Probing Electronic Communication in Covalently Linked Multiporphyrin Arrays. A Guide to the Rational Design of Molecular Photonic Devices

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ABSTRACT

Understanding electronic communication among the constituents in multicomponent macromolecular architectures is essential for the rational design of molecular devices for photonic, electronic, or optoelectronic applications. This Account describes studies aimed at understanding the mechanisms of electronic communication in porphyrin-based architectures that undergo excited-state energy migration and ground-state hole/electron hopping. Porphyrins are ideal building blocks for such constructs owing to their attractive and versatile physical properties and amenability to synthetic control. These properties have permitted the creation of covalently linked multiporphyrin arrays wherein the rates of excited-state energy migration and ground-state hole/electron hopping can be tuned over a wide range.

1. Introduction

The advent of rational approaches for the design and synthesis of molecular devices may usher in a new era in the field of materials chemistry. In this Account, we describe our work aimed at understanding the mechanisms of electronic communication in molecular architectures that undergo excited-state energy migration and ground-state hole/electron hopping. This work, inspired initially by the development of a light-harvesting antenna (Figure 1),[1] a molecular photonic wire,[2] and two types of molecular optoelectronic gates[3] (Figure 2), has yielded a

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foundation for the rational design of a wide range of molecular devices for photonic, electronic, or optoelectronic applications.

Our design and synthesis strategy has relied on a building block approach that uses porphyrinic molecules as the basic components. The porphyrins were chosen owing to their extraordinary versatility. In particular, the ground-state optical characteristics and excited-state properties (energy, lifetime, emission yield) can be tuned in a systematic manner via variation of the central metal as well as the substituents at the peripheral *meso*- or β-positions. The redox potentials of porphyrins can also be varied by ~1 V using the same architectural features. These properties and other design guidelines discovered during the course of this work have permitted us to create covalently linked multiporphyrin arrays wherein the rates of excited-state energy migration and ground-state hole/electron hopping can be tuned over a wide range. We have also explored how the properties of porphyrins can be exploited in conjunction with other pigments and redox-active agents. We are not aware of any other class of molecules that affords such attractive and versatile physical properties, is so amenable to synthetic control, and can be constituted in such a rich variety of architectures.

A central theme in our studies has been to use a "bottom-up" strategy for understanding the properties of large multiporphyrin architectures, such as the antenna, wire, and gates. In this approach, we first characterized dimers and trimers that are constituents of the larger architectures. We begin this Account with the results of our studies on these smaller constructs. These studies probed both excited-state electronic energy transfer and ground-state hole/electron hopping between porphyrins in a variety of arrays with different porphyrin constituents, linker types, and porphyrin—linker attachment motifs. We continue with a discussion of the mechanism(s) of electrochemical gating of excited-state energy flow. We conclude by describing how our studies have led to the rational design of other porphyrinic architectures with applications that extend beyond molecular photonics.

2. Excited-State Electronic Communication

A basic constituent of all the multiporphyrin arrays is a dimer comprised of two metalloporphyrins or one metalloporphyrin and one free-base (Fb) porphyrin joined by a linker molecule. In our prototypical dimer, the metal ions were Zn^{2+} or Mg^{2+} in metalloporphyrins or $2H^+$ in Fb porphyrins, and the linker was a diarylethyne unit. The diarylethyne linker is readily constructed[4] and is semi-rigid,[5] undergoing modest bending and allowing rotation of the porphyrin planes about the ethyne in fluid solution. Another important feature of this architecture is that the individual porphyrins are weakly coupled electronically,

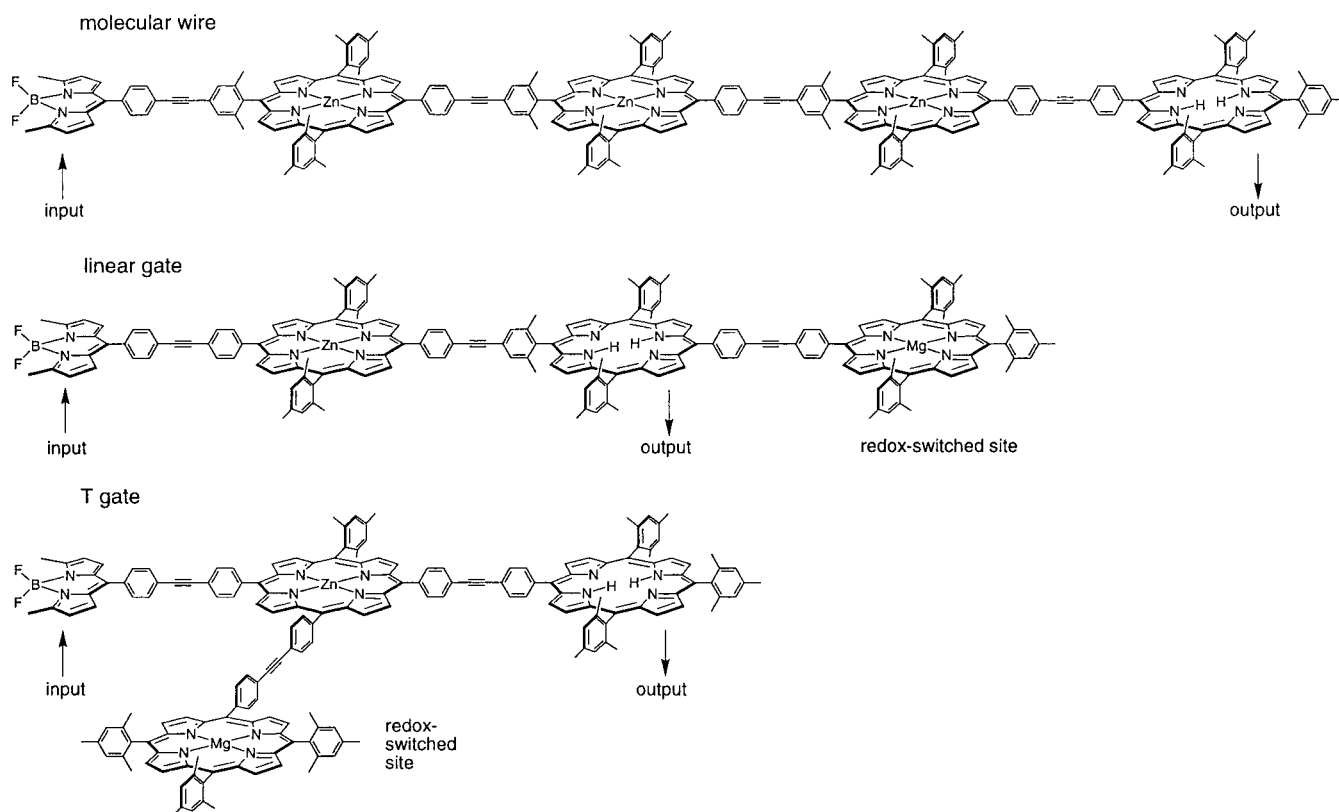* Address correspondence to any author. E-mail: holten@wuchem.wustl.edu, David.Bocian@ucr.edu, jlindsey@ncsu.edu.
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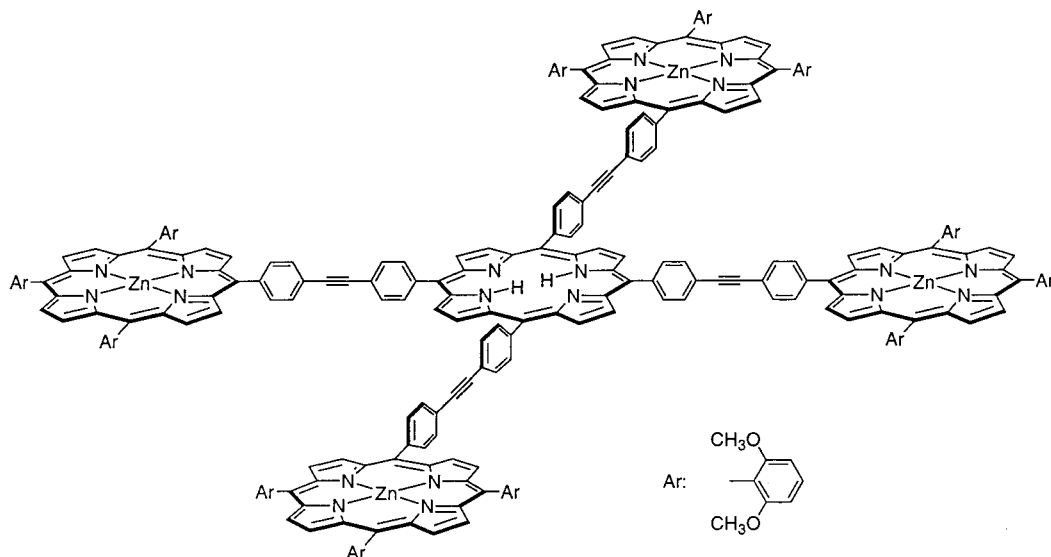
FIGURE 1. Light-harvesting antenna comprised of four Zn porphyrins and one Fb porphyrin.


FIGURE 2. Molecular wire and two optoelectronic gates. The molecular wire contains a boron-dipyrrin dye (input unit), three Zn porphyrins, and one Fb porphyrin (output unit). Each optoelectronic gate is comprised of a short molecular wire (boron-dipyrrin, Zn porphyrin, Fb porphyrin) and a redox-switched unit (Mg porphyrin).

such that the key optical, redox, and vibrational properties of a dimer (and larger array) are essentially the sum of those of the individual molecular components. Stated differently, the desired properties rationally designed into the individual chromophores or small assemblies are essentially retained when these units are joined, thus providing a foundation for predicting and understanding the properties of architectures of increasing complexity. This feature is essential for the success of the "bottom-up" strategy. On the other hand, if the electronic coupling

between the porphyrins were appreciable, each array would need to be considered as a "supermolecule" rather than the sum of individual pieces.[6] Both strategies are useful and can be melded to advantage when desired.[7] Our work has focused on arrays wherein the electronic coupling between diarylethyne-linked porphyrins is relatively weak but still more than sufficient to support facile energy and hole/electron transfer.

2.1. Mechanism of Electronic Communication. A key aspect of our studies of excited-state energy transfer in
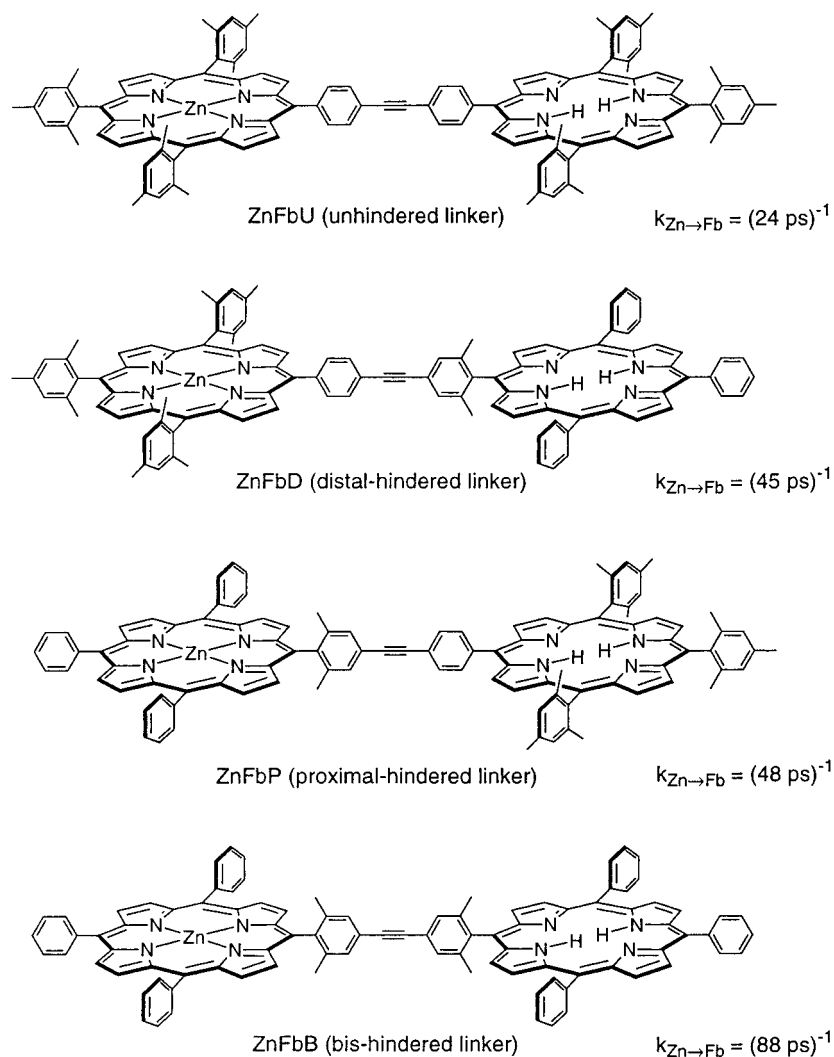
FIGURE 3. Series of dimers with progressively increased steric constraint on the linker.

porphyrin dimers of the general form ZnFb (or MgFb) was to elucidate the underlying mechanism. The salient unifying observation is that the energy-transfer rates are up to 25 times more rapid than would be anticipated for a through-space Förster energy-transfer process. This observation indicates that energy transfer occurs predominantly via a through-bond mechanism. The energy-transfer rates correspond to the tens to hundreds of picoseconds regime, consistent with the weak interporphyrin electronic coupling (a few wavenumbers at most). The through-bond nature of the process opens new avenues for controlling the rates and patterns of energy flow above and beyond those available in architectures in which through-space interactions dominate. In these latter systems, donor–acceptor distance, orientation, and energetics are the sole determinants of energy-transfer rates/efficiencies. These factors are supplemented in arrays utilizing through-bond transfer with additional design parameters that include torsional constraints, porphyrin–linker connection motif, and energies and electron density patterns involving the frontier molecular orbitals.

2.2. Effects of Torsional Mobility. Our early studies revealed that the torsional mobility of the porphyrin about the phenyl rings of the diarylethyne linker influences the extent of electronic communication between the constituent porphyrins.[8] Dimers incorporating methyl groups at the ortho positions of the linker phenyl rings restrict rotation toward coplanarity (Figure 3). As the degree of torsional constraint increases, the rate and efficiency of interporphyrin energy transfer systematically decreases. In parallel, the resonance enhancement of the Raman intensity of the $\nu_{C\equiv C}$ mode of the diarylethyne linker[9] systematically decreases.[10] The attenuation of these properties derives from diminished through-bond electronic communication (via reduced orbital overlap), as through-space communication is expected to be essentially identical along the series. Attenuated rates are also achieved by replacement of methyl by chloro groups on the linker.[11]

To elucidate the effects of porphyrin–porphyrin torsional mobility, a molecular square was prepared that locks four porphyrins (a dimer of dimers) in a mutually coplanar architecture with Zn and Fb porphyrins on alternating corners (*cyclo*-Zn_2Fb_2U) (Figure 4).[12] The energy-
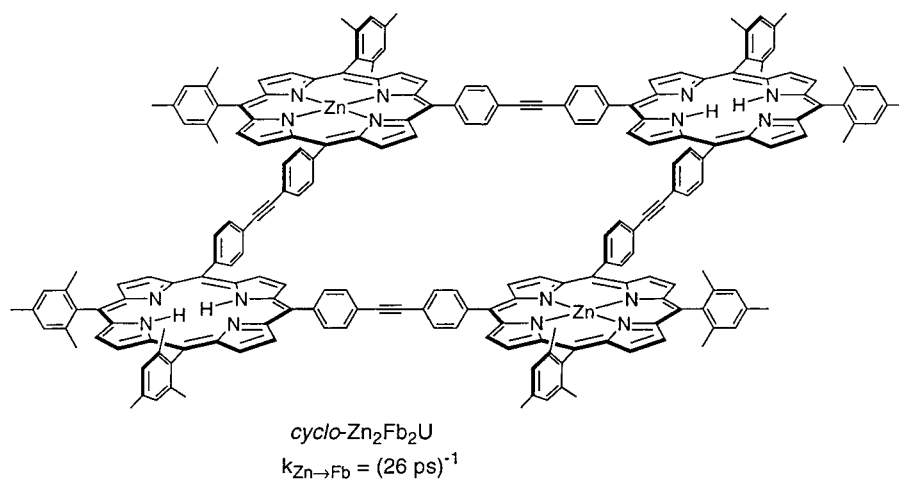
cyclo-Zn_2Fb_2U

$k_{Zn \rightarrow Fb} = (26 \text{ ps})^{-1}$

FIGURE 4. Molecular square designed to lock the porphyrins in a coplanar geometry.

R = *n*-hexyl

Osuka's dimer

$k_{Zn \rightarrow Fb} = (417 \text{ ps})^{-1}$

ZnFbU

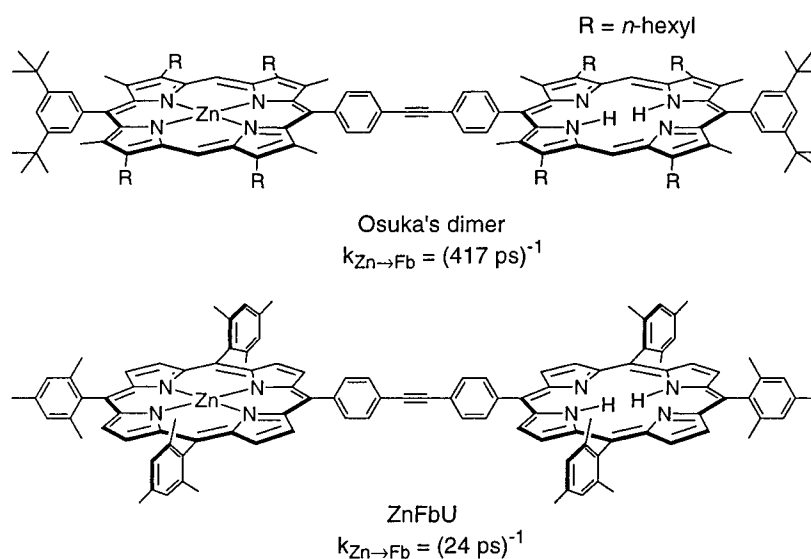$k_{Zn \rightarrow Fb} = (24 \text{ ps})^{-1}$

FIGURE 5. Two dimers with identical linkers yet very different energy-transfer rates.

transfer rate from the photoexcited Zn porphyrin to a neighboring Fb porphyrin, as well as the intensities of the ethyne $\nu_{C \equiv C}$ mode(s), of *cyclo*-Zn_2Fb_2U are comparable to those of the unconstrained ZnFbU dimer. Thus, the enforced coplanarity of the four porphyrin rings achieved by closure to the macrocyclic structure does not alter the through-bond electronic communication among the porphyrins. This result and others indicate that the fidelity of interporphyrin energy and hole/electron transfer is maintained in rigid/constrained structures.

2.3. Effects of Linker Attachment to the Porphyrin. While our diarylethyne-linked porphyrin arrays undergo rapid, highly efficient energy transfer, far slower ($\sim(417$ ps)$^{-1}$) and less efficient (78%) energy transfer was observed by Osuka et al.[13] in a dimer structurally similar to ZnFbU (Figure 5). The 17-fold attenuation in the energy-transfer rate is striking considering that ZnFbU and Osuka's dimer have identical diphenylethyne linkers. Thus, the differences in energy-transfer rates in the two dimers must derive from the nature of the porphyrins rather than the linker. In particular, ZnFbU has hydrogens at each of the

eight β-pyrrole positions and an aryl group at each of the four *meso*-positions, while Osuka's dimer has alkyl groups at all β-pyrrole positions and only two *meso*-aryl substituents.

The substitution pattern at the periphery of a porphyrin can alter the relative energies of the two nearly degenerate filled orbitals, $a_{2u}(\pi)$ and $a_{1u}(\pi)$, and thus which is the HOMO. The *meso*-aryl substitution pattern in ZnFbU makes the a_{2u} orbital the HOMO, thereby placing substantial electron density on the *meso*-carbon atoms to which the linker is appended. In contrast, the β-alkyl substitution pattern in Osuka's dimer should give the a_{1u} HOMO, which has nodes at *meso*-carbon linker attachment sites. We wondered whether electronic factors arising from the difference in orbital ordering could be the principal source of the disparate energy-transfer rates in the two dimers. To test this hypothesis, we prepared an analogue of ZnFbU, namely F_{30}ZnFbU, that has the same linker but substitutes pentafluorophenyl groups at all nonlinking *meso*-positions in order to manipulate the orbital energies (Figure 6).[14] The strong electron-with-
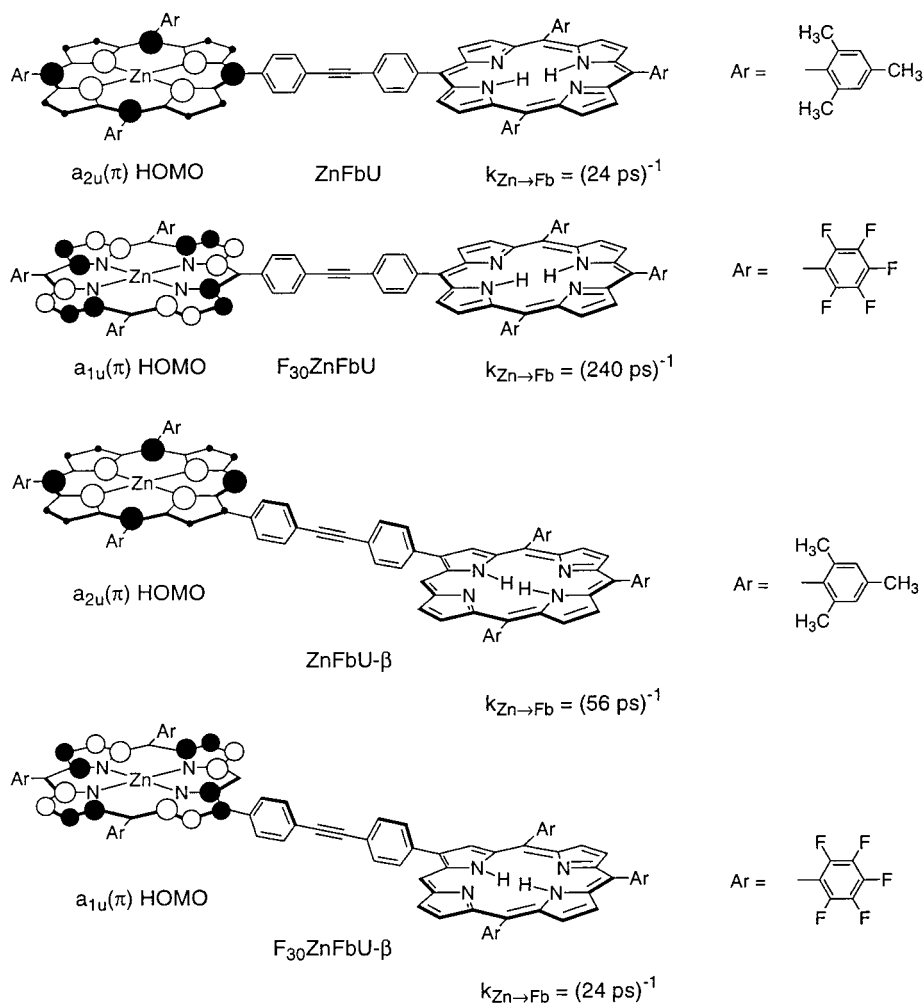
FIGURE 6. Four dimers designed to probe the interplay of orbital ordering and linker attachment site. The porphyrin frontier molecular orbitals are displayed for the Zn porphyrin.

drawing effects of the nonlinking *meso*-pentafluorophenyl groups preferentially stabilize the a_{2u} orbital of ZnFbU to an extent that the HOMO is switched to the a_{1u} orbital in F_{30}ZnFbU.

Comparison of energy transfer in ZnFbU versus F_{30}ZnFbU provides a direct probe of how orbital characteristics mediate through-bond interporphyrin electronic communication. Remarkably, the energy-transfer rate is 10 times slower in F_{30}ZnFbU than in ZnFbU [(240 ps)$^{-1}$ versus (24 ps)$^{-1}$], despite the same linker. This effect is readily ascribed to attenuated excited-state electronic coupling that stems from fluorination-induced a_{2u} stabilization to afford the a_{1u} HOMO, combined with changes in the electron density distribution in this orbital. Effects on the $e_g(\pi^*)$ LUMOs are far less important owing to the electron density distribution in these orbitals.[14]

The above results prompted the hypothesis that there should be interplay between orbital characteristics (and the effects used to tune them) and the site of linker attachment. This idea was tested using the β-diphenyl-ethyne-linked porphyrin dimers ZnFbU-β (nonlinking *meso*-mesityl substituents) and F_{30}ZnFbU-β (nonlinking pentafluorophenyl *meso*-substituents) (Figure 6).[15] The energy-transfer rate was found to be (56 ps)$^{-1}$ for ZnFbU-β

and (24 ps)$^{-1}$ for F_{30}ZnFbU-β.[16] Thus, the presence of pentafluorophenyl groups causes *enhancement* of electronic communication in the β-linked dimers but *attenuation* in the *meso*-linked dimers. These opposite effects follow because both pentafluorophenyl-substituted dimers have a_{1u} HOMOs (with β-pyrrole electron density), whereas both mesityl-substituted dimers have a_{2u} HOMOs (with *meso*-carbon electron density). Thus, optimal electronic communication is achieved by the combination of an a_{1u} HOMO with a β-linker or an a_{2u} HOMO with a *meso*-linker.

The results on this series of dimers clarify the origin of the different energy-transfer rates observed among multiporphyrin arrays and exemplify the interconnected roles of a_{1u}/a_{2u} orbital ordering, electron density distributions, and linker position in interporphyrin electronic communication, a point not appreciated prior to this study. More specifically, the findings demonstrate that the characteristics of the frontier orbitals and the position of attachment of a covalent linker (in addition to distance, orientation, and energetics) are key considerations in the design of multiporphyrin arrays for molecular photonics applications. The effects are not restricted to dimers but are manifested in larger multiporphyrin arrays.[17,18] These insights are also directly applicable to the widely studied
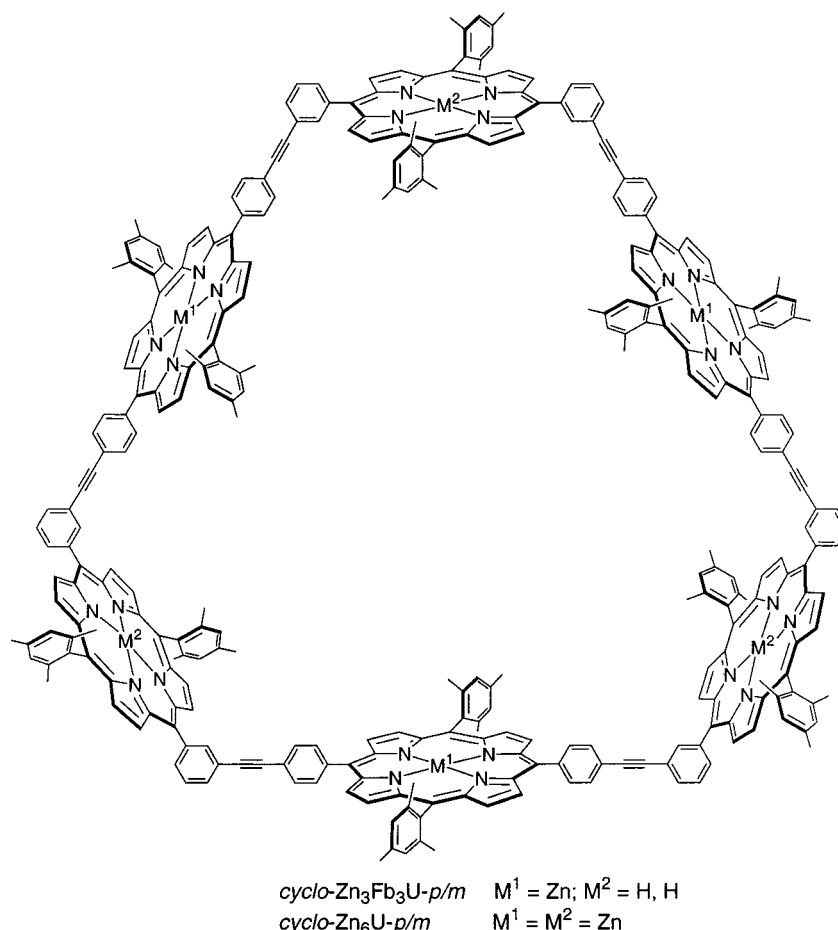
cyclo-Zn$_3$Fb$_3$U-*p/m*   M^1 = Zn; M^2 = H, H
cyclo-Zn$_6$U-*p/m*   M^1 = M^2 = Zn

FIGURE 7. Shape-persistent cyclic hexamer with alternating Zn and Fb porphyrins.

porphyrin-based electron-transfer processes. Given the importance of these effects, we synthesized and characterized a library of over 40 Fb, Mg, and Zn tetraarylporphyrins that bear *meso*-substituents with a wide range of halogenation patterns, thereby affording a set of porphyrin building blocks with explicit control over the characteristics of the frontier molecular orbitals.[19]

2.4. Effects of Porphyrin Attachment to the Linker. We prepared a cyclic hexameric architecture (*cyclo*-Zn$_3$-Fb$_3$U-*p/m*) comprised of three Fb porphyrins and three Zn porphyrins joined via diphenylethyne units (Figure 7).[20] To probe the energy-transfer dynamics in the dimeric motif of the cyclic hexamer, we examined dimers in which one porphyrin is linked at the *para* position of one phenyl ring in a diphenylethyne linker and the other is linked at the *meta* position of the other phenyl ring (ZnFbU-*p/m* and Zn$_2$U-*p/m*). The energy transfer proceeds via a linker-mediated through-bond mechanism, as occurs with the dimers described above which contain only *para* attachments (ZnFbU and Zn$_2$U). However, the energy-transfer rate of (34 ps)$^{-1}$ in ZnFbU-*p/m* is slower than that of (24 ps)$^{-1}$ in ZnFbU, despite the shorter center-to-center distance in the former case. This rate difference can be traced primarily to the larger electron density of the frontier molecular orbitals at the *para*- versus *meta*-position of each phenyl ring in the diphenylethyne linker.[20] These results indicate that the position of attachment of

the porphyrin to the linker can alter the electronic communication, analogous to the position of attachment of the linker to the porphyrins. The all-Zn analogue of the cyclic hexamer (*cyclo*-Zn$_6$U-*p/m*) has been employed as a host for binding a dipyridyl-substituted Fb porphyrin, thereby constituting a self-assembled light-harvesting array.[21]

2.5. Effects of Linker Architecture. Another logical step in understanding and tuning electronic communication was to explore the influence of the linker itself. To this end, the excited-state properties of two ZnFb porphyrin dimers employing a *p*-phenylene linker (Φ) were characterized.[22] The effect on orbitals/rates was also probed by employing mesityl groups (ZnFbΦ) or pentafluorophenyl rings (F$_{30}$ZnFbΦ) at the nonlinking *meso*-positions. The energy-transfer rate from the Zn porphyrin to the Fb porphyrin is (3.5 ps)$^{-1}$ for ZnFbΦ and (10 ps)$^{-1}$ for F$_{30}$-ZnFbΦ. These rates are considerably faster than those for the analogous diphenylethyne-linked dimers, namely (24 ps)$^{-1}$ for ZnFbU and (240 ps)$^{-1}$ for F$_{30}$ZnFbU. The differences arise from enhanced electronic coupling between the *p*-phenylene-linked porphyrins due to the shorter separation. This interporphyrin distance is sufficiently short that through-space coupling likely contributes appreciably to energy transfer (and to the diminished fluorination effect) but is still long enough to maintain the "bottom-up" strategy in which the relevant redox and
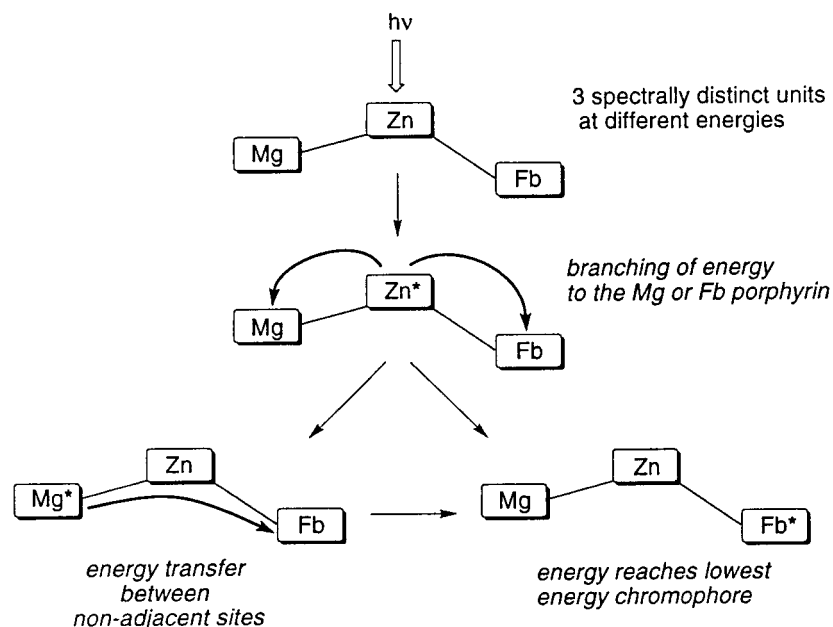
FIGURE 8. Generic design of trimers for probing nonadjacent energy-transfer processes.

photophysical characteristics of the units are basically retained in the arrays. Thus, *p*-phenylene-linked porphyrin constructs are attractive candidates for incorporation into extended multiporphyrin arrays for applications wherein larger electronic coupling and faster processes than those obtained with the diarylethyne linker are desirable.

2.6. Effects of Metalation State. Most of our studies examined arrays that contain all Zn, all Mg, a combination of Zn and Fb, or Mg and Fb porphyrins. To expand this combination of components, we examined other metal-loporphyrin dimers that retain the same diarylethyne linker and porphyrin substituents. One dimer consists of a Zn porphyrin and a Mg porphyrin (ZnMgU),[23] and the other incorporates a Cd porphyrin and a Fb porphyrin (CdFbU).[24] The rates of energy transfer are faster for ZnMgU ($(9 \text{ ps})^{-1}$) and CdFbU ($(15 \text{ ps})^{-1}$) than for ZnFbU ($(24 \text{ ps})^{-1}$) and MgFbU ($(31 \text{ ps})^{-1}$). Only for CdFbU does the yield of energy transfer (87%) drop below the near-quantitative ($\geq 99\%$) 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 how molecular/electronic properties can be manipulated to tune energy flow in multiporphyrin arrays.

2.7. Importance of Nonpairwise Interactions. Many of the concepts that emerged from studies of the porphyrin dimers were incorporated into trimers containing Mg, Zn, and Fb porphyrins having a variable linkage motif between the first two constituents (Figures 8 and 9).[25] Studies on trimers were undertaken as benchmarks for the optoelectronic gates and to quantify how nonpairwise interactions (electronic coupling) between nonadjacent (distant) sites might influence the properties of arrays.

The energy of the lowest excited singlet state of the three porphyrins in the trimers decreases in the order Zn > Mg ≫ Fb. Thus, excitation of the central Zn porphyrin leads to branched energy transfer, forming the excited Mg

porphyrin (Mg*) and the excited Fb porphyrin (Fb*). Our previous studies on the dimer components, showing that $k_{\text{Zn} \rightarrow \text{Fb}} = (24 \text{ ps})^{-1}$ in ZnFbU and $k_{\text{Zn} \rightarrow \text{Mg}} = (9 \text{ ps})^{-1}$ in ZnMgU, predicted a Zn* lifetime of 6.6 ps for the trimer with the *p,p*-linker attached to the *meso*-position of the Mg porphyrin. Indeed, τ_{Zn^*} was found to be between ~ 6.5 and ~ 10 ps for each of the four trimers, consistent with the work on the subunits and with the concept that the other three linker motifs should give slower energy transfer from Zn* to the Mg porphyrin. More importantly, energy subsequently flows from Mg* to the Fb porphyrin (i.e., from one end of the trimer to the other) with a rate constant in the range $(150 \text{ ps})^{-1}-(370 \text{ ps})^{-1}$, depending on the linker motif. This latter process does not involve uphill energy transfer from Mg* to form Zn* as a discrete intermediate state, as confirmed by studies at low temperature. Instead, energy transfer from Mg* to the Fb porphyrin utilizes the intervening Zn porphyrin as a superexchange mediator. It is noteworthy that superexchange mediation of electron transfer has been widely studied, but the importance of this mechanism for energy transfer had previously received little attention.

The nonpairwise interactions, while small relative to the (already weak) pairwise interactions, result in energy transfer among nonadjacent sites at a rate within 10-fold that of transfer between adjacent sites. Nonadjacent energy transfer at such rates has important implications for the energy-transfer characteristics of very large arrays where multiple energy-flow pathways are active, in particular for the optoelectronic gates (vide infra). Accurate modeling of the energy-transfer dynamics and efficiencies of such large assemblies must include these nonpairwise pathways. These effects may also be important for mediating electronic communication in other types of architectures such as photosynthetic antenna complexes and DNA.
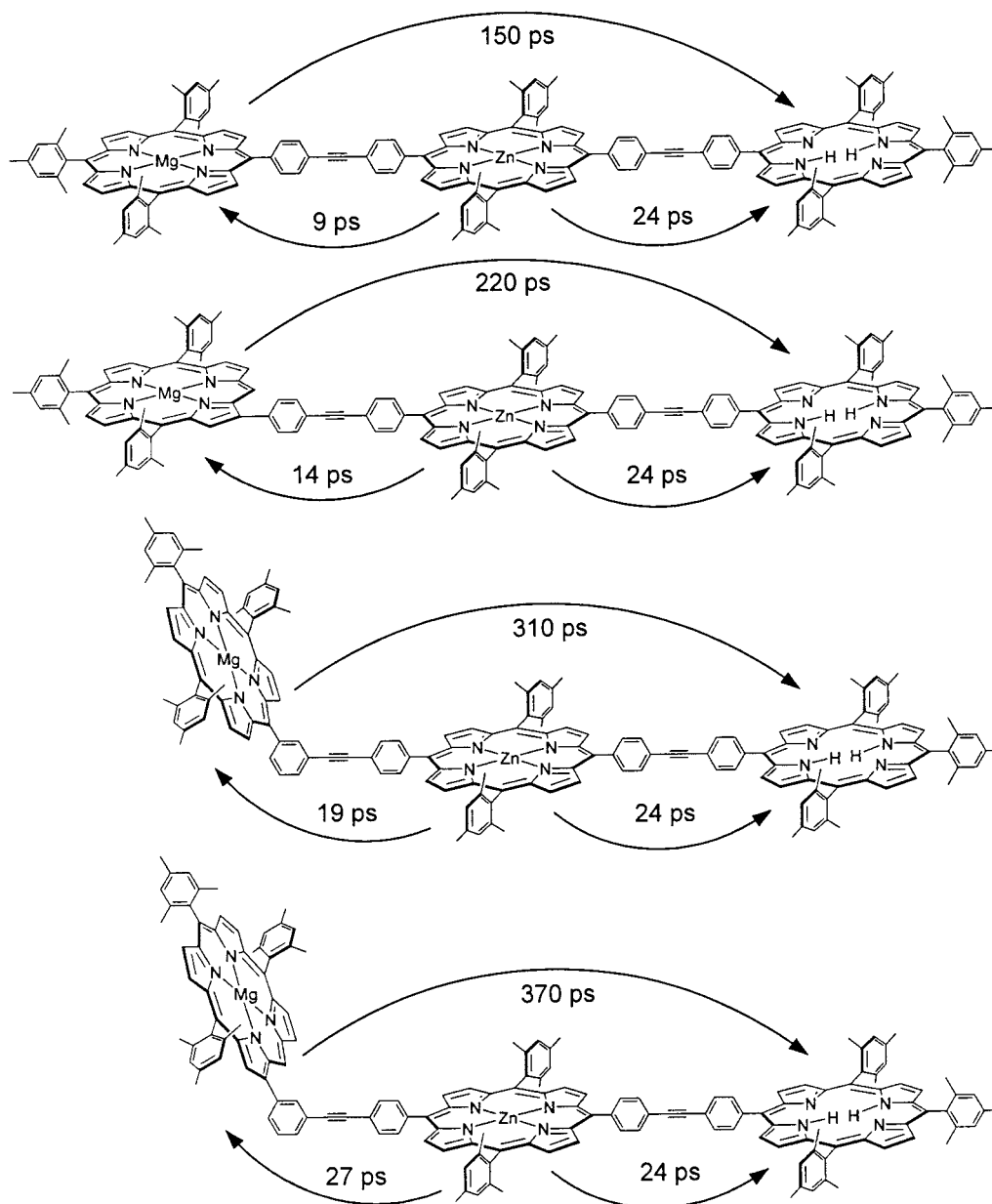
FIGURE 9. Set of MgZnFb trimers with different linker motifs and connectivity between the Mg and Zn porphyrins.

## 3. Ground-State Electronic Communication

Ground-state electronic communication in the multiporphyrin arrays was investigated in parallel with the excited-state behavior. Our approach to probe ground-state communication was to characterize the hole/electron-hopping properties of oxidized arrays containing multiple Zn porphyrin constituents (Figure 10), primarily the bis-Zn analogues of the ZnFb dimers described above. In addition, arrays containing three, five, or more porphyrins were studied. A primary motivation was to gain additional insight into the rates of charge-transfer processes that might occur, because we found that excited-state inter-porphyrin charge-transfer processes were much slower than the dominant energy-transfer pathway. Although the hole/electron-hopping rates in the electronic ground states of the oxidized arrays are not expected to be equal to the charge-transfer rates in the excited states, they provide a measure of the controlling factors.

We examined the oxidized arrays using a variety of techniques including electronic (absorption), vibrational (resonance Raman), and magnetic resonance (EPR) spectroscopy.[9] These studies revealed that the hole/electron hopping in oxidized arrays (regardless of porphyrin, linker, connectivity) is slow on the electronic/vibrational time scale ($10^{-13}-10^{-15}$ s), namely that the hole/electron is localized on a particular porphyrin constituent.

We observed quite different behavior on the much slower EPR time scale ($\sim10^{-7}$ s). In the case of oxidized diarylethyne-linked dimers such as Zn_2U, the hole/electron hops very rapidly between the porphyrins and is completely delocalized on this time scale. Although the exact rate could not be determined, it is $\geq(0.05 \ \mu s)^{-1}$.[9] The rate remains fast on the EPR time scale upon the addition

$Zn_2U^{\cdot+}$

monocation radical of Zn_4FbU
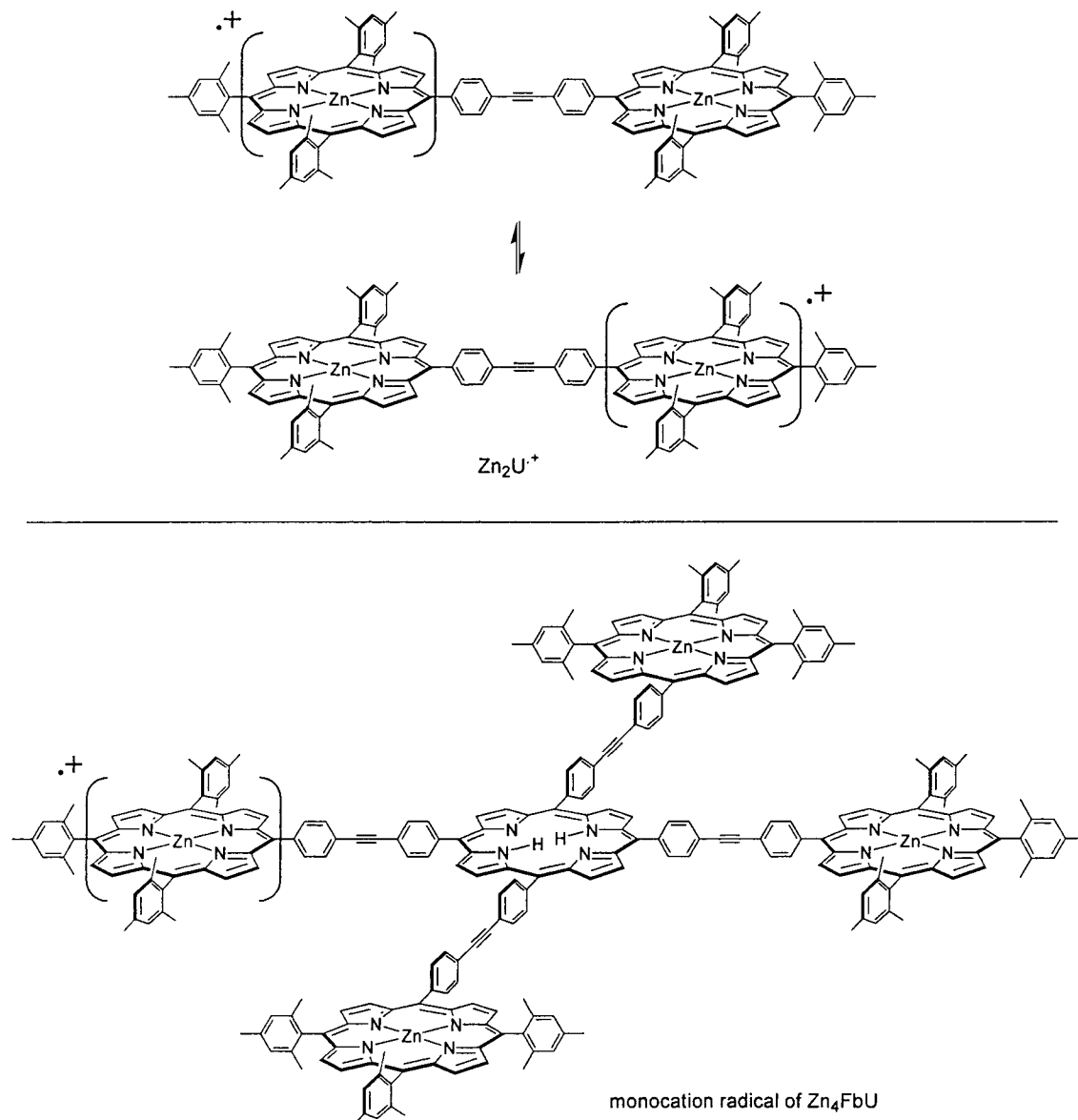
FIGURE 10. Ground-state hole hopping is a facile process both in the bis-Zn porphyrin dimers and in larger arrays wherein the Zn porphyrins are separated by an intervening Fb porphyrin.

of torsional constrains to the diarylethyne linker (see Figure 3).[10] In contrast, the hole/electron-hopping rate in the fluorinated bis-Zn complex $[F_{30}Zn_2U]^+$ (Figure 6) is at least 10-fold slower ($\leq(0.5\ \mu s)^{-1}$) than that for $[Zn_2U]^{+}$.[14] Similar trends are observed in the bis-Zn *p*-phenylene-linked dimers; namely, the rate of $\geq(0.05\ \mu s)^{-1}$ for $[Zn_2\Phi]^+$ is much more rapid than that of $\leq(2.5\ \mu s)^{-1}$ for $[F_{30}Zn_2\Phi]^{+}$.[22] In the case of the mono-oxidized bis-Zn analogues of the β-linked dimers $[Zn_2U\text{-}\beta]^+$ and $[F_{30}Zn_2U\text{-}\beta]^+$, the relative rates of hole/electron hopping are both $\geq(0.05\ \mu s)^{-1}$.[16] The rate is also influenced by the site of porphyrin attachment to the linker. For example, the hole/electron hopping for $[Zn_2U\text{-}p/m]^+$ is at least 10-fold slower than that for $[Zn_2U]^{+}$.[20]

We have also investigated ground-state hole/electron hopping in linear and right-angle trimers and in star-shaped pentamers (Figure 10) containing only Zn porphyrins or Zn porphyrins attached to a central Fb porphyrin (all with diarylethyne linkers).[9,10] In the case of the all-Zn-containing trimers and pentamer, the hole/electron hops rapidly on the EPR time scale and is completely delocalized over all of the Zn porphyrins. More interesting are the trimers and pentamer wherein an intervening Fb porphyrin separates the Zn porphyrins.[9,10] In these arrays, the hole cannot reside on the Fb porphyrin owing to its much higher oxidation potential relative to that of the Zn porphyrins. Nevertheless, the hole hops quite rapidly between the nonadjacent Zn porphyrins and is completely delocalized over the Zn porphyrins on the EPR time scale.

Collectively, the studies of ground-state hole/electron transfer indicate that this process is sensitive to the same structural/electronic properties that influence excited-state energy transfer. Again, of particular importance is the interplay between the characteristics of the frontier molecular orbitals and the porphyrin–linker motif. The fact that facile hole/electron hopping occurs between
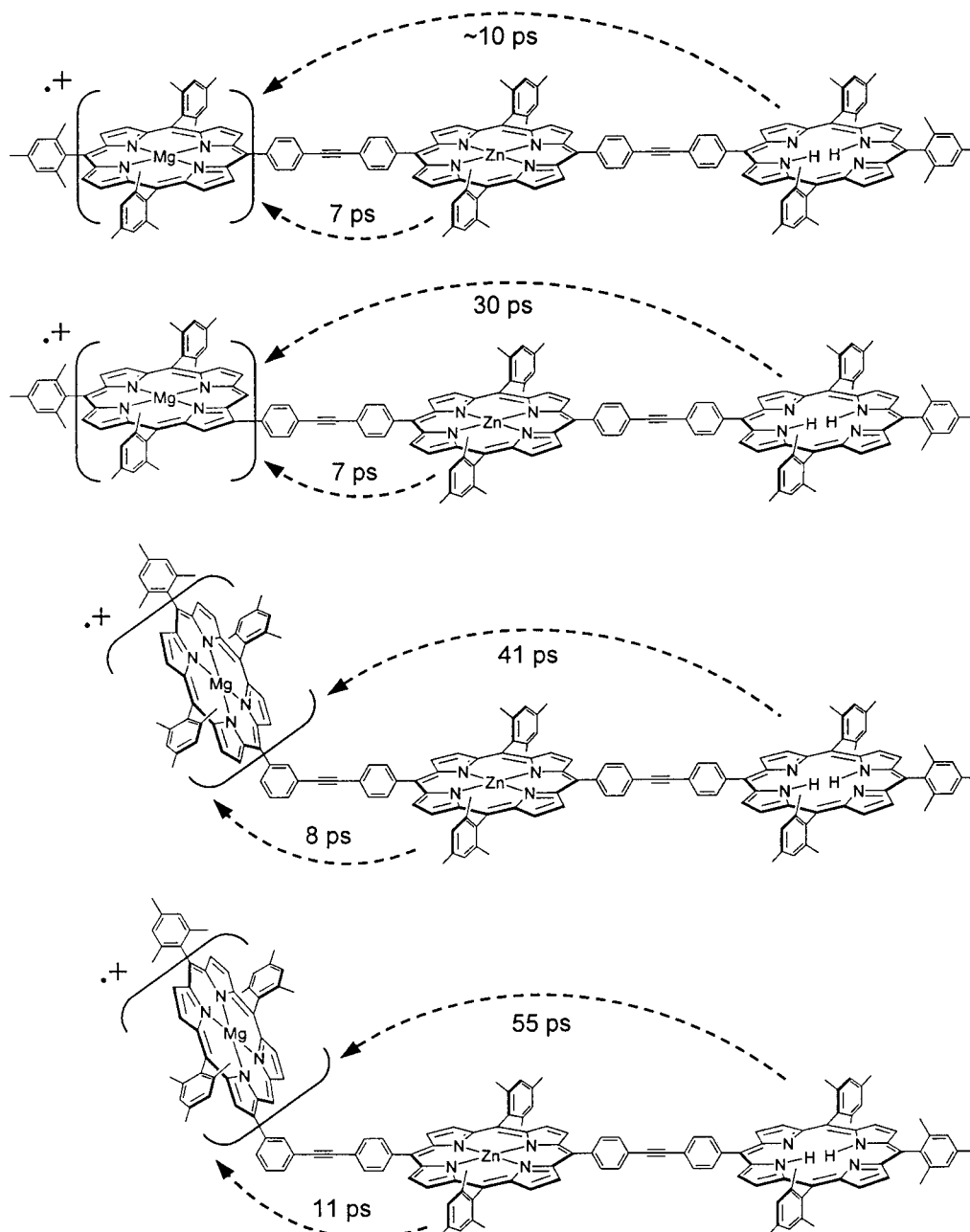
FIGURE 11. Gating in one-electron-oxidized MgZnFb trimers.

nonadjacent Zn porphyrins in arrays that contain an intervening Fb porphyrin indicates that nonpairwise superexchange interactions are important for mediating ground-state as well as excited-state electronic communication.

4. Gating of Excited-State Energy Flow

Having constructed a molecular photonic wire and other arrays that mediate excited-state energy migration, we synthesized two types of gates wherein a redox-switching site was employed to toggle the flow of excited-state energy.[3,26] The T gate and linear gate (Figure 2), constructed at the inception of this project,[3] were anticipated to function in quite different ways. In the T gate, the redox-switching unit was anticipated to function by intercepting the excited-state energy at the (short-lived) relay element (Zn porphyrin) prior to passage to the light-output unit, whereas in the linear gate, the redox-switching unit was required only to quench the (long-lived) excited state of the output unit.

We investigated the gating rate and mechanism in studies of energy transfer from Zn or Fb porphyrins to oxidized Mg porphyrins both in simple dimers and in the four trimers depicted in Figure 11.[27] The studies show that an oxidized porphyrin rapidly ($\sim$10 ps) quenches an adjacent excited porphyrin, which normally has a lifetime in the range 2–3 ns (Zn porphyrins) or 10–15 ns (Mg or Fb porphyrins). This quenching occurs by energy/charge transfer, followed by rapid ($<$10 ps) deactivation to the ground state. The overall quenching rate of $\sim$(10 ps)$^{-1}$ is
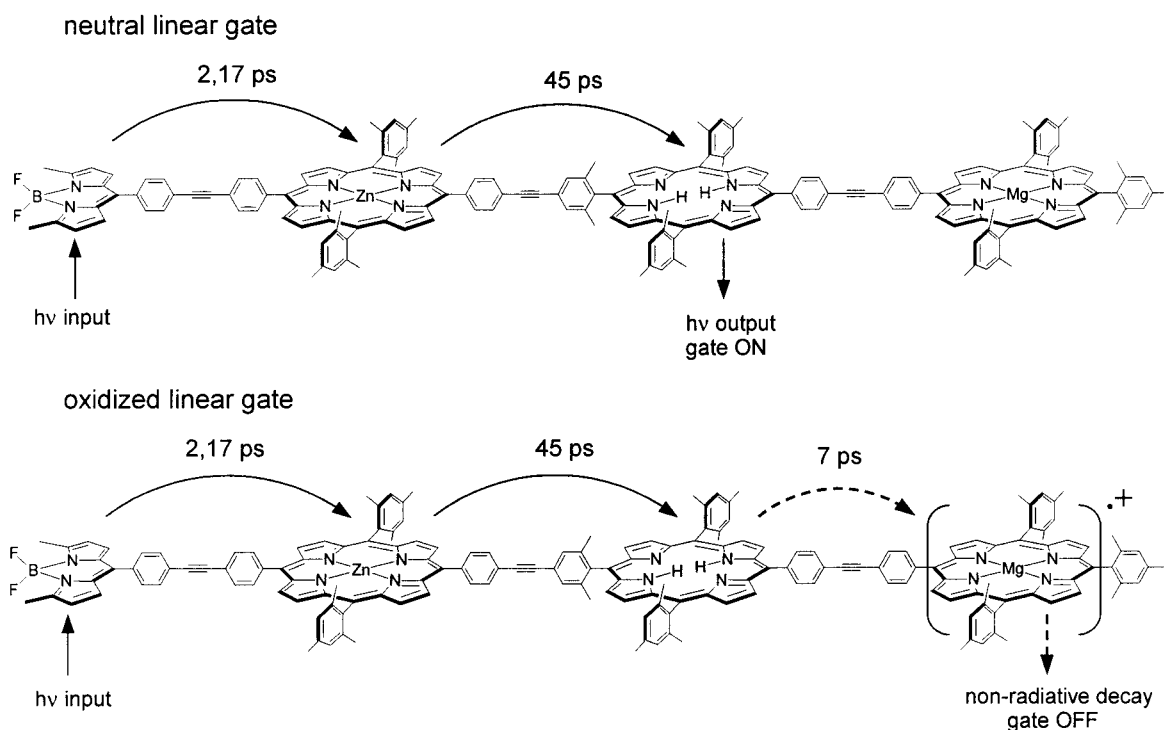
neutral linear gate

oxidized linear gate

FIGURE 12. Dynamics of gating in the linear gate.

comparable to the energy-transfer rate we have found between neutral porphyrins joined by the same diaryl-ethyne linker (within a factor of 3, depending on the porphyrins). The finding of a similar time scale when the acceptor is an oxidized porphyrin indicates that a linker-mediated through-bond mechanism again applies.

In addition to quenching involving neighboring por-phyrins, the excited Fb porphyrin is efficiently quenched by the nonadjacent Mg porphyrin π-cation radical in the oxidized MgZnFb trimers (Figure 11).[27] This process is analogous to the energy transfer from the excited Mg porphyrin to the distant Fb porphyrin in the neutral forms of the same arrays (Figure 9). The process again utilizes the intervening Zn porphyrin (and the two linkers) as a superexchange mediator. A quenching time of <100 ps between distant sites in the oxidized trimers is sufficiently short compared to the 13 ns lifetime of the excited Fb porphyrin that emission from the excited output element is quantitatively quenched. Furthermore, studies of the porphyrin trimers indicate that the gating rate can be tuned to a modest extent by altering the electronic coupling between porphyrin constituents by changing one of the two diphenylethyne linkage motifs. Other structural variations should permit the gating rate to be tuned over an even greater range.

Recently, we studied the dynamics of the energy-transfer processes in the linear and T-shaped optoelec-tronic gates themselves (Figures 12 and 13).[28] Both the dynamics and the mechanism of energy flow in the gates in the neutral (ON ≡ light output from Fb porphyrin) and oxidized (OFF ≡ emission quenched) forms are more complex than originally anticipated. Because energy trans-fer occurs very rapidly ($k_{Zn\rightarrow Mg} = (9 \text{ ps})^{-1}$) from a Zn

porphyrin to a Mg porphyrin joined via a diphenylethyne linker,[24] the majority of the energy in the neutral T gate initially flows to the (neutral) switching site rather than to the output unit. However, our studies on the MgZnFb trimers described above demonstrate that superexchange-mediated transfer from the Mg porphyrin will occur rapidly to the distant Fb porphyrin in the T-gate, thus maintaining the same efficiency of the ON state as in the linear gate. Similarly, the Mg porphyrin π-cation radical in the oxidized T gate quenches the energy arriving at the distant Fb porphyrin efficiently by superexchange, thus giving the same efficiency of the OFF state as in the linear gate. Hence, nonpairwise interactions involving distant neutral porphyrins or a neutral porphyrin and a distant π-cation radical are critical for the function of the T-gate architecture and will be equally applicable in other multiporphyrin assemblies.

5. Other Architectures and Applications

Our findings during the course of these studies have led us to a number of applications. For example, accessory pigments such as boron-dipyrrin[2,29] or perylene[7] dyes have been incorporated as energy donors in light-harvesting arrays. Phthalocyanines (Fb, Zn, Mg) have been employed as energy-transfer acceptors and bright fluorescent output elements in molecular photonic devices.[7,30−32] In each of these constructs, through-bond electronic communication provides the dominant mechanism for energy transfer. We also have examined a number of prototypical switching elements for use in molecular gates.[26] These molecules include ferrocene attached to a porphyrin or a phthalo-cyanine, and a derivative of Ru(bpy)$_3$ attached to a
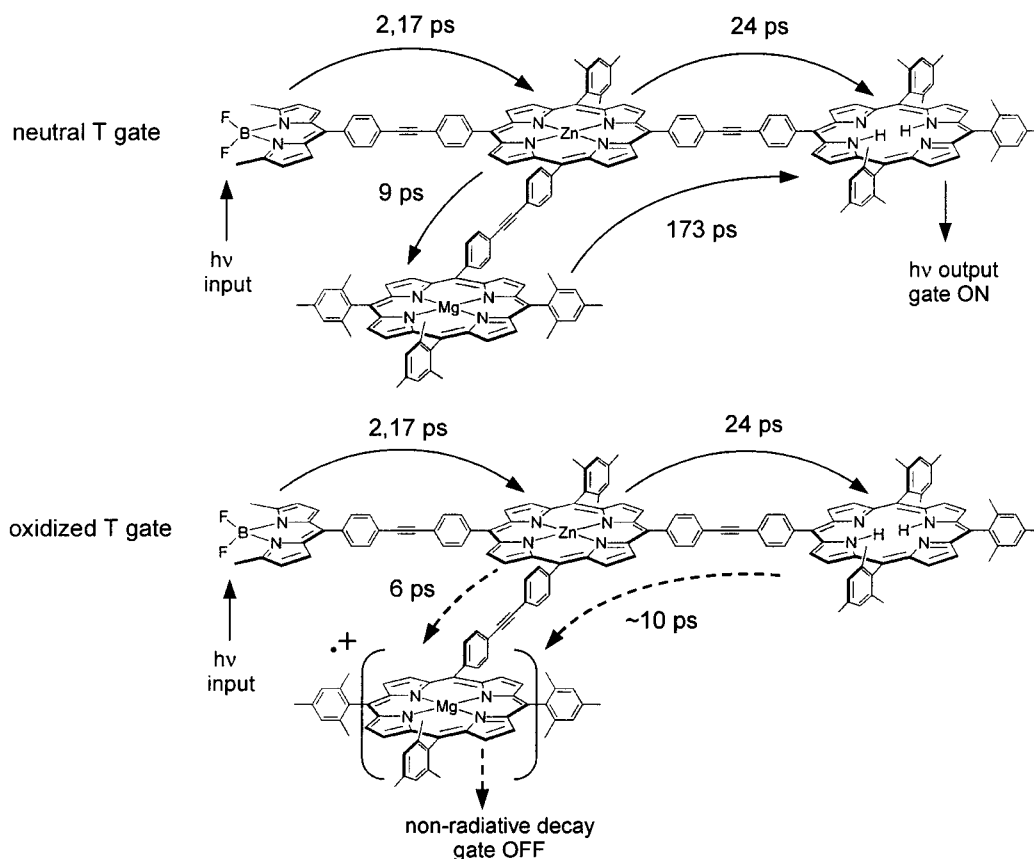
FIGURE 13. Dynamics of gating in the T gate.

porphyrin. The latter system was constructed as a proto-typical component for an all-optical gate. Recently we have extended our studies to all-porphyrin arrays containing up to 21 units, which serve as efficient light-harvesting energy funnels and hole-storage reservoirs.[33]

The facile hole-hopping processes and the stability of the oxidized multiporphyrin arrays led us to investigate the use of thiol-derivatized multiporphyrin constructs in self-assembled monolayers with the objective of creating a molecular-based information storage device utilizing the distinct redox states of the molecules.[34] Additionally, arrays with interleaving redox potentials enable storage of multiple bits of information.[35] This approach affords ultra-dense, low-power, electrically addressable information storage in an architecture that is scalable to molecular dimensions.

6. Conclusions

The principal findings of the studies described in this Account are as follows: Ultrafast excited-state energy transfer and ground-state hole-hopping occur predominantly via a linker-mediated through-bond mechanism involving both adjacent and distant sites. These processes can be systematically controlled by changes in (1) the steric interactions between the porphyrin and the linker, (2) the characteristics of the porphyrin frontier molecular orbitals, and (3) the site of porphyrin attachment to the linker and vice versa. Our findings provide a comprehensive understanding of the factors that control electronic communication in weakly coupled multiporphyrin arrays and serve as a foundation for the rational design of architectures for a number of applications.

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