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Light-Harvesting Chromophores with Metalated Porphyrin Cores for Tuned Photosensitization of Singlet Oxygen via Two-Photon Excited FRET

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Utilization of two-photon (TP) excited fluorescence resonance energy transfer (FRET) within a light-harvesting dendrimer has proven to be a reliable method for the enhancement of the effective TP absorption efficiency of many FRET acceptor molecules. This light-harvesting approach has enabled TP photosensitization of singlet oxygen from a porphyrin in both aqueous and organic media using wavelengths more transmissive to human body tissue (750−1000 nm). This ability to utilize near-infrared irradiation to induce photochemical reactions is especially attractive for applications including in vivo photochemistry, oxygen sensing, and photodynamic cancer therapy. In efforts to further the applicability of this concept, we synthesized an array of novel photosensitizers by metalation of the porphyrin core with aluminum, silver, and zinc. Time-resolved fluorescence, transient absorption measurements, and TP excitation experiments demonstrated efficient TP excited FRET to produce the porphyrin excited state triplet which subsequently generates singlet oxygen by the aluminum and zinc metalated species. Singlet oxygen photosensitization efficiency was found to be most efficient using aluminum followed by zinc and least efficient using silver. In fact, silver metalated photosensitizers were found to be nonfluorescent and incapable of generating a measurable amount of singlet oxygen. With the proper choice of inserted metals, it was possible to tune the efficiency of TP induced singlet oxygen production.

Introduction

The phenomenon of two-photon absorption (TPA) permits the excitation of chromophores with enhanced spatial selectivity, which is especially attractive for applications requiring near-infrared wavelengths at which biological media are transmissive and safe from photochemical damage.[1] Systems that utilize TPA to trigger desirable photochemical and photophysical processes are of great interest for in vivo photochemistry,[2] bioimaging,[3−5] oxygen sensing,[6] and phototherapies.[7−10] Unfortunately, chromophores traditionally used for these applications have low TPA efficiencies, making it too inefficient to be of practical use. For example, porphyrins and other tetrapyrrolic macrocycles are commonly used in photodynamic therapy (PDT) for cancer treatments because of their ability to efficiently generate singlet oxygen and their tendency to preferentially accumulate in tumor tissue but have a low TPA efficiency.[11] Improving the TPA efficiency of these photosensitizers, without changing their other desirable properties, could broaden the use of PDT to subcutaneous tumors and allow treatment to be precisely guided at the focal point of a laser beam.

Two major approaches to improving the TPA efficiencies of porphyrins have recently emerged. One notable approach

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(1) Fisher, W. G.; Partridge, W. P.; Dees, C.; Wachter, E. A. *Photochem. Photobiol.* **1997**, *66*, 141−155.
(2) Prasad, P. N. *Introduction to Biophotonics*; John Wiley & Sons: New York, 2003.
(3) Piston, D. W. *PLoS Biol.* **2005**, *3*, 960−962.
(4) Theer, P.; Hasan, M. T.; Denk, W. *Opt. Lett.* **2003**, *28*, 1022−1024.
(5) Bharali, D. J.; Lucey, D. W.; Jayakumar, H.; Pudavar, H. E.; Prasad, P. N. *J. Am. Chem. Soc.* **2005**, *127*, 11364−11371.
(6) Brinas, R. P.; Troxler, T.; Hochstrasser, R. M.; Vinogradov, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 11851−11862.
(7) Oar, M. A.; Serin, J. A.; Dichtel, W. R.; Fréchet, J. M. J.; Ohulchanskyy, T. Y.; Prasad, P. N. *Chem. Mater.* **2005**, *17*, 2267−2275.
(8) Dichtel, W. R.; Serin, J. M.; Edder, C.; Fréchet, J. M. J.; Matuszewski, M.; Tan, L. S.; Ohulchanskyy, T. Y.; Prasad, P. N. *J. Am. Chem. Soc.* **2004**, *126*, 5380−5381.
(9) Frederiksen, P. K.; McIlroy, S. P.; Nielsen, C. B.; Nikolajsen, L.; Skovsen, E.; Jorgensen, M.; Mikkelsen, K. V.; Ogilby, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 255−269.
(10) Karotki, A.; Kruk, M.; Drobizhev, M.; Rebane, A.; Nickel, E.; Spangler, C. W. *IEEE J. Sel. Top. Quantum Electron.* **2001**, *7*, 971−975.
(11) Kruk, M.; Karotki, A.; Drobizhev, M.; Kuzmitsky, V.; Gael, V.; Rebane, A. *J. Lumin.* **2003**, *105*, 45−55.

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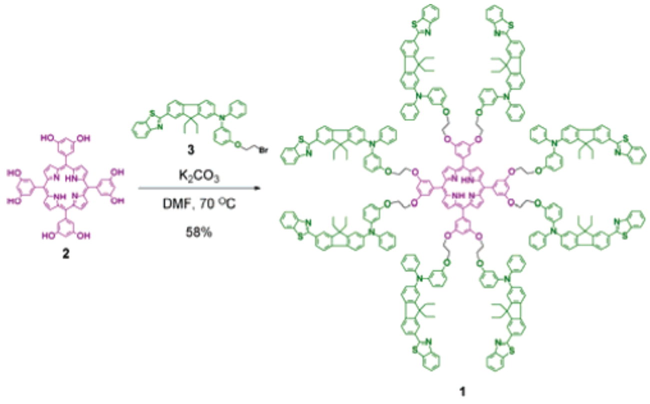
involves forming various π-conjugated butadiyne-linked porphyrin dimers, which has thus far produced systems with high TPA efficiency.[12−15] Another study with a meso-substituted porphyrin demonstrated a lesser increase in the TPA cross section and adequate singlet oxygen generation.[9] We recently reported an alternative approach,[7,8] in which an unmodified porphyrin chromophore is incorporated into a light-harvesting dendrimer[16,17] containing donor two-photon absorbing chromophores (TPACs) capable of efficient TPA and subsequent energy transfer to the porphyrin. Thus, the unmodified porphyrin retains its desirable photophysical properties, and the donor chromophores act as a TPA "antenna", funneling excited-state energy to the photosensitizer. This light-harvesting approach has enabled the demonstration of two-photon (TP) excited fluorescence resonance energy transfer (FRET) for enhanced production of singlet oxygen in both aqueous[7] and organic[8] media and has also shown promise for use in oxygen sensing applications.[6]

The proposed photophysical pathway for TP generation of singlet oxygen within our light-harvesting chromophore (**1**) occurs via TPA by the peripheral donor chromophores, FRET to the porphyrin, followed by intersystem crossing to the porphyrin triplet and sensitization of molecular oxygen to produce excited-state singlet oxygen.[7] Described herein are experiments confirming that light-harvesting chromophores enhance production of singlet oxygen under TPA conditions, as well as steady-state and time-resolved photophysical measurements that support the proposed energy transfer mechanism.[17] It is known that metalation strongly affects the photophysical properties of porphyrins;[18−20] therefore, various metalated derivatives were prepared and tested to tune singlet oxygen generation efficiencies of the porphyrins under TPA conditions.

Results and Discussion

Synthesis of Free-Base and Metalated Photosensitizers. The free-base porphyrin (**1**, Scheme 1), containing eight AF-343 donor TPACs,[21] was synthesized from tetrakis(3′,5′-dihydroxyphenyl)porphyrin[22,23] **2** and a TP absorbing AF-343 derivative **3**[21] in a dimethylformamide (DMF) solution with K_2CO_3. Complete functionalization of the porphyrin was

Scheme 1. Synthesis of the Free-Base Photosensitizer



confirmed using NMR and matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS).

For each metal, both a TPAC-functionalized and a TPAC-free photosensitizer were prepared to test their relative abilities for TP excited FRET and production of singlet oxygen. The metalated derivatives were formed using free-base (H_2) porphyrin photosensitizers **1** and tetrakis(3′,5′-dimethoxyphenyl)porphyrin[22,23] **4** as synthetic precursors (Scheme 2). The aluminum(III) complexes with an axial chloride ligand (**5** and **6**) were prepared by treating dichloromethane solutions of each porphyrin with diethyl aluminum chloride.[24] The zinc(II) complexes **7** and **8** were prepared by refluxing the porphyrins with zinc acetate in a 3:1 mixture of chloroform and methanol. The silver complexes were prepared by heating the porphyrins in chloroform with an excess of Ag(I) trifluoroacetate; the resulting disproportionation reaction yielded the Ag(II) porphyrin species (**9** and **10**) and silver metal. The yield of each metalation reaction was essentially quantitative, and the porphyrins were purified by extraction and/or passing the crude product through a short silica gel plug.

Steady-State Photophysical Characterization. Preparative thin-layer chromatography (TLC) purification of the chromophores was performed prior to photophysical measurements to ensure their purity. The steady-state absorption spectrum of **1** contains the characteristic peaks of the AF-343 donor **3** at 308 and 390 nm as well as the porphyrin Soret (or B) band at 421 nm and the Q bands between 500 and 670 nm (Figure 1). The spectrum is quite similar to the sum of the absorption spectra of the component chromophores (eight TPACs and one porphyrin), indicating the presence of all of the chromophores and the absence of any significant ground-state interactions.

A pronounced change in photophysical properties occurred upon insertion of each metal into the porphyrin core. The ground-state absorbance data for the porphyrin chromophores **6**, **8**, and **10** were overlaid with that of chromophore **4** (Figure 2B), which can be compared to the overlaid spectra of **1**, **5**, **7**, and **9** (Figure 2A). The characteristic coalescence and shift of the Q-bands upon metalation is also shown in the inset of Figure 2. It is interesting to note that the intensities of

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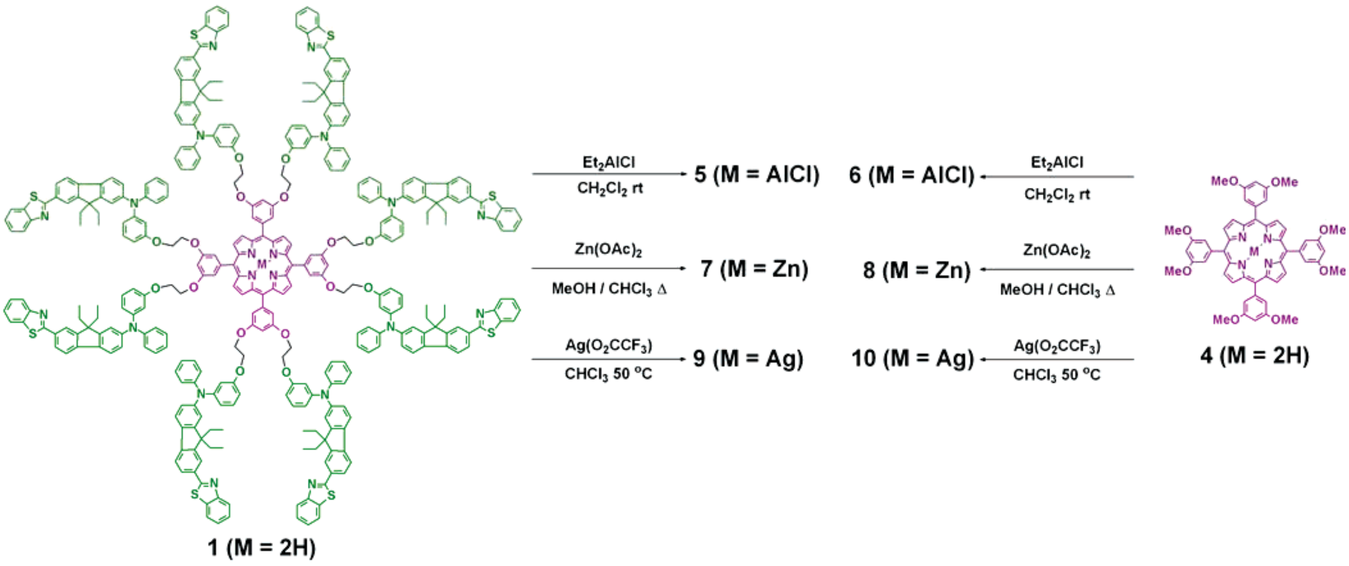
(12) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **2004**, *126*, 15352−15353.
(13) Karotki, A.; Drobizhev, M.; Dzenis, Y.; Taylor, P. N.; Anderson, H. L.; Rebane, A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 7−10.
(14) Ogawa, K.; Ohashi, A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Phys. Chem. B* **2005**, *109*, 22003−22012.
(15) Ogawa, K.; Ohashi, A.; Kobuke, Y.; Kamada, K.; Ohta, K. *J. Am. Chem. Soc.* **2003**, *125*, 13356−13357.
(16) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701−1710.
(17) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175−1185.
(18) Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1978−1985.
(19) Harriman, A. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1281−1291.
(20) Kalyanasundram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.
(21) Tan, L.-S.; Kannan, R.; Matuszewski, M. J.; Khur, I. J.; Feld, W. A.; Dang, T. D.; Dombroskie, A. G.; Vaia, R. A.; Clarson, S. J.; He, G. S.; Lin, T.-C.; Prasad, P. N. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *4797*, 171−178.
(22) James, D. A.; Arnold, D. P.; Parsons, P. G. *Photochem. Photobiol.* **1994**, *59*, 441−447.
(23) Gonsalves, A. M. A. R.; Varejao, J. M. T. B.; Pereira, M. M. *J. Heterocycl. Chem.* **1991**, *28*, 635−640.
(24) Sigman, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 5315−5316.

Scheme 2. Synthesis of the Metalated Photosensitizers



the peaks at roughly 395 nm and the Soret band at 420 nm vary, depending on the metal. The quantified absorbance data are given in Table 1 for the B-band and the Q-band maxima.

FRET between the AF-343 donor and the porphyrin acceptor was confirmed using fluorescence measurements of **1**, **3**, and **4** (Figure 3). Emission of **3** at 492 nm is observed upon excitation at 385 nm. This donor emission exhibits spectral overlap with the porphyrin Q bands (Figure 2), which is required for efficient FRET. Excitation of **1** at the same wavelength shows quenched donor emission and enhanced porphyrin acceptor emission with a 97% calculated energy transfer efficiency.[8]

Upon confirmation that the AF-343 (**3**) chromophore is capable of efficient energy transfer to the porphyrin under one-photon conditions, the corresponding experiments were performed using TP excitation at 780 nm using a femtosecond mode locked Ti:sapphire laser (Tsunami, Spectra-Physics) as the excitation source. Deuterated solvents were used for these experiments to facilitate comparison with oxygen luminescence studies (vide infra), which benefit from the enhanced lifetime of singlet oxygen in deuterated media. Excitation of **1** at 780 nm produced emission predominantly from the porphyrin, which was 17 times more intense than the emission from **4** under identical conditions (Figure 3B). This value is in line with literature data.[25,26] Thus, TP excited FRET was demonstrated to enhance production of porphyrin excited states using near-infrared irradiation.

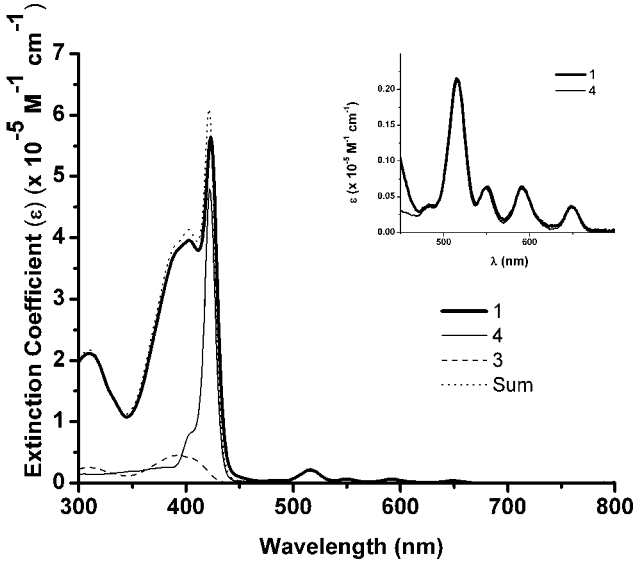


Figure 1. Quantified steady-state absorption spectra of **1**, **3**, and **4** in benzene at room temperature. The sum of the parts (eight TPACs plus one porphyrin) is also shown as a dotted line and overlays well with **1**. The inset highlights the Q-band region in more detail.

Fluorescence spectra of the Al−Cl, Zn, and Ag porphyrins obtained by directly exciting the porphyrin chromophore confirmed that the presence of the donor chromophores have little effect on the porphyrins' fluorescence quantum yields (Figure 4A). TP induced fluorescence spectra for each metalated complex bear similarity to the free-base system **1** (Figure 4B). For each metalated photosensitizer, a negligible amount of residual AF-343 emission is observed, suggesting efficient FRET to the porphyrin acceptor for the Al−Cl and Zn compounds (**5** and **7**, respectively). For the nonfluorescent Ag(II) complex **9**, it is unclear whether the AF-343 quenching mechanism is via FRET or electron transfer.[27] Quantified fluorescence data for the free-base and metalated chromophores are given in Table 2.

To confirm that the emission observed from **1** under 800 nm laser irradiation was indeed arising from a TPA process, the relative emission intensities of **1** and **3** were plotted over

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(25) Brousmiche, D. W.; Serin, J. M.; Fréchet, J. M. J.; He, G. S.; Lin, T. C.; Chung, S. J.; Prasad, P. N.; Kannan, R.; Tan, L. S. *J. Phys. Chem. B* **2004**, *108*, 8592−8600.

(26) Zheng, Q. D.; He, G. S.; Prasad, P. N. *Chem. Mater.* **2005**, *17*, 6004−6011.

(27) It should be noted that Ag(II) is formally a d^9 system in contrast to the close-shell d^0 and d^{10} configurations for Al(III)Cl and Zn(II). In general, the photophysical properties of metallophorphyrins with a d^0 or d^{10} metal ion are determined largely by the π electrons of the porphyrin ring, with small perturbation effects from the metal ion. On the contrary, when the central metal ion has partially filled d orbitals, the interactions of the d electrons with the π and π^* ortbitals of the porphyrin can lead to shorter-lived excited states and very low triplet-state quantum yields. Kubat, P.; Mosinger, J. *J. Photochem. Photobiol., A* **1996**, *96*, 93−97.

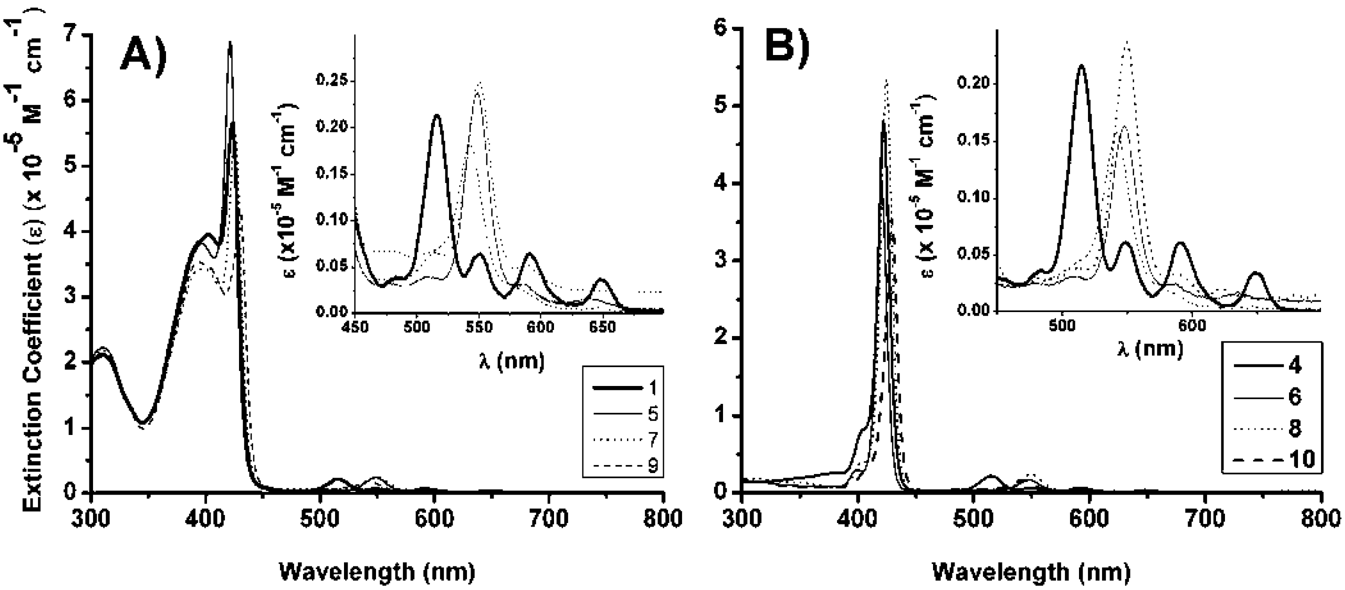

Figure 2. (A) Quantified ground-state absorption spectra of **1**, **5**, **7**, and **9**. (B) Quantified ground-state absorption spectra of **4**, **6**, **8**, and **10**. All data measured in air-saturated benzene. Insets: Expansion of the Q-band region.

Table 1. Ground State Absorbance Data Summarized (Benzene)

	B_{max} (nm)	ϵ ($\times 10^{-5}$ M^{-1} cm^{-1})	Q_{max} (nm)	ϵ ($\times 10^{-5}$ M^{-1} cm^{-1})
1	423	5.63	516	0.214
4	422	4.80	515	0.216
5	421	6.90	548	0.236
6	420	4.01	548	0.163
7	426	5.51	550	0.250
8	425	5.34	549	0.237
9	430	4.34	542	0.182
10	429	3.54	541	0.158

a range of laser powers (Figure 5). The quadratic dependence on laser power observed for both molecules is characteristic of TPA and supports the hypothesis that porphyrin excited states arise from TPA of the AF-343 donor chromophores, followed by efficient FRET.

Time-Resolved Fluorescence and Transient Absorption Characterization. To further confirm energy transfer from the TPA antennae to the central porphyrin, time-resolved fluorescence and transient absorption experiments were conducted. Time-resolved fluorescence measurements examine fluorescence growth and decay profiles at different wavelengths and can provide evidence of interrelated processes such as energy transfer. Reported in Table 2 and Figure 6 are the emission decay profiles of **1** in air-saturated benzene at 441 and 655 nm. A 400 nm excitation source was used, which predominately excites the AF-343 (**3**) portion of the molecule. The data were fitted using a reconvolution method of the instrument response function (IRF) producing χ^2 fitting values of 1−1.5. The emission at 441 nm, corresponding to TPAC emission, exhibits a sharp decay followed by a long-lived decay. Porphyrin emission at 655 nm exhibits a very short growth followed by a long-lived decay. The components of the growth and decay are outside the measurement range of the instrument (approximately 50 ps) and, therefore, are faster than our ability to measure. We assume that these fast components are due to energy transfer from the TPA chromophores to the porphyrin core. Thus, the emission at 441 nm yields biexponential lifetimes of <50 ps (τ_{S1}) and 1.47 ns (τ_{S2}), and the emission at 655 nm has a lifetime of 9.47 ns (τ_{S3}). These lifetimes closely match those observed for the TPAC **3** (1.61 ns)[28] and porphyrin **4** (8.97 ns).

The emission producing τ_{S2} is likely due to unquenched donor chromophores arising from less than 100% efficient FRET and a small amount of uncoupled TPAC **3** impurity (as observed by mass spectrometry). When time-resolved fluorescence data are used, the calculated FRET efficiency for **1** is >97% (see the experimental section for calculations). Less than quantitative FRET efficiency may result from imperfect spectral overlap and improper dipole conformations achieved through the flexible linker. The donor has a large fluorescence quantum yield, and thus emission from a small amount of unquenched donors may be expected. Although a fully selective excitation of the TPA moieties of **1** was not achieved, these data strongly support the occurrence of an energy transfer process.

Identical time-resolved fluorescence measurements were also performed on the metalated derivatives (Figure 7, Table 2). For **5** and **7** the initial fluorescence decay at 450 nm was outside the measurement range of our instrument and calculated to be approximately 50 ps, again indicating the occurrence of a fast energy transfer process with a τ_{S1} of less than 50 ps. For **9**, the initial decay at 450 nm was found to be 245 ps, indicating that energy transfer to the porphyrin is not as efficient for this compound. The calculated FRET efficiencies for **5** and **7** were >97% and for **9** was 85% (see experimental section for calculations). For all materials the long decay at 450 nm was approximately 1.5 ns, which compares well with compound **3** (1.61 ns) in air-saturated benzene. In the 650 nm region, the fluorescence lifetimes were also biexponential, with fast growth (<50 ps) followed by long decay for **5** and **7**. We did not observe any emission in the 650 nm region for compound **9**, which was expected, based on its low emission intensity in the steady-state

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(28) This value was measured using techniques reported in the experimental section of this publication for a nearly identical chromophore AF-240.[21]

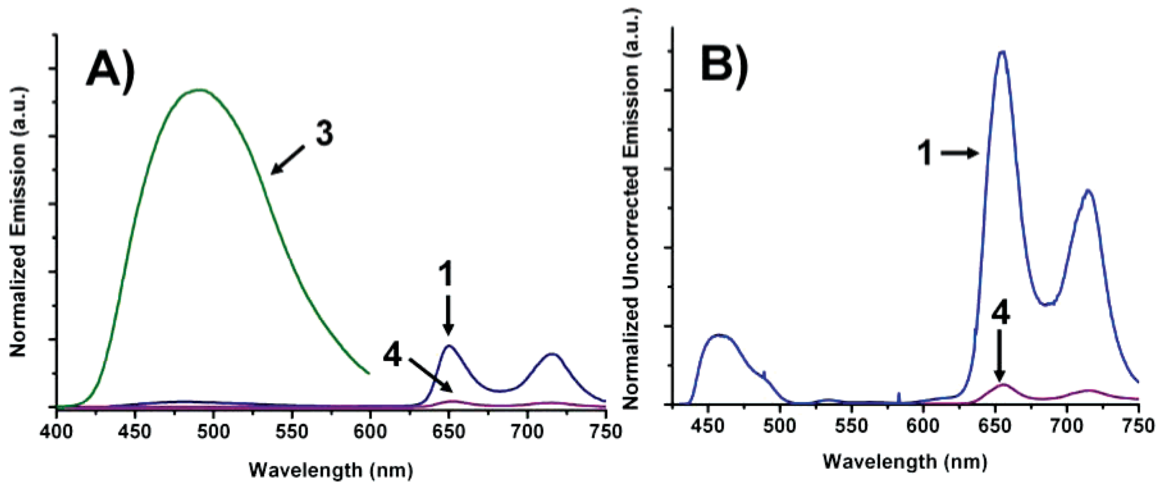

Figure 3. (A) Fluorescence spectra of **1**, **3**, and **4** in chloroform at room temperature under single-photon excitation ($\lambda_{ex} = 385$ nm) conditions normalized to the absorption spectra (Figure 2). Efficient FRET is demonstrated by quenched donor emission and enhanced porphyrin emission. (B) Normalized fluorescence spectra of **1** and **4** in benzene-d_6 upon TP excitation ($\lambda_{ex} = 780$ nm). The 17-fold enhancement in emission from **1** relative to **4** is due to FRET from the AF-343 donors excited via TPA.

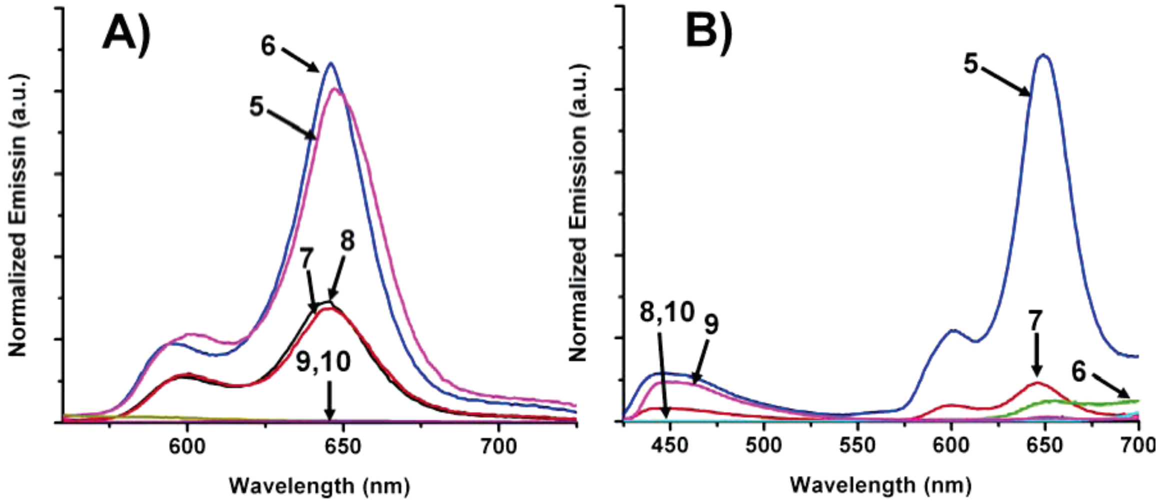

Figure 4. (A) Single-photon fluorescence spectra of the Al−Cl, Zn, and Ag derivatives, excited at their respective Q-band maxima and normalized to absorption intensity at that wavelength. The presence of the donor chromophores has little effect on the fluorescence quantum yields. (B) TP fluorescence spectra of the same complexes. For the Al−Cl and Zn complexes, the expected emission from the porphyrin is observed. AF-343 emission is quenched in the Ag complexes, but the nonfluorescent nature of the Ag complexes precludes drawing further conclusions about FRET in these systems.

Table 2. Summarized Fluorescence Maxima (Fl$_{max}$) and Fluorescence Lifetimes in Benzene for the Short-Lived (τ_{S1}) and Longer-Lived (τ_{S2}) Emission from the TPAC in Addition to Porphyrin Lifetimes (τ_{S3})

	Fl$_{max}$ (nm)	T_{S1} (ps)	T_{S2} (ns)	Fl$_{max}$ (nm)	T_{S3} (ns)
1	442	<50	1.47	655	9.47
4				655	8.97
5	446	<50	1.82	646	4.80
6				647	5.40
7	438	<50	1.42	647	1.61
8				647	1.61
9	441	245	1.49		
10					

measurements. The long decaying lifetimes were single exponential and varied depending on the metal. For **5** and **7**, the measured decays were 4.80 ns and 1.61 ns, respectively. These values correspond very well with those for **6** and **8**, which were 5.4 ns and 1.61 ns, respectively. The biexponential kinetics confirm that very efficient energy transfer also occurs in the metalated systems and that the porphyrin's fluorescence decay kinetics are strongly dependent on the embedded metal.

The time-resolved fluorescence data demonstrate that the singlet excited state of the TPA chromophore is quenched. To further confirm an energy transfer mechanism and resulting triplet production, nanosecond transient absorption measurements using laser flash photolysis were performed. Laser flash photolysis is a technique used to measure the triplet excited-state absorption ($T_1 - T_n$) that gives both spectral and kinetic information. Shown in Figure 8 are the overlaid transient absorption spectra of **1** and **4** in deoxygenated benzene upon excitation at 355 nm. The spectra are nearly identical, indicating only the formation of the porphyrin triplet state within the nanosecond laser pulse. If electron transfer were responsible for quenching of the donor fluorescence, the transients shown in Figure 8 would not be identical; this represents further evidence that efficient energy transfer is occurring in this system. The triplet decay lifetimes measured for **1** and **4** were 966 μs and 252 μs, respectively (Table 3). It is not clear why the triplet lifetime of the porphyrin in **1** is so much longer than that found for porphyrin **4**. It is possible that partial encapsulation of the

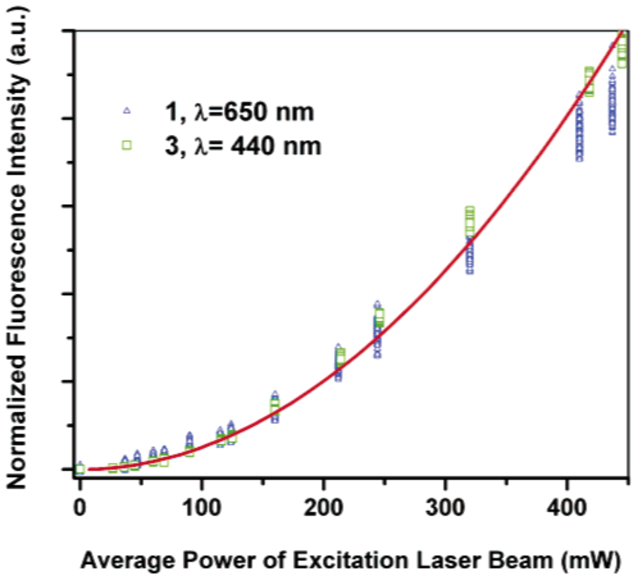

Figure 5. Normalized fluorescence intensity upon excitation of **1** (emission at 650 nm) and **3** (emission at 440 nm) at 780 nm in benzene-d_6 as a function of laser powers. The red line represents a least-squares fit of the data with a quadratic function ($y = ax^2$, where $a = 5.04 \times 10^{-6}$). The quadratic dependence observed for both **1** and **3** is indicative of a TPA process and is further evidence for efficient FRET in **1**.

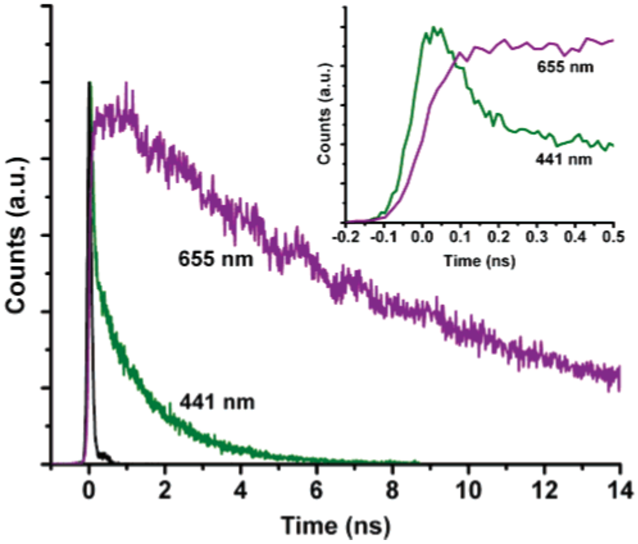

Figure 6. Time-resolved emission data of **1** in air-saturated benzene upon excitation at 400 nm with a 70 ps pulse. The IRF is shown above as the unlabeled trace. Inset: Magnification of the fast growth and decay region. The IRF trace is omitted for clarity.

porphyrin by the TPAC groups contributes to reduce triplet−triplet annihilation,[29−32] which is known to quench the triplet excited state. Observation of a transient absorption under TP excitation conditions proved to be beyond the sensitivity of the instrument.

Last, we looked at the nanosecond transient absorption of **5**, **6**, **7**, and **8** in deoxygenated benzene (Figure 8). For **5** and **7** the transient produced is undoubtedly due to the porphyrin and not the TPAC portion of the molecule, thus confirming effective energy transfer to the porphyrin. Triplet extinction coefficients and triplet quantum yields were also measured for **4**, **6**, and **8** (Table 3). Discrepancies between our values for **4** and those previously reported[33] may be due to errors in our singlet depletion method. We did not observe any transient absorption for **9** and **10** under the same conditions. Literature precedent has shown that Ag *meso*-tetraphenylporphyrin has a very short-lived triplet excited state that can only be observed on picosecond or shorter time scales.[34] This may be why we do not observe any triplet formation on the 50 ns limit of our experiment for compounds **9** and **10**. Fast intersystem crossing would also account for the low fluorescence intensities observed for **9** and **10** (vide supra).

Singlet Oxygen Generation. The efficiency of singlet oxygen generation of **1** upon TPA was evaluated by measuring its characteristic emission at 1270 nm.[7] Direct excitation of the porphyrin in **1** and **4** with a 532 nm laser gave singlet oxygen emission signals of comparable intensity (Figure 9A). The slightly higher intensity for **1** may be related to its longer triplet lifetime (Table 3). Upon switching the excitation source to a 780 nm laser, air-saturated benzene-d_6 solutions of **1** showed a measurable luminescence signal, whereas no detectable singlet oxygen emission was observed from solutions of **4** under the same conditions (Figure 9B).

Single-photon induced singlet oxygen emission from the metalated complexes indicate that the Al−Cl and Zn complexes are capable of efficiently generating singlet oxygen (Figure 10). However, the Ag complexes, in addition to being nonfluorescent, are also poor singlet oxygen generators. This result is not surprising because transient absorption measurements demonstrated that the Ag-metalated photosensitizer (**9**) produced no observable triplet excited states. If the triplet excited state of **9** is short-lived as suggested above, then second-order processes such as singlet oxygen generation are not expected to be efficient.

Singlet oxygen luminescence measurements were then performed on the metalated complexes under TPA conditions (Figure 11). The Al−Cl (**5**) and Zn (**7**) metalated complexes gave luminescence signals that outperformed their TPAC-free counterparts (**6** and **8**), which produced no measurable oxygen luminescence signals. As expected, the Ag metalated species (**9** and **10**) provided no measurable singlet oxygen emission signal upon TP excitation. For the metalloporphyrins, it should be noted that the trend in triplet quantum yield values is reflected in singlet oxygen luminescence intensities. This can be expected, assuming that these materials are quenched similarly by oxygen to produce singlet oxygen. At this time we have not measured the quantum yield for singlet oxygen production.

These results are direct evidence that the AF-343 donor chromophores significantly enhance singlet oxygen production of the porphyrin upon irradiation at 780 nm. In addition,

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(29) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74−91.

(30) Matos, M. S.; Hofkens, J.; Verheijen, W.; De Schryver, F. C.; Hecht, S.; Pollak, K. W.; Fréchet, J. M. J.; Forier, B.; Dehaen, W. *Macromolecules* **2000**, *33*, 2967−2973.

(31) Jin, R. H.; Aida, T.; Inoue, S. *J Chem. Soc., Chem. Commun.* **1993**, 1260−1262.

(32) Vinogradov, S. A.; Lo, L. W.; Wilson, D. F. *Chem.*−*Eur. J.* **1999**, *5*, 1338−1347.

(33) Katona, Z.; Grofcsik, A.; Baranyai, P.; Bitter, I.; Grabner, G.; Kubinyi, M.; Vidoczy, T. *J. Mol. Struct.* **1998**, *450*, 41−45.

(34) Chirvonyi, V. S.; Dzhagarov, B. M.; Timinskii, Y. V.; Gurinovich, G. P. *Chem. Phys. Lett.* **1980**, *70*, 79−83.

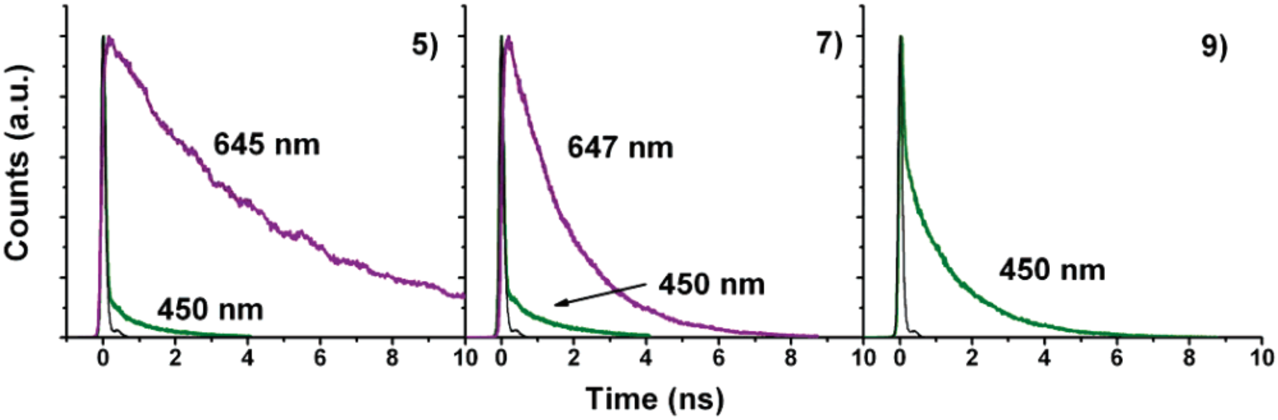

Figure 7. Time-resolved fluorescence decay of **5**, **7**, and **9** in air-saturated benzene. Data at 450 nm represents emission from the TPA antennae, and data in the 650 nm region are from the porphyrin. Samples were excited at 400 nm with a 70 ps pulse. The IRF is shown above as the unlabeled trace.

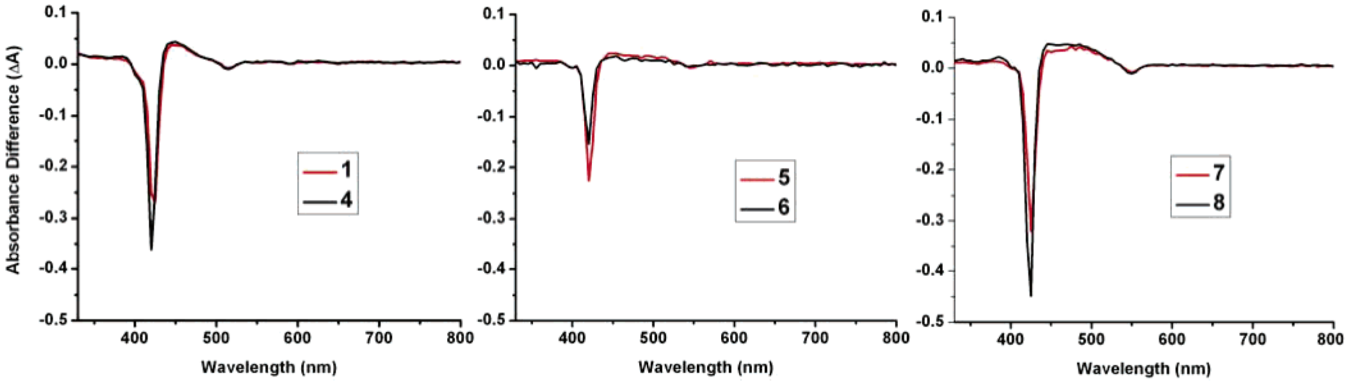

Figure 8. Transient absorption spectra of **1**, **4**, **5**, **6**, **7**, and **8** in deoxygenated benzene. The spectra were recorded immediately following irradiation of the sample with a 5 ns laser pulse (355 nm).

Table 3. Summarized Transient Triplet Absorbance ($T_1 - T_{n\max}$), Triplet Extinction Coefficient (ϵ_T), Triplet Lifetimes (τ_T), and Intersystem Crossing Quantum Efficiency (Φ_T)

	$T_1 - T_{n\max}$ (nm)	ϵ_T (M^{-1} cm^{-1})	τ_T (μs)	Φ_T
1	450		966	
4	450	53 800 ± 5400	252	0.66 ± 0.07
5	460		480	
6	460	45 100 ± 4500	384	0.92 ± 0.09
7	475		826	
8	476	49 400 ± 4900	251	0.87 ± 0.09
9				
10				

porphyrin photophysical properties are strongly dependent on the embedded metal. Overall, these data validate the proposed function and design of this light-harvesting chromophore for effectively enhancing TPA efficiency through FRET from a suitable donor.

Chemical Oxidation. The ability of **1** to generate singlet oxygen under TPA conditions was also evaluated by a chemical trapping method. 2,5-Dimethylfuran was chosen as a substrate because its reaction kinetics with singlet oxygen is zero order with respect to the furan over the concentration range used in the experiment and because it cleanly undergoes a [4 + 2] cycloaddition reaction to give an ozonide, which dimerizes to give a peroxide product as a single diastereomer (Figure 12).[35] Thus, the observed rate of product formation is a direct measure of the rate of singlet oxygen generation. Under TPA conditions, solutions containing **1** showed a threefold enhancement in reactivity relative to **4**. It is important to note that we believe this to be the minimum enhancement of reactivity between **1** and **4**. The low conversions observed for oxidations using **4** are subject to standard NMR integration errors and could be artificially high because of even small amounts of exposure to ambient light during the experiment. In addition, **4** may be capable of weak TPA;[36] therefore, small amounts of singlet oxygen that were undetectable using emission detection may become detectable via their participation in chemical oxidation. Despite these limitations, this experiment confirms that the AF-343 donor chromophores significantly increase the singlet oxygen generating ability of **1** under TPA conditions.

Conclusions and Outlook

Metalated and free-base porphyrin photosensitizers capable of TP excited FRET have been synthesized. The reported steady-state and time-resolved photophysical measurements give evidence of large transition moments, high donor fluorescence quantum efficiency, high acceptor extinction coefficient values, and good orbital overlap between donor emission and acceptor absorption. These are criteria that support a Coulombic energy transfer (FRET) mechanism.[17] This TP donor enhancement resulted in amplified singlet oxygen production, as evidenced by luminescence spectroscopy and chemical oxidation experiments. Differential meta-

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(35) Gollnick, K.; Griesbeck, A. *Tetrahedron* **1985**, *41*, 2057−2068.

(36) Drobizhev, M.; Karotki, A.; Kruk, M.; Rebane, A. *Chem. Phys. Lett.* **2002**, *355*, 175−182.

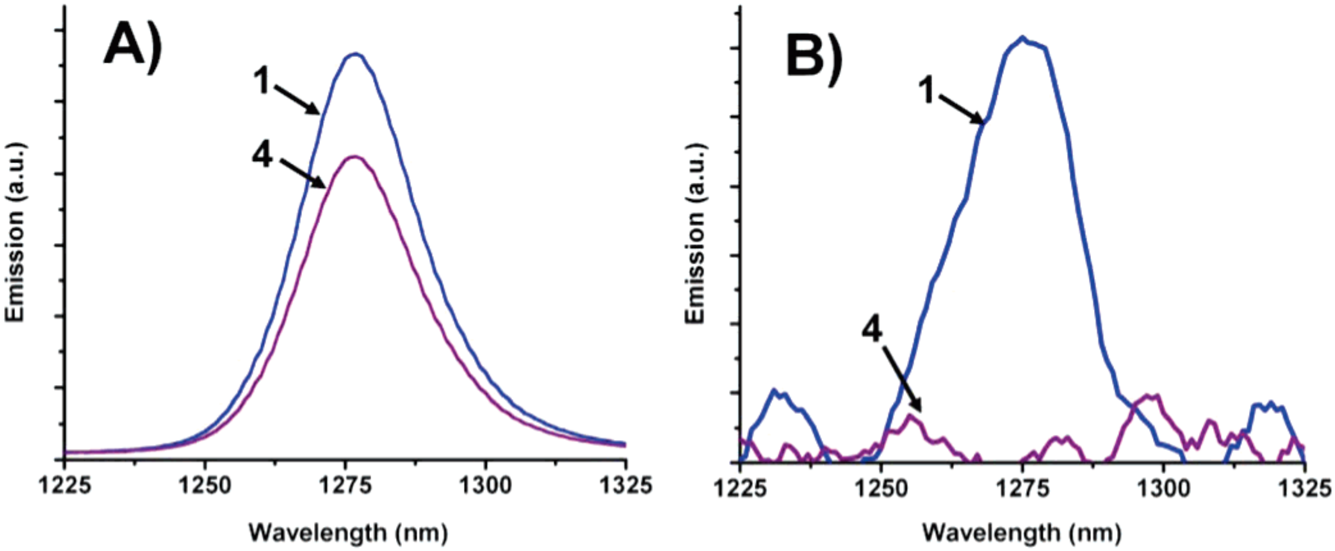

Figure 9. (A) Singlet oxygen emission spectra obtained from isoabsorbing oxygen-saturated benzene-d_6 solutions of **1** and **4** directly excited at the Q bands with a 532 nm laser. (B) Singlet oxygen emission spectra obtained from isoabsorbing, oxygen-saturated solutions of **1** and **4** in benzene-d_6 irradiated with a 780 nm laser. Oxygen luminescence is observed from the solution containing **1**, but the photosensitizer that lacked TPACs (**4**) produced no measurable oxygen emission signal. Baseline correction and Savitsky−Golay smoothing were applied to each spectrum.

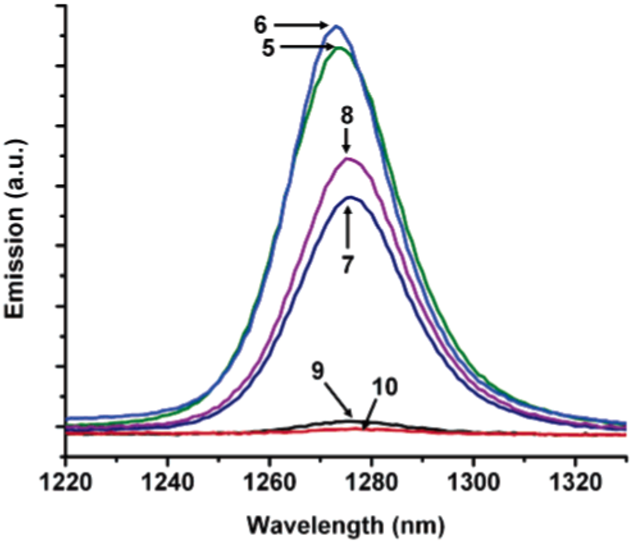

Figure 10. Singlet oxygen emission spectra obtained from isoabsorbing oxygen saturated benzene-d_6 solutions of the Al−Cl (**5** and **6**), Zn (**7** and **8**), and Ag (**9** and **10**) derivatives directly excited at the Q bands with a 532 nm laser.

lation of the porphyrin strongly influenced the quantum yields of the triplet excited states and thus directly affected the overall efficiency of singlet oxygen production. Transient absorption measurements of the Al−Cl, Zn, and Ag metalated derivatives showed triplet-state production only for the Al−Cl and Zn species. For the metalated porphyrins, an increased triplet quantum yield resulted in enhanced singlet oxygen production, as evidenced by increased singlet oxygen emission intensities.

Overall we have demonstrated that FRET can be used to enhance the efficiency of singlet oxygen production under TPA conditions. Furthermore, we have shown that singlet oxygen quantum yields can be readily tuned for metalated and free-base porphyrin photosensitizers. The utilization of TPA to trigger photochemical events may broaden the applicability and enhance the precision of many photochemical applications. Future work in our laboratories will include testing these metalated porphyrins for PDT and other applications that benefit from the features of TPA.

Experimental Section

General Techniques. The solvents used for absorbance and luminescence measurements were spectroscopic grade. Ground-state UV/vis absorption spectra were measured on either a Cary 50 UV−vis spectrometer or a Cary 500 spectrophotometer. Emission and excitation spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to a 2 nm band-pass on both excitation and emission monochromators. Samples for absorbance and emission experiments were measured in standard 1 cm quartz cells. All measurements were performed at room temperature. Time correlated single photon counting (Edinburgh Instruments OB 920 spectrometer) was utilized to determine singlet state lifetimes. The sample was pumped using a 70-ps laser diode at 401 nm. Emission was detected on a cooled microchannel plate photomultiplier tube. Data were analyzed using a reconvolution software package provided by Edinburgh Instruments. Nanosecond transient absorption measurements were carried out using the third harmonic (355-nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 8 mJ cm^{-2} at the excitation wavelength were typically used. A detailed description of the laser flash photolysis apparatus has been published earlier.[37] The molar absorption coefficients of the porphyrin triplet states were determined using the method of singlet depletion, which has been described previously.[37] Quantum yields for intersystem crossing were determined using the method of relative actinometry utilizing a ZnTPP in benzene actinometer ($\Phi T = 0.88$).[38] Matched optical densities of the porphyrins and ZnTPP at 355 nm were utilized in each determination.

TP excitation at 780 nm was performed using a Ti−sapphire laser (Spectra-Physics-Tsunami) pumped by a frequency-doubled

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(37) Rogers, J. E.; Cooper, T. M.; Fleitz, P. A.; Glass, D. J.; Mclean, D. G. *J. Phys. Chem. A* **2002**, *106*, 10108−10115.

(38) Lee, W. A.; Gratzel, M.; Kalyanasundaram, K. *Chem. Phys. Lett.* **1984**, *107*, 308−313.

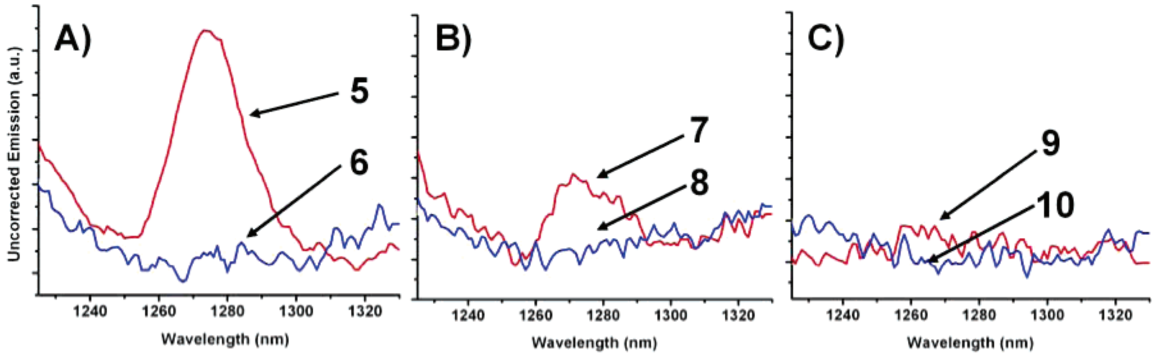

Figure 11. Singlet oxygen emission spectra obtained from isoabsorbing oxygen-saturated solutions in benzene-d_6 irradiated with a 780 nm laser. Baseline correction and Savitsky−Golay smoothing have been applied to each spectrum.

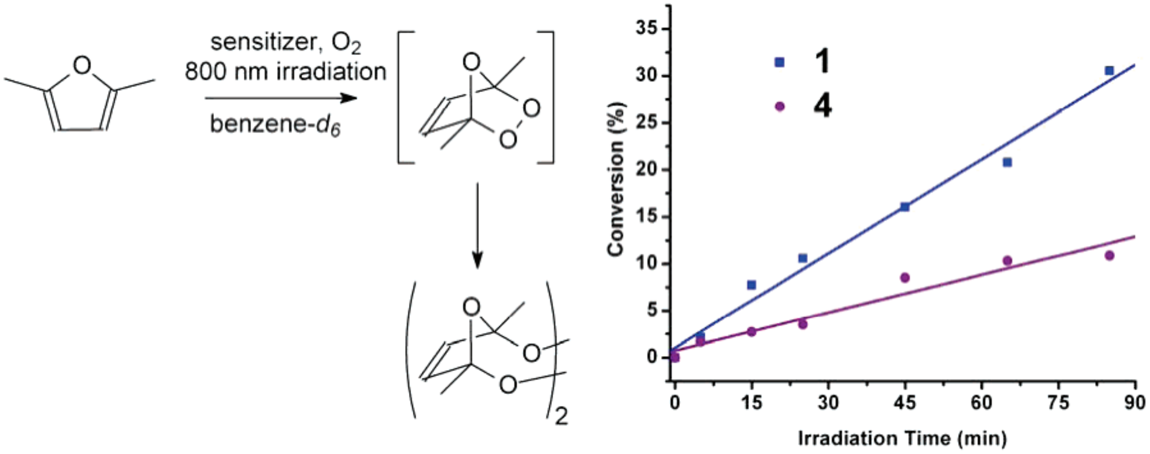

Figure 12. Photooxidation of 2,5-dimethylfuran in oxygen saturated benzene-d_6 solutions containing **1** or **4** as sensitizers using an 800 nm laser as the excitation source. The percent conversion was determined using NMR spectroscopy.

diode pumped solid-state laser (Spectra-Physics-Millennia). It provided 90 fs pulses at an 82 MHz repetition rate with an average power of 1.3 W. For single-photon fluorescence measurements, the Q-band optical density was kept below 0.l (2×10^{-7} M), and the samples were bubbled with N_2 for 5 min before measurement. TP fluorescence measurements were obtained at Q-band optical densities of 0.9 (1.7×10^{-6} M porphyrin concentration). Oxygen luminescence experiments were performed in solutions of benzene-d_6 using a 10^{-4} M sensitizer concentration.

Unless otherwise noted, all reagents were used as received and without further purification or were prepared according to literature procedures. Tetrahydrofuran (THF) and toluene were distilled under N_2 from sodium/benzophenone immediately prior to use. Acetonitrile was distilled under N_2 from CaH_2 immediately prior to use. Potassium carbonate was ground and stored in an oven (120 °C) prior to use. Chromatography was carried out with Merck silica gel for flash columns, 230−400 mesh, and preparative TLC was conducted on 1000 μm Whatman plates. Unless otherwise specified, extracts were dried over $MgSO_4$ and solvents were removed with a rotary evaporator at aspirator pressure. NMR spectra were measured in $CDCl_3$ with tetramethylsilane or solvent signals as the standards. High-resolution mass spectra (HRMS) were obtained with a Micromass LCT using electrospray ionization and Micromass ProSpec using fast atom bombardment (FAB). MALDI-TOF MS was performed on a PerSeptive Biosystems Voyager-DE, using *trans*-3-indoleacrylic acid as the matrix. The staff at University of California−Berkeley Analytical Facility performed elemental analyses.

Photooxidation of 2,5-dimethylfuran[35] was accomplished through 800 nm excitation using the aforementioned Ti−sapphire laser. Solutions of **1** and **4** (12.0 mg, 2.3×10^{-6} mol, and 1.85 mg, 2.2×10^{-6} mol, respectively), 2,5-dimethylfuran (7.45 μL, 6.73 mmol), 3.2 mL of benzene-d_6, and 16 μL of DMF were made in two separate NMR tubes. Upon saturation with oxygen, the solutions were irradiated, and the photooxidation progress was monitored using NMR spectroscopy.

Calculations of FRET efficiencies using the time correlated single photon counting data were done as follows.

$$^{1}\text{AF-343}^{*} \xrightarrow{k_d} \text{AF-343} \tag{1}$$

$$^{1}\text{AF-343}^{*} + \text{P} \xrightarrow{k_q} \text{AF-343} + {}^{1}\text{P}^{*} \tag{2}$$

$$k_{obs} = k_d + k_q[\text{P}] \tag{3}$$

$$f_q = (k_{obs} - k_d)/k_{obs} \tag{4}$$

For **1**, **5**, and **7** the efficiency of quenching was calculated to be >97%, but in the case of **9** it was only 85%. These values were calculated using the eqs 1−4. Equation 3 was simplified by making an assumption that the concentration of porphyrin (P) is not changed by porphyrin quenching, also known as a pseudo-first-order equation. In eq 4, the overall fraction quenched (f_q) was determined by measuring the change in the observed rate relative to that inherent in AF-343. First, the rate of quenching (k_q) was set to $1/\tau_{S1}$, which was $>2 \times 10^{10}$ M^{-1} s^{-1} for **1**, **5**, and **7** but for **9** was only 4.1×10^{9} M^{-1} s^{-1}. Finally, the value for k_d was set to $1/\tau_{S1}$ for the AF-343 (**3**), which was 6.2×10^{8} s^{-1} (1.61 ns). Theoretical FRET studies have been previously performed with analogous light harvesting systems.[17,39]

Preparation of Tetrakis(3′,5′-di(AF-343)phenyl)porphyrin (1). AF-343[21] (300 mg, 465 μmol), tetrakis(3′,5′-dihydroxyphenyl)-

porphyrin[22,23] (35 mg, 47 μmol), K_2CO_3 (100 mg, 719 μmol), and 18-crown-6 (12 mg, 45 μmol) were dissolved in 4 mL of dry DMF and stirred under argon at 70 °C for 4 days. The reaction was cooled to room temperature, and the mixture was poured in a separatory funnel containing 50 mL of CH_2Cl_2 and washed with water (100 mL) twice and brine (100 mL). The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The residue was taken up in a minimum amount of $CHCl_3$ and precipitated into 200 mL of 8:2 hexanes/ethyl acetate. The residue was filtered, collected, and further purified by column chromatography on silica gel ($CHCl_3$) to yield 144 mg of a dark purple solid (58%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.81$ (s, 2H), 0.34 (t, $J = 7$ Hz, 48H), 1.86−2.07 (m, 32H), 4.25 (br s, 16H), 4.36 (br s, 16H), 6.63 (d, $J = 8$ Hz, 8H), 6.71 (d, $J = 8$ Hz, 8H), 6.76 (br s, 8H), 6.95−7.03 (m, 20H), 7.10−7.15 (m, 32H), 7.17−7.24 (m, 16H), 7.33−7.39 (m, 16H), 7.45−7.50 (m, 24H), 7.83−7.89 (dd, 16H), 8.04−8.07 (m, 16H), 8.91 (br s, 8H). HRMS (MALDI) (m/z): ($M + H^+$) calcd, 5261.70; found, 5261.81. UV/vis (benzene): λ_{max} ($\epsilon \times 10^{-5}$): 310 (2.11), 403 (3.96), 423 (5.63), 516 (0.214), 551 (0.064), 592 (0.064), 647 (0.037). Fluorimeter (benzene, $\lambda_{ex} = 516$) λ_{em}: 655.

Preparation of 5,10,15,20-Tetrakis(3′,5′-dihydroxyphenyl)porphyrin (2).[22] 5,10,15,20-Tetrakis(3′,5′-dimethoxyphenyl)porphyrin[23] **4** (1.50 g, 1.75 mmol) was dissolved in 250 mL of dry CH_2Cl_2, and the solution was cooled to 0 °C. Boron tribromide (17.0 mL of a 0.91 M solution in CH_2Cl_2, 15.4 mmol) was added over a period of 0.5 h. It was stirred at room temperature for an additional 24 h. Excess reagent was quenched with methanol, 5 mL of triethylamine and 200 mL of water were added, and the mixture was stirred for 18 h. Evaporation of the organic solvent followed by addition of water, and filtration afforded the desired product as purple crystals (1.30 g, 100%). Characterization was in agreement with the literature.[22]

Preparation of AF-343 (3). AF-343 was prepared as described previously.[21]

Preparation of 5,10,15,20-Tetrakis(3′,5′-dimethoxyphenyl)porphyrin (4). The symmetrical free-base porphyrin 4 was prepared under Adler-Longo conditions using the published method. Characterization agreed with the literature reports.[23]

Preparation of Aluminum Chloride Tetrakis(3′,5′-di(AF-343)phenyl)porphyrin (5). Diethyl aluminum chloride (0.00270 mmol, 0.0015 mL of a 1.8 M solution in CH_2Cl_2) was added to a solution of **1** (0.010 g, 0.00190 mmol) in CH_2Cl_2 (0.2 mL) in a flame dried round-bottom flask under nitrogen. The mixture was stirred at room temperature for 1 h and was monitored for completion by observing changes in the Q-band region at 550 nm. When complete, the porphyrin solution was taken up in 5 mL of CH_2Cl_2, washed with 3 × 5 mL of 0.3 M $NaHSO_4$, and dried, and the solvent was removed. **5** (0.010 g) was isolated as an amorphous solid, requiring no further purification (99% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.35$ (dt, $J = 19$ Hz, 7 Hz, 48H), 1.86−2.07 (m, 32H), 4.25 (br d, 16H), 4.36 (br d, 16H), 6.63 (d, $J = 8$ Hz, 8H), 6.71 (d, $J = 8$ Hz, 8H), 6.76 (br s, 8H), 6.95−7.03 (m, 20H), 6.94−7.15 (m, 32H), 7.17−7.24 (m, 16H), 7.33−7.39 (m, 16H), 7.45−7.50 (m, 24H), 7.83−7.89 (m, 16H), 8.05−8.07 (m, 16H), 9.10 (br s, 8H). MALDI-TOF MS (m/z): calcd, 5322.13; found, 5322.45. UV/vis (benzene) λ_{max} ($\epsilon \times 10^{-5}$): 311 (2.22), 397 (3.81), 421 (6.90), 548 (0.236). Fluorimeter (benzene, $\lambda_{ex} = 549$) λ_{em}: 646.

Preparation of Aluminum Chloride 5,10,15,20-Tetrakis(3′,5′-dimethoxyphenyl)porphyrin (6). Diethyl aluminum chloride (0.0585 mmol, 0.0325 mL of a 1.8 M solution in toluene) was added to a solution of **4** (0.050 g, 0.0585 mmol) in CH_2Cl_2 (0.6 mL) in a flame dried round-bottom flask under nitrogen. The mixture was stirred at room temperature for 1 h and was monitored for completion by observing changes in the Q-band region at 550 nm. When complete, the porphyrin solution was taken up in 5 mL of CH_2Cl_2, washed with 3 × 5 mL of 0.3 M $NaHSO_4$, and dried, and the solvent was removed. **6** (0.051 g) was isolated as an amorphous solid, requiring no further purification (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.89$ (s, 24H), 6.53 (m, 4H), 6.90 (m, 8H), 9.10 (br s, 8H). MALDI-TOF MS (m/z): calcd, 916.39; found, 916.23. HRMS (FAB) (m/z): calcd for $C_{52}H_{44}AlN_4O_8$, 879.2975; found, 879.2957. UV/vis (benzene) λ_{max} ($\epsilon \times 10^{-5}$): 420 (4.01), 548 (0.163). Fluorimeter (benzene, $\lambda_{ex} = 548$) λ_{em}: 647.

Preparation of Zinc Tetrakis(3′,5′-di(AF-343)phenyl)porphyrin (7). A saturated methanol solution of zinc acetate (0.5 mL) was added to a solution of **1** (0.010 g, 0.00190 mmol) in $CHCl_3$ (3 mL) in a round-bottom flask under nitrogen. The mixture was refluxed for 3 h and was monitored for completion by observing changes in the Q-band region at 550 nm. When the reaction was complete, the porphyrin solution was cooled to room temperature, and 3 mL of an aqeous solution of KOAc (0.1 M) and ethylenediamine tetraacetic acid (EDTA, 0.01 M) was added. The biphasic mixture was stirred overnight at room temperature. The solution was taken up in a separatory funnel, washed with 3 × 3 mL of H_2O and dried, and the solvent was removed. **7** (0.010 g) was isolated as an amorphous solid, requiring no further purification (99% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.35$ (t, $J = 7$ Hz, 48H), 1.88−2.03 (m, 32H), 4.24 (br d, 16H), 4.35 (br d, 16H), 6.61 (d, $J = 8$ Hz, 8H), 6.68 (d, $J = 8$ Hz, 8H), 6.74 (br s, 8H), 6.93−7.00 (m, 20H), 7.07−7.14 (m, 32H), 7.17−7.25 (m, 16H), 7.33−7.39 (m, 16H), 7.45−7.52 (m, 24H), 7.85−7.87 (m, 16H), 8.02−8.03 (m, 16H), 8.98 (br s, 8H). MALDI-TOF MS (m/z): calcd, 5325.08; found, 5325.65. UV/vis (benzene) λ_{max} ($\epsilon \times 10^{-5}$): 310 (2.17), 398 (3.43), 426 (5.51), 550 (0.250). Fluorimeter (benzene, $\lambda_{ex} = 550$) λ_{em}: 647.

Preparation of Zinc 5,10,15,20-Tetrakis(3′,5′-dimethoxyphenyl)porphyrin (8). A saturated methanol solution of zinc acetate (5.0 mL) was added to a solution of **4** (0.100 g, 0.117 mmol) in $CHCl_3$ (100 mL) in a round-bottom flask under nitrogen. The mixture was refluxed for 6 h and was monitored for completion by observing changes in the Q-band region at 550 nm. When the reaction was complete, the porphyrin solution was cooled to room temperature, and 100 mL of an aqeous solution of KOAc (0.1 M) and EDTA (0.01 M) was added. The biphasic mixture was stirred overnight at room temperature. The solution was taken up in a separatory funnel, washed with 3 × 50 mL of H_2O and dried, and the solvent was removed. **8** (0.101 g) was isolated as an amorphous solid, requiring no further purification (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.89$ (s, 24H), 6.84 (t, $J = 2$ Hz, 4H), 7.37 (d, $J = 2$ Hz, 8H), 9.03 (s, 8H). HRMS (FAB) (m/z) calcd for $C_{52}H_{44}N_4O_8Zn$, 916.2451; found, 916.2440. Anal. Calcd for $C_{52}H_{44}N_4O_8Zn$: C, 68.01; H, 4.83; N, 6.10. Found: C, 68.17; H, 5.09; N, 5.75. UV/vis (benzene) λ_{max} ($\epsilon \times 10^{-5}$): 425 (5.34), 549 (0.237). Fluorimeter (benzene, $\lambda_{ex} = 549$) λ_{em}: 647.

Preparation of Silver Tetrakis(3′,5′-di(AF-343)phenyl)porphyrin (9). Silver(II) trifluoracetate (0.32 g, 0.146 mmol) was added to a solution of **1** (0.350 g, 0.067 mmol) in $CHCl_3$ (30 mL) in a round-bottom flask under nitrogen. The mixture was heated to reflux for 20 min and was monitored for completion by observing changes in the Q-band region at 550 nm. When the reaction was complete, the porphyrin solution was cooled to room temperature, and the solvent evaporated. The crude product was purified by filtration through a plug of silica gel using THF as the eluent. The THF was evaporated to give **9** (0.350 g) isolated as an amorphous solid, requiring no further purification (99% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.35$ (t, $J = 7$ Hz, 48H), 1.86−2.02 (m, 32H), 4.22

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(39) Neuwahl, F. V. R.; Righini, R.; Adronov, A.; Malenfant, P. R. L.; Fréchet, J. M. J. *J. Phys. Chem. B* **2001**, *105*, 1307−1312.

(br m, 32H), 6.60 (d, $J = 8$ Hz, 8H), 6.69 (d, $J = 8$ Hz, 8H), 6.74 (br s, 8H), 6.97−7.00 (m, 20H), 7.09−7.18 (m, 32H), 7.19−7.25 (m, 16H), 7.33−7.37 (m, 16H), 7.44−7.47 (m, 24H), 7.86−7.87 (m, 16H), 8.02−8.03 (m, 16H). MALDI-TOF MS (*m*/*z*): calcd, 5357.57; found, 5357.88. UV/vis (benzene) $\lambda_{\max}$ ($\epsilon \times 10^{-5}$): 310 (2.09), 394 (3.53), 430 (4.34), 542 (0.182).

Preparation of Silver 5,10,15,20-Tetrakis(3′,5′-dimethoxyphenyl)porphyrin (10). Silver(II) trifluoroacetate (0.078 g, 0.351 mmol) was added to a solution of **4** (0.100 g, 0.117 mmol) in $CHCl_3$ (25 mL) in a round-bottom flask under nitrogen. The mixture was heated to reflux for 20 min and was monitored for completion by observing changes in the Q-band region at 550 nm. The crude product was purified by filtration through a plug of silica gel using THF as the eluent. The THF was evaporated to give **10** (0.105 g) isolated as a purple powder, requiring no further purification (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.97$ (s, 24H), 6.91 (m, 4H), 7.28 (m, 8H). HRMS (FAB) (*m*/*z*): calcd for $C_{52}H_{44}AgN_4O_8$, 959.2210; found, 959.2193. Anal. Calcd for $C_{52}H_{44}AgN_4O_8$: C, 65.00; H, 4.62; N, 5.83. Found: C, 64.74; H, 4.77; N, 5.59. UV/vis (benzene) $\lambda_{\max}$ ($\epsilon \times 10^{-5}$): 429 (3.54), 541 (0.158).

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