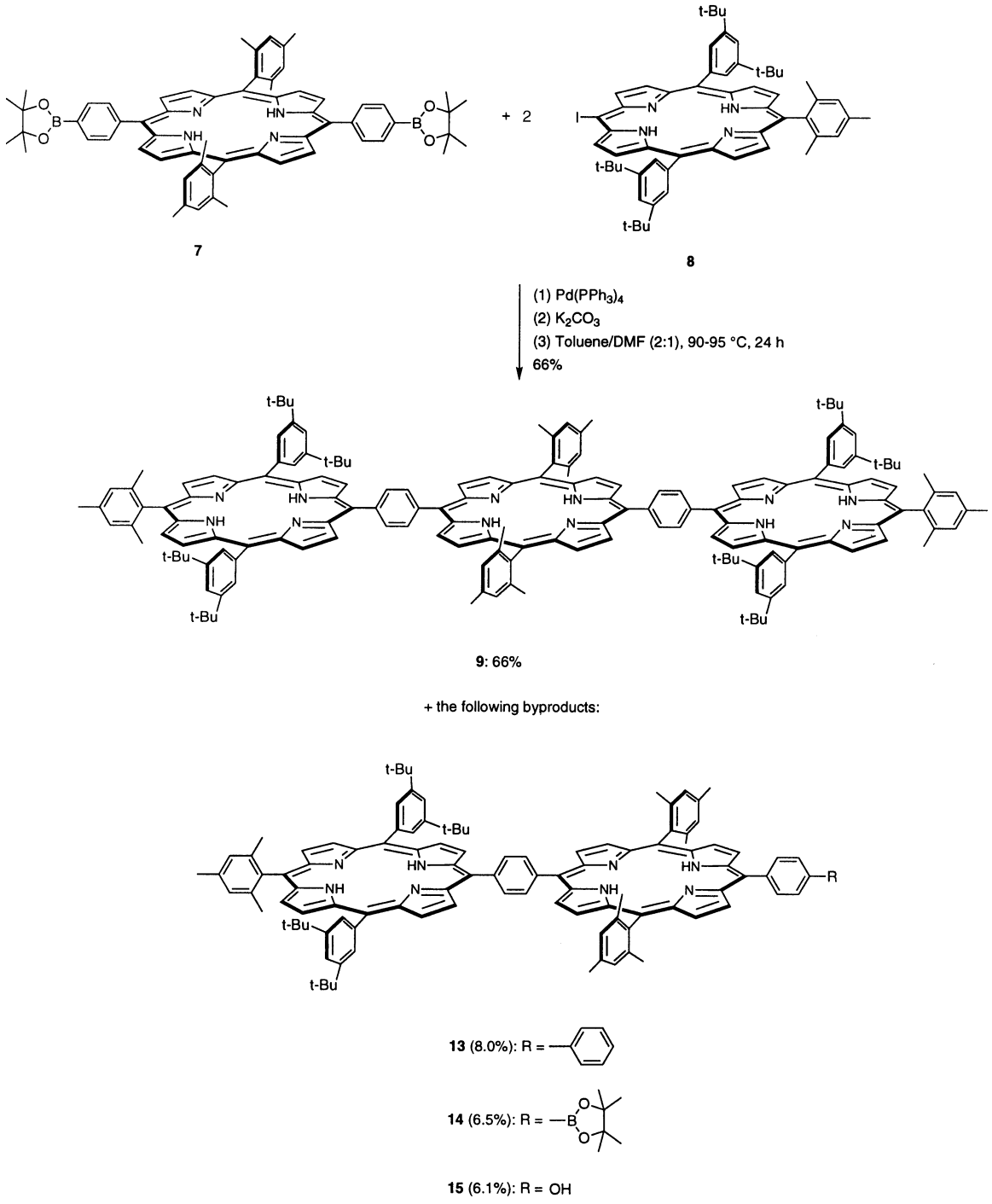
Figure 2. SEC traces of the crude reaction mixture from the formation of dimer **12** via Suzuki coupling. (A) Reaction mixture before adding the catalyst. (B) Reaction mixture after 3 h at 70°C. (C) Reaction mixture after 15 h at 90–95°C. The integrated intensities (uncorrected) were as follows: the desired dimer (t_R=10.75 min), 73.4%; monomeric porphyrins (t_R=11.28 min), 26.5%. (D) Purified dimer **12**.

The syntheses of porphyrin dimers joined across the *meso*-position and β-position by a *p*-phenylene unit has been achieved by Suzuki coupling of a β-substituted bromo-porphyrin and a *meso*-substituted dioxaborinane-porphyrin.[21] These reaction conditions employed a 3.4:1 ratio of the dioxaborinane-porphyrin/bromo-porphyrin with 10–15 mol% of $Pd(PPh_3)_4$ and 8 equiv. of K_2CO_3 in toluene for 48 h at 90–100°C, affording the desired porphyrin dimer in 88% yield. We investigated the Suzuki coupling reactions using stoichiometric amounts of the two porphyrins, because both porphyrin components are valuable and chromatographic workup is simplified if an excess of starting material is not present.[30,32] As shown in Scheme 8, equimolar amounts of dioxaborolane-porphyrin **6b** and iodo-porphyrin **8** were coupled in toluene/DMF (2:1) using $Pd(PPh_3)_4$ (15 mol%) and K_2CO_3 (2 molar equiv. relative to the porphyrin). We chose the mixture of toluene and DMF because tetraarylporphyrin monomers have good solubility in toluene, while K_2CO_3 has good solubility in DMF. The concentration of each porphyrin was 10 mM. The reaction was followed by analytical SEC (Fig. 2). After 3 h at 75°C, the reaction mixture consisted of the desired dimer (6.4%) and monomeric porphyrins (93.5%) by integrated intensities (uncorrected). Therefore, additional K_2CO_3 (6 molar equiv.) and $Pd(PPh_3)_4$ (15 mol%) were added and the temperature was raised to 90°C. The analytical SEC trace showed that most of the starting porphyrins were consumed after stirring for 15 h at 90°C (Fig. 2C). Purification of the crude product involved (1) silica gel chromatography to remove the inorganic salt and Pd species, (2) preparative SEC (THF) and (3) a final silica gel chromatography, affording the desired porphyrin dimer **12** in 70% yield (Fig. 2D).

We applied the conditions for the Suzuki coupling of an iodo-porphyrin and a dioxaborolane-porphyrin yielding the dimer (8 molar equiv. of K_2CO_3 and 30 mol% of $Pd(PPh_3)_4$ at 90°C for several hours) to prepare the phenylene-linked trimer **9** as shown in Scheme 9. In this two-site coupling reaction, the concentrations were as follows: iodoporphyrin **8**, 20 mM; bis(dioxaborolane)porphyrin **7**, 10 mM; K_2CO_3, 16 molar equiv. relative to porphyrin **7**; $Pd(PPh_3)_4$, 30 mol% relative to porphyrin **7**. Analytical SEC indicated that most of the starting porphyrins remained unreacted even after 6 h at 90°C (Fig. 3). Therefore, an additional amount of $Pd(PPh_3)_4$ (30 mol%) was added and the reaction was allowed to proceed for 18 h at 90–95°C. Analytical SEC showed complete consumption of the starting porphyrins.

The purification of the crude reaction mixture by silica column chromatography [$CHCl_3$/hexanes (2:1)] afforded four fractions (in order of elution): (1) the desired trimer **9**; (2) byproduct I (dimers); (3) byproduct II (dimer); and (4) monomeric species. Further purification of the trimer by preparative SEC (toluene) followed by final silica gel chromatography gave **9** in 66% yield (Fig. 3D). Preparative SEC purification (THF) of fraction 2 afforded one band as evidenced by analytical SEC; however, final silica column chromatography [$CHCl_3$/hexanes (2:1)] afforded clearly two bands, which were collected separately, affording dimer **13** (first purple band) and **14** (second purple band) in 8.0 and 6.5% yield, respectively. Similar purification of fraction 3 by preparative SEC (THF) and silica column chromatography [$CHCl_3$/hexanes (2:1)] afforded dimer **15** in 6.1% yield. In summary, the Suzuki coupling afforded a direct synthesis of the desired trimer (or dimer) upon reaction at the low concentrations typical in porphyrin chemistry.[‡] The requirement to use high-temperature conditions in the presence of base, as employed in the synthesis of trimer **9**, precluded the use of the Suzuki reaction to prepare diethynyl-substituted or other trimeric porphyrin building blocks.

[‡] Fu and co-workers recently reported extremely mild conditions for the Suzuki coupling of arylboronic acids with aryl halides.[31] Under their conditions, an aryl iodide and an aryl boronic acid (~1 M each) were coupled in excellent yield (94–98%) with $Pd_2(dba)_3$ (0.5 mol%), P(*t*-Bu)$_3$ (1.2 mol%) and KF (3.3 equiv.) in THF at room temperature for 3–20 h. Application of these conditions to prepare porphyrin dimer **12** using 10 mM of each porphyrin was not successful. A 10-fold increase in the loading of $Pd_2(dba)_3$ (5 mol%) and P(*t*-Bu)$_3$ (12 mol%) also gave no dimer. A reasonable interpretation is that the low solubility of porphyrinic substrates limits the types of Pd-mediated coupling conditions that can be employed.



Scheme 9.

2.5. Electronic spectra of *p*-phenylene-linked arrays

The absorption spectrum of the trimer **9** shows broadening and splitting of the Soret (B) band compared with that of the monomer **6b**, but the visible (Q) bands are essentially unchanged (Fig. 4). Dimer **12** exhibits broadening and splitting of the Soret band intermediate between that of a trimer and monomer **6b**. The unchanged visible bands are consistent with an excited singlet state that is unaffected by the juxtaposition of the three porphyrins via the *p*-phenylene bridges. These absorption spectral features resemble those observed previously for *p*-phenylene linked porphyrin trimers.[9,12,14,15] The fluorescence emission spectrum and emission intensity of **9** in toluene (λ_{exc}=520 nm, ϕ_f=0.13) closely resembled that of *meso*-tetraphenylporphyrin (ϕ_f=0.11), with peak emission wavelengths of **9** within 3 nm of those of *meso*-tetraphenylporphyrin. Nearly identical behavior was observed for the diethynyl-trimer **10**. In contrast, the *p*-phenylene linked trimer composed of β-substituted free base porphyrins gave a slightly broadened emission spectrum,[11] and the zinc chelates of the same type of trimer gave quite red-shifted and broadened emission spectra.[14,15] The essentially unaltered fluorescence spectrum and intensity compared with that of a monomeric free base

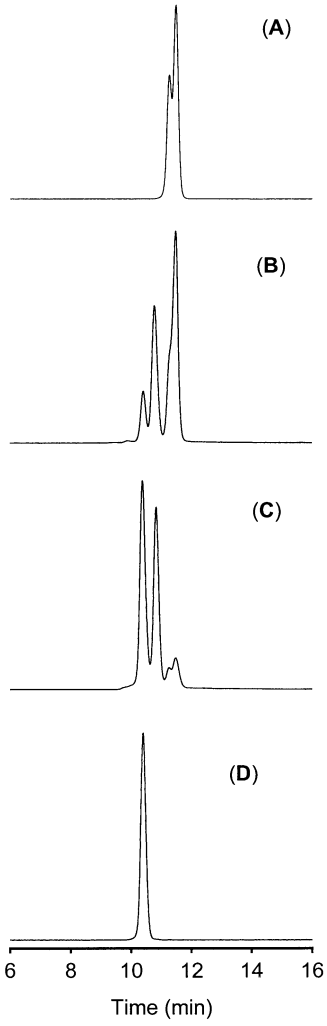


Figure 3. SEC traces of the crude reaction mixture from the formation of trimer **9** via Suzuki coupling. (A) Reaction mixture before adding the catalyst. (B) Reaction mixture after 6 h at 90–95°C. (C) Reaction mixture after 18 h at 90–95°C. The integrated intensities (uncorrected) were as follows: desired trimer (t_R=10.38 min), 49.0%; dimer species (t_R=10.84 min), 39.4%; monomeric species (t_R=11.26–11.48 min), 11.05%. (D) Purified trimer **9**.

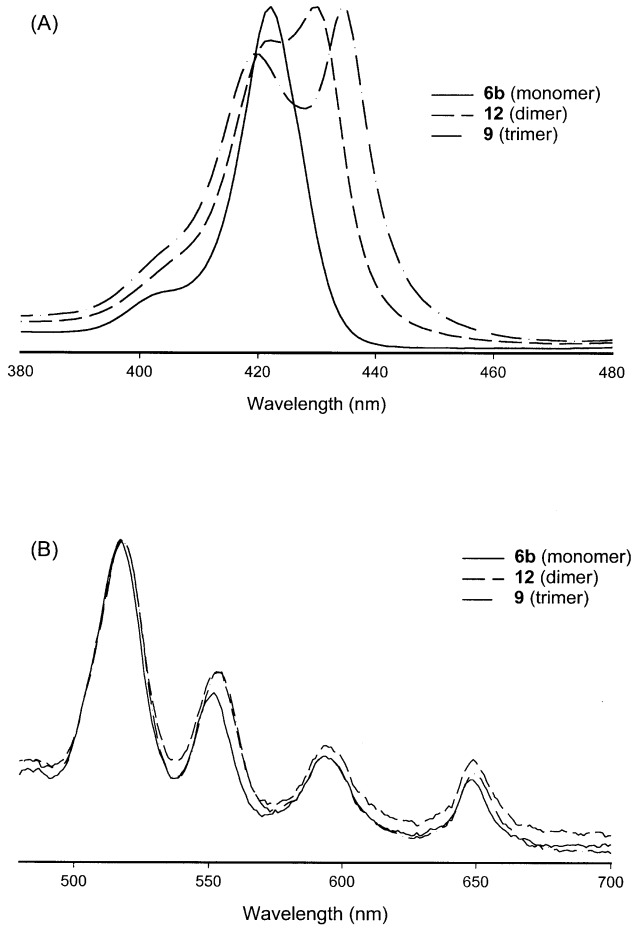


Figure 4. UV–Vis absorption spectra (normalized) of monomer (**6b**), dimer (**12**) and trimer (**9**) in toluene at room temperature: (A) Soret band region. (B) Q-band region.

tetraarylporphyrin indicates the integrity of the excited singlet state in the *p*-phenylene linked trimers, a desirable attribute of weakly coupled systems for photochemical applications.

3. Conclusions

Linear porphyrin trimers joined via *p*-phenylene linkers across the respective porphyrin *meso*-positions were successfully prepared both by condensation of a porphyrin-benzaldehyde+dipyrromethane and by Suzuki coupling of an iodo-porphyrin and a bis(dioxaborolane)-porphyrin. Both routes are convergent and proceed in a rational manner but employ conditions of somewhat complementary scope. The former route gave a lower yield (36%) but the reaction proceeded under mild conditions and a short time course (room temperature, 30–40 min). Diverse functional groups (e.g. iodo, trimethylsilylethynyl, triisopropylsilylethynyl) are known to survive these mild conditions.[16] The latter route offered higher yield (66%) but required more forcing conditions (90–95°C, 24 h in the presence of K_2CO_3). Functional groups such as the TMS-protected ethynyl unit are not expected to survive these conditions. Purification of the *p*-phenylene-linked porphyrin trimer was somewhat simpler in the Suzuki route.

4. Experimental

4.1. General

^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were collected in $CDCl_3$ unless noted otherwise. Absorption and fluorescence spectra were collected in toluene at room temperature. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix,[33] or by high resolution fast atom bombardment mass spectrometry (FAB-MS) using a matrix of nitrobenzyl alcohol and polyethylene glycol. Fluorescence quantum yields were determined in toluene at room temperature using chlorin-free *meso*-tetraphenylporphyrin (Φ_f=0.11;[34] λ_{em}=652, 718 nm) as a standard as described previously.[3] Anhydrous K_2CO_3, tetrabutylammonium fluoride (TBAF) (1.0 M

solution in THF), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), mesitaldehyde, 4-formylphenylboronic acid, and pinacol were used as received from Aldrich. The synthesis of the porphyrin monomers was performed without degassing.

4.2. Solvents

All solvents were dried by standard methods. Triethylamine and toluene were distilled from CaH_2. Anhydrous DMF (Aldrich), CH_2Cl_2 and $CHCl_3$ (Fisher, certified ACS grade, stabilized with 0.8% ethanol) were used as received.

4.3. Chromatography

Adsorption column chromatography was performed using flash silica gel (Baker, 60–200 mesh) or alumina (Fisher). Preparative-scale SEC was performed using BioRad Biobeads SX-1 in THF or in toluene (Fisher HPLC grade). Analytical scale SEC ($\lambda_{detection}$=420 nm) was performed as described previously to monitor the progress of the coupling reactions and assess the purity of the porphyrin oligomers.[35]

The known compounds 5-mesityldipyrromethane (**3a**),[24] 5-[4-(trimethylsilylethynyl)phenyl]dipyrromethane (**3b**),[25] dipyrromethane (**3d**),[24] 5-(4-formylphenyl)dipyrromethane (**3e**),[5] and 3,5-di-*tert*-butylbenzoyl chloride (**4**)[5] were prepared according to literature procedures.

4.3.1. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (2). To a suspension of 4-formylphenylboronic acid (5.02 g, 33.4 mmol) in dry ethyl ether (50 mL) was added pinacol (4.70 g, 40.1 mmol, 1.2 equiv.), causing the reaction mixture to turn to a clear solution after 30 min. After stirring for 15 h at room temperature, ethyl ether (100 mL) was added and the mixture was washed with H_2O. The organic layer was dried ($MgSO_4$) and chromatographed (silica, CH_2Cl_2), affording a slightly yellow oil. Trituration with hexanes gave a solid, which was filtered and dried affording a colorless solid (6.98 g, 90%): mp 58–59°C; ^{1}H NMR δ 10.05 (s, 1H), 7.96 (d, J=8.1 Hz, 2H), 7.87 (d, J=8.1 Hz, 2H), 1.36 (s, 12H); ^{13}C NMR δ 192.5, 138.0, 135.1, 128.6, 84.2, 24.8. Anal calcd for $C_{13}H_{17}BO_3$: C, 67.28; H, 7.38. Found: C, 67.42; H, 7.47.

4.3.2. 5-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]dipyrromethane (3c). Following a general procedure,[24] a mixture of pyrrole (35 mL, 0.50 mol) and aldehyde **2** (4.64 g, 20.0 mmol) was flushed with argon for 5 min and treated with TFA (154 μL, 2.00 mmol). The mixture was stirred for 5 min at room temperature and then quenched with triethylamine. Ethyl acetate (100 mL) was added and the mixture was washed with H_2O and dried (Na_2SO_4). Removal of solvent and excess pyrrole followed by chromatography [silica, CH_2Cl_2→CH_2Cl_2/ethyl acetate (95:5)] gave a slightly yellow oil. Trituration with hexanes afforded a colorless solid (2.50 g, 32%): mp 129–130°C; ^{1}H NMR δ 7.91 (s, br, 2H), 7.77 (d, J=8.1 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H), 6.70–6.69 (m, 2H), 6.17–6.14 (m, 2H), 5.91 (s, br, 2H), 5.49 (s, 1H), 1.34 (s, 12H); ^{13}C NMR δ 145.1, 135.0, 132.0, 127.7, 117.2, 108.2, 107.1, 83.7, 44.0, 24.8; Anal calcd for $C_{21}H_{25}BN_2O_2$: C, 72.43; H, 7.24; N, 8.04. Found: C, 72.06; H, 7.34; N, 7.97.

4.3.3. 1,9-Bis(3,5-di-*tert*-butylbenzoyl)-5-mesityldipyrromethane (5a). Following the general diacylation procedure,[5] a solution of 5-mesityldipyrromethane (2.64 g, 10.0 mmol) in toluene (200 mL) was treated with EtMgBr (50.0 mL, 50.0 mmol, 1.0 M in THF) for 30 min at room temperature followed by addition of 3,5-di-*tert*-butylbenzoyl chloride (6.33 g, 25.0 mmol, 2.5 equiv.). The mixture was stirred for 20 min at room temperature. Standard workup and chromatography [silica, CH_2Cl_2] followed by precipitation from methanol afforded a brown solid (3.55 g, 51%): mp >240°C (dec); ^{1}H NMR δ 11.28 (s, br, 2H), 7.56 (s, 4H), 7.53 (s, 2H), 6.92 (s, 2H), 6.61 (s, 2H), 6.24 (s, 1H), 5.96 (s, 2H), 2.31 (s, 3H), 2.29 (s, 6H), 1.29 (s, 36H), ^{13}C NMR δ 184.4, 150.0, 140.0, 137.9, 136.6, 133.9, 130.4, 130.0, 125.2, 124.0, 121.0, 110.0, 39.2, 34.8, 31.3, 21.1, 20.8. Calcd for $C_{48}H_{60}N_2O_2$: C, 82.71; H, 8.68; N, 4.02. Found: C, 82.66; H, 8.81; N, 4.00.

4.3.4. 1,9-Bis(3,5-di-*tert*-butylbenzoyl)-5-{4-[2-(trimethylsilyl)ethynyl]phenyl} dipyrromethane (5b). Following the general diacylation procedure,[5] a solution of dipyrromethane **3b** (1.57 g, 4.93 mmol) in toluene (90 mL) was treated with EtMgBr (24.7 mL, 24.7 mmol, 1.0 M in THF) for 30 min at room temperature followed by addition of 3,5-di-*tert*-butylbenzoyl chloride (3.12 g, 12.3 mmol, 2.5 equiv.). The mixture was stirred for 40 min at room temperature. Standard workup and chromatography [silica, CH_2Cl_2→CH_2Cl_2/ethyl acetate (98:2)] followed by precipitation (from a methanol solution upon addition of water) gave an amorphous solid (1.30 g, 35%): mp 168–170°C; ^{1}H NMR δ 11.97 (s, br, 2H), 7.58 (d, J=8.1 Hz, 2H), 7.54 (s, 6H), 7.48 (d, J=8.1 Hz, 2H), 6.54–6.52 (m, 2H), 5.94 (m, 2H), 5.71 (s, 1H), 1.29 (s, 36H), 0.25 (s, 9H); ^{13}C NMR δ 185.5, 150.2, 141.5, 137.8, 132.4, 131.1, 128.9, 125.4, 124.2, 122.1, 120.9, 111.1, 105.0, 94.1, 45.2, 34.8, −0.1; Anal. Calcd for $C_{50}H_{62}N_2O_2Si$: C, 79.95; H, 8.32; N, 3.73. Found: C, 79.75, H, 8.34, N, 3.73.

4.3.5. 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-formylphenyl)-20-mesitylporphyrin (6a). Following a standard procedure,[5] reduction of **5a** (2.79 g, 4.00 mmol) with $NaBH_4$ (7.60 g, 200 mmol) in THF/methanol (320 mL, 3:1) yielded the dipyrromethane-dicarbinol. Condensation of the latter with dipyrromethane **3e** (1.00 g, 4.05 mmol) in CH_3CN (1600 mL) containing TFA (3.70 mL, 30 mM) for 5 min, followed by oxidation with DDQ (2.72 g, 12.0 mmol) and standard workup gave a purple solid (467 mg, 12.8%): ^{1}H NMR δ 10.38 (s, 1H), 8.90 (d, J=4.5 Hz, 2H), 8.86 (d, J=4.5 Hz, 2H), 8.75 (d, J=5.1 Hz, 2H), 8.71 (d, J=5.1 Hz, 2H), 8.41 (d, J=8.1 Hz, 2H), 8.27 (d, J=8.1 Hz, 2H), 8.08 (s, 4H), 7.80 (s, 2H), 7.28 (s, 2H), 2.63 (s, 3H), 1.87 (s, 6H), 1.52 (s, 36H), −2.65 (s, br, 2H); LD-MS obsd 908.8; FAB-MS obsd 908.5387, calcd 908.5393 ($C_{64}H_{68}N_4O$).

4.3.6. 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-mesityl-20-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-porphyrin (6b). Following a standard procedure,[5] reduction of **5a** (0.697 g, 1.00 mmol) with $NaBH_4$ (1.90 g, 50.0 mmol) in THF/methanol (80 mL, 3:1) yielded the dipyrromethane-dicarbinol. The latter was condensed with **3c** (0.348 g, 1.00 mmol) in CH_3CN (400 mL) containing TFA (0.92 mL, 30 mM) for 5 min followed by oxidation with DDQ

(0.68 g, 3.0 mmol). Filtration through a pad of silica and chromatography (silica, CH_2Cl_2) afforded a purple solid (162 mg, 16%): ^{1}H NMR δ 8.87–8.84 (m, 4H), 8.80 (d, J=4.5 Hz, 2H), 8.69 (d, J=4.5 Hz, 2H), 8.23 (d, J=7.2 Hz, 2H), 8.18 (d, J=7.2 Hz, 2H), 8.08 (s, 4H), 7.78 (s, 2H), 7.27 (s, 2H), 2.62 (s, 3H), 1.86 (s, 6H), 1.53–1.50 (m, 48H), −2.66 (s, br, 2H); LD-MS obsd 1007.9; FAB-MS obsd 1007.6398, calcd 1007.6374 ($C_{69}H_{79}BN_4O_2$); λ_{abs} 422, 517, 552, 593, 648 nm; λ_{em} (λ_{ex}=520 nm) 651, 720 nm.

4.3.7. 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-mesitylporphyrin (6c). Following a standard procedure,[5] reduction of **5a** (1.04 g, 1.49 mmol) with $NaBH_4$ (2.78 g, 75.0 mmol) in THF/methanol (120 mL, 3:1) yielded the dipyrromethane-dicarbinol. The latter was condensed with dipyrromethane **3d** (219 mg, 1.50 mmol) in CH_3CN (600 mL) containing TFA (1.39 mL, 30 mM) for 5 min followed by oxidation with DDQ (1.02 g, 4.49 mmol). Standard workup and chromatography (silica, CH_2Cl_2) gave a purple solid (280 mg, 23%): ^{1}H NMR δ 10.20 (s, 1H), 9.33 (d, J=4.5 Hz, 2H), 9.05 (d, J=4.5 Hz, 2H), 8.91 (d, J=4.5 Hz, 2H), 8.74 (d, J=4.5 Hz, 2H), 8.12 (s, 4H), 7.80 (s, 2H), 7.27 (s, 2H), 2.62 (s, 3H), 1.84 (s, 6H), 1.55 (s, 36H), −2.82 (s, br, 2H); LD-MS obsd 803.9; FAB-MS obsd 804.5177, calcd 804.5131 ($C_{57}H_{64}N_4$).

4.3.8. 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-formylphenyl)-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (6d). Following the general procedure for the preparation of *trans*-AB_2C-porphyrins,[5] a sample of **5b** (1.46 g, 1.95 mmol) was reduced in THF/methanol (88 mL, 10:1) with $NaBH_4$ (1.52 g, 39.0 mmol, 20 equiv.). The resulting dipyrromethane-dicarbinol was condensed with dipyrromethane **3e** (488 mg, 1.95 mmol) in CH_3CN (800 mL) containing TFA (1.9 mL, 30 mM) for 5 min followed by oxidation with DDQ (1.36 g, 5.99 mmol). Standard workup and purification by chromatography (silica, CH_2Cl_2) afforded a purple solid (254 mg, 13.6%): ^{1}H NMR δ 10.38 (s, 1H), 8.92–8.90 (m, 4H), 8.82 (d, J=5.1 Hz, 2H), 8.78 (d, J=5.1 Hz, 2H), 8.41 (d, J=8.1 Hz, 2H), 8.28 (d, J=8.1 Hz, 2H), 8.17 (d, J=8.1 Hz, 2H), 8.07 (m, 4H), 7.87 (d, J=7.8 Hz, 2H), 7.81 (m, 2H), 1.52 (s, 36H), 0.37 (s, 9H), −2.74 (s, br, 2H); LD-MS obsd 961.7; FAB-MS obsd 963.5427, calcd 963.5397 ($C_{66}H_{70}N_4OSi$); λ_{abs} 423, 517, 553, 593, 650 nm; λ_{em} (λ_{ex}=520 nm) 653, 720 nm.

4.3.9. 5,15-Dimesityl-10,20-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]porphyrin (7). Following an early procedure[27] now known to give a small amount of scrambling,[16] a solution of 5-mesityldipyrromethane (1.05 g, 3.98 mmol) and aldehyde **2** (952 mg, 4.01 mmol) in $CHCl_3$ (500 mL) was treated with $BF_3{\cdot}O(Et)_2$ (210 μL, 3.3 mM) for 30 min at room temperature under argon. DDQ (1.36 g, 5.99 mmol) was added and the mixture was stirred for 1 h at room temperature. Triethylamine (230 μL, 3.3 mM) was added and the mixture was filtered through a pad of silica and washed with $CHCl_3$. Removal of solvent and chromatography (silica, CH_2Cl_2) afforded a purple solid (516 mg, 27%): ^{1}H NMR δ 8.78 (d, J=4.5 Hz, 4H), 8.67 (d, J=4.5 Hz, 4H), 8.24 (d, J=8.1 Hz, 4H), 8.18 (d, J=8.1 Hz, 4H), 7.28 (s, 4H), 2.63 (s, 6H), 1.83 (s, 12H), 1.50 (s, 24H), −2.65 (s, br, 2H); LD-MS obsd 949.2; FAB-MS obsd 950.5137, calcd 950.5114 ($C_{62}H_{64}B_2N_4O_4$).

4.3.10. 5,15-Bis(3,5-di-*tert*-butylphenyl)-10-iodo-20-mesitylporphyrin (8). Following a general procedure,[19,28] a stirred solution of porphyrin **6c** (201 mg, 0.249 mmol) and I_2 (44.5 mg, 0.175 mmol, 0.7 equiv.) in $CHCl_3$ (30 mL) was treated with a solution of [bis(trifluoroacetoxy)-iodo]benzene (86 mg, 0.20 mmol, 0.8 equiv.) in $CHCl_3$ (5 mL) followed by pyridine (10 drops). The mixture was stirred at room temperature. TLC [silica, CH_2Cl_2/hexanes (1:2)] showed iodination was complete after 40 min. The reaction mixture was diluted with CH_2Cl_2, washed with aqueous $Na_2S_2O_3$ and dried (Na_2SO_4). Chromatography [silica, CH_2Cl_2/hexanes (1:2)] afforded a purple solid which was washed with methanol (sonicated), filtered and dried (187 mg, 80%): ^{1}H NMR δ 9.68 (d, J=4.2 Hz, 2H), 8.90 (d, J=5.1 Hz, 2H), 8.79 (d, J=5.1 Hz, 2H), 8.65 (d, J=4.2 Hz, 2H), 8.06 (s, 4H), 7.80 (s, 2H), 7.25 (s, 2H), 2.60 (s, 3H), 1.85 (s, 6H), 1.53 (s, 36H), −2.61 (s, br, 2H); LD-MS obsd 928.2; FAB-MS obsd 931.4209, calcd 931.4176 ($C_{57}H_{63}IN_4$).

4.3.11. Trimer 9 (via the condensation/oxidation procedure). A solution of **6a** (36.4 mg, 0.0401 mmol) and 5-mesityldipyrromethane (10.6 mg, 0.0401 mmol) in CH_2Cl_2 (4.0 mL) was flushed with argon for 5 min; then TFA (30.9 μL, 100 mM) was added. The mixture was stirred for 40 min at room temperature. Analysis of an oxidized aliquot by LD-MS showed a significant peak at m/z=2305, corresponding to the desired trimer; no starting porphyrin peak was seen at this point. DDQ (13.6 mg, 0.060 mmol, 1.5 equiv.) was added and the mixture was stirred for 1 h at room temperature. Triethylamine (56 μL, 100 mM) was added. The mixture was filtered through a pad of alumina and washed with CH_2Cl_2. Chromatography [silica, CH_2Cl_2/hexanes (1:1)] gave a purple solid. The latter was dissolved in toluene (10 mL), treated with DDQ (13.6 mg, 0.060 mmol) and the mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was filtered through a pad of silica (CH_2Cl_2). Further purification by chromatography [SEC (THF); silica (CH_2Cl_2)] afforded a purple solid (16.8 mg, 36.4%): ^{1}H NMR δ 9.33–9.31 (m, 8H), 9.10 (d, J=4.5 Hz, 4H), 8.97–8.94 (m, 8H), 8.77 (d, J=4.5 Hz, 4H), 8.68 (s, 8H), 8.20 (m, 8H), 7.86 (m, 4H), 7.40 (s, 4H), 7.33 (s, 4H), 2.72 (s, 6H), 2.66 (s, 6H), 2.01 (s, 12H), 1.93 (s, 12H), 1.60 (s, 72H), −2.30 (s, br, 2H), −2.47 (s, br, 4H); LD-MS obsd 2301.4, calcd avg. mass 2305.1; λ_{abs} (log ε) 419 (5.76), 434 (5.83), 518 (4.80), 554 (4.57), 593 (4.32), 649 nm (4.24); λ_{em} (λ_{ex}=520 nm) 653, 720 nm (Φ_f=0.13).

4.3.12. Trimer 10. Following the general procedure described for the preparation of **9**, a solution of **6d** (250.4 mg, 0.260 mmol) and 5-mesityldipyrromethane (68.7 mg, 0.260 mmol) in CH_2Cl_2 (26 mL) was flushed with argon for 5 min. TFA (201 μL, 100 mM) was added and the mixture was stirred for 40 min at room temperature. Analysis of an oxidized aliquot by LD-MS showed a significant peak at m/z=2412, corresponding to the desired trimer; no starting porphyrin peak was seen at this point. DDQ (88.4 mg, 0.389 mmol, 1.5 equiv.) was added and

the mixture was stirred for 1 h at room temperature. Triethylamine (362 μL, 100 mM) was added. After stirring for 5 min, the mixture was filtered through a pad of alumina and washed with CH_2Cl_2. Chromatography (silica, CH_2Cl_2) gave a purple solid. The purple solid was dissolved in toluene (50 mL). DDQ (88.4 mg, 0.389 mmol) was added and the mixture was refluxed for 1 h, then the mixture was cooled to room temperature and filtered through a pad of silica ($CHCl_3$). Further chromatography [SEC (THF); silica (CH_2Cl_2)] afforded a purple solid (101.4 mg, 32.3%): ^{1}H NMR δ 9.32–9.30 (m, 8H), 9.09 (d, J=4.5 Hz, 4H), 8.98–8.94 (m, 8H) 8.86 (d, J=5.1 Hz, 4H), 8.69–8.63 (m, 8H), 8.22 (d, J=8.1 Hz, 4H), 8.18–8.17 (m, 8H) 7.90 (d, J=7.2 Hz, 4H), 7.86 (s, br, 4H), 7.39 (s, 4H), 2.71 (s, 6H), 2.00 (s, 12H), 1.58 (s, 72H), 0.29 (s, 18H), −2.32 (s, br, 2H), −2.58 (s, br, 4H); LD-MS obsd 2408.0, calcd avg. mass 2413.4; λ_{abs} (log ε) 420 (5.58), 435 (5.68), 519 (4.37), 555 (4.18), 594 (3.86), 650 nm (3.80); λ_{em} (λ_{ex}=520 nm) 654, 721 nm (Φ_f=0.15).

4.3.13. Trimer 11. A solution of trimer **10** (97 mg, 0.040 mmol) in $CHCl_3$/THF (16 mL, 1:1) was treated with tetrabutylammonium fluoride (TBAF) (88 μL, 0.088 mmol, 2.2 equiv., 1.0 M in THF) for 20 min at room temperature. Standard workup and chromatography [silica, $CHCl_3$/hexanes (2:1)] afforded a purple solid (82 mg, 90%): ^{1}H NMR δ 9.33–9.30 (m, 8H), 9.10 (d, J=4.5 Hz, 4H), 8.98 (d, J=4.2 Hz, 4H), 8.95 (d, J=4.5 Hz, 4H), 8.87 (d, J=4.2 Hz, 4H), 8.66 (s, 8H), 8.24 (d, J=8.1 Hz, 4H), 8.18 (m, 8H), 7.92 (d, J=8.1 Hz, 4H), 7.86 (s, 4H), 7.39 (s, 4H), 3.33 (s, 2H), 2.71 (s, 6H), 2.00 (s, 12H), 1.58 (s, 72H), −2.32 (s, br, 2H), −2.57 (s, br, 4H); LD-MS obsd 2264.3, calcd avg. mass 2269.0 ($C_{162}H_{154}N_{12}$); λ_{abs} 419, 434, 518, 554, 593, 649 nm; λ_{em} (λ_{ex}=520 nm) 654, 721 nm.

4.3.14. Dimer 12 (via Suzuki coupling). Samples of **6b** (30.2 mg, 0.0300 mmol), **8** (27.9 mg, 0.0300 mmol), anhydrous K_2CO_3 (8.3 mg, 0.060 mmol) and $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol, 15 mol%) were weighed into a 10 mL Schlenk flask. The flask was pump-purged with argon three times. Toluene/DMF (3.0 mL, 2:1) was added and the mixture was heated to 75°C under argon. Analytical SEC showed only 6% of product formation after 3 h. Additional amounts of K_2CO_3 (49.8 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) were added and the mixture was stirred for 15 h at 90°C. Analytical SEC indicated that most of the starting porphyrins were consumed. Chromatography [silica, $CHCl_3$/hexanes (3:2)] removed most of the unreacted porphyrin monomeric species. Preparative SEC (THF) removed the trace amount of remaining monomeric porphyrins. A final silica gel column [$CHCl_3$/hexanes (2:1)] afforded a purple solid (35.5 mg, 70.2%): ^{1}H NMR δ 9.30 (d, J=4.2 Hz, 4H), 9.07 (d, J=5.4 Hz, 4H), 8.92 (d, J=5.4 Hz, 4H), 8.75 (d, J=4.2 Hz, 4H), 8.62 (s, 4H), 8.18 (m, 8H), 7.84 (m, 4H), 7.31 (s, 4H), 2.64 (s, 6H), 1.91 (s, 12H), 1.57 (s, 72H), −2.50 (s, br, 4H); LD-MS obsd 1683.0, calcd avg. mass 1684.0 ($C_{120}H_{130}N_8$); λ_{abs} (log ε) 422(5.67), 430 (5.72), 518 (4.55), 553 (4.28), 594 (4.02), 649 nm (3.96); λ_{em} (λ_{ex}= 520 nm) 652, 720 nm (Φ_f=0.10).

4.3.15. Trimer 9 (via Suzuki coupling). Following the general procedure described for the preparation of dimer **12**, samples of **8** (55.9 mg, 0.0600 mmol), **7** (28.5 mg, 0.0300 mmol), K_2CO_3 (66.2 mg, 0.480 mmol) and $Pd(PPh_3)_4$ (10.4 mg, 9.0 μmol) were weighed into a 10 mL Schlenk flask. The flask was pump-purged with argon three times. Toluene/DMF (3.0 mL, 2:1) was added and the mixture was stirred at 90–95°C. Analytical SEC indicated incomplete consumption of the starting porphyrins after 6 h, therefore an additional amount of $Pd(PPh_3)_4$ (10.4 mg, 9.0 μmol) was added and the reaction mixture was stirred for 18 h at 90–95°C (total reaction time=24 h). Analytical SEC showed complete consumption of the starting materials at this point. The solvent was removed and the residue was chromatographed [silica, $CHCl_3$/hexanes (2:1)], affording four major bands (in order of elution): the desired trimer (first purple band, t_R=10.41 min); byproduct dimer (second purple band, t_R=10.77 min); byproduct dimer (third purple band, t_R=10.84 min) and monomeric porphyrin species (fourth purple band, t_R=11.28 min). The trimer fraction was further purified by chromatography [preparative SEC (toluene); silica ($CHCl_3$/hexanes, 2:1)] affording a purple solid (45.6 mg, 66%). The analytical data (^{1}H NMR, LD-MS, UV–Vis, fluorescence) were identical with those obtained from the porphyrin-benzaldehyde+dipyrromethane condensation route.

The dimer fraction (the second purple band) was further purified by preparative SEC (THF); however, TLC analysis showed two spots after the preparative SEC column chromatography. Silica chromatography [$CHCl_3$/hexanes (2:1)] afforded two purple bands (in order of elution): dimer **13** (3.8 mg, 8.0%); dimer **14** (3.2 mg, 6.5%). The dimer fraction (the third purple band) was further purified by chromatography [preparative SEC (THF); silica ($CHCl_3$/hexanes, 2:1)] to afford a purple solid: dimer **15** (2.8 mg, 6.1%).

4.3.16. Dimer 13. ^{1}H NMR δ 9.28–9.26 (m, 4H), 9.06 (d, J=4.5 Hz, 2H), 8.94–8.88 (m, 6H), 8.78–8.74 (m, 4H) 8.62 (s, 4H), 8.34 (d, J=8.1 Hz, 2H), 8.01 (d, J=8.1 Hz, 2H), 7.95 (d, J=7.2 Hz, 2H), 7.84 (m, 2H), 7.62 (t, J=7.2 Hz, 2H), 7.49 (t, J=7.2 Hz, 1H), 7.34 (s, 4H), 7.30 (s, 2H), 2.67 (s, 6H), 2.64 (s, 3H), 1.92–1.91 (m, 18H) 1.57 (s, 36H), −2.45 (s, br, 2H), −2.50 (s, br, 2H); LD-MS obsd 1577.4, calcd avg. mass 1578.1 ($C_{113}H_{108}N_8$).

4.3.17. Dimer 14. ^{1}H NMR δ 9.28–9.25 (m, 4H), 9.06 (d, J=4.2 Hz, 2H), 8.92 (d, J=4.5 Hz, 2H), 8.88 (d, J=5.1 Hz, 2H), 8.83 (d, J=5.1 Hz, 2H), 8.75–8.73 (m, 4H), 8.62 (s, 4H), 8.28 (d, J=8.1 Hz, 2H), 8.20 (d, J=8.1 Hz, 2H), 8.17 (m, 4H), 7.83 (m, 2H), 7.33 (s, 4H), 7.30 (s, 2H), 2.67 (s, 6H), 2.64 (s, 3H), 1.91 (s, 18H), 1.57 (s, 36H), 1.51 (s, 12H), −2.48 (s, br, 2H), −2.50 (s, br, 2H); LD-MS obsd 1625.9, calcd avg. mass 1628.0 ($C_{113}H_{115}N_8BO_2$).

4.3.18. Dimer 15. ^{1}H NMR δ 9.28–9.24 (m, 4H), 9.06 (d, J=4.2 Hz, 2H), 8.92 (d, J=4.5 Hz, 2H), 8.88–8.86 (m, 4H), 8.74 (d, J=5.1 Hz, 4H), 8.62 (s, 4H), 8.17 (m, 2H), 8.12 (d, J=8.7 Hz, 2H), 7.84 (m, 2H), 7.33 (s, 4H), 7.30 (s, 2H), 7.23–7.16 (m, 4H) 2.67 (s, 6H), 2.64 (s, 3H), 1.91 (s, 18H), 1.57 (s, 36H), −2.47 (s, br, 2H), −2.50 (s, br, 2H); LD-MS obsd 1517.9, calcd avg. mass 1518.0 ($C_{107}H_{104}N_8O$).

Acknowledgements

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy. 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. We acknowledge those individuals in our lab (Dr Toru Arai, Dr Polisetti Dharma Rao, Professor Chang-Hee Lee, Mr Christopher Wack) who performed early exploratory work on syntheses, primarily statistical in nature, of *p*-phenylene-linked arrays.

References

1. Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.*, in press.
2. Yang, S. I.; Lammi, R. K.; Seth, J.; Riggs, J. A.; Arai, T.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Phys. Chem.* **1998**, *102*, 9426–9436.
3. Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 11181–11193.
4. Youngblood, W. J.; Gryko, D. T.; Lammi, R. K.; Bocian, D. F.; Holten, D.; Lindsey, J. S. Manuscript in preparation.
5. Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344.
6. (a) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517–521. (b) Pullerits, T.; Sundström, V. *Acc. Chem. Res.* **1996**, *29*, 381–389.
7. Strachan, J. P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191–11201.
8. Cho, H. S.; Jeong, D. H.; Yoon, M.-C.; Kim, Y. H.; Kim, Y.-R.; Kim, D.; Jeoung, S. C.; Kim, S. K.; Aratani, N.; Shinmori, H.; Osuka, A. *J. Phys. Chem. A* **2001**, *105*, 4200–4210.
9. Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Müllen, K. *Adv. Mater.* **1992**, *4*, 737–739.
10. Sessler, J. L.; Capuano, V. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1134–1137.
11. Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618–4628.
12. Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054–3059.
13. Osuka, A.; Liu, B.-L.; Maruyama, K. *Chem. Lett.* **1993**, 949–952.
14. Osuka, A.; Tanabe, N.; Zhang, R.-P.; Maruyama, K. *Chem. Lett.* **1993**, 1505–1508.
15. Osuka, A.; Tanabe, N.; Nakajima, S.; Maruyama, K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 199–203.
16. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872.
17. Geier, III, G. R.; Littler, B. J.; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 701–711.
18. (a) Zhou, X.; Zhou, Z.-Y.; Mak, T. C. W.; Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2519–2520. (b) Chan, K. S.; Zhou, X.; Luo, B.-S.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1994**, 271–272. (c) Zhou, X.; Tse, M. K.; Wan, T. S. M.; Chan, K. S. *J. Org. Chem.* **1996**, *61*, 3590–3593. (d) Yoshida, N.; Shimidzu, H.; Osuka, A. *Chem. Lett.* **1998**, 55–56. (e) Kimura, M.; Shiba, T.; Muto, T.; Hanabusa, K.; Shirai, H. *Macromolecules* **1999**, *32*, 8237–8239. (f) Muzzi, C. M.; Medforth, C. J.; Voss, L.; Cancilla, M.; Lebrilla, C.; Ma, J.-G.; Shelnutt, J. A.; Smith, K. M. *Tetrahedron Lett.* **1999**, 6159–6162. (g) Tse, M. K.; Zhou, Z.-Y.; Mak, T. C. W.; Chan, K. S. *Tetrahedron* **2000**, *56*, 7779–7783.
19. Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 769–774.
20. Hyslop, A. G.; Kellett, M. A.; Iovine, P. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12676–12677.
21. Zhou, X.; Chan, K. S. *J. Org. Chem.* **1998**, *63*, 99–104.
22. Zhou, X.; Chan, K. S. *J. Chem. Soc., Chem. Commun.* **1994**, 2493–2494.
23. Deng, Y.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1066–1068.
24. Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396.
25. Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, C.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890–7901.
26. (a) Nicolas, M.; Fabre, B.; Marchand, G.; Simonet, J. *Eur. J. Org. Chem.* **2000**, 1703–1710. (b) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447–3450.
27. Ravikanth, M.; Strachan, J.-P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, *54*, 7721–7734.
28. Shanmugathasan, S.; Johnson, C. K.; Edwards, C.; Matthews, E. K.; Dolphin, D.; Boyle, R. W. *J. Porphyrin Phthalocyanines* **2000**, *4*, 228–232.
29. (a) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, 2887–2888. (b) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, 4251–4254. (c) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1401–1403.
30. (a) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266–5273. (b) Wagner, R. W.; Ciringh, Y.; Clausen, P. C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974–2983.
31. Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020–4028.
32. Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166–11180.
33. (a) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283–291. (b) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93–99.
34. Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1–13.
35. Li, J.; Ambroise, A.; Yang, S. I.; Diers, J. R.; Seth, J.; Wack, C. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 8927–8940.