Synthesis and Excited-State Photodynamics of a Molecular Square Containing Four Mutually Coplanar Porphyrins

Richard W. Wagner,[‖] Jyoti Seth,[†] Sung Ik Yang,[‡] Dongho Kim,[‡,§] David F. Bocian,*[,†]
Dewey Holten,*[,‡] and Jonathan S. Lindsey*[,‖]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204,
Department of Chemistry, University of California, Riverside, California 92521-0403, and
Department of Chemistry, Washington University, St. Louis, Missouri 63130-4889

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To examine the effect of restricted porphyrin−porphyrin rotation on energy transfer in diphenylethyne-linked porphyrin arrays, a square macrocyclic array of four porphyrins has been prepared that locks the porphyrins in a mutually coplanar architecture. The palladium-mediated coupling of Zn(II) 5,10-dimesityl-15,20-bis(4-ethynylphenyl)porphyrin and 5,10-dimesityl-15,20-bis(4-iodophenyl)porphyrin afforded the molecular square (*cyclo*-Zn_2Fb_2U) with zinc (Zn) and free base (Fb) porphyrins on alternating corners. The yield of *cyclo*-Zn_2Fb_2U is relatively insensitive to concentration with reactants at 5−0.5 mM but declines significantly at ≤0.05 mM. Transient absorption data from *cyclo*-Zn_2Fb_2U in toluene at room temperature indicate that the rate of energy transfer from the photoexcited Zn porphyrin to a neighboring Fb porphyrin is $(26\ \mathrm{ps})^{-1}$. A ZnFb porphyrin (ZnFbU) with an identical diphenylethyne linker but no constraints on rotation exhibits an identical energy-transfer rate. Resonance Raman spectroscopy shows that the intensities of the $\nu_{C\equiv C}$ mode(s) of the *cyclo*-Zn_2Fb_2U are comparable to those of ZnFbU, indicating that the extent of electronic coupling between the ethyne groups and the π-systems of the porphyrins is comparable in the two types of arrays. Thus, the geometric constraints imposed by the closure to the macrocyclic structure, including the enforced coplanarity of the four porphyrin rings, do not alter the through-bond electronic communication among the porphyrins.

Introduction

Over the past several years, we have prepared multi-porphyrin arrays that undergo excited singlet-state energy transfer and serve as photon funnels,[1] molecular wires,[2] and optoelectronic gates.[3] In each of these arrays, the porphyrins are joined covalently via a semirigid diarylethyne linker.[4] The energy-transfer process involves a minor contribution from a Förster through-space (TS) mechanism and a dominant contribution from a through-bond (TB) electron-exchange process that is mediated by the diarylethyne linker.[5−10] To understand the relationship between the nature of the diarylethyne linker and the energy-transfer process, we have prepared a variety of dimers, a prototypical example of which is shown in Scheme 1.[6−10] The diarylethyne linker holds the porphyrins at relatively fixed distances, but two distinct types of motions can occur involving the two porphyrins and their adjacent aryl groups in the linker. (1) The two porphyrins can rotate freely with respect to each other about the cylindrically symmetric ethyne bond, while the respective porphyrin−aryl group dihedral angles remain fixed. (2) One or both aryl groups of the linker can rotate toward coplanarity with the adjacent porphyrin, while maintaining a fixed porphyrin−porphyrin dihedral angle. Accordingly, the molecules in fluid solution are expected to experience a wide variety of geometries via combinations of these motions.

Assessing the effects of limited motion of the porphyrins is important for gauging the performance of multi-porphyrin arrays that are deposited on solid substrates, a key requirement for their application as devices. To lock the porphyrins in a mutually coplanar geometry, we sought to prepare a multi-porphyrin array having a cis-substituted porphyrin at each corner of a square. Most of our studies of energy transfer have examined the rate of energy transfer from an excited zinc (Zn) porphyrin to a free base (Fb) porphyrin. The comparison of the rate of energy transfer in the coplanar geometry with that of the freely rotating dimers required the Zn and Fb porphyrins to be arranged at alternating corners of the square.

Molecular squares are conceptually simple but have received limited attention until recently.[11] A common

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[†] University of California.

[‡] Washington University.

[§] Permanent address: Spectroscopy Lab, Korea Research Institute of Standards and Science, P.O. Box 102, Yusong, Taejon 305-600, Korea.

[‖] North Carolina State University.

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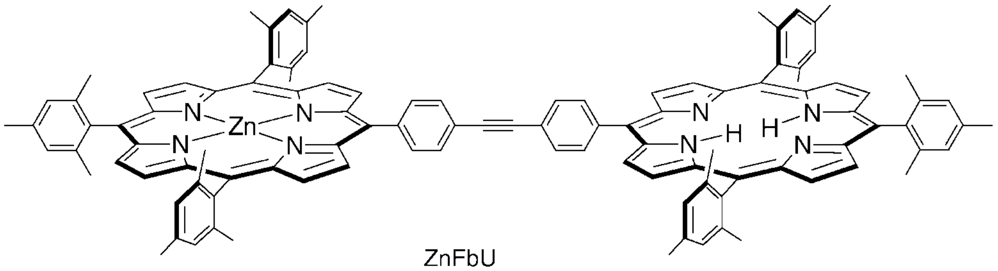
Scheme 1. ZnFbU Porphyrin Dimer with Free Rotation of the Porphyrins



ZnFbU

motif in molecular squares involves the use of a transition metal at each of the corners of the square.[12] Other molecular squares have been prepared using charge-transfer template effects.[13] Arrays containing four porphyrins have been prepared by the cyclization of a butadiyne-linked linear tetramer assisted by a template,[14] self-assembly via hydrogen bonds,[15] coordination of *meso*-pyridyl groups and transition metals,[16] coordination of *meso*-pyridyl groups to the central metal ion of a porphyrin,[17] and direct covalent attachment of porphyrins at the *meso*-positions.[18] The study of energy transfer required the preparation of a square array of four porphyrins with Zn porphyrins and Fb porphyrins at opposite corners of the square. In this paper, we describe the palladium-mediated coupling of Zn(II) 5,10-dimesityl-15,20-bis(4-ethynylphenyl)porphyrin (**1**) and 5,10-dimesityl-15,20-bis(4-iodophenyl)porphyrin (**2**), affording the molecular square (*cyclo*-Zn_2Fb_2U) where the zinc (Zn) and free base (Fb) porphyrins are on alternating corners. We also have determined the rate of energy transfer in *cyclo*-Zn_2Fb_2U using time-resolved absorption spectroscopy and have probed the mechanism of electronic communication using resonance Raman (RR) spectroscopy.

Results and Discussion

We investigated the preparation of *cyclo*-Zn_2Fb_2U via the palladium-mediated coupling of diethynyl Zn porphyrin (**1**) and diiodo Fb porphyrin (**2**) as shown in Scheme 2. Successful formation of *cyclo*-Zn_2Fb_2U via the coupling of **1** and **2** requires three intermolecular reactions followed by one intramolecular cyclization. To quickly assess this synthetic route, a few pilot reactions were performed using the coupling conditions that have been optimized for these types of porphyrin substrates (each porphyrin at 2.5 mM, 0.75 mM Pd_2dba_3, 6 mM $AsPh_3$, 5:1 toluene/triethylamine, and no copper cocatalysts, at 25−35 °C under argon).[19] The reactions were monitored by analytical SEC and laser desorption mass spectrometry (LD-MS). Although the analytical SEC trace of the crude reaction mixture was quite complex, the LD-MS spectrum of the same mixture showed the parent ion for *cyclo*-Zn_2Fb_2U at *m/z* 3008. This experimental protocol quickly established that *cyclo*-Zn_2Fb_2U could be formed using the route outlined in Scheme 2.

We investigated the effects of reaction concentration and reagent ratios on the yield of *cyclo*-Zn_2Fb_2U. Reactions were followed by analytical SEC, and the fractional amounts of higher-molecular weight material (HMWM), *cyclo*-Zn_2Fb_2U, and lower-molecular weight material (LMWM, which includes any unreacted starting material) were determined (Table 1). Under the standard coupling conditions,[19] HMWM was the major product formed, all starting material was consumed, and the reactions were complete in 30 (35 °C) or 60 min (25 °C) (entries 1 and 2 in Table 1). Upon reaction at 5−10-fold lower concentrations with constant reactant and reagent ratios, the yield of HMWM declined slightly and the yields of *cyclo*-Zn_2Fb_2U and LMWM increased slightly (entries 3, 5, and 6). Decreasing the concentration of porphyrin reactants, but not of reagents, shifted the product distribution from HMWM to LMWM with little effect on the yield of *cyclo*-Zn_2Fb_2U (entry 4). Reactions at 100−1000-fold lower concentrations with constant reactant and reagent ratios gave exclusively LMWM (entries 7 and 8). The reactions at lower concentrations were noticeably slower in forming *cyclo*-Zn_2Fb_2U, with changes in product distribution still occurring between 24 and 48 h for the reactions in entries 3−6.

The preparative synthesis of *cyclo*-Zn_2Fb_2U was performed using the same conditions that were used for entry 2 (Table 1), which provided the best compromise between reaction rate and yield. Thus, the reaction of 0.105 mmol of porphyrins **1** and **2** (185 mg total) for 2 h at 35 °C afforded the analytical SEC trace shown in

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Scheme 2. Synthesis of *cyclo*-Zn_2Fb_2U

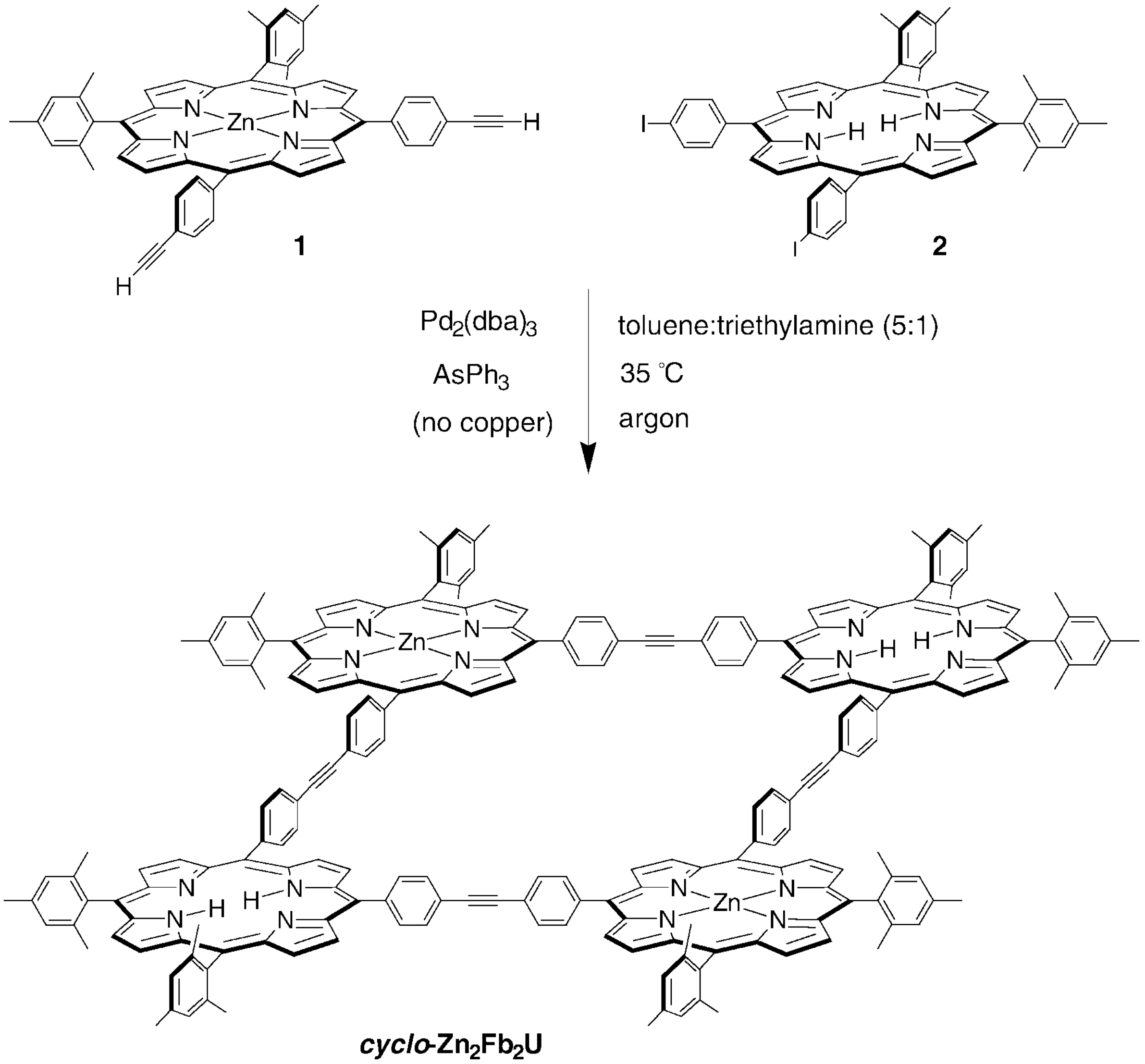

Table 1. Effects of Reaction Conditions on the Formation of *cyclo*-Zn_2Fb_2U[a]

						relative percent[b]		
entry	[**1**] and [**2**] (mM)	[Pd_2dba_3] (mM)	[$AsPh_3$] (mM)	T (°C)[c]	time (h)[d]	HMWM	*cyclo*-Zn_2Fb_2U	LMWM
1	2.5	0.75	6	25	1[e]	65	22	13[f]
2	2.5	0.75	6	35	0.5[g]	62	23	15[f]
3	0.5	0.15	1.2	25	24.5	56	26	18[h]
4	0.5	0.75	6	25	26	26	12	62[h]
5	0.25	0.075	0.6	25	64	45	20	35[h]
6	0.25	0.075	0.6	35	60	53	26	21[h]
7	0.025	0.0075	0.06	25	17	0	0	100[i]
8	0.0025	0.00075	0.006	25	17	0	0	100[i]

[a] All reactions were performed in toluene/triethylamine (5:1) under argon. [b] Relative percentages were determined by vertical lines from the troughs on either side of the *cyclo*-Zn_2Fb_2U peak to the baseline, thereby affording three sections of the chromatogram: higher-molecular weight material (HMWM), *cyclo*-Zn_2Fb_2U, and lower-molecular weight material (LMWM, including any unreacted starting material) (see Experimental Section). [c] Reactions at 25 °C were performed under argon in a glovebox, and reactions at 35 °C were carried out under argon on the benchtop. [d] The times indicated are the last data point before terminating the reaction unless noted otherwise. [e] No further reaction occurred at 2 h. [f] No unreacted starting material was observed. [g] No further reaction occurred at 1 h. [h] New peaks obscured the region of the starting materials. [i] Nearly entirely unreacted starting material.

Figure 1. The *cyclo*-Zn_2Fb_2U was purified using a combination of SEC and silica chromatography, with monitoring of the product purity by analytical SEC and LD-MS. In addition to the peak corresponding to *cyclo*-Zn_2Fb_2U, peaks also were present corresponding to linear trimer (iodoethyne and diiodo), linear pentamer (diiodo), and linear hexamer (iodoethyne), but not linear tetramer. The crude reaction mixture was filtered to remove palladium species and then passed over a preparative SEC column. Fractions containing *cyclo*-Zn_2Fb_2U (identified by LD-MS) were combined. The residual impurities were removed by chromatography on flash silica, affording *cyclo*-Zn_2Fb_2U in 7% yield. Figure 1 also shows the analytical SEC trace and LD-MS spectrum of pure *cyclo*-Zn_2Fb_2U. The SEC retention time of *cyclo*-Zn_2Fb_2U (25.5 min) is identical to that of ZnFbU.

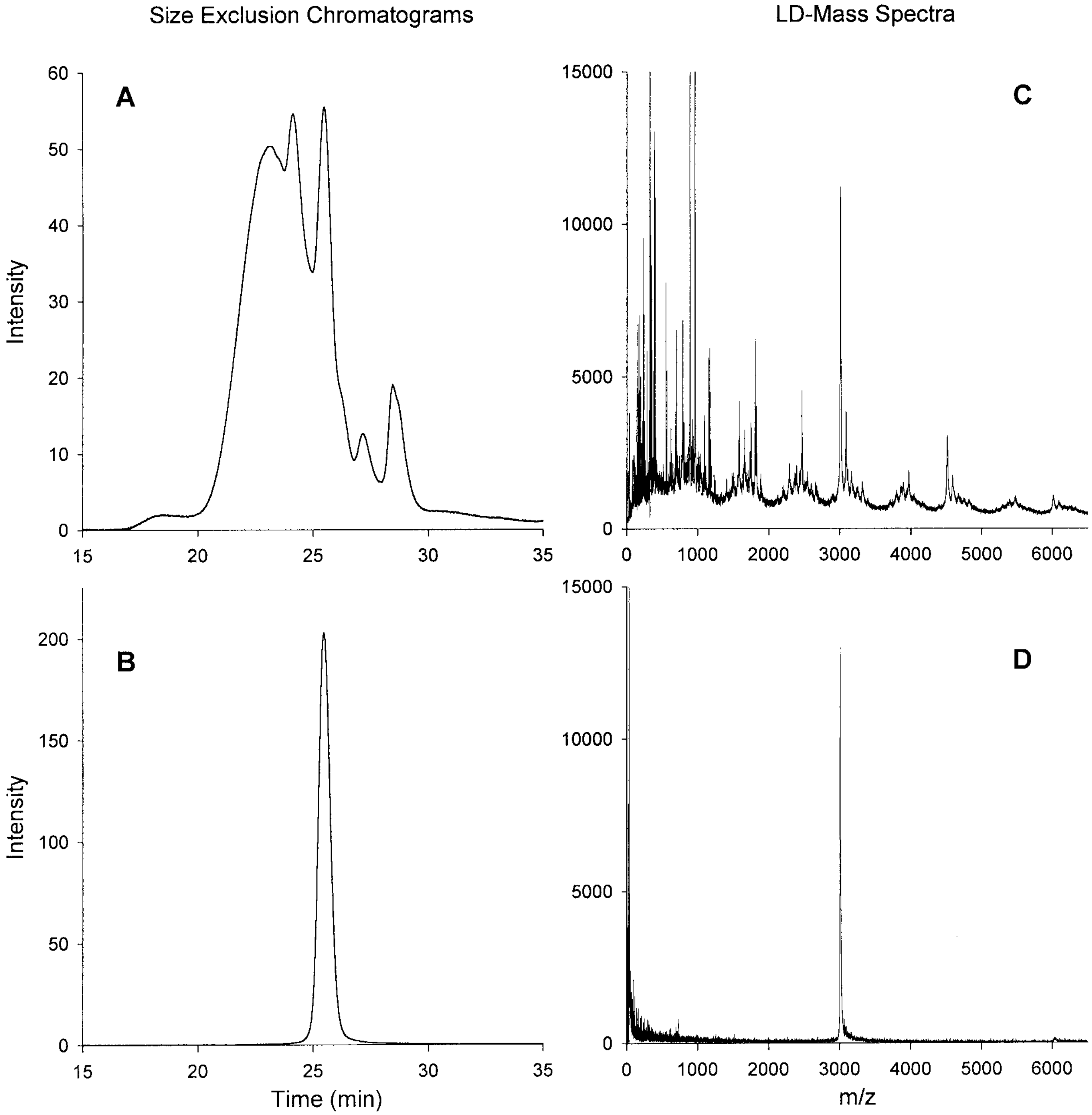

Figure 1. (A) Analytical size exclusion chromatogram of the crude reaction mixture from the synthesis of *cyclo*-Zn_2Fb_2U. The *cyclo*-Zn_2Fb_2U exhibits a t_R of 25.5 min. (B) Analytical size exclusion chromatogram of purified *cyclo*-Zn_2Fb_2U. (C) LD-MS of the crude reaction mixture (full scale corresponds to an intensity of 86 800 for *m*/*z* 321.7). (D) LD-MS of purified *cyclo*-Zn_2Fb_2U.

The *cyclo*-Zn_2Fb_2U is sufficiently soluble in $CHCl_3$ and in toluene for routine handling, chromatography, and spectroscopic measurements. Upon treatment of *cyclo*-Zn_2Fb_2U with methanolic zinc acetate, the *cyclo*-Zn_4U was isolated in 94% yield. This complex was poorly soluble in all solvents examined (toluene, $CHCl_3$, CS_2, tetrachloroethane, and *o*-dichlorobenzene).

The absorption spectrum of *cyclo*-Zn_2Fb_2U in toluene at room temperature shows a λ_{max} at 429 nm with a fwhm of 13.8 nm, to be compared with ZnFbU which has a λ_{max} at 426 nm with a fwhm of 13.3 nm.[7] The absorption spectrum of *cyclo*-Zn_2Fb_2U is essentially the sum of the spectra of the component parts, indicating relatively weak electronic interactions among the porphyrins. Illumination of *cyclo*-Zn_2Fb_2U at 550 nm, where the Zn porphyrin absorbs predominantly, affords emission almost exclusively from the Fb porphyrin. The static fluorescence emission spectra and fluorescence excitation spectra indicate the yield of energy transfer is essentially quantitative in *cyclo*-Zn_2Fb_2U. In arrays having such a high yield of energy transfer, the efficiency is best characterized using transient spectroscopy.

Transient Absorption Spectroscopy. The rate of energy transfer from the photoexcited Zn porphyrin to the Fb porphyrin subunits of *cyclo*-Zn_2Fb_2U was assessed using transient absorption spectroscopy. The complex in toluene at room temperature was excited using a 120 fs pulse at 550 nm, which predominantly pumps the Zn porphyrin component of the array. The spectra spanning the early (<1 ps) and late (>30 ps) domains are essentially the same over the region monitored (450−600 nm) as those reported previously for ZnFbU[7] and thus are not shown here. The spectra acquired immediately after the excitation flash are dominated by bleaching of

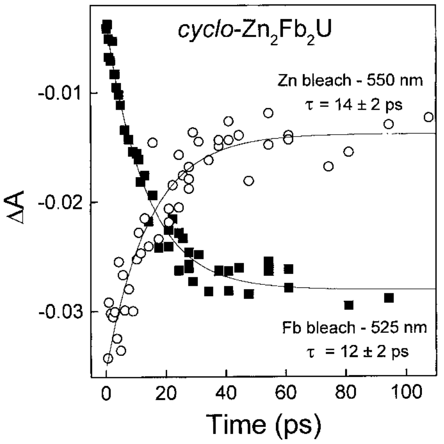

Figure 2. Time-resolved absorption data for *cyclo*-Zn_2Fb_2U in toluene at room temperature. The decay of the bleaching in the Q(1,0) ground-state band of the Zn porphyrin (550 nm) is shown with the open circles. The growth of the $Q_Y(1,0)$ bleaching of the Fb porphyrin (525 nm) is shown with the filled squares. The lines show single-exponential fits giving time constants of 14 ± 2 and 12 ± 2 ps, respectively.

the ground-state absorption bands of the Zn porphyrin near 550 and 590 nm imbedded on a broad featureless excited-state absorption; these early spectra contain relatively little Fb porphyrin bleaching. Spectra at progressively later times show decay of the bleaching of the Zn porphyrin ground-state bands and growth of bleaching in the ground-state absorption bands of the Fb porphyrins. The spectrum has reached a constant shape by about 30 ps. The decay of the bleaching in the Q(1,0) ground-state band of the Zn porphyrin (550 nm) and the growth of the $Q_Y(1,0)$ bleaching of the Fb porphyrin are shown in Figure 2. Also shown are single-exponential fits giving time constants of 14 ± 2 and 12 ± 2 ps, respectively. Since these values are the same within experimental error, the data indicate that the decay of photoexcited Zn porphyrin (Zn*) is directly accompanied by formation of the excited Fb porphyrin (Fb*). For all subsequent discussion, an average value of 13 ps will be used for the Zn* lifetime in the array.

The weak electronic coupling between the diarylethyne-linked porphyrins permits the energy-transfer rates (k_{trans}) and efficiencies (Φ_{trans}) to be estimated from the measured rate of decay of Zn* in the array (τ_{DA}) and that of the appropriate Zn porphyrin monomer (τ_D) using the following formulas:

$$1/\tau_D = k_{rad} + k_{isc} + k_{ic} \tag{1}$$

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

$$2k_{trans} = 1/\tau_{DA} - 1/\tau_D \tag{3}$$

$$\Phi_{trans} = 2k_{trans}\tau_{DA} = 1 - \tau_{DA}/\tau_D \tag{4}$$

These equations assume there are no other pathways for depopulating the Zn* in the arrays other than the intrinsic processes [radiative decay (rad), intersystem crossing (isc), and internal conversion (ic)] also present in the benchmark Zn porphyrin monomer. The close matching of the excitation spectra and absorption spectra for *cyclo*-Zn_2Fb_2U indicates a high yield of energy transfer and supports this assumption. However, within experimental uncertainty, we cannot exclude the possibility of a small amount (≤10%) of electron transfer from the Zn* state. Furthermore, the yield of reverse energy transfer (from the Fb porphyrin to the Zn porphyrin) is negligible due to the energy difference of the respective excited states.

In the *cyclo*-Zn_2Fb_2U, the Zn* has two neighboring Fb porphyrins to which energy transfer can occur. Consequently, the total rate for depopulating the excited state via energy transfer is $2k_{trans}$, where k_{trans} is the rate for transfer to a single Fb porphyrin. This expression in eq 2 allows direct comparison of k_{trans} in *cyclo*-Zn_2Fb_2U with that in dimers such as ZnFbU, which are comprised of one Zn porphyrin and one Fb porphyrin. Given a value for τ_{DA} of 13 ps for *cyclo*-Zn_2Fb_2U, and a measured value for τ_D of ~2.4 ns for an appropriate monomeric Zn porphyrin, $k_{trans} = (26\ \text{ps})^{-1}$. In addition, the yield of energy transfer (Φ_{trans}) in *cyclo*-Zn_2Fb_2U is 99.5%. For ZnFbU, the corresponding value for k_{trans} is $(26\ \text{ps})^{-1}$ and for Φ_{trans} is 99.0%.[7] Though *cyclo*-Zn_2Fb_2U and ZnFbU have identical rates of energy transfer (k_{trans}) between Zn* and a neighboring Fb porphyrin, the presence of two energy-transfer acceptors (Fb porphyrins) for Zn* in *cyclo*-Zn_2Fb_2U versus ZnFbU accounts for the higher energy-transfer yield in the former.

We previously have shown that the energy-transfer rate in this family of diarylethyne-linked porphyrin arrays is dominated by a TB mechanism mediated by the linker, rather than a Förster TS process.[7,9,10] In ZnFbU, rotation about the ethyne causes the orientation term (κ^2) in the Förster mechanism to take on values from 1.25 (coplanar porphyrins) to 1.0 (perpendicular porphyrins). We assumed the dynamically averaged limit, in which case the κ^2 value = 1.125. In *cyclo*-Zn_2Fb_2U the κ^2 term equals 1.25. The resulting slight increase in the rate of Förster TS transfer [from $(750\ \text{ps})^{-1}$ in ZnFbU to $(680\ \text{ps})^{-1}$ in *cyclo*-Zn_2Fb_2U] is negligible compared with the rate of TB energy transfer.[20] The identical rates of energy transfer in ZnFbU and *cyclo*-Zn_2Fb_2U indicate the respective TB energy-transfer processes have nearly identical rates. We turned to RR spectroscopy to probe the electronic communication process in *cyclo*-Zn_2Fb_2U.

RR Spectroscopy. The high-frequency regions of the B-state excitation (λ_{ex} = 457.9 nm) RR spectra of *cyclo*-Zn_2Fb_2U and *cyclo*-Zn_4U are shown in Figure 3. For comparison, the RR spectra of the previously characterized dimers, ZnFbU and Zn_2U,[7] are also included in the figure. The scattering characteristics of the porphyrin skeletal modes of the two tetramers are similar to those of the dimers and are generally unremarkable. The key spectral feature shown in the figure is the ethyne stretching mode, $\nu_{C\equiv C}$, which is observed at ~2215 cm^{-1} and exhibits substantial RR intensity (relative to the porphyrin modes) for both tetramers. The salient observations are as follows. (1) The frequencies of the $\nu_{C\equiv C}$ mode(s) of *cyclo*-Zn_2Fb_2U and *cyclo*-Zn_4U essentially identical to one another and identical to those of ZnFbU and Zn_2U. This observation indicates that there is negligible vibrational coupling between the four $\nu_{C\equiv C}$ vibrations of the tetramers. Accordingly, the four modes are best characterized as independent oscillators with

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(20) Assuming the observed energy-transfer rate is due to the additive effects of TB (k_{TB}) and TB (k_{TS}) processes ($k_{trans} = k_{TB} + k_{TS}$), then the fractional amounts of through-bond contribution (χ_{TB}) and through-space contribution (χ_{TS}) can be estimated by $\chi_{TB} = k_{TB}/k_{trans}$ where $\chi_{TB} + \chi_{TS} = 1$.[7] For *cyclo*-$Zn_2Fb_2U$, $k_{TB} = (27\ \text{ps})^{-1}$, $k_{TS} = (680\ \text{ps})^{-1}$, and χ_{TB} = 96%.

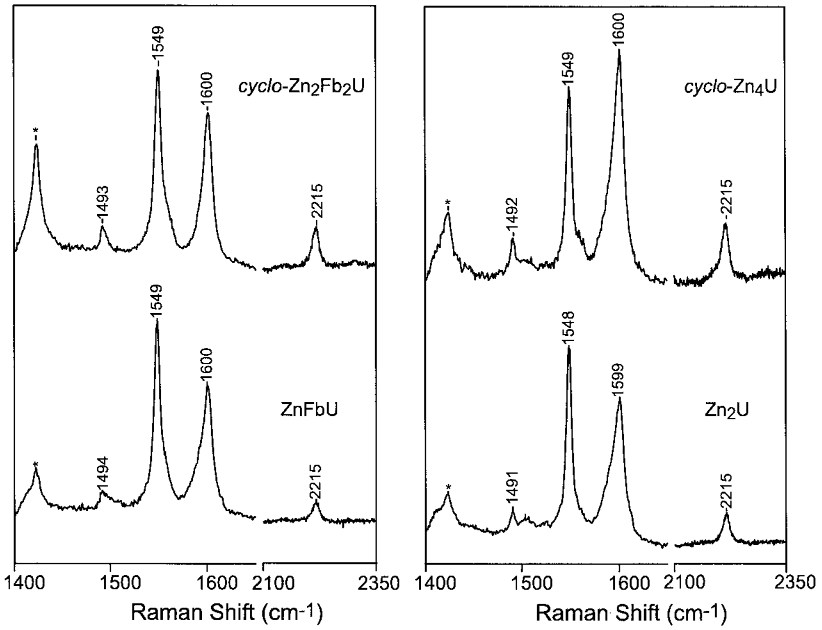

Figure 3. High-frequency regions of the B-state excitation (λ_{ex} = 457.9 nm) RR spectra of *cyclo*-Zn_2Fb_2U and *cyclo*-Zn_4U in CH_2Cl_2 solutions obtained at 295 K.

identical frequencies. This behavior is fully consistent with the large spatial separation between the different ethyne groups. (2) The RR intensity of the $\nu_{C\equiv C}$ mode(s) of *cyclo*-Zn_2Fb_2U and *cyclo*-Zn_4U is, to within experimental error, double that of the analogous modes of ZnFbU and Zn_2U (using the intensity of the porphyrin ν_2 mode at ~1550 cm^{-1} as a reference). The doubled intensity of the $\nu_{C\equiv C}$ mode(s) of the tetramers relative to that of the dimers is expected if the RR intensities of the four independent $\nu_{C\equiv C}$ modes of the former arrays are identical to one another and identical to those of the single $\nu_{C\equiv C}$ mode(s) of the latter. The doubled RR intensity of the $\nu_{C\equiv C}$ mode(s) of the tetramers relative to that of the dimers occurs because the ratio of ethyne groups to porphyrins is 1:1 in the former arrays and 1:2 in the latter.

The observation that the RR intensities of the $\nu_{C\equiv C}$ mode(s) of *cyclo*-Zn_2Fb_2U and *cyclo*-Zn_4U are comparable to those of ZnFbU and Zn_2U indicates that the extent of electronic coupling between the ethyne groups and the π-systems of the porphyrins is comparable in the two types of arrays. Thus, the additional geometric constraints imposed by the closure to the cyclic structure in the tetramers do not significantly impede electronic communication. This view is consistent with the observation that the energy-transfer rate in *cyclo*-Zn_2Fb_2U is essentially identical to that in ZnFbU.

Implications for the Design of Molecular Photonic Devices. The ability to deposit synthetic multiporphyrin arrays on substrates and in films is critical for device applications. Assessing the effects of limited motion of the porphyrins is important for gauging the performance of the molecular devices that are deposited on a solid substrate. The effects of changes in porphyrin−porphyrin dihedral angles on the Förster TS energy-transfer process are readily calculated (vide supra). However, the effects of constrained motion of the porphyrins as well as the porphyrin−aryl angle on the TB energy-transfer process are not readily accessible. We previously attempted to gain information about constrained motion by placing ZnFbU in various rigid environments, but the results were difficult to interpret.[21] The enforced coplanarity of the porphyrins in *cyclo*-Zn_2Fb_2U provides for an unambiguous assessment of the effects of a rigid environment. The key observation is that the energy-transfer rate in *cyclo*-Zn_2Fb_2U is identical to that in ZnFbU. Thus, the TB energy-transfer rate is unchanged upon constraining the porphyrins in a coplanar geometry. Prior studies of derivatives of ZnFbU having torsionally constrained linkers showed that the TB electronic communication process is dependent on the ability of the *meso*-phenylene unit of the linker to rotate toward coplanarity with the adjoining porphyrin.[7] While we have no direct information concerning the torsional motion of the diphenylethyne linkers in *cyclo*-Zn_2Fb_2U, the unchanged rate of energy transfer compared with that of ZnFbU suggests that this type of motion is similar in the two types of arrays and, therefore, unimpeded by the enforced coplanarity of the Zn and Fb porphyrins. Collectively, the behavior of *cyclo*-Zn_2Fb_2U and ZnFbU suggests that diphenylethyne-linked multiporphyrin arrays can be deposited on substrates with little expected change in the energy-transfer dynamics.

Experimental Section

General. Tetrabutylammonium fluoride on silica gel (1.0−1.5 mmol of F/g of resin), triphenylarsine, and tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) were purchased from Aldrich and used as received. Triethylamine was distilled from CaH_2. Toluene was distilled from $LiAlH_4$. CH_2Cl_2 (Fisher, reagent grade) and hexanes (Fisher, reagent grade) were used as received. Glass fiber filters (Fisherbrand 6G) were purchased from Fisher. ^1H NMR spectra (300 MHz, General Electric GN 300NB instrument), absorption spectra (Cary 3 instrument), and emission spectra (Spex FluoroMax instrument) were collected routinely. Flash chromatography was performed on Baker flash silica. Preparative SEC was performed on Bio-Rad Bio-Beads SX-1 beads. Mass spectra were obtained via laser desorption (Bruker Proflex II instrument)

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[21] ZnFbU in a viscous liquid (castor oil) at room temperature exhibits a k_{trans} of ~$(40\ ps)^{-1}$. In a frozen glass (*n*-butylbenzene) at 150 K, k_{trans} = $(59\ ps)^{-1}$.[7]

in the absence of an added matrix[22] or fast atom bombardment (JEOL HX110HF mass spectrometer, ion source at 40 °C, CsKI or polyethylene glycol standards, 10 ppm elemental compositional accuracy for the porphyrin monomers).

Analytical Size Exclusion Chromatography. Analytical SEC was performed with a Hewlett-Packard 1090 HPLC apparatus using 500 Å (300 mm × 7.8 mm), 1000 Å (300 mm × 7.5 mm), and 100 Å (300 mm × 7.5 mm) HP columns (5 μm) in series eluting with THF (flow rate = 0.8 mL/min, void volume ~ 16.0 min) with quantitation at 420 nm.[6] The analysis of the product distributions of the reactions forming *cyclo*-Zn_2Fb_2U could only be done semiquantitatively due to the poor resolution of the peaks in the SEC traces of the crude reaction mixtures. The area for the *cyclo*-Zn_2Fb_2U was assigned as the peak between the midpoint of the trough between the HMWM and the midpoint of the trough between the *cyclo*-Zn_2Fb_2U and the LMWM. The HMWM was assigned as all of the porphyrins eluting before the *cyclo*-Zn_2Fb_2U. The LMWM was assigned as all of the porphyrins, including unreacted starting material, eluting after the *cyclo*-Zn_2Fb_2U. The fractional distribution of products was determined by cutting sections of the chromatograms and weighing on an analytical balance.

Optimization Studies. In general, the Pd-coupling reactions were performed using our previously optimized conditions for porphyrin substrates.[19] Reactions were run at 25 or 35 °C under argon in a Vacuum Atmospheres glovebox or at 35 °C under argon on the benchtop. Reactions were monitored by periodically removing aliquots and analyzing by analytical SEC.

RR Spectroscopy. The RR spectra were recorded on a computer-controlled Spex Industries 1403 double monochromator equipped with a thermoelectrically cooled Hamamatsu R928 photomultiplier tube and a photon-counting detection system. RR spectra of samples in CH_2Cl_2 solutions (concentration ~ 0.05 mM) in a sealed capillary tube were obtained. The excitation wavelength (λ_{ex} = 457.9 nm) was provided by the output of an Ar ion (Coherent Innova 400-15UV) laser. The spectra were collected at 1 cm^{-1} intervals at a rate of 1 s/point. The incident powers were approximately 6 mW. The spectral slit width was ~3 cm^{-1}.

Transient Absorption Spectroscopy. Transient absorption data were acquired as described elsewhere.[23] Samples (~0.2 mM in toluene) in 2 mm path length cuvettes at room temperature were excited at 10 Hz with a 120 fs, 550 nm, 2−4 μJ flash from an optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system (Spectra Physics). Absorption changes were monitored using a white-light probe flash generated in water with the residual 800 nm light (~0.4 mJ per pulse) from the Ti:sapphire/OPA system. On each laser flash, spectral data across the 450−600 nm region were obtained, and data from 300 flashes were averaged to achieve a ΔA resolution of ±0.005. 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. The kinetic data shown in Figure 2 were generated by averaging the ΔA values in the range of 520−525 nm (for the Fb porphyrin bleaching) or in the range 550−555 nm (for the Zn porphyrin bleaching) at each delay time (−10 to 200 ps) and then plotting these values as a function of time. The kinetic traces were then fit to a function consisting of a single exponential and a constant using a nonlinear least-squares algorithm.

Zn(II) 5,10-Dimesityl-15,20-bis(4-ethynylphenyl)porphyrin (1). This compound was isolated from reaction mixtures originally used to prepare 5,10,15-trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin.[6] The crude reaction mixtures from several condensations of 4 equiv of pyrrole, 3 equiv of mesitaldehyde, and 1 equiv of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde were combined (totaling a reaction mixture equivalent to 20 mmol of pyrrole in 2 L). This mixture was concentrated and passed over a silica column (1:1 CH_2Cl_2/hexanes) affording the six porphyrins (900 mg) free from dark pigments and quinone species. The mixture of six porphyrins (450 mg, half of the original mixture) was dissolved in 100 mL of $CHCl_3$ and metalated with $Zn(OAc)_2 \cdot 2H_2O$ (219 mg, 1 mmol, 10 mL of methanol). After metalation was complete, the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and rotary evaporated affording a purple solid. The product mixture was dissolved in 10 mL of CH_2Cl_2, and then 20 mL of hexanes was added. The solution was loaded onto a silica column (6.8 cm × 12 cm, 2:1 hexanes/CH_2Cl_2). Six bands were observed with the following composition: (1) Zn(II) tetramesitylporphyrin, (2) Zn(II) 5,10,15-trimesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (280 mg, 12.4%), (3) Zn(II) 5,15-dimesityl-10,20-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin, (4) Zn(II) 5,10-dimesityl-15,-20-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin, (5) Zn(II) 5-mesityl-10,15,20-tris{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin, and (6) Zn(II) tetrakis{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin. The porphyrins in bands 3−5, which were not needed in the original synthetic work, were flushed from the column with CH_2Cl_2 and rotary evaporated to dryness as a mixture. Several sets of reactions were treated in this manner, and the mixtures of porphyrins from bands 3−5 were combined, yielding 400 mg of porphyrins. Final separation was achieved by dissolving the mixture in 20 mL of CH_2Cl_2, adding 10 mL of hexanes, and chromatographing the solution on a silica column (6.8 cm × 12 cm, 1:2 hexanes/CH_2Cl_2). The second band comprised Zn(II) 5,10-dimesityl-15,20-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin. This overall procedure was done twice, affording a total of 425 mg: ^1H NMR ($CDCl_3$) δ 0.39 (s, 18 H), 1.83 (s, 12 H), 2.63 (s, 6 H), 7.27 (s, 4 H), 7.89 (AA′BB′, 4 H), 8.19 (AA′BB′, 4 H), 8.75 (s, 2 H), 8.78 (d, J = 4.5 Hz), 8.83 (d, J = 4.5 Hz, 2 H), 8.89 (s, 2 H); $C_{60}H_{56}N_4Si_2Zn$, calcd exact mass 952.3335, obsd m/z 951.9 (LD-MS), obsd m/z 952.3303 (FAB-MS); λ_{abs} (toluene) 423, 550 nm.

A sample of Zn(II) 5,10-dimesityl-15,20-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (230 mg, 0.24 mmol) was dissolved in 30 mL of toluene. Then 960 mg of tetrabutylammonium fluoride on silica was added. After 30 min, the deprotection was complete as evidenced by silica TLC (1:1 CH_2Cl_2/hexanes). The organic layer was washed with 50 mL of 10% $NaHCO_3$ and 50 mL of H_2O, dried (Na_2SO_4), filtered, and concentrated to dryness. Column chromatography on silica (4.8 cm × 7 cm, 2:1 hexanes/CH_2Cl_2) afforded 175 mg (90%) of porphyrin: ^1H NMR ($CDCl_3$) δ 1.83 (s, 12 H), 2.63 (s, 6 H), 3.31 (s, 2 H), 7.27 (s, 4 H), 7.89 (AA′BB′, 4 H), 8.19 (AA′BB′, 4 H), 8.75 (s, 2 H), 8.78 (d, J = 4.5 Hz, 2 H), 8.83 (d, J = 4.5 Hz, 2 H), 8.89 (s, 2 H); $C_{54}H_{40}N_4Zn$, calcd exact mass 808.2544, obsd m/z 807.0 (LD-MS), obsd m/z 808.2542 (FAB-MS); λ_{abs} (toluene) 423, 550.

5,10-Dimesityl-15,20-bis(4-iodophenyl)porphyrin (2). We previously reported the isolation of **2** from the mixture of free base porphyrins.[6] To decrease the volume of solvent and to enhance the resolution of the cis and trans isomers, the mixture of porphyrins was freed from quinone and polypyrromethene impurities and then metalated with $Zn(OAc)_2 \cdot 2H_2O$. The desired **Zn2** was isolated from reactions that used a 3:1 mesitaldehyde:4-iodobenzaldehyde ratio as we were initially interested in isolating 5,10,15-trimesityl-20-(4-iodophenyl)porphyrin. Samples of the zinc chelates were dissolved in a minimum amount of CH_2Cl_2, and then hexanes were added to achieve the desired nonpolar solvent mixture. Column chromatography (silica, hexanes/CH_2Cl_2) gave **Zn2** as the fourth band off of the column.

A sample of **Zn2** (725 mg, 0.72 mmol) was dissolved in 100 mL of CH_2Cl_2 and treated with TFA (385 μL, 5.0 mmol). The demetalation was complete after 10 min as evidenced by silica TLC, absorption, and fluorescence excitation spectroscopy. Triethylamine (1.17 mL, 8.4 mmol) was added, and the reaction mixture was stirred for another 10 min. The solution was then washed three times with 10% $NaHCO_3$ and once with

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H_2O, dried (Na_2SO_4), filtered, and rotary evaporated to give 679 mg (100%) of the Fb porphyrin as a purple solid. The analytical data were consistent with an authentic sample.[6]

***cyclo*-Zn$_2$Fb$_2$U.** Samples of zinc ethynylporphyrin **1** (85 mg, 105 μmol) and free base iodoporphyrin **2** (100 mg, 105 μmol) were added to a 100 mL one-neck round-bottom flask containing 42 mL of toluene/triethylamine (5:1). The flask was fitted with a 15 cm reflux condenser, through which a drawn glass pipet was mounted for deaeration with argon. The reaction vessel headspace including the condenser was deaerated with argon at a high flow rate for 5 min. The solution was then deaerated by immersing the pipet in the solution and gently bubbling argon for 30 min. The condenser was then elevated, leaving the pipet in the solution, and $Pd_2(dba)_3$ (29 mg, 32 μmol) and $AsPh_3$ (77 mg, 252 μmol) were added. The condenser was replaced, and argon was bubbled through the solution for another 5 min. At this point, the pipet was removed from the reaction mixture and positioned about 2 cm above the solution. The flask was then placed in an oil bath preheated to 35 °C. The argon flow rate was increased slightly, and the reaction was allowed to proceed. After 2 h, the reaction mixture was concentrated to dryness. The mixture was dissolved in 2 mL of toluene and then passed through a glass fiber filter plug positioned in a pipet to remove palladium species. The mixture of porphyrins was then concentrated to dryness, dissolved in 2 mL of toluene, and then placed on top of a preparative SEC column (Bio-Beads SX-1 poured into toluene). Gravity elution afforded the product as the third band. The *cyclo*-Zn$_2$Fb$_2$U-containing fractions were concentrated to dryness, dissolved in 3 mL of CH_2Cl_2/hexanes (2:1), and purified on silica (3 cm diameter × 10 cm, poured into 2:1 CH_2Cl_2/hexanes) with gravity elution. A small amount of unidentified porphyrin eluted quickly, followed by *cyclo*-Zn$_2$Fb$_2$U. Concentration of the appropriate fractions gave 11.4 mg (7%). A similar reaction with 50 mg of **2** (53 μmol) gave 5.6 mg (7.0%): ^{1}H NMR ($CDCl_3$) δ -2.73 (bs, 4 H), 1.90 (s, 48 H), 2.55 (s, 24 H), 7.32 (s, 16 H), 8.20 (AA′BB′, 8 H), 8.31, 8.35 (m, 24 H), 8.69 (s, 4 H), 8.77, 8.79 (m, 8 H), 8.87 (d, $J = 4.5$ Hz, 4 H), 8.93 (d, $J = 5.1$ Hz, 4 H), 8.97 (s, 4 H), 9.02 (d, $J = 5.1$ Hz, 4 H), 9.06 (s, 4 H); $C_{208}H_{156}N_{16}Zn_2$, calcd exact mass 3005.1, obsd m/z 3005.2 (LD-MS), obsd m/z 3008.0 (FAB-MS); λ_{abs} (toluene) 429 (fwhm = 13.8 nm), 516, 551, 591, 648 nm; λ_{em} (toluene) 653, 721 nm.

***cyclo*-Zn$_4$U.** A sample of *cyclo*-Zn$_2$Fb$_2$U (5.0 mg, 1.7 μmol) was dissolved in 5 mL of toluene/$CHCl_3$ (1:1), and then a methanolic solution of $Zn(OAc)_2 \cdot 2H_2O$ (1.0 mg, 4.6 μmol, 250 μL of methanol) was added. The reaction mixture was stirred at room temperature and was monitored by fluorescence excitation spectroscopy. After 12 h, the reaction mixture was washed with 10% $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated, affording 5.0 mg (94%) of a purple solid: ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 1.88 (s, 48 H), 2.64 (s, 24 H), 7.27 (s, 16 H), 8.07 (AA′BB′, 16 H), 8.30 (AA′BB′, 16 H), 8.74 (s, 8 H), 8.82 (d, $J = 4.5$ Hz, 8 H), 8.99 (d, $J = 4.5$ Hz, 8 H), 9.03 (s, 8 H); $C_{208}H_{152}N_{16}Zn_4$, calcd exact mass 3128.9552, obsd m/z 3136.6 (LD-MS). High-resolution FAB-MS was carried out at greater than unit resolution. Though the signal-to-noise level was insufficient to allow measurement of the nominal exact mass ion, the base peak in the isotope cluster was observed at m/z 3137: λ_{abs} (toluene) 430, 552, 591 nm; λ_{em} (toluene) 598, 648 nm.

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Supporting Information Available: Copies of ^{1}H NMR spectra of **2**, *cyclo*-Zn$_2$Fb$_2$U, and *cyclo*-Zn$_4$U (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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