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Synthesis of Swallowtail-Substituted Multiporphyrin Rods

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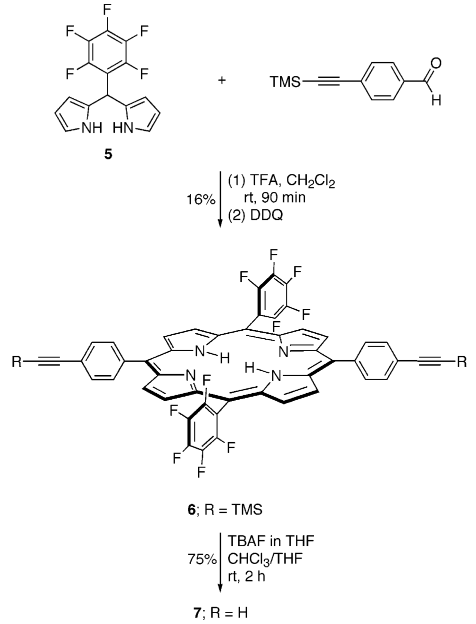
Abstract: The availability of multiporphyrin arrays with defined architectures and good solubility in organic solvents is essential for a wide variety of physical studies. Herein the synthesis of linear multiporphyrin arrays (triads, tetrad, pentad) bearing solubilizing 7-tridecyl (swallowtail) groups is presented. The rodlike arrays are composed of zinc porphyrins at the termini and 1, 2, or 3 free base porphyrins at the core. The free base porphyrins in the tetrad and pentad are joined to each other via *p*-phenylene linkers whereas the zinc porphyrins in each array are attached to the core free base porphyrins via 1,4-diphenylethyne linkers. The arrays are designed for studies of interporphyrin electronic communication.

A wide variety of molecular constructs containing multiple porphyrins have been prepared to serve as light-harvesting arrays, optoelectronic gates, charge-separation units, and charge-storage reservoirs.[1−6] The design of molecular architectures with prescribed electronic properties (energy transfer, electronic switching, charge separation/storage) requires a firm understanding of the mechanisms of electronic communication between interacting constituents. We previously prepared a series of multiporphyrin arrays for studies of ground-state electronic communication. The method for examining ground-state electronic communication involved hole-hopping in partially oxidized arrays. The arrays examined include (1) dimers of zinc porphyrins,[7,8] (2) linear or right-angle triads with zinc porphyrins at the termini of the linear array and a free base porphyrin at the core,[9] and (3) star-shaped pentads with four zinc porphyrins at the periphery and a free base porphyrin at the core.[7] Despite the larger size of the pentads, hole-hopping occurred between zinc porphyrins in a triad motif owing to the star-shaped architecture.

SCHEME 1



A chief problem encountered upon examination of the linear triads was the limited solubility of the compounds. Indeed, adequate solubility for electrochemical studies could only be achieved in mixtures of chlorinated solvents (e.g., CH_2Cl_2 and $CHCl_3$).[9] The previous arrays incorporated porphyrins bearing mesityl groups at all nonlinking meso positions (**Triad-1**, Chart 1). We recently showed that 7-tridecyl ("swallowtail") groups impart solubility to meso-substituted porphyrin building blocks without affecting the physical properties of the macrocycles.[10] Herein we present the synthesis of a series of rodlike arrays composed of multiple swallowtail-substituted porphyrins, including four triads, one tetrad, and one pentad. The triads enable in-depth studies of electronic communication while the tetrad and pentad enable examination of whether hole-hopping persists over longer distances than that in the triad arrays.

The four triads (**Triad-2**−**5**) are shown in Chart 1. **Triad-2** bears swallowtail substituents at nonlinking meso positions of the terminal porphyrins and mesityl substituents at nonlinking meso positions of the central free base porphyrin. **Triad-3** is a zinc-chelated derivative of **Triad-2**. **Triad-4** bears swallowtail groups at the terminal porphyrins while the free base porphyrin bears pentafluorophenyl groups to tune the energy levels of the porphyrin molecular orbitals. **Triad-5** bears swallowtail and mesityl groups in the reversed pattern of that in **Triad-2**. The tetrad or pentad each incorporates zinc porphyrins at the termini and two or three free base porphyrins as the intervening unit (Chart 2). The linker between the free base porphyrins is a *p*-phenylene unit,

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CHART 1

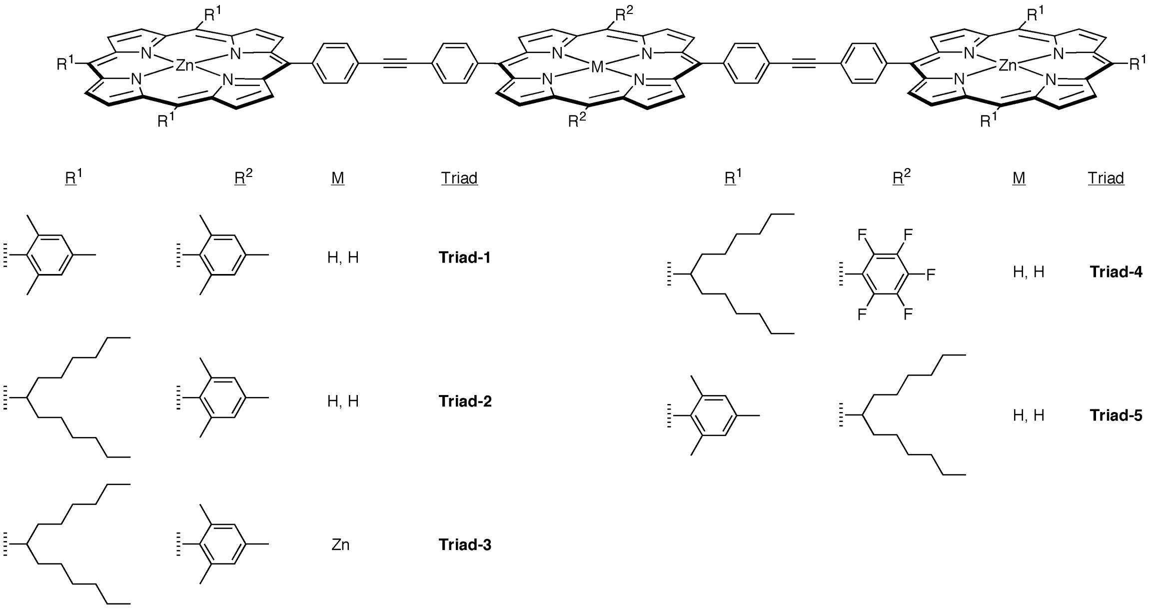


CHART 2

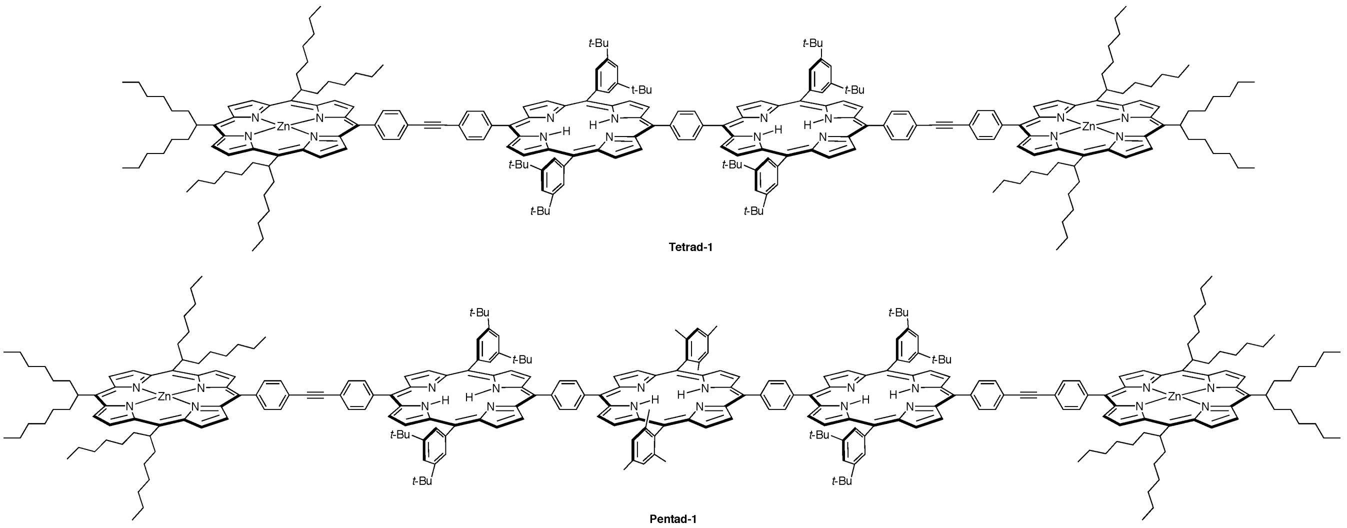
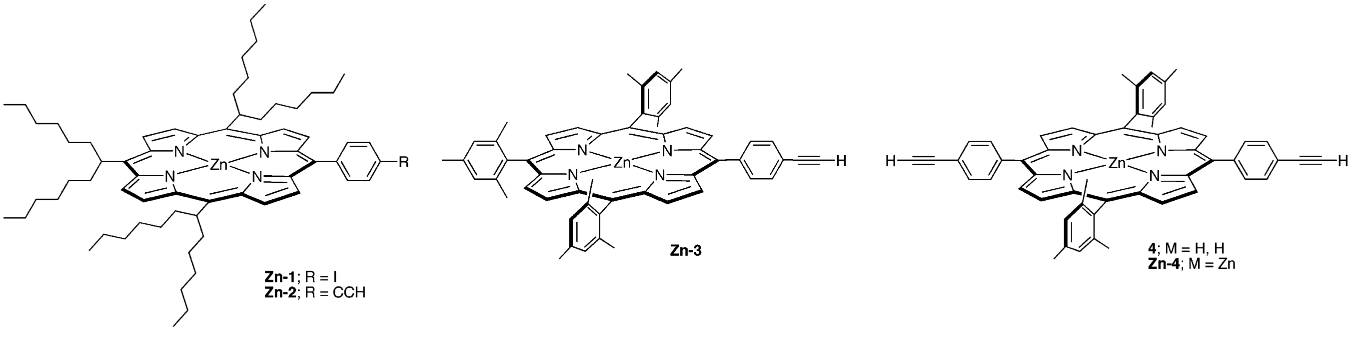


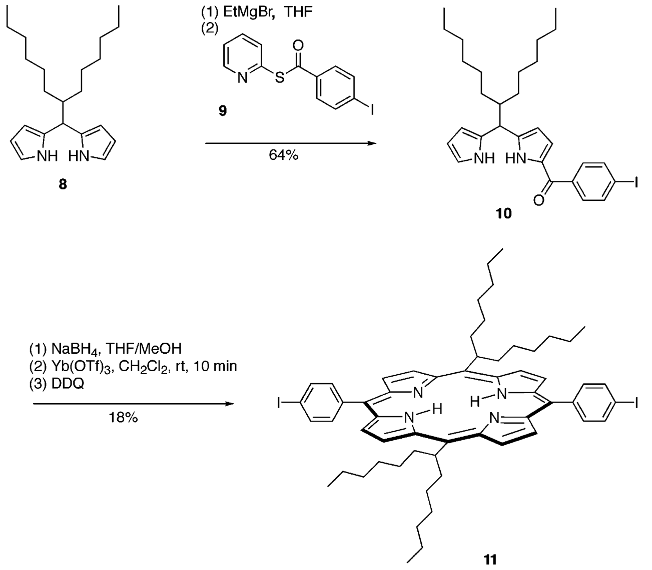
CHART 3



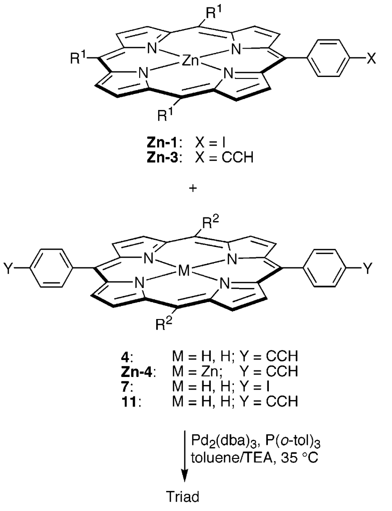
which affords enhanced electronic coupling between the porphyrins compared with that of the diphenylethyne unit.[3] Each array is pseudocentrosymmetric along the long axis (ignoring torsional motions and NH tautomerism) and the two terminal porphyrins are identical with one another.

The general approach for synthesis of the triads entailed a Sonogashira reaction with a difunctional core porphyrin and 2 equiv of the monofunctional terminal porphyrin. Porphyrin building blocks **Zn-1**,[10] **Zn-2**,[10] **Zn-3**,[11] **4**,[12] and **Zn-4**[12] are known compounds (Chart 3). Condensation of dipyrromethane **5**[13] and 4-(2-(trimeth-

SCHEME 2

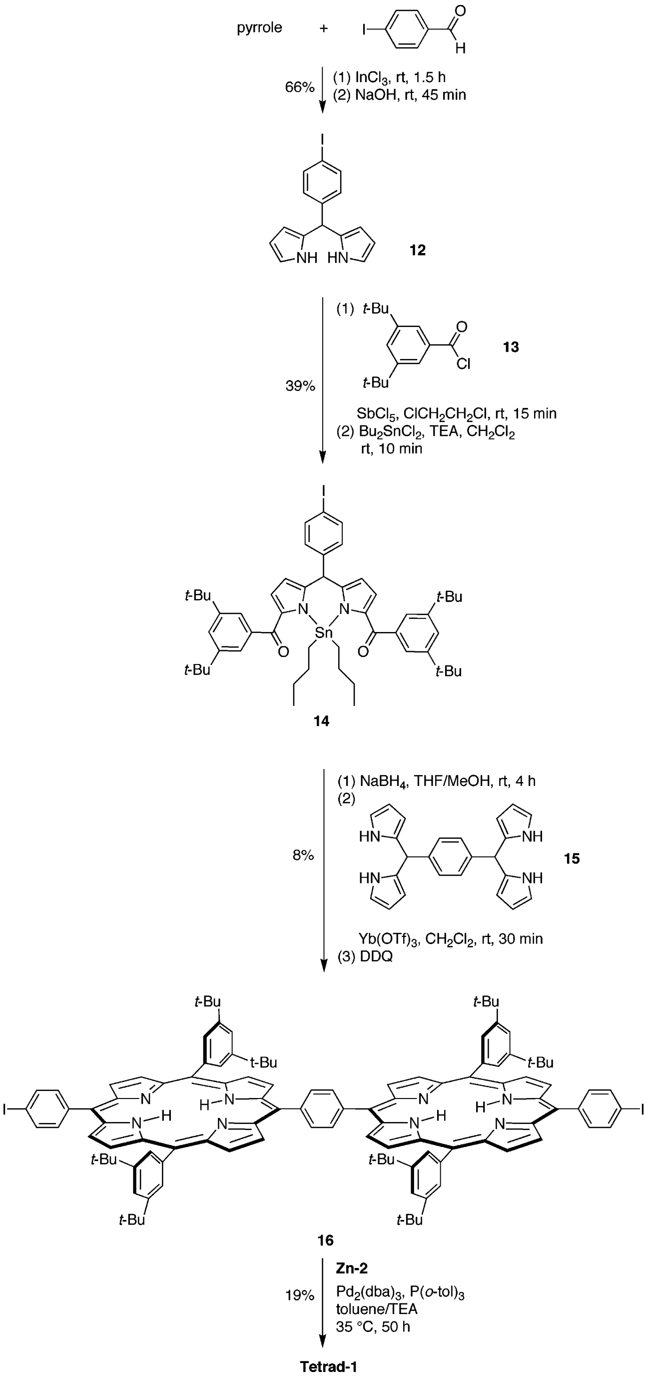


SCHEME 3



Reactants	Triad	% yield
Zn-1 + **4**	**Triad-2**	87
Zn-1 + **Zn-4**	**Triad-3**	57
Zn-1 + **7**	**Triad-4**	37
Zn-3 + **11**	**Triad-5**	61

SCHEME 4



ylsilyl)ethynyl)benzaldehyde with catalysis by TFA[14] followed by oxidation with DDQ afforded porphyrin **6** in 16% yield. Subsequent treatment with TBAF in THF gave ethynyl porphyrin **7**, a free base precursor for the synthesis of **Triad-4**, in 75% yield (Scheme 1). Acylation of dipyrromethane **8**[10] with pyridyl benzothioate **9**[15] led to 1-acyldipyrromethane **10**. Reduction of **10** and self-condensation[15] of the resulting carbinol in CH_2Cl_2 containing $Yb(OTf)_3$[16] followed by oxidation with DDQ gave porphyrin **11**, required for the synthesis of **Triad-5**, in 18% yield (Scheme 2). The condensation of a dipyrromethane-carbinol can be achieved with a mild Lewis acid such as $Yb(OTf)_3$ in CH_2Cl_2[15] or by trifluoroacetic acid in CH_3CN,[16] though the former conditions generally are superior in terms of diminished propensity to acidolysis of the dipyrromethane and greater ease of purification of the resulting porphyrin.

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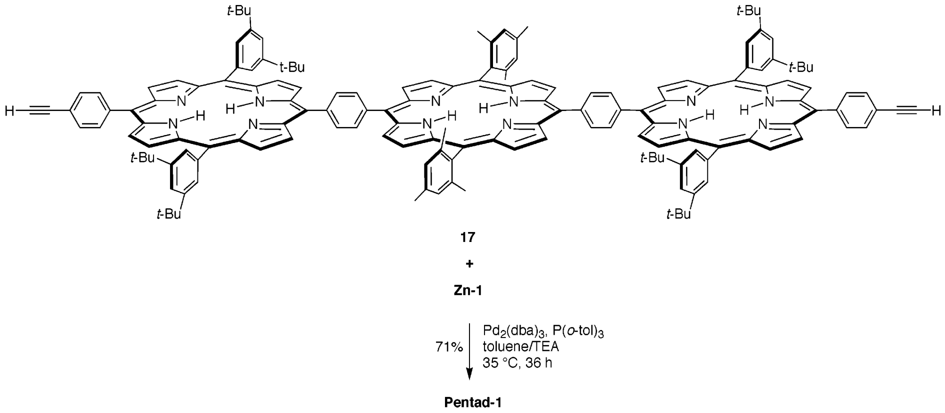
SCHEME 5



The synthesis of the triads is summarized in Scheme 3. The Sonogashira reaction was performed under copper-free conditions in toluene/TEA (5:1) at 35 °C in the presence of Pd$_2$(dba)$_3$ and P(*o*-tol)$_3$.[17] In each case, the desired triad was isolated by a straightforward combination of adsorption chromatography and size exclusion chromatography. The yields ranged from 37% to 87%. **Triad-2**, **Triad-3**, and **Triad-4**, which bear swallowtail groups at the porphyrin termini, exhibit satisfactory solubility (>5 mg/mL) in common organic solvents (e.g., toluene, CH$_2$Cl$_2$, CHCl$_3$, THF) for routine handling, characterization, and physical studies. By contrast, **Triad-5**, which has swallowtail groups at the central porphyrin, was less soluble in the same solvents. In general, the swallowtail-substituted porphyrin arrays are more soluble than the corresponding mesityl-substituted porphyrin arrays (e.g., **Triad-1**).

The synthetic approach toward the target tetrad and pentad similarly entailed Sonogashira coupling of a core unit of *p*-phenylene-linked free base porphyrins and the terminal swallowtail-substituted zinc porphyrin. The reaction of 4-iodobenzaldehyde with excess pyrrole containing InCl$_3$[13] afforded dipyrromethane **12** in 66% yield (Scheme 4). Diacylation of **12** was carried out with 3,5-di-*tert*-butylbenzoyl chloride (**13**)[18] under catalysis by SbCl$_5$.[19] Treatment of the mixture with dibutyltin dichloride[10] and TEA gave the corresponding diacyldipyrromethane−tin complex **14** in 39% yield. Reduction of **14** with NaBH$_4$ in THF/methanol for 4 h gave the dipyrromethane−dicarbinol. Reaction of the latter with 1,4-bis(dipyrromethyl)benzene (**15**)[20,21] in CH$_2$Cl$_2$ containing Yb(OTf)$_3$[16] followed by oxidation with DDQ afforded the difunctional dimer **16** in 8% yield. Although the overall yield of **16** was low, the starting materials are readily available in sizable quantities.

The coupling reactions to form the tetrad and pentad were performed under the standard conditions for Pd-mediated reactions of iodo and ethynyl porphyrins. The reaction of dimer **16** and porphyrin **Zn-2** was complicated by the incomplete dissolution of the dimer (**16**) at the start of the reaction. **Tetrad-1** was obtained in 19% yield (Scheme 4). The low yield is attributed to the low solubility of **16** and the formation of trimeric byproducts (as shown by analytical SEC). On the other hand, the Pd-mediated coupling of triad **17**[22] and porphyrin **Zn-2**[10] afforded **Pentad-1** in 71% yield (Scheme 5). As with the triads, the tetrad and pentad were purified by straightforward combination of adsorption and size exclusion chromatography. Both **Tetrad-1** and **Pentad-1** exhibit satisfactory solubility (>5 mg/mL) in a variety of common organic solvents. Studies of electronic communication in the various rodlike arrays can now be undertaken and will be reported elsewhere.

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Supporting Information Available: Full Experimental Section including characterization data (NMR spectra, mass spectra) for all new compounds, as well as analytical SEC traces for the arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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