Synthesis and Properties of Star-Shaped Multiporphyrin−Phthalocyanine Light-Harvesting Arrays

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Light-harvesting arrays containing four porphyrins covalently linked to a phthalocyanine in a star-shaped architecture have been synthesized. Cyclotetramerization of an ethyne-linked porphyrin−phthalonitrile in 1-pentanol in the presence of $MgCl_2$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded the all-magnesium porphyrin−phthalocyanine pentad in 45% yield. Similar reaction using $Zn(OAc)_2{\cdot}2H_2O$ afforded the all-zinc porphyrin−phthalocyanine pentad in 15% yield. Arrays with different metals (free base, Mg, Zn) in the porphyrin and phthalocyanine macrocycles have been prepared by selective demetalation and metalation steps. This approach provides rapid and convergent access to multiporphyrin−phthalocyanine arrays in diverse metalation states. The arrays are reasonably soluble in organic solvents such as toluene, THF, and CH_2Cl_2. The arrays exhibit strong absorption in the blue and red regions. Time-resolved and static optical measurements indicate that intramolecular singlet-excited-state energy transfer from the porphyrin to the phthalocyanine moiety is extremely rapid (picoseconds) and efficient. Ground-state electronic communication among the porphyrins is indicated by rapid hole/electron hopping among the metalloporphyrins in the arrays as detected by EPR measurements on the singly oxidized pentads. These physical measurements indicate that the porphyrin−phthalocyanine pentads possess favorable characteristics for light harvesting and other photonics applications.

Introduction

Natural photosynthetic systems employ elaborate light-harvesting complexes to capture dilute sunlight and funnel the captured energy to the reaction center through rapid and efficient transfer processes.[1] The light-harvesting complexes in the natural system are generally composed of chlorophylls (or bacteriochlorophylls) assembled in protein matrices that absorb over a wide spectral range. The challenge of creating artificial mimics of the light-harvesting complexes has prompted the development of routes to a diverse collection of multiporphyrin arrays. Examples of covalently linked architectures comprised of five or more porphyrins and their method of preparation include the following: (1) *dendritic arrays* with stilbene linkers formed via successive Wittig reactions,[2] diphenylethyne linkers constructed via Pd-coupling reactions,[3] or a combination of diphenylethyne and ester linkers prepared via Pd-coupling and Mitsunobu reactions,[4] (2) *windmill arrays* with direct *meso*−*meso* linkages formed via oxidative coupling,[5] (3) *sheetlike arrays* with Pd-coordinated pyridyl linkages prepared via self-assembly,[6] (4) *star-shaped arrays* with diphenylethyne linkers formed via Pd-coupling reactions,[7,8] oligophenylethyne linkers prepared via Pd-coupling reactions,[9] phenylene linkers constructed via condensations of a porphyrin aldehyde,[10,11] phenylenevinylene linkers formed via Wittig reactions,[12] or benzoxyphenyl linkers joined via alkylation,[13] (5) *linear arrays* with phenylene linkers formed via porphyrin aldehyde + dipyrromethane condensations[14] or 1,3,5-triazine−aniline units constructed via condensation of amino porphyrins and cyanuric acid,[15] (6) *cyclic arrays* with diphenylbutadiyne linkers formed via Cu-coupling reactions[16] or diphenylethyne linkers prepared via Pd-coupling reactions,[17] and

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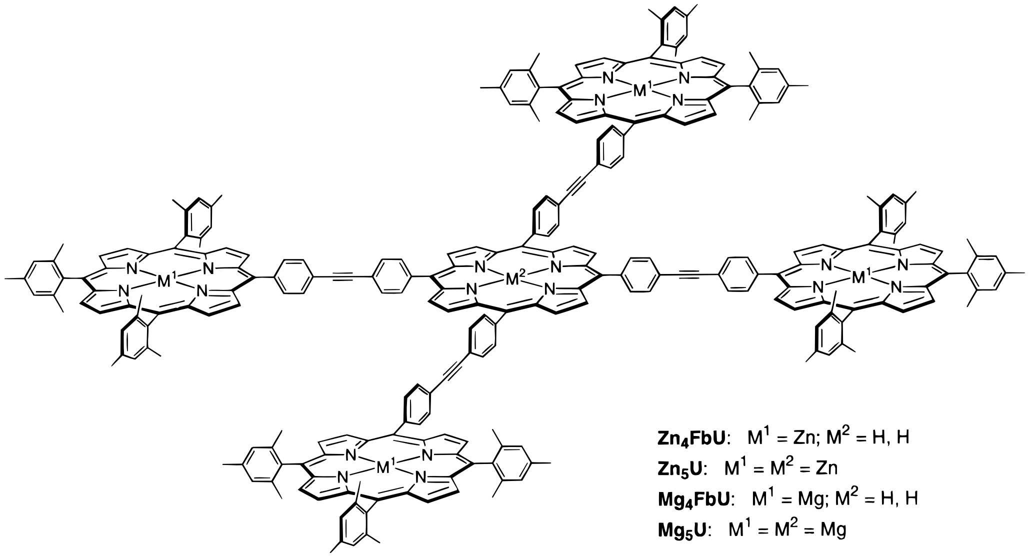
Chart 1



Zn_4FbU: M^1 = Zn; M^2 = H, H
Zn_5U: M^1 = M^2 = Zn
Mg_4FbU: M^1 = Mg; M^2 = H, H
Mg_5U: M^1 = M^2 = Mg

(7) *backbone polymeric arrays* with oligophenylenevinylene linkers formed via Wittig reactions[18] or condensation of porphyrin aldehydes and active methylene units[19] or phenylethyne linkers synthesized via Pd-coupling reactions.[20]

A star-shaped light-harvesting array that we previously synthesized and studied is shown in Chart 1. This architecture functions as an energy funnel when the peripheral porphyrins are metalated (Zn or Mg) and the core porphyrin is in the free base (Fb) form.[7,8] The peripheral metalloporphyrins provide a large cross section for light harvesting. The absorption of light is followed by energy transfer to the energetically lower-lying Fb porphyrin. The energy-transfer rate in toluene at room temperature is ~$(20\ \mathrm{ps})^{-1}$ in both Mg_4FbU and Zn_4FbU, and in both cases the yields of energy transfer are >99%. The photoinduced energy-transfer process occurs predominantly by a through-bond mechanism mediated by the diphenylethyne linker. To probe the electronic interactions between the porphyrins in their ground electronic states, the arrays were oxidized and hole/electron hopping was examined.[21] In the singly oxidized all-Zn or all-Mg pentameric arrays, the hole is delocalized over the five metalloporphyrins on the EPR time scale. In the singly oxidized M_4Fb arrays, the hole is delocalized over the four metalloporphyrins. The rapid hole/electron hopping in the oxidized arrays is indicative of ground-state electronic communication between the porphyrins mediated by the diphenylethyne linker.

The results obtained with the star-shaped pentamer and related multiporphyrin arrays prompted the synthesis and investigation of a new generation of light-harvesting arrays. Our objectives included the following:

(1) Increased spectral coverage. Porphyrins absorb strongly in the blue but weakly in the red, whereas chlorophylls and bacteriochlorophylls absorb strongly both in the blue and in the red. In contrast, phthalocyanines absorb strongly in the red region (600−700 nm) but weakly in the blue.[22] A mixed system of porphyrins and phthalocyanines that retains the essential electronic features of the respective pigments should absorb strongly both in the blue and in the red, thereby covering a large part of the solar spectrum. While many multiporphyrin arrays have been prepared,[2−20] relatively few arrays comprised of multiple phthalocyanines[23] and even fewer porphyrin−phthalocyanine dyads[24,25] and tetraporphyrin−phthalocyanine pentads[26] have been prepared. Examination of the spectroscopic properties of several such dyads revealed efficient energy transfer from porphyrin to phthalocyanine.[24,25,27] A further attraction of a porphyrin−phthalocyanine combination is that the lowest singlet electronic state of a phthalocyanine lies lower in energy than that of a porphyrin regardless of metalation state.[28] Thus, an inherent energy funnel exists even with identical metals in the two types of chromophores, unlike the all-porphyrin arrays where differential metalation states are necessary to achieve directed energy flow.

(2) Enhanced electronic communication. A Zn porphyrin and Fb porphyrin (each having a_{2u} HOMOs) joined at the *meso*-positions by a diphenylethyne linker exhib-

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ited a photoinduced energy-transfer rate with a rate of (24 ps)$^{-1}$ (ref 29) whereas the analogue with a *p*-phenylene linker underwent energy transfer with a rate of (3.5 ps)$^{-1}$.[30] We sought to examine the energy-transfer rate with a phenylethyne linker, where the ethyne moiety is directly attached to a phthalocyanine.

(3) Convergent synthesis without Pd-mediated coupling reactions.[31] The star-shaped porphyrin arrays were prepared by the Pd-mediated coupling of a monoethynyl Zn porphyrin and a tetraiodo Fb porphyrin. The Pd-mediated coupling reactions are well-suited for preparing small arrays, but purification becomes increasingly difficult as the size of the array increases.[32] We sought to investigate the use of phthalocyanine formation for the direct assembly of a star-shaped energy-funnel architecture.

In this paper, we report the convergent synthesis of star-shaped light-harvesting arrays comprised of four porphyrins and a core phthalocyanine. This synthetic route complements the Pd-mediated coupling employed in the synthesis of a related set of porphyrin−phthalocyanine dyads.[33] Excited-state energy transfer in the pentads has been examined by static and time-resolved absorption and fluorescence spectroscopies. Ground-state electronic communication has been investigated by EPR studies of hole/electron hopping in the oxidized complexes.

Results and Discussion

1. Synthesis. Strategy. The synthesis of ethyne-linked porphyrin−phthalocyanine pentads could proceed via two distinct strategies. In one approach, porphyrin and phthalocyanine building blocks (a tetraiodophthalocyanine and an ethynylporphyrin, or a tetraethynylphthalocyanine and an iodoporphyrin) are subjected to a Pd-mediated coupling process,[31,32] which is compatible with different metals in the porphyrin and phthalocyanine building blocks. This strategy mirrors that used in the synthesis of a star-shaped porphyrin−phthalocyanine complex involving condensation of an aminoporphyrin with a phthalocyanine tetraanhydride.[26] Limitations of the Pd-mediated coupling approach include (1) incomplete reaction, which would afford a mixture composed of phthalocyanines with various numbers of appended porphyrins, and (2) side reactions, which result in increasingly difficult separation as the size of the array increases.[32] Moreover, the core tetraiodo- and tetraethynylphthalocyanine, which have been prepared for polymerization studies, are practically insoluble in organic solvents, making purification and handling difficult.[34]

A complementary approach elaborates the phthalocyanine from a porphyrin−phthalonitrile in a final cyclotetramerization step. Precedent for this route is seen in the variety of large groups that have been attached to phthalonitriles for cyclization to the corresponding substituted phthalocyanine.[35] Indeed, porphyrin−phthalocyanine dyads (but not pentads) have been prepared by mixed reaction of a porphyrin−phthalonitrile and a second phthalonitrile in excess.[24,25] Formation of the phthalocyanine in the last step imposes some restrictions on the range of available porphyrin and phthalocyanine metalation states, as metal templating is used to facilitate phthalocyanine formation. An attractive feature of this route is that the Pd-mediated coupling reactions are used only in preparing small-molecule precursors, where purification is more manageable. These considerations prompted us to pursue the synthesis of the porphyrin−phthalocyanine pentads via the phthalonitrile cyclotetramerization strategy.

Porphyrin−phthalocyanine Pentads. Treatment of 4-iodophthalonitrile and 4-ethynylbenzaldehyde under Pd-mediated coupling conditions (triethylamine/THF (3:1) at 35 °C in the presence of Pd$_2$(dba)$_3$ and AsPh$_3$) gave phthalonitrile−benzaldehyde (**1**) in 86% yield (Scheme 1). These general conditions have been used extensively in the synthesis of multiporphyrin arrays, where the yields in preparing porphyrin dimers are approximately 60−70%.[36] A mixed condensation of **1**, mesitaldehyde, and pyrrole via the two-step one-flask method in CHCl$_3$ with BF$_3$·O(Et)$_2$ (BF$_3$−ethanol cocatalysis)[37] at room temperature followed by oxidation with DDQ afforded a mixture of porphyrins. Because the porphyrins bear different numbers of polar groups (mesityl, 3,4-dicyanophenyl), the desired ethyne-linked porphyrin−phthalonitrile (**2**) was easily isolated in 20% yield after one flash silica column (Scheme 1).

The methods for preparing phthalocyanines from phthalonitrile usually involve high-temperature conditions.[38] One of the milder methods to obtain phthalocyanines involves heating phthalonitrile in 1-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and a metal salt.[39] We employed this method with the free base porphyrin−phthalonitrile. Porphyrin−phthalonitrile (**2**) is soluble in 1-pentanol at room temperature. Thus, condensation of **2** in 1-pentanol with MgCl$_2$ in the presence of DBU at 140 °C under argon for 24 h afforded

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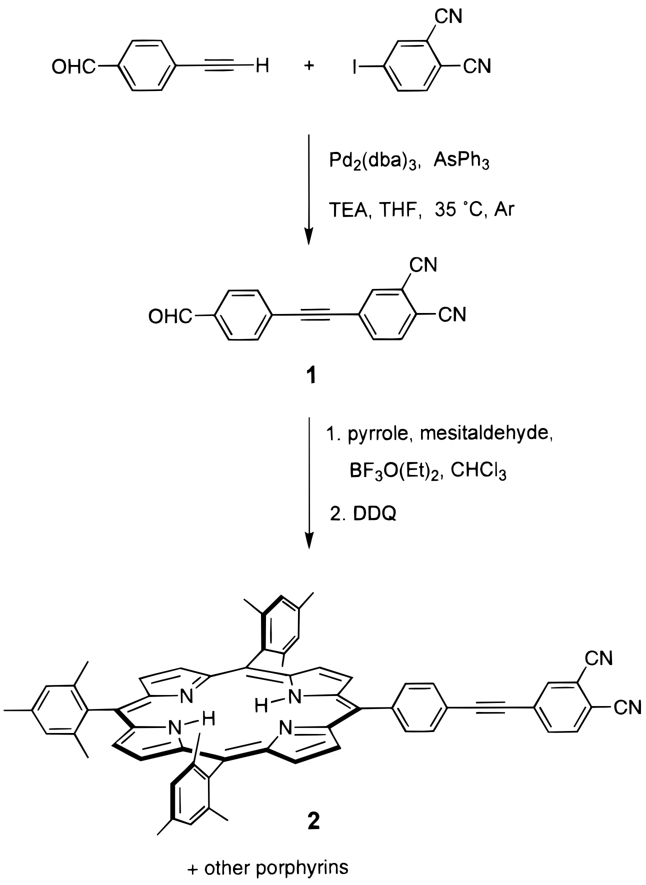
Scheme 1



a very dark green mixture. Chromatography on one alumina column removed nearly all of the non-phthalocyanine species, and one subsequent size exclusion chromatography (SEC) column gave the all-magnesium porphyrin−phthalocyanine pentad $(MgP)_4MgPc$ in 45% yield (Scheme 2). The similar treatment of **2** using zinc acetate instead of magnesium chloride gave the all-zinc porphyrin−phthalocyanine pentad $(ZnP)_4ZnPc$ in 15% yield. The difference in yields of the Mg versus Zn pentad mirrors the phthalocyanine yields observed with the two metals with simple phthalonitriles. Indeed, of a variety of metals examined with simple phthalonitriles, magnesium was one of the most effective in forming phthalocyanines.[40] The facile metal insertion that occurs under the phthalocyanine-forming conditions is not surprising; zinc insertion in porphyrins and phthalocyanines occurs under mild conditions, and the conditions for phthalocyanine formation resemble those used in classical methods for magnesium insertion.[41] In neither reaction was any free base porphyrinic component isolated from the reaction mixture. In the phthalocyanine-forming reaction, there are four expected regioisomers due to the two possible positions of substitution of each ethyne at the periphery of the phthalocyanine; such species were not resolved by column chromatography in either reaction.

The ^1H NMR spectrum of each pentad recorded in THF-d_8 showed multiple peaks from the phthalocyanine aromatic protons, consistent with the presence of regioisomers (see the Experimental Section). The presence of four regioisomers from such phthalocyanine-forming reactions is well-known and expected.[42] The IR spectrum of each array was devoid of nitrile peaks as well as peaks in the region 1650−1800 cm^{-1}, indicating the absence of impurities typically observed in crude samples from phthalocyanine-forming reactions. The pentads obtained display good solubility in organic solvents such as toluene, methylene chloride, or THF. The solubility of the porphyrin−phthalocyanine pentads can be attributed both to the bulky nature of the peripheral porphyrin groups and to the existence of regioisomers. Given that unsubstituted phthalocyanines are practically insoluble in organic solvents, it appears that the four trimesitylporphyrin macrocycles serve as solubilizing groups.

Selective Metalation and Demetalation of Porphyrin−Phthalocyanine Pentads. The photochemical properties of metalloporphyrins and metallophthalocyanines depend significantly on the nature of the metal. In designing light-harvesting arrays, it is desirable for the energy-transfer donor unit to have a long-lived excited singlet state. For porphyrins, this requirement is met by Mg ($\tau \approx 9$ ns) or the free base ($\tau \approx 13$ ns) more so than Zn ($\tau \approx 2$ ns).[8] On the other hand, for applications such as light harvesting or directed energy flow, it is desirable to avoid non-energy-transfer quenching reactions such as electron transfer. To examine various combinations of metals for efficacy in energy-transfer (and avoidance of excited-state quenching) processes, we examined the preparation of mixed-metal complexes of the porphyrin−phthalocyanine arrays. Three distinct demetalation/metalation manipulations were performed (Scheme 3).

(1) Selective demetalation. Magnesium porphyrins are labile toward acids, and even chromatography on silica gel will cause demetalation of magnesium porphyrins and chlorins.[41,43] However, magnesium phthalocyanines are less labile toward demetalation, with no demetalation occurring for magnesium phthalocyanines even after they are stirred for several hours in the presence of silica gel. Thus, stirring $(MgP)_4MgPc$ for 12 h in CH_2Cl_2 containing silica gel gave $(H_2P)_4MgPc$ in 74% yield. No demetalation of the phthalocyanine moiety was observed at the end of the reaction as verified by laser-desorption mass spectrometry and absorption spectroscopy.

(2) Selective metalation. Treatment of a solution of $(H_2P)_4MgPc$ in $CHCl_3$ with zinc acetate at room temperature afforded $(ZnP)_4MgPc$ in nearly quantitative yield. Though the reaction was carried out overnight with a large excess of zinc acetate, no transmetalation of magnesium by zinc in the phthalocyanine moiety was observed.

(3) Comprehensive demetalation. Treatment of $(MgP)_4MgPc$ with TFA gave the all-free base pentad $(H_2P)_4H_2Pc$ in 68% yield. Alternatively, treatment of $(ZnP)_4MgPc$ with TFA in a manner similar to that of $(MgP)_4MgPc$ also afforded $(H_2P)_4H_2Pc$ in 70% yield. In principle, $(H_2P)_4H_2Pc$ could also be prepared by cyclotetramerization of **2** in the absence of metal salts; however, condensation under Shiraishi conditions without a metal template generally affords a much lower yield of the phthalocyanine.[39,40]

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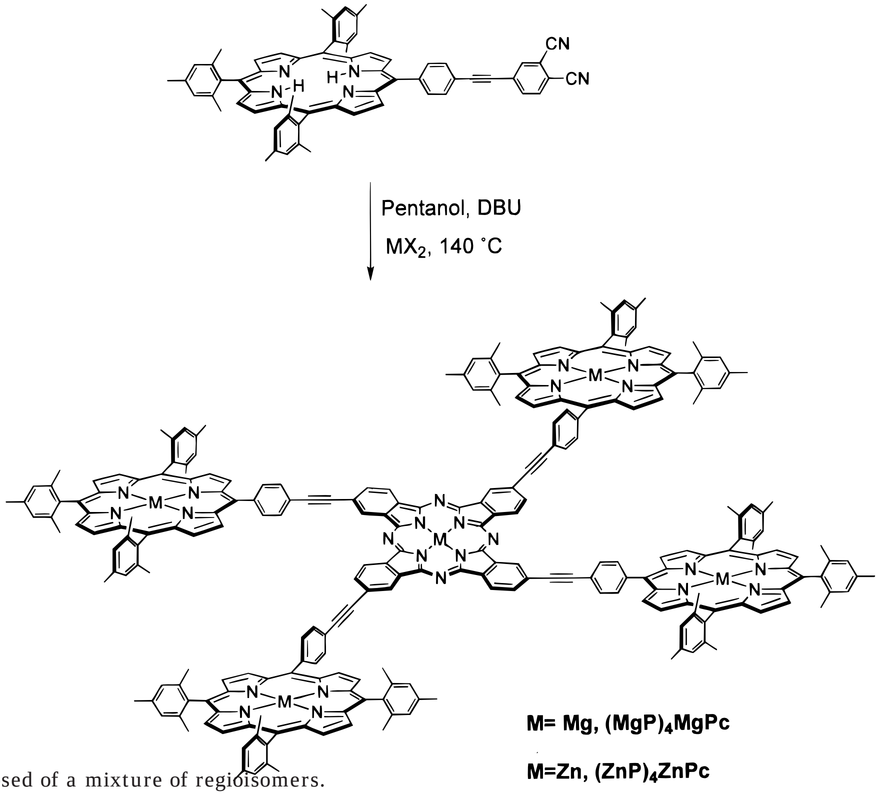
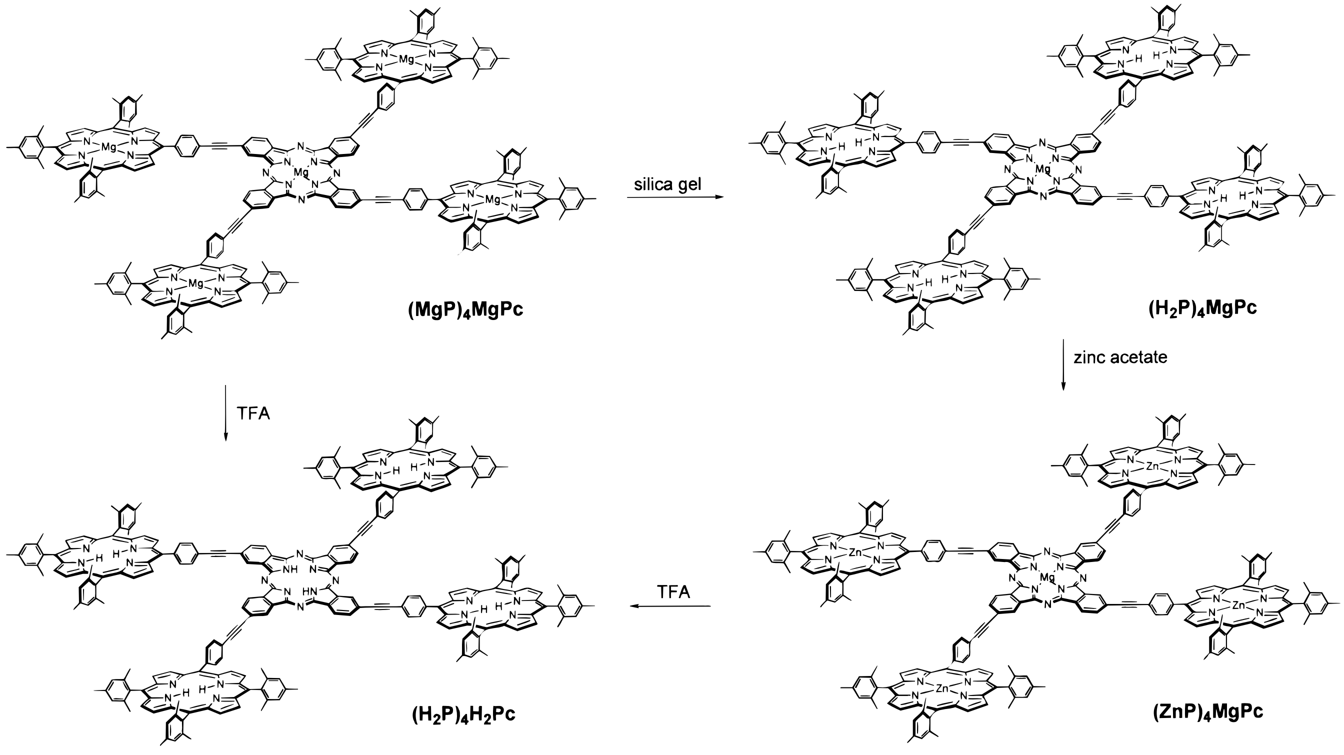
Scheme 2. Convergent Synthesis of Porphyrin-Phthalocyanine Pentads



[a] Each pentad is composed of a mixture of regioisomers.

Scheme 3. Selective Metalation and Demetalation of Porphyrin−Phthalocyanine Pentads



2. Physical Properties of the Neutral Complexes. Absorption Spectra. The absorption spectrum in toluene of each pentad resembles, but does not equal, the sum of the spectra of the corresponding monomeric components. A representative example is shown for $(H_2P)_4H_2Pc$ in toluene at room temperature (Figure 1). The absorption spectrum of each pentad is dominated by the intense Soret band of the multiple porphyrin constituents near 420 nm. The net molar absorption coefficient of the porphyrin Soret band in each pentad is approximately 1.4×10^6 M^{-1} cm^{-1} with only slight broadening (fwhm = ~14 nm) compared with monomeric porphyrins. The weaker Q-bands of the porphyrins lie between 500 and 650 nm, with the exact wavelengths depending on the metalation state; for example, the absorption near 515 nm in Figure 1 is the $Q_Y(1,0)$ band

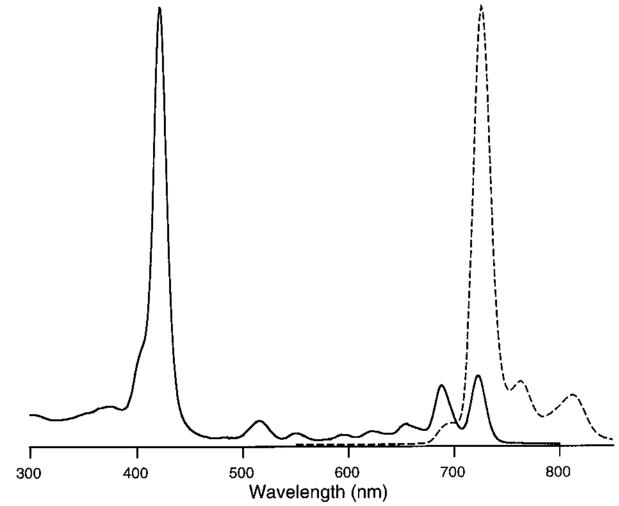


Figure 1. Absorption (solid line) and fluorescence emission (dashed line, $\lambda_{exc} = 515$ nm) spectra of $(H_2P)_4H_2Pc$ in toluene at room temperature. The porphyrin Soret band ($\epsilon_{421\ nm} = 1.5 \times 10^6\ M^{-1}\ cm^{-1}$), phthalocyanine Q(0,0) band ($\epsilon_{723\ nm} = 2.3 \times 10^5\ M^{-1}\ cm^{-1}$), and weaker bands from 500 to 700 nm provide effective absorption across a broad range. Excitation of the porphyrin (515 nm) is followed by efficient energy transfer to the phthalocyanine. The latter fluoresces with high intensity ($\Phi_f = 0.76$).

of the free base porphyrin units of $(H_2P)_4H_2Pc$. The Soret band of the phthalocyanine core component lies near 350 nm, and the Q-bands of this unit give rise to the relatively strong absorption near 720 nm ($\epsilon \approx 2.5 \times 10^5\ M^{-1}\ cm^{-1}$) and 690 nm. The phthalocyanine Q(0,0) bands in all the pentads are red shifted ~20 nm relative to those in tetra-*tert*-butylphthalocyanine ($(t\text{-Bu})_4H_2Pc$)[44] and its Mg and Zn chelates $(t\text{-Bu})_4MgPc$[44] and $(t\text{-Bu})_4ZnPc$;[27] the red shift is ~10 nm relative to those in phthalocyanine monomers bearing a total of either eight heptyl groups or six heptyl groups and one ethyne group at the peripheral carbons of the fused benzene rings.[33] This red shift is attributed to extension of the conjugated π-system involving the four phenylethynyl linkers from the attached porphyrins.

Fluorescence Properties. Upon excitation of $(H_2P)_4H_2Pc$ at 515 nm, where the porphyrin is the dominant absorber, fluorescence was observed exclusively from the phthalocyanine moiety (Figure 1). These results indicate very efficient photoinduced intramolecular energy transfer from the porphyrin to the phthalocyanine. Similar results were observed for $(ZnP)_4ZnPc$, $(ZnP)_4MgPc$, and $(H_2P)_4MgPc$. The fluorescence yields of the phthalocyanine components in these four pentads, obtained upon excitation of either the porphyrin or the phthalocyanine, are similar to those of phthalocyanine reference monomers (Table 1). For example, the fluorescence properties of tetra-*tert*-butylphthalocyanine ($(t\text{-Bu})_4H_2Pc$) and its metal chelates are as follows: $(t\text{-Bu})_4H_2Pc$, $\Phi_f = 0.77$, $\tau = 5.3$ ns;[44] $(t\text{-Bu})_4MgPc$, $\Phi_f = 0.84$, $\tau = 4.9$ ns;[44,45] $(t\text{-Bu})_4ZnPc$, $\Phi_f = 0.23$, $\tau = 3.3$ ns.[27] We have obtained similar results for phthalocyanine monomers bearing a total of either eight heptyl groups or six heptyl groups and one ethyne group at the peripheral carbons of the fused benzene rings.[33] The approximate (Φ_f, τ) values for both series are (0.77, 5.5 ns), (0.62, 5.4 ns), and (0.38, 2.8 ns) for the free base, Mg, and Zn complexes, respectively.

Two differences from the static emission properties of the other pentads are observed in the case of $(MgP)_4MgPc$. (1) Some emission is observed from the Mg components, and can be ascribed largely if not completely to the greater photolability of this array, liberating monomeric MgP. (2) The emission yield of the phthalocyanine core obtained upon excitation of the porphyrin is reduced by 40−50% from the reference monomers. We ascribe this finding to a contribution of charge transfer involving the excited porphyrin and the ground-state phthalocyanine core. This conclusion is based on the greater ease of oxidation of Mg porphyrins relative to the Zn and free base analogues, and results of extensive studies on a series of porphyrin−phthalocyanine dyads.[33]

Fluorescence lifetimes of the phthalocyanine core unit in selected porphyrin−phthalocyanine pentads were determined by fluorescence modulation spectroscopy in which both the phase shift and modulation amplitude were monitored. The results are included in Table 1. The free base and magnesium phthalocyanines have lifetimes of about 4.5 ns, whereas the zinc analogue has a value of about 2.5 ns. These lifetimes are similar to those found for benchmark phthalocyanine monomeric reference compounds. As is the case for phthalocyanine monomers, the error limits on the emission lifetimes for the phthalocyanine in each pentad are larger than normal because of potential complexities such as effects of aggregation. In particular, aggregation tends to lengthen the phthalocyanine lifetimes as concentrations are increased (even in the several micromolar range), and the effect is more pronounced along the series pentads < dyads < monomers.[33] This difference can account for any potential slight shortening of the phthalocyanine lifetimes in the pentads compared to the monomers, although a minor contribution of charge transfer cannot be ruled out. Nonetheless, the comparable fluorescence lifetime of the central phthalocyanine in each array and the reference monomer indicates that appending multiple porphyrins via phenylethyne units does not significantly perturb the excited-state properties of the phthalocyanine component. Due to rapid energy transfer to the phthalocyanine, the photoexcited porphyrins in the porphyrin−phthalocyanine arrays were far too weakly emissive (vide supra) and short-lived (vide infra) to monitor via fluorescence spectroscopy. Therefore, the decay properties of the excited porphyrins were monitored using time-resolved absorption spectroscopy.

Transient Absorption Spectra. The energy-transfer rate from the photoexcited porphyrin constituents to the ground-state phthalocyanine of selected pentads was assessed using transient absorption spectroscopy. Representative data for $(H_2P)_4H_2Pc$ are shown in Figure 2. Excitation of the porphyrin with a 130 fs pulse at 420 nm causes the absorption difference spectra ($\Delta A = A_{excited\ state} - A_{ground\ state}$) at early times to be dominated by bleaching of the porphyrin Soret band near 420 nm (solid spectrum in Figure 2). However, even at 0.2 ps after excitation, bleaching is observed to some degree in the ground-state absorption bands of the phthalocyanine, notably in the Q-bands near 685 and 720 nm. The bleaching in the phthalocyanine bands even at this early time after excitation may arise from several factors, the predominant of which appears to be an extremely fast

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Table 1. Excited-State Properties of Porphyrin−Phthalocyanine Arrays[a]

array	porphyrin lifetime (ps)[b]	phthalocyanine lifetime (ns)	phthalocyanine Φ_f[c]	$(k_{trans}^{-1})_{avg}$[d] (ps)	Φ_{trans} (%)
$(H_2P)_4H_2Pc$	1.2 ± 0.2 (62%) 13 ± 3 (38%)	4.6 ± 0.7	0.76	5.6	>99
$(MgP)_4MgPc$	0.8 ± 0.3 (68%) 15 ± 3 (32%)	4.3 ± 0.7	~0.4[e]	5.3	~60[e]
$(ZnP)_4ZnPc$	0.9 ± 0.3 (55%) 7 ± 2 (45%)	2.4 ± 0.4	0.38	3.6	>99

[a] All data acquired in toluene at room temperature. The energy-transfer rates and efficiencies are obtained using eqs 1 and 2. [b] Average of values from decay of the porphyrin bleaching and growth of the phthalocyanine bleaching in transient absorption measurements. [c] Phthalocyanine fluorescence yield (±15%) obtained upon excitation of the porphyrin near 420 nm. These yields were determined using *meso*-tetraphenylporphyrin as a reference ($\Phi_f = 0.11$), a method that also reproduced literature values for the corresponding phthalocyanine monomers. [d] Derived assuming a lifetime for the photoexcited porphyrin that is the amplitude-weighted average value given in the second column (obtained using porphyrin-Soret excitation). [e] The yields of phthalocyanine fluorescence and porphyrin-to-phthalocyanine energy transfer are reduced for $(MgP)_4MgPc$ relative to the other pentads due to competing electron transfer from the photoexcited porphyrin (see the text).

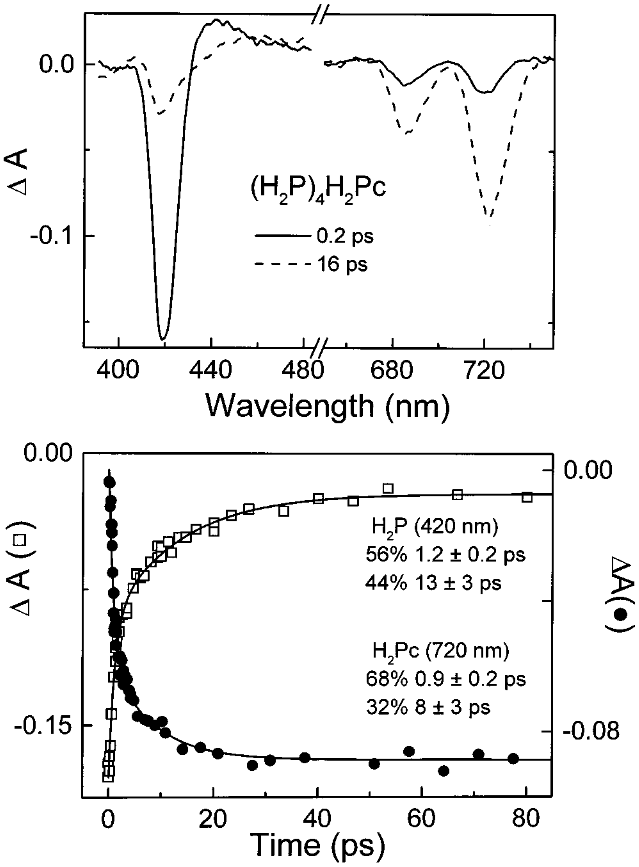

Figure 2. Time-resolved absorption data for $(H_2P)_4H_2Pc$ in toluene at 298 K, acquired using excitation of the porphyrin components with a 130 fs flash at 420 nm. The top panel shows absorption difference spectra corresponding to the porphyrin excited state (solid) and the phthalocyanine excited state (dashed). The bottom panel gives kinetic data for decay of bleaching in the porphyrin Soret band (open squares) and growth of bleaching in the phthalocyanine Q-band (closed circles). Date before $t = 0$ and along the instrument rise are not shown for clarity.

(~1 ps) component of energy transfer from the photoexcited porphyrin to the ground-state phthalocyanine. At increasing times after excitation, the bleaching in the porphyrin Soret band diminishes dramatically, reflecting decay of the porphyrin component to the ground electronic state. Concomitantly, the bleaching in the phthalocyanine bands in the Q-region increases (see the dashed spectrum taken at 16 ps in Figure 2). In this longer-time spectrum, there appears to be a proportionately larger increase in the apparent bleaching near 720 nm than at 685 nm. The most significant contribution to this effect stems from the presence of stimulated emission in the longer-wavelength feature (fluorescence stimulated by the white light probe pulse). Over the next tens of picoseconds, the spectrum shows only a minor evolution from the spectrum at 16 ps, mainly in the amplitude of the feature at 720 nm.

The time evolution of the decay of porphyrin Soret bleaching near 420 nm and of the growth of the phthalocyanine bleaching near 720 nm for $(H_2P)_4H_2Pc$ is dual exponential in nature. Representative kinetic data and dual-exponential fits are given in the lower panel of Figure 2. It can be seen that the time constant pairs in the two regions are in good agreement, with average values of ~1 and ~10 ps having ~60/40 relative amplitudes. Very similar transient absorption characteristics and time profiles were observed for the $(MgP)_4MgPc$ and $(ZnP)_4ZnPc$ pentads (Table 1). Essentially the same behavior was also observed for $(H_2P)_4H_2Pc$ using Q-region excitation at 550 nm. The latter finding indicates that the dual-exponential behavior is not associated with energy or electron transfer associated with the S_2 (Soret) versus S_1 (Q) states of the porphyrin components. The biphasic kinetic behavior cannot be ascribed to a subpopulation of a particular porphyrin−phthalocyanine regioisomer, because the same dual-exponential kinetics were observed in the related porphyrin−phthalocyanine dyads where no regioisomers are present.[33] Possible origins of the dual-exponential behavior and other complexities are discussed in the context of the studies on the dyads where comparisons among a large body of data can be made.[46] One candidate for the ~10 ps component is intermolecular energy transfer involving two closely associated arrays.

Energy-Transfer Rates and Mechanisms. The transient absorption data, as well as the static and time-resolved fluorescence data, lead to the assessment that energy transfer from the photoexcited porphyrin units to the central phthalocyanine core in the arrays is a rapid

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(46) For $(H_2P)_4H_2Pc$, the growth of bleaching in the 685 nm band occurs essentially completely with the ~1 ps component, with perhaps a very minor subsequent decay over the time scale of about 10 ps. For the other metal-containing pentads, the splitting in the ground-state spectrum is not observed, and so the presence or extent of this phenomenon cannot be cleanly delineated in those arrays. This difference in the contribution of the slow component to the rise of the bleaching in the two Q-bands of $(H_2P)_4H_2Pc$ is not directly connected with the origin of the dual-exponential decay of the porphyrin excited state and the behavior for the growth of the phthalocyanine lowest excited singlet state, but rather may reflect dynamics within the phthalocyanine manifold after energy transfer. These dynamics in free base phthalocyanines may involve symmetry effects associated with the proton axis with respect to the site(s) of linker attachment.

and highly efficient process. The efficiency is only reduced when ultrafast electron transfer from the photoexcited porphyrin to the phthalocyanine can occur in arrays such as $(MgP)_4MgPc$ where the thermodynamics of the process are favorable. The major fraction of the energy-transfer process appears to occur with a time constant of about 1 ps, with a somewhat lesser amount occurring with a time constant of about 10 ps. To assess the overall rate and efficiency of excited-state energy transfer, an amplitude-weighted average of the two components will be used for the lifetime of the photoexcited porphyrin in the arrays. Note that these lifetimes are at least 400-fold shorter (and up to about 2000-fold shorter) than the lifetimes of the relevant photoexcited monomeric porphyrin reference compounds (Table 1). This difference, as with the reduced emission yields of the porphyrins in the arrays, reflects the high efficiency of energy transfer to the central phthalocyanine unit.

The rate and yield of excited-state energy transfer in each array can be derived using the following expressions:

$$1/\tau_{\mathrm{D}} = k_{\mathrm{rad}} + k_{\mathrm{isc}} + k_{\mathrm{ic}} \tag{1}$$

$$1/\tau_{\mathrm{DA}} = k_{\mathrm{rad}} + k_{\mathrm{isc}} + k_{\mathrm{ic}} + k_{\mathrm{trans}} \tag{2}$$

$$k_{\mathrm{trans}} = 1/\tau_{\mathrm{DA}} - 1/\tau_{\mathrm{D}} \tag{3}$$

$$\Phi_{\mathrm{trans}} = k_{\mathrm{trans}}\tau_{\mathrm{DA}} = 1 - \tau_{\mathrm{DA}}/\tau_{\mathrm{D}} \tag{4}$$

Here, τ_{DA} is the excited-state lifetime of the excited porphyrin donor in the presence of the phthalocyanine acceptor, τ_{D} is the excited-state lifetime of the benchmark porphyrin monomer, k_{trans} is the energy-transfer rate, and Φ_{trans} is the energy-transfer efficiency. These equations assume that, besides energy transfer, there are no pathways for depopulating the excited porphyrin (P*) in the arrays other than the intrinsic processes (radiative decay (rad), intersystem crossing (isc), internal conversion (ic)) also present in the monomer. The transient absorption and static emission data support this assumption. However, within experimental uncertainty we cannot exclude the possibility of a small amount of electron transfer from the photoexcited porphyrin.

Table 1 gives the energy-transfer rate constants and yields obtained by application of eqs 1−4 to the excited-state lifetimes. The rate of excited-state energy transfer in each case is effectively given by the amplitude-weighted average excited-state lifetime of $\sim(5\ \mathrm{ps})^{-1}$. The energy-transfer yield is >99% except for $(MgP)_4MgPc$, where electron transfer provides an alternative decay channel for the porphyrin excited state. For $(H_2P)_4H_2Pc$ and $(ZnP)_4ZnPc$, the efficiency would not fall below 99% even if one based the calculation solely using the slower component of the energy transfer (~10 ps), and would be even closer to 99.9% if the major component of the porphyrin excited-state decay time (~1 ps) were used. Hence, although there is a complexity associated with the dual-exponential kinetics in these porphyrin−phthalocyanine arrays, the data are unequivocal in indicating an extremely rapid energy-transfer process.

3. Physical Properties of the Oxidized Complexes. The oxidation products of $(ZnP)_4ZnPc$ and $(MgP)_4MgPc$ were examined explicitly to assess the mobility of the hole/electron(s) among the MP arms of each star-shaped array. These studies were motivated by our earlier work on the pentaporphyrin array Zn_4FbU, which revealed that hole/electron hopping rates between the ZnP constituents are $10^7\ \mathrm{s}^{-1}$ (or faster).[21] The rapid hole/electron hopping in Zn_4FbU indicates that the central Fb constituent serves as an effective superexchange mediator. This role for the Fb constituent in the all-porphyrin arrays is dictated by the fact that the hole cannot physically reside on this porphyrin due to its substantially higher oxidation potential compared with the Zn porphyrin.[47] The oxidation potential of the Pc unit is anticipated to be much higher still than that of the corresponding porphyrin due to the electron-withdrawing influence of the four additional nitrogen atoms;[48] accordingly, the hole cannot reside on this constituent of the $(MP)_4MPc$ complexes. The issue in question is whether the MPc constituent of the pentads functions as an efficient superexchange mediator for hole/electron hopping.

The pentad $(ZnP)_4ZnPc$ exhibits two $E_{1/2}$ values at 0.61 and 0.89 V (vs Ag/Ag^+; $E_{1/2}$ $(FeCp_2/FeCp_2^+) = 0.22$ V). These potentials are essentially identical to those of the first and second oxidations of monomeric Zn porphyrins with the same aryl substituents.[49] Quantitative coulometry of $(ZnP)_4ZnPc$ indicates that the lowest potential peak is due to four overlapped one-electron oxidations of the Zn porphyrins. Square wave voltammetry shows that this peak is slightly asymmetric, owing to small differences in the $E_{1/2}$ values of the overlapping one-electron oxidations of the Zn porphyrins. This behavior directly parallels that previously observed for the Zn constituents of the Zn_4FbU array.[21] The redox behavior of $(MgP)_4MgPc$ is different from that of $(ZnP)_4ZnPc$. In particular, the Mg complex exhibits a single broad wave at ~0.39 V and no other resolved features. Cycling the potential resulted in degradation of the complex, as evidenced by the appearance of new features that were irreproducible with successive scans. Due to the instability of the oxidation products of $(MgP)_4MgPc$, spectroscopic studies of these π-cations were not pursued. It is noteworthy that phthalocyanines bearing other types of redox-active units, such as four ferrocene groups[50] or eight tetrathiafulvalene groups,[51] also exhibited complex electrochemical behavior.

The UV−vis absorption characteristics of oxidation products of $(ZnP)_4ZnPc$ (not shown) are typical of those of other porphyrin π-cation radicals, namely, blue-shifted B-bands (relative to the neutral complexes) and very weak, broad bands in the visible and near-infrared regions.[47] The absorption spectra of the oxidized complexes appear to be a superposition of neutral and cationic species. This observation and the results of the electrochemical studies are consistent with weak interactions between the constituent porphyrins.[52−54]

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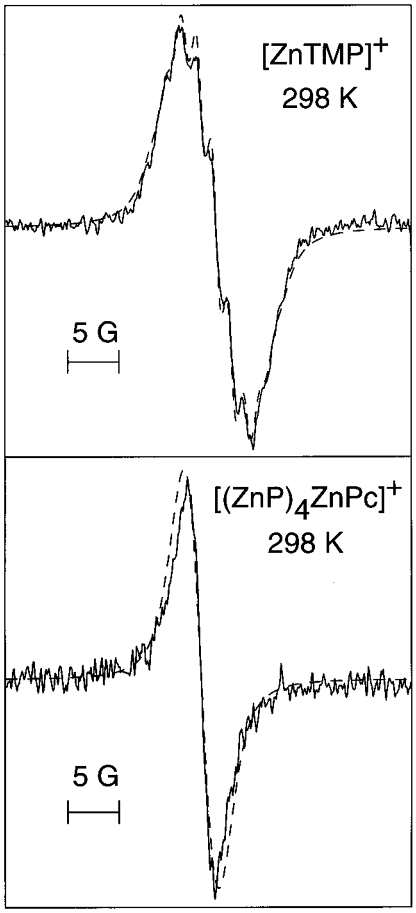

Figure 3. EPR spectra of $[(ZnP)_4ZnPc]^+$ and $[ZnTMP]^+$ in $CH_2Cl_2/CHCl_3$ (1:1) at 298 K. The dashed lines shown are simulated spectra.

The EPR spectrum of the one-electron oxidation product of $(ZnP)_4ZnPc$ at 298 K is shown in Figure 3. For comparison, the spectrum of the one-electron oxidation product of zinc tetramesitylporphyrin (ZnTMP) is also shown in the figure. In liquid solution, $[ZnTMP]^+$ exhibits a partially resolved nine-line hyperfine pattern due to interaction of the unpaired electron with the four pyrrole ^{14}N nuclei ($a(^{14}N) \approx 1.5$ G). This hyperfine pattern is characteristic of a $^2A_{2u}$ porphyrin π-cation radical.[55] The liquid solution EPR spectrum of $[(ZnP)_4ZnPc]^+$ exhibits a much narrower line than $[ZnTMP]^+$, with no resolved hyperfine structure. Simulations of the EPR spectrum of $[(ZnP)_4ZnPc]^+$ indicate that the line shape can be reasonably well accounted for by reducing the hyperfine coupling by a factor of 4 and quadrupling the number of interacting nuclei, while holding the line width constant (dashed line in the figure). If the constraint on the line width is relaxed, an essentially perfect fit to the EPR spectrum can be achieved. This behavior indicates that the hole/electron of $[(ZnP)_4ZnPc]^+$ is completely delocalized on the EPR time scale.[47,49] This time scale is determined by the ^{14}N hyperfine coupling, which is ~4 MHz. Thus, the hole/electron hopping rate in $[(ZnP)_4ZnPc]^+$ must be considerably faster (i.e., $\geq 10^7$ s^{-1}). The hole/electron hopping characteristics of $[(ZnP)_4ZnPc]^+$ exactly parallel those previously observed for $[Zn_4FbU]^+$.[21] Accordingly, the central ZnPc unit in $(ZnP)_4ZnPc$ is an effective superexchange mediator for hole/electron hopping.

Conclusion

Porphyrin–phthalocyanine light-harvesting arrays have been prepared by cyclotetramerization of substituted phthalonitriles. This straightforward method permits the easy isolation of the desired arrays by column chromatography. The complementary absorption properties of porphyrin and phthalocyanine chromophores make them ideal components of light-harvesting systems. Excited-state energy transfer from the porphyrin constituents to the phthalocyanine core in the arrays is rapid and generally extremely efficient, despite some complexities associated with dual-exponential behavior and charge transfer in limited cases where the thermodynamics are appropriate. Similarly, ground-state hole/electron hopping is rapid on the EPR time scale for the singly oxidized all-metal pentads. These results indicate that electronic communication is very effective among the constituents of these arrays. The efficient convergent synthesis and efficient light-harvesting properties augurs well for the construction of larger multiporphyrin–phthalocyanine light-harvesting arrays by this approach.

Experimental Section

General Procedures. ^1H NMR spectra were collected at 300 MHz. Mass spectra of porphyrins and multiporphyrin–phthalocyanine arrays were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix.[56] High-resolution fast atom bombardment (FAB) mass spectrometry of the arrays was carried out at greater than unit resolution. Signal-to-noise levels were not sufficient to allow measurement of the nominal exact mass ion, but the base peak in the isotope cluster was observed. Triphenylarsine, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used as received from Aldrich. 4-Iodobenzaldehyde was obtained from Karl Industries, Ltd.

Solvents. All solvents were dried by standard methods. CH_2Cl_2 (Fisher, reagent grade) and $CHCl_3$ (Fisher, certified ACS grade, stabilized with 0.75% ethanol) were distilled from K_2CO_3. Simple distillation does not significantly alter the ethanol content. Toluene (Fisher, certified ACS) and triethylamine (Fluka, puriss) were distilled from CaH_2. Pyrrole (Acros) was distilled at atmospheric pressure from CaH_2. All other solvents were used as received.

Chromatography. Adsorption column chromatography was performed using alumina (Fisher A-540, 80–200 mesh), grade V alumina,[8] or flash silica gel (Baker, 60–200 mesh). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1. A preparative scale glass column was packed using Bio-Beads SX-1 in tetrahydrofuran and eluted with gravity flow. Following purification, the SEC column was washed with two volume equivalents of solvents used.

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Analytical scale SEC was performed to assess the purity of the arrays. Analytical SEC columns (styrene−divinylbenzene copolymer) were purchased from Hewlett-Packard and Phenomonex. Analytical SEC was performed with a Hewlett-Packard 1090 HPLC using 100 Å (7.5 × 300 mm) columns eluting with THF (flow rate 0.8 mL/min). Sample detection was achieved by absorption spectroscopy using a diode array detector with quantitation at 420 and 354 nm (±10 nm bandwidth).

Static Absorption and Emission. Static absorption and fluorescence measurements were performed as described previously.[8,57] Nondeaerated samples with an absorbance ≤ 0.15 at λ_{exc} were used for the emission measurements; the detection band-pass was 4−5 nm, and the spectra were corrected for the detection-system spectral response. Emission quantum yields were measured relative to *meso*-tetraphenylporphyrin ($\Phi_f = 0.11$).[58]

Time-Resolved Fluorescence. Fluorescence lifetimes were determined by modulation (phase shift) techniques using a Spex Tau2 spectrometer. Samples (1−50 μM) in toluene were deaerated by bubbling with N_2. Samples were excited at several wavelengths in the Soret- and Q-band regions, and the emission at wavelengths >680 nm was detected using a long-pass filter. Modulation frequencies from 20 to 300 MHz were utilized, and both the fluorescence phase shift and modulation amplitude were analyzed in modeling the data. Lifetimes of a number of control samples obtained by this technique were found to be the same as obtained by us or others using time-resolved techniques.[59]

Time-Resolved Absorption. Transient absorption data were acquired as described elsewhere.[30,60] In short, samples (~0.2 mM in toluene) in 2 mm path length cuvettes at room temperature were excited at 10 Hz with a ~130 fs, 4−7 μJ pulse at 420 or 550 nm from an optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system (Spectra Physics). Transient absorption difference spectra were obtained using broad-band detection methods utilizing a ~130 fs white light probe pulse. The time evolution of the spectra was obtained by varying the pump−probe delay with an optical delay pump pulse. The kinetic data shown in Figure 2 were generated by averaging the ΔA values in 10 nm intervals about the specified center wavelength, namely, 420 nm for the porphyrin bleaching and 685 or 718 nm for the phthalocyanine bleaching. The kinetic traces were then fit to a function consisting of either a single or dual exponential plus a constant using a nonlinear least squares algorithm (taking into account the instrument rise and pre-zero-time data, which are not shown in Figure 2 for clarity).

Electrochemistry. The oxidized complexes were prepared and manipulated in a glovebox as previously described.[21] The solvent used for the studies consisted of a 1:1 mixture of $CH_2Cl_2/CHCl_3$. This mixture was used because the solubility in pure CH_2Cl_2 was poor. Tetrabutylammonium hexafluorophosphate (0.1 M) (Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) was used as the supporting electrolyte. The potentials reported are vs Ag/Ag$^+$; $E_{1/2}(FeCp_2/FeCp_2^+) = 0.22$ V. The integrity of the samples was checked by cyclic voltammetry after oxidation. For (ZnP)$_4$ZnPc, the cyclic voltammograms were reproducible upon repeated scans and exhibited no scan-rate dependence in the 20−100 mV/s range. For (MgP)$_4$MgPc, the π-cation radical species could not be generated quantitatively due to instability of the complex (vide supra). For all of the oxidized complexes, spectroscopic studies were performed immediately after oxidation and transfer of the samples to an optical cuvette or quartz capillary.

EPR Spectroscopy. The EPR spectra were recorded as previously described.[21] The sample concentrations for all of the experiments were typically 0.05 mM. The microwave power and magnetic field modulation amplitude were typically 5.7 mW and 0.32 G, respectively.

Syntheses. The synthesis of each complex was performed as follows.

4-[2-(3,4-Dicyanophenyl)ethynyl]benzaldehyde (1). Samples of 4-iodophthalonitrile[61] (0.98 g, 3.85 mmol), 4-ethynylbenzaldehyde[62] (0.50 g, 3.85 mmol), $Pd_2(dba)_3$ (35.6 mg, 0.04 mmol), and $AsPh_3$ (95.0 mg, 0.31 mmol) were added to a 25 mL three-neck round-bottom flask equipped with a condenser. The reaction vessel headspace including the condenser was deaerated with a high flow rate of argon for 30 min. Then deaerated triethylamine (15 mL) and THF (5 mL) were added via a syringe, and argon was purged through the vessel for another 5 min. At this point the argon flow was decreased, the reaction vessel was immersed in an oil bath at 35 °C, and the mixture was stirred overnight. Upon completion of the reaction as judged by TLC, CH_2Cl_2 (100 mL) was added to the reaction mixture to dissolve the product, and the resulting solution was washed with 5% $NaHCO_3$, H_2O, and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the resulting brown solid was redissolved in CH_2Cl_2/hexanes (3:2), and loaded onto a silica gel column (3.5 × 25 cm) packed with the same solvent. Elution with CH_2Cl_2/hexanes (3:2) afforded $AsPh_3$ as the first colorless fraction, followed by a brown band and then a yellow band which contained traces of uncharacterized species. The desired compound then eluted as a colorless band, which after removal of the solvent afforded 0.85 g (86%) of a white solid: mp 155−156 °C; IR (neat film) ν 2212 (CN), 1696 (CO), 1599, 1205, 1157, 833, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70−7.73 (m, 2 H), 7.84−7.86 (m, 2 H), 7.91−7.96 (m, 3 H), 10.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 88.99, 95.23, 114.78, 115.13, 115.20, 116.65, 127.41, 128.67, 129.87, 132.71, 133.78, 135.91, 136.33, 136.65, 191.33; HRMS (EI) calcd for $C_{17}H_{18}N_2O$ 256.0637, found 256.0628. Anal. Calcd: C, 79.68; H, 3.15; N, 10.93. Found: C, 79.80; H, 3.10; N, 10.92.

5,10,15-Trimesityl-20-{4-[2-(3,4-dicyanophenyl)ethynyl]-phenyl}porphyrin (2). Samples of mesitaldehyde (0.79 mL, 5.3 mmol), **1** (453 mg, 1.77 mmol), and pyrrole (0.49 mL, 7.1 mmol) were condensed in $CHCl_3$ (700 mL) with $BF_3 \cdot O(Et)_2$ (0.86 mL of 2.5 M stock solution in $CHCl_3$) at room temperature for 1 h. Then DDQ (1.22 g, 5.38 mmol) was added, and after the mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was then dissolved in CH_2Cl_2/hexanes (1:1, 50 mL) and passed through a short silica gel column to remove the non-porphyrinic components from the crude reaction mixture. The resulting mixture of porphyrins was redissolved in CH_2Cl_2/hexanes (2:3) and loaded onto a flash silica gel column (6 × 10 cm). Elution with the same solvent afforded tetramesitylporphyrin, and then elution with CH_2Cl_2/hexanes (1:1) gave the desired compound as the second band, affording 320 mg (20%) of a purple solid: IR (neat film) ν 3309 (NH), 2917 (CH), 2209 (CN), 1592, 1467, 1347, 1211, 1189, 965, 851, 802, 737 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −2.57 (s, 2 H), 1.85 (s, 18 H), 2.63 (s, 9 H), 7.28 (s, 6 H), 7.85−8.07 (m, 5 H), 8.24 (d, $J = 8.1$ Hz, 2 H), 8.64 (m, 4 H), 8.69 (d, $J = 5.3$ Hz, 2 H), 8.74 (d, $J = 5.3$ Hz, 2 H); LD-MS calcd av mass 891.1, obsd 889.5; HRMS (FAB) calcd for $C_{63}H_{50}N_6$ 890.4097, found 890.4144; λ_{abs} (toluene) 421, 516, 549, 593, 650 nm.

2(3),9(10),16(17),23(24)-Tetrakis{2-[4-(magnesium-5,-10,15-trimesityl-20-porphinyl)phenyl]ethynyl}phthalocyaninatomagnesium [(MgP)$_4$MgPc]. A mixture of **2** (100

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mg, 0.11 mmol), $MgCl_2$ (100 mg, 1.1 mmol), and two drops of DBU in dry 1-pentanol (4 mL) was heated at reflux with stirring under an argon atmosphere. The reaction mixture started to change from red to green after 1 h, and the reaction mixture was refluxed for 24 h. After being cooled to room temperature, the green mixture was poured into a solution of CH_3OH/H_2O (5:1, 20 mL). The resulting precipitate was collected by centrifugation and washed with CH_3OH. Column chromatography on alumina (grade V, 4 × 20 cm) with toluene/ethyl acetate (10:1) gave two bands (red first and then green), the second band of which (green) was the desired compound. Further purification was achieved by dissolving the desired compound in THF and chromatography on a preparative SEC column packed with THF (3 × 45 cm). Gravity elution afforded the desired compound as the first band, affording 46.5 mg (45%) of a purple solid: IR (neat film) ν 2917, 1609, 1477, 1200, 1060, 997, 799, 721 cm^{-1}; ^1H NMR (THF-d_8) δ 1.80−1.90 (m, 72 H), 2.44−2.62 (m, 36 H), 7.21−7.31 (m, 24 H), 8.16−8.40 (m, 16 H), 8.48−8.85 (m, 32 H), 9.63−9.71 (m, 4 H), 9.87, 9.92 (m, 4 H), 10.84 (br s, 4 H); LD-MS calcd av mass for $C_{252}H_{192}N_{24}Mg_5$ 3677.8, obsd 3675.0; HRMS (FAB) obsd 3677.3; λ_{abs} (toluene) 310, 365, 427, 566, 608, 710 nm.

2(3),9(10),16(17),23(24)-Tetrakis{2-[4-(5,10,15-trimesityl-20-porphinyl)phenyl]ethynyl}phthalocyanine[$(H_2P)_4H_2Pc$]. A sample of $(MgP)_4MgPc$ (10 mg, 2.7 μmol) was dissolved in $CHCl_3$ (10 mL), then TFA (1 mL) was added, and the solution was stirred under argon for 1 h. Dichloromethane (20 mL) was then added, and the solution was washed carefully with 5% $NaHCO_3$, then triethylamine (1 mL) was added, and the resulting solution was washed again with 5% $NaHCO_3$ and then dried (Na_2SO_4). After removal of the solvent, the solid was dissolved in a minimum volume of toluene and loaded onto a flash silica gel column (3.5 × 12 cm). Elution with toluene afforded the desired compound as the first (green-brown) band. Removal of the solvent and washing the resulting solid with methanol afforded 6.6 mg (68%) of a black solid: IR (neat film) ν 3316 (NH), 2921, 1605, 1467, 1215, 1093, 1013, 970, 799, 740 cm^{-1}; ^1H NMR (THF-d_8) δ −2.56 (br s, 10 H), 1.30−1.62 (m, 72 H), 2.44−2.53 (m, 36 H), 6.65−7.21 (m, 24 H), 8.18−9.03 (m, 48 H), 9.08−9.37 (m, 8 H), 10.84 (m, 4 H); LD-MS calcd av mass for $C_{252}H_{202}N_{24}$ 3566.5, obsd 3565.3; HRMS (FAB) obsd 3565.8; λ_{abs} (log ϵ) (toluene) 421 (6.17, fwhm = 15 nm), 515 (4.90), 688 (5.29), 723 (5.37) nm. Alternatively, a solution of $(ZnP)_4MgPc$ (6.0 mg, 1.6 μmol) in $CHCl_3$ (10 mL) was treated with TFA (1 mL), and the reaction mixture was worked up and the product purified in identical fashion, affording 3.9 mg (70%) of a black solid.

2(3),9(10),16(17),23(24)-Tetrakis{2-[4-(5,10,15-trimesityl-20-porphinyl)phenyl]ethynyl}phthalocyaninatomagnesium [$(H_2P)_4MgPc$]. To a solution of $(MgP)_4MgPc$ (10 mg, 2.7 μmmol) in CH_2Cl_2 (10 mL) was added silica gel (1.0 g). The mixture was stirred overnight at room temperature under an argon atmosphere with shielding from ambient light. Upon completion of the demetalation as judged by LD-MS, the reaction mixture was filtered under vacuum through a fritted glass funnel, and the filtrate was washed with CH_2Cl_2/ethyl acetate (1:1) until it was colorless. The filtrate was then evaporated to dryness under reduced pressure, and purified by column chromatography (silica gel, 3.5 × 10 cm, toluene/ethyl acetate; 20:1), affording the desired product as a green-brown band. Removal of the solvent and washing the solid with methanol afforded 7.2 mg (74%) of a black solid: IR (neat film) ν 3313 (NH), 2914, 1610, 1464, 1345, 1210, 1081, 968, 800, 736 cm^{-1}; ^1H NMR (THF-d_8) δ −2.44, −2.37 (m, 8 H), 1.78−1.94 (m, 72 H), 2.43−2.62 (m, 36 H), 7.21−7.33 (m, 24 H), 8.25−8.43 (m, 16 H), 8.59−8.95 (m, 32 H), 9.62−9.68 (m, 4 H), 9.86, 9.92 (m, 4 H), 10.83, 10.85 (m, 4 H); LD-MS calcd av mass for $C_{252}H_{200}N_{24}Mg$ 3588.8, obsd 3592.6; HRMS (FAB) obsd 3588.5; λ_{abs} (log ϵ) (toluene) 421 (6.21, fwhm = 16 nm), 516 (4.96), 551 (4.63), 702 (5.37) nm.

2(3),9(10),16(17),23(24)-Tetrakis{2-[4-(zinc-5,10,15-trimesityl-20-porphinyl)phenyl]ethynyl}phthalocyaninatomagnesium [$(ZnP)_4MgPc$]. To a solution of $(H_2P)_4$-MgPc (6.0 mg, 1.7 μmol) in $CHCl_3$ (15 mL) was added $Zn(OAc)_2{\cdot}2H_2O$ (20 mg, 0.091 mmol) in CH_3OH (2 mL), and the reaction mixture was stirred magnetically at room temperature overnight under an argon atmosphere. The metalation was complete as judged by TLC and LD-MS. The green-brown mixture was then diluted with $CHCl_3$ (25 mL), washed with 5% $NaCHCO_3$, dried (Na_2SO_4), and filtered and the solvent removed under reduced pressure. Column chromatography on flash silica gel (3.5 × 10 cm) eluting with toluene/ethyl acetate (20:1) gave the product as a black solid. The solid was suspended in methanol, centrifuged, and dried under vacuum, affording 6.18 mg (96.2%): IR (neat film) ν 2914, 1611, 1483, 1449, 1332, 1198, 1087, 998, 798 cm^{-1}; ^1H NMR (THF-d_8) δ 1.79−1.93 (m, 72 H), 2.42−2.62 (m, 36 H), 7.21−7.31 (m, 24 H), 8.22−8.40 (m, 16 H), 8.58−8.74 (m, 24 H), 8.84−8.93 (m, 8 H), 9.62−9.70 (m, 4 H), 9.87−9.92(m, 4 H), 10.83, 10.84 (m, 4 H); LD-MS calcd av mass for $C_{252}H_{192}N_{24}$-$MgZn_4$ 3842.3, obsd 3844.5; HRMS (FAB) obsd 3842.4; λ_{abs} (log ϵ) toluene 424 (6.10, fwhm = 14 nm), 551 (4.83), 634 (4.59), 702 (5.29) nm.

2(3),9(10),16(7),23(24)-Tetrakis{2-[4-(zinc-5,10,15-trimesityl-20-porphinyl)phenyl]ethynyl}phthalocyaninatozinc [$(ZnP)_4ZnPc$]. A mixture of **2** (50 mg, 0.055 mmol), zinc acetate (50 mg, 0.30 mmol), and two drops of DBU in dry 1-pentanol (2 mL) was heated at reflux for 36 h with stirring under an argon atmosphere. After being cooled to room temperature, the green mixture was poured into a solution of CH_3OH/H_2O (5:1, 15 mL). The resulting precipitate was collected by centrifugation and washed with CH_3OH. Column chromatography on silica gel (3.5 × 20 cm) eluting with toluene/ethyl acetate (20:1) afforded the desired compound as the first band. The compound obtained was further purified by dissolving it in THF with chromatography on a preparative SEC column (3 × 45 cm) packed with THF. Gravity elution afforded the desired compound as the first band. Removal of solvent and washing the solid with methanol afforded 8.0 mg (15%) of a purple solid: IR (neat film) ν 2918, 1613, 1494, 1336, 1204, 1090, 998, 798, 723 cm^{-1}; ^1H NMR (THF-d_8) δ 1.79−1.85 (m, 72 H), 2.43−2.55 (m, 36 H), 7.13−7.29 (m, 24 H), 8.34−8.45 (m, 16 H), 8.57−8.98 (m, 32 H), 9.40−9.64 (m, 8 H), 10.84, (br s, 4 H); LD-MS calcd av mass for $C_{252}H_{192}N_{24}$-Zn_5 3883.4, obsd 3888.9; HRMS (FAB) obsd 3883.1; λ_{abs} (log ϵ) (toluene) 421 (6.21, fwhm = 14 nm), 550 (4.93), 631 (4.74), 701 (5.49) nm.

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Supporting Information Available: ^1H NMR and LD-MS spectra for all porphyrins and porphyrin−phthalocyanine arrays, and absorption and fluorescence spectra for all porphyrin−phthalocyanine arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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