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Building-Block Synthesis of Porphyrin Light-Harvesting Arrays

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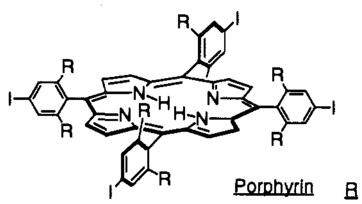
Photosynthetic organisms employ light-harvesting complexes to capture dilute sunlight and funnel energy to the reaction centers.[1] Light-harvesting complexes are remarkable in achieving efficient energy migration among hundreds of pigments with avoidance of non-energy transfer quenching processes. Understanding light-harvesting phenomena at the molecular level is a major objective of photosynthesis research and might also provide the foundation for the design of synthetic molecular devices.[2] Synthetic porphyrin-based light-harvesting arrays are essential for probing the effects of molecular organization on energy migration processes. Covalent arrays of five or more porphyrins have been prepared,[3,4] but the combination of desired attributes in a light-harvesting model system, i.e., architectural rigidity, organic solubility, and incorporation of numerous porphyrins in controlled metalation states, including metalloporphyrins and free base porphyrins, has heretofore not been met.

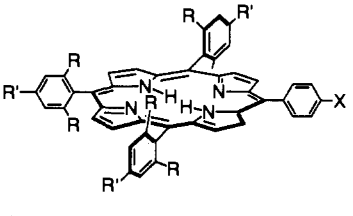
In this communication we report a convergent strategy for preparing rigid, soluble arrays of covalently-linked porphyrins in various metalation states. The strategy employs readily available tetraarylporphyrins as modular building blocks. The porphyrins bear peripheral iodo or ethynyl groups and are facially-encumbered to suppress aggregation. The free base or metalloporphyrins are then joined via homogeneous Pd-mediated coupling reactions under basic conditions to give a desired assembly. We believe that this building-block approach provides an ideal route to model light-harvesting compounds.

Porphyrins **1** and **2** bearing four peripheral iodo groups were prepared from the corresponding aldehyde and pyrrole.[5,6] Monofunctionalized porphyrins **3–5** were prepared in 10% yield via mixed aldehyde condensations using the conditions for synthesis of facially-encumbered porphyrins.[6] Desilylation afforded the monoethynyl porphyrins **6** and **7**.

The synthesis of ethyne-linked porphyrin dimers was examined in order to establish coupling conditions suitable for the synthesis of arrays. The major constraints were to achieve high yield, minimize butadiyne-linked dimer formation,[7] not alter metalation states, and maintain solubility of the reaction components, a key requirement for extension to syntheses of larger arrays. The best results were obtained with a catalytic amount of Pd(PPh$_3$)$_4$[8] in pyridine:triethylamine (3:1) at 100 °C. Reaction of Zn-**3** (0.4 mM) and **6** (0.44 mM) for 2 h afforded the ethyne-linked porphyrin dimer in 83% yield and the butadiyne-linked porphyrin dimer (11%). Equivalent results were obtained with **3** and Zn-**6**. Control reactions showed no demetalation of zinc porphyrins or adventitious metalation of free base porphyrins under the same conditions at prolonged reaction times.



Porphyrin	R
1	H
2	CH$_3$



Porphyrin	R	R'	X
3	CH$_3$O	H	I
4	CH$_3$O	H	(CH$_3$)$_3$Si-C≡C–
5	CH$_3$	CH$_3$	(CH$_3$)$_3$Si-C≡C–
6	CH$_3$O	H	H-C≡C–
7	CH$_3$	CH$_3$	H-C≡C–

This coupling method was applied to the synthesis of pentameric arrays of porphyrins. A tetraiodo porphyrin was employed as the core unit to prevent the butadiyne side reaction from subverting the synthesis of the pentamer target. The reaction of **1** (1.5 mM) and monoethynylporphyrin Zn-**6** (6.7 mM) for 12 h under the same conditions afforded a small amount of higher molecular weight material, the pentamer, butadiynyl dimer, unreacted starting material, and several intermediates as detected by GPC analysis. Chromatography (silica gel, 4% ethyl acetate in methylene chloride) afforded the pentamer **8** (M = Zn, M′ = H,H) in 50% yield (supplementary material). The pentamer is soluble in methylene chloride (>6 mM), toluene (~0.2 mM), or tetrahydrofuran (~0.1 mM). This pentamer is distinguished from two pentamers of similar architecture[3] in comprising a rigid scaffolding and exhibiting organic solubility. Though the center-to-center porphyrin distances are fixed (19.4 Å from peripheral to core porphyrins by CPK models), the porphyrins can freely rotate about the ethyne unit.

The absorption spectrum of **8** differs slightly from the component parts. The Soret region shows no splitting, but the absorption is slightly red-shifted (λ_{max} 428 nm) and broadened (fwhm 20 nm) from that of Zn-**6** (423 nm) and a model free base core porphyrin (422 nm). The visible absorption bands are essentially a superposition of the spectra of the individual free base and zinc porphyrin components.

The fluorescence spectrum of **8** (Figure 1) is dominated by emission from the core free base porphyrin. The fluorescence spectrum is identical upon excitation either in the Soret region or at 547 nm (where the zinc porphyrin absorption is 7.4 times that of the free base). The zinc porphyrin emission yield (Φ_f = 0.0038) is diminished 12-fold compared with a corresponding monomeric zinc porphyrin. The core free base porphyrin emission yield (Φ_f = 0.12) appears relatively unaffected by the four peripheral zinc porphyrins. The fluorescence excitation spectrum (Figure 1) nearly matches the absorption throughout the spectrum. The yield of energy transfer from zinc to free base porphyrins is

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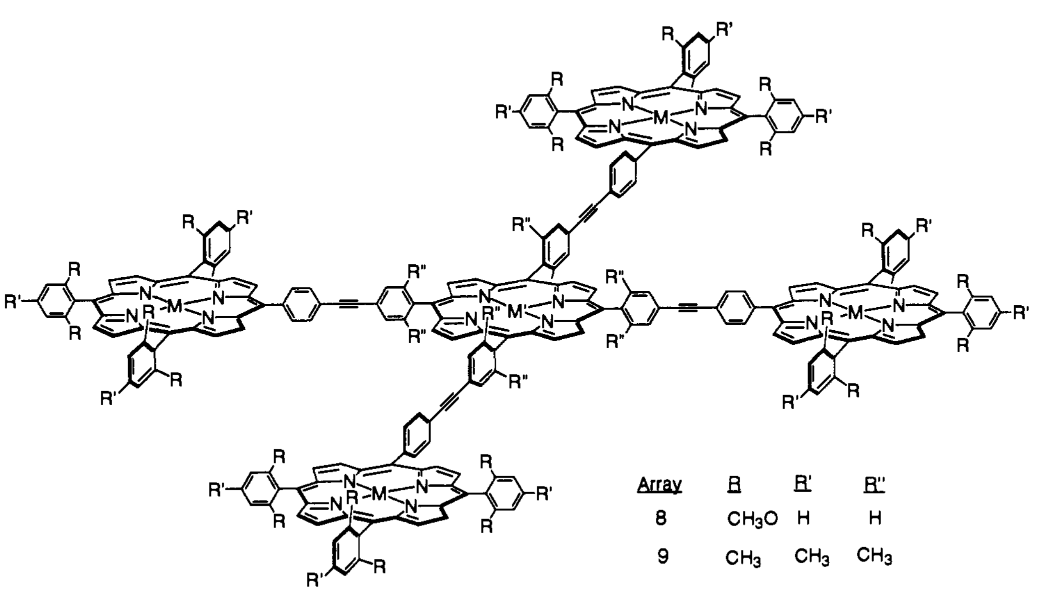

Array	R	R'	R''
8	CH_3O	H	H
9	CH_3	CH_3	CH_3

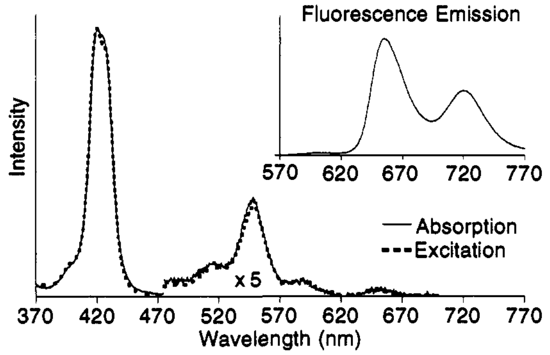

Figure 1. Absorption, fluorescence excitation (λ_{em} 721 nm), and fluorescence emission (λ_{ex} 421 or 547 nm) spectra of **8** in CH_2Cl_2 at 303 K. The weak fluorescence of the zinc porphyrins (601, 648 nm; assumed 1:4 ratio) is partially obscured by the fluorescence of the core free base porphyrin (656, 721 nm). The absorption and fluorescence excitation spectra were fitted by normalization at the Soret bands.

estimated to be ~90%, based on the fluorescence quenching of the zinc porphyrins and on the near-matching of the excitation and absorption spectra.[9] Though efficient energy transfer is expected if the Förster mechanism[10] is operative, time-resolved measurements are essential for probing the photophysical mechanisms involved in concentration of photonic energy at the array core.

Arrays with porphyrins in various metalation states are readily available either by direct joining of premetalated building blocks or by metalation/demetalation of arrays. The all free base (M, M' = H,H) or all zinc pentameters (M, M' = Zn) exhibited fluorescence emission yields typical of monomeric porphyrins, indicating the absence of non-energy transfer quenching interactions. Copper-containing arrays such as Zn_4Cu-**8** exhibited strong quenching of the peripheral zinc porphyrins ($\Phi_f = 0.0033$); the core copper porphyrin also quenched the peripheral free base porphyrins ($\Phi_f = 0.021$) in $(H,H)_4Cu$-**8**. Pentamer **9** (M = Zn, M' = H,H), prepared from Zn-**7** and **2** by the same strategy, was nearly identical to **8** in its light-harvesting properties. The photochemical properties of these and related arrays are currently under investigation.

In summary, this synthetic approach enables incorporation of peripherally-functionalized, facially-encumbered, free base porphyrins or metalloporphyrins in rigid but soluble molecular architectures. The diphenylethyne spacer provides rigid center-to-center distances, is constructed from readily available tetraarylporphyrin building blocks, and appears to be of appropriate length for efficient light-harvesting. A key feature of this synthetic strategy is that the tetraarylporphyrins are intrinsic building blocks and comprise an integral part of the array scaffolding. This approach should provide a robust pathway to larger arrays resembling those found in the natural photosynthetic systems.

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Supplementary Material Available: Experimental details for the synthesis of **8**, including gel permeation, ^1H NMR, mass, and absorption data (7 pages). Ordering information is given on any current masthead page.

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(10) The Förster mechanism predicts 92% energy transfer from zinc to free base porphyrins in this architecture ($J = 4.5 \times 10^{-14}$ cm^6 mmol^{-1}; $\kappa^2 = 1.125$ assuming dynamic averaging during the donor excited-state lifetime by rotation about the ethyne unit). See: Dale, R. E.; Eisinger, J. *Biopolymers* **1974**, *13*, 1573–1605.