Effects of Metalation State (Free Base, Mg, Zn, Cd) on Excited-State Energy Transfer in Diarylethyne-Linked Porphyrin Dimers

Philippe Hascoat,[†] Sung Ik Yang,[‡] Robin K. Lammi,[‡] Jennifer Alley,[‡] David F. Bocian,*[§] Jonathan S. Lindsey,*[†] and Dewey Holten*[‡]

Departments of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204,
Washington University, St. Louis, Missouri 63130-4899, and University of California,
Riverside, California 92521-0403

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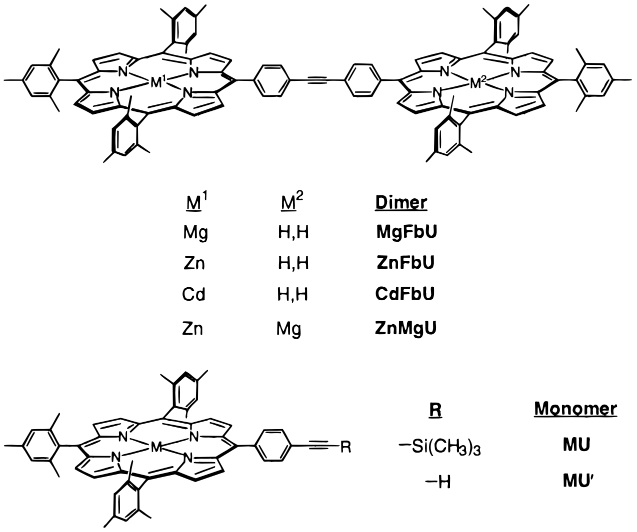
The ground- and excited-state properties of two new porphyrin dimers have been examined using static and time-resolved optical techniques. One dimer consists of a zinc porphyrin and a magnesium porphyrin (ZnMgU), and the other dimer consists of a cadmium porphyrin and a free base (Fb) porphyrin (CdFbU). In both arrays, the porphyrins are joined by a diarylethyne linker at one meso position with mesityl groups at the nonlinking meso positions. The rates of photoinduced energy transfer are faster for ZnMgU ((9 ps)$^{-1}$) and CdFbU ((15 ps)$^{-1}$) than found previously for ZnFbU ((24 ps)$^{-1}$) and MgFbU ((31 ps)$^{-1}$). Only for CdFbU does the yield of excited-state energy transfer (87%) drop below the near-quantitative (≥99%) level, and this effect derives solely from competition with a very short inherent lifetime (∼100 ps) of the photoexcited Cd porphyrin. The results further illustrate (1) the efficacy of this dimeric architecture for ultrafast excited-state energy transfer, (2) how molecular/electronic properties can be manipulated to tune photoinduced energy flow in multiporphyrin arrays, and (3) key factors impacting effective inter-porphyrin electronic communication, including porphyrin orbital tuning.

Introduction

As part of a program in the design of multiporphyrin arrays for molecular photonics,[1−4] we have constructed and studied a variety of porphyrin dimers and a host of monomeric building blocks.[5−14] One basic dimeric unit has two porphyrins joined by a semirigid diarylethyne linker[15] (Figure 1). We have gained detailed insights into key elements, such as porphyrin orbital characteristics,[10,13] in controlling linker-mediated inter-porphyrin electronic communication in these arrays. The studies have shown that molecular tuning (central metal ion, electron-donating/releasing ability of nonlinking porphyrin substituents, steric hindrance on the diarylethyne linker, linker−porphyrin attachment site) affords at least an order of magnitude variation in the rate of photoinduced energy transfer (∼(24 ps)$^{-1}$ to ∼(240 ps)$^{-1}$), as well as parallel effects on ground-state hole/electron hopping in the monooxidized bis(metallo) analogues.[9−13]



M^1	M^2	Dimer
Mg	H,H	**MgFbU**
Zn	H,H	**ZnFbU**
Cd	H,H	**CdFbU**
Zn	Mg	**ZnMgU**

R	Monomer
$-Si(CH_3)_3$	**MU**
$-H$	**MU′**

Figure 1. Structures of porphyrin dimers and monomers.

[†] North Carolina State University.
[‡] Washington University.
[§] University of California.

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In the present paper, we have extended our studies of porphyrin arrays containing a Zn or Mg porphyrin linked to a free base (Fb) porphyrin (i.e., ZnFbU and MgFbU in Figure 1) to include two additional dimers. We have synthesized and characterized ZnMgU, which represents the first member in the series that contains two different metal porphyrins. (The photophysics of several mixed-metal porphyrin dimers employing different linkers have been investigated previously.[16]) We have also investigated CdFbU, which represents the first member that contains a third-row metal ion, with possible amplified metal electronic effects. These dimers afford further insights into the factors underlying electronic communication in these architectures.

Results

Synthesis. The structures of the relevant compounds are given in Figure 1. Cadmium tetraphenylporphyrin (CdTPP) and the ethynyl porphyrin building blocks (CdU′ and CdU) were prepared by mild but nonquantitative cadmium insertion into the corresponding Fb porphyrin with 200 equiv of $Cd(OAc)_2$ in $CHCl_3$/MeOH (7:3) at room temperature for 15 h. Chromatography on alumina gave <0.1% Fb porphyrin as judged by fluorescence excitation spectra. The Cd porphyrins are even more labile than Mg porphyrins and must be handled carefully (e.g., exposure to neutral alumina in toluene for 12 h leads to complete demetalation). CdFbU was prepared in 75% yield from CdU′ and a free base (Fb) monoiodo porphyrin (5,10,15-trimesityl-20-(4-iodophenyl)porphyrin) using the Pd-coupling reaction[9,17−19] previously developed for the synthesis of multiporphyrin arrays containing Fb, Zn, and Mg porphyrins (e.g., ZnFbU and MgFbU).[9,19] The dimer ZnMgU was prepared in 90% yield by treating ZnFbU with MgI_2 (10 equiv) and DIEA (20 equiv) in CH_2Cl_2 at room temperature with stirring for 45 min, followed by column chromatography. This gentle method affords quantitative metalation and is compatible with the presence of the Zn porphyrin.[20] Complete descriptions of the synthetic methods, analytical data, and other experimental procedures are given in the Supporting Information.

Static and Time-Resolved Absorption and Emission Spectra. Q-region electronic absorption and fluorescence spectra (corresponding to transitions between the ground state and lowest excited singlet state) for the monomeric building blocks of the dimers are shown in Figure 2. These spectra are similar to those reported previously for these or related compounds.[6,7,9,14] The absorption spectra of the metalloporphyrins contain a moderately strong Q(1,0) band, flanked by the Q(0,0) and Q(2,0) bands. The corresponding Q(0,0) and Q(0,1) features are seen in the fluorescence spectra (dashed). The absorption spectrum of FbU contains the *x*- and *y*-polarized Q(1,0)/Q(0,0) pairs of bands, and the emission spectrum contains the $Q_x(0,0)$ and $Q_x(0,1)$ features.

The absorption spectra of ZnMgU and CdFbU, like those of ZnFbU and MgFbU studied previously,[7,9] are essentially given by the sum of the spectra of the monomeric building blocks. This finding indicates relatively weak (but not insignificant) electronic interactions between the porphyrin constituents. The fluorescence from ZnMgU in toluene occurs essentially exclusively from the Mg porphyrin even when the Zn porphyrin is preferentially excited. This result reveals effectively quantitative energy transfer from the photoexcited Zn porphyrin (Zn*) to the ground-state Mg porphyrin. Parallel findings were obtained previously concerning highly efficient energy transfer from the excited metal porphyrin to the Fb porphyrin in ZnFbU and MgFbU.[7,9] In the case of CdFbU, a very small amount of Cd porphyrin emission is observed when this constituent is excited (in addition to the dominant Fb porphyrin fluorescence). This result indicates a somewhat lower efficiency of photoinduced energy transfer from Cd* to Fb in CdFbU.

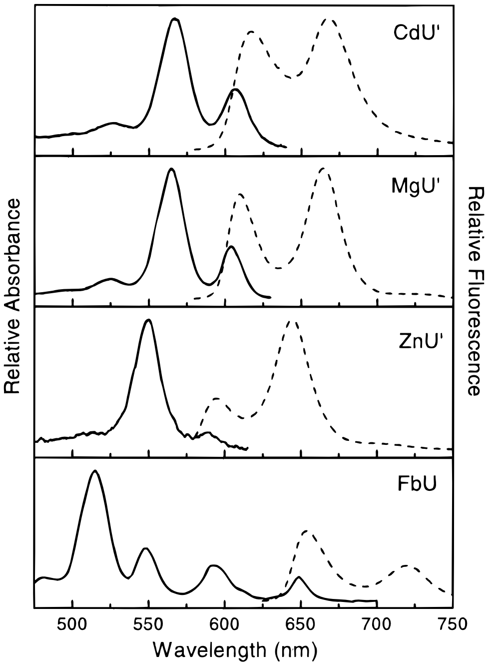

Figure 2. Visible-region (Q-band) ground-state absorption spectra (solid) and excited-state fluorescence spectra (dashed) of monomeric building blocks in toluene. The absorption spectra are normalized to the Q(1,0) band ($Q_Y(1,0)$ for FbU′), and the emission spectra, to the Q(0,1) band. The absorption spectrum of each dimer is essentially given by sums of the appropriate pairs of these absorption spectra.

The rates and efficiencies of photoinduced energy transfer for ZnMgU and CdFbU in toluene were quantitated using time-resolved absorption measurements. The procedures and analyses parallel those described previously for ZnFbU and MgFbU and other multiporphyrin arrays.[7,9−13] Representative data for ZnMgU are shown in Figure 3. The absorption difference spectrum at 1 ps after excitation with a 130 fs flash at 548 nm shows bleaching in the prominent Q(1,0) and weaker Q(0,0) ground-state bands of the Zn porphyrin near 550 and 590 nm, respectively (see ZnU′ absorption spectrum in Figure 2). The feature at 590−600 nm also contains Zn* Q(0,0) stimulated emission (involving the white-light probe pulse), and the feature near 640 nm is the corresponding Q(0,1) stimulated emission band (see ZnU′ emission spectrum in Figure 2). Thus, the 1 ps spectrum for ZnMgU is due primarily to Zn*, with some contribution from Mg* in a fraction of the dimers in which the Mg porphyrin was excited. A similar analysis of the spectrum at 30 ps in Figure 3 shows that this spectrum can be ascribed essentially exclusively to Mg*. The Mg* state subsequently decays with a lifetime of about 6 ns, as determined by emission lifetime measurements (Table 1).

Representative kinetic data for key absorption-difference spectral features for ZnMgU in toluene are also shown in Figure

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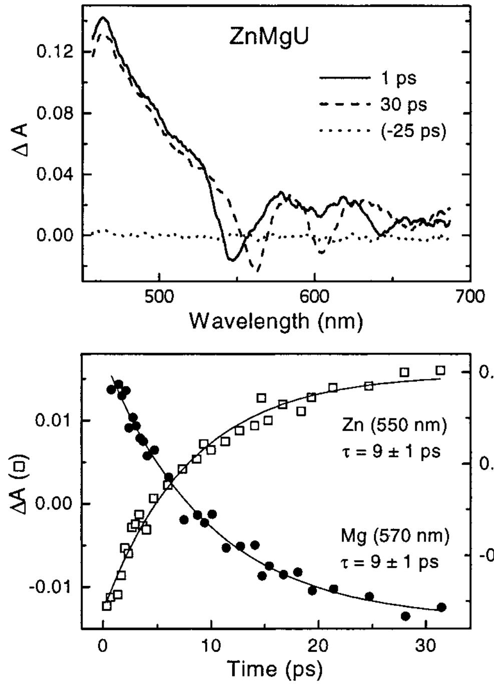

Figure 3. Top: Representative time-resolved absorption difference spectra for ZnMgU in toluene elicited by excitation with a 130 fs flash at 548 nm. Bottom: Representative kinetic data and fits. For clarity the data before zero time, during the instrument rise, and at longer delays (to ~60 ps) are not shown.

Table 1. Excited-State Lifetimes and Emission Yields[a]

compd[b]	donor τ (ps)[c]	acceptor τ (ns)[d]	acceptor Φ_f[e]
		Dimers	
ZnMgU	9 ± 1	5.8 ± 0.3	0.17
CdFbU	13 ± 2	6.6 ± 0.6[f]	0.05
ZnFbU	24 ± 2	13.1 ± 0.6	0.13[g]
MgFbU	31 ± 3	13.1 ± 0.6	0.13[h]
		Monomers	
ZnU′		2.4 ± 0.2[i]	0.033[i]
MgU′		9.7 ± 0.4	0.16
CdU′		0.10 ± 0.03[j]	≤0.002[k]
FbU′		13.3 ± 0.5[i]	0.13[i]

[a] Data in toluene at room temperature unless noted otherwise. [b] The first member of the dimer is the excited-state energy-transfer donor, and the second is the acceptor. [c] Donor porphyrin lifetimes measured by transient absorption spectroscopy. [d] Acceptor porphyrin (in the dimers) and monomer porphyrin lifetimes measured by fluorescence modulation (phase-shift) spectroscopy. For the monomers, similar values are found for the MU, MTPP, and metallo–tetramesitylporphyrin analogues.[14] [e] Acceptor porphyrin (in the dimers) and monomer porphyrin fluorescence yields (±10%) determined relative to ZnTPP (0.033[27]) or FbTPP (0.11[28]). For the monomers, similar values are found for the MU, MTPP, and metallo–tetramesitylporphyrin analogues.[14] [f] The lifetime is 8.6 ± 0.6 ns in DMSO. [g] From refs 7 and 9. [h] From ref 9. [i] From ref 14. [j] This value was obtained from transient absorption measurements (the corresponding value for CdTPP is 90 ± 10 ps). The emission lifetime of 0.13 ± 0.06 ns measured for CdU′ is in good agreement. [k] The same value is found for CdTPP (a literature value is 0.0004[29]).

3. The bleaching near 550 nm due mainly to Zn* decays with a time constant of 9 ps. The bleaching near 570 nm due mainly to Mg* simultaneously grows with the same time constant. These findings give a Zn* lifetime in ZnMgU of 9 ± 1 ps. Similar measurements give a Cd* lifetime in CdFbU of 13 ± 2 ps (not shown). These lifetimes are included in Table 1 along with values determined previously for Zn* in ZnFbU (24 ps) and Mg* in MgFbU (31 ps). For reference, this table also includes the excited-state lifetimes of the energy-transfer-acceptor porphyrins in these dimers along with data for benchmark monomers.

Excited-State Energy-Transfer Rates and Yields. The parameters for photoinduced energy transfer in ZnMgU and CdFbU were obtained using eqs 1–4, where, τ_{DA} is the excited-

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

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

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

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

state lifetime of the donor in the presence of the acceptor (e.g., Zn* in ZnMgU), τ_D is the excited-state lifetime of the benchmark porphyrin monomer (e.g. ZnU′), k_{trans} is the energy-transfer rate, and Φ_{trans} is the energy-transfer efficiency. These equations assume that, besides energy transfer, there are no pathways for depopulating the excited donor porphyrin in the arrays other than the intrinsic processes (radiative decay (rad), intersystem crossing (isc), internal conversion (ic)) also present in the monomer. The transient absorption and static emission data support this assumption. However, within experimental uncertainty, we cannot exclude the possibility of a small amount of charge transfer from Zn* to Mg in ZnMgU or from Cd* to Fb in CdFbU in toluene.[21]

Analysis of the excited-state lifetime data in Table 1 using eqs 1–4 gives a rate and an efficiency of photoinduced energy transfer from Zn* to Mg in ZnMgU of $(9\ \text{ps})^{-1}$ and >99%. The corresponding values for energy transfer from Cd* to Fb in CdFbU are $(15\ \text{ps})^{-1}$ and 87%. Thus, excited-state energy transfer is extremely fast in both new dimers. The lower efficiency in CdFbU derives essentially entirely from energy transfer in this dimer having to compete with a very short excited-state lifetime ($\tau_D \sim 100$ ps) of the photoexcited Cd porphyrin as reflected by the CdU′ and CdTPP reference compounds (Table 1). In turn, the short lifetime for the cadmium porphyrin monomers can be traced to the effect of the heavy metal to enhance singlet–triplet intersystem crossing (k_{isc} in eq 1), which also gives a corresponding reduction in fluorescence yield relative to Fb porphyrins and metallo analogues with lighter metals (Table 1). The energy-transfer rates and efficiencies for ZnMgU and CdFbU are collected in Table 2 along with the results obtained previously for ZnFbU and MgFbU.

Discussion

Both ZnMgU and CdFbU exhibit faster photoinduced energy-transfer rates than those we have found previously for ZnFbU and MgFbU. The rates along this series are $(9\ \text{ps})^{-1}$, $(15\ \text{ps})^{-1}$, $(24\ \text{ps})^{-1}$, and $(31\ \text{ps})^{-1}$, respectively. All the complexes except CdFbU exhibit near-quantitative (≥99%) energy-transfer yields. The robustness of these architectures toward excited-state energy flow is manifested by the fact that the yield is still almost 90% in CdFbU despite competition with the extremely short (~100 ps) inherent lifetime of the excited Cd porphyrin. The characteristics of ZnMgU make it an attractive building block for extended arrays requiring ultrafast and efficient energy transfer. This unit also may be used in gating applications wherein ground- or excited-state redox processes can be made opera-

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(21) The fluorescence lifetime and emission yield data in Table 1 indicate that there may be some electron transfer after the formation of Mg* in ZnMgU and Fb* in CdFbU.

Table 2. Energy-Transfer Properties and Possible Contributing Factors for the Dimers

dimer[a]	k_{trans}^{-1} (ps)[b]	Φ_{trans}[c]	J_{Dexter} (/eV)[d]	$10^{14}J_{\mathrm{Forster}}$ ($\mathrm{cm^6\ mmol^{-1}}$)[e]	Q-band ratio[f]	d orbital availability[g]
ZnMgU	9	>0.99	0.087	1.6	0.10, 0.34	+, 0
CdFbU	15	0.87	0.31	1.9	0.42, 0.30	++, 0
ZnFbU	24	0.99	0.51	2.9	0.10, 0.30	+, 0
MgFbU	31	>0.99	0.33	2.0	0.34, 0.30	0, 0

[a] The first member of the U-linked dimer is the photoexcited donor porphyrin, and the second is the acceptor. [b] Inverse of the energy-transfer rate calculated from eq 3 and the lifetimes in Table 1. [c] Energy-transfer efficiency calculated from eq 4. [d] Dexter energy-overlap integral calculated (using PhotochemCAD)[30] from the spectra in Figure 2.[25] [e] Förster spectral overlap integral calculated (using PhotochemCAD)[30] from the spectra in Figure 2.[7,13,24] [f] The Q(0,0)/Q(1,0) integrated-intensity ratio (donor porphyrin, acceptor porphyrin) obtained from the ground-state absorption spectra in Figure 2. For each macrocycle, a larger Q-band ratio indicates a larger $a_{2u}-a_{1u}$ orbital-energy spacing and thus a greater contribution of the a_{2u} HOMO to the linker-mediated electronic coupling (see text).[23] [g] Qualitative representation (donor porphyrin, acceptor porphyrin) of the availability of metal d orbitals (particularly d_{xz} and d_{yz}) for mixing with the porphyrin e_g LUMOs and thus modulating linker-mediated inter-porphyrin electronic coupling (see text).

tive.[3,9] Although CdFbU is also a viable candidate on the basis of its fast energy-transfer rate, this dimer is less attractive overall because of its somewhat lower efficiency and the more labile character of the Cd porphyrins relative to the other metalloporphyrins. Collectively, the results on these four dimers demonstrate the efficacy of photoinduced energy transfer in these diarylethyne-linked architectures.

Our previous studies on ZnFbU, MgFbU, and various analogues (with changes in electron-donating/releasing porphyrin substituents, linker architecture, linker site, etc.) have revealed several important aspects of excited-state energy transfer and ground-state hole/electron hopping in these systems.[7,9−13] These features include the following. (1) Excited-state energy transfer is dominated by a linker-mediated through-bond mechanism, with a much smaller contribution from a through-space process. (2) The characteristics (nature, energy spacings/orderings, and electron-density distributions) of the porphyrin frontier molecular orbitals together with the site of linker attachment substantially modulate inter-porphyrin electronic communication.

The relative contributions of the porphyrin filled $a_{2u}(\pi)$ and $a_{1u}(\pi)$ orbitals to the relevant wave functions derive from the fact that the a_{2u} orbital places substantial electron density[22] at the meso carbons to which the linker is attached (Figure 1) whereas the a_{1u} orbital has nodes at these positions (but electron density at the β-pyrrole carbons).[10,13] Analysis of the Q-band ratios in the ground-state absorption spectra of the monomer units[14] in terms of the four-orbital model[22] indicates that the $a_{2u}-a_{1u}$ energy spacing and thus the contribution of the a_{2u} orbital decreases along the series Cd > Mg > Fb > Zn.[23] The characteristics of the $e_g(\pi^*)$ LUMOs and the overall electron density in the macrocycle also contribute to the effective linker-mediated inter-porphyrin electronic coupling.[12,13] The LUMO contribution to this coupling in principle could be affected by the overlap of the porphyrin e_g orbitals with the metal d_{xz} and d_{yz} orbitals; this factor would be more effective for Cd than for Zn (3d versus 2d) and not possible for Mg and Fb. Porphyrin−porphyrin energy matching in the dominant through-bond (Dexter) mechanism and spectral overlap in the lesser-contributing through-space (Förster) mechanism also play a role. Analysis of the absorption and emission spectra in Figure 2 using the appropriate methods[6,13,24,25] indicates that both overlap integrals decrease along the series ZnFbU > CdFbU ∼ MgFbU > ZnMgU (Table 2).

The relatively small variation in the energy-transfer rate among the four dimers indicates that the rate must be controlled by the interplay of a variety of factors, with no single factor making a dominant contribution. Regardless, the following comparisons are worth noting (Table 2). (1) There appears to be no correlation among the Dexter (or Förster) overlap integrals and the energy-transfer rates. For example, the rate in ZnMgU ($(9\ \mathrm{ps})^{-1}$) is over 2-fold faster than that in ZnFbU ($(24\ \mathrm{ps})^{-1}$) even though the Dexter overlap integral is 5-fold larger (and the Förster integral 2-fold larger) in the latter dimer. This finding should not be taken to mean that energy overlap is unimportant but rather that other factors are more significant among the arrays. These factors include (a) electronic interactions involving the spatial characteristics of relevant orbitals (vide supra) and (b) energy matching involving not only the porphyrin donor/acceptor *states* in the Dexter formalism but also the energy relationships between the porphyrin and linker *orbitals* in a superexchange formalism.[26] Of course, both factors a and b are contributions to the linker-mediated inter-porphyrin electronic coupling. (2) The faster rate in CdFbU ($(15\ \mathrm{ps})^{-1}$) than in MgFbU ($(31\ \mathrm{ps})^{-1}$) appears to reflect a greater contribution of the a_{2u} HOMO and/or d orbital participation in the former array. (3) The fact that the fastest rate is observed in the mixed-metal complex ZnMgU may reflect in part an effect of symmetry on the electron density distributions in the porphyrin frontier MOs (particularly the e_g LUMOs, which are degenerate in the D_{4h} metalloporphyrins). In particular, neither porphyrin in ZnMgU has the distinct x and y axes that are defined by the central protons in the Fb porphyrin acceptor of the other dimers (CdFbU, ZnFbU, MgFbU), especially with respect to the linker site. Analogous symmetry (and associated electron density distribution) effects also may be operative in the β-pyrrole-linked ZnFb dimers we have studied recently.[13]

Although the relative contributions of the above factors among the members of our dimer series are not precisely delineated, it is noteworthy that these parameters are all associated with porphyrin orbital characteristics and the manner in which they modulate the linker-mediated inter-porphyrin electronic coupling. From a purely operational point of view, all four diarylethyne-linked porphyrin dimers (ZnMgU, CdFbU, ZnFbU, MgFbU) exhibit extremely fast and highly efficient

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(23) According to the four-orbital model,[22] the oscillator strength of the Q(0,0) absorption band is related to the energy spacing (not ordering) between the porphyrin nearly degenerate filled a_{2u} and a_{1u} orbitals. In comparing the Q(0,0) integrated intensity among a series of porphyrins, it is convenient to normalize the value to the Q(1,0) band, which has a relatively constant oscillator strength because this band derives its intensity primarily from vibronic coupling with the intense near-UV Soret transition. Concerning the ordering of the a_{2u} and a_{1u} orbitals, the former is higher than the latter among the metal porphyrins studied here (meso-substituted Zn, Mg, and Cd complexes) and this appears to be true for the Fb analogue as well (see ref 14).

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photoinduced energy transfer. Accordingly, all of these architectures are of potential utility in extended multiporphyrin arrays designed for molecular photonics applications.

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Supporting Information Available: A complete Experimental Section including schemes and detailed descriptions for the syntheses, analytical data, and spectroscopic methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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