

Swallowtail Porphyrins: Synthesis, Characterization and Incorporation into Porphyrin Dyads

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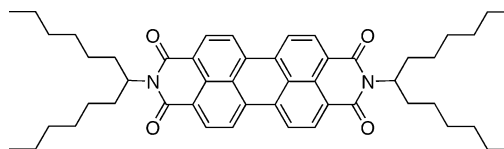
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The incorporation of symmetrically branched tridecyl (“swallowtail”) substituents at the meso positions of porphyrins results in highly soluble building blocks. Synthetic routes have been investigated to obtain porphyrin building blocks bearing 1–4 swallowtail groups. Porphyrin dyads have been synthesized in which the zinc or free base (Fb) porphyrins are joined by a 4,4'-diphenylethyne linker and bear swallowtail (or *n*-pentyl) groups at the nonlinking meso positions. The swallowtail-substituted Zn₂- and ZnFb-dyads are readily soluble in common organic solvents. Static absorption and fluorescence spectra and electrochemical data show that the presence of the swallowtail groups slightly raises the energy level of the filled a_{2u}(π) HOMO. EPR studies of the π-cation radicals of the swallowtail porphyrins indicate that the torsional angle between the proton on the alkyl carbon and p-orbital on the meso carbon of the porphyrin is different from that of a porphyrin bearing linear pentyl groups. Regardless, the swallowtail substituents do not significantly affect the photophysical properties of the porphyrins or the electronic interactions between the porphyrins in the dyads. In particular, time-resolved spectroscopic studies indicate that facile excited-state energy transfer occurs in the ZnFb dyad, and EPR studies of the monocation radical of the Zn₂-dyad show that interporphyrin ground-state hole transfer is rapid.

Introduction

One of the challenges in creating molecules with nanoscale dimensions lies in achieving a defined 3-dimensional architecture while maintaining adequate solubility in appropriate solvents. Solubility is essential for carrying out synthetic transformations, purification procedures, and diverse physical studies. The solubility problem is significant with planar aromatic compounds such as porphyrins and is exacerbated in arrays composed of multiple porphyrins in defined architectures. Indeed, the limited solubility of multiporphyrin arrays often constrains their synthetic manipulation and limits their size. The most prevalent meso substituents that have been employed to increase the solubility over that of meso-tetraphenylporphyrins include 3,5-di-*tert*-butylphenyl,^{1–4} mesityl,^{2,5,6} and pentyl⁷ groups. The develop-

CHART 1



ment of facile syntheses of multiporphyrin arrays would benefit from new substituents that impart high solubility in organic solvents.

Attractive candidates to reach the goal of relatively high solubility are the readily available swallowtail substituents, which are symmetrically branched alkyl groups. Langhals introduced swallowtail substituents into the poorly soluble 3,4,9,10-perylene diimide chromophore to achieve increased solubility (Chart 1).⁸ The high solubility of the resulting swallowtail perylene diimides prompted us to consider the use of swallowtail substituents with porphyrins.

A number of porphyrins bearing branched alkyl groups at the meso positions have been prepared over the years. The branched alkyl substituents include isopropyl,⁹

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isobutyl,¹⁰ isopentyl,¹¹ *tert*-butyl,¹² cyclopropyl,¹³ cyclohexyl,¹⁴ and adamantyl¹⁵ groups. A major motivation for many of the studies was to explore the effects of bulky substituents on structural deformation of the porphyrin macrocycle. Such substituents include the *tert*-butyl group, which causes significant deformation, and the isopropyl group, which causes very little deformation. Evidence for deformation of the macrocycle stems from X-ray characterization, electronic spectroscopy, and electrochemistry.^{15–17} The isopropyl and isopentyl groups are examples of short swallowtail substituents. The resulting porphyrins generally contained four identical branched-chain substituents, without synthetic handles for elaboration into arrays.

In this paper, we describe methodology for the synthesis of porphyrins bearing 1–4 swallowtail substituents. The swallowtail substituents have 13 carbons, are symmetrically branched about carbon 7, and are attached at the porphyrin meso positions. The swallowtail groups have been incorporated into precursors employed in the rational synthesis of porphyrins, including dipyrromethanes and acyldipyrromethanes. Dyads composed of a zinc porphyrin and a free base (Fb) porphyrin or two zinc porphyrins have been prepared, where each porphyrin bears three swallowtail substituents at the nonlinking meso positions and the porphyrins are joined via a diphenylethyne linker. The electrochemical and photophysical properties of the swallowtail-containing compounds have been investigated along with excited-state energy transfer in the ZnFb dyad and ground-state hole transfer in the monocation of the Zn₂ dyad. Collectively, these studies reveal that the swallowtail substituents provide good solubility without significantly altering the photophysical properties of the porphyrins or the electronic interactions in dyads.

Results and Discussion

1. Synthesis of Swallowtail Porphyrins. Porphyrins Bearing Four Swallowtail Groups.

The synthesis of A₄-porphyrins requires access to the precursor

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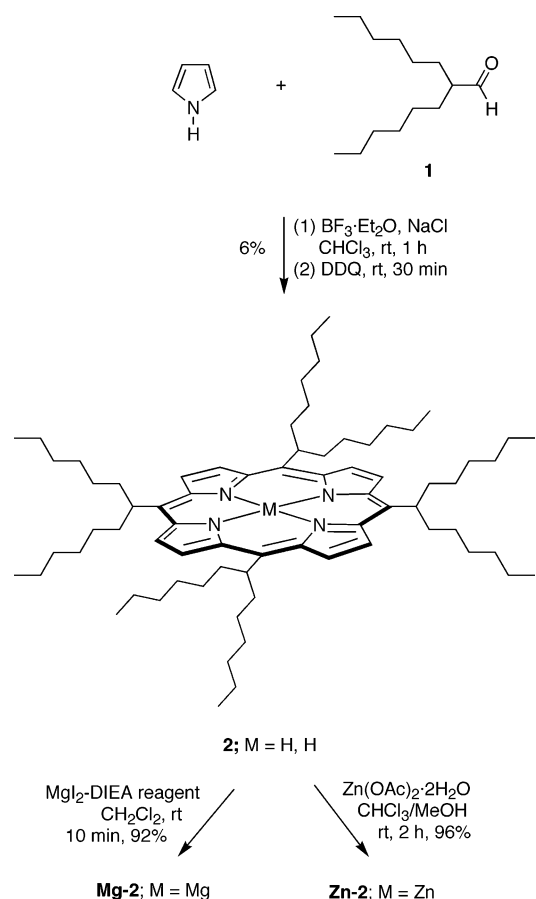
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SCHEME 1



aldehyde. The required 7-formyltridecane (**1**) was prepared according to literature procedures¹⁸ by the Wittig reaction of 7-tridecanone and (methoxymethyl)triphenylphosphonium ylide followed by acid hydrolysis. Condensation of **1** with pyrrole in CHCl_3 (containing 0.13 M ethanol) using $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ in the presence of NaCl¹⁹ followed by oxidation with DDQ afforded porphyrin **2** in 6% yield. The porphyrin bears four swallowtail groups at the meso positions (Scheme 1). Attempts to improve the yield by increasing the concentration of $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ from 3.3 to 26 mM and that of the starting materials from 10 to 150 mM as previously reported¹² for small branched alkyl aldehydes (pivalaldehyde, 2-methylpropanal) did not give yield improvements in this case. Indeed, the yield of porphyrin **2** was <1% under the high-concentration conditions. Acid screening experiments were performed with the following acid catalysts that have been examined in other porphyrin-forming reactions:²⁰ TFA, $\text{BF}_3 \cdot \text{O}(\text{Et})_2$, TFA/ $\text{BF}_3 \cdot \text{O}(\text{Et})_2$, $\text{BF}_3 \cdot \text{O}(\text{Et})_2/\text{EtOH}$, $\text{BF}_3 \cdot \text{O}(\text{Et})_2/\text{NaCl}$, SnCl_4 , SiCl_4 , TiCl_4 , montmorillonite K₁₀, $\text{Sc}(\text{OTf})_3$, InCl_3 , and MgBr_2 . However, these acid-catalyzed conditions failed to give a satisfactory yield of porphyrin **2**.

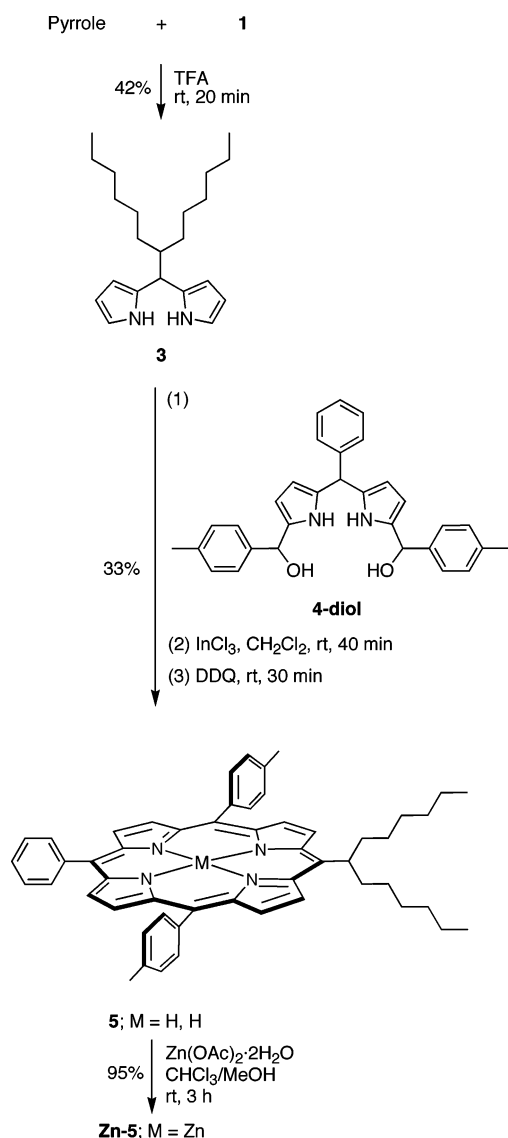
Treatment of **2** under standard conditions with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ at room temperature for 2 h afforded porphyrin **Zn-2** in 96% yield. The analogous magnesium

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SCHEME 2



insertion was achieved by treatment of a solution of **2** in CH₂Cl₂ with a freshly prepared solution of MgI₂ in diethyl ether containing DIEA,²¹ affording porphyrin **Mg-2** in 92% yield.

Porphyrins Bearing One Swallowtail Group. A₃B-porphyrins are readily available by reaction of an A₃-dipyrromethane-dicarbino and a B-dipyrromethane.²² Dipyrromethanes are key intermediates in the synthesis of porphyrins bearing distinct patterns of substituents. The condensation of aldehyde **1** with excess pyrrole^{23,24} was carried out at room temperature in CH₂Cl₂ containing TFA. The resulting 5-(tridec-7-yl)dipyrromethane (**3**) was obtained by Kugelrohr distillation as a viscous yellow liquid in 42% yield (Scheme 2).

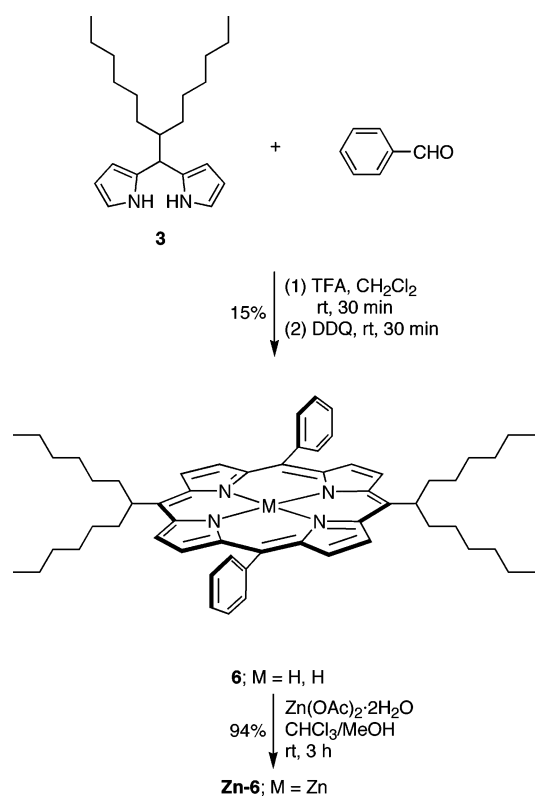
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SCHEME 3



Treatment of 1,9-diacetyldipyrromethane **4**²² with NaBH₄ in dry THF/methanol (10:1) afforded the corresponding dipyrromethane-dicarbino **4-diol** as a colorless foam. Condensation of the latter with dipyrromethane **3** using new acid catalysis conditions (InCl₃ in CH₂Cl₂ at room temperature)²⁵ followed by oxidation with DDQ gave porphyrin **5** (33% yield), an A₃B-porphyrin that bears one swallowtail substituent. Treatment of **5** with Zn(OAc)₂·2H₂O gave **Zn-5** in 95% yield.

Porphyrins Bearing Two Swallowtail Groups. *trans*-A₂B₂-Porphyrins are readily prepared by the reaction of a dipyrromethane and an aldehyde, given that the dipyrromethane does not undergo acidolysis followed by undesired recombination of reactive fragments (i.e., scrambling) during the condensation.²⁶ Condensation of dipyrromethane **3** and benzaldehyde in CH₂Cl₂ under TFA catalysis followed by oxidation with DDQ gave the desired *trans*-A₂B₂-porphyrin **6** in 15% yield. No other porphyrins were observed by analysis of the crude reaction mixture with laser-desorption mass spectrometry (LD-MS).²⁷ These conditions are known to afford reaction without noticeable acidolytic scrambling for sterically hindered dipyrromethanes,²⁷ and apparently work well for dipyrromethane **3**. Treatment with Zn(OAc)₂·2H₂O gave porphyrin **Zn-6** in 94% yield (Scheme 3).

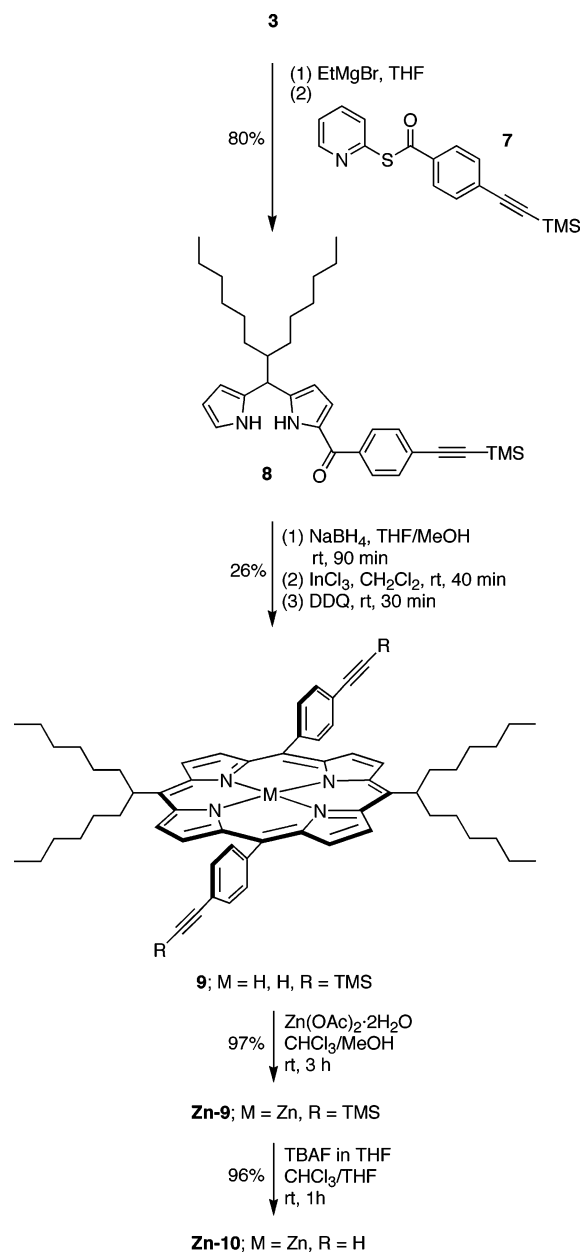
An alternative route to *trans*-A₂B₂-porphyrins employs the self-condensation of an AB-dipyrromethane-mono-

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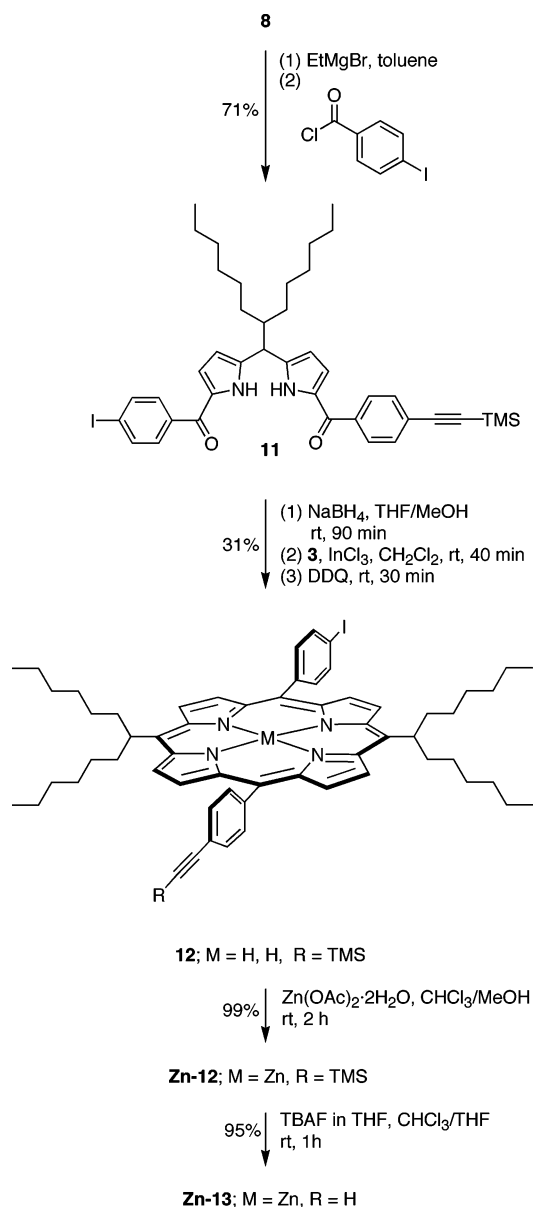
SCHEME 4



carbinol.²⁸ Dipyrrromethane **3** was subjected to monoacylation with the pyridyl benzothioate **7**,²⁸ affording the ethynyl-substituted 1-acetyldipyrrromethane **8**. Reduction of **8** gave the dipyrromethane-monocarbinol, which underwent self-condensation in the presence of InCl_3 in CH_2Cl_2 . Subsequent oxidation with DDQ gave the desired *trans*- A_2B_2 -porphyrin **9** in 26% yield (Scheme 4). The yield of the dipyrromethane-monocarbinol self-condensation approach giving **9** was higher (26% vs 15%) than that of the aldehyde + dipyrromethane route giving **6**. Metalation and deprotection gave the diethynyl porphyrin **Zn-10**, which can be used for Glaser coupling.

trans- AB_2C -Porphyrins are readily available by reaction of an AB_2 -dipyrrromethane-dicarbinol and a C-dipyrrromethane.²² The synthesis of such a porphyrin bearing two swallowtail substituents, one iodo group, and

SCHEME 5



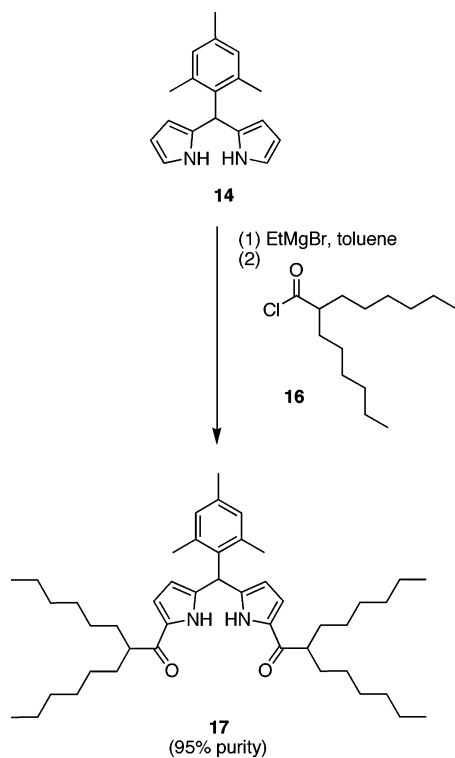
one ethyne group is shown in Scheme 5. Acylation of the ethynyl-substituted 1-acetyldipyrrromethane **8** with 4-iodobenzoyl chloride gave 1,9-diacetyldipyrrromethane **11**. Reduction of the latter and condensation of the resulting dipyrromethane-dicarbinol with dipyrromethane **3** afforded the *trans*- AB_2C -porphyrin **12** in 31% yield. Zinc insertion and cleavage of the TMS group gave porphyrin **Zn-13**, which can be used for Sonogashira coupling.

It is noteworthy that an alternative approach toward *trans*- A_2B_2 -porphyrins or *trans*- AB_2C -porphyrins bearing two swallowtail substituents employs the swallowtail substituents attached to the carbons at the 1- and 9-positions of the dipyrromethane-dicarbinol. However, this route proved infeasible on the basis of the results described in the next section.

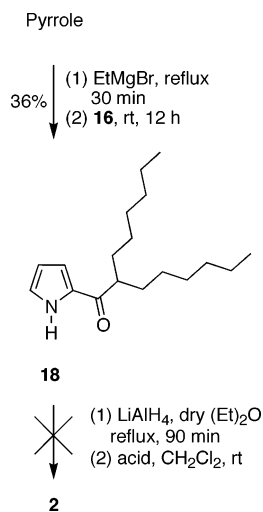
Porphyrins Bearing Three Swallowtail Groups. A_3B -Porphyrins are readily available by reaction of an A_3 -dipyrrromethane-dicarbinol and a B-dipyrrromethane.²² We explored the rational synthesis of porphyrins bearing three swallowtail groups, which requires the preparation

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SCHEME 6



SCHEME 7

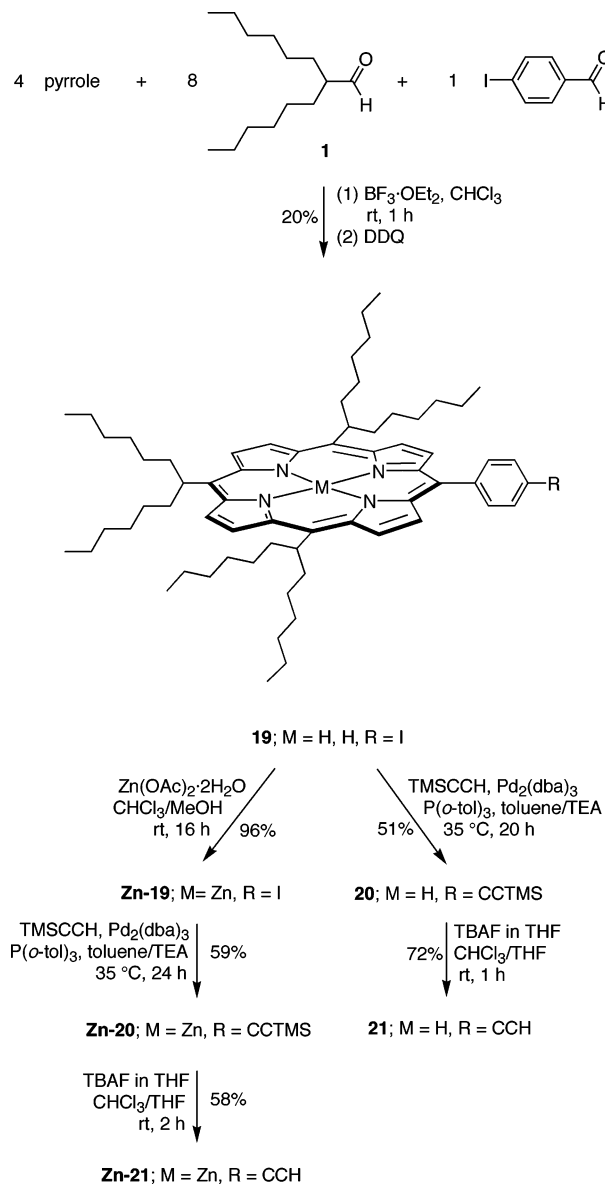


of a dipyrromethane-dicarbonyl bearing swallowtail groups at the α -carbon positions. Oxidation of aldehyde **1** with KMnO₄ led to carboxylic acid **15**²⁹ (81% yield), which was converted to acid chloride **16** upon reaction with SOCl₂ as previously reported.³⁰ Acylation of 5-mesityldipyrromethane (**14**)²³ via the dipyrromethane Grignard reagent²² proceeded slowly, affording a mixture of the 1-acyldipyrromethane and the target 1,9-diacyl dipyrromethane (**17**). The mixture proved difficult to separate and the corresponding 1,9-diacyl dipyrromethane (**17**) was obtained in only ~10% yield and ~95% purity (Scheme

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SCHEME 8



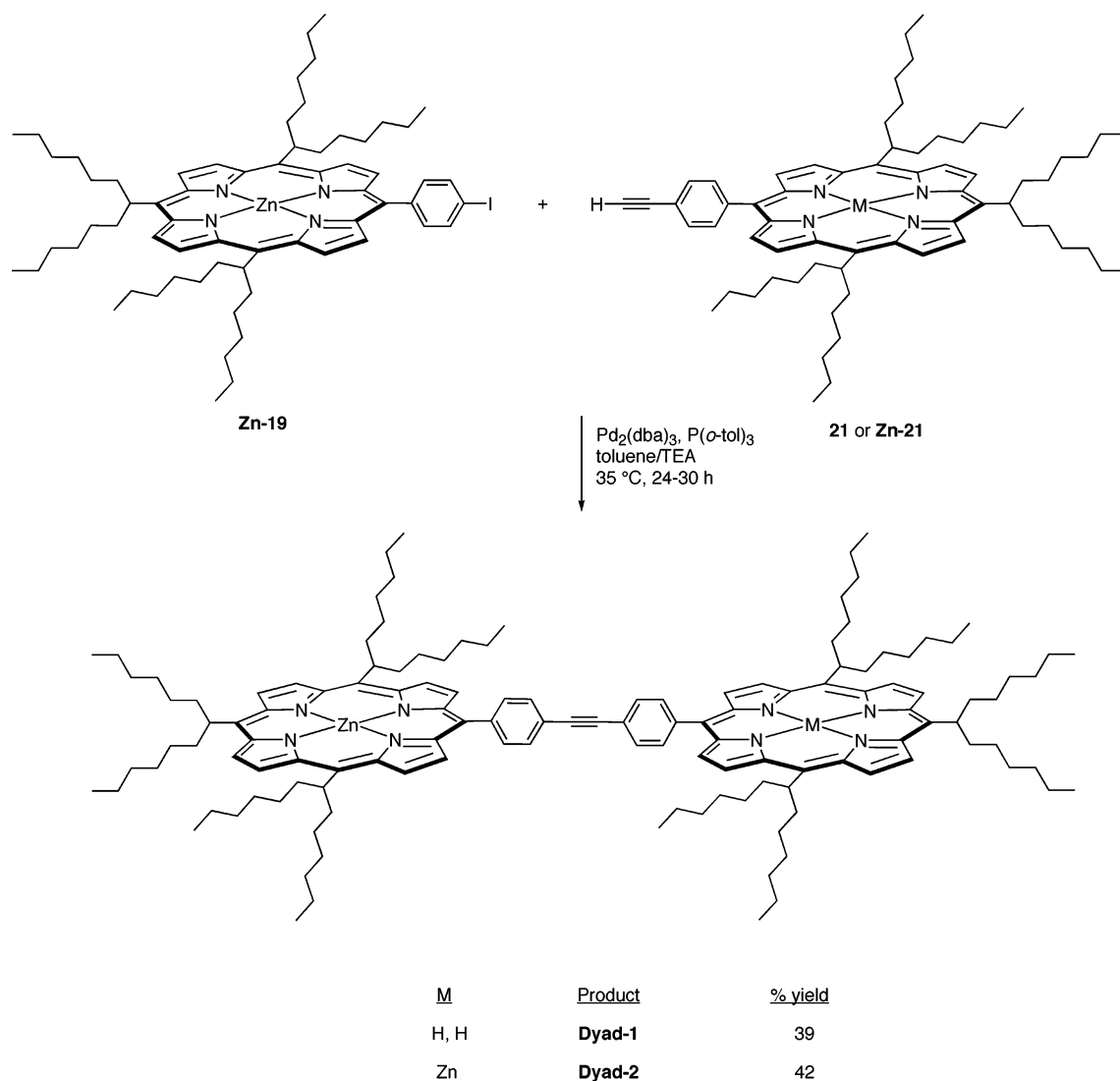
6). Application of a tin-complexation method,³¹ which facilitates purification of a wide variety of 1,9-diacyl dipyrromethanes, was fruitless as **17** failed to give a tin complex.

Treatment of **17** (95% purity) with NaBH₄ in THF/methanol (10:1) at room temperature or at 40 °C failed to give clean reduction to the corresponding dicarbonyl. Although no evidence was obtained to confirm the presence of the dicarbonyl, the crude mixture was worked up and reacted with dipyrromethane **14** in the presence of InCl₃ in CH₂Cl₂ at room temperature, followed by the addition of DDQ. No trace of porphyrin was observed. We examined a simpler substrate, a pyrrole-carbinol bearing a swallowtail substituent, because pyrrole-carbinols are known to readily give porphyrin.³² Reaction of the swallowtail acid chloride **16** and the pyrrole

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SCHEME 9



Grignard reagent afforded acyl-pyrrole **18** (Scheme 7). Treatment of **18** with LiAlH_4 for 90 min in refluxing diethyl ether gave incomplete reduction. The resulting crude product was subjected to acid catalysis (TFA, $\text{BF}_3 \cdot \text{O}(\text{Et})_2$, or InCl_3) and oxidation; however, no porphyrinic product was observed. Further studies are required to develop suitable reaction conditions for use with dipyrromethanes bearing swallowtail groups at the 1- and 9-positions. The absence of such conditions precludes rational syntheses of porphyrins bearing three meso-swallowtail substituents.

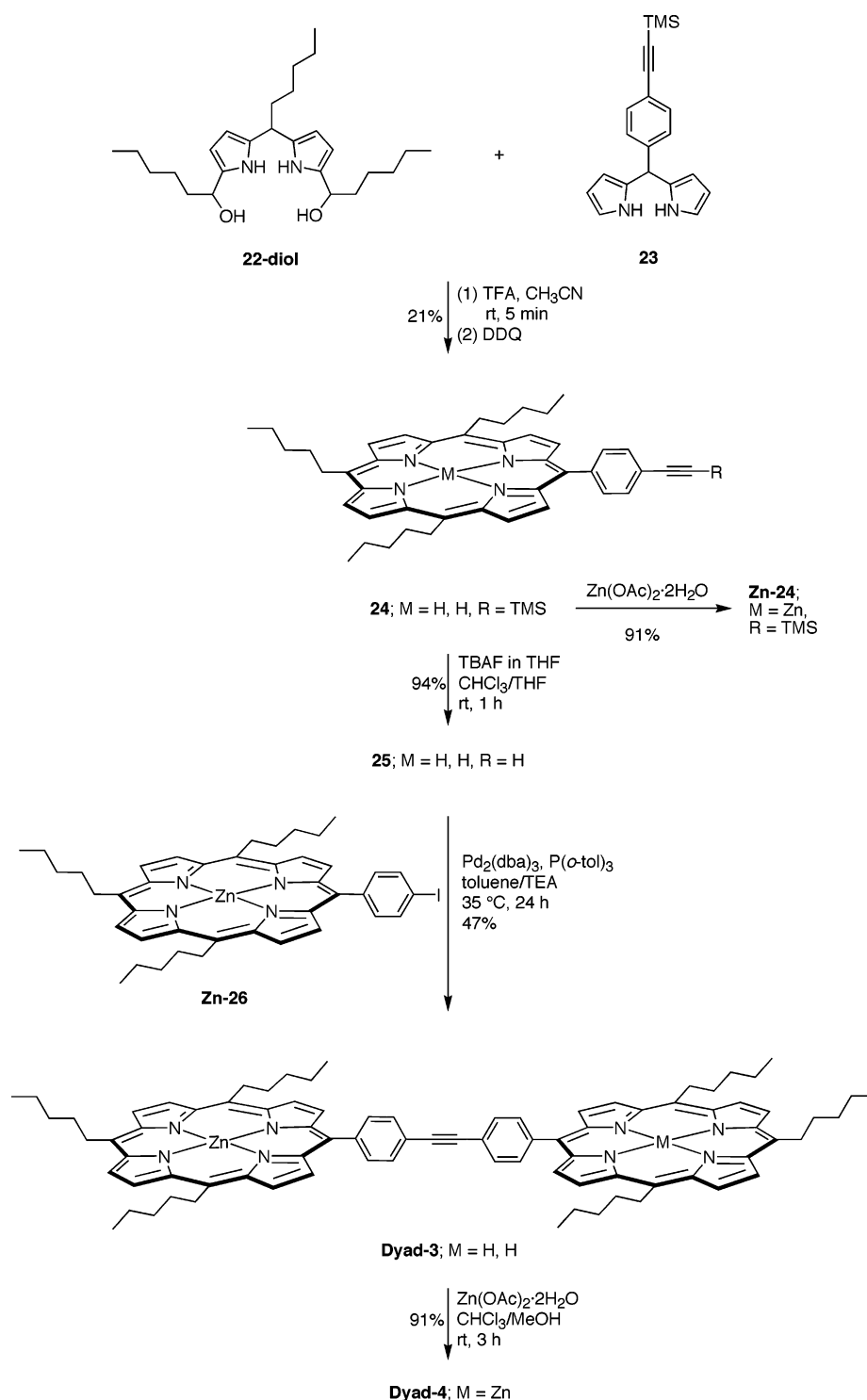
We turned to the use of statistical condensations for the synthesis of A_3B -porphyrins bearing three swallowtail groups. Condensation of pyrrole, aldehyde **1** and 4-iodobenzaldehyde in 4:8:1 ratio with $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ in CHCl_3 followed by oxidation with DDQ gave **19** in 20% yield (Scheme 8). This ratio was found to be effective in terms of yield and convenience of isolating porphyrin **19** from the byproduct tetra-swallowtail porphyrin **2**, which have similar chromatographic R_f values. Subsequent reaction with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ gave **Zn-19** in 96% yield. The similar mixed-condensation strategy with pyrrole, aldehyde **1** and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde predominantly afforded porphyrins containing three or four

ethyne groups without significant amounts of the desired porphyrin **20**, despite employing up to a 4:15:1 ratio of pyrrole, aldehyde **1**, and 4-[2-(trimethylsilyl)ethynyl]benzaldehyde. However, the Pd-coupling of porphyrin **19** and trimethylsilylacetylene gave porphyrin **20** in 51% yield. Subsequent TMS cleavage with TBAF led to ethynyl-porphyrin **21** in 72% yield. Similarly, the Pd-coupling of **Zn-19** and (trimethylsilyl)acetylene gave **Zn-20**, which upon treatment with TBAF in THF gave ethynyl-porphyrin **Zn-21** in good yield.

2. Synthesis of Porphyrins Dyads. Swallowtail-Porphyrin Dyads. Diphenylethyne-linked dyads in which each porphyrin bears three swallowtail groups were prepared to investigate the electronic communication in these types of arrays. Both Zn_2 and ZnFb dyads were prepared, the former to investigate ground-state hole-hopping in monocation radical species and the latter to investigate excited-state energy transfer in neutral complexes. The syntheses of **Dyad-1** and **Dyad-2** are summarized in Scheme 9.

The Pd-coupling reaction was performed in toluene/TEA (5:1) at 35 °C in the presence of $\text{Pd}_2(\text{dba})_3$ and $\text{P}(o\text{-tol})_3$ under standard conditions for Sonogashira coupling of porphyrins in dilute solution in the absence of copper.³³

SCHEME 10



Porphyrin **Zn-19** was reacted with **21** or **Zn-21**, affording the ZnFb array **Dyad-1** or the Zn₂ array **Dyad-2** in 39% or 42% yield, respectively. The reactions were monitored by analytical size exclusion chromatography (SEC).³³ The dyads were purified by a three-column chromatography sequence of silica, preparative SEC, and silica columns. As expected, both porphyrinic arrays exhibit good solubil-

ity in common organic solvents such as CH₂Cl₂, CHCl₃, and THF.

Pentyl-Porphyrin Dyads. To compare the effect of the branched alkyl groups on the electronic communication within the porphyrin dyads versus that of linear alkyl chains, we synthesized **Dyad-3** and **Dyad-4**, which contain *n*-pentyl substituents at the meso positions of the macrocycle framework instead of swallowtail groups as in **Dyad-1** and **Dyad-2**. Reduction of diacyldipyrromethane **22**²² with NaBH₄ in THF/methanol followed

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by condensation of the resulting dipyrromethane-dicarbonyl **22-diol** and dipyrromethane **23**³⁴ in CH₃CN containing TFA gave porphyrin **24** in 21% yield (Scheme 10). Porphyrin **Zn-24**, a benchmark compound for **Dyad-3**, was obtained in 91% yield upon treatment of **24** with Zn(OAc)₂·2H₂O. Cleavage of the TMS group by TBAF afforded porphyrin **25** (94% yield), which has been prepared previously by a slightly different route.³⁵ The Pd-coupling of porphyrins **25** and **Zn-26** (prepared in 95% yield by metalation of its free base counterpart **26**)³⁶ was performed under the same conditions as described for **Dyad-1** and **Dyad-2**. The desired ZnFb **Dyad-3** was obtained in 47% yield. Treatment of **Dyad-3** with Zn(OAc)₂·2H₂O afforded the Zn₂ product **Dyad-4** in 91% yield. Reaction monitoring and purification was performed as described for **Dyad-1** and **Dyad-2**. **Dyad-3** is soluble in common organic solvents such as CH₂Cl₂, CHCl₃, and THF, whereas **Dyad-4** could be dissolved in THF but only partially in CH₂Cl₂ and CHCl₃.

3. Physicochemical Properties of the Neutral Swallowtail Porphyrins. Static Absorption and Fluorescence Spectra. Figure 1 shows electronic ground-state absorption spectra (solid) and excited-state fluorescence spectra (dashed) of Zn porphyrins containing 0 (**ZnTPP**), 1 (**Zn-5**), 2 (**Zn-6** and **Zn-9**), and 4 (**Zn-2**) swallowtails, with aryl groups at the other meso positions. The optical spectra for ZnFb **Dyad-1** along with monomeric reference porphyrins (**Zn-20** and **20**) containing three swallowtails per porphyrin are shown in Figure 2. The corresponding spectra for the analogues containing three pentyl groups per porphyrin instead of swallowtails (**Dyad-3**, **Zn-24**, and **24**) are given in Figure 3. The wavelengths of the Q(0,0) absorption and emission maxima along with fluorescence quantum yields and lifetimes of the lowest excited singlet state for all of these compounds are summarized in Table 1. The key aspects of these static optical data are described in the following:

(1) Swallowtails do not significantly perturb the photophysical properties of the porphyrins relative to *meso*-tetraarylporphyrins (e.g., **ZnTPP**) and analogues bearing meso alkyl substituents such as *n*-pentyl groups. For example, the replacement of four aryl rings by four swallowtails in Zn porphyrins causes only a ~5 nm red shift in the origin optical transitions (Figure 1A and E). This effect can be accounted for by minor electronic perturbations of alkyl versus aryl substituents, given that compounds with three swallowtails have virtually the same spectra as the pentyl analogues (Figures 2A versus 3A).

(2) The minor Q-band red shifts observed upon replacement of multiple aryl rings by either swallowtails or pentyl groups is accompanied by a slight increase in the intensity of the Q(0,0) absorption band (~595 nm) with respect to the Q(1,0) band (cf. features at ~595 and ~555 nm in Figure 1A versus E). According to the four-orbital model,³⁷ this change can also be accounted for by the effect of meso alkyl groups, which raise the filled a_{2u}(π)

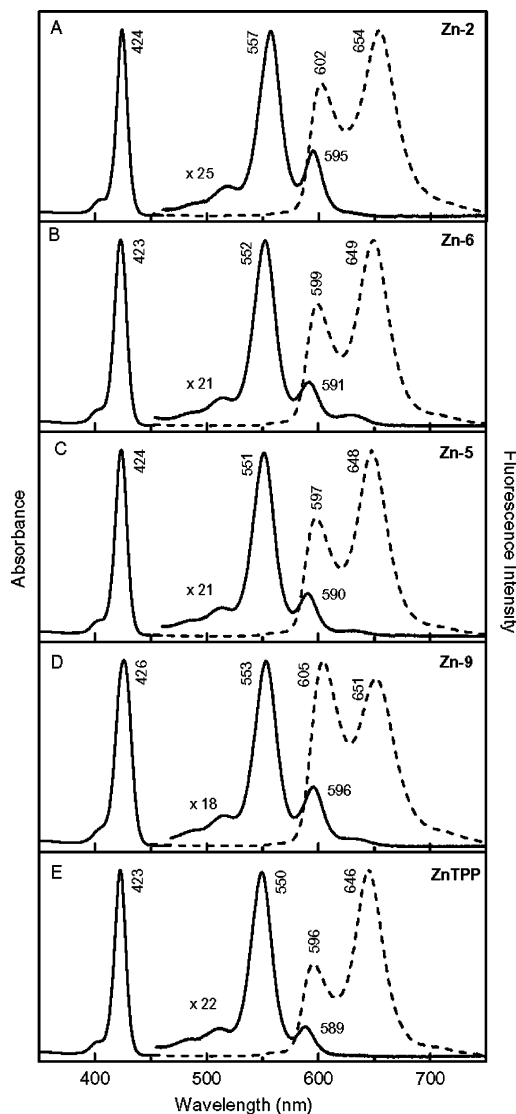


FIGURE 1. Electronic absorption spectra (solid) and fluorescence spectra (dashed) for the indicated porphyrins in toluene at room temperature. The absorption spectra in the 450–750 nm region have been multiplied by the factors shown. The emission spectra were acquired using Soret excitation. Spectra in the respective regions have been normalized to the same peak intensity, and the maxima (± 1 nm) are indicated.

HOMO slightly further above the filled a_{1u}(π) orbital (relative to meso aryl-substituted porphyrins).

(3) The above-mentioned comparisons of optical spectra as well as the fluorescence quantum yields (~0.03) and excited-state lifetimes (~2 ns) in Table 1 demonstrate that swallowtail groups cause little if any of the nonplanar distortions that occur in molecules with multiple bulky substituents such as zinc(II)-*meso*-tetra-*tert*-butylporphyrin. These nonplanar distortions result in broadened and red-shifted (by 50 nm or more) optical spectra as well as fluorescence yields and excited-state lifetimes that are reduced by over an order of magnitude from planar analogues ($\Phi_f < 10^{-4}$ and $\tau \sim 10$ ps).^{15,17}

(4) The spectra of the diphenylethyne-linked **Dyad-1** that contains three swallowtails at the nonlinking meso positions of the macrocycles is well approximated by the sum of the spectra of the Zn porphyrin and Fb porphyrin

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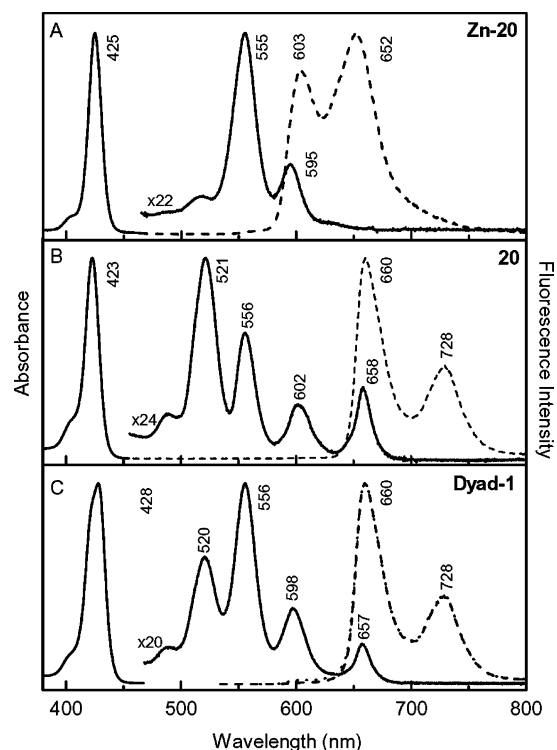


FIGURE 2. Optical spectra for swallowtail-containing **Dyad-1** and reference porphyrins. The other conditions are as in Figure 1.

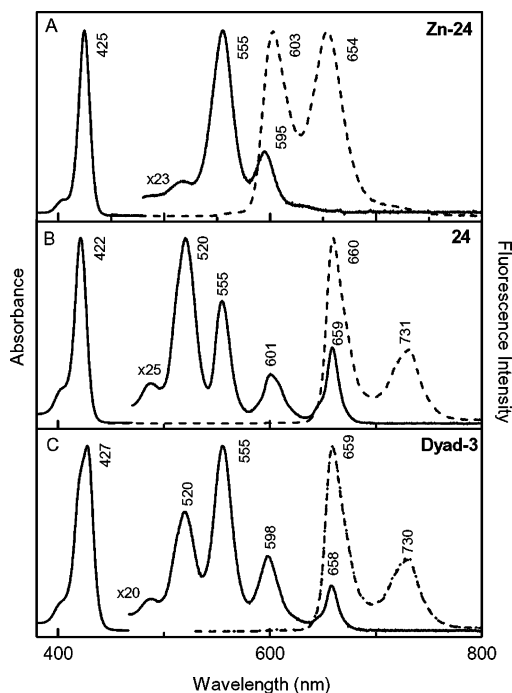


FIGURE 3. Optical spectra for pentyl-containing **Dyad-3** and reference porphyrins. The other conditions are as in Figure 1.

constituents in the photophysically relevant Q-band region (500–650 nm; Figure 2). This finding reflects the relatively weak interporphyrin electronic interactions in these dyads. The same result is found here for the pentyl-containing **Dyad-3** (Figure 3) and previously³⁸ for aryl-containing analogues. Thus, the swallowtails do not significantly modulate the electronic interactions between

TABLE 1. Absorption, Fluorescence, and Electrochemical Properties of Swallowtail Porphyrins^a

porphyrin	no. of alkyl groups ^b	no. of aryl groups ^c	λ_{abs} (nm)	λ_{em} (nm)	Φ_{f}^d	τ^e (ns)	$E_{1/2}^f$ (V)
Zn-2	4 ST	0	595	602	0.023	1.9	+0.25
Zn-6	2 ST	2	591	599	0.031	2.3	+0.38
Zn-9	2 ST	2	596	605	0.045	2.2	<i>g</i>
Zn-5	1 ST	3	590	597	0.032	2.1	+0.42
Zn-20	3 ST	1	595	603	0.026	2.3	+0.33
20	3 ST	1	658	660	0.13	10.3	<i>g</i>
Zn-24	3 Pn	1	595	603	0.053	2.4	<i>g</i>
24	3 Pn	1	659	660	0.071	11.2	<i>g</i>
ZnTPP	0	4	588	596	0.035 ^h	2.3 ^b	+0.50
FbTPP	0	4			0.11 ⁱ	13 ^j	<i>g</i>
Dyad-1	3 ST	1	657	660	0.14 ^k	10.4	+0.34
Dyad-2	3 ST	1					+0.34
Dyad-3	3 Pn	1	658	659	0.13 ^k	9.6	+0.37
Dyad-4	3 Pn	1					+0.36

^a In toluene at room temperature except for the $E_{1/2}$ values. ^b ST is a swallowtail group and Pn is an *n*-pentyl chain. ^c The aryl groups are combinations of phenyl, *p*-tolyl, mesityl, and H- or TMS-terminated ethynylphenyl groups; the differences can give rise to small variations in electronic properties. ^d Fluorescence quantum yield determined using Soret excitation relative to $\Phi_{\text{f}} = 0.030$ for zinc tetraphenylporphyrin (ZnTPP) and/or $\Phi_{\text{f}} = 0.11$ for free base tetraphenylporphyrin (FbTPP) in toluene. ^e Lifetime of the lowest excited singlet state determined using fluorescence modulation (phase shift) techniques. ^f First oxidation potential for the compound in $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1) containing 0.1 M Bu_4NPF_4 vs Ag/Ag^+ ; $\text{FeCp}^2/\text{FeCp}^{2+} = 0.19$; scan rate = 0.1 V s^{-1} ; values are $\pm 0.03 \text{ V}$. ^g Not determined. ^h Values in the ranges $\Phi_{\text{f}} = 0.02\text{--}0.05$ and $\tau = 1.9\text{--}2.6 \text{ ns}$ have been found for reference zinc porphyrins including ZnTPP, zinc tetramesitylporphyrin, and analogues bearing ethynylphenyl or alkyl groups. ⁱ Values in the ranges $\Phi_{\text{f}} = 0.09\text{--}0.12$ and $\tau = 12.5\text{--}13.5 \text{ ns}$ have been found for reference Fb porphyrins including FbTPP, tetramesitylporphyrin, and analogues bearing ethynylphenyl or alkyl groups. ^j Obtained using primary excitation of the Fb unit at 515 nm; the value obtained using excitation of the Zn unit (along with some Fb excitation) at 551 nm is 0.11. ^k Obtained using primary excitation of the Fb unit at 519 nm; the value obtained using excitation of the Zn unit (along with some Fb excitation) at 554 nm is 0.11.

the porphyrin constituents in the arrays, as is further demonstrated by the excited-state energy-transfer and ground-state hole-hopping dynamics described below.

Time-Resolved Absorption Spectra and Energy-Transfer Characteristics of Dyads. Facile energy transfer from the Zn porphyrin to the Fb porphyrin in the swallowtail-containing array **Dyad-1** is demonstrated by several observations. First, fluorescence from this dyad is observed basically exclusively from the Fb constituent even upon excitation of the Zn porphyrin, just as is observed for the pentyl analogues and previously³⁹ for the aryl counterparts (see fluorescence spectra in Figures 2C and 3C and Fb porphyrin fluorescence yields with either excitation wavelength in Table 1). Second, the transient absorption difference spectra in Figure 4 show that bleaching of the $Q_{\text{y}}(1,0)$ band of the Fb porphyrin in **Dyad-1** develops with a $\sim 20 \text{ ps}$ time constant as energy flows to this component following

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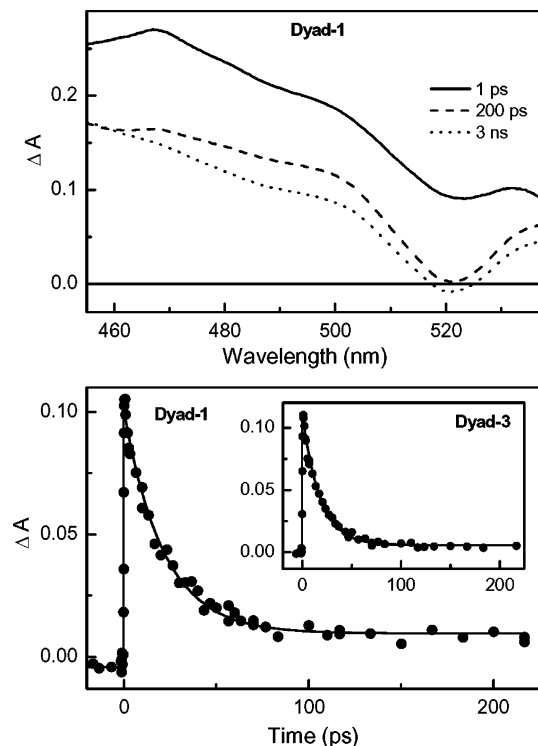


FIGURE 4. Representative time-resolved absorption spectra and kinetic profiles for **Dyad-1** in toluene at room temperature obtained using excitation with a 565-nm 130-fs flash (top panel). The fit to the data at 525 nm for **Dyad-1** in the lower panel is the convolution of the instrument response with an exponential plus a constant, giving a time constant of 22 ps. The average of this value with the time constant of 18 ps from the fit to the kinetic profile at 465 nm gives a lifetime of the excited Zn porphyrin of 20 ± 3 ps. The same lifetime is obtained for **Dyad-3**, as can be seen from the data at 465 nm in the inset to the lower panel.

principal excitation of the Zn porphyrin with a 130-fs 550 nm flash. Third, the lifetime of the excited singlet state of the Zn porphyrin in swallowtail **Dyad-1** is 20 ± 3 ps (Figure 4), the same as in pentyl **Dyad-3** (Figure 4 inset) and basically the same as the value of 24 ± 4 ps found previously³⁹ for the dyad containing mesityl groups at the nonlinking meso positions. These lifetimes are all significantly shorter than the value of ~ 2 ns in the reference Zn porphyrins, affording energy-transfer rates on the order of $\sim (20 \text{ ps})^{-1}$ and efficiencies of $>99\%$. Thus, the use of swallowtails at the nonlinking positions in diphenylethyne-linked dyads does not diminish energy transfer in these systems.

4. Physicochemical Properties of the Oxidized Swallowtail Porphyrins. Electrochemistry. The $E_{1/2}$ values for the first oxidation of various monomers and dyads are given in Table 1. In the case of the ZnFb dyads, $E_{1/2}$ values are for the Zn porphyrins. The $E_{1/2}$ values for the swallowtail porphyrins are generally in the range of those found previously for porphyrins substituted with alkyl and/or aryl groups at the meso carbons.^{40,41} Consistent with previous studies, the $E_{1/2}$ value shifts to lower

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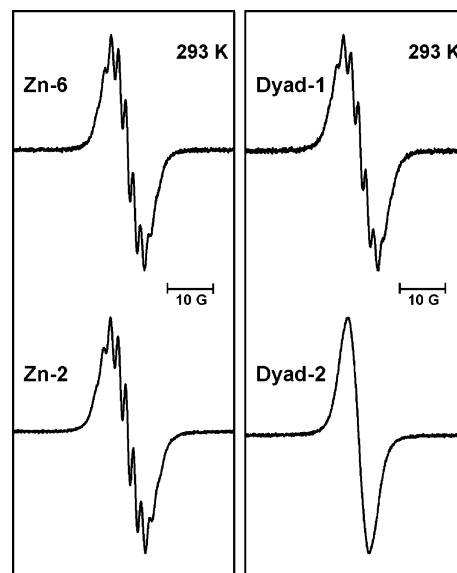


FIGURE 5. Room-temperature X-band EPR spectra of **[Zn-6]⁺** and **[Zn-2]⁺** (left panel) and **[Dyad-1]⁺** and **[Dyad-2]⁺** (right panel).

potential as the number of alkyl groups increases,⁴¹ reflecting the electron-donating characteristics of the swallowtail group.

EPR Spectra and Hole-Hopping Characteristics of the Dyads. The EPR spectra of the π -cation radicals of the swallowtail porphyrins bearing two and four swallowtail groups, **[Zn-6]⁺** and **[Zn-2]⁺**, are shown in Figure 5 (left panel). The spectra are quite similar and exhibit a nine-line ¹⁴N hyperfine pattern that is typical for porphyrins in which the electronic ground state is ²A_{2u} (as is expected for meso-substituted complexes).^{41,42,42–45} The spectra of the π -cation radicals of the swallowtail porphyrins containing one and three groups (not shown) are very similar to those shown in Figure 5 (left panel). The most notable characteristic of the EPR spectra of the π -cation radicals of the monomeric swallowtail porphyrins is that no hyperfine features are observed for the proton(s) on the branching meso-connected carbon(s) of the swallowtail(s). In this respect, the EPR spectra of the swallowtail porphyrins are from those of porphyrins bearing linear meso-alkyl groups. The EPR spectra of these latter complexes typically exhibit substantial hyperfine splittings due to the protons on the first carbon of the alkyl chain.^{41,42}

The absence of proton hyperfine structure for the π -cation radicals of the swallowtail porphyrins provides insight into the torsional angle of the CR₂H group with respect to the porphyrin plane. In particular, the proton

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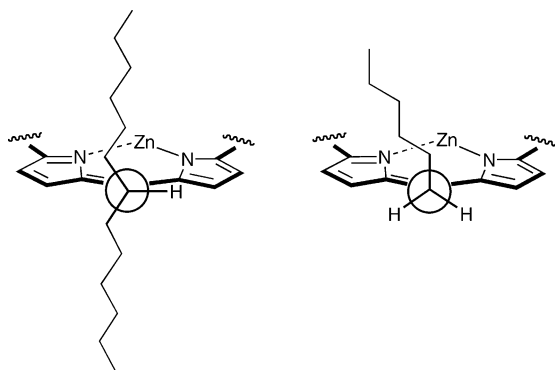


FIGURE 6. Newman projections of the torsional angles for meso substituents in swallowtail (left panel) versus linear alkyl (right panel) substituted porphyrins.

hyperfine coupling exhibits a $\cos^2 \theta$ dependence, where θ is the torsional angle between the proton on the alkyl carbon and the p-orbital on the meso carbon atom of the porphyrin. The absence of proton hyperfine splitting in the swallowtail porphyrins indicates that $\theta \approx 90^\circ$, i.e., the proton is in the plane of the porphyrin ring, as shown in Figure 6 (left structure). Thus, the two hexyl chains of the swallowtails project above and below the porphyrin ring, respectively. In the case of porphyrins bearing linear meso alkyl-substituted porphyrins, $\theta \approx 60^\circ$, i.e., the two protons on the first carbon of the alkyl chain are on the same side of the porphyrin plane and the second carbon of the alkyl chain is in the same plane as the p-orbital of the porphyrin meso carbon, as shown in Figure 6 (right structure).⁴² The different torsional angles for the swallowtail versus linear alkyl groups reflect the different steric constraints experienced by these two types of groups.

The EPR characteristics of the monocation radical of the Zn_2 -dyad, **[Dyad-2]⁺**, permit the investigation of hole transfer between the two swallowtail porphyrins in the array. In this regard, our previous EPR studies of monocation radicals of Zn_2 porphyrin dyads in which the ground state of the porphyrin is $^2A_{2u}$ have shown that the hole rapidly transfers between the two porphyrins on the EPR time scale.³⁸ The rapid hole transfer is evidenced by a narrowed EPR line shape with no resolved hyperfine structure. This same behavior is exhibited by the monocation radical of the swallowtail Zn_2 -dyad, **[Dyad-2]⁺**, as can be seen via comparison of the EPR spectrum of this array with that of the ZnFb analogue, **[Dyad-1]⁺** (Figure 5, right panel). In the latter dyad, the hole is localized on the Zn porphyrin and cannot transfer owing to the much higher oxidation potential of the Fb

porphyrin.⁴⁰ As can be seen, the EPR signal of **[Dyad-2]⁺** exhibits no resolved hyperfine structure and is narrower than that of the **[Dyad-1]⁺**. The spectrum of **[Dyad-1]⁺** is similar to that of the monomeric swallowtail porphyrin π -cations (Figure 5, left panel). Accordingly, the swallowtail substituents do not have any effect on the qualitative aspects of the hole-transfer process.

Outlook

The results obtained define approaches for the synthesis of porphyrins bearing 1–4 swallowtail substituents. A key limitation is the inability to reduce the 7-tridecyl group attached to the keto group of a 1-acyl-dipyrromethane with $NaBH_4$, though the swallowtail substituent can be located at the 5-position of the dipyrromethane. In the synthesis of porphyrin building blocks, this present limitation leads to the use of statistical methods for the synthesis of porphyrins bearing three swallowtail substituents (A_3B -porphyrins) or two swallowtail substituents at adjacent meso positions (*cis*- A_2B_2 -porphyrins), while rational methods can be employed for porphyrins that bear one swallowtail substituent (AB_3 -porphyrin) or two swallowtail substituents at opposite meso positions (*trans*- A_2B_2 - or *trans*- AB_2C -porphyrins). The fact that the swallowtail substituents do not significantly alter the electronic or photophysical properties of porphyrins makes these molecules excellent building blocks for the construction of large arrays, where the solubility imparted by the swallowtails is beneficial for performing detailed physicochemical studies. We are currently implementing the swallowtail design in large multiporphyrin arrays and probing the ground and excited-state electronic communication in these architectures.

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Supporting Information Available: Complete Experimental Section including procedures for the synthesis of all new compounds; 1H NMR spectra for all new compounds; ^{13}C NMR spectra for all new non-porphyrin compounds; and LD-MS and/or MALDI-MS spectra for all new porphyrins. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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