Glaser-Mediated Synthesis and Photophysical Characterization of Diphenylbutadiyne-Linked Porphyrin Dyads

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The Pd-mediated Glaser coupling of a zinc monoethynyl porphyrin and a magnesium monoethynyl porphyrin affords a mixture of three 4,4′-diphenylbutadiyne-linked dyads comprised of two zinc porphyrins (**Zn-pbp-Zn**), two magnesium porphyrins (**Mg-pbp-Mg**), and one metalloporphyrin of each type (**Zn-pbp-Mg**). The latter is easily isolated due to the greater polarity of the magnesium versus the zinc chelate. Exposure of **Zn-pbp-Mg** to silica gel results in selective demetalation, affording **Zn-pbp-Fb** where Fb = free base porphyrin. This synthesis route employs the magnesium porphyrin as a latent form of the Fb porphyrin, thereby avoiding copper insertion during the Glaser reaction, and as a polar entity facilitating separation. The absorption spectrum of **Zn-pbp-Mg** or **Zn-pbp-Fb** is the sum of the spectra of the component parts, while in each case the fluorescence spectrum upon illumination of the Zn porphyrin is dominated by emission from the Mg or Fb porphyrin. Time-resolved absorption spectroscopy shows that the energy-transfer rate constants are (11 ps)$^{-1}$ and (37 ps)$^{-1}$ for **Zn-pbp-Mg** and **Zn-pbp-Fb**, respectively, corresponding to energy-transfer quantum yields of 0.995 and 0.983, respectively. The calculated Förster through-space rates are (1900 ps)$^{-1}$ and (1100 ps)$^{-1}$ for **Zn-pbp-Mg** and **Zn-pbp-Fb**, respectively. Accordingly, the through-bond process dominates for both dyads with a through-bond:through-space energy-transfer ratio of ≥97:1. Collectively, the studies show that the 4,4′-diphenylbutadiynyl linker supports fast and efficient energy transfer between Zn and Mg or Fb porphyrins.

Introduction

As part of a program in the design and synthesis of light-harvesting materials, we have constructed a variety of multiporphyrin arrays in which the porphyrins are joined via covalent linkers. The absorption of light by the porphyrins is followed by rapid singlet energy migration among these elements, ultimately terminating at the porphyrin with the lowest energy singlet excited state. In the course of our studies, we have investigated various dyads comprised of porphyrins in different metalation states to probe the rates, efficiencies, and mechanisms of energy transfer.[1] The metalation states include zinc (Zn), magnesium (Mg), and the free base (Fb); the combinations of metalation states include ZnFb, MgFb, and ZnMg. In ZnFb dyads containing a 4,4′-diphenylethyne linker (Chart 1), the energy-transfer rate is (24 ps)$^{-1}$, while in dyads containing a 1,4-phenylene linker, the rate is (3 ps)$^{-1}$.[2,3] In ZnMg dyads with a 4,4′-diphenylethyne linker, the rate is (9 ps)$^{-1}$.[4] For all of these dyads, the dominant mechanism of energy transfer is through-bond rather than through-space in nature. More recently, we have capitalized on the fast, efficient through-bond energy-transfer characteristics of the dyads by incorporating the ZnMg motif into extended architectures (light-harvesting rods) for use in molecular-based solar cells.[5]

The porphyrin dyads incorporating the diphenylethyne linker were constructed via the Sonogashira reaction,[6] whereas those with the 1,4-phenylene linker were constructed via aldehyde-pyrrole condensation reactions or the Suzuki reaction.[7] Both the Sonogashira and Suzuki reactions yield a number of side products that impose limitations in the preparation of multiporphyrin arrays. In contrast, the Glaser reaction, which yields a diphenylbutadiyne unit,[8] is relatively clean and potentially far better suited for preparing covalently linked multiporphyrin architectures. Indeed, the Glaser reaction has been previously used to construct a number of diphen-

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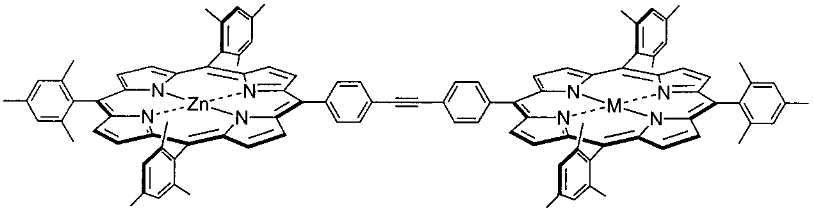
Chart 1



Zn-pep-Fb, M = H,H $k_{trans} = (24\ ps)^{-1}$

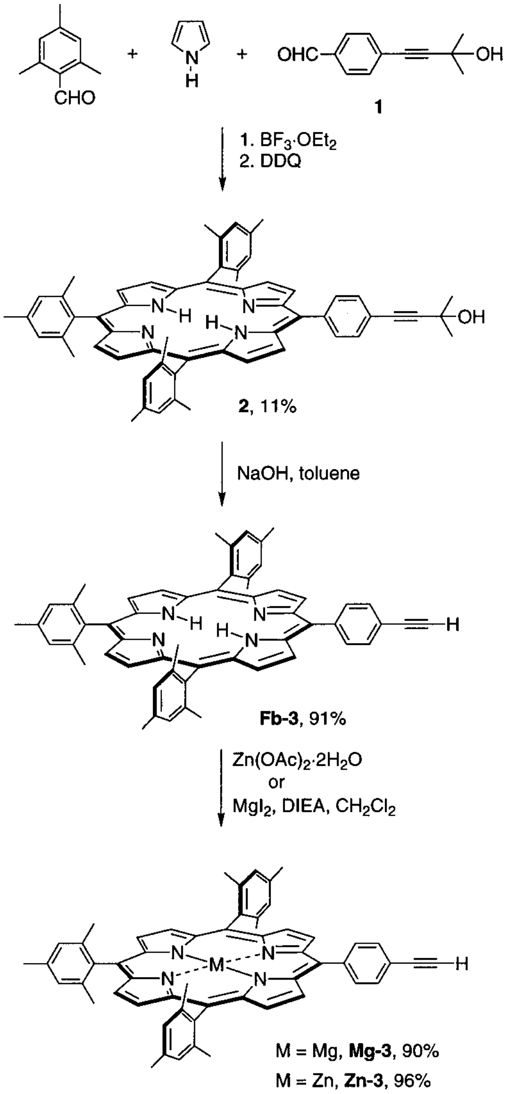
Zn-pep-Mg, M = Mg $k_{trans} = (9\ ps)^{-1}$

ylbutadiyne-linked multiporphyrin complexes.[6,9–11] Diphenylbutadiyne-linked porphyrins have also been prepared via condensation of a diphenylbutadiyne-dialdehyde + dipyrromethane.[12] Despite the potentially interesting photophysical characteristics of porphyrin arrays linked via a diphenylbutadiyne group, properties such as the rates and yields of energy transfer have not been reported for these arrays.

Knowledge of the extent of electronic communication in diphenylbutadiyne-linked porphyrin arrays is essential for assessing the utility of this linker motif for constructing light-harvesting elements and other porphyrin-based molecular photonic devices. One key limitation has been the lack of a simple route to dyads linked with a diphenylbutadiyne unit wherein the two porphyrins contain different metals. In this note, we address this issue and report a simple method for obtaining mixed metatalloporphyrin 4,4′-diphenylbutadiyne-linked dyads, including ZnFb and ZnMg combinations. We also probe electronic communication in these dyads by investigating the energy-transfer rates and yields.

Results and Discussion

Scheme 1



The Glaser reaction employs a copper reagent for the dimerization of ethynes. Fb porphyrins readily undergo copper insertion. Because Mg chelates of meso-substituted porphyrins can be readily prepared and then demetalated under conditions that do not alter the integrity of a Zn porphyrin,[13–15] we planned to use magnesium chelation to protect the desired Fb porphyrin from Cu insertion. The synthesis of the requisite metal chelate of 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin is shown in Scheme 1. The synthesis of the monoethynyl Fb porphyrin building block via our previous approach (mixed condensation of mesitaldehyde, 4-[2-(trimethylsilyl)ethynyl]benzaldehyde, and pyrrole)[9] required lengthy purification. To facilitate separation of the desired monoethynyl porphyrin, we employed the more polar 2-hydroxyisopropyl unit as the ethyne protecting group. Thus, a mixed-aldehyde condensation[9] of mesit-

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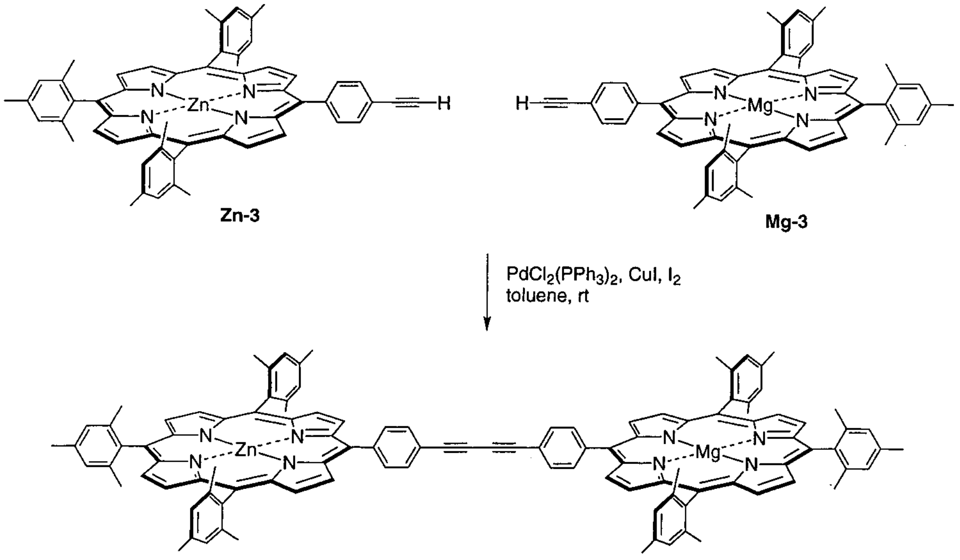
Scheme 2

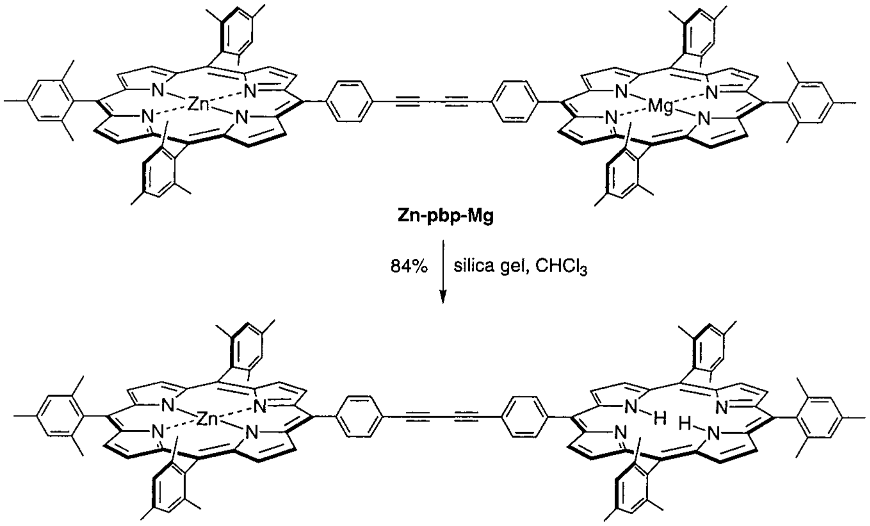


Zn-3

Mg-3

Zn-pbp-Mg (46%)
+ two dimers:
Zn-pbp-Zn
Mg-pbp-Mg

Scheme 3



Zn-pbp-Mg

Zn-pbp-Fb

aldehyde, aldehyde **1**,[16] and pyrrole was performed using BF$_3$−ethanol cocatalysis[17] at a high concentration.[18] A mixture of porphyrins was obtained, from which the desired monoethynyl porphyrin **2** was readily isolated by chromatography (Scheme 1). Subsequent cleavage of the hydroxyisopropyl group afforded the desired Fb porphyrin **Fb-3** in gram quantities. The corresponding chelate **Zn-3** or **Mg-3** was obtained by reaction at room temperature either with Zn(OAc)$_2$·2H$_2$O or with MgI$_2$ in the presence of DIEA (heterogeneous magnesium insertion conditions[13]), respectively.

A Glaser coupling reaction of an equimolar mixture of **Zn-3** and **Mg-3** was performed using the standard conditions for this Pd-mediated reaction: diisopropylamine as the base, Pd(PPh$_3$)$_2$Cl$_2$ and CuI as the catalysts, and I$_2$ as the oxidant[19] (Scheme 2). As expected from this statistical reaction, three diphenylbutadiyne-linked products (**Mg-pbp-Mg**, **Zn-pbp-Mg**, and **Zn-pbp-Zn**) were formed. The three dyads were easily separated due to the significant polarity difference imparted by the respective metals, affording the desired dyad **Zn-pbp-Mg** in 46% yield. Mg porphyrins are readily demetalated by treatment with silica gel, while Zn porphyrins are not.[13−15] Treatment of **Zn-pbp-Mg** with silica gel in CHCl$_3$ at room temperature caused selective demetalation of the magnesium porphyrin, affording the desired **Zn-pbp-Fb** dyad in 84% yield (Scheme 3). In this manner, the Mg chelate serves as (1) a polar site that facilitates separation of the hybrid product and (2) a protective group that upon removal affords the Fb

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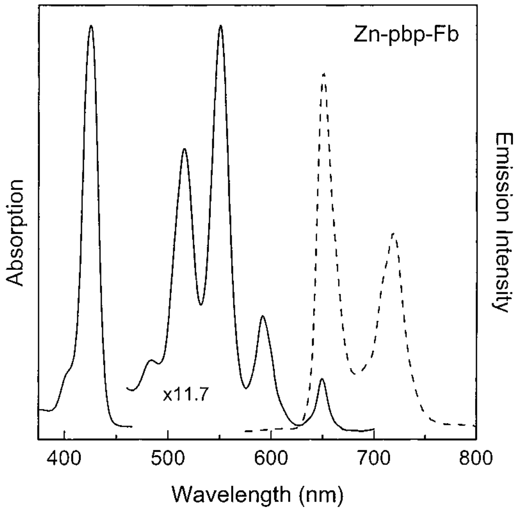

Figure 1. Absorption spectrum (solid) and fluorescence spectrum (dashed) for **Zn-pbp-Fb** in toluene at room temperature. The emission was obtained with 550 nm excitation (an identical spectrum was obtained using excitation at 515 nm).

porphyrin. This statistical route is complementary to the Cadiot−Chodkiewicz route for directed formation of butadiyne linkers.[8]

Spectroscopy. Absorption and emission spectra of **Zn-pbp-Fb** are shown in Figure 1. The ground-state spectrum of the dyad (solid line) is approximately the sum of spectra of its constituent monomers. The same is true for the analogous diphenylethyne-linked dyad **Zn-pep-Fb** (also called ZnFbU).[2] A combined Zn and Fb porphyrin Soret band occurs at 424 nm. The Zn porphyrin Q(2,0), Q(1,0), and Q(0,0) bands occur at 513, 550, and 591 nm, respectively. The following are the Fb porphyrin Q-bands: $Q_y(2,0)$, 483 nm; $Q_y(1,0)$, 515 nm; $Q_y(0,0)$, 550 nm; $Q_x(1,0)$, 592 nm; $Q_x(0,0)$, 650 nm. The emission spectrum of the dyad was obtained using two different excitation wavelengths. The fluorescence data shown in Figure 1 (dashed line) were elicited by excitation of both the Fb and Zn porphyrins (but not simultaneously in the same dyad) at 550 nm. Although the Zn porphyrin was excited in a significant fraction of the arrays, the spectrum contains only the Fb porphyrin fluorescence features, namely, Fb $Q_x(0,0)$ at 651 nm and Fb $Q_x(0,1)$ at 719 nm. The same emission spectrum is obtained upon direct excitation of the Fb porphyrin at 515 nm. Comparison of optically matched samples at this wavelength gives a Fb porphyrin emission quantum yield of $\Phi_f = 0.13$ in the dyad, which is comparable to the value of 0.12 for the **Fb-3** reference monomer.[15] In addition, the emission spectrum of the Fb porphyrin in **Zn-pbp-Fb** is essentially unchanged from that of **Fb-3**. Similar results were obtained for the **Zn-pbp-Mg** dyad: again, the ground-state spectrum is approximately the sum of the monomer spectra; the emission spectrum arises solely from the Mg porphyrin (λ_{em} 613 and 666 nm), even when the Zn porphyrin is preferentially excited.

The static absorption and emission results indicate the following. (1) The electronic interactions between porphyrins across the diphenylbutadiyne linker are relatively weak (but not insignificant). (2) Efficient energy transfer occurs from the Zn porphyrin to the Fb or Mg porphyrin in **Zn-pbp-Fb** or **Zn-pbp-Mg**, respectively. (3) The emission properties of the acceptor porphyrin are essentially unchanged from those of the isolated chromophore. These findings are similar to those made previously for the corresponding diphenylethyne-linked dyads (e.g., **Zn-pep-Fb**).[2]

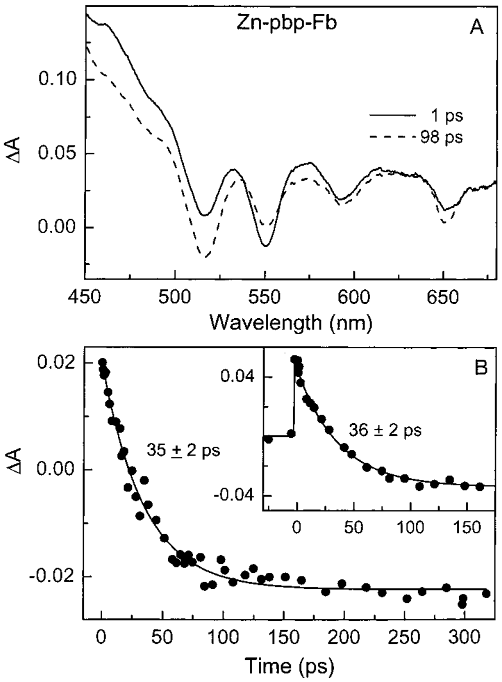

Figure 2. (A) Transient absorption difference spectra for **Zn-pbp-Fb** in toluene at room temperature obtained using 130 fs excitation flashes at 440 nm. (B) Time profile and single-exponential fit at 515 nm (referenced to ΔA at 553 nm) obtained using 440 nm excitation flashes (as in panel A). The inset to panel B gives a time profile and single-exponential fit at 515 nm obtained using 550 nm excitation flashes.

Transient absorption spectroscopy was used to probe energy transfer in both dyads, exciting primarily the Zn porphyrin in each case. Spectra and kinetics from experiments on **Zn-pbp-Fb** are shown in Figure 2. The absorption difference spectra in panel A were obtained by preferentially (but not exclusively) exciting the Zn porphyrin with 130 fs pulses at 440 nm. Shortly (1 ps) after excitation (solid line), the spectrum contains bleaching in the Zn porphyrin ground-state Q(1,0) and Q(0,0) bands at 550 and 592 nm, respectively. Because the Fb porphyrin is excited in a fraction of the arrays, the Zn porphyrin bleaches are superimposed on the Fb $Q_y(0,0)$ and $Q_x(1,0)$ features at the same wavelengths. The bleach of the Fb $Q_y(1,0)$ band occurs at 515 nm, and both Fb $Q_x(0,0)$ bleaching and Fb* $Q_x(0,0)$ stimulated emission occur at 650 nm. In the 98 ps spectrum (dashed), the Fb bleach at 515 nm has increased in amplitude and the Zn bleach at 550 nm has decayed. This finding indicates that energy transfer has occurred from the Zn porphyrin to the Fb porphyrin (denoted Zn* → Fb) in the fraction of the arrays in which the Zn porphyrin was initially excited. Kinetic analysis was performed on data in several spectral regions. The main portion of Figure 2B shows a time profile and single-exponential fit at 515 nm (referenced against data at 553 nm); in the inset, data from a separate experiment with 550-nm excitation are shown. These measurements and those in adjacent wavelength regions give nearly identical results, with an average Zn* lifetime of 36 ± 3 ps.

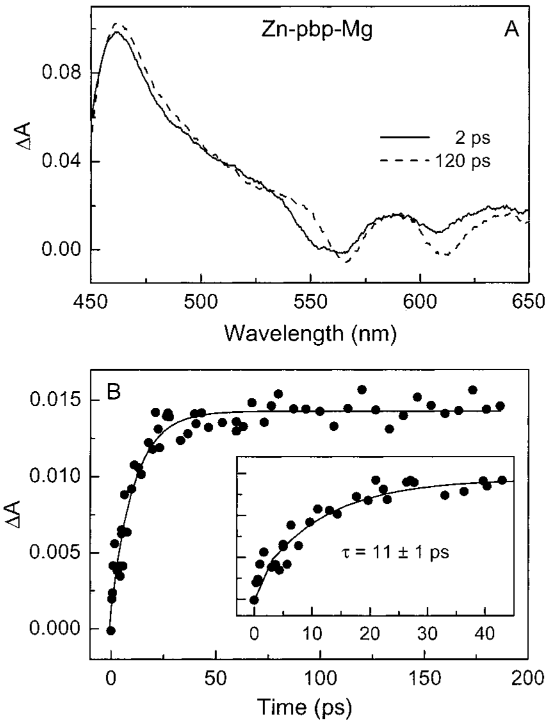

Figure 3. Transient absorption data for **Zn-pbp-Mg** in toluene at room temperature, obtained using 130 fs excitation flashes at 413 nm. (A) Absorption difference spectra. (B) Time profile monitored at 553 nm and a single-exponential fit. The inset to panel B shows the same data and fit using a reduced time axis and the same ΔA scale.

Table 1. Energy-Transfer Rates and Efficiencies for the Dyads[a,b]

	Zn-pep-Fb	Zn-pbp-Fb	Zn-pep-Mg	Zn-pbp-Mg
$(k_{\mathrm{trans}})^{-1}$	24	37	9	11
Φ_{trans}	0.99	0.98	>0.99	>0.99
R (Å)[c]	19.3	21.6	19.3	21.6
$(k_{\mathrm{TB}})^{-1}$	25	38	9.1	11
$(k_{\mathrm{TS}})^{-1}$	590	1100	970	1900
χ_{TB}	0.959	0.967	0.991	0.994
χ_{TS}	0.041	0.033	0.009	0.006

[a] Overall energy transfer rates and efficiencies were calculated from eqs 1−4 using τ_D = 2.4 ns. [b] Through-bond rates and efficiencies were calculated from eqs 5 and 6 and the calculated through-space rate from the Förster equation. Forster calculations were performed (using PhotochemCAD[21]) for samples in toluene at room temperature. [c] Note that the previous Forster calculation[2] employed R = 20 Å rather than 19.3 Å for the 4,4′-diphenylethyne-linked dyads. An average value for the TS contribution ((720 ps)$^{-1}$) was reported.[2] Spectral overlap terms (J values) for the ZnFb and ZnMg dyads were 3.0 × 10^{-14} and 1.8 × 10^{-14} cm^6/mmol, respectively.

Similar transient absorption experiments were performed on **Zn-pbp-Mg**, exciting primarily the Zn porphyrin at 413 nm (Figure 3). Again, because selective excitation is not possible, bleaching of both the Zn- and Mg-porphyrin ground-state bands is evident shortly after excitation (2 ps spectrum, solid). The Zn Q(1,0) bleach near 550 nm decays with time, and the Mg Q(1,0) bleach at 565 nm and Q(0,0) bleach and stimulated emission near 610 nm develop, as is evident in the 120 ps spectrum (dashed). The time profiles in several wavelength regions were again fit well by single-exponential functions, giving a Zn* lifetime of 11 ± 1 ps (Figure 3B).

Rates and Yields of Energy Transfer. The rate constants and yields of energy transfer in the dyads were calculated using eqs 1−4.

$$\tau_{\mathrm{D}} = (k_{\mathrm{f}} + k_{\mathrm{ic}} + k_{\mathrm{isc}})^{-1} \tag{1}$$

$$\tau_{\mathrm{DA}} = (k_{\mathrm{f}} + k_{\mathrm{ic}} + k_{\mathrm{isc}} + k_{\mathrm{trans}})^{-1} \tag{2}$$

$$\Phi_{\mathrm{f}} = k_{\mathrm{f}}/(k_{\mathrm{f}} + k_{\mathrm{ic}} + k_{\mathrm{isc}} + k_{\mathrm{trans}}) \tag{3}$$

$$\Phi_{\mathrm{trans}} = k_{\mathrm{trans}}/(k_{\mathrm{f}} + k_{\mathrm{ic}} + k_{\mathrm{isc}} + k_{\mathrm{trans}}) \tag{4}$$

In these equations, τ_D is the excited-state lifetime of the (donor) porphyrin monomer (Zn* in **Zn-3**; τ_D = 2.4 ns),[3] τ_{DA} is the Zn* excited-state lifetime of the donor in the presence of the acceptor (Zn* τ_{DA} = 36 ps in **Zn-pbp-Fb**; τ_{DA} = 11 ps in **Zn-pbp-Mg**), k_{trans} is the energy-transfer rate constant, and Φ_{trans} is the energy-transfer efficiency. These equations assume that, other than energy transfer, there are no pathways for depopulating the excited state of the donor porphyrin in the dyads that do not also exist in the porphyrin monomers (radiative decay, intersystem crossing, and internal conversion, with rate constants k_{f}, k_{isc}, and k_{ic}, respectively). The transient absorption and static emission data support this assumption; however, we cannot exclude the possibility of a small amount of charge transfer from donor to acceptor in each array.

Using these equations, we calculated Zn* → Fb energy transfer in **Zn-pbp-Fb** to occur with a rate constant of (37 ps)$^{-1}$ and an efficiency of 0.983. In **Zn-pbp-Mg**, Zn* → Mg energy transfer occurs with a rate constant of (11 ps)$^{-1}$ and an efficiency of 0.995. These rates can be compared to those for the corresponding diphenylethyne-linked dyads, namely, (24 ps)$^{-1}$ for ZnFbU and (9 ps)$^{-1}$ for ZnMgU. Thus, the rates observed in the 4,4′-diphenylbutadiyne-linked dyads are only slightly slower than those with the diphenylethyne linker. On the other hand, the addition of one more p-phenylene unit in the linker (giving a phenylethynyl-phenyl-ethynylphenyl linker) results in transfer with a rate constant of (156 ps)$^{-1}$.[20]

The rather small changes in the rate of energy transfer in going from the diphenylethyne linker to the diphenylbutadiyne linker are readily interpreted upon consideration of the mechanism of energy transfer. We have shown that the observed energy-transfer rate (k_{trans}) is the sum of those for through-bond (TB) and through-space (TS) processes:[1,2]

$$k_{\mathrm{trans}} = k_{\mathrm{TB}} + k_{\mathrm{TS}} \tag{5}$$

$$\chi_{\mathrm{TB}} = k_{\mathrm{TB}}/k_{\mathrm{trans}} \tag{6}$$

$$\chi_{\mathrm{TB}} + \chi_{\mathrm{TS}} = 1 \tag{7}$$

where the fraction of TB or TS process is given by χ_{TB} or χ_{TS}, respectively. The rate of TS energy transfer for each of the complexes was calculated,[21] affording values for $(k_{\mathrm{TS}})^{-1}$ of (1900 ps)$^{-1}$ and (1100 ps)$^{-1}$ for **Zn-pbp-Mg** and **Zn-pbp-Fb**, respectively (Table 1). Accordingly, for both dyads, the TB process provides the dominant mechanism of transfer. Indeed, the ratio of TB:TS transfer was ≥97:1 for both dyads. This ratio is slightly greater than the 96:4 ratio for the diphenylethyne-linked dyads. Thus, the falloff in rate is less pronounced for the TB process than

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it is for the TS process in going from the 4,4′-diphenylethyne to 4,4′-diphenylbutadiyne linker.

In summary, porphyrin dyads linked via a diphenylbutadiyne can be readily constructed. Mixed-metallo and metallo-Fb dyads can be easily obtained because the synthetic route employs a Mg porphyrin as a polar handle, which both facilitates the isolation of the desired hybrid product and protects the Fb porphyrin from copper insertion. The diphenylbutadiyne linker provides for rapid and efficient energy transfer between the porphyrins in the dyad. The rates and yields of energy transfer are comparable to those supported by a diphenylethyne linker. The comparable energy-transfer dynamics supported by 4,4′-diphenylbutadiyne versus 4,4′-diphenylethyne linkers in porphyrin dyads can be rationalized in terms of the similarities in relevant structural/electronic properties: (a) average deformation angle, 31 versus 26°;[22] (b) porphyrin center-center distance, 21.6 versus 19.3 Å; and (c) the HOMO−LUMO gap, 3.78 versus 4.08 eV (based on the long wavelength transition: 327.9 versus 303.5 nm, respectively[23]). Thus, the diphenylbutadiyne unit is a suitable linker for use in multiporphyrin constructs for light-harvesting and energy-funneling applications.

Experimental Section

General. All reagents and solvents were obtained from Fisher or Aldrich, were reagent grade, and were used as received unless noted otherwise. The $CHCl_3$ contained 0.75% ethanol. Toluene was spectroscopic grade. Molecular modeling to determine center-to-center distances was performed using PCModel v7.5 (Serena Software 2000). Laser-desorption mass spectrometry (LD-MS) was performed in the absence of a matrix.[24]

Spectroscopy. Static fluorescence and static and time-resolved absorption studies were performed on samples in toluene at room temperature. The solutions contained ambient concentrations of dissolved oxygen.

Static Absorption and Fluorescence Spectroscopy. Static absorption (Cary) and fluorescence (Spex Fluoromax) measurements were performed as described previously.[3,15] For the absorption measurements, a 0.5 nm data interval, a scan speed of 600 nm/min, and a spectral bandwidth of 1 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.

Time-Resolved Absorption Spectroscopy. Transient absorption data were obtained at room temperature as discussed elsewhere.[3,15] Samples (from ~0.1 to 0.2 mM in toluene) in 2 mm path length cuvettes were excited at 10 Hz with 130 fs, 30−40 μJ pump pulses and probed with white light pulses of comparable duration.

5-[4-(3-Methyl-3-hydroxy-1-butyn-1-yl)phenyl]-10,15,-20-trimesitylporphyrin (2). Following a standard procedure[9,17] at a higher concentration,[18] a solution of 4-(3-methyl-3-hydroxy-1-butyn-1-yl)benzaldehyde (**1**)[16] (2.75 g, 14.6 mmol, 18.3 mM), mesitaldehyde (6.4 mL, 44 mmol, 55 mM), and pyrrole (4.0 mL, 58 mmol, 73 mM) in $CHCl_3$ (800 mL) was treated with $BF_3{\cdot}OEt_2$ (1.8 mL, 14 mmol, 18 mM). The mixture was stirred at room temperature for 1.5 h. Then, a solution of DDQ (12 g, 53 mmol) in THF (100 mL) was added, and the mixture was stirred for 1 h. The mixture was concentrated to one-fourth of the original volume and passed over a short silica column (CH_2Cl_2). Fractions containing porphyrins were concentrated and chromatographed [silica, CH_2Cl_2/hexanes (1:1)]. A second chromatography column [silica, CH_2Cl_2/hexanes (1:3)] afforded pure compound (1.33 g, 11%): ^{1}H NMR δ −2.53 (s, 2H), 1.80 (s, 6H), 1.88 (s, 18H), 2.65 (s, 9H), 7.31 (s, 6H), 7.83, 7.86 (AA′BB′, 2 × 2H), 8.6−8.8 (m, 8H); LD-MS found 822.4; FAB-MS found 822.4323, calcd 822.4298 ($C_{58}H_{54}N_4O$); λ_{abs} (CH_2Cl_2) 419, 514, 549, 591, 646 nm.

5-(4-Ethynylphenyl)-10,15,20-trimesitylporphyrin (Fb-3). A solution of **2** (608 mg, 0.749 mmol) in toluene (50 mL) was treated with powdered NaOH (500 mg, 12.5 mmol), and the reaction mixture was refluxed for 4 h. After cooling, the reaction mixture was directly poured on a dry silica pad (6 × 15 cm). The title product was eluted with toluene (514 mg, 91%). Physical properties concur with published data.[9]

Zn(II)-5-(4-Ethynylphenyl)-10,15,20-trimesitylporphyrin (Zn-3). A solution of **Fb-3** (200 mg, 0.262 mmol) in CH_2Cl_2 was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (1.15 g, 5.24 mmol) in methanol (20 mL). The mixture was stirred overnight at room temperature and poured into aqueous $NaHCO_3$. The organic layer was dried, filtered, and chromatographed [silica, CH_2Cl_2/hexanes (1:1)] to afford the title porphyrin (207 mg, 96%). Physical properties concur with published data.[6]

Mg(II)-5-(4-Ethynylphenyl)-10,15,20-trimesitylporphyrin (Mg-3). A solution of **Fb-3** (150 mg, 0.196 mmol) in CH_2Cl_2 (20 mL) was treated with DIEA (0.683 mL, 3.92 mmol) and MgI_2 (556 mg, 2.00 mmol). The mixture was stirred at room temperature. After 10 min, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous $NaHCO_3$. The organic layer was dried and evaporated. The residue was chromatographed [alumina, toluene/acetone (4:1)] to obtain the title product (142 mg, 90% yield). Physical properties concur with published data.[25]

1-[4-[Zn(II)-5,10,15-Trimesityl-20-porphinyl]phenyl]-4-[4-[Mg(II)-5,10,15-trimesityl-20-porphinyl]phenyl]-1,3-butadiyne (Zn-pbp-Mg). Following a standard procedure,[19] a solution of **Zn-3** (60 mg, 72 μmol) and **Mg-3** (57 mg, 72 μmol) in toluene (5 mL) was treated with $Pd(PPh_3)_2Cl_2$ (4.0 mg, 5.7 μmol), CuI (0.5 mg, 3 μmol), I_2 (9.0 mg, 36 μmol), and diisopropylamine (0.6 mL). (Note that this reaction employed 0.5 equiv of I_2 rather than the specified quantity[19] of 1 equiv.) The reaction mixture was stirred at room temperature in the dark for 1 h. Analytical SEC showed complete reaction. The reaction mixture was directly loaded onto an alumina column (CH_2Cl_2). The amount of ethyl acetate in the eluent was slowly increased. The second main fraction contained almost pure title compound. The crude product was chromatographed [alumina (typically 4 × 30 cm), CH_2Cl_2, and then CH_2Cl_2/ethyl acetate (9:1)], affording the pure title compound (53 mg, 46%): ^{1}H NMR δ 1.86 (m, 36H), 2.65 (m, 18H), 7.2−7.4 (m, 12H), 7.9−8.3 (m, 8H), 8.6−9.0 (m, 16H); LD-MS found 1614.8; FAB-MS found 1610.6504, calcd 1610.6430 ($C_{110}H_{90}N_8MgZn$); λ_{abs} (CH_2Cl_2) 430, 553, 607 nm.

1-[4-[Zn(II)-5,10,15-Trimesityl-20-porphinyl]phenyl]-4-[4-[5,10,15-trimesityl-20-porphinyl]phenyl]-1,3-butadiyne (Zn-pbp-Fb). Following a standard procedure,[15] a solution of **Zn-pbp-Mg** (105 mg, 65.1 μmol) in $CHCl_3$ (250 mL) was treated with 78.6 g of silica. The mixture was stirred overnight at room temperature in the dark. The silica slurry was poured into a vacuum-fitted funnel, and the porphyrinic material was washed through, leaving a pale green residue on the silica. The filtrate was dried over Na_2SO_4, and solvent was removed. The residue was chromatographed [silica, $CHCl_3$/hexanes (3:2)]. The title compound eluted as the first red band, affording a purple solid (87 mg, 84% yield): ^{1}H NMR δ −2.51 (s, 2H), 1.90 (m, 36H), 2.67 (m, 18H), 7.2−7.4 (m, 12H), 8.0−8.4 (m, 8H), 8.6−9.0 (m, 16H); LD-MS found 1589.27;

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FAB-MS found 1588.6697, calcd 1588.6736 ($C_{110}H_{92}N_8Zn$); λ_{abs} (CH_2Cl_2) 424, 515, 550, 592, 649 nm.

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Supporting Information Available: ^{1}H NMR spectra and LD-MS spectra for all new compounds, fluorescence emission spectra of **Zn-pbp-Mg** and **Zn-pbp-Fb**, and an overlay of emission spectra of Zn porphyrin and Mg porphyrin monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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