# Long-Lived, Charge-Shift States in Heterometallic, Porphyrin-Based **Dendrimers Formed via Click Chemistry**

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### Supporting Information

ABSTRACT: A series of multiporphyrin clusters has been synthesized and characterized in which there exists a logical gradient for either energy or electron transfer between the porphyrins. A central free-base porphyrin (FbP), for example, is equipped with peripheral zinc(II) porphyrins (ZnP) which act as ancillary light harvesters and transfer excitation energy to the FbP under visible light illumination. Additional energy-transfer steps occur at the triplet level, and the series is expanded by including magnesium(II) porphyrins and/or tin(IV) porphyrins as chromophores. Light-induced electron transfer is made possible by incorporating a gold(III) porphyrin (AuP<sup>+</sup>) into the array. Although interesting by themselves, these clusters serve as control compounds by which to understand the photophysical processes occurring within a three-stage dendrimer comprising an AuP<sup>+</sup> core, a second layer formed from four FbP



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units, and an outer layer containing 12 ZnP residues. Here, illumination into a peripheral ZnP leads to highly efficient electronic energy transfer to FbP, followed by charge transfer to the central AuP<sup>+</sup>. Charge recombination within the resultant charge-shift state is intercepted by secondary hole transfer to the ZnP, which occurs with a quantum yield of around 20%. The final charge-shift state survives for some microseconds in fluid solution at room temperature.

# INTRODUCTION

Multiporphyrin dendrimers are desirable target molecules for use as large-scale photon collectors, or light-harvesting arrays, in artificial photosynthesis. Indeed, the spherical branch symmetry is well-suited for the realization of large absorption cross-sections and for channeling accumulated photons or electronic charge toward the center or periphery according to the nature of the dendrimer. Changing the metal cation coordinated to the porphyrin ring can generate a wide range of pigments, each displaying a distinctive absorption spectrum, that combine to cover a broad absorption window and at high absorptivity.<sup>1-4</sup> Such properties are key requisites for the design of efficacious solar concentrators.<sup>5</sup> Furthermore, the increasing density of pigment molecules brought about with each incremental layer creates opportunities for intercompartmental processes, such as excited-state annihilation,<sup>6</sup> energy- and/or electron-transfer reactions,<sup>7–10</sup> and quenching events.<sup>11</sup> By arranging the pigments in preferred sequences, additional possibilities might arise for the spatial isolation of light-induced, charge-separated states, in turn leading to long-lived redox species.<sup>12</sup> A particularly attractive feature of tetrapyrrolic-based dendrimers is the capability to combine both options and thereby produce tailor-made optoelectronic devices able to run under ambient light conditions. This could lead to new molecular materials able to generate and store several

oxidative or reductive equivalents in close proximity.<sup>13</sup> In this way, it might become feasible to consider multielectron redox reactions leading to fuel production or water oxidation.<sup>14</sup> The light-harvesting antenna present in photosynthetic reaction centers, which organize 9 or 18 (bacterio)chlorophylls into discrete cyclic arrangements,<sup>15</sup> is a convincing illustration of the validity of these basic principles.<sup>16</sup>

Numerous multiporphyrin arrays have been prepared by iterative Sonogashira cross-coupling reactions,  $^{17-20}$  by the Williamson nucleophilic reaction,  $^{21-24}$  or by way of nucleophilic aromatic substitutions.<sup>25</sup> Such systems rely on covalent bonding to assemble the individual porphyrins into logical superstructures. Supramolecular-based dendrimers assembled by way of strong coordinative bonds with zinc,<sup>26–28</sup> phosphorus, and tin porphyrins are also known.<sup>9,29–31</sup> Furthermore, efficient electronic energy-<sup>32</sup> and electron-transfer<sup>33</sup> processes have been described for several of these systems, and it should be stressed that, in certain cases, unusually long-lived, charge-separated states have been reported.<sup>34</sup> In seeking to extend the field, it might be noted that the synthesis of heteronuclear multiporphyrin dendrimers is a nontrivial task inasmuch as high-yielding reactions must

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be used to limit defects and to reach higher generations. To this end, the copper-catalyzed Huisgen cycloaddition reaction, commonly referred to as "click chemistry", is a powerful tool for such applications.<sup>35–38</sup> This type of connection has been used successfully to link porphyrin substrates to various ancillary functions.<sup>39–50</sup> Herein, we continue to apply click chemistry to assemble functional porphyrin-based residues,<sup>40,51–53</sup> with the specific intention of preparing layered heterometallic dendrimers.

The main design principle behind this synthetic work has been to create a large superstructure with the capability to harvest photonic energy over most of the visible range and to utilize this excitation energy to bring about efficacious charge separation. A further requirement is that the resultant charge-separated state should be relatively long-lived and have the promoted electron localized at a single porphyrin residue. This latter feature is necessary for the array to function as a light-harvesting unit for organic solar cells or dye-injection photoelectrochemical devices. To realize such units, we have adapted our earlier work<sup>54–56</sup> with electron affinic gold(III) porphyrins. Thus, the starting point for assembly of the dendrimer is a gold(III) tetraarylporphyrin, which will operate as the ultimate electron acceptor.<sup>57</sup> The complementary electron donor is a free-base porphyrin (FbP), attached nearby to the gold(III) porphyrin (AuP<sup>+</sup>) and forming the first layer. To provide for spatial isolation of the chargeseparated state, a layer of zinc(II) porphyrins is added. This strategy allows for the redox gradient that should drive hole transfer from the oxidized free-base porphyrin to one of the attached zinc(II) porphyrins. In addition, highly efficient electronic energy transfer should be expected<sup>58</sup> from the zinc(II) porphyrin (ZnP) to an adjacent free-base porphyrin, thereby fulfilling the need to collect photons over a wide spectral window. Energy transfer in such systems can involve both singlet and triplet excited states<sup>59</sup> such that the overall quantum efficiency for the charge-separation event should be high. The limiting efficiency, therefore, might be set by the effectiveness of the subsequent hole-transfer step.

# RESULTS AND DISCUSSION

**Synthesis.** The molecular formula of the target dendrimer, **D2(Fb)**, is presented in Chart 1, together with structural representations of some relevant control compounds. Synthesis of these porphyrin-based dendrimers calls for three key building blocks, **3**, **6**, and 7 (Schemes 1 and 2). The fully symmetrical tetrakis-5,10,15,20-(4-(azidomethyl)phenyl)porphyrin, **2**, was prepared in 12% overall yield by condensation of the known 4-(azidomethyl)benzaldehyde, **1**,<sup>60</sup> with pyrrole as catalyzed by BF<sub>3</sub>—OEt<sub>2</sub> in dichloromethane (Scheme 1). The corresponding free-base porphyrin **2** was subsequently metalated with gold(III) using standard conditions,<sup>61</sup> namely, KAuCl<sub>4</sub> in refluxing acetic acid, to afford **3** in 40% yield.

Mixed aldehyde condensation of **1** with 4-((trimethylsilyl)ethynyl)benzaldehyde, **4**,<sup>62</sup> with pyrrole gave porphyrin **5** in 4% yield. In spite of the low yield for this transformation, the onestep synthesis and its facile purification by column chromatography, due to the high polarity of the azido groups, enable isolation of pure samples of porphyrin **5** in significant quantities. Metalation of **5** with magnesium(II) was accomplished according to the conditions developed by Lindsey and co-workers.<sup>63</sup> Ethynylporphyrin 7 was prepared by condensation of 3,5-di*tert*-butylbenzaldehyde and 4-(3-methyl-3-hydroxybut-1-yn-1-yl)benzaldehyde with pyrrole followed by deprotection with sodium hydroxide in refluxing toluene as previously reported by Lindsey and co-workers.<sup>64</sup> The methylhydroxybutynyl protecting group was preferred over the classical trimethylsilyl unit since it provides easier separation of porphyrin byproduct via column chromatography, because of the relatively high polarity of the alcohol compared to the corresponding di*-tert*-butyl derivative. The Huisgen cycloaddition reaction between the above porphyrin building blocks was conducted with copper(II) sulfate as catalyst using ascorbic acid as reducing agent in dimethylformamide. Reaction proceeds smoothly at 50 °C and gave high yields. The resultant reaction mixture was best purified by size-exclusion chromatography, where the triazole groups bind strongly to the stationary phase (Scheme 2).

It was found that the magnesium porphyrin (MgP) in **10** and **D2** could be selectively demetalated with phosphoric acid in tetrahydrofuran without removal of the zinc(II) cations from the peripheral porphyrins. All of the new compounds were characterized by <sup>1</sup>H NMR spectroscopy and high-resolution mass spectrometry, except dendrimers **D2**(**Fb**) and **D2**(**Mg**), which failed to give a MALDI-TOF signal, most likely because of the high molecular weights (>15 000 g/mol) of these compounds.

Electrochemistry. The dendrimers and relevant synthons were studied by cyclic voltammetry and differential pulse voltammetry in deoxygenated CH2Cl2 containing background electrolyte to determine the half-wave potentials of each porphyrin in the array. The most easily oxidized porphyrin is MgP  $(E_{\text{OX}} = +0.66 \text{ V vs SCE})$ , closely followed by ZnP  $(E_{\text{OX}} = +0.74 \text{ Vs SCE})$ V vs SCE), and finally by FbP ( $E_{OX}$  = +1.02 V vs SCE). These derived values are in line with earlier work on simpler metalloporphyrins,<sup>65</sup> thereby indicating that the triazole linker does not perturb the electronic properties of the porphyrin. The AuP<sup>+</sup> unit cannot be oxidized within the available electrochemical window imposed by the solvent. This potential gradient creates the driving force by which to move a positive hole formed at the FbP to a ZnP-forming part of the outer periphery in D2(Fb), but this process is thermodynamically uphill for D2(Mg). All of the electrochemical steps are quasi-reversible and highly reproducible. Similar values are observed in N,N-dimethylformamide (DMF) solution.

For D2(Fb), the first reduction wave corresponds to addition of an electron to AuP<sup>+</sup> ( $E_{\text{RED}} = -0.57$  V vs SCE). Again, this situation is fully consistent with earlier work,<sup>66</sup> where it has been concluded that the actual site of reduction is the metal cation and not the porphyrin ring.<sup>67</sup> At higher reductive potentials, the FbP unit is reduced with a characteristic  $E_{\rm RED}$  of -0.89 V vs SCE in CH<sub>2</sub>Cl<sub>2</sub>. Finally, the outermost ZnP units are reduced  $(E_{\text{RED}} = -1.35 \text{ V vs SCE})$ . In examining this system it was noted that whereas the ratio of the intensities of the ZnP oxidation wave and the AuP<sup>+</sup> reduction wave in dendrimer D1 is close to 4:1, the same ratio for dendrimer D2(Fb) is much higher than expected. This effect can be attributed to shielding by the ZnP (and FbP) moieties that prevents close approach of AuP<sup>+</sup> to the working electrode. This phenomenon has been noted before in electrochemical studies with dendrimers<sup>68</sup> and is reminiscent of the situation known to occur in certain redox enzymes where the protein matrix insulates the internal catalytic site and prevents fast electron exchange with the electrode.<sup>69</sup> Similar effects and halfwave potentials were found for D2(Mg), with the MgP unit being the most difficult species to reduce ( $E_{\text{RED}} = -1.42 \text{ V vs SCE}$ ).

Absorption and Fluorescence Spectroscopy. The absorption spectrum recorded for the target dendrimer D2(Fb) in DMF is shown as Figure 1 and contains a rich variety of overlapping



Chart 1. Molecular Formulas and Generic Abbreviations for the Compounds Studied in this Work<sup>a</sup>

<sup>a</sup>S refers to synthon, D refers to dendrimer, and the numeral refers to the level of evolution.

transitions across the visible region. Assignment is made on the basis of the various control compounds, supplemented with the corresponding monomeric porphyrins. The Soret band appears as a strong transition centered at 421 nm but cannot be resolved into individual components. Across the Q-region, the absorption spectrum has the appearance of a linear combination of the individual porphyrin spectra, indicating little ground-state electronic interaction between the pigments. This property is consistent with the saturated linkage used to connect the porphyrins. The presence of AuP<sup>+</sup> is evidenced by the intensification of the absorbance at 550 nm and the presence of a shoulder at 515 nm, which is the consequence of the overlap of its Q-bands, which show peaks at 515 and 550 nm, with those of ZnP, which appear

respectively at 550 and 590 nm. The FbP unit shows absorption bands at 591 and 648 nm, as well as Q-bands obscured by the stronger transitions localized on ZnP. Thus, FbP can be illuminated selectivity at 648 nm, but AuP<sup>+</sup> does not possess a unique absorption spectral feature and cannot be excited with any real degree of selectivity. Because of the large number of ZnP chromophores and their preferential absorption at 550 nm, this pigment can be excited with around 85% selectivity. The absorption spectrum of the magnesium porphyrin (MgP) cannot be distinguished from that of the ZnP such that spectra recorded for S(Mg) or D2(Mg) (see insert to Figure 1) lack the diagnostic information found for D2(Fb). Accordingly, selective excitation of these two porphyrins is not possible. Scheme 1. Synthetic Route to the Key Porphyrin Building Blocks 3 and 6  $^{a}$ 



<sup>*a*</sup> Reagents and conditions: (a)  $Et_2O.BF_3$ ,  $CH_2Cl_2$ , 12 h, r.t. then DDQ, r.t., 1 h, (11%). (b) HAuCl\_4.3H\_2O, NaOAc, acetic acid, 120 °C, 2 h, (40%). (c)  $Et_2O.BF_3$ ,  $CH_2Cl_2$ , 12 h, r.t. then DDQ, r.t., 1 h, (4%). (d) diisopropylethylamine, MgI\_2,  $CH_2Cl_2$ , 60 °C, 3 h, (66%).

The photophysical properties of S(Fb) have been reported earlier<sup>52</sup> and provide clear evidence for rapid energy transfer from ZnP to the central FbP, at both singlet and triplet excited-state levels. The rate constant for singlet energy transfer from ZnP to FbP, as measured by time-resolved fluorescence spectroscopy, is  $4.8 \times 10^9 \text{ s}^{-1}$  and indicates that the probability for energy transfer in this system exceeds 90%. The residual excited-singlet state of ZnP produced upon excitation undergoes intersystem crossing to form the corresponding triplet-excited state.<sup>59</sup> This latter species transfers excitation energy to the attached FbP with a rate constant of  $1.1 \times 10^8$  s<sup>-1</sup>. In contrast, no spectroscopic evidence could be obtained to indicate light-induced electron transfer between the porphyrin units. Consequently, the excitedstate lifetimes of the FbP unit remain comparable to those recorded for the corresponding monomeric porphyrin. Thus, the singlet-excited-state lifetime ( $\tau_{\rm S} = 6.1$  ns) is reduced slightly relative to that of the monomeric reference compound ( $\tau_{\rm S}$  = 6.3 ns) but the corresponding triplet lifetime recorded for the FbP unit present in S(Fb) ( $\tau_{\rm T}$  = 370  $\mu$ s) is somewhat longer than that recorded for the control compound ( $\tau_{\rm T} = 325 \,\mu s$ ).

Energy transfer from ZnP to AuP<sup>+</sup> in the corresponding compound D1(Zn), where AuP<sup>+</sup> replaces FbP, is thermodynamically uphill and unlikely to take place. However, in DMF solution fluorescence from the ZnP unit is quenched by a factor of ca. 12-fold relative to the ZnP reference compound. Timeresolved emission profiles recorded for ZnP fluorescence for D1 in DMF were monoexponential and allowed calculation of  $\tau_s$  as being 175 ps, compared to  $\tau_s = 2.2$  ns for the control. In this case, quenching of the S<sub>1</sub> state localized on the ZnP unit is attributed to electron transfer to the AuP<sup>+</sup>, as was reported for several related molecular dyads comprising ZnP and AuP<sup>+</sup> terminals.<sup>70</sup> There is a significant thermodynamic driving force for this process ( $\Delta G^0 = -0.79$  eV) in D1, and laser flash photolysis studies confirm the transient formation of the relevant charge-shift state (see later). For the corresponding free-base porphyrin analogue, **D1(Fb)**, fluorescence from the peripheral porphyrin is also quenched relative to the isolated reference compound, the decrease being about 3.5-fold in DMF solution. Time-resolved emission spectroscopy indicates that the S<sub>1</sub> lifetime of the FbP module is reduced to ca. 1.4 ns compared to 6.3 ns for the control. Again, fluorescence quenching is attributed to a charge-shift reaction for which the thermodynamic driving force is -0.32 eV.

The photophysical properties recorded for S(Mg) are difficult to interpret because neither porphyrin can be excited with meaningful selectivity, even allowing for the stoichiometry. Indeed, the difference in absorption maxima for the Q-bands of ZnP and MgP in DMF is less than 10 nm. There are marked differences, however, in both fluorescence quantum yield ( $\Phi_{\rm F}$ ) and excited-state lifetime ( $\tau_{\rm S}$ ) recorded for the monomeric MgP and ZnP reference compounds that can be used to follow the course of reaction. Thus, because of the internal heavy-atom effect,<sup>71</sup> fluorescence from ZnP ( $\Phi_{\rm F}$  = 0.033;  $\tau_{\rm S}$  = 2.2 ns) is quenched relative to that from MgP ( $\Phi_F = 0.086$ ;  $\tau_S = 7.7$  ns). Excitation of S(Mg) in DMF at 510 nm gives a time-resolved emission decay profile that is best fit to dual-exponential kinetics, as might be expected, at all monitoring wavelengths. The two lifetimes extracted by global fitting routines are 1.2 and 3.8 ns. This situation requires partial quenching of both excited states in the cluster relative to their respective reference compound. For direct excitation into the ZnP unit, quenching could involve both electron abstraction ( $\Delta G^{\circ} = -0.09 \text{ eV}$ ) from the ground-state MgP and electronic energy transfer. Electron transfer from the excited-singlet state of MgP to a nearby ZnP ( $\Delta G^{\circ} = -0.05 \text{ eV}$ ) is also possible following excitation into MgP, while excitation energy transfer is thermodynamically uphill by a small amount. Tentatively, we assign the shorter lifetime to the ZnP unit, but this could not be proven by experiment. Such behavior is also possible at the triplet level, but again the triplet energies are rather close.<sup>58</sup> This leads to a complex equilibrium mixture of triplet states that interconvert on the sub-microsecond time scale.

Preferential excitation at 550 nm of the ZnP units present in the target dendrimer D2(Fb) leads to weak fluorescence characteristic of the ZnP S<sub>1</sub> state (Figure 2). Time-resolved fluorescence decay profiles recorded at wavelengths where only the ZnP unit emits indicate a lifetime of 160 ps, compared to 190 ps as recorded for S(Fb) under the same conditions. Fluorescence excitation spectra recorded for emission wavelengths where fluorescence from the FbP dominates the profile confirm that photons absorbed by ZnP are transferred in almost quantitative yield to the FbP unit.

Thus, quenching is attributed to rapid electronic energy transfer within the dendrimer, in accordance with the behavior illustrated above for S(Fb). However, the  $S_1$  state localized on the FbP unit is somewhat quenched in the dendrimer compared to the synthon. Thus, the fluorescence lifetimes recorded for the FbP units in D2(Fb) and S(Fb), respectively, are 1.3 and 6.1 ns in DMF solution at ambient temperature (Figure 3). At the same time, the fluorescence quantum yields measured following selective excitation into the FbP unit at 610 nm confirmed that the corresponding  $S_1$  state is quenched by a factor of ca. 5-fold in the dendrimer compared to the synthon. Clearly, the difference between the two compounds can be traced to the presence of the central AuP<sup>+</sup> fragment in D2(Fb). According to the electrochemical results, there is a substantial thermodynamic driving ( $\Delta G^0 = -0.34 \text{ eV}$ ) for electron transfer from the  $S_1$  state resident

Scheme 2. Click Chemistry Reactions for the Preparation of the Dendron D1(Zn) and the Two-Stage Dendrimers<sup>a</sup>



<sup>*a*</sup> Reagents and conditions: (a) CuSO<sub>4</sub> · 5H<sub>2</sub>O, ascorbic acid, DMF, 50 °C, 4 days (75–99%). (b) K<sub>2</sub>CO<sub>3</sub>, MeOH, CH<sub>2</sub>Cl<sub>2</sub>, rt, 2 h (99%). (c) H<sub>3</sub>PO<sub>4</sub>, THF, rt, 1 h (99%).

on the FbP residue to a nearby AuP<sup>+</sup> unit. We will return to this point in the next section.

For dendrimer D2(Mg) in DMF solution, excitation at 560 nm gives rise to rather weak emission that appears consistent with that expected from the ZnP unit, with little contamination from the MgP unit. It must be stressed, however, that the two spectral profiles are quite similar, and consequently it is difficult to be quantitative on this point. More informative are the time-resolved emission profiles recorded after statistical excitation into the ZnP unit. Like the situation found for S(Mg), fluorescence decay curves recorded for D2(Mg) are dual-exponential across the entire wavelength range. The averaged emission lifetimes,

derived by global analysis, are 150 ps and 1.1 ns, with the latter being the more intense at all monitoring wavelengths. These values are to be compared to those derived for the ZnP ( $\tau_S = 1.2 \text{ ns}$ ) and MgP units ( $\tau_S = 3.8 \text{ ns}$ ) present in **S(Mg)**. It is difficult to arrive at a logical interpretation as to why the fluorescence lifetime for the ZnP residue should shorten in the dendrimer, since it is remote from the central AuP<sup>+</sup>, but the MgP is able to undergo light-induced electron transfer ( $\Delta G^\circ = -0.83 \text{ eV}$ ) to the AuP<sup>+</sup> unit. Consequently, we assign the longer lifetime to ZnP and the shorter lifetime to MgP. Clearly, this situation requires that the S<sub>1</sub> state localized on the MgP unit in **D2(Mg)** is heavily involved in electron transfer to the central porphyrin. A similar



Figure 1. Absorption spectrum recorded for D2(Fb) in DMF. The Soret region is shown after dilution of the solution. The insert shows the corresponding Q-band region as recorded for D2(Mg) in DMF.



Figure 2. Fluorescence spectrum recorded for D2(Fb) in DMF at room temperature. The excitation wavelength was 550 nm, and the region corresponding to emission from the ZnP unit is shown as an expansion.

situation arises for the triplet manifold since laser flash photolysis studies made with 25 ns temporal resolution failed to detect any transient species. In contrast, the triplet-state lifetime ( $\tau_T$ ) recorded for the monomeric MgP reference compound in deoxygenated DMF is 290  $\mu$ s. A similar triplet lifetime was found for **S(Mg)** ( $\tau_T = 265 \,\mu$ s), although this cannot be attributed solely to MgP since the triplet states localized on MgP and ZnP are almost isoenergetic. Nonetheless, the triplet-state resident on MgP must be quenched in the dendrimer relative to that for the synthon in deoxygenated DMF at ambient temperature. This effect can be ascribed to electron transfer to the AuP<sup>+</sup>.

We now summarize the various processes occurring in the multicomponent arrays by way of Table 1. The two key fluorescence quenching events relate to electronic energy transfer (EET) and light-induced electron transfer (EIT) within the cluster while the accompanying thermodynamic parameters refer to the energy gap between relevant electronic levels ( $\Delta E_{\rm SS}$ ) or the change in Gibbs free energy ( $\Delta G^{\circ}$ ) associated with electron transfer. The rate constants ( $k_{\rm EET}$  or  $k_{\rm EIT}$ ) are derived from time-resolved emission spectroscopy by comparing fluorescence life-times for a particular chromophore in the cluster with the isolated control compound in DMF, using the same excitation wave-length. In general, the electron-transfer rates reflect the driving force for that process but give no useful information about the



Figure 3. Time-resolved fluorescence profiles recorded for D2(Fb) in DMF solution at room temperature. The instrumental response function is shown as a gray curve superimposed onto the experimental data points: (a) fluorescence from the ZnP unit and (b) fluorescence from the FbP unit.

Table 1. Summary of Main Fluorescence Quenching Events
Deduced from Time-Resolved Emission Spectroscopy for the
Various Clusters in DMF Solution

compd	process	donor	acceptor	$-\Delta G^{\circ a}/\mathrm{eV}$	$k^{b}/(10^{8} \text{ s}^{-1})$
S(Fb)	EET	ZnP*	FbP	0.19	48
S(Mg)	ElT	MgP	ZnP*	0.09	3.8
	ElT	MgP*	ZnP	0.05	2.3
D1(Zn)	ElT	ZnP*	$AuP^+$	0.79	53
D1(Fb)	ElT	FbP*	$AuP^+$	0.32	5.6
D2(Fb)	EET	ZnP*	FbP	0.19	58
	ElT	FbP*	$AuP^+$	0.32	6.1
D2(Mg)	ElT	MgP	ZnP*	0.09	3.8
	ElT	MgP*	$AuP^+$	0.83	65
<sup>a</sup> For EET electron	substitute	$\Delta E_{\rm SS}$ .	$^{b}k_{\rm EET}$ for	energy transfer	and $k_{\rm EIT}$ for

underlying mechanism. The time scales for electron transfer within the various clusters seem to be on the order of some hundreds of picoseconds which means that competing processes need to be fast.

**Transient Absorption Spectroscopy.** Starting first with **D1**-(**Zn**) in deoxygenated DMF, laser flash photolysis studies were carried out with excitation at 532 nm using a 30 ps laser pulse. Immediately after excitation, the transient absorption records show the presence of the S<sub>1</sub> state associated with the ZnP unit. This species possesses a reasonably characteristic spectral signature<sup>72</sup> with strong absorption at around 450 nm and distinctive bleaching signals at longer wavelengths. The S<sub>1</sub> state decays via first-order kinetics with a lifetime of 140 ps, derived from global analysis, leading to increased absorptivity across most of the spectral window and the evolution of a new spectral profile (Figure 4). On the basis of earlier work,<sup>70</sup> this latter transient species can be identified as being the charge-shift state formed as a result of electron transfer from the ZnP S<sub>1</sub> state to the nearby



Figure 4. Transient absorption spectral records showing the reaction profile after selective excitation into the ZnP unit present in D1(Zn) in DMF solution at room temperature. Delay times are as follows: 30, 60, 100, 200, 300, 400, 600, 800 and 1000 ps. The insert shows a typical kinetic trace recorded at 460 nm.

Scheme 3. Representation of the Events That Follow from Selective Excitation of the ZnP Unit Present in D1(Zn)



AuP<sup>+</sup>. The thermodynamic driving force for this process, calculated on the basis of the cyclic voltammetry results, is estimated to be ca. -0.8 eV. It is notable that the rate constant for the forward charge-shift step ( $k_{\rm CSR} = 6.7 \times 10^9 \, {\rm s}^{-1}$ ) derived from the transient absorption studies is in fair agreement with that obtained from time-resolved emission spectroscopy  $(k_{\rm CSR} = 5.3 \times 10^9 \, {\rm s}^{-1})$ . Global analysis applied to the transient absorption spectral records indicates that the charge-shift state decays with a lifetime of ca. 290 ps to restore the ground state, without intermediate population of a triplet species. Indeed, the small amount of ZnP triplet state formed in competition to electron transfer can be seen after decay of the charge-shift state. By necessity, the  $T_1$  state is formed for those conformations that do not favor electron transfer at the S1 level. The lifetime of the  $T_1$  state for D1(Zn) is decreased to only 25 ns, compared to 280  $\mu$ s found for the isolated control compound. Quenching is attributed to intramolecular electron transfer to form the triplet charge-shift state, for which the driving force is ca. -0.28 eV. In this case, decay of the charge-shift state occurs faster than the forward reaction, probably because of an accompanying change in conformation to favor electron transfer. The overall behavior deduced for D1(Zn) is illustrated by way of Scheme 3.

Similar experiments made with compound D1(Fb) in deoxygenated DMF confirmed the presence of the S<sub>1</sub> state localized on FbP at the end of the laser pulse.<sup>72,73</sup> Here, excitation was



**Figure 5.** Transient absorption spectral records showing the reaction profile after selective excitation into the ZnP unit present in **D1(Fb)** in DMF solution at room temperature. Delay times are as follows: 0.05, 0.20, 0.60, 1.0, 2.0, 4.0, and 8.0 ns. The insert shows a typical kinetic trace recorded at 518 nm.

made at 598 nm where only the FbP absorbs. The transient signal decays with a lifetime of 1.1 ns to form the triplet-excited state<sup>73</sup> of the FbP unit in low yield (Figure 5). This latter species is most likely formed by way of intersystem crossing from the S1 state. It decays with a lifetime of 190  $\mu$ s, which is not too dissimilar from that measured for the control compound ( $\tau_{\rm T}$  = 325  $\mu$ s) under identical conditions. Thus, the triplet state does not enter into electron-transfer reactions with the nearby AuP<sup>+</sup>, most likely because of unfavorable thermodynamics ( $\Delta G^{\circ} = +0.12$  eV). Quenching of the S1 state is attributed to the charge-shift reaction, as outlined above on the basis of the time-resolved emission spectroscopy. Since the charge-shift state is not seen clearly in the flash photolysis records, we surmise that charge recombination occurs on a time scale comparable to that of the forward chargeshift reaction. The transient absorption spectral records were closely interrogated at 493 nm, which represents an isosbestic point for the FbP excited singlet and triplet states but where the charge-shift state is expected to show significant absorption. Simulation of the temporal profile collected at this wavelength, on the basis that it evolves with a lifetime of 1.1 ns, suggests the charge-shift state has a lifetime less than 0.7 ns. This can be compared with that derived for the species formed for D1(Zn) under related conditions. Although the charge-shift state associated with D1(Fb) has to dissipate more vibrational energy during the reverse step ( $\Delta G_{\text{CSR}} = -1.59 \text{ eV}$ ) relative to D1(Zn) where  $\Delta G_{\text{CSR}} = -1.31$  eV, it is able to undergo intersystem crossing to the local triplet-state resident on FbP. This latter process might serve to offset the full effects<sup>74</sup> of the Marcus inverted region."

Laser flash photolysis studies made with S(Fb) in deoxygenated DMF confirmed the presence of the S<sub>1</sub> state localized on ZnP at the end of the laser pulse<sup>72</sup> Again, this S<sub>1</sub> state decayed much faster than that of the isolated reference compound ( $\tau_s = 2.2$  ns), with the derived lifetime of 180 ps being in very good agreement with that determined by time-resolved fluorescence spectroscopy ( $\tau_s = 190$  ps). Electron transfer is unlikely in this system because of unfavorable thermodynamics, but energy transfer is a strong possibility and has been introduced already to account for the fluorescence spectral results. This situation was confirmed by transient absorption spectroscopy, as indicated in Figure 6 for S(Fb). Thus, decay of the ZnP S<sub>1</sub> state is matched by



Figure 6. Transient absorption spectral records showing the reaction profile after selective excitation into the ZnP unit present in S(Fb) in DMF solution at room temperature. Delay times are as follows: 0.05, 0.10, 0.20, 0.30, 0.50, 0.75, 3.0, 6.0, and 10.0 ns. The insert shows typical kinetic traces recorded at 508 and 582 nm.



**Figure 7.** Decay trace recorded at 508 nm for the ZnP triplet excited state of **S(Fb)** in DMF. Note that the residual signal is due to the triplet state of the FbP unit.

formation of the S<sub>1</sub> state associated with the FbP unit.<sup>73</sup> This effect is most noticeable by the fast decay process occurring at 508 nm and the concomitant growth of a signal at 582 nm (Figure 6). The efficiency of electronic energy transfer in S(Fb) is around 92%, with the residual S1 state primarily undergoing intersystem crossing to the triplet state. The resultant metastable species also transfers excitation energy to the FbP unit,<sup>27</sup> as indicated by the laser flash photolysis records. In this case, kinetic measurements were made at wavelengths (i.e., 493, 510, 567, and 588 nm) corresponding to isosbestic points between the transient absorption signals recorded for the excited-singlet and triplet states localized on the FbP unit. The transient decay seen under these conditions is due entirely to the ZnP triplet state, which decays with an averaged lifetime of 9 ns (Figure 7). The overall behavior is illustrated by way of Scheme 4. Laser flash photolysis studies carried out with S(Mg) were inconclusive other than to confirm the shortened S<sub>1</sub> lifetimes and the presence of low concentrations of triplet species that decayed on the microsecond time scale.

Attention now turns to the target dendrimer G2(Fb) in DMF solution. The dominant chromophore is the ZnP unit, which can be illuminated with modest selectivity at 560 nm. Under such conditions, weak fluorescence is observed in the region expected for ZnP, but the quantum yield is reduced to only 0.003 while the

Scheme 4. Representation of the Events That Follow from Selective Excitation of the ZnP Unit Present in S(Fb)



emission lifetime is decreased to 175 ps. On the basis of the work described above, fluorescence quenching can be attributed to electronic energy transfer to an FbP fragment within the dendrimer. Although EET is highly efficient in this system, fluorescence from the FbP is also quenched; in this case, quenching is due to light-induced electron transfer to a nearby AuP<sup>+</sup>. Indeed, the emission lifetime for the FbP unit in D2(Fb) is reduced to 0.85 ns compared to 6.1 ns found for S(Fb). In this case, the timeresolved fluorescence decay profile does not fit particularly well to a single-exponential step and is better described in terms of dual-exponential kinetics. This behavior most likely is a reflection of hindered mobility of the FbP unit in the second-level dendrimer. Now, the best fit to the decay curves has lifetimes of 0.60 ns (70%) and 1.05 ns (30%), which are taken to represent two different families of conformers. Apart from this effect, the general situation found for D2(Fb) closely resembles that described for the lower level dendrimer D1(Fb). A marked difference, however, is that there is a pronounced fall in the yield of the excited-triplet state of FbP in the larger dendrimer as seen on relatively slow time scales. There is, in addition, a further transient species that cannot be resolved for D1(Fb) under the same conditions, and this species possesses the characteristic spectral features of the charge-shift state.38

Detailed analysis of the transient absorption spectral records obtained for D2(Fb) in DMF indicates that the charge-shift state evolves on sub-nanosecond time scales but does not decay within a 10 ns temporal window. On much longer time scales (Figure 8), it is seen that the charge-shift state coexists with the tripletexcited state of the FbP unit and survives for some tens of microseconds. Indeed, global analysis protocols indicate that the charge-shift state possesses a lifetime of ca.  $60 \,\mu s$  in DMF at room temperature. It is most likely that this charge-shift state forms by way of hole transfer from the FbP  $\pi$ -radical cation, this being part of the primary charge-shift state, to a nearby ZnP. There is a modest thermodynamic driving force for this process ( $\Delta G^{\circ} = -0.28 \text{ eV}$ ). The transient absorption spectra are fully consistent with this hypothesis in that the profile derived for the long-lived charge-shift state clearly bears the characteristic signature of the ZnP  $\pi$ -radical cation (see Supporting Information). Thus, transient differential absorption spectra were compiled for the charge-shift states formed between ZnP/AuP<sup>+</sup> and FbP/AuP<sup>+</sup> on the basis of the individual spectra obtained by spectroelectrochemistry. These spectra are similar but differ in the region where the Q-bands of the porphyrins are bleached. The net result is that the charge-shift spectrum involving the FbP shows pronounced bleaching at ca. 660 nm whereas that formed from the ZnP has its principal bleaching region centered at ca. 560 nm. The charge-shift state derived for D2(Fb) after subtraction of the contribution due to the FbP triplet-excited



**Figure 8.** Transient absorption spectral records showing the reaction profile after selective excitation into the ZnP unit present in **D2**(Fb) in deoxygenated DMF solution at room temperature. Delay times are as follows: 0.01, 10, 20, 40, 60, 100, 150, and 250  $\mu$ s. The insert shows a typical kinetic trace recorded at 503 nm, which is an isosbestic point for the triplet state of the FbP unit.

Scheme 5. Representation of the Events That Follow from Selective Excitation of the ZnP Unit Present in D2(Fb)



state agrees well with the latter spectrum but not the former (see Supporting Information).

Within experimental limits, decay of the charge-shift state follows first-order kinetics and is independent of the concentration of D2(Fb) and of laser intensity. The quantum yield, being much less than unity, can be estimated as follows: The  $S_1$  state associated with the FbP fragment is populated with 93% probability by way of EET from the ZnP chromophore. Light-induced charge shift with the central AuP<sup>+</sup> unit accounts for some 85% of this S<sub>1</sub> state, the remainder decaying by way of fluorescence and intersystem crossing to the T<sub>1</sub> state. For the isolated FbP control compound, the T<sub>1</sub> state is formed with a quantum yield of 0.70 and we assume that the same relative probability holds for the dendrimer. There is a further crop of the T1 state because of triplet-triplet energy transfer from the ZnP. Thus, the overall quantum yield for formation of the FbP T<sub>1</sub> state in the dendrimer is ca. 15%. The molar absorption coefficient of this species is  $6500 \text{ M}^{-1} \text{ cm}^{-1}$  at 780 nm. On the basis of spectro-electrochemical measurements made with D1(Zn), the molar absorption coefficients of the ZnP  $\pi$ -radical cation and the AuP neutral radical respectively are 7100 and 5800  $M^{-1}$  cm<sup>-1</sup> at 493 nm, where the FbP triplet does not contribute to the transient signal. From the relative absorbance values for the two species we reach the

conclusion that the secondary charge-shift state is formed with a quantum yield of ca. 20%. The overall behavior is summarized in Scheme 5.

The long-lived charge-shift state is not observed for D2(Mg), where any electron-transfer chemistry is complete within a few nanoseconds of excitation. Here, it is not possible to selectively excite either ZnP or MgP units; in principle the AuP<sup>+</sup> unit could be selectively illuminated at 525 nm, but there is too much competitive absorption by the ZnP, this being in large excess, to make such studies viable. The photophysical properties differ from those mentioned for S(Mg) and are difficult to interpret in detail because of competitive light absorption and multiple quenching pathways. In this case, the system does not facilitate hole transfer to spatially isolate the redox pair and serves to emphasize the importance of setting up a suitable redox gradient within the dendrimer.

## CONCLUSIONS

The new porphyrin-based building blocks described herein provide straightforward access to the first series of heterometallic, multiporphyrin dendrimers by making use of the so-called click chemistry. The approach is exemplified by the synthesis of a three-layer dendrimer comprising 17 porphyrin modules arranged in a rational sequence. A key strength of the synthetic protocol relates to the mild deprotection of the TMS group in synthon 6 followed by the copper-catalyzed Huisgen cycloaddition with the azido porphyrin, which is almost quantitative. A second advantage of this strategy concerns the opportunity to modify the sequence of porphyrin-based modules within the assembly, which is an important feature by which to control the directionality of energy or electron transfer. In this study, we have reported on the first and second dendrimer generations, but it seems reasonable to anticipate that the iterative reactions of dendron 10 with any metal porphyrin 5 would provide access to higher generations. Dendrimers made to date are readily soluble in DMF and show no signs of aggregation of individual porphyrins. According to the photophysical measurements, these dendrimers demonstrate energy- and electron-transfer reactions with relatively high yield that are of potential interest for solar energy conversion.

The best performance is provided by D2(Fb) where highly efficient EET is followed by successive electron-transfer steps that lead to long-lived, charge-separated species in modest yield. The limitation of this system is set by the relatively slow chargeshift reaction in which the FbP donates an electron to the nearby AuP<sup>+</sup> fragment. Subsequent hole transfer to a peripheral ZnP unit struggles to compete with primary charge recombination, although the resultant secondary charge-shift state survives for ca. 60  $\mu$ s in DMF at room temperature. It is difficult to see how to increase the overall efficiency of this basic design since the system represents a critical balance of competing events, each of which is subjected to thermodynamic control. Perhaps a different approach is warranted. Thus, the synthetic strategy is easily modified to enable the replacement of the interior FbP layer with one formed from tin(IV) porphyrins (SnP). Illumination of the outermost ZnP modules should lead to light-induced electron transfer to one of the SnP units.<sup>76</sup> The resultant SnP  $\pi$ -radical anion<sup>77</sup> is able to reduce the central AuP<sup>+</sup>, leading to the same secondary charge-shift state as characterized for D2(Fb). Preliminary investigations made with S(Sn), where the corresponding  $Sn^{1V}P$ replaces the FbP in S(Fb), confirm that the first step occurs with

high efficiency, although it is not possible to selectively illuminate ZnP. There is now a modest driving force for reduction of  $AuP^+$ , which might be competitive with charge recombination. An advantage of this sequence is that the ZnP triplet state is also capable of reducing SnP so few photons are lost. Likewise, any photons absorbed directly by SnP will be used to drive the same electron-transfer reaction.

# ASSOCIATED CONTENT

**Supporting Information.** Text giving experimental details for the synthesis of all new compounds and for making the photophysical measurements and figures showing comparative differential spectra for the two charge-shift states associated with D2(Fb). This material is available free of charge via the Internet at http://pubs.acs.org.

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