A Tightly Coupled Linear Array of Perylene, Bis(Porphyrin), and Phthalocyanine Units that Functions as a Photoinduced Energy-Transfer Cascade

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We have prepared a linear array of chromophores consisting of a perylene input unit, a bis(free base porphyrin) transmission unit, and a free base phthalocyanine output unit for studies in artificial photosynthesis and molecular photonics. The synthesis involved four stages: (1) a rational synthesis of *trans*-AB_2C-porphyrin building blocks each bearing one meso-unsubstituted position, (2) oxidative, meso,meso coupling of the zinc porphyrin monomers to afford a bis(zinc porphyrin) bearing one phthalonitrile group and one iodophenyl group, (3) preparation of a bis(porphyrin)−phthalocyanine array via a mixed cyclization involving the bis(free base porphyrin) and 4-*tert*-butylphthalonitrile, and (4) Pd-mediated coupling of an ethynylperylene to afford a perylene−bis(porphyrin)−phthalocyanine linear array. The perylene−bis(porphyrin)−phthalocyanine array absorbs strongly across the visible spectrum. Excitation at 490 nm, where the perylene absorbs preferentially, results in fluorescence almost exclusively from the phthalocyanine ($\Phi_f = 0.78$). The excited phthalocyanine forms with time constants of 2 ps (90%) and 13 ps (10%). The observed time constants resemble those of corresponding phenylethyne-linked dyads, including a perylene−porphyrin ($\leq$0.5 ps) and a porphyrin−phthalocyanine (1.1 ps (70%) and 8 ps (30%)). The perylene−bis(porphyrin)−phthalocyanine architecture exhibits efficient light-harvesting properties and rapid funneling of energy in a cascade from perylene to bis(porphyrin) to phthalocyanine.

Introduction

One of our objectives is to construct multipigment arrays that strongly absorb visible light and funnel the resulting excited-state energy rapidly and efficiently to a designated site.[1−4] Such arrays can serve as light-harvesting elements in artificial photosynthetic systems or as wires in molecular photonic devices. One means of directing the flow of energy toward the final energy acceptor involves the use of a systematic energy cascade along a sequential array of pigments.[5] We have constructed two examples of such a system (**1**[6] and **2**[7]) that incorporate a boron-dipyrrin dye (input), one or three zinc porphyrins (transmission unit), and a free base porphyrin (output) (Chart 1). The positioning of input and output units at opposite ends of the linear array enables detection of the flow of energy from one end of the assembly to the other. In the case of **1** or **2**, preferential excitation of the boron-dipyrrin dye input unit results in emission almost exclusively from the free base porphyrin output unit.

We sought to refine the design of **1** and **2** by incorporating different pigments with characteristics that would extend the range of possible applications and by employing linkers that provide stronger electronic coupling among the pigments and thus faster rates of photoinduced energy transfer. The design we chose (**3**) is shown in Chart 1. The changes to the composition of array **3** relative to **1** and **2** are as follows:

(1) For the input unit, a perylene unit is employed in place of the boron-dipyrrin dye. The well studied perylene dye, perylene-3,4,9,10-bis(dicarboximide), exhibits strong absorption in the spectral region between the porphyrin Soret and Q bands ($\epsilon_{490\ \mathrm{nm}} \sim$50,000 M^{-1} cm^{-1}),[8] near-unity fluorescence quantum yield,[9] a long and monophasic fluorescence lifetime ($\sim$3.8 ns),[10] and very high photostability.[9] Perylene−porphyrin[11] and perylene−phthalocyanine[12] dyads that incorporate perylene−bis(imides)

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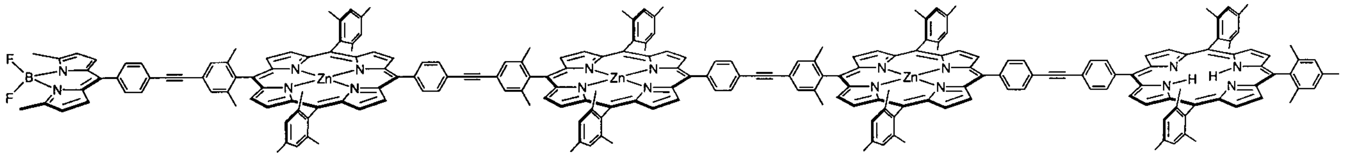
Chart 1



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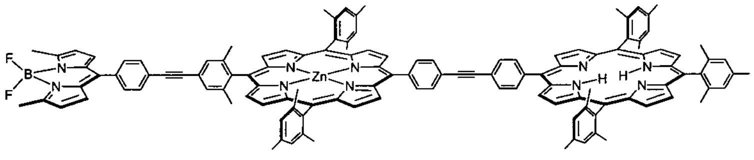

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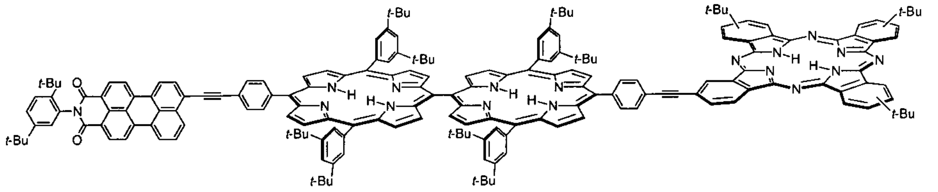
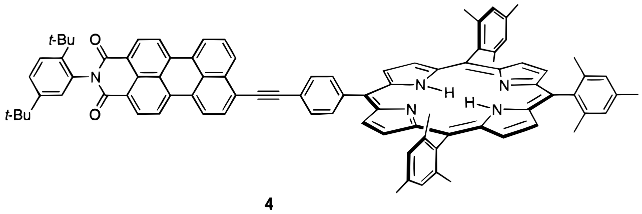


3

have been reported. Perylene–monoimide dyes also have been prepared and exhibit attractive absorption features,[13] though much less is known about their excited-state properties. Based on considerations of the effects of orbital ordering on electronic communication and electron-density distributions,[14] we chose a perylene monoimide dye rather than a bis(imide) dye for use as the input unit (vide infra). We have recently found that excited-state energy transfer from a perylene monoimide to a free base porphyrin via an ethynylphenyl linker (**4**) is extremely fast (≤0.5 ps).[7]



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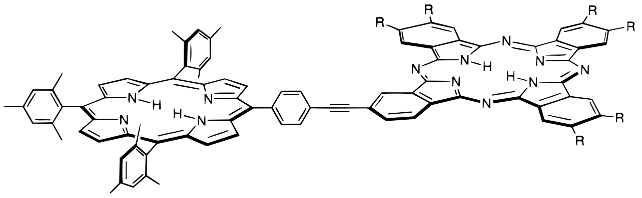
(2) For the output unit, a free base phthalocyanine is employed in place of the free base porphyrin. Phthalocyanines absorb very strongly in the red and can emit with a very high fluorescence quantum yield (0.7–0.8). We recently studied the energy-transfer properties of phenylethynyl-linked porphyrin–phthalocyanine dyads[15] (and star-shaped pentads)[16] and observed strong absorption in the blue and red as well as rapid (≤10 ps) energy transfer from porphyrin to the phthalocyanine. A variety of free base and metalated porphyrin–phthalocyanine combinations were examined. A dyad comprised of a free base porphyrin and a free base phthalocyanine (**5**) gave a high yield (>98%) of energy transfer without noticeable photochemical side reactions.



5 R = *n*-heptyl

Furthermore, the excited-state energy characteristics are such that downhill energy flow from a porphyrin to a phthalocyanine can be achieved independent of the metalation states of the units, providing advantages in the design, synthesis, and utility of the devices.[1,15,16] In particular, free base porphyrins can be used as energy-transfer donors or transmission elements with free base phthalocyanines as acceptors; in contrast, when zinc porphyrins and free base porphyrins are used exclusively in arrays, the latter must serve as the energy-transfer acceptor.

(3) For the transmission unit, we sought to incorporate a meso,meso-linked porphyrin dimer. Osuka and coworkers have pioneered the synthesis of all-meso-linked multiporphyrin arrays comprised of up to 128 porphyrins.[17–23] To our knowledge, energy-transfer studies

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of such meso,meso-linked arrays have not been performed with input and output units on opposite ends of a linear array. The combination of perylene, meso,meso-linked porphyrins, and phthalocyanine is anticipated to absorb strongly across the visible spectrum, enhancing the light-harvesting capabilities of the array.

(4) For the linker joining the pigments, we employed a phenylethyne unit in place of the diphenylethyne unit in order to facilitate stronger interpigment electronic coupling and more rapid rates of energy transfer.

We also sought to refine the synthetic methodology for constructing linear arrays of pigments. The synthesis of **1** and **2** involved the repetitive use of Pd-coupling reactions, requiring extensive chromatography at each stage of the synthesis. In our recent synthesis of multi-porphyrin−phthalocyanine arrays,[1,16] we employed complementary chemistries in successive stages of the synthetic plan. The latter approach avoids accumulation of similar byproducts at each stage and affords the opportunity for distinct purification regimens following each stage of synthesis. The synthesis of a linear array comprised of perylene, bis(porphyrin), and phthalocyanine units requires reactions involving porphyrin formation, phthalocyanine formation, meso,meso-coupling, and Pd-coupling methods.

In this paper, we present the synthesis of a linear array of perylene, meso,meso-linked porphyrin dimer, and phthalocyanine chromophores (**3**). Examination of the static absorption and fluorescence spectra in toluene reveal strong absorption across the visible spectrum and efficient funneling of energy from perylene to phthalocyanine. The photodynamics of energy transfer have been investigated by time-resolved absorption spectroscopy.

Results

Synthesis Approach. We sought to prepare a sequential array containing perylene, meso,meso-linked porphyrin dimer, and phthalocyanine chromophores in a linear or star-shaped architecture. The strategy we intended to utilize involved the following steps: (1) Pd-mediated coupling of the perylene and a porphyrin yielding a perylene−porphyrin dyad, (2) the synthesis of a porphyrin−phthalocyanine pentad (star-shaped architecture) or dyad (linear architecture) by cyclization of a porphyrin−phthalonitrile, and (3) the oxidative meso,-meso-coupling of the perylene−porphyrin dyad with the porphyrin−phthalocyanine pentad or dyad. The investigation of this route revealed unanticipated difficulties with these various chemistries. The route that succeeded involved oxidative coupling to give the meso,meso-linked porphyrin dyad bearing one iodo group and one phthalonitrile moiety, conversion to the phthalocyanine to give the bis(porphyrin)−phthalocyanine, and Pd-mediated coupling to attach the perylene unit to the functionalized bis(porphyrin) to give the linear array (**3**).

Preparation of Building Blocks. The synthesis of a perylene dye building block employs chemistry established by Langhals and co-workers. The 2,5-di-*tert*-butylphenyl group was selected as one *N*-aryl substituent to enhance the solubility, chemical stability, and light fastness.[8−10,13] For rapid through-bond energy transfer, the linker should be attached at sites where the frontier molecular orbitals of the donor and acceptor have high electron density.[14] For porphyrins bearing electron-rich groups at the meso positions, the a_{2u} orbital is generally the HOMO. The a_{2u} orbital has considerable electron density at the meso carbons but little density at the β-pyrrole positions. Accordingly, such porphyrins should be joined to the linker at the meso rather than the β-position.[14] For perylenes, the orbital coefficients at the 3, 4, 9, and 10 positions are large,[24] consistent with a significant influence by the 3,4,9,10-substituents (and little or no influence by the *N*-substituents)[25] on the absorption spectra. Due to the very large orbital coefficient at the 9-position,[24] substitution at this site appeared particularly attractive for enabling efficient linker-mediated electronic communication between the perylene and the porphyrin. Accordingly, we decided to synthesize a perylenedicarboximide derivative bearing an ethyne at the 9-position. Bromination of the perylene mono-imide **6** as described by Feiler et al.[13] afforded **7** (Scheme 1). Subsequent Pd-mediated coupling[26] with trimethylsilylacetylene gave the ethyne-substituted perylene dye **8**, which was deprotected using Bu_4NF on silica gel to give the ethynyl perylene dye **9**. Treatment of **9** with iodobenzene under Pd-coupling conditions afforded the phenyl-capped ethynylperylene (**10**) for use as a photophysical reference compound.

The requisite porphyrin building blocks are of the trans-AB_2C type, which can be prepared using a rational synthesis that we recently developed.[27,28] In this approach, a dipyrromethane and a dipyrromethane-dicarbinol are reacted under mild nonscrambling conditions to give the corresponding porphyrin. The dipyrromethanes are produced in a one-flask synthesis, and the dipyrromethane-dicarbinols are obtained by diacylation of the dipyrromethane followed by reduction. Thus, reaction of **11**[29] and **13**[30] afforded porphyrin **14** in 18% yield (Scheme 2). However, the solubility of **14** was poor despite the presence of two 4-*tert*-butylphenyl groups. In an effort to prepare more soluble porphyrin building blocks, **12**[29] and **13** were reacted to give porphyrin **15**, which bears two 3,5-di-*tert*-butylphenyl groups. The solubility of **15** is high and rivals that of porphyrins bearing *meso*-mesityl groups. It is noteworthy that no detectable scrambling of the meso substituents was observed in the preparation of porphyrins **14** and **15**.

The synthesis of porphyrin−phthalocyanine arrays (pentads or dyads) where the porphyrin has a free meso site is best accomplished using a trans porphyrin bearing one phthalonitrile group and one free meso site. We have previously prepared porphyrin−phthalocyanine pentads by cyclization of an A_3B-type porphyrin bearing

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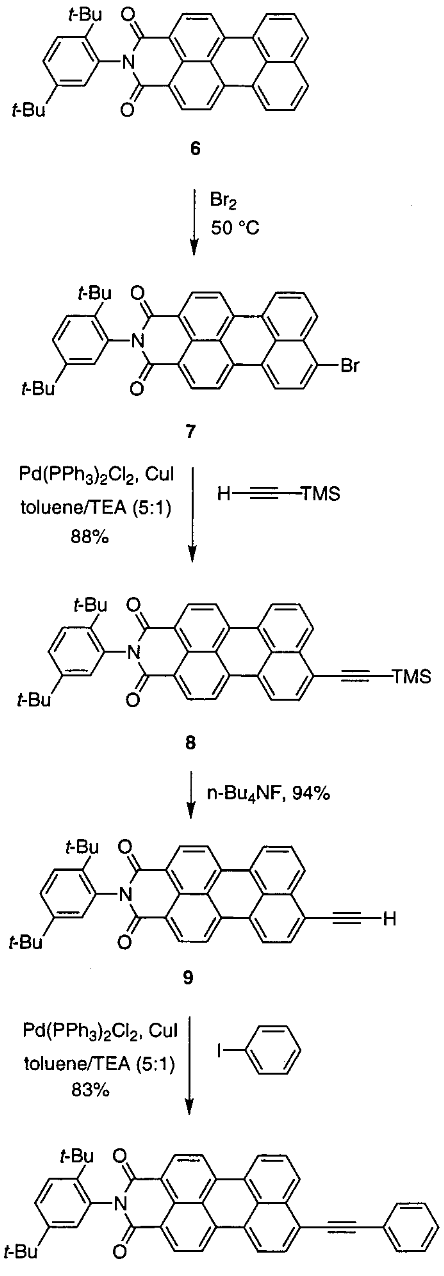
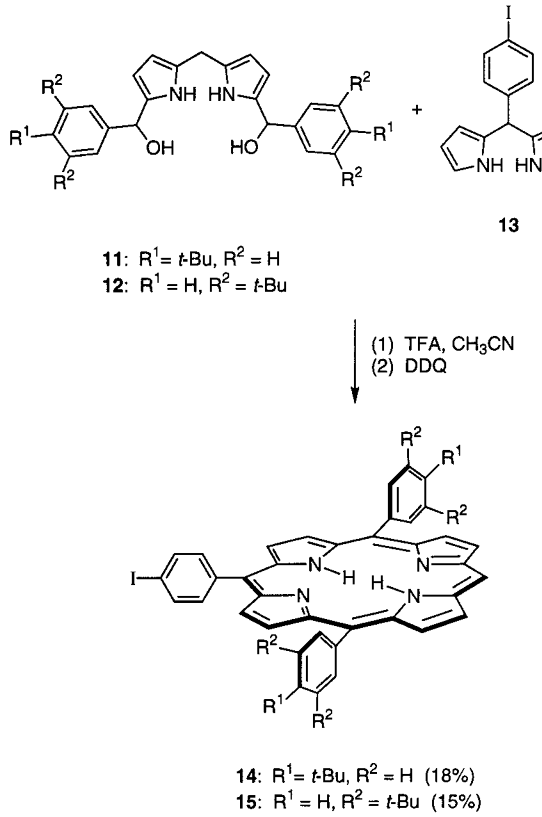
Scheme 1



Scheme 2



a phthalonitrile group[16] and porphyrin–phthalocyanine dyads by mixed cyclization of the same porphyrin–phthalonitrile and an alkyl-substituted phthalonitrile.[15] The synthesis of a trans porphyrin bearing one phthalonitrile group and one free meso site is shown in Scheme 3. Treatment of 5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-dipyrromethane (**16**, not shown)[27] with K_2CO_3 afforded the unprotected ethyne **17**,[28] which was coupled with 4-iodophthalonitrile[31] to give the desired dipyrromethane **18** on a multigram scale. The reaction of **18** and **11** under the standard conditions for dipyrromethane + dipyrromethane-dicarbinol coupling afforded porphyrin **19** in 23% yield. The solubility of **19** was poor, so **18** and **12** were reacted to give **20**, which proved to be more soluble. Again, no detectable scrambling of the meso substituents was observed in the preparation of porphyrins **19** and **20**.

Routes to Arrays. Perylene–porphyrin dyads were prepared by coupling an ethynylperylene dye (**9**) with the meso-unsubstituted porphyrin **14** or **15** under Pd-mediated conditions that are compatible with porphyrins,[32] affording the corresponding dyads **22** or **23** (Scheme 4). Though the solubility of **14** was poor, the addition of the perylene unit in dyad **22** greatly increased the solubility. A perylene–porphyrin dyad of interest as a photochemical benchmark was prepared in similar manner by first coupling the ethynylperylene dye (**9**) and iodo-substituted zinc porphyrin (**21**) to give **Zn-4** in 88% yield (Scheme 5). The zinc porphyrin **21** is conveniently obtained upon separation of a mixture of zinc porphyrins following a mixed-aldehyde condensation.[33] Demetalation with TFA then gave the desired reference dyad **4** containing the free base porphyrin.

We initially sought to prepare a star-shaped array with a phthalocyanine at the core and perylene–bis(porphyrin) units as radial arms. In our prior syntheses of porphyrin-phthalocyanine light-harvesting arrays from porphyrin-phthalonitriles,[1,15,16] the classical Linstead conditions[34] (lithium pentoxide in refluxing pentanol) afforded higher yields than the more modern Shiraishi conditions[35] (DBU and a metal salt in refluxing pentanol). The cyclization of **19** under Linstead conditions gave the characteristic color changes of a typical phthalocyanine forming reaction, but the product **24** could not be isolated, presumably due to the insolubility of the products (Scheme 6). The

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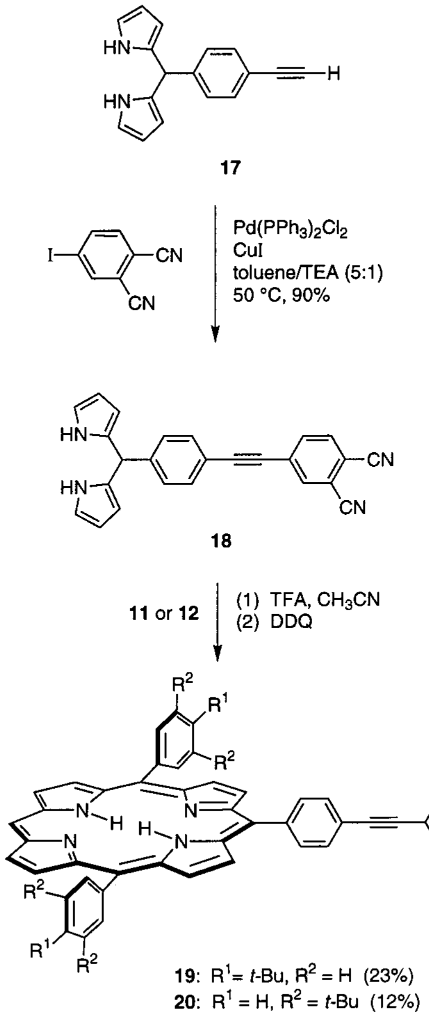
Scheme 3



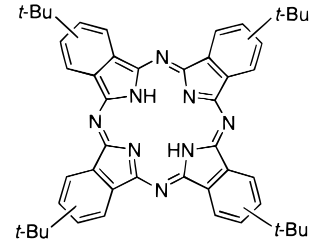
cyclization of **20** under the same conditions gave the desired pentad **25** in 32% yield. The star-shaped array **25** is similar to those prepared previously except for the lone unsubstituted meso position on each porphyrin. The metalation of **25** with zinc acetate resulted in formation of the array comprised of four zinc porphyrins and one free base phthalocyanine (**Zn25**), as evidenced by the characteristic absorption spectrum, emission spectrum (free base phthalocyanine band at 725 nm), and intense molecule ion peak observed upon LD-MS analysis. The selective metalation of a porphyrin in a porphyrin−phthalocyanine array has been demonstrated previously.[15,16] Treatment of **Zn-25** with excess perylene−porphyrin **Zn-22** under oxidative coupling conditions ($AgPF_6$, DMA, $CHCl_3$, room temperature) slightly modified[29] from those originally developed by Osuka[17,22] afforded a complex mixture of products in which incomplete coupling was observed and purification proved to be difficult. This result prompted a change of strategy that led us to develop a perylene−porphyrin−porphyrin trimer (**27**), which incorporated a phthalonitrile group for subsequent phthalocyanine formation.

A route to the perylene−bis(porphyrin) triad **Zn-27** is shown in Scheme 7. Oxidative coupling of **Zn-15** and **Zn-20** gave the zinc porphyrin dyad **Zn-26** (45% yield), as well as the homocoupled product of **Zn-15** (30% yield) and the homocoupled product of **Zn-20** (23% yield) (assignments of homocoupled products based on LD-MS). The products were readily separated by chromatography on silica. The Pd-mediated coupling of **Zn-26** and ethynylperylene **9** afforded **Zn-27** in 82% yield.

The cyclization of **Zn-27** to form the phthalocyanine at the core of a star-shaped array proved to be unsuccessful. The reaction under Linstead conditions resulted in decomposition of the perylene dye, and no product was obtained upon use of Shiraishi conditions. Attempts to construct a linear array by a mixed cyclization of **Zn-27** and 4-*tert*-butylphthalonitrile under Shiraishi conditions also failed, as did the similar reaction of **Zn-26** (or free base **26**) and 4-*tert*-butylphthalonitrile.

We then turned to the preparation of a linear array with the desired sequence of perylene, bis(porphyrin), and phthalocyanine units. Treatment of free base bis(porphyrin) **26** and 4-*tert*-butylphthalonitrile under Linstead conditions afforded the desired bis(porphyrin)−phthalocyanine triad **28** in 30% yield (Scheme 8). The final reaction in the synthesis of the linear array involved the Pd-mediated coupling of **28** and **9**, affording **3** in 58% yield. Note that **3** exists as a number of isomers. There are four possible regioisomers due to the position of the *tert*-butyl groups at the periphery of the phthalocyanine moiety, two isomers due to the orientation of the 2,5-di-*tert*-butylphenyl group attached to the perylene dye, and other (interconverting) isomers due to the orientation of the N−H protons at the core of the phthalocyanine and the two porphyrins.

To serve as a benchmark for photochemical studies, meso,meso-linked porphyrin dimer **30** was prepared by the route shown in Scheme 9. Oxidative meso,meso-coupling of **29** afforded **Zn-30** in 83% yield (obtained previously from a mixed meso,meso-coupling reaction[29]). Demetalation of **Zn-30** with TFA gave the free base **30** in 95% yield. Tetra-*tert*-butylphthalocyanine **31** served as a spectroscopic reference compound for the phthalocyanine unit in **3**.



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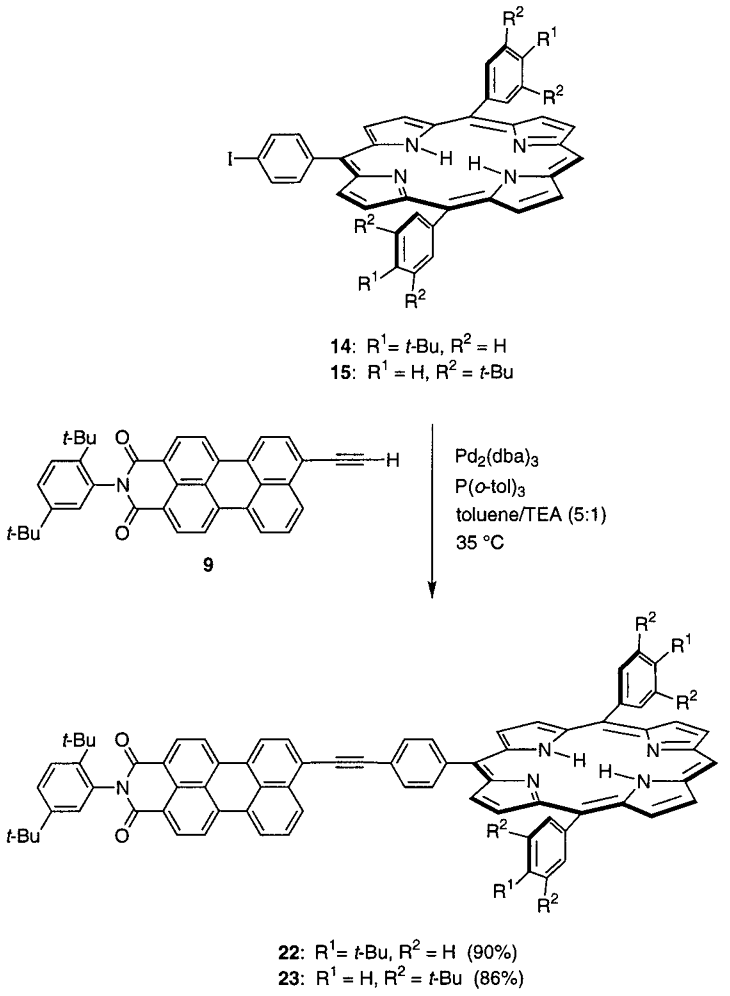
Absorption and fluorescence spectra. The absorption spectrum of **3** in toluene at room temperature is shown in Figure 1. The linear array **3** absorbs strongly across much of the visible region. Figure 1 also shows spectra of reference compounds representing the subunits of **3**: the phenylethynylperylene monoimide (**10**), the meso,meso-linked porphyrin dimer (**30**), and tetra-*tert*-butylphthalocyanine (**31**). The spectrum of the linear array resembles but does not match the sum of the spectra of the component parts, due largely to the effects of the ethynylphenyl linker on the perylene and the phthalocyanine units.

The dramatic splitting of the porphyrin Soret bands (~418 and ~455 nm) is characteristic of the meso,meso-linked porphyrin motif,[17,20−23] as is apparent for both **3** and **30**; the four, weaker porphyrin visible bands extend from $Q_Y(1,0)$ at ~525 nm to $Q_X(0,0)$ at ~660 nm. The

Scheme 4



14: R^1 = t-Bu, R^2 = H
15: R^1 = H, R^2 = t-Bu

9

22: R^1 = t-Bu, R^2 = H (90%)
23: R^1 = H, R^2 = t-Bu (86%)

perylene (with the ethynylphenyl linker attached in both **3** and **10**) has three resolved vibronic features: the (0,0) band at ~530 nm (which overlaps the porphyrin Q(1,0) band but is 1.3-fold more intense), the (1,0) band at ~480 nm that falls between the porphyrin Soret and Q features, and the (2,0) band (which appears as a shoulder on the (1,0) feature) that underlies the longer-wavelength porphyrin Soret component. The absorption bands of the phenylethynyl-substituted perylene in **10** or **3** lie approximately 15 or 30 nm to the red of those in the unsubstituted perylene monoimide **6** (which has its (0,0) band at ~505 nm) reflecting very effective electronic communication between the perylene and the ethynylphenyl linker (and an appended porphyrin).[7] The phthalocyanine absorption characteristics in **3** differ slightly from those of tetra-*tert*-butylphthalocyanine (**31**). However, similar spectral changes were evident in the porphyrin−phthalocyanine dyad **5**, which incorporates the same ethynylphenyl linker and a phthalocyanine substituted with six heptyl groups.[15] Accordingly, the spectral differences observed in the phthalocyanine absorption bands in linear array **3** versus the phthalocyanine reference compound **31** cannot be attributed to regioisomers but instead arise from electronic and symmetry effects due to the appended ethynylphenyl linker in the porphyrin−phthalocyanine motif.

The fluorescence spectrum of **3** in toluene at room temperature upon excitation at 490 nm is shown in Figure 2. At 490 nm, the perylene absorbs ~60% of the light, the bis(porphyrin) ~40%, and the phthalocyanine only several percent. Emission occurs almost exclusively from the phthalocyanine moiety. The perylene emission is decreased by at least 200-fold relative to the isolated chromophore **10** (which has $\Phi_f = 0.95^7$). No discernible band due to the porphyrin emission is evident (expected at 665 nm), though any such emission would be partially obscured by the short-wavelength shoulder on the phthalocyanine emission spectrum. The fluorescence quantum yield of **3** upon illumination in the phthalocyanine band is 0.78, to be compared with 0.77 for tetra-*tert*-butylphthalocyanine (**31**).[36] The excitation spectrum of **3** (λ_{em} = 697 nm) closely matches the absorption spectrum from 350 to 650 nm. In summary, the static fluorescence data are consistent with (1) essentially quantitative energy transfer from the perylene and the bis(porphyrin) to the phthalocyanine, and (2) intense emission from the phthalocyanine that is undiminished from that of the isolated chromophore.

Time-Resolved Absorption and Fluorescence Studies. The perylene−bis(porphyrin)−phthalocyanine array **3** was excited at 529 nm, where the perylene absorbs preferentially (perylene ~60% of the light, bis(porphyrin) ~40%, phthalocyanine only a few percent; see Figure 1). The rate of photoinduced energy transfer from the excited perylene to the ground-state phthalocyanine

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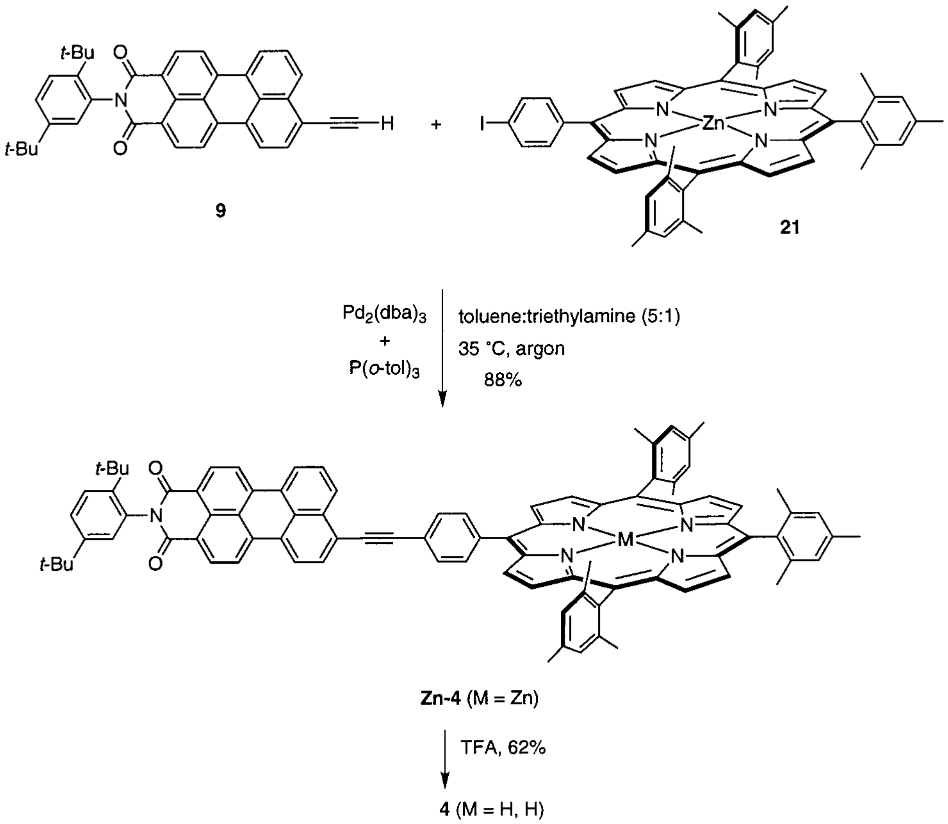
[36] Teuchner, K.; Pfarrherr, A.; Stiel, H.; Freyer, W.; Leupold, D. *Photochem. Photobiol.* **1993**, *57*, 465−471.

Scheme 5



component (via the intervening porphyrin dimer) was assessed by monitoring the growth of the phthalocyanine bleach near 700 nm (Figure 3). This feature develops very rapidly between 0.2 and 4 ps after excitation, nearly reaching its maximum amplitude; a small amount of additional growth occurs between 4 and 49 ps after excitation.[37] Kinetic analysis of data in the 695−700 nm region (Figure 4) shows that 90% of the excitation arrives on the phthalocyanine with a time constant of 2.0 ± 0.1 ps; 10% arrives more slowly, in 13 ± 5 ps.

A similar experiment was performed on the bis(porphyrin)−phthalocyanine array **28**, which lacks the perylene unit. The bis(porphyrin) was excited at 526 nm. The phthalocyanine bleach near 700 nm again developed with dual-exponential kinetics, with time constants of 1.3 ± 0.3 ps (70%) and 13 ± 5 ps (30%).

Lifetimes of the excited singlet states of the isolated chromophores and of the phthalocyanine component of the array were measured using fluorescence modulation (phase shift) spectroscopy. The phthalocyanine unit in array **2** has an excited-state lifetime of 6.0 ± 0.5 ns, which is the same as that measured for tetra-*tert*-butylphthalocyanine **31** (both solutions contain dissolved oxygen). The finding of the same phthalocyanine lifetime in the array and the monomeric reference compound is in accord with the essentially identical phthalocyanine fluorescence yield in the two systems. The excited-state lifetime of the isolated meso,meso-linked porphyrin dimer **30** of 9.7 ± 0.5 ns (degassed; 8.0 ± 0.5 ns undegassed) is slightly shorter than that of reference monomers such as free base tetramesitylporphyrin (~13 ns degassed; ~10 undegassed).[15,38] The excited-singlet-state lifetimes and fluorescence yields of the perylene reference compounds in toluene are as follows: 4.8 ns and 0.99 for unsubstituted perylene **6**, 3.9 ns and 0.97 for ethynylperylene **9**, and 3.4 ns and 0.95 for phenylethynylperylene **10**.[7]

Discussion

A linear array of pigments that functions as an energy cascade can serve as a light-harvesting element in artificial photosynthesis or as a wire in molecular photonic devices. In both applications, strong absorption and efficient energy funneling are desirable, though the nature of the output of the energy cascade differs. In artificial photosynthesis, the linear array would deliver energy to a reaction center and thus fluorescence would not be the desired output (though a long-lived excited singlet state of the last excited component in the array is highly desirable). In molecular photonic devices, a very bright fluorescence output would be attractive in a number of applications. A bright output element is also useful in fundamental studies of energy flow. An attractive design for achieving an energy cascade involves the sequential arrangement of pigments having a progressive increase in long-wavelength absorption band (i.e., progressive decline in excited-state energy). The

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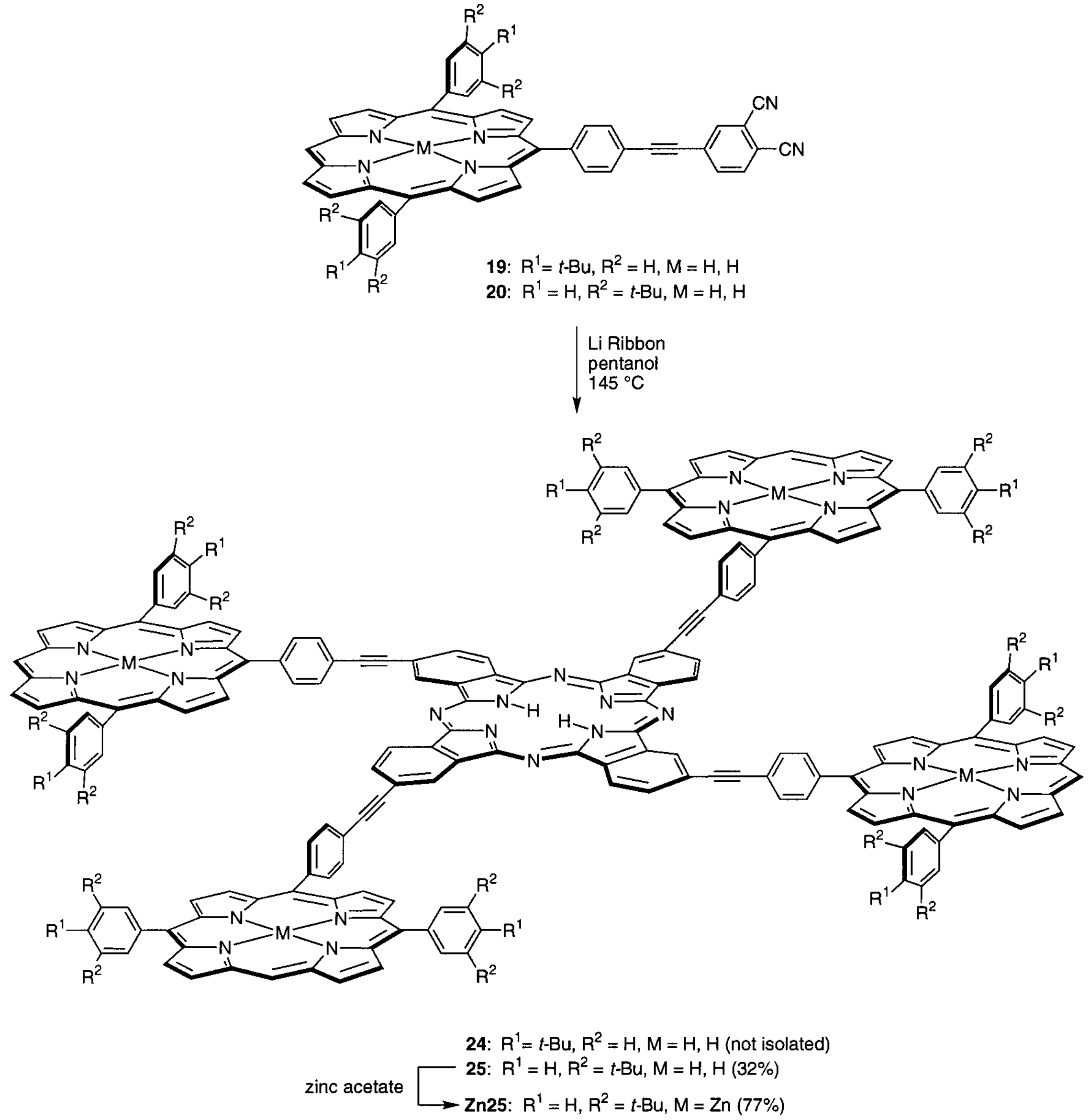
[37] The small phthalocyanine bleach at ~700 nm in the 0.2 ps spectrum (about 8% of the ultimate amplitude) can be attributed to two sources: (1) direct excitation of the phthalocyanine in a small fraction of the arrays and (2) ultrafast energy transfer with a time constant of ~1 ps from the fraction of the bis(porphyrin)s that were excited (judging from results on the porphyrin−phthalocyanine dyad **5**, where similar small early-time phthalocyanine bleaching in a small fraction of the arrays was observed).[15] Similarly, a small change in the shape of the bleaching spectrum at early times similar to that seen in Figure 2 was found for the porphyrin−phthalocyanine dyads **5** and ascribed to energy relaxation within the phthalocyanine and other effects.[15]

[38] Yang, S. I.; Seth, J.; Strachan, J. P.; Gentemann, S.; Kim, D.; Holten, D.; Lindsey, J. S.; Bocian, D. F. *J. Porphyrins Phthalocyanines* **1999**, *3*, 117−147.

Scheme 6



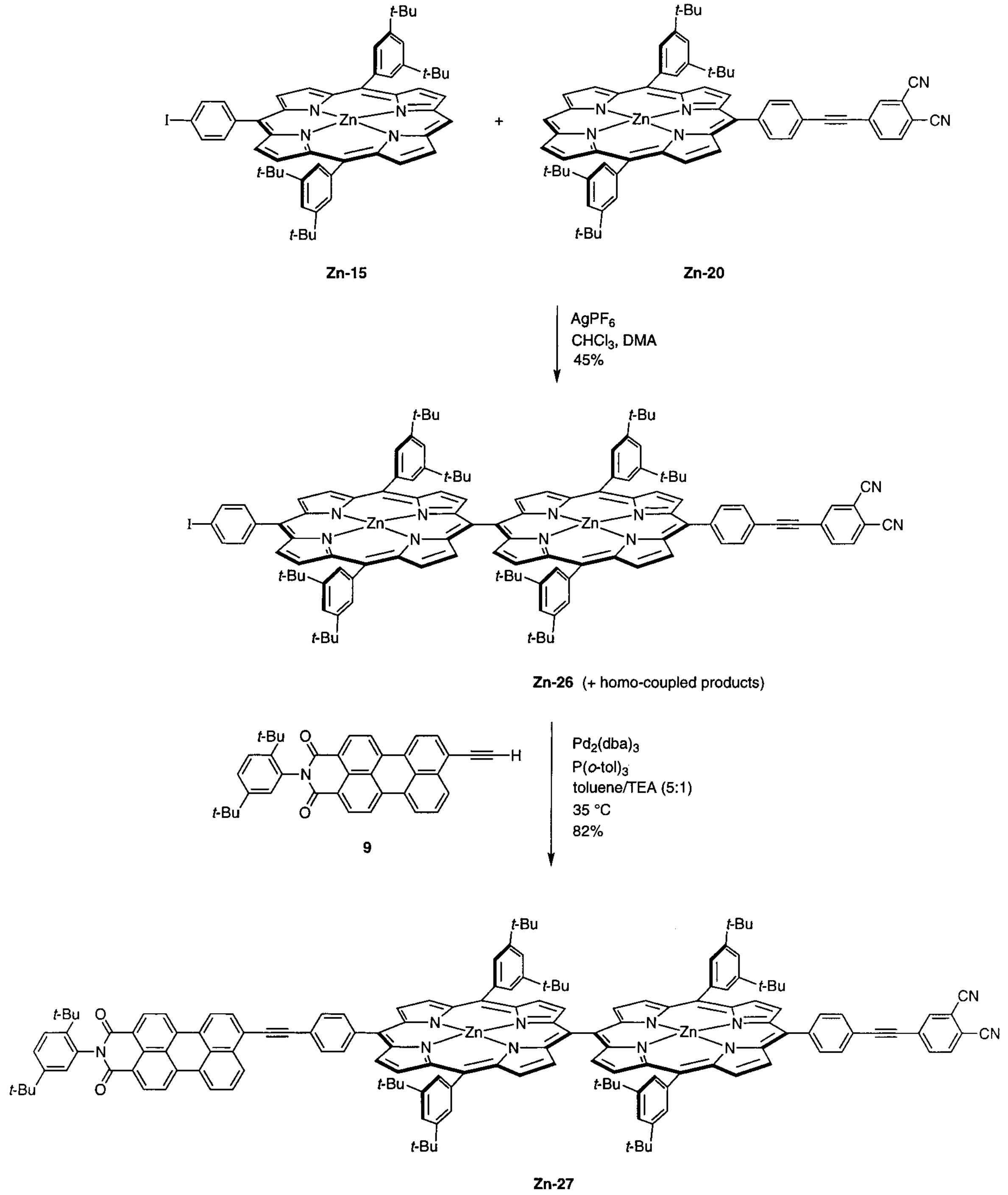
synthesis of such an array must yield pigments joined by appropriate linkers such that energy flows in a rapid manner without deleterious photoreactions. The new array **3** possesses these favorable characteristics.

Synthetic Strategy. One approach to the synthesis of linear arrays involves the sequential attachment of modular building blocks in proceeding from one end to the other. Ideally, such an approach would employ no statistical reactions, involve minimal chromatography, and afford the desired target molecule in a minimum number of steps.[1] In developing a route to **3**, we encountered a number of limitations in synthetic methodology that precluded a straightforward linear synthesis of the array. Chief among these limitations are (1) the absence of a directed route to AB-type meso,meso-linked porphyrin dyads and (2) the lack of a simple and rational method for preparing A_3B-type phthalocyanine building blocks. Furthermore, the incompatibility of the perylene monoimide dye with phthalocyanine-forming conditions (lithium pentoxide in refluxing pentanol) required that the perylene not be present when the phthalocyanine is formed.

The successful synthesis of **3** employed the following sequence of steps: (1) rational synthesis of porphyrin building blocks containing one unsubstituted meso site, one functional group (iodo or phthalonitrile moiety), and two 3,5-di-*tert*-butylphenyl groups for increased solubility (**15**, **20**); (2) a statistical reaction of two porphyrin building blocks to form the AB-type meso,meso-linked bis(porphyrin) bearing one iodo group and one phthalocyanine moiety (**26**); (3) a statistical reaction of the bis(porphyrin) with 4-*tert*-butylphthalonitrile yielding the corresponding A_3B-type phthalocyanine (**28**), and (4) Pd-mediated coupling to attach the perylene (**9**) to the bis(porphyrin)−phthalocyanine unit. Though the use of statistical reactions is unattractive, in both cases the polarity differences of the various components were sufficient to enable straightforward chromatographic separation. This route provided access to the desired linear array **3** for photochemical studies.

Energy-Transfer Rates and Yields. Excitation of the perylene and bis(porphyrin) components of **3** (with ~60/40 relative absorption at either 490 or 529 nm) results in rapid arrival of energy on the phthalocyanine

Scheme 7



component. The excitation arrives predominantly (90%) on the phthalocyanine with a time constant of 2 ps; the remainder (10%) arrives in 13 ps. Even the slower time constant is over 2 orders of magnitude shorter than the excited-state lifetimes of the isolated perylene and bis(porphyrin) chromophores (3.4 ns for **10**, 9.7 ns for **30**). This simple comparison and the fact that fluorescence occurs almost exclusively from the phthalocyanine regardless of which chromophore is excited are evidence of the extremely fast and efficient funneling of energy from perylene to bis(porphyrin) to phthalocyanine.

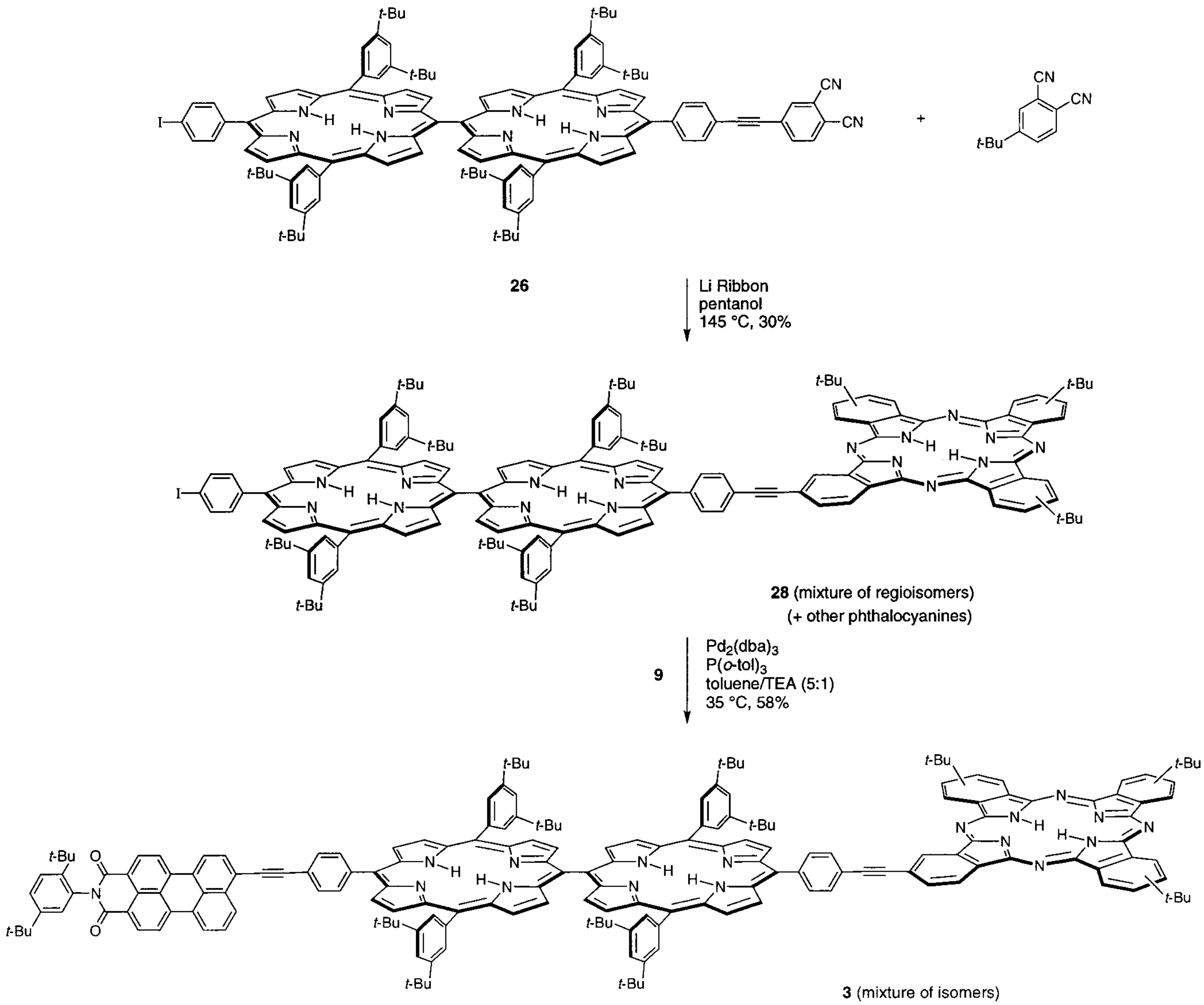
The measured 2-ps (major) and 13-ps (minor) time constants reflect the excited-state decay properties of the photoexcited perylene (PMI*) and/or bis(porphyrin) (P_2*) members of array **3**. These decay pathways include the energy-transfer processes given in eqs 1 and 2.

$$\mathrm{PMI^*{-}P_2{-}Pc} \rightarrow \mathrm{PMI{-}P_2^*{-}Pc} \qquad (1)$$

$$\mathrm{PMI{-}P_2^*{-}Pc} \rightarrow \mathrm{PMI{-}P_2{-}Pc^*} \qquad (2)$$

These two processes will occur sequentially upon direct absorption by the perylene component, and both sequentially and in parallel upon absorption of both the perylene and bis(porphyrin) components. The latter is the case for the 529-nm excitation wavelength used in the time-resolved absorption experiments, which produce PMI* in ~60% of the arrays and P_2* in ~40%. These events make difficult the determination of the rate constants for

Scheme 8



energy-transfer processes (1) and (2) from experiments on the perylene–bis(porphyrin)–phthalocyanine array **3** alone. However, it can be concluded from the 2-ps dominant lifetime component in **3** and lifetimes of 3.4 ns and 9.7 ns for reference compounds **10** and **31**, respectively,[39] that the rate constant and yield for each transfer step must be $\geq$ (3 ps)$^{-1}$ and >99%.

To deduce the rate constants for the sequential energy-transfer steps (1) and (2), the 2-ps (90%) and 13-ps (10%) lifetime components found in the perylene–bis(porphyrin)–phthalocyanine array **3** can be compared with the values found in the subunits and reference compounds. Following excitation of the bis(porphyrin) in the iodo-bis(porphyrin)–phthalocyanine compound **28**, P_2^* decays and the excited phthalocyanine Pc* forms by energy-transfer process (2) in two parts: a major component with a time constant of 1.3 ps (70%) and a minor component with a time constant of 13 ps (30%). Similar results were found for the porphyrin–phthalocyanine dyad **5**, in which the excited porphyrin shows a dual-exponential decay with time constants of 1.1 ps (70%) and 8 ps (30%).[15,16] The fluorescence yield and lifetime of the phthalocyanine in **5** are essentially the same as those of the isolated chromophore, indicating the absence of deleterious quenching processes. In perylene–porphyrin dyad **4**, energy transfer occurs from PMI* to the porphyrin with a rate constant of $\geq$(0.5 ps)$^{-1}$.[7] The photoexcited porphyrin in **4** in toluene has the same excited-state lifetime and fluorescence yield as in benchmark monomeric porphyrins, again indicating the absence of deleterious quenching processes.

Thus, the predominant 2-ps time constant for the arrival of excitation on the phthalocyanine in the perylene–bis(porphyrin)–phthalocyanine (**3**) is in line with the rates observed in the dyads. In particular, this value is essentially the sum of the time constants of 1.3 ps found in the bis(porphyrin)–phthalocyanine **28** (or 1.1 ps in porphyrin-phthalocyanine **5**) and $\leq$0.5 ps in perylene-porphyrin **4** (plus <1 ps for equilibration/relaxation events within the bis(porphyrin)). It is also clear that the 13 ps minor (10%) component to the growth of excitation on the phthalocyanine in **3** is associated with energy

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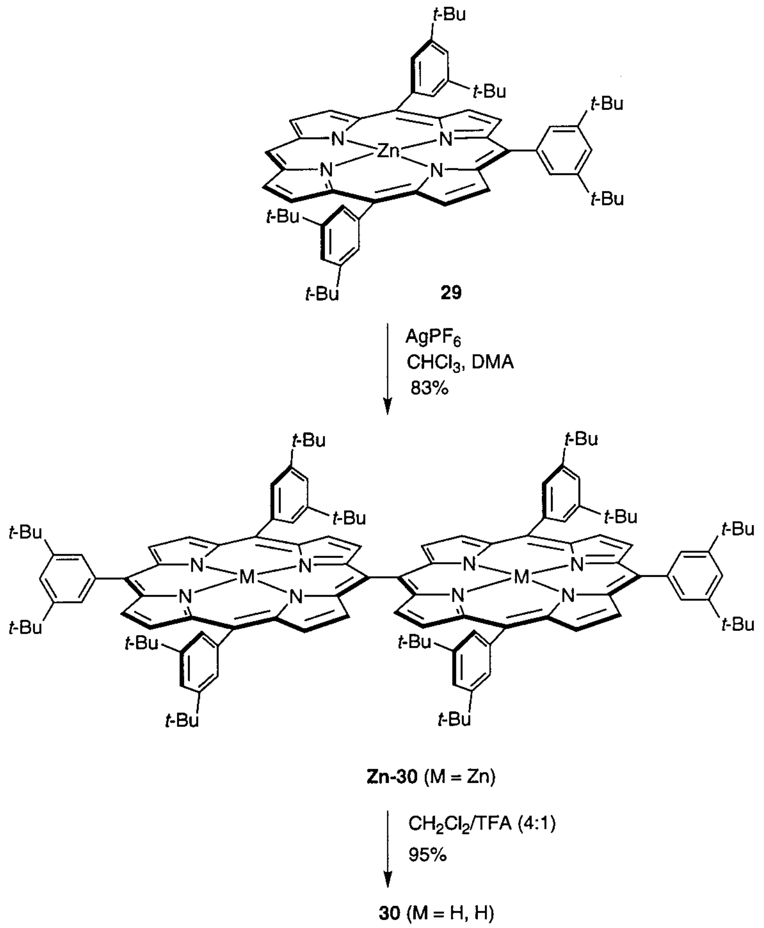
[39] The rate constant for each step is derived using the formula $k_{\text{trans}} = 1/\tau_{\text{DA}} - 1/\tau_{\text{D}}$ where $1/\tau_{\text{DA}} = k_{\text{rad}} + k_{\text{isc}} + k_{\text{ic}} + k_{\text{trans}}$ and $1/\tau_{\text{D}} = k_{\text{rad}} + k_{\text{isc}} + k_{\text{ic}}$. The yield is determined using the formula $\Phi_{\text{trans}} = k_{\text{trans}} \cdot \tau_{\text{DA}} = 1 - \tau_{\text{DA}}/\tau_{\text{D}}$. These equations assume that no processes other than energy transfer, fluorescence, internal conversion, and intersystem crossing contribute to the decay properties of PMI* and P_2^* in **3**. This assumption is valid for **3**, based on our work on perylene–porphyrin dyads[7] and porphyrin–phthalocyanine dyads and pentads.[15,16]

Scheme 9



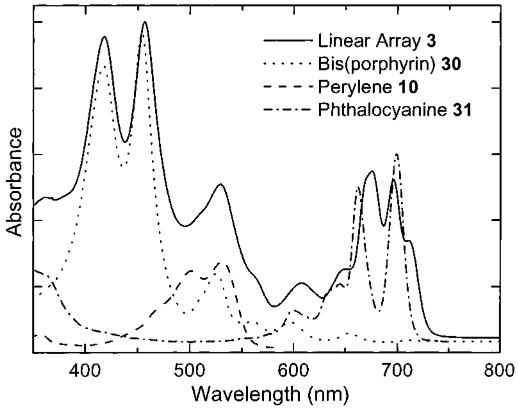


Figure 1. Ground-state absorption spectra in toluene at room temperature of the linear array **3** and reference compounds; the latter are scaled appropriately in intensity to best match the spectrum of **3**.

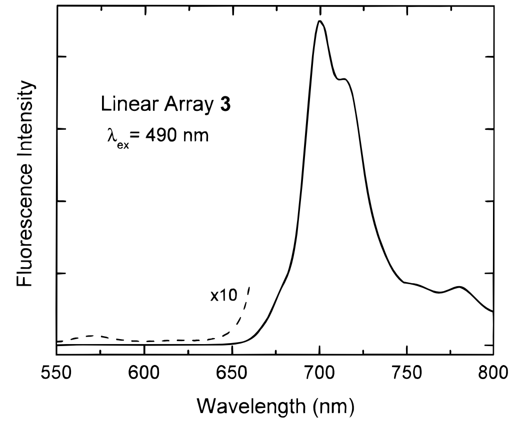


Figure 2. Fluorescence spectrum of linear array **3** in toluene at room temperature (λ_{ex} 490 nm).

transfer from the bis(porphyrin) to the phthalocyanine, as such a component is also found in dyads **28** and **5**,[15] which lack the perylene subunit. The origin of this minor component is not known but is a feature of all phenylethyne-linked porphyrin-phthalocyanine arrays that we have examined.[15,16] The ultrafast energy-transfer dynamics in this tightly coupled system stem from the nature of the input and output chromophores, the phenylethyne linkers, and the strong electronic interactions within the bis(porphyrin) transmission unit.[23,40]

Comparison of Linear Array (3) with the First-Generation Arrays (1) and (2). The perylene−bis(porphyrin)−phthalocyanine array **3** exhibits many favorable light-harvesting and energy-funneling characteristics, including the following: (1) good spectral coverage across the blue and red regions, (2) ultrafast and essentially quantitative energy transfer from the perylene end to the phthalocyanine end of the array, and (3) emission from the phthalocyanine acceptor that is as bright and long-lived as in the isolated chromophore. The properties of **3** are particularly favorable relative to the original wires (**1** and **2**) that contained a boron-dipyrrin input dye, one or three zinc porphyrin transmission

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[40] Bhuiyan, A. A.; Seth, J.; Yoshida, N.; Osuka, A.; Bocian, D. F. *J. Phys. Chem.* in press.

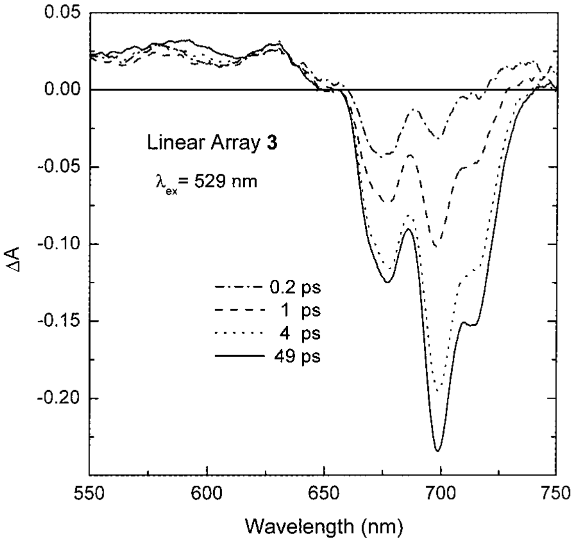
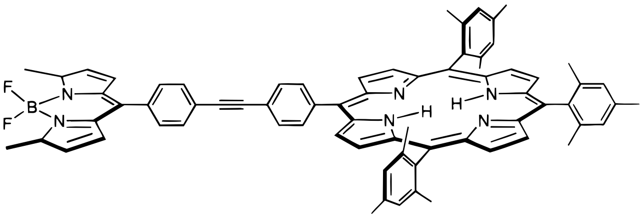


Figure 3. Time-resolved absorption difference spectra of linear array **3** in toluene at room temperature at several times after excitation with a 130-fs flash at 529 nm.

elements, a free base porphyrin output unit, and diphenylethyne linkers. The advantages of **3** compared to the components and linkers employed in **1** and **2** can be seen from the following considerations.

In a boron-dipyrrin–porphyrin dyad (**32**), which represents the input section of **1** and **2**, energy transfer occurs from the excited boron-dipyrrin dye to the free base porphyrin in dual-exponential fashion with rate constants of (2.9 ps)$^{-1}$ (36%) and (24 ps)$^{-1}$ (64%) (due to two excited-state conformers of the dye).[2] By comparison,



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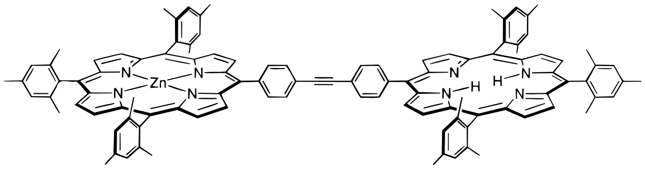
energy transfer in **3** proceeds with a rate that is fast ($\geq$(3 ps)$^{-1}$) and single exponential. The perylene also has modestly strong absorption in the blue-green region that complements the extended coverage in the blue region afforded by the bis(porphyrin) linker (due to the split Soret bands) and by the phthalocyanine in the red.

In a diphenylethyne-linked zinc porphyrin–free base porphyrin dyad (**33**), which represents the output section of **1** and **2**, energy transfer occurs with a rate constant of (24 ps)$^{-1}$.[4]



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By comparison, the rate of energy transfer from porphyrin to phthalocyanine with a phenylethyne linker is much faster (1.1 ps porphyrin lifetime for the dominant process). One drawback of the phthalocyanine is that there is a second, minor component to the excited-state dynamics associated with the porphyrin–phenylethyne–phthalocyanine motif that has a time constant of ~10 ps.[15] The phthalocyanine absorbs strongly in the red and has a lower-energy excited state than the porphyrin transmission element irrespective of the metalation states of these components, permitting use of free base porphyrins as energy-transfer donors. The free base phthalocyanine in **3** emits with the same high efficiency ($\Phi_f = 0.78$) and lifetime (6 ns) as in the isolated chromophore, indicating the absence of charge-transfer or other quenching processes involving the bis(porphyrin) unit. In contrast, the emission efficiency of the free base porphyrin in **1** is 0.12.[6] Thus, there are many advantages of using a porphyrin–phenylethyne–phthalocyanine output section relative to a diphenylethyne-linked zinc porphyrin and free base porphyrin as in the original wires **1** and **2**.

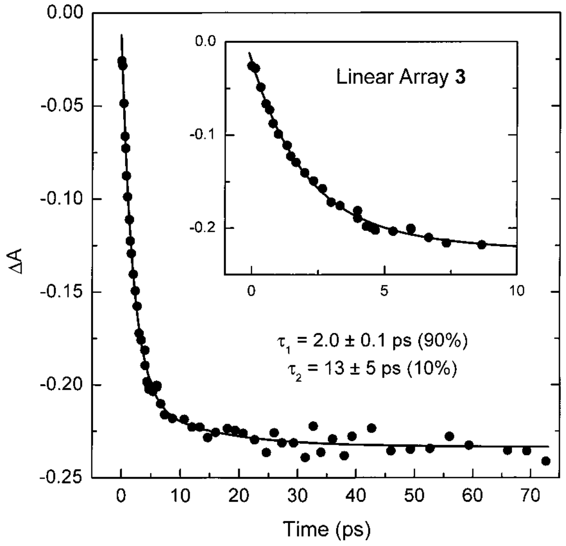

Figure 4. Kinetic data and dual-exponential fit for linear array **3** in toluene showing Δ*A* averaged over the 695–700 nm region as a function of time after excitation (see Figure 3). The phthalocyanine bleaching develops (as excitation arrives via energy transfer from the bis(porphyrin) unit) with time constants of 2 ps (90%) and 13 ps (10%). The inset shows an expanded view of the data at early times. The data before $t = 0$ and during the flash are omitted for clarity.

While our studies of end-to-end photoinduced energy transfer in **1** and **2** are still in progress, the results in hand indicate that the overall transfer process in **3** is approximately 5–10 times faster than the single-step transfer process in a diphenylethyne-linked boron-dipyrrin–porphyrin dyad (**32**) or zinc porphyrin–free base porphyrin dyad (**33**). Thus, phenylethyne-linked perylene and phthalocyanine components appear ideal as input and output units for use in porphyrin-based energy-transfer systems. The meso,meso-linked transmission unit affords rapid energy transfer. In summary, we have constructed and characterized a perylene–bis(porphyrin)–phthalocyanine array that has superior light-harvesting and energy-funneling properties compared to our first-generation wires (**1** and **2**), including long-distance ultrafast energy-transfer dynamics.

Experimental Section

General Methods. ^{1}H NMR spectra were collected at 300 MHz in $CDCl_3$ unless otherwise stated. All absorption and emission spectra were collected in toluene. Mass spectra of porphyrins and porphyrin-containing compounds were obtained via laser desorption mass spectrometry (LD-MS) in the absence of an added matrix.[41] A full presentation of the LD-MS spectra of the arrays is available in the Supporting Information. High-resolution fast atom bombardment mass spectrometry (FAB-MS) studies of the compounds were carried out at greater than unit resolution unless stated otherwise. All chemicals were used as received from Aldrich. The porphyrins prepared by rational synthesis were examined for scrambling by LD-MS analysis of crude reaction mixtures.[42]

Solvents. All solvents were dried by standard methods. Toluene (Fisher, certified ACS) and triethylamine (Fluka, puriss) were distilled from CaH_2, and tetrahydrofuran (Fisher, histological grade) was distilled from Na/benzophenone. Tetrahydrofuran (Fisher, HPLC grade) and all other solvents were used as received.

Chromatography. Adsorption column chromatography was performed using flash silica gel (Baker, 60−200 mesh) or alumina (Fisher A-540, 80−200 mesh). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1.[43] 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 2 volume equiv of solvents used.

General Procedure for Pd-Coupling Reactions. Two methods for Pd-mediated coupling were employed. For the coupling of nonporphyrinic species where copper could be employed, the method of Ames was used ($Pd(PPh_3)_2Cl_2$ + CuI).[26] For porphyrins, a copper-free Pd-coupling method was employed ($Pd_2(dba)_3$, P(*o*-tol)$_3$).[32] The iodo and ethynyl substrates and the Pd reagents were placed in a Schlenk flask, which was evacuated and purged with argon three times. The argon flow rate was increased, the threaded stopcock was removed, and deaerated distilled toluene and triethylamine were added in succession by gastight syringe. The threaded stopcock was replaced, the argon flow rate was reduced and the Schlenk flask was immersed in an oil bath held at a constant temperature. When the reaction was finished the flask was cooled to room temperature and the solvents were removed under reduced pressure. To remove Pd species the mixture generally was filtered through a short silica column.

Physical Methods. (1) General. Static fluorescence and static and time-resolved absorption studies were performed on samples in toluene at room temperature.

(2) Static Absorption and Fluorescence Spectroscopy. Static absorption (Cary 100) and fluorescence (Spex Fluoromax) measurements were performed as described previously.[15,16] For the absorption measurements, a 1-nm data interval, a scan speed of 600 nm/min, and a spectral bandwidth of 2 nm were used. Fluorescence measurements utilized ∼2 μM samples, 5-nm band-pass in both excitation and detection paths, and a right-angle geometry. Emission spectra were corrected for the sensitivity of the detection system. Tetra-*tert*-butylphthalocyanine served as a fluorescence standard (Φ_f = 0.77).[36] The solutions contained ambient concentrations of dissolved oxygen.

Time-Resolved Fluorescence Spectroscopy. Fluorescence lifetimes were measured using fluorescence modulation (phase shift) methods on a Spex Tau2 spectrofluorimeter as described previously.[15,16] Modulation frequencies from 10 to 40 MHz were typically utilized for the samples studied here, and both the fluorescence phase shift and amplitude modulation were used in modeling the data. Samples (∼5 μM) were excited in an appropriate Q band and the emission over the entire profile isolated with appropriate colored glass filters. The solutions either contained ambient concentrations of dissolved oxygen or were deoxygenated by bubbling with N_2 as indicated.

Time-Resolved Absorption Spectroscopy. Transient absorption data were obtained at room temperature as discussed elsewhere.[16] Samples (∼0.1 to 0.2 mM in toluene) were placed in a 5-mm path length cuvette and stirred with a magnetic stir bar. Samples were excited at 10 Hz with 130 fs, 25−30 μJ pump pulses and probed with white light pulses of comparable duration. Each spectrum was acquired at a specific pump−probe delay time using 2D-detection and represents the average of data from 300 laser pulses. Kinetic data were generated by averaging the ΔA values in specific wavelength ranges (e.g., 695−700 nm) for the entire set of pump−probe delay times and plotting these values as a function of time. A nonlinear least-squares algorithm was used to fit the kinetic traces to functions consisting of either a single or double exponential plus a constant.

Perylene−Bis(porphyrin)−Phthalocyanine (3). Following a general Pd-coupling procedure,[32] a mixture of **28** (0.016 g, 6.8 μmol), ethynylperylene **9** (0.004 g, 6.8 μmol), $Pd_2(dba)_3$ (0.005 g, 5 μmol), and P(*o*-tol)$_3$ (0.011 g, 36 μmol) in toluene/triethylamine (14 mL, 5:1) was reacted in a Schlenk flask at 35 °C for 2 h. The crude reaction mixture was evaporated to dryness, chromatographed (silica, toluene), chromatographed (SEC, THF), and chromatographed (silica, toluene/ethyl acetate, 10:1) to afford a black solid (0.011 g, 58% yield): ^{1}H NMR (500 MHz) δ −2.10 to −1.90 (m, 4H), −1.50 (br s, 2H), 0.70−2.00 (m, 117H), 6.30−9.60 (m, 60H); LD-MS obsd 2771.1; FAB-MS (unit resolution) obsd 2759.4, calcd exact mass 2758.5 ($C_{192}H_{183}N_{17}O_2$); λ_{abs} (log ϵ) 418 (5.26), 457 (5.28), 530 (4.98), 606 (4.54), 674 (5.00), 696 (4.99) nm; λ_{em} 700, 714, 780 nm.

Perylene−Ethynylphenyl−Zinc Porphyrin (Zn-4). Following a general Pd-coupling procedure,[32] a mixture of **9** (0.016 g, 0.033 mmol), zinc(II)-5,10,15-trimesityl-20-(4-iodophenyl)-porphyrin (**21**)[33] (0.028 g, 0.032 mmol), $Pd_2(dba)_3$ (4.3 mg, 4.4 μmol), and P(*o*-tol)$_3$ (0.011 g, 0.036 mmol) in toluene/triethylamine (13 mL, 5:1) was reacted in a Schlenk flask at 35 °C for 1 h. The crude reaction mixture was filtered through Celite, rotary evaporated to dryness, chromatographed on silica (CH_2Cl_2/hexanes, 3:1), chromatographed (SEC, THF), and recrystallized (ethanol) to afford a purple solid (0.042 g, 88%): R_f (silica, CH_2Cl_2/hexanes) = 0.27; ^{1}H NMR δ 1.31 (s, 9H), 1.34 (s, 9H), 1.85 (s, 18H), 2.64 (s, 9H), 7.05 (m, 2H), 7.28 (s, 6H), 7.47 (m, 1H), 7.61 (m, 1H), 7.86 (m, 2H), 8.06 (m, 4H), 8.31 (m, 2H), 8.57 (m, 2H), 8.60 (m, 2H), 8.75 (m, 8 H), 8.91 (m, 2H); LD-MS obsd 1339.1; FAB-MS obsd 1333.52, calcd exact mass 1333.52, ($C_{91}H_{75}N_5O_2Zn$); λ_{abs} 423, 515, 550 nm.

4. A solution of **Zn-4** (30 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) was treated with TFA (250 μL, 5 vol %) and the solution was stirred for 2 h (with monitoring by fluorescence spectroscopy). The crude reaction mixture was dissolved in CH_2Cl_2, washed with $NaHCO_3$, washed with water, dried (Na_2SO_4), rotary evaporated to dryness, chromatographed on silica (CH_2Cl_2/hexanes, 5:1), and recrystallized (ethanol) to afford a purple solid (18 mg, 62%): ^{1}H NMR δ −2.12 (s, 2H), 1.31 (s, 9H), 1.34 (s, 9H), 1.84 (s, 18H), 2.61 (s, 9H), 7.05 (d, J = 2.1 Hz 1H), 7.24 (m, 4H), 7.44 (dd, J = 8.7, 2.1 Hz, 1H), 7.58 (d, J = 8.7, 1H), 7.80 (m, 2H), 7.98 (d, J = 7.8, 1H), 8.05 (d, J = 8.1 Hz, 2H), 8.27 (d, J = 8.1 Hz, 2H), 8.48 (m, 5H), 8.67 (m, 9 H), 8.80 (d, J = 5.1 Hz, 2H); LD-MS obsd 1275.2; FAB-MS obsd 1271.61, calcd exact mass 1271.61 ($C_{91}H_{77}N_5O_2$); λ_{abs} 420, 515, 591, 651 nm.

***N*-(2,5-Di-*tert*-butylphenyl)-9-[2-(trimethylsilyl)ethynyl]-perylene-3,4-dicarboximide (8).** Following a general Pd-coupling procedure,[26] a mixture of **7**[13] (0.200 g, 0.34 mmol), trimethylsilylacetylene (60 μL, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.024 g, 0.03 mmol), and CuI (0.005 g, 0.02 mmol) in toluene/triethylamine (60 mL, 5:1) was reacted in a Schlenk flask for 2 h at 50 °C. The crude reaction mixture was filtered through Celite, evaporated to dryness, and chromatographed (silica, $CHCl_3$/hexanes, 10:1) to afford a red solid (0.18 g, 88%): mp >270 °C; R_f (silica, $CHCl_3$) = 0.36; ^{1}H NMR δ 0.38 (s, 9H, Si), 1.30 (s, 9H), 1.33 (s, 9H), 7.05 (m, 1H), 7.11 (s, 1H), 7.44 (m, 4H), 7.67 (m, 5H), 8.28 (m, 1H), 8.39 (m, 2H), 8.62 (m, 2H);

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FAB-MS obsd 605.2779, calcd exact mass 605.2750 ($C_{41}H_{39}NO_2Si$); λ_{abs} 523, 493 nm.

***N*-(2,5-Di-*tert*-butylphenyl)-9-ethynylperylene-3,4-dicarboximide (9).** A mixture of **8** (0.051 g, 0.082 mmol) and tetrabutylammonium fluoride on silica (0.120 g, 0.1−0.15 mmol) 10 mL of dry THF was stirred for 0.5 h under argon. The reaction mixture was filtered through Celite, evaporated to dryness, and chromatographed (silica, $CHCl_3$/hexanes, 10:1) to afford a red solid (0.042 g, 94%): $R_f = 0.27$ (silica, $CHCl_3$); ^{1}H NMR (mixture of diastereomers) δ 1.31 (s, 9H), 1.34 (s, 9H), 3.67 (s, 1H), 7.05 (m, 1H), 7.11 (m, 1H), 7.44 (m, 4H), 7.65 (m, 4H), 7.77 (m, 1H), 8.28 (m, 1H), 8.37 (m, 4H), 8.62 (m, 2H); FAB-MS obsd 533.2356 calcd exact mass 533.2355 ($C_{38}H_{31}NO_2$); λ_{abs} (log ϵ) 517, 486 (4.45) nm.

***N*-(2,5-Di-*tert*-butylphenyl)-9-(phenylethynyl)perylene-3,4-dicarboximide (10).** Following a general Pd-coupling procedure,[26] a mixture of **9** (20.0 mg, 0.038 mmol), iodobenzene (5 μL, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7 mmol), and CuI (5 mg, 0.02 mmol) in toluene/triethylamine (12 mL, 5:1) was reacted in a Schlenk flask at 50 °C for 2 h. The crude reaction mixture was filtered through Celite, evaporated to dryness, and chromatographed (silica, $CHCl_3$/hexanes, 10:1) to afford a red solid (0.015 g, 83%): mp >270 °C; ^{1}H NMR δ 1.31 (s, 9H), 1.34 (s, 9H), 7.04 (d, $J = 2.1$ Hz, 1H), 7.46 (m, 4H), 7.60 (m, 1H), 7.73 (m, 3H), 7.88 (d, $J = 8.1$ Hz, 1H), 8.48 (m, 5H), 8.67 (dd, $J = 8.1, 1.5$ Hz, 2H); FAB-MS obsd 609.2703, calcd exact mass, 609.2668 ($C_{44}H_{35}NO_2$); λ_{abs} (log ϵ) 358, 433, 501 (4.56), 531 (4.60) nm.

5,15-Bis(4-*tert*-butylphenyl)-10-(4-iodophenyl)porphyrin (14). Following a rational synthesis,[28] a solution of **11**[29] (0.63 g, 1.3 mmol) and 5-(4-iodophenyl)dipyrromethane (**13**)[30] (0.45 g, 1.3 mmol) in acetonitrile (660 mL) was treated with TFA (1.2 mL, 16 mmol) and stirred for 4.5 min. DDQ (1.2 g, 5.3 mmol) was added followed by triethylamine (1.2 mL, 16 mmol), and the reaction mixture was stirred for 1 h. The crude reaction mixture was filtered through a pad of alumina (CH_2Cl_2), followed by a pad of silica (CH_2Cl_2), evaporated to dryness, and washed with hot ethanol to afford purple crystals (0.18 g, 18% yield): ^{1}H NMR δ −3.01 (s, 2H), 1.63 (s, 18H), 7.79, 816 (AA′BB′, 2 × 2H) 7.95, 8.07 (AA′BB′, 2 × 2H), 8.83 (d, 2H, $J = 5.1$ Hz), 8.96 (d, 2H, $J = 5.1$ Hz), 9.06 (d, 2H, $J = 5.1$ Hz), 9.33 (d, 2H, $J = 4.2$ Hz), 10.22 (s, 1H); LD-MS obsd 779.6; FAB-MS obsd 776.2369, calcd exact mass 776.2376 ($C_{46}H_{44}N_4I$); λ_{abs} 416, 510, nm.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-iodophenyl)porphyrin (15). Following a rational synthesis,[28] a solution of **12**[29] (1.0 g, 1.7 mmol) and **13**[30] (0.60 g, 1.7 mmol) in acetonitrile (660 mL) was treated with TFA (1.5 mL, 20 mmol) and stirred for 5 min. DDQ (1.5 g, 6.8 mmol) was added followed by triethylamine (2.8 mL, 20 mmol) and the reaction mixture was stirred for 1 h. The crude reaction mixture was purified by the same procedure for **14**, affording purple crystals (0.23 g, 15% yield): ^{1}H NMR δ −2.96 (s, 2H), 1.55 (s, 36H), 7.80−7.90 (m, 2H), 7.92−8.20 (m, 8H), 8.85 (d, 2H, $J = 4.5$ Hz), 8.96 (d, 2H, $J = 5.1$ Hz), 9.07 (d, 2H, $J = 4.2$ Hz), 9.35 (d, 2H, $J = 5.1$ Hz), 10.23 (s, 1H); LD-MS obsd 890.3; FAB-MS obsd 888.3643, calcd exact mass 888.3628 ($C_{54}H_{57}N_4I$); λ_{abs} 416, 509, 585 nm.

Zn(II)-5,15-Bis(3,5-di-*tert*-butylphenyl)-10-(4-iodophenyl)porphyrin (Zn-15). A solution of **15** (0.20 g, 0.22 mmol) in $CHCl_3$/MeOH (25 mL, 3:2) was treated with zinc acetate (4.8 g, 22 mmol), and the reaction mixture was stirred overnight. The crude reaction mixture was washed with H_2O and dried (Na_2SO_4). The crude product was then chromatographed (alumina, CH_2Cl_2/hexanes, 3:1, then CH_2Cl_2) affording a purple solid (0.20 g, 97% yield): ^{1}H NMR δ 1.55 (s, 36H), 7.80−7.88 (m, 2H), 7.90−8.30 (m, 8H), 8.96 (d, 2H, $J = 5.1$ Hz), 9.06 (d, 2H, $J = 5.1$ Hz), 9.16 (d, 2H, $J = 4.2$ Hz), 9.43 (d, 2H, $J = 4.2$ Hz), 10.29 (s, 1H); LD-MS obsd 952.9; FAB-MS obsd 950.2742, calcd exact mass 950.2763 ($C_{54}H_{55}N_4IZn$); λ_{abs} 420, 546 nm.

5-[4-[2-(3,4-Dicyanophenyl)ethynyl]phenyl]dipyrromethane (18). Following a general Pd-coupling procedure,[26] a mixture of **17**[28] (3.4 g, 14 mmol), 4-iodophthalonitrile[15,31] (3.6 g, 14 mmol), $Pd(Ph_3P)_2Cl_2$ (0.98 g, 0.14 mmol), and CuI (0.13 g, 0.71 mmol) in toluene/triethylamine (20 mL, 5:1) was reacted in a Schlenk flask at 50 °C for 0.5 h. The crude reaction mixture was filtered through Celite, washed with CH_2Cl_2, and evaporated to dryness. The crude product was chromatographed (silica, (CH_2Cl_2/hexanes, 10:1) and recrystallized from ethanol to afford light-orange crystals (4.7 g, 90% yield): mp 187 °C; ^{1}H NMR δ 5.50 (s, 1H), 5.89 (s, 2H), 6.10−6.23 (m, 2H), 6.65−6.80 (m, 2H), 7.24 (d, 2H, $J = 8.1$ Hz), 7.49 (d, 2H, $J = 8.1$ Hz), 7.70−7.95 (m, 3H), 8.00 (br s, 2H); ^{13}C NMR δ 43.99, 85.88, 107.57, 108.65, 114.22, 114.60, 115.22, 116.35, 117.64, 119.90, 128.78, 129.40, 131.64, 132.25, 133.50, 135.55, 136.01, 144.37; FAB-MS obsd 372.1375, calcd exact mass 372.1375 ($C_{25}H_{16}N_4$).

5,15-Bis(4-*tert*-butylphenyl)-10-[4-[2-(3,4-dicyanophenyl)ethynyl]phenyl]porphyrin (19). Following a rational synthesis,[28] a mixture of **11**[29] (2.5 g, 5.4 mmol) and **18** (2.0 g, 5.4 mmol) in acetonitrile (2.1 L) was treated with TFA (4.9 mL, 22 mmol) and the reaction mixture was stirred for 4.5 min. DDQ (4.9 g, 22 mmol) was added followed by triethylamine (9.0 mL, 65 mmol) and the reaction mixture was stirred for 1 h. The crude reaction mixture was purified by the same procedure as for **14**, affording purple crystals (0.99 g, 23% yield): ^{1}H NMR δ −3.01 (s, 2H), 1.63 (s, 18H), 7.70−8.20 (m, 15H), 8.83 (d, 2H, $J = 4.5$ Hz), 8.96 (d, 2H, $J = 4.5$ Hz), 9.07 (d, 2H, $J = 4.5$ Hz), 9.34 (d, 2H, $J = 5.1$ Hz), 10.22 (s, 1H); LD-MS obsd 803.3; FAB-MS obsd 800.3628, calcd exact mass 800.3627 ($C_{56}H_{44}N_6$); λ_{abs} 417, 510, 585 nm; λ_{em} 645, 711 nm.

5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-[2-(3,4-dicyanophenyl)ethynyl]phenyl]porphyrin (20). Following a rational synthesis,[28] a solution of **12**[29] (1.0 g, 1.7 mmol) and **18** (0.63 g, 1.7 mmol) in acetonitrile (660 mL) was treated with TFA (1.5 mL, 20 mmol) and the solution was stirred for 5 min. Then DDQ (1.5 g, 6.8 mmol) was added followed by triethylamine (2.8 mL, 20 mmol), and the reaction mixture was stirred for 1 h. The crude reaction mixture was purified by the same procedure as for **14**, affording purple crystals (0.19 g, 12% yield): ^{1}H NMR δ −2.94 (s, 2H), 1.55 (s, 36H), 7.80−8.00 (m, 6H), 8.05−8.30 (m, 7H), 8.84 (d, 2H, $J = 4.5$ Hz), 8.98 (d, 2H, $J = 4.5$ Hz), 9.08 (d, 2H, $J = 5.1$ Hz), 9.36 (d, 2H, $J = 4.2$ Hz), 10.25 (s, 1H); LD-MS obsd 914.9; FAB-MS obsd 912.4857, calcd exact mass 912.4879 ($C_{64}H_{60}N_6$); λ_{abs} 417, 510, 544, 586 nm; λ_{em} 645, 711 nm.

Zn(II)-5,15-Bis(3,5-di-*tert*-butylphenyl)-10-[4-[2-(3,4-dicyanophenyl)ethynyl]phenyl]porphyrin (Zn-20). A solution of **20** (0.18 g, 0.20 mmol) in $CHCl_3$/MeOH (20 mL, 7:3) was treated with zinc acetate (4.4 g, 20 mmol), and the reaction mixture was stirred overnight. The crude reaction mixture was washed with H_2O, dried (Na_2SO_4), and chromatographed (silica, CH_2Cl_2/hexanes, 3:1), affording a purple solid (0.19 g, 96% yield): ^{1}H NMR δ 1.55 (s, 36H), 7.80−8.00 (m, 6H), 8.05−8.35 (m, 7H), 8.95 (d, 2H, $J = 4.5$ Hz), 9.08 (d, 2H, $J = 5.1$ Hz), 9.17 (d, 2H, 4.5 Hz), 9.44 (d, 2H, $J = 4.5$ Hz), 10.31 (s, 1H); LD-MS obsd 976.2; FAB-MS obsd 974.4025, calcd exact mass 974.4014 ($C_{64}H_{58}N_6Zn$); λ_{abs} 427, 557 nm; λ_{em} 606, 650 nm.

Perylene−Porphyrin Dyad (22). Following a general Pd-coupling procedure,[32] a mixture of **13** (0.069 g, 0.089 mmol), ethynylperylene **9** (0.048 g, 0.089 mmol), $Pd_2(dba)_3$ (0.012 g, 14 μmol), and P(*o*-tol)$_3$ (0.033 g, 0.011 mmol) in toluene/triethylamine (72 mL, 5:1) was reacted in a Schlenk flask at 35 °C for 2.5 h. The crude reaction mixture was evaporated to dryness, chromatographed (silica, CH_2Cl_2/hexanes, 3:1), chromatographed by SEC (THF), and evaporated to afford a purple solid (0.091 g, 90% yield): ^{1}H NMR δ −3.07 (s, 2H), 1.35 (s, 9H), 1.36 (s, 9H), 1.64 (s, 18H), 7.08 (d, 1H, $J = 2.4$ Hz), 7.45−7.52 (m, 1H), 7.55−7.65 (m, 2H), 7.75−7.87 (m, 5H), 8.08, 8.34 (AA′BB′, 2 × 2H), 8.15−8.30 (m, 6H), 8.25 (m, 4H), 8.54 (d, 1H, $J = 8.1$ Hz), 8.61 (d, 2H, $J = 8.1$ Hz), 8.92 (d, 2H, $J = 5.1$ Hz), 9.00 (d, 2H, $J = 5.4$ Hz), 9.06 (d, 2H, $J = 5.1$ Hz), 9.30 (d, 2H, $J = 5.1$ Hz), 10.16 (s, 1H); LD-MS obsd 1186.7; FAB-MS obsd 1181.5612, calcd exact mass 1181.5608 ($C_{84}H_{71}N_5O_2$); λ_{abs} 416, 510 nm; λ_{em} 646, 711 nm.

Perylene−Zinc Porphyrin Dyad (Zn-22). A solution of **22** (0.040 g, 0.034 mmol) in $CHCl_3$/MeOH (12 mL, 2:1) was treated with zinc acetate (0.74 g, 3 mmol), and the reaction mixture was stirred overnight. The crude reaction mixture was then washed with H_2O, dried (Na_2SO_4), and chromatographed (alumina, CH_2Cl_2, then ethyl acetate), affording a purple solid (0.036 g, 97% yield): ^{1}H NMR δ 1.37 (s, 9H), 1.42 (s, 9H), 1.66 (s, 18H), 7.07 (d, 1H, $J = 2.1$ Hz), 7.48−7.51 (m, 1H), 7.62−7.69 (m, 3H), 7,75−8.70 (m, 19H), 9.03−9.13 (m, 6H), 9.28 (d, 2H, $J = 4.2$ Hz), 10.05 (s, 1H); LD-MS obsd 1248.8; FAB-MS obsd 1243.4739, calcd exact mass 1243.4743 ($C_{84}H_{69}N_5O_2Zn$); λ_{abs} 420, 543 nm; λ_{em} 597, 642 nm.

Perylene−Porphyrin Dyad (23). Following the general Pd-coupling procedure,[32] a mixture of porphyrin **15** (0.014 g, 0.022 mmol), ethynylperylene **9** (0.008 g, 0.02 mmol), $Pd_2(dba)_3$ (0.002 g, 2 μmol), and P(*o*-tol)$_3$ (0.006 g, 20 μmol) in toluene/triethylamine (6 mL, 5:1) was reacted in a Schlenk flask at 35 °C for 1.5 h. The crude reaction mixture was evaporated to dryness, chromatographed (silica, CH_2Cl_2/hexanes, 4:1), chromatographed (SEC, THF), and evaporated to afford a purple solid (0.018 g, 86% yield): ^{1}H NMR δ −3.00 (s, 2H), 1.36 (s, 9H), 1.37 (s, 9H), 1.57 (s, 36H), 7.09 (d, 1H, $J = 2.1$ Hz), 7.45−7.90 (m, 7H), 8.00−8.40 (m, 11H), 8.50−8.65 (m, 3H), 8.95 (d, 2H, $J = 4.5$ Hz), 9.01 (d, 2H, $J = 5.4$ Hz), 9.07 (d, 2H, $J = 4.5$ Hz), 9.32 (d, 2H, $J = 4.2$ Hz), 10.18 (s, 1H); LD-MS obsd 1299.8; FAB-MS obsd 1293.68, calcd exact mass 1293.69 ($C_{92}H_{87}N_5O_2$); λ_{abs} (log ϵ) 417 (5.61), 510 (4.88), 642 (3.78) nm; λ_{em} 645, 711 nm.

Star-Shaped Porphyrin−Phthalocyanine Pentad (25). Following a standard procedure,[1,34] a solution of pentanol (2.5 mL) was treated with lithium ribbon (16 mg) and the mixture was stirred at 90 °C until the lithium had reacted. The reaction mixture was cooled to room temperature, and 50 mg of **20** was added; the reaction mixture was heated to 145 °C for 2 h and then cooled to room temperature. The reaction mixture was dissolved in CH_2Cl_2, washed with MeOH/H_2O (100 mL, 3:1), washed with H_2O, dried (Na_2SO_4), and chromatographed (silica, toluene/ethyl acetate, 20:1) affording a purple-brown solid (0.016 g, 32% yield). A satisfactory ^{1}H NMR spectrum was not obtained: LD-MS obsd 3670.6, calcd avg mass 3654.8; λ_{abs} (log ϵ) 419 (5.87), 510 (4.56), 546 (4.60), 689 (4.69), 721 (4.74) nm; λ_{em} 725 nm.

Star-Shaped Zinc Porphyrin−Phthalocyanine Pentad (Zn-25). A solution of **25** (0.081 g, 0.022 mmol) in $CHCl_3$/MeOH (10 mL, 7:3) was treated with zinc acetate (1.9 g, 8.9 mmol), and the reaction mixture was stirred overnight. The crude reaction mixture was washed with H_2O, dried (Na_2SO_4), and chromatographed (silica, toluene), affording a green solid (0.053 g, 77% yield). A satisfactory ^{1}H NMR spectrum was not obtained: LD-MS obsd 3905.4, calcd avg mass 3908.3; λ_{abs} 421, 544, 686, 722 nm; λ_{em} 725 nm.

Iodo-Bis(zinc porphyrin)−Phthalonitrile (Zn-26). Following a slight modification[29] of a procedure developed by Osuka,[17,22] a solution of **Zn-20** (0.079 g, 0.081 mmol) and **Zn-15** (0.077 g, 0.081 mmol) in $CHCl_3$ (50 mL) was treated with $AgPF_6$ (0.031 g, 0.12 mmol) and DMA (250 μL), and the reaction mixture was stirred under argon for 1.5 h. The crude reaction mixture was then washed with H_2O, dried (Na_2SO_4), and evaporated to dryness. The crude product was chromatographed (silica, CH_2Cl_2/hexanes, 3:1) yielding three fractions composed of the homocoupled product of **Zn-15** (30% yield), the title compound, and the homo-coupled product of **Zn-20** (23% yield) (assignment of these products stems from LD-MS). The second fraction was further chromatographed by SEC (THF) to afford a red-brown solid (0.071 g, 45% yield): ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 72H), 7.65−7.75 (m, 4H), 7.80−8.40 (m, 23 H), 8.72 (d, 4H, $J = 4.2$ Hz), 8.95−9.10 (m, 8H); LD-MS obsd 1932.8; FAB-MS obsd 1922.66, calcd exact mass 1922.66 ($C_{118}H_{111}N_{10}IZn_2$); λ_{abs} 422, 462, 560 nm.

Iodo-Bis(porphyrin)−Phthalonitrile (26). A solution of **Zn-26** (0.050 g, 0.02 mmol) in CH_2Cl_2/TFA (4:1) was stirred overnight. The crude reaction mixture was then washed with 0.1 M NaOH (100 mL), dried (Na_2SO_4), and chromatographed (alumina, CH_2Cl_2/hexanes, 1:1) affording a brown solid (0.044 g, 95% yield): ^{1}H NMR δ −2.17 (s, 2H), −2.15 (s, 2H), 1.45 (s, 72H), 7.70−7.80 (m, 4H), 7.85−8.40 (m, 23 H), 8.64 (d, 4H, $J = 5.1$ Hz), 8.85−9.00 (m, 8H); LD-MS obsd 1803.5; FAB-MS obsd 1798.84, calcd exact mass 1798.84 ($C_{118}H_{115}N_{10}I$); λ_{abs} (log ϵ) 419 (5.26), 457 (5.32), 525 (4.66), 596, 655 nm.

Perylene−Bis(zinc porphyrin)−Phthalonitrile (Zn-27). Following a general Pd-coupling procedure,[32] a mixture of **Zn-26** (0.060 g, 0.031 mmol), ethynylperylene **9** (0.017 g, 0.031 mmol), $Pd_2(dba)_3$ (0.005 g, 5 μmol), and P(*o*-tol)$_3$ (0.011 g, 36 μmol) in toluene/triethylamine (14 mL, 5:1) was reacted in a Schlenk flask at 35 °C for 2 h. The crude reaction mixture was evaporated to dryness, chromatographed (silica, CH_2Cl_2/hexanes, 3:1), and chromatographed (SEC, THF) to afford a purple solid (0.059 g, 82% yield): ^{1}H NMR δ 1.33 (s, 9H), 1.34 (s, 9H), 1.44 (s, 36H), 1.45 (s, 36H), 7.06 (d, 2H, $J = 2.1$ Hz), 7.27−7.63 (m, 3H), 7.69−7.75 (m, 4H), 7.80−8.20 (m, 20H), 8.30−8.80 (m, 15H), 8.95−9.15 (m, 8H); LD-MS obsd 2337.3; FAB-MS obsd 2327.97, calcd exact mass 2327.99 ($C_{156}H_{141}N_{11}O_2Zn_2$); λ_{abs} 422, 463, 560, 604 nm; λ_{em} 625, 657 nm.

Perylene−Bis(porphyrin)−Phthalonitrile (27). A solution of **Zn-27** (0.010 g, 4.3 μmol) in CH_2Cl_2/TFA (4:1) was stirred overnight. The crude reaction mixture was then washed with 0.1 M NaOH (50 mL), dried (Na_2SO_4), and chromatographed (alumina, CH_2Cl_2/hexanes, 1:1), affording a reddish-brown solid (0.075 g, 80% yield): ^{1}H NMR δ −2.15 (s, 2H), −2.13 (s, 2H), 1.33 (s, 9H), 1.35 (s, 9H), 1.44 (s, 36H), 1.45 (s, 36H), 7.05 (d, 2H, $J = 2.1$ Hz), 7.27−7.65 (m, 3H), 7.70−7.75 (m, 4H), 7.80−8.20 (m, 20H), 8.30−8.80 (m, 15H), 8.85−9.00 (m, 8H); LD-MS obsd 2214.7; FAB-MS obsd 2204.15, calcd exact mass 2204.16 ($C_{156}H_{145}N_{11}O_2$); λ_{abs} (log ϵ) 419 (5.34), 457 (5.38), 530 (5.08), 597 (4.38), 656 (4.18) nm; λ_{em} 636, 728 nm.

Iodo−Bis(porphyrin)−Phthalocyanine (28). Following a standard procedure,[1,34] a solution of pentanol (5 mL) was treated with lithium ribbon (0.061 g, 8.8 mmol) and the reaction mixture was stirred at ~90 °C until the lithium had reacted. The reaction mixture was cooled to room temperature and **25** (0.025 g, 14 μmol) and 4-*tert*-butylphthalonitrile (0.023 g, 0.13 mmol) were added; then the reaction mixture was heated to 145 °C and stirred for 3 h. The reaction mixture was cooled to room temperature, dissolved in CH_2Cl_2, washed with H_2O/MeOH (100 mL, 1:1), dried (Na_2SO_4), chromatographed (silica, toluene), chromatographed (SEC, THF), and chromatographed (silica, toluene) to afford a green solid (0.010 g, 30%). ^{1}H NMR (500 MHz) δ −3.1 to −2.4 (m, 2H), −2.10 to −2.00 (m, 4H), 1.45 (s, 36H), 1.47 (s, 36H), 1.96 (m, 27H), 7.65−9.30 (m, 48H)]; LD-MS obsd 2360.1; FAB-MS obsd 2353.12, calcd exact mass 2353.15 ($C_{154}H_{153}N_{16}I$); λ_{abs} (log ϵ) 418 (5.38), 456 (5.43), 526 (4.78), 608 (4.63), 674 (5.15), 696 (5.11) nm.

Meso,Meso-Linked Bis(zinc porphyrin) (Zn-30). Following a slight modification[29] of a procedure developed by Osuka,[17,22] a solution of **29**[29] (0.030 g, 0.032 mmol) in $CHCl_3$ (16 mL) was treated with $AgPF_6$ (0.031 g, 0.12 mmol) and DMA (80 μL), and the mixture was stirred under argon for 1 h. The crude reaction mixture was then washed with H_2O (100 mL), dried (Na_2SO_4), and chromatographed (silica, $CHCl_3$), affording a red-brown solid (0.025 g, 83% yield): ^{1}H NMR δ 1.46 (s, 72H), 1.59 (s, 36H), 7.65−7.90 (m, 6H), 8.05−8.25 (m, 16 H), 8.74 (d, 4H, $J = 5.1$ Hz), 9.00−9.20 (m, 8H); LD-MS obsd 1880.7, 1817.7 [$M^+ - Zn$], 1866.0 [$M^+ - 15$], 1912.1 [$M^+ + 31$], 1946.7 [$M^+ + 66$]; FAB-MS obsd 1870.99, calcd exact mass 1870.99 ($C_{124}H_{142}N_8Zn_2$); λ_{abs} 421, 460, 559 nm; λ_{em} 623, 660 nm.

Meso,Meso-Linked Bis(porphyrin) (30). A solution of **Zn-30** (0.023 g, 0.012 mmol) in CH_2Cl_2/TFA (15 mL, 4:1) was stirred overnight. The crude reaction mixture was then washed with 0.1 M NaOH (100 mL), dried (Na_2SO_4), and chromatographed (alumina, CH_2Cl_2/hexanes, 1:1), affording a brown solid (0.020 g, 95% yield): ^{1}H NMR δ −2.10 (s, 4H), 1.45 (s, 72H), 1.58 (s, 36H), 7.65−7.90 (m, 6H), 8.05−8.20 (m, 16 H), 8.64 (d, 4H, $J = 4.5$ Hz), 8.90−9.05 (m, 8H); LD-MS obsd 1754.8; FAB-MS obsd 1747.16, calcd exact mass 1747.17 ($C_{124}H_{146}N_8$); λ_{abs} (log ϵ) 417 (5.40), 454 (5.45), 525 (4.80), 596 (4.28), 654 (3.92) nm; λ_{em} 662, 727 nm.

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Supporting Information Available: ^{1}H NMR for all new compounds (except **25**), absorption spectra for all perylene compounds, fluorescence spectra for perylenes **9** and **10**, and LD-MS, absorption, and fluorescence spectra for all porphyrin containing compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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