JOURNAL OF
Materials
CHEMISTRY

Synthesis and excited-state photodynamics of phenylethyne-linked porphyrin–phthalocyanine dyads†

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Received 3rd August 1999, Accepted 25th October 1999

Free base, zinc and magnesium mono-ethynyl phthalocyanines have been prepared as building blocks for constructing phthalocyanine-containing molecular devices. The phthalocyanine building blocks were prepared by the statistical reaction of 4,5-diheptylphthalonitrile and 4-(3-hydroxy-3-methylbut-1-ynyl)phthalonitrile, followed by chromatographic separation and subsequent deprotection. Seven porphyrin–phthalocyanine dyads in various metalation states have been prepared (M^1PM^2Pc; M^1, $M^2 = Zn^{2+}$, Mg^{2+}, or $2H^+$). $ZnPH_2Pc$ and ZnPZnPc were synthesized by Pd-coupling reactions of an ethynylphthalocyanine and an iodoporphyrin. Five other dyads (H_2PH_2Pc, $MgPH_2Pc$, MgPMgPc, H_2PMgPc, ZnPMgPc) were prepared by selective metalation and demetalation reactions starting from $ZnPH_2Pc$, based on the stability differences of metalloporphyrins and metallophthalocyanines. Transient absorption and static emission experiments indicate the following: (1) Excited singlet-state intramolecular energy transfer from the porphyrin to the phthalocyanine moiety is very fast ($\leqslant 10$ ps). (2) The efficiency of the energy-transfer process is very high (typically $\geqslant 90\%$), and is greatest in dyads in which competing charge transfer is inhibited on energetic grounds (*e.g.* $>98\%$ for H_2PH_2Pc). (3) Charge transfer involving the excited phthalocyanine and the porphyrin occurs to a limited degree (typically $<10\%$) depending on the redox characteristics of the chromophores. (4) The desirable strong emission properties of monomeric phthalocyanines are retained in most of the dyads ($\Phi_f = 0.37$–0.75). This paper establishes the foundation for utilizing phthalocyanines as strong-red absorbers, energy-transfer acceptors, and bright emitters in conjunction with porphyrin-based molecular photonic devices.

Introduction

As part of a program in molecular photonics, we have created covalently linked multiporphyrin arrays that function as energy funnels,[1] a molecular photonic wire[2] or optoelectronic gates.[3] In each case, excited-state energy transfer occurs from a metalloporphyrin (ZnP or MgP) to a free base porphyrin (H_2P), followed by emission of light from the free base porphyrin. Directed energy transfer occurs as a consequence of the energetically lower lying excited state of the free base porphyrins. The free base porphyrin is conveniently incorporated into porphyrin-based arrays but is not an ideal emitter due to its relatively low fluorescence quantum yield (*e.g.*, H_2TPP has $\Phi_f = 0.11$).[4] In order to tune and refine the building blocks for molecular photonic devices, we investigated other chromophores as alternative candidates for bright emitters to incorporate into the porphyrin-based arrays.

Among the chromophores considered, phthalocyanines (Pc) appeared to be ideal emitters in conjunction with porphyrin constituents for the following reasons: (1) Phthalocyanines and porphyrins display complementary optical transitions.[5,6] In particular, the lowest energy absorption of phthalocyanines is red shifted and more intense than that of porphyrins, and the Soret band of the phthalocyanine is blue-shifted and weaker than that of the porphyrin. (2) The fluorescence quantum yields of phthalocyanines are typically 6–10 times higher than those of the porphyrin counterparts.[7,8] (3) The emission spectra of phthalocyanines do not significantly overlap with those of porphyrins. (4) Phthalocyanines are much harder to oxidize than the corresponding porphyrins.[9] The latter feature enables electrochemical oxidation of a porphyrin gating element to be performed in the presence of a phthalocyanine. (5) The distinctly different energy levels of phthalocyanine and porphyrin macrocycles make it feasible to perform a global metalation of all porphyrin and phthalocyanine units in a molecular array while maintaining a directed energy-transfer process (from metalloporphyrin to metallophthalocyanine). This last consideration, which bears on synthesis design rather than photophysical properties, enables conditions that cause metalation/demetalation to be employed early in the synthesis. All pigments can then be metalated identically in the last step of the synthesis. Such manipulations are not available when metalloporphyrins and free base porphyrins are employed to achieve directed energy transfer.

We recently prepared a series of star-shaped arrays composed of four or eight peripheral porphyrins and one core phthalocyanine (Chart 1).[10] These arrays serve as light-harvesting architectures with good spectral coverage in the blue and red provided by the porphyrin and phthalocyanine, respectively. The incorporation of a phthalocyanine as a strong-red absorber and bright emitter in a molecular wire or optoelectronic gate requires the ability to attach a phthalocyanine to the molecular device at one site. In order to probe

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†Details of the syntheses of compounds **1**–**6** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/jm/a9/a906273d/, otherwise available, together with other experimental data, from BLDSC (SUPPL. NO. 57671, pp. 40) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

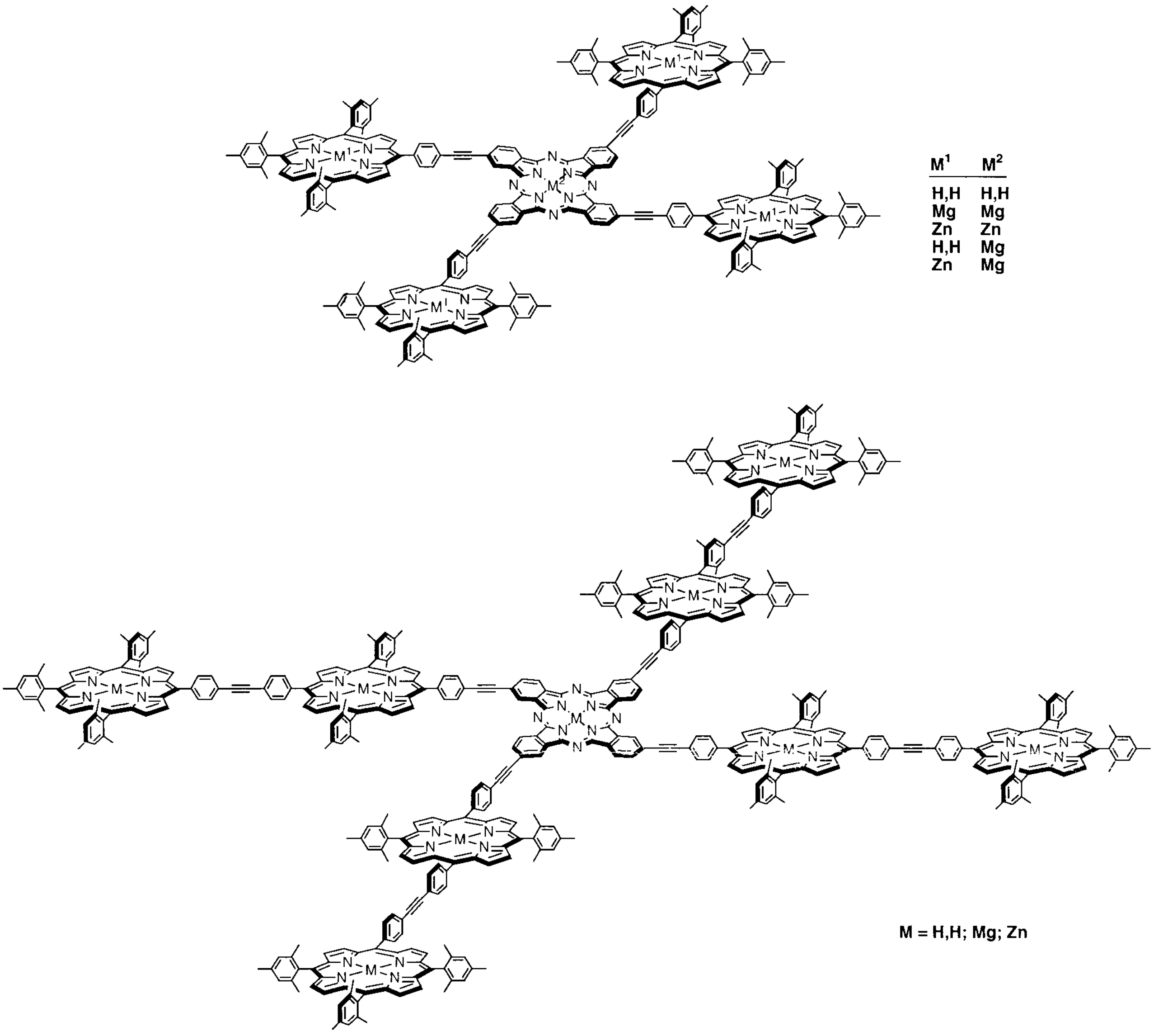


Chart 1 Porphyrin–phthalocyanine light-harvesting arrays. Each array is comprised of a mixture of regioisomers.

the pairwise interactions between covalently-linked porphyrin and phthalocyanine chromophores, as occurs in the porphyrin–phthalocyanine pentamers and nonamers,[10] and as an anticipated design motif in molecular wires or gates, we sought to prepare a family of covalently-linked porphyrin–phthalocyanine dyads. Despite the widespread use of phthalocyanine monomers, relatively few such porphyrin–phthalocyanine dyads have been constructed.[11,12] Some specific methods have been described for preparing unsymmetrical phthalocyanines such as polymer supported methods,[13] stepwise synthetic procedures,[14] and the ring enlargement reaction of subphthalocyanines.[15] Still, the most common method remains the reaction of two different phthalonitriles.[16] This procedure usually presents two problems: (1) The mono-substituted phthalocyanine must be separated by chromatography from the statistical mixture of four phthalocyanines. (2) In a reaction of two mono-substituted phthalonitriles, each of the four phthalocyanine products is in turn comprised of a mixture of regioisomers.[17] Difficulties in handling these mixtures is one major detraction of phthalocyanines.

Each covalently-linked porphyrin–phthalocyanine dyad that has been reported previously is composed of a mixture of structural isomers.[12] These dyads were prepared *via* a statistical reaction of a porphyrin-phthalonitrile and a mono-substituted phthalonitrile (*e.g.*, 4-*tert*-butylphthalonitrile). To avoid regioisomers in the phthalocyanine component of molecular arrays, we elected to synthesize a phthalocyanine bearing one ethyne and six solubilizing *n*-heptyl groups. In this paper, we report the synthesis of the mono-ethynyl phthalocyanine building block *via* a statistical reaction. Seven porphyrin–phthalocyanine dyads having various metalation states have been prepared by Pd-mediated coupling or *via* selective metalation/demetalation reactions. Static and time-resolved optical measurements indicate that energy transfer from the porphyrin to the phthalocyanine is fast and efficient in spite of complexities such as dual-exponential behavior, competition with charge transfer (generally < 10%) and aggregation (minimized at low concentrations). This work establishes the fundamentals for the synthesis of arrays containing porphyrins and phthalocyanines for applications in molecular photonics and has enabled the pairwise interactions of porphyrins and phthalocyanines to be examined in detail.

Results and discussion

1. Synthesis

Strategy. In preparing target systems such as dyads or larger arrays, the ideal phthalocyanine building blocks should exhibit the following properties: (1) bear a reactive handle such as an ethyne or iodo group for Pd-mediated coupling reactions, (2) retain the intrinsically high fluorescence quantum yield of phthalocyanines, (3) be available as a pure compound rather than a mixture of regioisomers, and (4) exhibit sufficient solubility and stability in common organic solvents for routine handling and spectroscopic examination. The phthalocyanine building blocks were designed to meet these criteria.

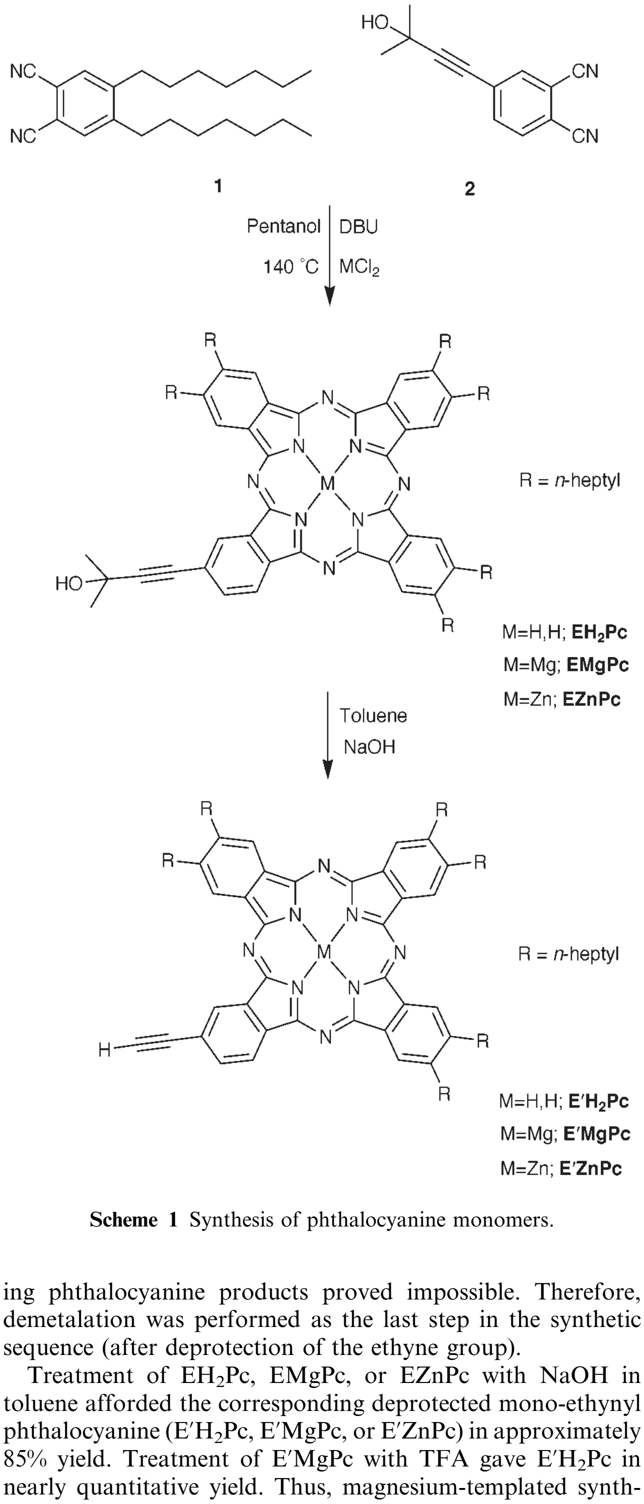
The synthetic handle on the phthalocyanine was chosen to be the ethyne rather than the iodo group for two reasons. (1) We want to perform various syntheses starting at the emitter end of a multichromophore array or device (*i.e.*, the phthalocyanine). The available protecting-group strategies require that bifunctional building blocks have one iodo group and one trimethylsilylethynyl group.[18] The former group is used for immediate coupling while the latter is deprotected only when subsequent coupling reactions to extend the array are to be performed. Hence the terminal mono-substituted building block must bear an ethynyl group for coupling with the iodo site on the bifunctional building block. (2) The ethynyl-substituted phthalocyanine is needed as a benchmark for comparison with the photophysical and other properties of the phthalocyanine-containing arrays.

In order to obtain a soluble mono-ethynyl phthalocyanine building block without regioisomers, a 4,5- or 3,6-disubstituted phthalonitrile can be used in the mixed reaction. Though there are no reports about regiospecific substituent effects on the solubility of phthalocyanines, the reported fluorescence-yield (Φ_F) values of phthalocyanines with substituents at the β(2,3)-positions (derived from 4,5-substituted phthalonitriles) do not differ markedly from those of the unsubstituted phthalocyanines,[19] while the Φ_F values with substituents at the α(1,4)-positions (derived from 3,6-substituted phthalonitriles) decrease significantly with increasing number of substituents. For 2,3,9,10,16,17,23,24-octaalkylphthalocyanines containing alkyl chains with odd numbers of carbons, the maximum solubility was observed with heptyl groups.[20] Thus, we chose 4,5-diheptylphthalonitrile as one starting material for preparing phthalocyanines.

Phthalocyanine building blocks. The starting materials for preparing the mono-ethynyl phthalocyanines, 4,5-diheptylphthalonitrile (**1**)[20,21] and 4-(3-hydroxy-3-methylbut-1-ynyl)phthalonitrile (**2**)[22] are known compounds. We have made slight improvements to the syntheses of these compounds starting from 1,2-dichlorobenzene and 4-nitrophthalonitrile. These procedures are described in the Supplementary Information.

The reaction of **1** and **2** (1 : 6 ratio) was carried out in *n*-pentanol in the presence of a metal salt and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 140 °C under an argon atmosphere for 24 h (Scheme 1). These conditions, developed by Shiraishi,[23] have proved applicable for the synthesis of a wide variety of phthalocyanines.[6,24] The reaction was performed in the absence of a metal salt in order to obtain the free base phthalocyanine, or in the presence of $MgCl_2$ or $Zn(OAc)_2 \cdot 2H_2O$ to obtain the corresponding metal chelate. Due to the differences in polarities of the four phthalocyanines produced in the statistical reaction, the desired mono-ethynyl phthalocyanine was easily separated in each case. The isolated yields of the mono-ethynyl phthalocyanine ranged from 3% for the protected ethynyl free base phthalocyanine (EH_2Pc) to 28% for the corresponding magnesium chelate (EMgPc). The low yield of EH_2Pc is attributable to lack of a metal template in the reaction and limited solubility. The solubility of the phthalocyanines increases in order of $EH_2Pc < EZnPc < EMgPc$.

An attempt to prepare EH_2Pc by acid-induced demetalation of EZnPc or EMgPc failed due to the lability of the 3-hydroxy-3-methylbut-1-ynyl group. Treatment of EMgPc with trifluoroacetic acid (TFA) resulted in demetalation but also loss of the 3-hydroxy-3-methylbut-1-ynyl group. Separation of the resulting phthalocyanine products proved impossible. Therefore, demetalation was performed as the last step in the synthetic sequence (after deprotection of the ethyne group).

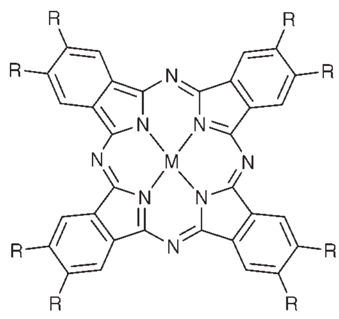


Scheme 1 Synthesis of phthalocyanine monomers.

Treatment of EH_2Pc, EMgPc, or EZnPc with NaOH in toluene afforded the corresponding deprotected mono-ethynyl phthalocyanine ($E'H_2Pc$, E′MgPc, or E′ZnPc) in approximately 85% yield. Treatment of E′MgPc with TFA gave $E'H_2Pc$ in nearly quantitative yield. Thus, magnesium-templated synthesis producing EMgPc followed by deprotection and demetalation proved to be the most attractive route to $E'H_2Pc$.

During the course of the statistical syntheses of the phthalocyanine building blocks, we isolated the octaheptylphthalocyanines ($(n\text{-heptyl})_8$MPc (Chart 2), which have previously been synthesized by Nishi *et al.*[20] These molecules serve as references for the photophysical properties of the mono-ethynyl hexaheptyl phthalocyanine monomers and the porphyrin–phthalocyanine dyads.

Porphyrin–phthalocyanine dyads. We have developed a Pd-mediated reaction for coupling iodo- and ethynyl-substituted porphyrin building blocks in dilute solution without alteration of the porphyrin metalation state. The conditions for the Pd-mediated reaction include use of tris(dibenzylideneacetone)di-



R = *n*-heptyl

M = H,H; **R_8H_2Pc**

M = Mg; **R_8MgPc**

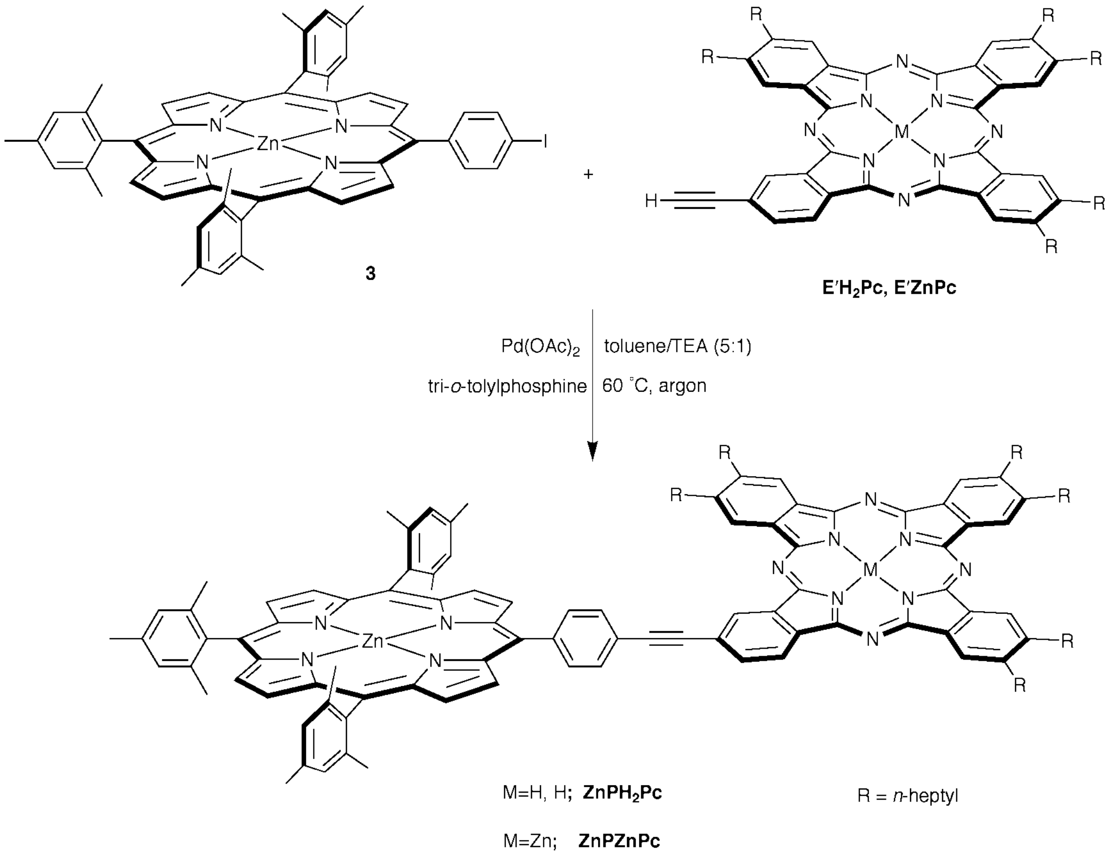
M = Zn; **R_8ZnPc**

Chart 2

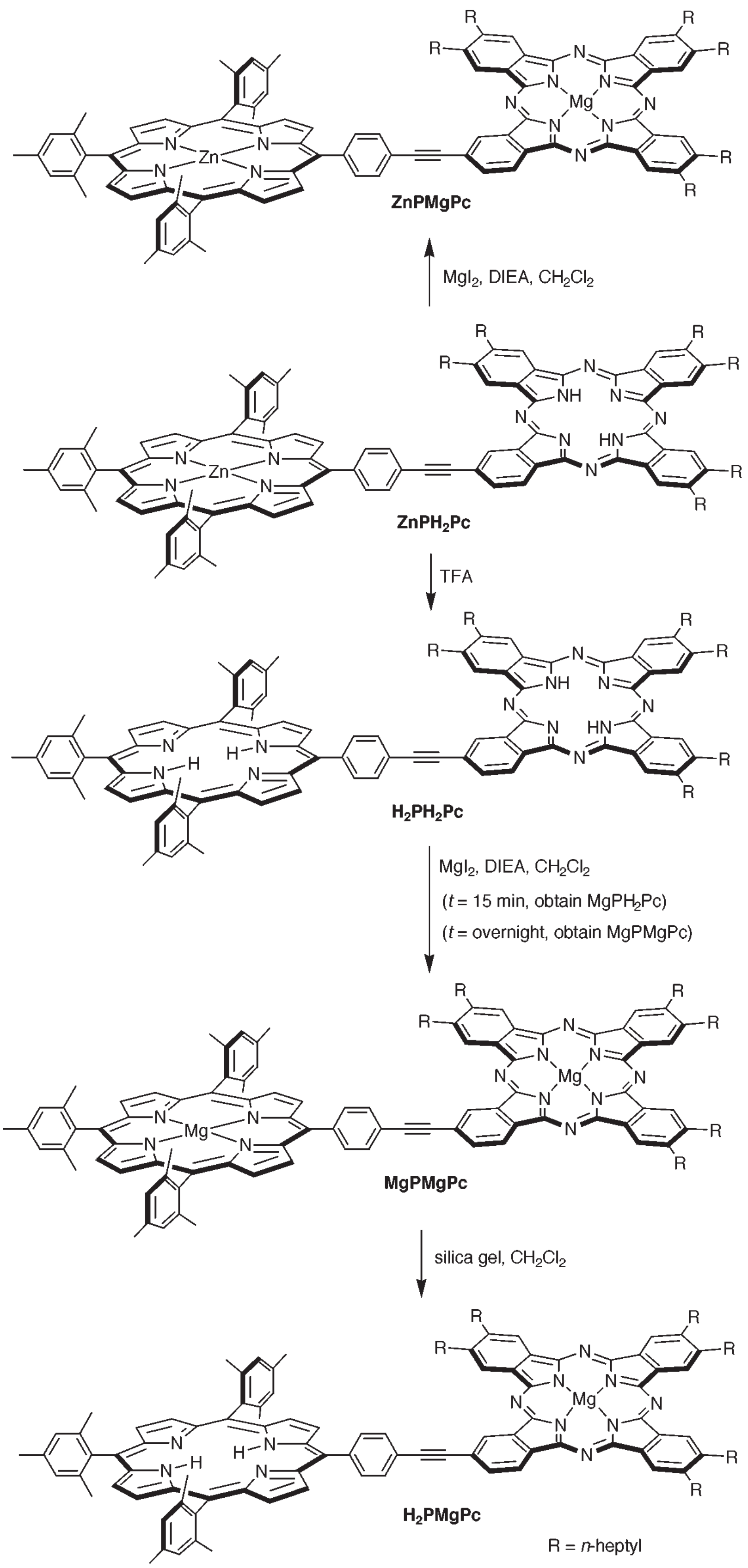
palladium(0) [$Pd_2(dba)_3$] and $AsPh_3$ in toluene–triethylamine (5 : 1) at 35 °C with 2.5 mM porphyrin reactants.[25] The reaction is generally complete in 2 h and isolated yields are ~60%. This reaction has been used to prepare multiporphyrin arrays[1–3,18] and phthalocyanine dimers.[26] However, due to the relatively low solubility of the phthalocyanine, the reaction between zinc 5,10,15-trimesityl-20-(4-iodophenyl)porphyrin[27] (**3**) and E′H_2Pc (~1.6 mM each) under the same conditions was not complete after 7 h and various by-products were observed. Therefore, we applied a new set of coupling conditions involving $Pd(OAc)_2$ and tri-*o*-tolylphosphine in toluene–triethylamine (5 : 1) at 60 °C, which gives fewer by-products.[28] The higher temperature was attractive for increasing the solubility of the phthalocyanine. Under these modified conditions, the coupling of **3** and E′H_2Pc was complete in ~3.5 h, affording the corresponding dyad $ZnPH_2Pc$ (Scheme 2). During the purification of $ZnPH_2Pc$, we found that traces of phthalocyanine starting material were very difficult to remove either by adsorption chromatography or preparative size exclusion chromatography (SEC). Upon using a slight excess of **3**, no ethynyl phthalocyanine starting material was detected by analytical SEC at the end of the reaction (~3.5 h), and the resulting dyad $ZnPH_2Pc$ was easily purified by adsorption chromatography followed by SEC in 54% yield. The similar reaction of **3** and E′ZnPc afforded the dyad ZnPZnPc in 50% yield.

Selective metalation and demetalation reactions. In order to probe the pairwise interactions of the porphyrin and phthalocyanine, various central metals can be used to tune the characteristics of the molecular orbitals and states and thus the photophysical properties of the dyad. A specific issue is to identify particular combinations of metals that give rise to deleterious excited-state quenching processes or (photo)chemical instability. In principle, all the desired dyads could be obtained directly by Pd-mediated coupling reactions as described above. However, given the different stabilities of a metalloporphyrin *versus* a metallophthalocyanine, we investigated the use of selective metalation or demetalation procedures as routes to some of the dyads with different combinations of central metals (Scheme 3). We have previously investigated a limited set of demetalation/metalation procedures in the porphyrin–phthalocyanine pentamers.[10]

Treatment of H_2PH_2Pc with the heterogeneous magnesium insertion conditions (MgI_2 and DIEA in CH_2Cl_2)[29] at room temperature for 15 min resulted in metalation of the porphyrin but not the phthalocyanine, and the complex $MgPH_2Pc$ was obtained in 79% yield. Upon stirring overnight, the all-magnesium complex MgPMgPc was obtained. Such differences in rates of magnesium insertion in porphyrins and phthalocyanines have been noted previously.[30] The similar magnesium



Scheme 2 Pd-mediated synthesis of ethyne-linked porphyrin–phthalocyanine dyads.



Scheme 3 Selective metalation and demetalation procedures.

insertion reaction starting with $ZnPH_2Pc$ gave the desired ZnPMgPc as well as some MgPMgPc due to transmetalation of the zinc porphyrin. An attempt to avoid this side reaction by decreasing the amount of MgI_2 failed to suppress porphyrin transmetalation without also decreasing the extent of magnesium insertion into the phthalocyanine. As a result, a large excess of MgI_2 must be used to make the insertion of magnesium into the phthalocyanine go to completion. The desired ZnPMgPc was then obtained by chromatographic separation of the reaction mixture.

Treatment of $ZnPH_2Pc$ with TFA gave the free base dyad H_2PH_2Pc in nearly quantitative yield. Treatment of MgPMgPc with silica gel in CH_2Cl_2 for 4 h at room temperature gave H_2PMgPc with no observable demetalation of the phthalocyanine moiety. The latter process reflects the increased kinetic lability (toward acid) with increased electron richness of the magnesium porphyrinic macrocycle. The four additional nitrogens in a phthalocyanine macrocycle compared with a porphyrin render the former less electron rich and hence more resistant toward demetalation. Indeed, when a mixture of E′MgPc and silica gel in CH_2Cl_2 was stirred for 5 h, no demetalation was observed as determined by TLC analysis and absorption spectroscopy. Thus, metalation/demetalation procedures (Scheme 3) can be used to complement Pd-coupling methods (Scheme 2) to prepare porphyrin–phthalocyanine dyads in various desired combinations of metalation states.

2. Physical properties of the monomeric phthalocyanine building blocks

The mono-ethynyl hexaheptyl phthalocyanines ($E'H_2Pc$, E′MgPc, E′ZnPc; Scheme) were characterized by absorption spectroscopy, fluorescence spectroscopy, LD-MS, high resolution FAB-MS, and ^1H NMR spectroscopy. The ^1H NMR spectrum of $E'H_2Pc$ was recorded in toluene-d_8 and displayed reasonably well-resolved peaks. The ^1H NMR spectra of E′MgPc and E′ZnPc in toluene-d_8 displayed broad peaks, especially in the aromatic region. In pyridine-d_5, the spectra of E′MgPc and E′ZnPc displayed well-resolved peaks both in the aromatic and alkyl regions with resonance patterns similar to those of $E'H_2Pc$. Axial ligation of pyridine to the metallophthalocyanines appears to reduce the effects of aggregation on the NMR spectra of these molecules.

The electronic absorption spectra of the mono-ethynyl hexaheptyl phthalocyanine monomers exhibit the expected strong absorption in the red region. The Q bands are split due to the combination of reduced symmetry and the electronic effects of the ethyne group. This effect is not seen for monomers such as $(n\text{-heptyl})_8MPc$[19] (Chart 1) or $(tert\text{-butyl})_4MPc$.[8] The fluorescence emission spectra of the mono-ethynyl hexaheptyl phthalocyanines are similar to those of $(n\text{-heptyl})_8MPc$ or $(tert\text{-butyl})_4MPc$, exhibiting only a small (typically ~2 nm) shift between the Q(0,0) absorption and emission maxima as well as approximate mirror symmetry relative to the absorption spectra.

Both the electronic absorption and emission spectra of the mono-ethynyl phthalocyanine monomers exhibit effects of aggregation similar to those observed for other phthalocyanines.[31a] These effects are observed at concentrations of several micromolar, and include increasing absorbance on the shorter-wavelength side of the Q(0,0) absorption band (*e.g.*, near 650 nm) and increasing emission on the shorter- and longer-wavelength sides of the Q(0,0) emission band with relative amplitudes that depend on the excitation wavelength. Additionally, inner-filter effects are observed on the emission spectra at higher concentrations due to the combination of the high oscillator strength of the Q(0,0) absorption and the large spectral overlap with the fluorescence.[31b] In order to minimize the effects of aggregation on the static optical spectra and emission yields, data were typically acquired at sub-micromolar concentrations.

As expected, the $E'H_2Pc$, E′MgPc, and E′ZnPc monomers exhibit high fluorescence quantum yields ($\Phi_F = 0.76$, 0.69, and 0.41, respectively; Table 1). These values are similar to those for phthalocyanines lacking ethynes such as the corresponding free-base and metal-containing octaheptyl phthalocyanines[19] (Table 1) and tetra-*tert*-butyl phthalocyanines.[8,12b] Thus, the mono-ethynyl hexaheptyl phthalocyanines are attractive candidates as light emitters in molecular photonic devices.

3. Physical properties of the porphyrin–phthalocyanine dyads

All of the dyads displayed enhanced solubility compared with their phthalocyanine monomer counterparts. Each dyad has been characterized by analytical SEC, absorption and fluorescence spectroscopy, LD-MS, high resolution FAB-MS and ^1H NMR spectroscopy. The data are given in the Experimental section and Supplementary Information. Key results are described in the following sections.

NMR spectra. To minimize aggregation phenomena, ^1H NMR spectra of the dyads comprised of metallophthalocyanines were collected in pyridine-d_5, while the ^1H NMR spectra of those containing free base phthalocyanines were collected in $CDCl_3$. All of these dyads displayed similar proton resonance patterns, which are roughly the sum of the corresponding component monomers (though $MgPH_2Pc$ gave only moderately resolved peaks). It is noteworthy that the resonance due to the inner NH-protons could be clearly distinguished for the free base porphyrin *versus* free base phthalocyanine (due to the different chemical shifts caused by the two macrocycles). These resonances provided a convenient diagnostic for the free-base units in the dyads obtained by metalation and demetalation reactions.

Static absorption and fluorescence spectra. The electronic absorption spectra of all the dyads in toluene are very similar to those of an equimolar mixture of the corresponding component monomers. For example, in the spectrum of H_2PH_2Pc shown in Fig. 1, the strong band near 420 nm is the porphyrin Soret band and the weaker bands near 515 and 550 nm are the porphyrin $Q_y(1,0)$ and $Q_x(0,0)$ bands, respectively; the even weaker Q_x components expected near 590 and 650 nm underlie the phthalocyanine absorption in this region. Similarly, the broad band near 350 nm is the phthalocyanine Soret band. Except for the very weak porphyrin Q_x bands just noted, the absorption to the red of 600 nm is composed of the phthalocyanine Q bands, with the prominent features between ~670 nm and ~720 nm being the $Q_x(0,0)$ and $Q_y(0,0)$ bands, each split due to the mono-ethyne substituent as in the monomers (*vide supra*). Furthermore, for each dyad the phthalocyanine fluorescence spectrum obtained upon excitation of this component (*e.g.*, in its Soret band near 350 nm) is essentially the same as that of the corresponding mono-ethynyl hexaheptyl monomer. As in the case of the monomers, the optical spectra and emission yields of the dyads were typically measured at sub-micromolar concentrations to minimize the effects of aggregation. Collectively, these observations indicate the absence of strong electronic interactions between the porphyrin and phthalocyanine that would otherwise perturb the desirable inherent spectral characteristics of each component.

Fluorescence yields. In each array, illumination of the porphyrin component results in fluorescence exclusively from the phthalocyanine. For example, the emission from H_2PH_2Pc obtained either with excitation in the Soret band (418 nm) or a Q band (515 nm) is essentially the same as that obtained for the $E'H_2Pc$ monomer (maximum near 710 nm) with no clear evidence of emission from the porphyrin (expected maximum near 650 nm) (Fig. 1). Similar behavior is observed for the other dyads. The energy-transfer efficiency can be quantitated by analysis of the yield of fluorescence from the porphyrin and the phthalocyanine obtained by excitation of the porphyrin, and the yield of fluorescence from the phthalocyanine obtained upon direct excitation of the phthalocyanine (Table 1). In particular, the phthalocyanine fluorescence yield with porphyrin excitation reflects the combination of (1) energy transfer to the phthalocyanine, (2) quenching processes that compete with the inherent deactivation processes of the photoexcited

Table 1 Excited-state properties of porphyrin–phthalocyanine dyads and appropriate monomers[a]

		Phthalocyanine					Porphyrin	
Compound	Porphyrin lifetime/ps[b]	Lifetime/ns[c]	$\Phi^{M}_{f,Pc}$ (measured)[d]	$\Phi^{D,Pc}_{f,Pc}$ (measured)[e]	$\Phi^{D,P}_{f,Pc}$ (measured)[f]	$\Phi^{D}_{CT,Pc}$ (calc)[g]	$\Phi^{D}_{CT,P}$ (calc)[h]	$\Phi^{D}_{ENT,P}$ (calc)[i]
Dyads:								
H_2PH_2Pc	1.1 ± 0.2 (70%) 8 ± 2 (30%)	5.3 ± 0.7		0.75 ± 0.02 (0.73)	0.75 ± 0.02	$\leqslant 0.02$	< 0.02	> 0.98
$ZnPH_2Pc$	0.9 ± 0.2 (80%) 9 ± 2 (20%)	5.2 ± 0.7		0.74 ± 0.03 (0.71)	0.67 ± 0.03	0.05	0.07	0.93
$MgPH_2Pc$	0.9 ± 0.2 (75%) 14 ± 3 (25%)	4.9 ± 0.7		0.68 ± 0.03 (0.67)	0.46 ± 0.03	0.11	0.28	0.72[j]
H_2PMgPc	0.8 ± 0.2 (43%) 4 ± 1 (57%)	4.7 ± 0.7		0.64 ± 0.04 (0.60)	0.64 ± 0.04	0.10	< 0.02	> 0.98
ZnPMgPc	0.8 ± 0.3 (43%) 11 ± 2 (57%)	4.5 ± 0.7		0.62 ± 0.04 (0.58)	0.54 ± 0.04	0.13	0.09	0.91
MgPMgPc	0.6 ± 0.1 (63%) 5 ± 1 (37%)	4.4 ± 0.7		0.43 ± 0.04 (0.56)	0.36 ± 0.04	0.19	0.29	0.71[j]
ZnPZnPc	0.9 ± 0.2 (65%) 13 ± 2 (35%)	2.3 ± 0.4		0.37 ± 0.03 (0.35)	0.33 ± 0.03	0.12	0.08	0.92
Monomers:[k]								
FbU	$13.3 \pm 0.5 \times 10^3$							
H_2TMP	$13.2 \pm 0.5 \times 10^3$							
MgU	$10.0 \pm 0.4 \times 10^3$							
MgTMP	$8.9 \pm 0.4 \times 10^3$							
ZnU	$2.4 \pm 0.2 \times 10^3$							
ZnTMP	$2.4 \pm 0.2 \times 10^3$							
$E'H_2Pc$		5.6 ± 0.7	0.76 ± 0.02					
R_8H_2Pc		5.5 ± 0.7	0.76 ± 0.02					
E′MgPc		5.5 ± 0.7	0.69 ± 0.06					
R_8MgPc		5.3 ± 0.7	0.70 ± 0.06					
E′ZnPc		2.7 ± 0.4	0.41 ± 0.03					
R_8ZnPc		2.9 ± 0.4	0.42 ± 0.03					

[a] All data were acquired in toluene at room temperature. [b] The excited singlet-state lifetimes for the porphyrins in the dyads were determined *via* transient absorption measurements. The values for the porphyrin monomers have been reported previously.[35] [c] The excited singlet-state lifetimes for the monomeric phthalocyanines are the average values from time-correlated single photon counting and fluorescence modulation (phase shift) methods (see text). [d] Fluorescence yields of the phthalocyanine monomers obtained using Soret (355 nm) excitation of the phthalocyanine referenced to values of 0.11 (H_2TPP),[4] 0.033 (ZnTPP),[4] and (*tert*-butyl)$_4$Pc, (0.77).[8] [e] Fluorescence yields of the porphyrin–phthalocyanine dyads obtained using Soret (355 nm) excitation of the phthalocyanine (referenced to the standards noted in footnote *d*). The same values within experimental error were obtained for selected complexes using phthalocyanine excitation at 675 nm: H_2PH_2Pc (0.75), $MgPH_2Pc$ (0.70), MgPMgPc (0.46). The values in parentheses are the expected phthalocyanine fluorescence yields in the dyads calculated from the lifetime data and monomer fluorescence yields using eqn. (4b) of Appendix 1. [f] The phthalocyanine fluorescence yields obtained using porphyrin Soret (420 nm) excitation. [g] Calculated yields of the $PPc^* \rightarrow P^+Pc^-$ charge-transfer process of the excited phthalocyanine in the dyads using eqn. (5b) of Appendix 1 along with the phthalocyanine fluorescence yields ($\Phi^{D,Pc}_{f,Pc}$) obtained for each dyad by averaging the measured value in column 5 and the value in parentheses in column 5 calculated from the lifetime data. [h] Calculated yield of the $P^*Pc \rightarrow P^+Pc^-$ charge-transfer process of the photoexcited porphyrin obtained using eqn. (7) of Appendix 1. [i] Calculated yield of the $P^*Pc \rightarrow PPc^*$ energy-transfer process obtained using either eqn. (8a) or (8b) of Appendix 1. [j] The energy-transfer yields may be somewhat larger than indicated because of greater (photo)chemical instability of these dyads with concomitant effects on the emission yields. [k] The nomenclature for the monomeric porphyrins is as follows: FbU is 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin. MgU and ZnU are the corresponding chelates of FbU. H_2TMP is 5,10,15,20-tetramesitylporphyrin, and MgTMP and ZnTMP are the corresponding metal chelates. The nomenclature for the monomeric phthalocyanines is given in Scheme 1.

porphyrin, and (3) subsequent quenching processes in the excited phthalocyanine that compete with its inherent deactivation processes. A measure of the latter quenching processes is provided by the phthalocyanine fluorescence yield in the dyad obtained with direct excitation of phthalocyanine and comparison with the fluorescence of the phthalocyanine monomer. The most likely excited-state quenching process in either the porphyrin or the phthalocyanine involves electron or hole transfer (forming the oxidized porphyrin and reduced phthalocyanine).[32] In this regard, charge transfer in porphyrin–phthalocyanine complexes has been observed previously.[12b] Analysis of the emission yield data for the various dyads using standard methods[33] and equations given in Appendix 1 reveals that the yield of photoinduced energy transfer from the porphyrin to phthalocyanine typically exceeds 90% and is basically quantitative (> 98%) for H_2PH_2Pc (Table 1). Furthermore, the analysis shows that the yields of the charge-transfer quenching processes (which track the ease of oxidation of the porphyrin: $H_2P < ZnP < MgP$) typically have values of < 10% and are negligible for H_2PH_2Pc (Table 1). Thus, the desired highly efficient photoinduced energy transfer from the porphyrin to the phthalocyanine and subsequent bright emission from the phthalocyanine are both generally obtained and can be optimized by choice of the porphyrin and phthalocyanine constituents of the dyad.

Fluorescence lifetimes. Fluorescence lifetimes for both the phthalocyanine component of the porphyrin–phthalocyanine dyads and the phthalocyanine reference monomers were determined by fluorescence modulation (phase and amplitude) techniques.[34] The lifetimes for the representative monomers and dyads were also obtained using time-correlated-single-photon-counting (TCSPC) spectroscopy. Fluorescence lifetimes for the relevant porphyrin monomers have been reported previously.[35] The excited-state decays of the porphyrins in the porphyrin–phthalocyanine dyads were determined by time-resolved absorption as described below.

The monomeric free base and magnesium phthalocyanines have lifetimes of ~5.5 ns and the zinc chelates have lifetimes of ~2.8 ns (Table 1). The lifetimes of the excited phthalocyanine components of the dyads are typically somewhat shorter than the values in the appropriate monomers. The extent of the lifetime shortening typically tracks the redox characteristics of the constituents, like the fluorescence yields. In fact, the

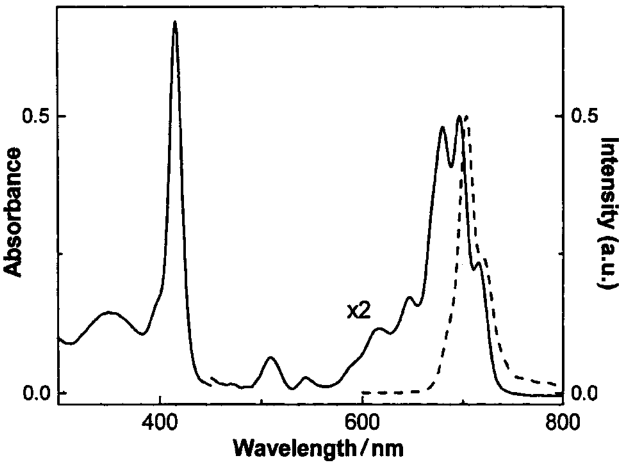


Fig. 1 Absorption (solid line) and fluorescence emission (dashed line, $\lambda_{\text{exc}} = 550$ nm) spectra of H_2PH_2Pc in toluene. The region of the absorption spectrum >430 nm has been multiplied ×2. The corresponding red-region absorption and emission maxima have been normalized to the same peak amplitude.

phthalocyanine excited-state lifetime for a given dyad *versus* the monomer can be used to calculate an expected phthalocyanine fluorescence yield. In basically all cases, the calculated value is in excellent agreement with the value measured from the static emission measurements using phthalocyanine excitation (fifth column in Table 1). Thus, the emission lifetime measurements fully support the conclusions drawn above from the emission yield measurements. In particular, the charge-transfer quenching processes in the excited phthalocyanine components of the dyads typically have <10% yields and are essentially nonexistent in the array H_2PH_2Pc.

Transient absorption spectra. The rate of energy transfer from the photoexcited porphyrin to the ground-state phthalocyanine in each dyad was assessed using transient absorption spectroscopy. Data were acquired in both the blue and red spectral regions under the same experimental conditions. Representative data for H_2PH_2Pc are shown in Fig. 2. Each of the arrays was excited using a 130 fs pulse at 420 nm, which predominantly pumps the porphyrin component of each array (see ground state absorption spectrum in Fig. 1). Hence, the absorption difference spectra ($\Delta A = A_{\text{excited-state}} - A_{\text{ground-state}}$) at early times are dominated by bleaching of the porphyrin Soret band (solid spectrum in Fig. 2). However, even at 0.2 ps after excitation, some bleaching is already observed in the ground state absorption bands of the phthalocyanine, notably in the red (Q_Y) bands between 670 and 720 nm. The bleaching in the phthalocyanine bands even at this early time after excitation is dominated by an extremely fast (~1 ps) component of P*Pc→PPc* energy transfer (*vide infra*). At increasing times after excitation, the bleaching in the porphyrin Soret band diminishes dramatically, reflecting return of the porphyrin component to the ground electronic state. Concomitantly, the bleaching in the phthalocyanine bands in the Q_Y region increases (see dashed spectrum taken at 16 ps in Fig. 2). Note that it is clear from the longer-time spectrum that the apparent bleaching near 700 nm (and 715 nm) is larger than that at 685 nm, which does not match the relative magnitudes of the features in the ground state spectrum shown in Fig. 1. This effect can be understood in terms of the enhanced contribution to the longer-wavelength features of excited-state stimulated emission (fluorescence stimulated by the white-light probe pulse) in addition to ground-state bleaching. These contributions to the transient spectra are in keeping with the characteristics of the static optical spectra (Fig. 1). Only small changes occur in the spectrum over the next tens of picoseconds (not shown). Given the spectral characteristics, the 16-ps spectrum in Fig. 2 can be assigned predominantly to the photoexcited phthalocyanine, resulting from the energy transfer process $H_2P^*H_2Pc \rightarrow H_2PH_2Pc^*$.

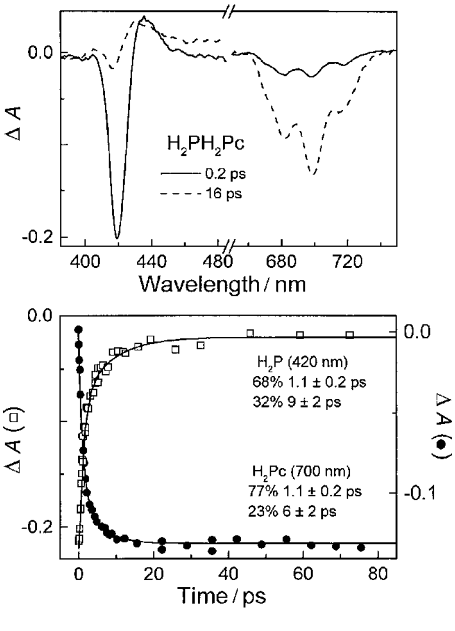


Fig. 2 Time-resolved absorption data for H_2PH_2Pc in toluene at 298 K, acquired using excitation of the porphyrin components with a 130 fs flash at 420 nm. The top panel shows absorption difference spectra corresponding to the porphyrin excited state (solid) and the phthalocyanine excited state (dashed). 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). Data before $t = 0$ and along the instrument rise are not shown for clarity.

The time profiles for decay of the porphyrin Soret bleaching near 420 nm and the growth of the phthalocyanine bleaching (and stimulated emission) near 700 nm for H_2PH_2Pc are both dual exponential in nature. Representative kinetic data and dual-exponential fits are given in the lower panel of Fig. 2. It can be seen that the time constant pairs in the two regions are in good agreement, with average values of ~1 ps and ~7 ps with ~70/30 relative amplitudes. Similar lifetimes, as well as similar transient absorption spectra in general, are observed for all the porphyrin–phthalocyanine dyads (Table 1).[36] Among the possibilities for the dual-exponential excited-state behavior,[37] the most likely stems from some aggregation of the dyads. (The ~10 μM sample concentrations required to obtain reliable kinetic data in both the porphyrin and phthalocyanine bleachings in the same sample are higher than the 0.3–0.8 μM concentrations employed for the fluorescence yield measurements.) In particular, in a fraction of the dyads, the porphyrin component of one molecule may interact closely with the phthalocyanine component of another. In such a mixture, the intramolecular process (porphyrin-to-phthalocyanine) could be responsible for one (*e.g.* the fast) kinetic component and an intermolecular process could give rise to the other component.

Energy-transfer rates and mechanisms. The transient absorption data, like the static fluorescence data, lead to the assessment that energy transfer from the photoexcited porphyrin to the phthalocyanine in the dyads is a very rapid and efficient process. However, the quantitative analysis of the energy transfer dynamics is complicated by the observation of two kinetic components in both the decay of the photoexcited porphyrin and formation of the excited phthalocyanine (with the major fraction having a time constant of ~1 ps and a lesser amount occurring with a time constant of ~10 ps).

An estimate for the energy-transfer parameters is most readily obtained by considering H_2PH_2Pc in toluene (for which ancillary quenching processes such as charge transfer are found to be negligible (*vide supra*)). The biphasic decay gives an amplitude-weighted lifetime of the photoexcited porphyrin of ~5 ps. This lifetime is at least 40-fold shorter than the lifetimes of the benchmark porphyrin monomers (Table 1). Thus, the rate of porphyrin-to-phthalocyanine energy transfer is substantially faster than the rates of the intrinsic processes for depopulation of the photoexcited porphyrin. These results can be used in conjunction with the standard equations[10a] to obtain an energy-transfer rate of $\sim(5\ \text{ps})^{-1}$ and an energy-transfer efficiency of >99% for the $P^*Pc \rightarrow PPc^*$ process in H_2PH_2Pc. This value is in excellent agreement with that deduced from the emission-yield measurements. For the other dyads, the energy-transfer rates remain $>(10\ \text{ps})^{-1}$ and the yields are typically >90% considering that the ancillary quenching processes (such as charge transfer) in the photoexcited porphyrin are modest or negligible in nonpolar media (*vide supra*).

Our previous studies on related all-porphyrin-containing arrays with the constituents connected by diarylethyne linkers have shown that excited-state energy-transfer is predominantly through-bond (TB) in nature and that through-space (TS) processes make a relatively minor contribution to the overall energy-transfer rate.[38] In analogs where the two porphyrins are connected by a *p*-phenylene linker, the TS process makes a larger contribution than in the diarylethyne-linked arrays due to the shorter inter-porphyrin distance. In some respects, the linker architecture in the present porphyrin–phthalocyanine arrays may be more similar to the *p*-phenylene-linked all-porphyrin arrays than the diarylethyne-linked all-porphyrin arrays. In fact, the average energy-transfer rate of $\sim(5\ \text{ps})^{-1}$ in the porphyrin–phthalocyanine dyads is comparable to the value of $(3.5\ \text{ps})^{-1}$ in the *p*-phenylene-linked zinc-porphyrin free base-porphyrin dimer and is faster than the rate of $(24\ \text{ps})^{-1}$ in the corresponding diphenylethyne-linked zinc-porphyrin free base-porphyrin dimer.[38] However, it is difficult to accurately assess the relative contributions of the TB and TS mechanisms in the porphyrin–phthalocyanine dyads due to (1) uncertainties in the exact value of the energy transfer rate in dyads due to the presence of the $\sim(1\ \text{ps})^{-1}$ and $\sim(10\ \text{ps})^{-1}$ values, and (2) the effects of aggregation on the spectra used to calculate the Förster overlap integrals[39] for evaluating the TS process. By analogy with our previous work on the porphyrin–porphyrin systems, it is likely that the TB process makes a significant contribution in the porphyrin–phthalocyanine dyads. However, like the *p*-phenylene-linked porphyrin dimers, the TS process may make an important contribution to photoinduced energy transfer in the porphyrin–phthalocyanine dyads as well.

Conclusion

Phthalocyanine building blocks bearing an ethyne moiety are ideal building blocks for the introduction of phthalocyanines into porphyrin-containing molecular photonic devices. The homo- and hetero-bimetallic porphyrin–phthalocyanine linked dyads have been prepared by coupling reactions as well as selective metalation and demetalation strategies. The phthalocyanines exhibit strong absorption in the red and high fluorescence quantum yields and are well-suited as bright emitters in porphyrin-based molecular devices. Energy transfer from photoexcited porphyrin to phthalocyanine is rapid and efficient. Among the seven dyads, non-energy-transfer quenching in either the porphyrin or phthalocyanine is essentially nonexistent for H_2PH_2Pc and is negligible (<10%) for most of the other dyads with the exception of the Mg-containing species. Collectively, the studies reported herein establish the foundation for the synthesis of devices such as photonic wires and gates containing multiple porphyrins and phthalocyanines.

Experimental

General

^1H NMR spectra (300 MHz, IBM FT-300), absorption spectra (HP 8451A, Cary 3), and fluorescence spectra (Spex FluoroMax) were collected routinely. Phthalocyanines, porphyrins, and dyads were analyzed by laser desorption mass spectrometry (LD-MS) without a matrix using a Bruker Proflex II, and by high resolution fast atom bombardment (FAB) on a JEOL (Tokyo, Japan) HX 110HF mass spectrometer. Porphyrins and phthalocyanines can be analyzed effectively by LD-MS without the use of matrices.[40] Commercial sources provided 4-nitrophthalonitrile (Acros), 4-iodobenzaldehyde (Karl Industries, Inc.), and 2-methylbut-3-yn-2-ol (Janssen Chimica). Unless otherwise indicated, all other reagents were obtained from Aldrich Chemical Company, and all solvents were obtained from Fisher Scientific.

Chromatography

Adsorption column chromatography was performed using alumina (Fisher A-540, 80–200 mesh), grade V alumina,[1b] 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 (4.8 × 60 cm) was packed using Bio-Beads SX-1 in toluene, and eluted with gravity flow. Following purification, the SEC column was washed with two volume equivalents of toluene.

Analytical scale SEC was performed to assess the purity of the dyads and to monitor the progress of the coupling reactions between the corresponding porphyrin and phthalocyanines. 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 (300 × 7.5 mm) columns eluting with THF (flow rate = 0.8 mL min^{-1}). Reaction monitoring was performed by removing aliquots from the reaction mixture and diluting with THF (Fisher, HPLC grade). Sample detection was achieved by absorption spectroscopy using a diode array detector with quantitation at 420 and 354 nm (±10 nm bandwidth).

Solvents

All solvents were dried by standard methods prior to use. 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.

Static absorption and emission

Static absorption (HP8451A, Cary 3, Perkin-Elmer Lambda 3B) and fluorescence (Spex Fluoromax or Fluorolog II) measurements were performed as described previously.[1b,38] Non-deaerated samples with an absorbance $\leqslant 0.15$ at λ_{exc} (0.3–0.8 μM) were used for the key emission measurements, although more concentrated samples were investigated; 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 appropriate reference monomers (ZnTPP, $\Phi_f = 0.033$;[4] H_2TPP, $\Phi_f = 0.11$;[4] (*tert*-butyl)$_4$Pc, $\Phi_f = 0.77$, ref. 8).

Time-resolved fluorescence

Fluorescence lifetimes were obtained by two methods. Samples for both methods were deaerated (by bubbling with N_2 or repetitive freeze–pump–thaw cycles) in toluene. The lifetimes reported herein were obtained with samples having concentrations of 0.5–1 μM, although concentrations as high as 10 μM were investigated. In the first method, lifetimes were determined by fluorescence modulation (phase shift) techniques using a Spex Tau2 spectrometer. Samples were excited at several wavelengths in the Soret- and Q-band regions and the emission at wavelengths >680 nm detected through 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 the second method, fluorescence lifetimes were measured by time-correlated single photon counting spectroscopy with an instrument having a response of about 30 ps. The samples were excited at several wavelengths in the Soret- and Q-band regions and detected at several wavelengths using a monochromator with a bandpass of 10 nm.

Time-resolved absorption

Transient absorption data were acquired as follows.[1b,37b] Samples (~10 μM in toluene) in 2 mm pathlength 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). Absorption changes were monitored (Princeton Instruments dual-diode array system) using a white-light probe flash generated in water with the residual 800-nm light (~0.3 mJ per pulse) from the Ti : sapphire–OPA system. (The probe flash contained approximately equal contributions of both polarizations with respect to the linearly polarized pump pulse.) On each laser flash, spectral data in a 250 nm window were obtained, and data from 300 flashes were averaged to achieve a ΔA resolution of better than ±0.005. Absorption changes in the blue and red regions (acquired under the same excitation and sample conditions) were then combined to make Fig. 2. Spectra at different pump-probe delay times were acquired by changing the path length over which the probe light traveled with respect to the pump pulse. Time profiles were obtained by averaging the ΔA values in 10 nm intervals about the specified wavelength, which was typically 420 nm for the porphyrin bleaching and 685 or 700 nm for the phthalocyanine bleaching. The kinetic traces were then fitted to a function consisting of a single or dual exponential plus a constant (along with the instrument response) using a nonlinear least squares algorithm.

2-(3-Hydroxy-3-methylbut-1-ynyl)-9,10,16,17,23,24-hexaheptylphthalocyanine (EH_2Pc)

A mixture of 1,2-dicyano-4,5-diheptylbenzene (**1**) (780 mg, 2.4 mmol), 4-(3-hydroxy-3-methylbut-1-ynyl)phthalonitrile (**2**) (84 mg, 0.40 mmol), and a catalytic amount (two drops) of DBU in dry *n*-pentanol (8 mL) was heated at reflux for 24 h with stirring under an argon atmosphere. After cooling to room temperature, the blue–green reaction mixture was poured into a solution of CH_3OH–H_2O (5 : 1, 60 mL). The resulting precipitate was collected by centrifugation and washed with CH_3OH. Column chromatography on silica gel with toluene–ethyl acetate (20 : 1) gave three bands, of which the second band ($R_f = 0.40$) was found to be the product. Removal of the solvent afforded 15 mg (3.1%) of a blue solid. ^1H NMR (300 MHz, toluene-d$_8$) δ 9.39 (s, 1H, ArH), 8.67–9.02 (m, 7H, ArH), 8.06 (d, 1H, $J = 7.8$ Hz, ArH), 2.90–3.22 (m, 12H, alkyl H), 1.81–1.97 (m, 18H, alkyl H), 1.45–1.65 (m, 12H, alkyl H), 1.02–1.06 (m, 36H, alkyl H), 0.83–0.87 (m, 18H, alkyl H), −2.45 (br s, 2H, NH); LD-MS *m/z* 1183.1 (M^+); HRMS (FAB) calcd. for $C_{79}H_{108}N_8O$ 1184.8646, found 1184.8677; λ_{abs} (toluene) 351, 649, 678, 700 nm.

2-(3-Hydroxy-3-methylbut-1-ynyl)-9,10,16,17,23,24-hexaheptylphthalocyaninatomagnesium(II) (EMgPc)

A mixture of 1,2-dicyano-4,5-diheptylbenzene (**1**) (900 mg, 2.78 mmol), 4-(3-hydroxy-3-methylbut-1-ynyl)phthalonitrile (**2**) (97 mg, 0.46 mmol), $MgCl_2$ (150 mg, 1.58 mmol) and two drops of DBU in dry *n*-pentanol (9 mL) was heated at reflux for 24 h with stirring under an argon atmosphere. After cooling to room temperature, the blue–green reaction mixture was poured into a solution of CH_3OH–H_2O (5 : 1, 60 mL). The resulting precipitate was collected by centrifugation and washed with CH_3OH. Column chromatography on grade V alumina with toluene–ethyl acetate (10 : 1) afforded four bands, of which the second band was found to be the title compound. Removal of the solvent afforded 158 mg (28.5%) of a blue solid. ^1H NMR (300 MHz, pyridine-d$_5$) δ 9.98 (s, 1H, ArH), 9.71–9.76 (m, 7H, ArH), 8.33 (d, 1H, $J = 8.1$ Hz, ArH), 7.61 (s, 1H, OH), 3.22–3.37 (m, 12H, alkyl H), 1.93–2.04 (m, 18H, alkyl H), 1.56–1.70 (m, 12H, alkyl H), 1.34–1.45 (m, 36H, alkyl H), 0.92 (m, 18H, alkyl H); LD-MS *m/z* 1206.5 (M^+); HRMS (FAB) calcd. for $C_{79}H_{106}N_8OMg$ 1206.8227, found 1206.8301; λ_{abs} (toluene) 357, 622, 682, 695 nm.

2-(3-Hydroxy-3-methylbut-1-ynyl)-9,10,16,17,23,24-hexaheptylphthalocyaninatozinc(II) (EZnPc)

A mixture of **1** (780 mg, 2.4 mmol), **2** (84 mg, 0.40 mmol), zinc acetate (100 mg, 0.50 mmol) and two drops of DBU in dry *n*-pentanol (8 mL) was heated at reflux for 24 h with stirring under an argon atmosphere. After cooling to room temperature, the reaction mixture was poured into a solution of CH_3OH–H_2O (5 : 1, 60 mL). The resulting precipitate was collected by centrifugation and washed with CH_3OH. Column chromatography on silica gel with toluene–ethyl acetate (10 : 1) gave three bands, of which the second band ($R_f = 0.19$) was found to be the title compound containing trace amounts of 2,3,9,10,16,17,23,24-octaheptylphthalocyaninatozinc. After a second column, 42 mg (8.4%) of the pure title compound was obtained as a blue solid. ^1H NMR (300 MHz, pyridine-d$_5$) δ 9.95 (s, 1H, ArH), 9.58–9.69 (m, 7H, ArH), 8.35 (d, 1H, $J = 8.1$ Hz, ArH), 7.63 (s, 1H, OH), 3.20–3.38 (m, 12H, alkyl H), 1.98–2.06 (m, 18H, alkyl H), 1.62–1.72 (m, 12H, alkyl H), 1.26–1.46 (m, 36H, alkyl H), 0.92 (m, 18H, alkyl H); LD-MS *m/z* 1249.1 (M^+); HRMS (FAB) calcd. for $C_{79}H_{106}N_8OZn$ 1246.7781, found 1246.7791; λ_{abs} (toluene) 354, 617, 680, 693 nm.

2-Ethynyl-9,10,16,17,23,24-hexaheptylphthalocyanine ($E'H_2Pc$)

A mixture of EH_2Pc (10 mg, 0.0085 mmol) and NaOH (0.5 g) in toluene (50 mL) was heated at reflux with stirring under an argon atmosphere. The reaction was monitored by TLC and was found to be complete after 3 h. The resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and loaded onto a short silica gel column (toluene–ethyl acetate 10 : 1). The desired product eluted as a single blue band ($R_f = 0.96$) giving 7.8 mg (82%) of a blue solid. ^1H NMR (300 MHz, toluene-d$_8$) δ 9.43 (s, 1H, ArH), 8.94 (d, 1H, $J = 8.1$ Hz, ArH), 8.81, 8.75 (m, 4H, ArH), 8.55, 8.52 (m, 2H, ArH), 8.07 (d, 1H, $J = 7.5$ Hz, ArH), 3.17 (s, 1H, ethynyl H), 2.79–3.12 (m, 12H, alkyl H), 1.74–2.00 (m, 12H, alkyl H), 1.40–1.71 (m, 12H, alkyl H), 0.99–1.12 (m, 36H, alkyl H), 0.73–0.97 (m, 18H, alkyl H), −2.77 (s, 2H, NH); LD-MS *m/z* 1128.3 (M^+); HRMS (FAB) calcd. for $C_{76}H_{102}N_8$ 1126.8227, found 1126.8182; λ_{abs} (toluene) 350, 657, 677, 699 nm.

2-Ethynyl-9,10,16,17,23,24-hexaheptylphthalocyaninatomagnesium(II) (E′MgPc)

A mixture of EMgPc (83 mg, 0.069 mmol) and powdered NaOH (0.5 g) in toluene (50 mL) was heated at reflux with stirring under an argon atmosphere. The reaction was monitored by TLC (alumina, toluene–ethyl acetate 20 : 1) and was found to be complete after 2 h. The resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated and loaded onto a short alumina column (grade V, toluene–ethyl acetate 10 : 1), and the blue band ($R_f = 0.67$) was collected, affording 65 mg (82%) of the desired product. ^{1}H NMR (300 MHz, pyridine-d$_5$) δ 10.02 (s, 1H, ArH), 9.60–9.70 (m, 7H, ArH), 8.42 (d, 1H, $J = 8.1$ Hz, ArH), 4.53 (s, 1H, ethynyl H), 3.22–3.35 (m, 12H, alkyl H), 1.98–2.12 (m, 12H, alkyl H), 1.56–1.73 (m, 12H, alkyl H), 1.35–1.48 (m, 36H, alkyl H), 0.93 (m, 18H, alkyl H); LD-MS *m*/*z* 1148.1 (M$^+$); HRMS (FAB) calcd. for $C_{76}H_{100}N_8Mg$ 1148.7921, found 1148.7981; λ_{abs} (toluene) 357, 621, 681, 695 nm.

2-Ethynyl-9,10,16,17,23,24-hexaheptylphthalocyaninatozinc(II) (E′ZnPc)

A mixture of compound EZnPc (20 mg, 0.016 mmol) and NaOH (0.5 g) in toluene (50 mL) was heated at reflux with stirring under an argon atmosphere. The reaction was monitored by TLC and was found to be complete after 2 h. The resulting mixture was cooled to room temperature and filtered. The filtrate was concentrated, and loaded onto a short silica gel column (toluene–ethyl acetate 10 : 1). The desired product eluted as a single blue band ($R_f = 0.67$) giving 16 mg (86%) of a blue solid. ^{1}H NMR (300 MHz, pyridine-d$_5$) δ 9.98 (s, 1H, ArH), 9.47–9.65 (m, 7H, ArH), 8.44 (d, 1H, $J = 8.1$ Hz, ArH), 4.58 (s, 1H, ethynyl H), 3.19–3.37 (m, 12H, alkyl H), 1.94–2.11 (m, 12H, alkyl H), 1.57–1.76 (m, 12H, alkyl H), 1.24–1.50 (m, 36H, alkyl H), 0.95 (m, 18H, alkyl H); LD-MS *m*/*z* 1190.7 (M$^+$); HRMS (FAB) calcd. for $C_{76}H_{100}N_8Zn$ 1188.7362, found 1188.7316; λ_{abs} (toluene) 354, 616, 679, 692 nm.

Synthesis of 2-ethynyl-9,10,16,17,23,24-hexaheptylphthalocyanine (E′H$_2$Pc) from the corresponding magnesium complex

A solution of E′MgPc (50 mg, 0.044 mol) in $CHCl_3$ (25 mL) was treated with TFA (5 mL) and stirred for 15 min at room temperature. The dark green mixture was then diluted with $CHCl_3$ (25 mL), washed successively with H_2O (1 × 50 mL), 5% $NaHCO_3$ (3 × 50 mL) and H_2O (1 × 50 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The blue solid obtained was then washed with methanol, and dried *in vacuo* to afford 45 mg (92%) of the free base phthalocyanine.

1-[4-(Zinc(II)-5,10,15-trimesitylporphin-20-yl)phenyl]-2-[2-(9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (ZnPH$_2$Pc)

Samples of **3** (18.6 mg, 19.9 μmol), E′H$_2$Pc (21.3 mg, 18.9 μmol), palladium acetate (0.84 mg, 3.78 μmol) and tri-*o*-tolylphosphine (4.6 mg, 15 μmol) 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 1 h. Then 10 mL of deaerated toluene and 2 mL of deaerated triethylamine were added *via* a syringe, and argon was purged through the vessel for another 5 min. At this point the argon flow was decreased and the reaction vessel immersed in an oil bath at 60 °C. The reaction was allowed to proceed at 60 °C with magnetic stirring and the reaction progress was checked by analytical SEC. Upon completion (3 h) of the reaction, the solution was concentrated to dryness, redissolved in 2 mL of toluene–hexane (3 : 2), and chromatographed on a flash silica gel column with toluene–hexane (3 : 2). The porphyrin–phthalocyanine dyad as well as some higher molecular weight material eluted as a single green band. The fractions were collected, concentrated to dryness, dissolved in 2 mL of toluene, and placed on the top of a preparative SEC column. Gravity elution afforded three major bands with the desired dyad as the second band. The dyad-containing fractions were collected and concentrated to dryness. The resulting solid was then suspended in methanol, centrifuged, and dried *in vacuo* to give 19.5 mg (53.6%) of a green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 1H, ArH), 9.07 (d, 2H, $J = 5.1$ Hz, β-pyrrole), 8.86–8.88 (m, 3H, β-pyrrole and ArH), 8.70–8.74 (m, 8H, β-pyrrole and ArH), 8.53 (m, 1H, ArH), 8.45 (d, 2H, $J = 7.8$ Hz, ArH), 8.36 (m, 1H, ArH), 8.28 (d, 2H, $J = 7.2$ Hz, ArH), 8.22 (d, 1H, $J = 7.2$ Hz, ArH), 7.30 (s, 6H, ArH), 2.95–3.28 (m, 12H, alkyl H), 2.64 (s, 9H, $ArCH_3$), 2.06–2.11 (m, 12H, alkyl H), 1.88 (s, 18H, $ArCH_3$), 1.50–1.82 (m, 48H, alkyl H), 0.95–1.01 (m, 18H, alkyl H), −2.45 (br s, 2H, NH); LD-MS *m*/*z* 1927.3 (M$^+$); HRMS (FAB) calcd. for $C_{129}H_{146}N_{12}Zn$ 1927.11, found 1927.12; λ_{abs} (toluene) 353, 424, 550, 621, 652, 683, 700, 719 nm.

1-[4-(Zinc(II)-5,10,15-trimesitylporphin-20-yl)phenyl]-2-[2-(zinc(II)-9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (ZnPZnPc)

Following the same procedure as for ZnPH$_2$Pc, samples of **3** (9.8 mg, 10.5 μmol), E′ZnPc (11.3 mg, 9.46 μmol), palladium acetate (0.42 mg, 1.89 μmol) and tri-*o*-tolylphosphine (2.3 mg, 7.6 μmol) were reacted. Upon completion (3.5 h) of the reaction, the solution was concentrated to dryness, redissolved in ~2 mL of toluene–ethyl acetate (20 : 1), and loaded onto a flash silica gel column with toluene–ethyl acetate (20 : 1) as the eluent. The porphyrin–phthalocyanine dyad as well as some higher molecular weight material eluted as a single green band. The fractions were collected and concentrated to dryness. The mixture was then dissolved in 1 mL of toluene and placed on the top of a preparative SEC column. Gravity elution afforded three major bands with the desired dyad as the second band. The dyad-containing fractions were combined and concentrated to dryness. The resulting solid was then suspended in methanol, centrifuged, and dried *in vacuo* to give 9.8 mg (50%) of a green solid. H NMR (300 MHz, pyridine-d$_5$) δ 10.19 (s, 1H, ArH), 9.58–9.78 (m, 7H, ArH), 9.26 (d, 2H, $J = 4.2$ Hz, β-pyrrole), 9.12 (d, 2H, $J = 4.5$ Hz, β-pyrrole), 8.99–9.05 (m, 4H, β-pyrrole), 8.65 (d, 1H, $J = 7.2$ Hz, ArH), 8.46 (d, 2H, $J = 8.1$ Hz, ArH), 8.32 (d, 2H, $J = 8.1$ Hz, ArH), 7.28, 7.35 (s, 6H, ArH), 3.26–3.42 (m, 12H, alkyl H), 2.54, 2.60 (m, 9H, $ArCH_3$), 1.86–2.06 (m, 30H, $ArCH_3$ and alkyl H), 1.61–1.70 (m, 12H, alkyl H), 1.36–1.50 (m, 36H, alkyl H), 0.94 (m, 18H, alkyl H); LD-MS *m*/*z* 1991.7 (M$^+$); HRMS (FAB) calcd. for $C_{129}H_{144}N_{12}Zn_2$ 1927.11, found 1927.12; λ_{abs} (toluene) 355, 423, 550, 618, 641, 681, 699 nm.

1-[4-(5,10,15-Trimesitylporphin-20-yl)phenyl]-2-[2-(9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (H$_2$PH$_2$Pc)

A sample of ZnPH$_2$Pc (10 mg, 5.2 μmol) was dissolved in $CHCl_3$ (15 mL) and treated with TFA (50 μL). The demetalation was complete after 15 min as evidenced by TLC analysis (alumina, toluene–hexane 3 : 2). Triethylamine (200 μL) was then added and the reaction mixture was stirred for another 15 min. The solution was diluted with 15 mL of $CHCl_3$, washed with 5% $NaHCO_3$ (3 × 30 mL) and water (1 × 30 mL), dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The desired product was obtained as a green solid, 9.5 mg (98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (s, 1H, ArH), 8.90–8.99 (m, 3H, β-pyrrole and ArH), 8.68–8.81 (m, 10H, β-pyrrole and ArH), 8.59 (m, 1H, ArH), 8.41–8.44 (m, 3H, ArH), 8.21–8.28 (m, 3H, ArH), 7.31 (s, 6H, ArH), 3.00–3.27 (m, 12H, alkyl H), 2.62 (s, 9H, $ArCH_3$), 1.96–2.62 (m, 12H, alkyl H), 1.91 (s, 18H, $ArCH_3$), 1.34–1.85 (m, 48H, alkyl H), 0.99 (m, 18H, alkyl H), −2.38 (br s, 2H, NH), −2.47 (s, 2H, NH); LD-MS *m*/*z* 1864.4 (M$^+$); HRMS (FAB) calcd. for

$C_{129}H_{148}N_{12}$ 1865.20, found 1865.18; λ_{abs} (toluene) 354, 421, 516, 550, 621, 652, 684, 700, 719 nm.

1-[4-(Magnesium(II)-5,10,15-trimesitylporphin-20-yl)phenyl]-2-[2-(9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (MgPH$_2$Pc)

To a solution of H_2PH_2Pc (10 mg, 5.3 µmol) in CH_2Cl_2 (1.5 mL) were added MgI_2 (50 mg, 0.18 mmol) and *N*,*N*-diisopropylethylamine (80 µL, 0.45 mmol).[29] The reaction mixture was stirred magnetically at room temperature under an argon atmosphere for 15 min. The dark green mixture was then diluted with 25 mL of CH_2Cl_2, washed with 5% $NaHCO_3$ (3 × 25 mL), dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure. Column chromatography on alumina (grade V) eluting with toluene followed by toluene–ethyl acetate (40 : 1) gave the product as a green solid. The solid was suspended in methanol, centrifuged, and dried under vacuum affording 8.0 mg (79%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 1H, ArH), 8.90 (m, 3H, β-pyrrole and ArH), 8.67 (m, 6H, β-pyrrole and ArH), 8.51 (m, 4H, β-pyrrole and ArH), 8.22–8.35 (m, 7H, ArH), 7.23 (m, 6H, ArH), 2.88–3.21 (m, 12H, alkyl H), 2.63 (s, 9H, $ArCH_3$), 0.99–1.70 (m, 96H, $ArCH_3$ and alkyl H), −2.56 (s, 2H, NH); LD-MS calcd. avg. mass for $C_{129}H_{146}N_{12}Mg$ 1888.9, obsd. 1885.6; λ_{abs} (toluene) 352, 429, 566, 619, 652, 684, 700, 719 nm.

1-[4-(Magnesium(II)-5,10,15-trimesitylporphin-20-yl)phenyl]-2-[2-(magnesium(II)-9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (MgPMgPc)

To a solution of H_2PH_2Pc (12 mg, 6.4 µmol) in CH_2Cl_2 (2 mL) were added MgI_2 (80 mg, 0.28 mmol) and *N*,*N*-diisopropylethylamine (100 µL, 0.56 mmol). The reaction mixture was stirred magnetically at room temperature overnight under an argon atmosphere. The metalation was complete as evidenced by TLC (alumina, toluene–ethyl acetate 20 : 1, $R_f = 0$) and absorption spectroscopy. Workup as for MgPH$_2$Pc afforded 11.6 mg (94.4%) of the desired product. ^{1}H NMR (300 MHz, pyridine-d$_5$) δ 10.27 (s, 1H, ArH), 9.77–9.86 (m, 7H, ArH), 9.21 (d, 2H, $J = 5.1$ Hz, β-pyrrole), 9.06 (d, 2H, $J = 4.5$ Hz, β-pyrrole), 8.91–8.97 (m, 4H, β-pyrrole), 8.63 (d, 1H, $J = 8.1$ Hz, ArH), 8.46 (d, 2H, $J = 8.1$ Hz, ArH), 8.27 (d, 2H, $J = 7.8$ Hz, ArH), 7.35, 7.28 (m, 6H, ArH), 3.28–3.38 (m, 12H, alkyl H), 2.56, 2.54 (m, 9H, $ArCH_3$), 1.87–2.05 (m, 30H, $ArCH_3$ and alkyl H), 1.58–1.68 (m, 12H, alkyl H), 1.27–1.49 (m, 36H, alkyl H), 0.94 (m, 18H, alkyl H); LD-MS *m*/*z* 1911.5 (M^+); HRMS (FAB) calcd. for $C_{129}H_{144}N_{12}Mg_2$ 1909.13, found 1909.14; λ_{abs} (toluene) 356, 428, 566, 682, 701 nm.

1-[4-(5,10,15-Trimesitylporphin-20-yl)phenyl]-2-[2-(magnesium(II)-9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (H$_2$PMgPc)

To a solution of MgPMgPc (10 mg, 5.2 µmol) in CH_2Cl_2 (10 mL), silica gel (1.0 g) was added. The mixture was stirred at room temperature under an argon atmosphere with shielding from ambient light. TLC analysis (alumina, toluene–ethyl acetate 20 : 1) showed the reaction was complete after 4 h. The resulting mixture was vacuum filtered through a fritted glass funnel, and washed with CH_2Cl_2–ethyl acetate (2 : 1) until the filtrate was colorless (~20 mL of solvent). The filtrate was evaporated to dryness and purified by column chromatography (alumina, grade V, toluene–ethyl acetate, 50 : 1), affording the desired product as a green solid. The product was suspended in methanol, centrifuged and dried under vacuum, giving 6.0 mg (61%). ^{1}H NMR (300 MHz, pyridine-d$_5$) δ 10.26 (s, 1H, ArH), 9.77–9.87 (m, 7H, ArH), 9.18 (d, 2H, $J = 5.1$ Hz, β-pyrrole), 8.97–9.04 (m, 6H, β-pyrrole), 8.63 (d, 1H, $J = 8.1$ Hz, ArH), 8.41 (d, 2H, $J = 8.1$ Hz, ArH), 8.32 (d, 2H, $J = 8.1$ Hz, ArH), 7.28, 7.34 (s, 6H, ArH), 3.28–3.34 (m, 12H, alkyl H), 2.54–2.59 (m, 9H, $ArCH_3$), 1.86–2.14 (m, 30H, $ArCH_3$ and alkyl H), 1.55–1.71 (m, 12H, alkyl H), 1.24–1.47 (m, 36H, alkyl H), 0.93 (m, 18H, alkyl H), −1.92 (s, 2H, NH); LD-MS *m*/*z* 1888.5 (M^+); HRMS (FAB) calcd. for $C_{129}H_{146}N_{12}Mg$ 1887.16, found 1887.15; λ_{abs} (toluene) 357, 421, 516, 550, 680, 699 nm.

1-[4-(Zinc(II)-5,10,15-trimesitylporphin-20-yl)phenyl]-2-[2-(magnesium(II)-9,10,16,17,23,24-hexaheptylphthalocyaninyl)]ethyne (ZnPMgPc)

To a solution of ZnPH$_2$Pc (10 mg, 5.2 µmol) in CH_2Cl_2 (2 mL) were added MgI_2 (50 mg, 0.18 mmol) and *N*,*N*-diisopropylethylamine (50 µl, 0.28 mmol).[29] The reaction mixture was stirred magnetically at room temperature under an argon atmosphere. After 6 h, the metalation appeared complete as judged by TLC and absorption spectroscopy. The dark green mixture was diluted with 30 mL of CH_2Cl_2, washed with 5% $NaHCO_3$ (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated to ~1 mL. Column chromatography on alumina (grade V) with CH_2Cl_2 afforded a light green band of residual starting material ZnPH$_2$Pc. Further elution with CH_2Cl_2–ethyl acetate (10 : 1) gave a green band of the desired product that was collected and evaporated to dryness. The resulting green solid was suspended in methanol, centrifuged, and dried under vacuum, affording 3.5 mg (35%). (Further elution with CH_2Cl_2–ethyl acetate (1 : 1 to 1 : 10) afforded another green band, which was ascertained by MS to be the dyad MgPMgPc; this side product was not characterized further.) ^{1}H NMR (300 MHz, pyridine-d$_5$) δ 10.26 (s, 1H, ArH), 9.77–9.87 (m, 7H, ArH), 9.24 (d, 2H, $J = 4.5$ Hz, β-pyrrole), 9.10 (d, 2H, $J = 5.1$ Hz, β-pyrrole), 8.99–9.05 (m, 4H, β-pyrrole), 8.65 (d, 1H, $J = 7.8$ Hz, ArH), 8.42 (d, 2H, $J = 8.1$ Hz, ArH), 8.27 (d, 2H, $J = 7.2$ Hz, ArH), 7.28, 7.35 (s, 6H, ArH), 3.28–3.35 (m, 12H, alkyl H), 2.54, 2.60 (m, 9H, $ArCH_3$), 1.86–2.06 (m, 30H, $ArCH_3$ and alkyl H), 1.60–1.66 (m, 12H, alkyl H), 1.31–1.47 (m, 36H, alkyl H), 0.93 (m, 18H, alkyl H); LD-MS *m*/*z* 1950.1 (M^+); HRMS (FAB) calcd. for $C_{129}H_{144}N_{12}ZnMg$ 1949.08, found 1949.08; λ_{abs} (toluene) 357, 424, 551, 656, 682, 701 nm.

Supplementary information available

Copies of ^{1}H NMR spectra and absorption spectra of E′H$_2$Pc, E′MgPc, E′ZnPc. ^{1}H NMR, absorption, fluorescence emission, and LD-MS spectra for all porphyrin-phthalocyanine dyads. Refined experimental procedures for preparing **1**–**6** (39 pages).

Appendix 1 Analysis of the photophysical data

The expressions relating the measured lifetimes, yields and microscopic rate constants for the depopulation pathways of the excited phthalocyanine monomer and the excited phthalocyanine in the dyads are as follows:

$$\tau^{M}_{Pc} = [k_{rad} + k_{isc} + k_{ic}]^{-1} \tag{1}$$

$$\Phi^{M}_{f,Pc} = k_{rad}\cdot[k_{rad} + k_{isc} + k_{ic}]^{-1} = k_{rad}\cdot\tau^{M}_{Pc} \tag{2}$$

$$\tau^{D}_{Pc} = [k_{rad} + k_{isc} + k_{ic} + k_{CT}]^{-1} \tag{3}$$

$$\Phi^{D,Pc}_{f,Pc} = \frac{k_{rad}}{k_{rad} + k_{isc} + k_{ic} + k_{CT}} = k_{rad}\cdot\tau^{D}_{Pc} \tag{4a}$$

$$\Phi^{D,Pc}_{f,Pc} = \tau^{D}_{Pc}\cdot\Phi^{M}_{f,Pc}/\tau^{M}_{Pc} \tag{4b}$$

$$\Phi^{D}_{CT,Pc} = \frac{k_{CT}}{k_{rad} + k_{isc} + k_{ic} + k_{CT}} \tag{5a}$$

$$\Phi^{\mathrm{D}}_{\mathrm{CT,Pc}} = 1 - \left[\Phi^{\mathrm{D,Pc}}_{\mathrm{f,Pc}} / \Phi^{\mathrm{M}}_{\mathrm{f,Pc}}\right] \quad (5b)$$

Here, $\tau^{\mathrm{D}}_{\mathrm{Pc}}$ is the excited-state lifetime of the excited phthalocyanine in the dyad (*i.e.*, in the presence of the porphyrin), $\Phi^{\mathrm{D,Pc}}_{\mathrm{f,Pc}}$ is the corresponding phthalocyanine fluorescence quantum yield in the dyad (measured using direct excitation of the phthalocyanine), $\tau^{\mathrm{M}}_{\mathrm{Pc}}$ is the excited-state lifetime of the benchmark phthalocyanine monomer, and $\Phi^{\mathrm{M}}_{\mathrm{f,Pc}}$ is the corresponding monomer fluorescence quantum yield. Also, $\Phi^{\mathrm{D}}_{\mathrm{CT,Pc}}$ is the quantum yield of the PPc*→P$^+$Pc$^-$ charge-transfer process of the excited phthalocyanine in the dyad. These equations assume that the rate constants for the intrinsic processes (radiative fluorescence decay (rad), intersystem crossing (isc), internal conversion (ic)) of the phthalocyanine are the same in the monomer and in the corresponding dyad. The equations also assume that the only additional process for depopulating the excited phthalocyanine in the dyad is charge transfer (CT) to the appended porphyrin (for each dyad energy transfer to the porphyrin is uphill, and fluorescence yield and lifetime measurements were done at concentrations where aggregation is minimal). The transient absorption and static emission data support these assumptions.

A similar set of expressions can be written for the excited porphyrin monomers and the excited porphyrin component of the dyads. The principal difference is that the excited porphyrin in the dyad has two new depopulation pathways in addition to the intrinsic processes (fluorescence, internal conversion, intersystem crossing). The intrinsic processes have a combined quantum yield of unity in the monomer and a combined quantum yield $\Phi^{\mathrm{D}}_{\mathrm{intrinsic,P}}$ in the dyads. The new depopulation channels are the P*Pc→P$^+$Pc$^-$ charge-transfer process (quantum yield $\Phi^{\mathrm{D}}_{\mathrm{CT,P}}$) and the P*Pc→ PPc* energy transfer process (quantum yield $\Phi^{\mathrm{D}}_{\mathrm{ENT,P}}$). These latter two processes dominate the decay of the excited porphyrin in each dyad such that both the fluorescence yield and excited-state lifetimes are reduced by several orders of magnitude relative to the appropriate porphyrin monomer (Table 1). Thus, the yield of the intrinsic processes ($\Phi^{\mathrm{D}}_{\mathrm{intrinsic,P}}$) in eqn. (6a) can be neglected relative to the other terms and eqn. (6b) is valid to a high degree of approximation.

$$\Phi^{\mathrm{D}}_{\mathrm{intrinsic,P}} + \Phi^{\mathrm{D}}_{\mathrm{CT,P}} + \Phi^{\mathrm{D}}_{\mathrm{ENT,P}} = 1 \quad (6a)$$

$$\Phi^{\mathrm{D}}_{\mathrm{CT,P}} + \Phi^{\mathrm{D}}_{\mathrm{ENT,P}} \approx 1 \quad (6b)$$

Finally, the yield of the P*Pc→P$^+$Pc$^-$ charge-transfer process can be derived by comparing (relative to the phthalocyanine monomer) the intensity of the phthalocyanine fluorescence in the dyad obtained using direct excitation of the phthalocyanine ($\Phi^{\mathrm{D,Pc}}_{\mathrm{f,Pc}}$ in eqn. (4) above) *versus* the intensity of the phthalocyanine fluorescence in the dyad obtained using excitation of the porphyrin ($\Phi^{\mathrm{D,P}}_{\mathrm{f,Pc}}$), using eqn. (7). Then, the yield of the P*Pc→PPc* energy-transfer process can be obtained from eqn. (8a) (obtained by combining eqn. (6b) and (7)) or eqn. (8b) (obtained by combining eqn. (5b), (6b), and (7)). For example, eqn. (7) and (8a) indicate that if charge-transfer quenching of the porphyrin were negligible (as are the intrinsic decay pathways, *vide supra*) compared to energy transfer to the phthalocyanine, then the intensity of phthalocyanine fluorescence would be the same whether the porphyrin or phthalocyanine were excited (for equal numbers of photons being absorbed).

$$\Phi^{\mathrm{D}}_{\mathrm{CT,P}} = [\Phi^{\mathrm{D,Pc}}_{\mathrm{f,Pc}} - \Phi^{\mathrm{D,P}}_{\mathrm{f,Pc}}] / \Phi^{\mathrm{M}}_{\mathrm{f,Pc}} \quad (7)$$

$$\Phi^{\mathrm{D}}_{\mathrm{ENT,P}} = 1 - [\Phi^{\mathrm{D,Pc}}_{\mathrm{f,Pc}} - \Phi^{\mathrm{D,P}}_{\mathrm{f,Pc}}] / \Phi^{\mathrm{M}}_{\mathrm{f,Pc}} \quad (8a)$$

$$\Phi^{\mathrm{D}}_{\mathrm{ENT,P}} = \Phi^{\mathrm{D}}_{\mathrm{CT,Pc}} + \Phi^{\mathrm{D,P}}_{\mathrm{f,Pc}} / \Phi^{\mathrm{M}}_{\mathrm{f,Pc}} \quad (8b)$$

Acknowledgements

This research was supported by a grant from the NSF (CHE-9707995). Fluorescence measurements by D.K. and H.S.C. at KRISS were supported by the Creative Research Initiatives of the Ministry of Science and Technology of Korea. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center and the NSF.

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32 Support for the view that $P^*Pc \rightarrow P^+Pc^-$ and $PPc^* \rightarrow P^+Pc^-$ are the most likely non-energy-transfer quenching processes derives from the following. (1) Since phthalocyanines are very difficult to oxidize,[9,10a] the most likely charge-transfer product involves oxidation of the porphyrin and reduction of the phthalocyanine. (2) The yields of the quenching processes generally increase as the oxidation potential of the porphyrin decreases (*i.e.*, easier oxidization along the series $H_2PH_2Pc < ZnPH_2Pc < MgPH_2Pc$), and the yield of $P^*Pc \rightarrow PPc^*$ energy transfer concomitantly decreases (Table 1). (3) For the H_2PH_2Pc dyad (for which both the $PPc^* \rightarrow P^+Pc^-$ and $P^*Pc \rightarrow P^+Pc^-$ processes are negligible in toluene), the P* emission dramatically quenches when the polarity of the solvent is increased by addition of 20% dimethyl sulfoxide or acetonitrile to toluene. It is noteworthy that the addition of significantly more of the polar solvent caused a broadening and decrease in intensity of the porphyrin Soret band (a reversible effect). This complicating factor, involving likely changes in axial ligation of metal-containing chromophores and/or changes in aggregation equilibria with solvent polarity, precludes carrying out meaningful studies of the solvent dependence of charge-transfer phenomena in these systems.

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34 Obtaining consistent lifetime results for the phthalocyanines required great care with sample conditions. Even at sample concentrations of 3–10 μM, up to two-fold variations in lifetime with concentration (and excitation/detection wavelength) were observed (*e.g.*, 4–8 ns for $E'H_2Pc$). These variations reflect a combination of aggregation and inner-filter effects that can either increase or decrease the measured lifetime from the actual value.[31] The lifetimes given in Table 1 are for low concentrations (<1 μM) and are in good agreement for the fluorescence modulation and TCSCP technique on samples (mainly the monomers) in which both techniques are employed.

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37 The finding that the exact time constants and relative amplitudes of the components change somewhat with detection wavelength is consistent with the view that an intermolecular process involving the interaction of two dyads may make a significant contribution to the dual-exponential kinetic behavior. Other potential contributors to the dual-exponential behavior that were considered include the following. (1) Charge transfer involving the second-excited state (B) *versus* lowest-excited state (Q) of the porphyrin with different overall rates is eliminated as a significant contributor by the previous finding of the same dual-exponential behavior for the $(H_2P)_4H_2Pc$ pentamer upon excitation of either the porphyrin B (Soret) or Q bands.[10a] (2) The presence of more than one ground- or excited-state conformer is another possibility, although we have not seen such dual-exponential behavior in either the diarylethyne-linked or *p*-phenylene-linked porphyrin–porphyrin dyads.[37] However, we have seen such behavior in covalently-linked porphyrin boron–dipyrrin complexes involving photoinduced conformational changes in the latter component. See: F. Li, S. I. Yang, Y. Ciringh, J. Seth, C. H. Martin III, D. L. Singh, D. Kim, R. R. Birge, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1998, **120**, 10001.

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Paper a906273d