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Photoinduced Electron Transfer within Porphyrin-Containing Poly(amide) Dendrimers

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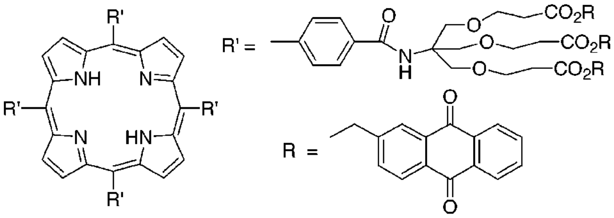
ABSTRACT



The synthesis and photophysical characterization of a series of free base porphyrin-containing polyamide dendrimers terminated with anthraquinone groups (FbP-Ga-AQ$_n$, $a = 1$–3, $n = 12$, 36, 108) are described. Substantial quenching (58–75%) of the porphyrin fluorescence of FbP-Ga-AQ$_n$ is observed when compared to the analogous ethyl-terminated dendrimers (FbP-Ga-Et$_n$) in steady-state fluorescence experiments and is attributed to intramolecular electron transfer. Time-resolved fluorescence experiments were fit to 2–3 exponentials, indicating multiple orientations for electron transfer, consistent with the flexible nature of these dendrimers.

Photosynthesis has evolved over time to promote a series of ultrafast photoinduced electron transfers from an electronically excited “special pair” of chlorophylls to a quinone.[1] Replicating the results of this process using synthetically derived photosynthetic mimics is important from the joint perspectives of understanding the factors that influence photosynthesis[2−8] and for potential use as alternative fuel sources.[9] Thus, one of the primary goals of such research is to separate electronic charges for durations such that the resulting chemical potential can be utilized, for example, to drive solar energy cells. Research in this area has ranged from molecules containing electron-donor and electron-

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[1] For recent reviews of the events occurring in the photosynthetic reaction center, see: (a) Rüttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1−24. (b) Yachandra, V. K.; Sauer, K.; Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927−2950. (c) Arnett, D. C.; Moser, C. C.; Dutton, P. L.; Scherer, N. F. *J. Phys. Chem. B* **1999**, *103*, 2014−2032.

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acceptor units connected by rigid[4,5] or flexible[8] bridging groups to multicomponent arrays,[7] supramolecular assemblies,[10] and polymers[11] that contain more than two electron-donor and electron-acceptor groups.

The chemistry of dendrimers has expanded exponentially in recent years[12] and is driven in part by the desire to utilize the inherent structural properties of these unique macromolecules. Dendrimers have recently been shown[13] to be amenable for mediating vectorial energy transfer in a manner reminiscent of the light-harvesting complex in photosynthesis.[14] Irradiation of appropriate energy donor units positioned on the dendrimer periphery resulted in Förster transfer[15] of the excitation energy to energy-accepting core units. Because of the large absorption cross section of the energy donor groups at the termini in these dendrimers, such donor–acceptor arrangements are ideal for light-harvesting purposes. A similar arrangement of donor–acceptor groups to initiate photoinduced electron transfer (ET), however, is *not* ideal for mimicking the charge-separating steps in the photosynthetic reaction center. Such an approach, consisting of a dendrimer with terminal porphyrin donors and an electron-accepting core, is inherently flawed due to the likely rapid dissipation of excitation energy resulting from energy transfer among terminal donor groups or collisional deactivation of the terminal excited state donors, both processes of which are energy-wasting. A more ideal approach places the electron-donor group in the core and the electron-acceptor groups at the terminal positions. We have used this rationale to synthesize and examine the photophysical properties of dendrimers containing porphyrin cores and terminal quinone groups.[16] Herein, we describe the synthesis and preliminary photophysical studies of a series of flexible, Newkome-style[17] dendrimers (Figure 1, **FbP-Ga-AQ$_n$**, $a = 1-3$, $n = 12, 36, 108$), containing free base tetraphenylporphyrin cores and anthraquinone (AQ) terminal groups. These dendrimers are designed to undergo ET from the photoexcited porphyrin core to the anthraquinone moieties at the dendrimer terminus.

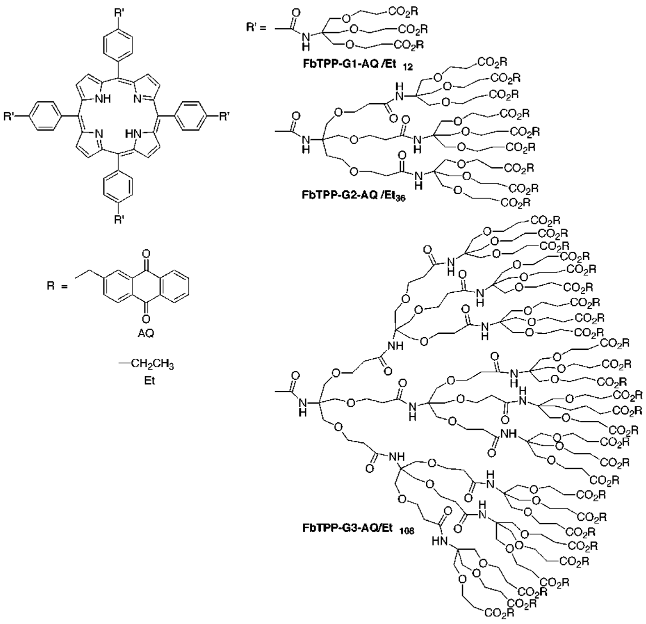

Figure 1. Dendrimers **FbP-Ga-Et$_n$** and **FbP-Ga-AQ$_n$**.

Dendrimers **FbP-Ga-AQ$_n$** were synthesized by a mixed convergent/divergent route.[16,18] The yields of the individual steps in each reaction were generally high (i.e., 70–85%), although overall yields of pure dendrimers[18] ranged from 7 to 16% depending upon generation number. Dendrimers **FbP-Ga-AQ$_n$** (and the analogous ethyl-terminated dendrimers, **FbP-Ga-Et$_n$**) are soluble in $CHCl_3$, CH_2Cl_2, dimethylacetamide (DMAc), and DMSO and are moderately soluble in THF. Absorption spectra (Table 1) of dendrimers **FbP-Ga-Et$_n$** exhibit a slight red-shift in their absorption bands relative to tetraphenylporphyrin (TPP). Similar red-shifts in porphyrin-containing Newkome[19] and Fréchet[13,20] dendrimers have been attributed to an increase of electron density at the porphyrin resulting from back-folding of the dendrimer arms. Replacement of the ethyl groups with AQ groups (**FbP-Ga-AQ$_n$**) results in a more pronounced red-shift that increases with generation number (Table 1). The increased red-shift in **FbP-Ga-AQ$_n$** relative to **FbP-Ga-Et$_n$** is presumably due to $\pi-\pi$ interactions between the anthraquinone groups and the porphyrin core. Importantly, these red-shifts indicate that

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Table 1. Summary of Photophysical Data for Dendrimers **FbP-Ga-AQ*n*** and **FbP-Ga-Et*n***

dendrimer	solvent	Soret (nm)	Q-band (nm)[a]	emission maxima (nm)	τ_1[b] (ns)	τ_2[b] (ns)	τ_3[b] (ns)	k_{ET}[b] (s^{-1})	Φ_{AQ}/Φ_{Et}[c]	τ_{AQ}/τ_{Et}[d]
TPP	$CHCl_3$	419	645	651 715	9.25					
FbP-G1-Et$_{12}$	$CHCl_3$	420	647	651 717	9.13					
FbP-G2-Et$_{36}$	$CHCl_3$	421	647	651 717	9.65					
FbP-G3-Et$_{108}$	$CHCl_3$	421	647	651 718	9.79					
FbP-G1-AQ$_{12}$	$CHCl_3$	424	650	655 719	3.99 (43%)	2.28 (54%)	0.46 (3%)	2.28×10^8	0.24	0.32
FbP-G2-AQ$_{36}$	$CHCl_3$	427	653	656 723	4.21 (70%)	2.11 (28%)	0.39 (2%)	1.78×10^8	0.27	0.37
FbP-G3-AQ$_{108}$	$CHCl_3$	429	655	657 724	6.75 (82%)	2.12 (15%)	0.48 (3%)	6.83×10^7	0.42	0.60
TPP	DMAc	417	646	650 715	12.2					
FbP-G1-Et$_{12}$	DMAc	419	647	650 717	12.1					
FbP-G2-Et$_{36}$	DMAc	420	647	650 718	11.9					
FbP-G3-Et$_{108}$	DMAc	420	647	651 718	11.8					
FbP-G1-AQ$_{12}$	DMAc	422	649	653 718	4.72 (89%)	1.75 (10%)	0.019 (1%)	1.46×10^8	0.30	0.36
FbP-G2-AQ$_{36}$	DMAc	426	653	656 721	5.40 (78%)	2.17 (21%)	0.034 (1%)	1.30×10^8	0.25	0.39
FbP-G3-AQ$_{108}$	DMAc	428	654	657 723	9.17 (81%)	3.96 (17%)	0.59 (1%)	3.86×10^7	0.38	0.69

[a] Only the position of the longest wavelength Q-band is reported. [b] See ref 18. [c] Relative to the fluorescence of the corresponding ethyl-terminated dendrimer, **FbP-Ga-Et*n***. Quantum yields were calculated using standard methods. [d] Ratio of lifetimes, where τ_{AQ} is the measured fluorescence lifetime of the appropriate anthraquinone-terminated dendrimer and τ_{Et} is the measured fluorescence lifetime of the analogous ethyl-terminated dendrimer.

dendrimers **FbP-Ga-AQ*n*** are flexible enough to allow the porphyrin and quinone groups to become spatially close to one another.

Steady-state fluorescence measurements indicate substantial quenching of the porphyrin fluorescence in AQ-terminated dendrimers, compared to both TPP and dendrimers **FbP-Ga-Et*n*** (Figure 2, Table 1). Because the only difference between **FbP-Ga-AQ*n*** and **FbP-Ga-Et*n*** is the presence of the terminal AQ groups, fluorescence quenching in **FbP-Ga-AQ*n*** can be attributed to ET from the porphyrin core to the terminal AQ groups.[21] Steady-state fluorescence measurements at a variety of dendrimer concentrations[18] indicate that inter-dendrimer electron transfer is not responsible for the fluorescence quenching, and fluorescence quenching thus occurs via intramolecular ET. The fluorescence quantum yields (Table 1) indicate efficient quenching at *all* generations, with the most efficient quenching occurring at generations one and two.

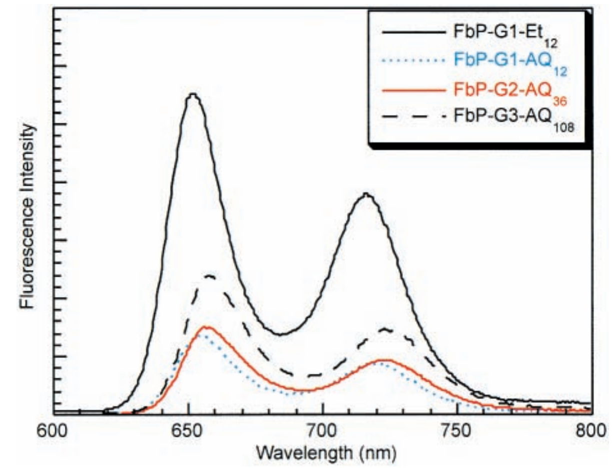

Figure 2. Steady-state fluorescence spectra of **FbP-G1-Et$_{12}$** and **FbP−Ga-AQ*n*** ($a = 1-3$, $n = 12, 36, 108$) in $CHCl_3$.

Time-correlated single-photon counting (TCSPC) measurements[18] indicate fluorescence lifetimes of ~9 and 12 ns for **FbP-Ga-Et*n*** in $CHCl_3$ and DMAc, respectively. These values are only slightly sensitive to generation number. TCSPC measurements on **FbP-Ga-AQ*n*** reveal much shorter decays that were best fit (i.e., $\chi^2 < 1.15$) using a three-component global analysis (Table 1). The time-resolved measurements are generally consistent with the fluorescence quantum yield results (Table 1, Φ_{AQ}/Φ_{Et} vs τ_{AQ}/τ_{Et}). Experimental rate constants for ET (k_{ET}) were determined[18] (Table 1) and indicate k_{ET} is more rapid for **FbP-G1-AQ$_{12}$** and **FbP-G2-AQ$_{36}$** than **FbP-G3-AQ$_{108}$**.

Preliminary Monte Carlo stochastic dynamics (MCSD) calculations[16] in the gas phase and in $CHCl_3$ indicate that the branches in **FbP-Ga-AQ*n*** are quite flexible. A large percentage of these conformations showed one to two branches with short porphyrin−AQ distances (i.e., 3−8 Å), consistent with calculations on other flexible dendrimers.[22] Marcus theory[23] requires k_{ET} to decrease exponentially with both donor−acceptor coupling strength and distance. The

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(21) The lowest energy singlet excited state of AQ is 2.94 eV (Zalesskaya, G. A.; Blinov, S. I. *Sov. Phys. Dokl.* **1985**, *30*, 297−299), substantially higher than that of **FbP-Ga-AQ*n*** (1.90 eV), ruling out energy transfer as the process responsible for fluorescence quenching.

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rate constants for **FbP-G1-AQ$_{12}$** and **FbP-G2-AQ$_{36}$** are 2.28 × 10^8 and 1.78 × 10^8 s^{-1}, respectively, while the porphyrin−AQ through-bond distance increases from ∼16 to ∼26 Å.[24] Such a large increase in distance should result in a much larger decrease in k_{ET} than is observed if a through-bond ET mechanism is operative. In addition, ET proceeding through saturated bonds, over a distance of ∼16 Å (the porphyrin−AQ edge-to-edge distance measured for **FbP-G1-AQ$_{12}$**), is expected to result in much slower values for k_{ET} than we have observed. Considering the flexible nature of **FbP-Ga-AQ$_n$** and the large number of conformers having short porphyrin−anthraquinone distances, we therefore conclude ET occurs efficiently by a through-space mechanism. We have obtained similar results for zinc porphyrin analogues of **FbP-Ga-AQ$_n$** (i.e., **ZnP-Ga-AQ$_n$**). These zinc porphyrin dendrimers have a free energy for electron transfer ($\Delta G_{ET} = -0.28$ eV) that is approximately 0.4 eV more exothermic than that of **FbP-Ga-AQ$_n$**. These results will be reported in due course.[16]

In conclusion, we have synthesized a series of flexibly linked, porphyrin-containing anthraquinone terminated dendrimers, **FbP-Ga-AQ$_n$**, that undergo rapid through-space photoinduced electron transfer. A through-bond mechanism was discounted because k_{ET} did not scale with the increase in generation number. Picosecond transient absorption and pump−probe experiments are currently in progress and will be reported in due course together with the molecular dynamics calculations.

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Supporting Information Available: Full synthetic details for the synthesis of dendrimers **FbP-Ga-Et$_n$** and **FbP-Ga-AQ$_n$**, as well as photophysical measurement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] MacSpartan 4.0, Wavefunction, Inc.; 18401 Von Karman Ave., #370. Irvine, CA 92715.