

Picosecond Dynamics of Energy Transfer in Porphyrin–Sapphyrin Noncovalent Assemblies

Stacy L. Springs,[†] David Gosztola,[‡] Michael R. Wasielewski,^{*,†,§} Vladimír Král,[†] Andrei Andrievsky,[†] and Jonathan L. Sessler^{*,†}

Contribution from the Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, Argonne National Laboratory, Chicago, Illinois, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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Abstract: The picosecond dynamics of noncovalent ensembles for energy transfer based on anion chelation are reported. The photoactive noncovalent complexes are assembled via salt-bridge formation between carboxyl-containing porphyrin photodons and a monoprotinated pentapyrrolic sapphyrin acceptor. These complexes are formed with a K_a of ca. 10^3 M^{-1} upon mixing the receptor and substrate in their respective free-acid and free-base forms in CD_2Cl_2 (as judged by ^1H NMR spectroscopic means). Upon irradiation at 417 nm, singlet–singlet energy transfer from the porphyrin to the sapphyrin subunit takes place readily with energy transfer dynamics that are consistent with a Förster-type mechanism. The title systems thus appear to be prototypic of a new kind of noncovalent energy transfer modeling that is predicated on the use of anion chelation.

Introduction

The light harvesting complexes of photosynthetic organisms contain many chromophores (primarily chlorophylls and bacteriochlorophylls, but also carotenoids and other pigments), noncovalently associated and elaborately arranged such that the energy is funneled rapidly over large distances and in high

quantum yield to a reaction center protein.¹ A desire to reproduce and understand the functional and mechanistic features of these natural multi-chromophore arrays has driven chemists, biologists, and engineers to study energy transfer events in both native constructs and synthetic model systems for many years. One approach to energy transfer modeling has been to link covalently, through chemical synthesis, various high- and low-energy redox-active chromophores. There are many examples of this approach, most of which use mixed metalloporphyrin systems or other highly stable transition metal complexes.^{2–4} Unfortunately, this approach requires a reasonably high synthetic investment. Nonetheless, it has allowed experimental verification of various orientation-related aspects of Förster energy transfer theory and has greatly enhanced our understanding of relevant natural processes.

Another, more recent approach uses noncovalent forces (i.e., hydrogen bonds, salt bridges, metal–ligand coordinate bonds)

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[‡] Argonne National Laboratory.

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to associate the requisite donor and acceptor for subsequent energy transfer events.^{5,6} This approach is more biomimetic, the synthesis is more straightforward, i.e., subunits of an array are synthesized, not the entire array, and once prepared, the individual subunits may be used in a "mix and match" way to assemble noncovalently a variety of ensembles.

In this paper, the molecular recognition and energy transfer dynamics of photoactive, noncovalent complexes assembled from carboxylate-bearing porphyrins and anion binding sapphyrins are described.⁷ The sapphyrins, originally reported by Woodward and Johnson,^{8–10} and more recently studied in detail by Sessler,^{11,12} are pentapyrrolic "expanded porphyrin" macrocycles that differ from their simpler porphyrin "cousins" in several important ways. Containing five, rather than four pyrrole subunits, the sapphyrins do not coordinate cations readily. However, when mono- or diprotonated, they act as excellent receptors for a variety of *anions*, including fluoride and phosphate, and to a lesser extent other halides and carboxylates.^{13–18} The sapphyrins are characterized by red-shifted absorption and emission bands and first excited singlet states that are ca. 0.20 eV lower in energy than those of the porphyrins (vide infra).

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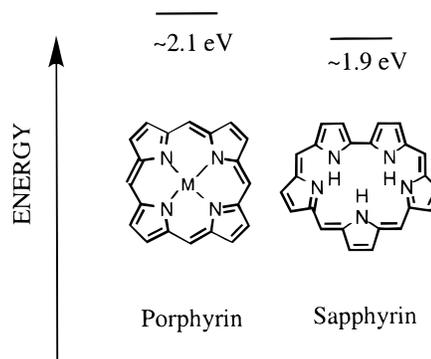


Figure 1. Typical values for the lowest excited singlet state energy levels of porphyrin and sapphyrin.

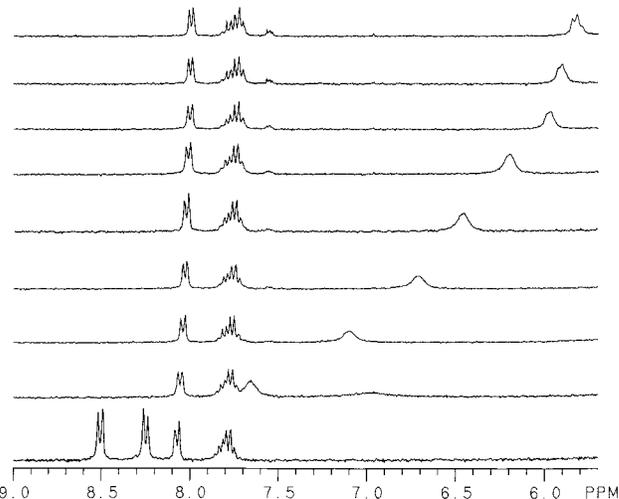


Figure 2. Stacked plot of proton NMR spectra showing the upfield shift of *m*-carboxyphenyl resonances of **2** as a function of increasing [**1**] in CD₂Cl₂ ([**2**] = 1.7 × 10⁻³ M; [**1**] = 3 × 10⁻⁴ to 6 × 10⁻³ M).

It was an appreciation of the above features which led us to consider that it might be possible to design sapphyrin-based systems, wherein anion binding is used to establish donor–acceptor interactions. Such systems could constitute a new approach to energy transfer modeling and one that could be particularly germane to the problem of understanding how salt bridges influence long-range energy- and electron-transfer events. They would also allow the photophysics of sapphyrins to be studied in detail. This ancillary objective is important since, despite being known for more than 30 years, the excited state dynamics of this expanded porphyrin have yet to be explored. The majority of available porphyrin-containing models for energy transfer consist of metalloporphyrin/free-base porphyrin covalent assemblies where the presence of a metal (usually Zn(II)) is used to establish the unidirectional energy gradient necessary.² However, the expanded porphyrins (e.g. sapphyrin, texaphyrin) inherently have different energetic and excited state properties than their porphyrin cousins, and could be useful chromophores in multicomponent arrays for vectorial energy transfer (see Figure 1). Indeed, we have recently shown that Y(III) texaphyrin (the first excited singlet state of which lies approximately 0.2 eV below that of sapphyrin) is capable of quenching the steady-state fluorescence emitted by sapphyrin in oligonucleotide conjugates.¹⁹

Ensembles **I** and **II** were designed to be prototypic of this new approach to energy-transfer modeling. Here, the key

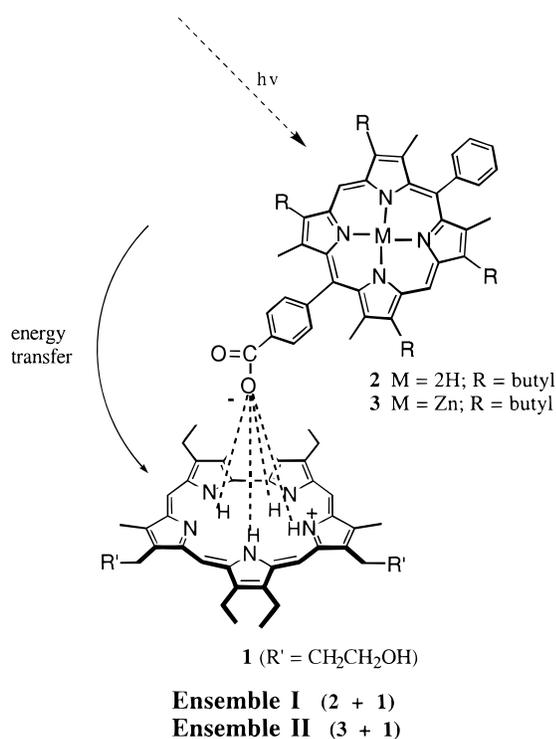
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Table 1. Association Constants for Ensembles I–III

ensemble	K_a	solvent
I	$(2.6 \pm 0.5) \times 10^3 \text{ M}^{-1}$	CD_2Cl_2
II	$(7.1 \pm 0.9) \times 10^2 \text{ M}^{-1}$	1% MeOD/99% CD_2Cl_2
III ^a	$(2.0 \pm 0.3) \times 10^3 \text{ M}^{-1}$ $(9.46 \pm 0.21) \times 10^3 \text{ M}^{-1}$	CD_2Cl_2 CD_2Cl_2

^a Ensemble III is a complex between monoprotonated sapphyrin **1** and *p*-toluate anion. The first value recorded and those for Ensembles I and II were collected in a manner where the monocarboxylate concentration was held constant and the concentration of sapphyrin was varied. The second value reported for Ensemble III is a complex between 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin and *p*-toluate, and in this case, the concentration of a 1:1 mixture of *p*-toluic acid and **1** was varied.

predicative assumptions were that (1) a readily accessible carboxyl-substituted porphyrin (**2** or **3**) could serve as both a simple-to-bind anionic substrate and a high-energy donor and (2) the protonated sapphyrin moiety **1** would function both as the geometry-inducing, carboxylate-binding receptor and the critical (low) energy acceptor. With these assumptions in mind, it was expected, based on earlier studies of an energetically similar, but covalently linked, sapphyrin–porphyrin pseudodimer,⁴ that irradiation of the porphyrin subunit in **I** or **II** would lead to excitation transfer to the sapphyrin “sink”, with the rate of this energy transfer being modulated, at least to some extent, by the presence of the salt bridge and the donor-to-acceptor orientation it establishes.



Results and Discussion

Molecular Recognition. To establish that ensembles **I** and **II** would in fact form under simple equilibrium mixing conditions, standard ¹H NMR binding titrations were carried out (cf., Figure 2). In the case of ensemble **I**, standard curve fitting procedures resulted in an association constant of $K_a = (2.6 \pm 0.5) \times 10^3 \text{ M}^{-1}$ in CD_2Cl_2 .^{7,20–24} (This and other K_a values are given in Table 1.)

When the methyl ester **4** was used in place of **2**, no shifts in the carboxyl-bearing phenyl signals were observed. However, upfield shifts in resonances corresponding to the methine protons

of **4** could be curve fit to yield an association constant of $K_a = (4.0 \pm 0.3) \times 10^2 \text{ M}^{-1}$. These changes are attributed to the presence of a slightly offset, π – π stacked complex between **4** and **1** at the high concentrations used for the ¹H NMR binding studies. However, because no shifts in the carboxyl-bearing phenyl signals were observed in the control, in the case of **I**, the changes associated with the carboxyphenyl protons provide a direct measure of salt-bridge binding (only).

The zinc porphyrin monoacid **3** is less soluble than its free base counterpart in dichloromethane. In fact, at concentrations where it was reasonable to perform a ¹H NMR binding study, **3** was not soluble. As a result, the ¹H NMR binding studies were carried out in 1% MeOD/99% CD_2Cl_2 . An $8.35 \times 10^{-4} \text{ M}$ solution of **3** (as the free acid) was titrated with **1** (at a concentration range of 0–12 mM) and the *m*-carboxyphenyl resonances of **3** monitored as a function of [**1**]. The association constant for this pair (Ensemble **II**) was smaller than that for the corresponding free-base system Ensemble **I** (measured in CD_2Cl_2). Specifically, an association constant of $(7.1 \pm 1.0) \times 10^2 \text{ M}^{-1}$ was determined by using standard curve fitting procedures.^{20–24} In the case of the control experiment with the methyl ester **5**, a binding constant could not be determined. Slight upfield changes in the chemical shift of the methine protons of **5** upon addition of **1** were observed, but these changes, when plotted against [**1**], gave a straight line with no curvature or plateau region, indicating that the association constant is too small to be measured under the conditions of the experiment. The solubility of **1** did not permit higher concentrations (10^{-2} M) of **1** to be used. It thus proved impossible to determine a reliable K_a value in this case. Regardless, it is clear that under the conditions of the subsequent photophysical experiments, there is little to no π – π stacked complex present.

While it was expected that the stoichiometry of the porphyrin–sapphyrin complex would be 1:1, it was considered possible that a 2:1 (or higher order) complex could be present in solution. Thus, the complex stoichiometry was experimentally determined by using a continuous variation (Job) plot. To effect this particular solution phase study, it was necessary to use *p*-toluic acid rather than the porphyrin monoacids **2** or **3** for the simple reason that this smaller acid is more soluble in dichloromethane. The Job plot of the ¹H NMR titration data indicates that the stoichiometry of the complex is indeed 1:1 (see Figure 3).

In addition to the above binding studies, the ¹H NMR spectra of a 1:1 mixture of *p*-toluic acid and 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin as a function of concentration were recorded in dichloromethane. The data were then treated with a curve-fitting algorithm for determining association constants from such a dilution experiment.²⁰ From this analysis, an association constant of $(9.46 \pm 0.21) \times 10^3 \text{ M}^{-1}$ was determined. Unfortunately, because of solubility limitations, this analytical method could not be used in the case of Ensembles **I** and **II**. Still, this study does provide important confirmation of the fact that monoprotonated sapphyrin will bind carboxylate anions in dichloromethane.

Gas-Phase and Solid-State Complexation.

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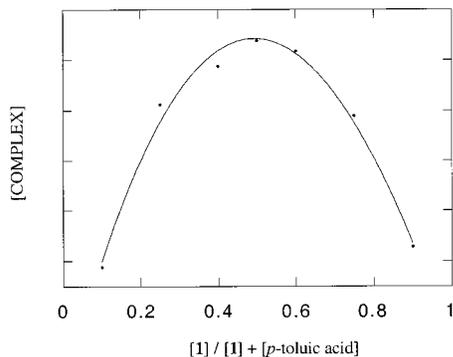
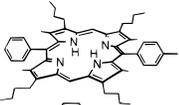
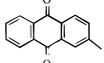
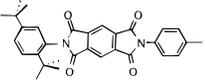


Figure 3. A continuous variation (Job) plot of *p*-toluic acid and **1** in CD_2Cl_2 .

Table 2. High-Resolution Mass Spectrometric Data for 1:1 Complexes between **1** and Various Monocarboxylate Anions

RCO_2^-	High Resolution FAB Mass Spectral Analysis	
	Calculated	Observed
	1446.9148	1446.9150
	782.4641	782.4645
	912.4717	912.4700
	898.4188	898.4213
	1184.6224	1184.6233

the solution-phase binding studies discussed above, evidence was also obtained that is consistent with ensemble formation occurring in the gas phase and in the solid state. In the first case, high-resolution mass spectrometric evidence for the complexation of a variety of carboxylates with the monoprotonated form of saphyrin was obtained from fast atom bombardment (FAB) mass spectrometric analyses.²⁵ The results of these studies, summarized in Table 2, serve to confirm that supramolecular complexes between protonated **1** and various mono-carboxylates are formed under the matrix desorption/gas-phase conditions of the experiment. Importantly, in the case of the porphyrin monoacid, this interpretation is supported by the fact that when the corresponding porphyrin monoester (**4** or **5**) and saphyrin (**1**) are submitted for analysis under the same conditions, no evidence of complexation is observed.

Further confirmation for the contention that protonated saphyrins can bind carboxylate anions comes from a recent X-ray diffraction study of the benzoic acid salt of saphyrin.²⁶ The resulting structure, reproduced in Figure 4, reveals that the orientation of the phenyl ring with respect to the saphyrin macrocycle is enforced by chelation of the carboxylate oxyanion. Further, this same crystallographic study highlights the presence of hydrogen bonds between the carboxylate oxyanion of benzoate and the N–H protons of the saphyrin macrocycle as well as an ancillary C–H...N close contact (2.38 Å). This contact presumably reflects a hydrogen bonding interaction between the benzoate anion and the unprotonated pyrrole nitrogen of the saphyrin macrocycle. This interaction, if

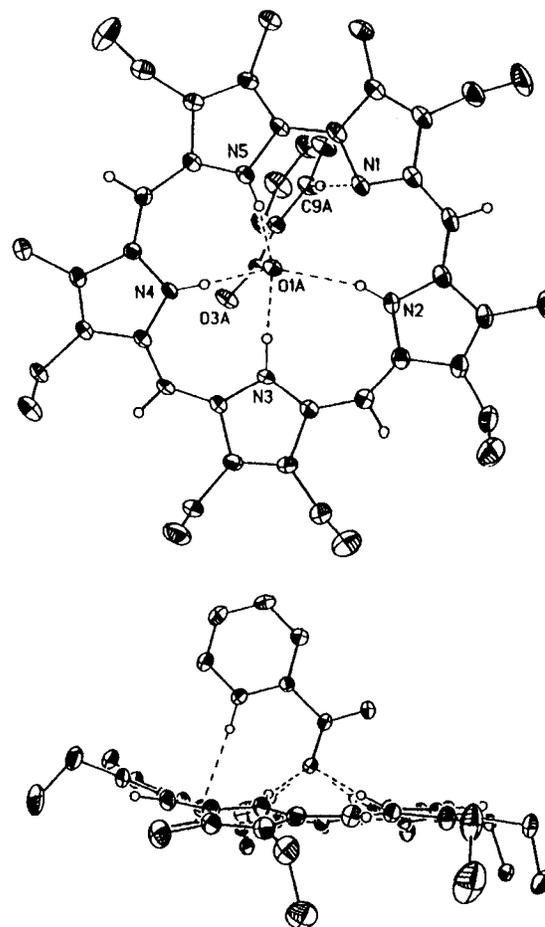


Figure 4. Top and side views of the single-crystal X-ray structure of a 1:1 inner-sphere, neutral complex of benzoate anion with monoprotonated saphyrin. Select hydrogen atoms have been omitted for clarity. Thermal ellipsoids are scaled to the 30% probability level.²⁶

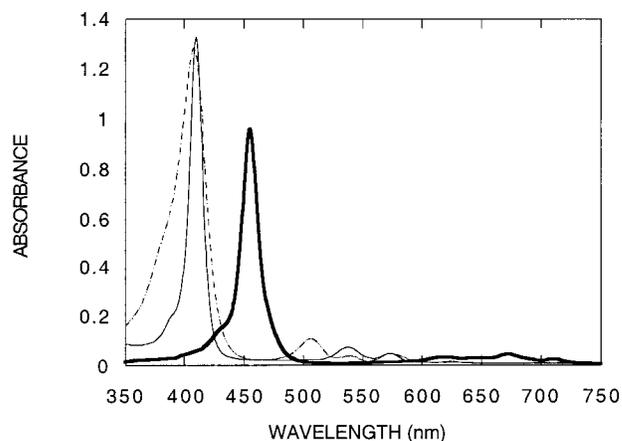


Figure 5. Ground-state absorbance spectra of **2** (---), **3** (—), and **1** (—) in dichloromethane.

persistent in solution, might serve to strengthen the complex. It could also lock in place the relative orientation of the phenyl ring and saphyrin. In any event, this crystal structure, considered in conjunction with our solution-phase ^1H NMR data, leads us to infer that in the porphyrin–saphyrin assemblies the two chromophores are likely to be oriented perpendicular to one another with the porphyrin lying “over” the saphyrin plane. To the extent such assumptions are correct, a center-to-center distance of 12.5 Å is expected between the two pyrrole-based chromophores.

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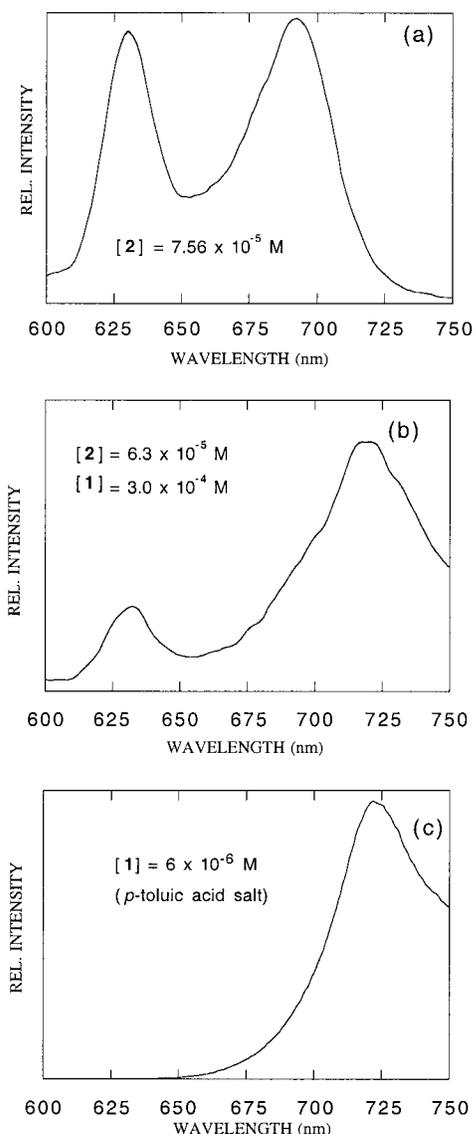


Figure 6. Corrected steady-state fluorescence spectra of (a) **2**, (b) **2** + **1**, and (c) the *p*-toluic acid salt of **1** in dichloromethane. Excitation was effected at 409 nm in the case of (a) and (b) and at 450 in the case of (c).

Ground-State Absorbance Spectra. Once the above predicative molecular recognition work was complete, a variety of ground-state absorbance and steady-state fluorescence measurements were made in an effort to characterize the intraensemble energy transfer characteristics of systems **I** and **II**. The ground-state absorbance spectra of the tetrabutylammonium salts of the free-base porphyrin monoacid **2** and the zinc(II) substituted porphyrin **3** as well as the *p*-toluic acid salt of sapphyrin **1** are shown in Figure 5. The spectra of the carboxylic acid substituted porphyrins are nearly identical with the corresponding unsubstituted diphenylporphyrins, the porphyrin methyl esters **4** and **5**, and the tetrabutylammonium salts of the porphyrin monoacids. Porphyrins **2** and **3** both obey Beer's law in dichloromethane at concentrations of 10^{-4} M and below. At the concentrations used for photophysical experiments ($[1] \sim 10^{-4}$ M, $[2/3] \sim 10^{-5}$ M), the spectra of the porphyrin (tetrabutylammonium salts of **2** or **3**), the *p*-toluic acid salt of sapphyrin, and the mixture of the porphyrin and sapphyrin were recorded. The spectral characteristics and the absorbance at the excitation wavelength

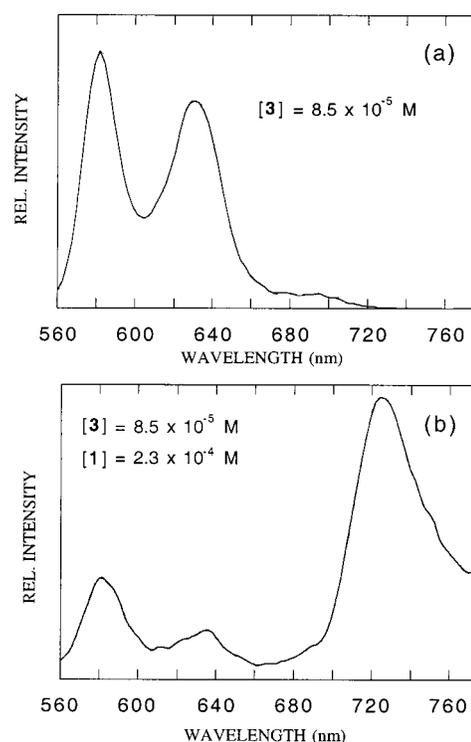


Figure 7. Corrected steady-state fluorescence spectra of (a) **3** and (b) **3** + **1** in dichloromethane. Excitation was effected at 409 nm.

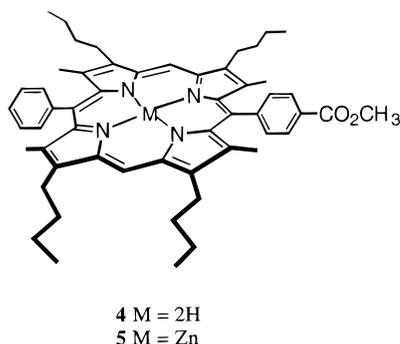
of the “complex” were observed to correspond well to the sum of the independent porphyrin and sapphyrin features. This observation, in conjunction with other solution-phase evidence, supports the contention that there is little or nothing in the way of π – π stacking occurring between the porphyrin-monoacids **2** and **3** and sapphyrin **1** at low concentrations, including explicitly those relevant to the photophysical analyses described below.

Fluorescence Emission Spectra. When **2** in dichloromethane is excited at 409 nm, an emission characteristic of a free base porphyrin is observed (Figure 6). However, upon addition of four molar equivalents of sapphyrin **1**, the porphyrin fluorescence is significantly quenched and a new emission band appears at 722 nm that is characteristic of the fluorescence spectrum of the mono-*p*-toluic acid salt of sapphyrin. Addition of methanol (10% v/v) almost fully restores the porphyrin fluorescence. Likewise, in the case of Ensemble **II**, when sapphyrin **1** is added to the zinc(II) substituted porphyrin-monoacid **3**, the fluorescence is quenched and a new emission band is observed (Figure 7). This new band corresponds to the emission of the *p*-toluic acid salt of sapphyrin. The addition of the hydrogen-bonding solvent, methanol, also serves to restore the porphyrin fluorescence in this case. When the esterified control porphyrins **4** and **5** are used in place of the corresponding acids, and under identical conditions, the porphyrin fluorescence is only marginally quenched by the addition of sapphyrin **1**. These observations are consistent with energy transfer occurring from the excited singlet state of the porphyrin to sapphyrin within the noncovalent assemblies **I** and **II** but not in those instances when the porphyrin acid group is blocked (i.e., when **4** or **5** is mixed with **1**). This conclusion, in favor of energy transfer, as opposed to electron transfer, is based on the observation of a strong fluorescence emission at 722 nm. Such an emission would not be expected from the radical species that would likely be produced as

Table 3. Photophysical Properties of Porphyrin and Sapphyrin Macrocycles

macrocycle	λ_{max} (nm)		$E_{(0,0)}$ (eV) ^a	Φ_f^b	τ_s (ns)	τ_t (μ s)
	Soret (nm)	Q-bands (nm)				
2	408	506, 540 574, 625	2.0	0.09	12.3	
2 (tetrabutyl- ammonium salt)	408	506, 540 574, 625		0.09		
4	408	506, 540 574, 625		0.08		
3	409	537, 573	2.1	0.07	1.65	2.5
3 (tetrabutyl- ammonium salt)	409	538, 573		0.07		
5	409	538, 573		0.07		
1 (<i>p</i> -toluic acid salt)	453	622, 674	1.9	0.03		34

^a Excited-state energy levels were calculated from the intersection between the absorbance and fluorescence spectra. ^b Quantum yields were calculated by comparison to a known reference (free-base tetraphenylporphyrin) according to standard methods.³⁴



the result of an intraensemble electron-transfer process.

As a control for the above study, we felt it important to compare the photophysical properties of the free acid forms of the carboxylic acid functionalized porphyrins **2** and **3**, their tetrabutylammonium salts, and the corresponding methyl esters (i.e., **4** and **5**). In particular, we felt it important to check whether attachment of a carboxylate functionality, essential for the formation of donor–acceptor assemblies **I** and **II**, affects the basic photophysical behavior of an octaalkyl 5,15-diaryl porphyrin. As can be seen from Table 3, the spectral characteristics of the acid, carboxylate, and esterified forms of free-base porphyrin **2** resemble those of typical porphyrins and, importantly, are virtually identical with one another. The same is true for the corresponding series of zinc(II) derivatives.

Femtosecond Transient Absorption Spectroscopic Measurements. In an effort to characterize more fully the presumed intraensemble energy-transfer processes, transient absorbance measurements were carried out.²⁷ In Figure 8 the difference absorption spectra of **2** (top trace) and **1** (bottom trace) in dichloromethane are shown, respectively. In the spectrum of **2**, features characteristic of the $S_0 \leftarrow S_n$ transient absorption spectrum of a free-base porphyrin can be seen. This spectrum reveals characteristic bleaches that correspond in wavelength to the four Q-band absorbances of the ground state. The trough observed at 695 nm is also a characteristic feature of porphyrin transient absorption spectra and results from stimulated emission.²⁸ In the bottom trace of Figure 8 the transient absorption spectrum of the *p*-toluic acid salt of sapphyrin is shown. Here,

(27) Previously, time-resolved luminescence measurements were made on Ensemble **I** in an attempt to characterize the intraensemble energy transfer. However, the assignment of the observed time-resolved luminescence changes, although correct in a qualitative sense, was later found to be quantitatively inaccurate due to interfering Raman scatter from the sapphyrin macrocycle.

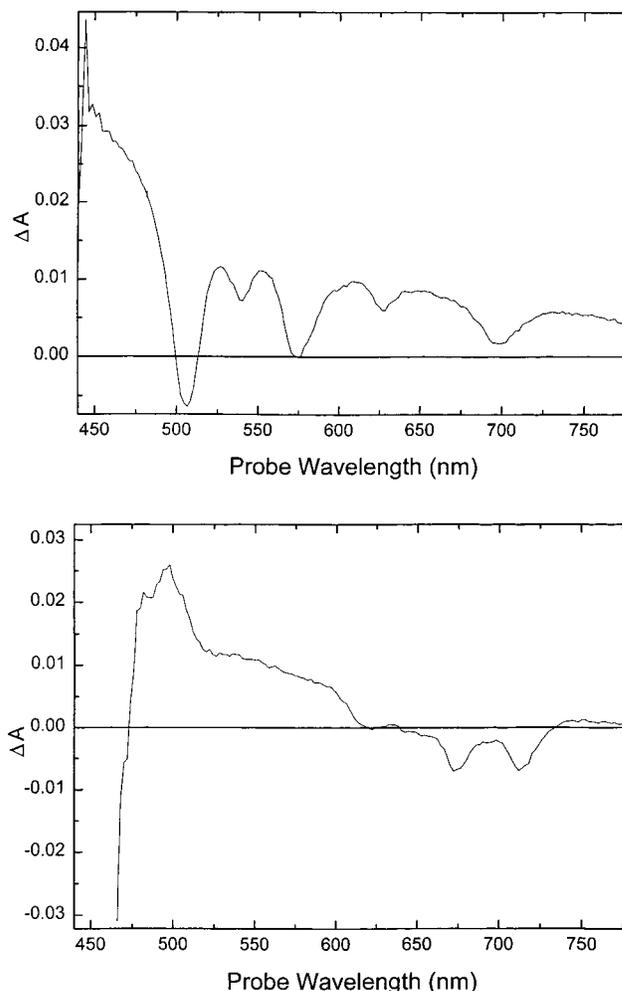


Figure 8. Transient absorption spectrum of **2** in dichloromethane recorded 15 ps after excitation with a 417 nm laser pulse (top trace). Transient absorption spectrum of **1** in dichloromethane recorded 30 ps after photoexcitation with a 417 nm laser pulse (bottom trace).

two troughs at 670 and 720 nm, corresponding to the Q-band absorbances of the ground state, are observed.

When a mixture of **1** and **2** (Ensemble **I**) is excited at 417 nm at early time (5 ps), a spectrum that has features of both **1** and **2** is observed (see Figure 9). For instance, the ground-state bleaches at 506, 540, 573, and 624 nm of the free-base porphyrin **2** are present, as are the Q-band bleaches of sapphyrin at 670 and 720 nm. This is because, under the conditions of the experiment with Ensemble **I** ($[2] = 6.35 \times 10^{-5}$ M; $[1] = 3.78 \times 10^{-4}$ M) the relative OD of **2** to **1** is 2.4 at the excitation wavelength. Thus, in these experiments some proportion of sapphyrin in solution is being directly excited. Despite this inherent loss of efficiency and the resulting experimental complications, when a spectrum at a later time (80 ps) is taken, it is evident that the spectral characteristics of this mixture are very different. First, the Q-band bleaches, which are ascribed to the porphyrin excited singlet state, have all but disappeared. Second, additional bleaching is observed in the region corresponding to photoexcited sapphyrin. The net result is that at 80 ps, the spectrum looks identical with that of an excited sapphyrin macrocycle alone. These spectral changes are thus consistent with a mechanism wherein excitation transfer from the excited state of the porphyrin to sapphyrin occurs. This generates the

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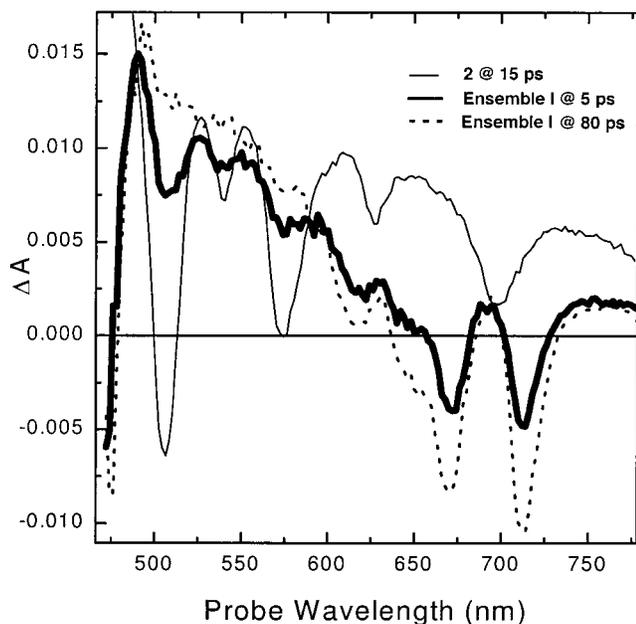


Figure 9. Transient absorption spectra of **2** in dichloromethane 15 ps after excitation with a 417 nm laser pulse (—), and a mixture of **1** + **2** (Ensemble **I**) in dichloromethane 5 ps (---) and 80 ps (---) after excitation with a 417 nm laser pulse.

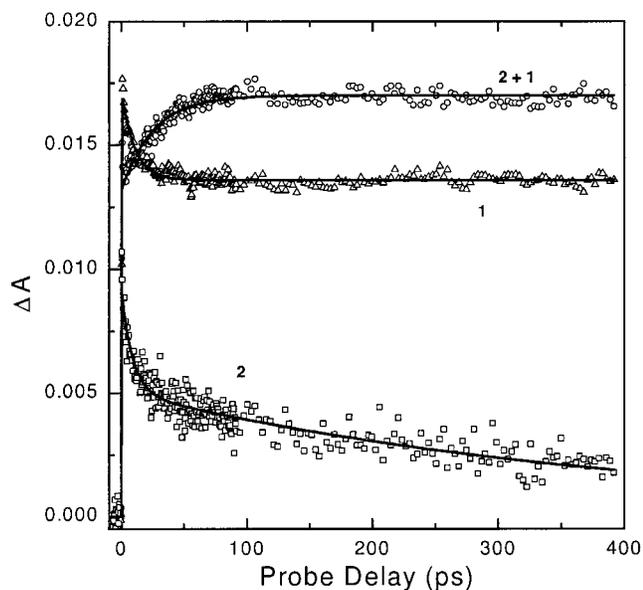


Figure 10. Transient spectral changes of **2**, **1**, and **2** + **1** (Ensemble **I**) monitored at 500 nm in dichloromethane and recorded after a 417 nm laser pulse. The kinetics of **1** and **2** consist of an instrument limited rise to form the excited states, **1**^{*} and **2**^{*}. In contrast, the kinetics of Ensemble **I** consist of an instrument-limited rise followed by a slower continued increase in absorption with a time constant $\tau = 25$ ps. The 25 ps component is due to energy transfer from **2**^{*} to **1**.

ground state of the porphyrin and the excited state of sapphyrin and results in the disappearance of the spectral features characteristic of the porphyrin excited singlet state. It also results in the appearance of spectral features characteristic of sapphyrin.

When Ensemble **I** is photoexcited at 417 nm the spectral changes at 500, 650, and 715 nm (see Figures 10–12) indicate that the change in the absorbance at the Q_y (1,0) band of the porphyrin and the changes in the Q (1,0) and Q (0,0) bands of the sapphyrin macrocycle occur on a similar time scale. Such a finding supports the reasonable conjecture that these two processes are connected. Following the initial instrument-limited rise, a positive absorption change at 500 nm occurs in 25 ps (Figure 10) while the corresponding bleach at 650 (Figure 11)

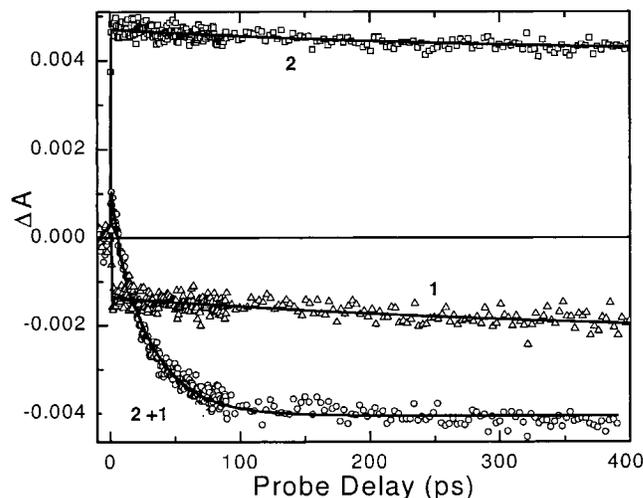


Figure 11. Transient spectral changes of **2**, **1** (*p*-toluic acid salt), and **2** + **1** (Ensemble **I**) in dichloromethane recorded at 650 nm after a 417 nm laser pulse. The free-base porphyrin **2** undergoes an instrument limited $+\Delta A$ to generate **2**^{*}; however, sapphyrin **1** undergoes an instrument limited bleach ($-\Delta A$) of the ground state during the formation of **1**^{*}. In the case of the complex (resulting from mixing **2** and **1**), a weak initial $+\Delta A$ transient followed by a slower $-\Delta A$ bleach is seen. The lifetime of the $-\Delta A$ component is 30 ps. The initial rise is due to the formation of **2**^{*} and the slower bleach is due to energy transfer to form the excited state of **1**.

and 715 nm (not shown) occurs in 30 and 22 ps, respectively. When a hydrogen bond disrupting solvent such as methanol is added, these time-dependent changes are no longer observed. Since methanol serves to break up the noncovalent complex (this contention is supported by ¹H NMR evidence *vide supra*), this critical change in aspect is taken as supporting further the critical conclusion that the spectral changes observed when **I** is irradiated in the absence of methanol result from *intracomplex* energy transfer.

It is clear that in the presence of methanol, all changes and time-dependent features consistent with intracomplex energy transfer are lost. For instance, the 25 ps rise at 500 nm is absent in the presence of methanol (Figure 12a). Instead, a decay is observed, and this decay is similar to the decay observed at 500 nm following photoexcitation of **2** alone. This decay may arise from vibrational relaxation within the S₁ or from S₂ → S₁ decay of the porphyrin second excited singlet state. Importantly, this decay is not observed in the regions of the porphyrin spectrum where the Q-band bleaches of sapphyrin are monitored. Taken together, these results are consistent with a scenario wherein intracomplex singlet–singlet energy transfer is occurring from porphyrin to sapphyrin within the anion-chelation based complex (Ensemble **I**).

In addition to the free-base porphyrin systems, the Zn(II)-metalated porphyrin-monoacid **3** was also studied both alone and as part of a supramolecular model system (Ensemble **II**). In the case of the latter noncovalent complex, experiments analogous to those described above were performed and the relevant **3**^{*} → **1** energy transfer times found to be on the order of 6 ps. In Figure 13 the difference transient absorption spectra for **3** and **3** + **1** recorded at 5 and 80 ps after the laser pulse are shown from top to bottom, respectively.

The transient spectrum of **3** (Figure 13 top) shows the Q-band bleach and stimulated emission features characteristic of an excited singlet state of a zinc(II) diarylporphyrin. As illustrated by Figure 13 (middle), a spectrum of Ensemble **II** (**[3]** = 6.23 × 10⁻⁵ M, **[1]** = 3.18 × 10⁻⁴ M) recorded at 5 ps after the laser pulse displays, in analogy to Ensemble **I**, the Q (1,0) and Q (0,0) bleaches characteristic of an excited zinc(II) diarylpor-

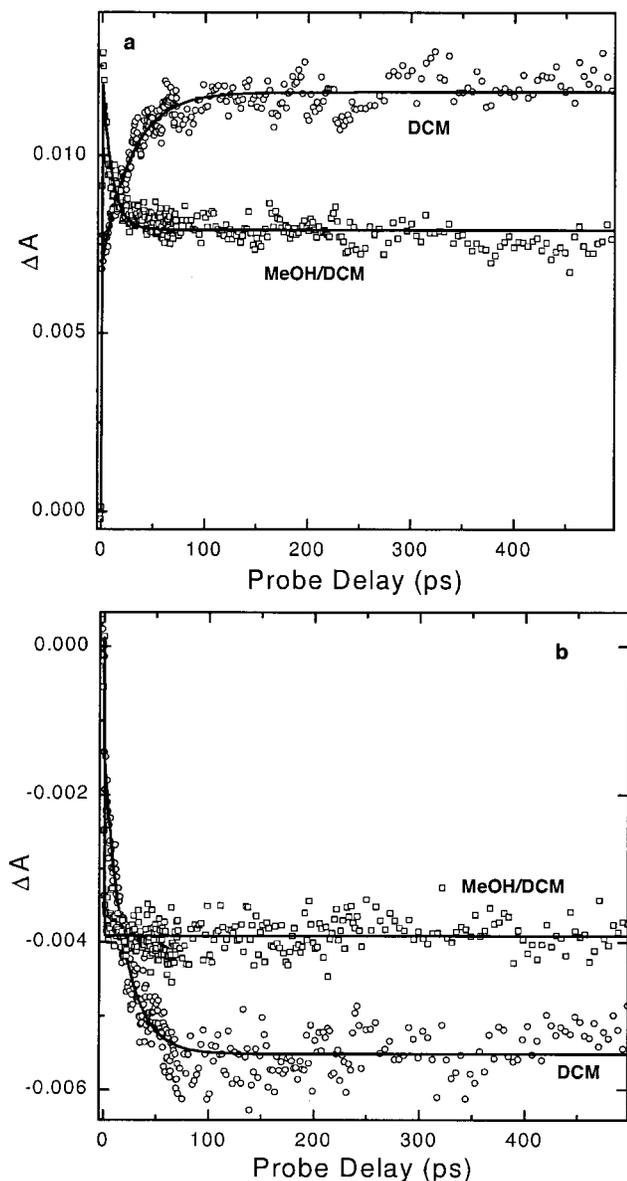


Figure 12. (a) Transient absorption kinetics of **2** + **1** (Ensemble **I**) at 500 nm in dichloromethane (DCM) and in a 30/70 mixture of methanol/dichloromethane. The addition of methanol (MeOH) inhibits formation of the complex by disrupting salt bridge formation. The kinetics at 500 nm in the presence of methanol resemble the kinetics of both **1**^{*} and **2**^{*} (see Figure 10) and provide no indication of energy transfer. (b) Transient absorption kinetics of **2** + **1** (Ensemble **I**) at 650 nm in dichloromethane and in a 30/70 mixture of methanol/dichloromethane. The addition of methanol inhibits formation of the complex by disrupting salt bridge formation. The kinetics at 650 nm in the presence of methanol are dominated by **1**^{*} indicating that no energy transfer is occurring.

phyrin. By contrast, the transient absorption spectrum recorded at 80 ps after the laser pulse (Figure 13 bottom) shows only spectral features characteristic of an excited sapphyrin singlet state.

When the kinetics of the spectral changes occurring after photoexcitation are monitored at 538 nm, a time constant $\tau = 7$ ps is obtained; this presumably corresponds to energy transfer from the first excited singlet state of **3** (**3**^{*}) to **1**. Similar values are also obtained when the kinetics are monitored at 613 or 713 nm. Independent of chosen monitoring wavelength, it is found that adding methanol has a profound effect. Specifically, as in the case of Ensemble **I**, the rapid transient changes ascribed to **3**^{*} → **1** energy transfer are no longer observed. This is consistent with the proposed model wherein fast **3**^{*} → **1** energy

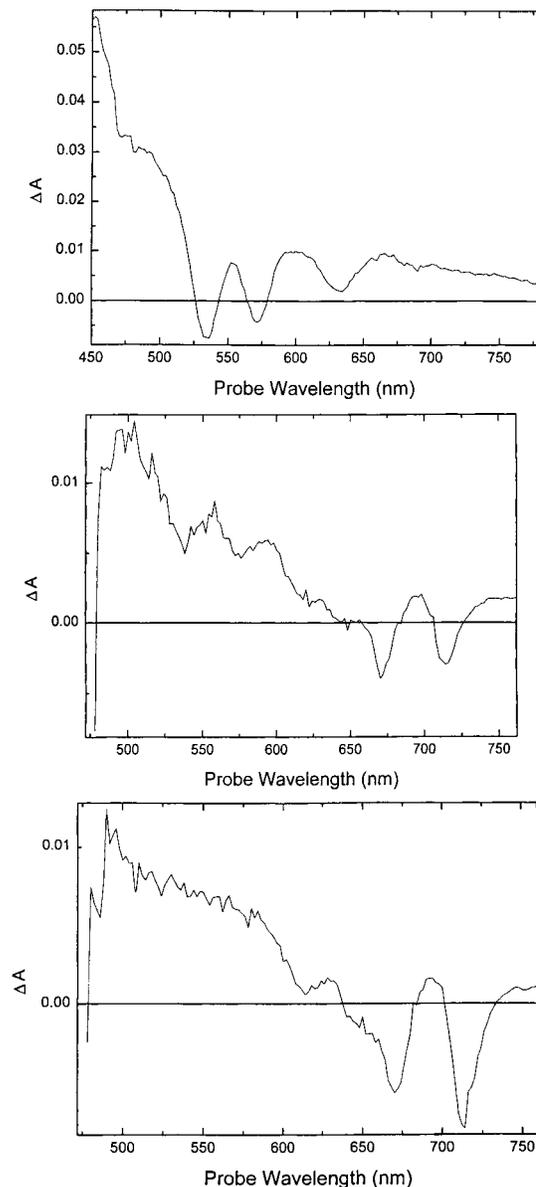


Figure 13. Transient absorbance spectra of **3** (top trace) and **3** + **1** (Ensemble **II**) at 5 ps (middle trace) and 80 ps (bottom trace) after excitation with a 417 nm laser pulse in dichloromethane.

transfer only takes place within the confines of the anion-chelation based complex Ensemble **II**.

From the time constants established with use of transient absorption spectroscopy, rate constants for energy transfer from (**2**^{*} to **1**) and (**3**^{*} to **1**) were determined according to eq 1 and found to be 4.3×10^{10} and $1.1 \times 10^{11} \text{ s}^{-1}$ for Ensembles **I** and **II**, respectively. Here, τ_0 is the fluorescence lifetime of the donor subunit and τ is the average of the energy transfer rise and decay times as recorded at six different wavelengths following photoexcitation of mixtures of (**2** and **1**) or (**3** and **1**).

$$k_{\text{ET}} = 1/\tau - 1/\tau_0 \quad (1)$$

The proposed intraensemble energy transfer is thought to be occurring via a Förster mechanism.²⁹ Although both Förster (dipole–dipole) and Dexter³⁰ (exchange) mechanisms are possible for singlet–singlet energy transfer, the magnitude of the rate constants can be rationalized by using Förster theory alone

(29) Förster, T. *Discuss. Faraday Soc.* **1959**, 27, 7.

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Table 4. Overlap Integrals and Calculated Rate Constants for Förster Energy Transfer within Porphyrin–Sapphyrin Ensembles **I** and **II**

ensemble	J_F (mmol/cm ⁻⁶)	R_c (Å)	κ^2	calc k_{ET} (s ⁻¹)	obs k_{ET} (s ⁻¹)
I	1.43×10^{-13}	12.5	0.69	5.0×10^{10}	4.3×10^{10}
II	2.43×10^{-13}	12.5	0.69	1.1×10^{11}	1.6×10^{11}

without the need to invoke a contribution from a Dexter mechanism. For Förster-type energy transfer, the calculated rate constants can be determined by using eq 2 where K is an orientation factor that describes the relative orientation of the donor and acceptor dipoles, Φ_F is the quantum yield of fluorescence of the donor, J_F is the overlap integral, n is the refractive index of dichloromethane, τ_s is the singlet state lifetime of the photodonor, and R_c is the center-to-center distance between chromophores. Here, the relevant overlap integrals (J_F), given in Table 4, are determined according to eq 3, where $F(\nu)$ is the fluorescence intensity at wavenumber ν and ϵ is the molar extinction coefficient of the Q_y absorption bands of the acceptor.

$$k_{ET} = \frac{(8.8 \times 10^{-25})K^2\Phi_F J_F}{n^4\tau_s R_c^6} \quad (2)$$

$$J_F = \frac{\int F(\nu)\epsilon(\nu)\nu^{-4} d\nu}{\int F(\nu) d\nu} \quad (3)$$

As can be seen in Table 4, the observed rate constants correspond quite well to those calculated from Förster theory. The fast energy transfer in Ensembles **I** and **II** is ascribable in part to the large overlap integrals between porphyrin and sapphyrin. The quantum efficiencies calculated by using eq 4 appear to be nearly quantitative.

$$\Phi = 1 - \tau/\tau_0 \quad (4)$$

That is, for every photoexcited complex, energy transfer occurs. However, it is important to point out that the overall reaction efficiency is not quantitative. This is because, as mentioned before, approximately 40% of the excitation of Ensembles **I** or **II** goes into exciting the sapphyrin macrocycle directly. To increase the reaction efficiency, more selective excitation of the porphyrin subunit must be achieved. Ideally, this could be done by increasing the association constant between the anionic substituted porphyrin and sapphyrin such that only one molecule of sapphyrin need be present for every porphyrin to be complexed.

Conclusions

In conclusion, we have demonstrated a new approach to non-covalent energy transfer model construction that involves the use of sapphyrin-based anion recognition. In principle, this is an approach of considerable versatility in that a range of anions in addition to carboxylates could be used to establish the critical noncovalent interaction. In addition, we have demonstrated that sapphyrin is an excellent low-energy partner for porphyrins; the described ensembles undergo fast excitation transfer with high efficiency. Thus, it appears that sapphyrin could be a useful component in multi-chromophoric arrays for multi-step energy-transfer events. Finally, a number of other expanded porphyrin systems with different anion binding characteristics and different optical properties could be employed.

Experimental Section

General Information. All solvents and chemicals were of reagent or spectral grade quality, purchased commercially and used without further purification except as noted in the materials section below.

Column chromatography was performed on Merck type 60 (230–400 mesh) silica gel. Thin-layer chromatography (TLC) was performed on commercially prepared silica gel plates purchased from Whatman International, Inc.

Absorbance spectra were recorded on a Beckman DU-640 spectrophotometer. Steady-state fluorescence spectra were recorded on a Perkin-Elmer LS5 instrument. Proton NMR spectra were recorded on either General Electric QE-300 (300 MHz), Bruker 250 (250 MHz), or Bruker AMX-500 (500 MHz) instruments. Carbon NMR spectra were recorded at 75 or 125 MHz with either a QE-300 (300 MHz) or a Bruker AMX-500 (500 MHz) spectrometer, respectively. Nonlinear least-squares NMR curve fits were performed by using the Whitlock algorithm,³¹ EQNMR,³² or the commercially available Kaleidagraph program.

High-resolution mass spectra (HRMS) were recorded with a Bell and Howell 21-110B instrument. For fast atom bombardment mass spectrometric (FAB) measurements, nitrobenzyl alcohol (NBA) was used as the matrix. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, Georgia).

Fluorescence lifetimes were measured by time correlated single photon counting with use of a mode-locked, synchronously pumped, cavity-dumped Rhodamine 6G dye laser. The excitation wavelength used was typically 573 nm, and the emission was collected at a variety of wavelengths between 600 and 700 nm.

Femtosecond transient absorption studies were carried out by using a system that has been described previously.³³ Briefly, the amplified output of a Ti:sapphire laser (300 μ J, 835 nm) was split and 95% was frequency doubled to serve as the pump beam. Samples were typically excited with 0.5–1 μ J, 150 fs, 417 nm pulses. The remaining 5% of the amplified 835 nm light was used to generate a white light continuum probe; this was done by focusing the beam into a piece of sapphire. The probe beam was polarized at the magic angle (54.7°) with respect to the pump beam. Amplified photodiodes were used to detect single wavelengths of the probe light after it passed through a monochromator (SPEX model 270M). The photodiode outputs were digitized and recorded with a personal computer. Multiexponential rise and decay fits to the data were determined by using the Levenberg–Marquardt algorithm.

Materials. The free-base form of sapphyrin **1** was obtained as described earlier.¹⁵ Compounds **2–4** were prepared as described previously.⁷ Dichloromethane over calcium hydride was distilled prior to use. Trifluoroacetic acid (protein sequencing grade) was purchased from Sigma Chemical Company. Anhydrous dichloromethane was purchased from Aldrich Chemical Co. (Sure-Seal). All other solvents used were reagent grade quality and used without further purification unless otherwise noted. Tetrabutylammonium salts were generated by the addition of 1 equiv of tetrabutylammonium hydroxide (1 M in methanol, (Aldrich)) to the free acid in dry dichloromethane or methanol.

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