A Noncovalent Assembly for Energy Transfer Based on Anion Chelation

Vladimír Král, Stacy L. Springs, and Jonathan L. Sessler*

Department of Chemistry and Biochemistry and Center for Fast Kinetics Research University of Texas at Austin, Austin, Texas 78712

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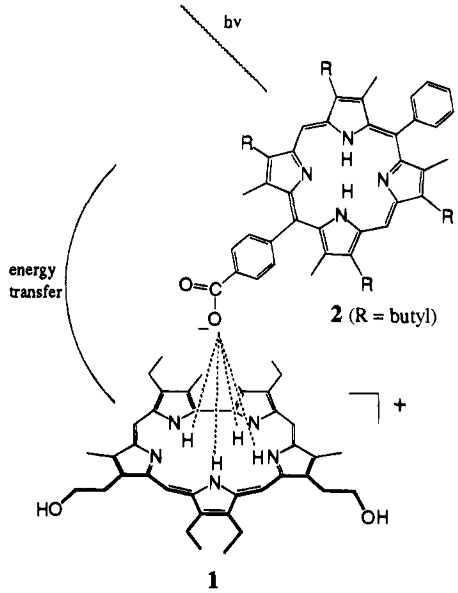
Considerable debate within the electron transfer/photosynthetic modeling community continues to be devoted to the question of how specific protein pathways might, or might not, be influencing long-range biological electron and energy transfer events.[1] Much of this debate has been concerned with salt bridges, and this, in turn, has focused renewed attention on electrostatically linked, noncovalently assembled, donor−acceptor conjugates.[2] Unfortunately, the available assemblies, which could serve as simple salt-bridge-containing energy or electron transfer model systems, are all characterized by a face-to-face[2−4] orientation between the relevant redox active partners. Thus, there is a clear need at present for electrostatically assembled donor−acceptor systems that enforce alternative geometries. Here, we report such a system (ensemble **I**). It is based on salt bridge formation between a carboxyl-bearing porphyrin photodonor and an anion-binding protonated sapphyrin acceptor.



I

The sapphyrins (e.g., **1**) are pentapyrrolic macrocycles that differ from their simpler porphyrin "cousins" in several important ways. The sapphyrins, for instance, do not coordinate cations readily. However, when mono- or diprotonated, they act as excellent receptors for a variety of *anions* including halides, phosphates, sulfates, and carboxylates.[5] In addition, the sapphyrins are green, not purple, and are characterized by red-shifted absorption and emission bands.[5] Finally, they possess first excited singlet states that are ca. 0.20−0.25 eV lower in energy than those of the porphyrins.[6,7]

An appreciation of the above features led us to consider that it might be possible to design sapphyrin-based systems, such as **I**, wherein anion binding is used to establish the critical donor-to-acceptor interactions. In system **I**, which was designed to be prototypic of this seemingly new approach to salt bridge electron and/or energy transfer modeling, the key predicative assumptions were that (1) a readily accessible[8] carboxyl-substituted porphyrin (**2**) could serve both as a well-understood, biologically-relevant photodonor and a simple-to-bind anionic substrate, while (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 pseudo-dimer,[7] that irradiation of the porphyrin subunit in **I** 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.

Despite the above predictions, it was actually not known at the outset of the present study whether simple monomeric carboxylate anions would bind to protonated sapphyrins with high affinity in organic solvents. Previous work had served only to establish that (1) trifluoroacetate anions are bound to monooxosapphyrin derivatives in the solid state[9] and that (2) covalently linked sapphyrin dimers could chelate selected dicarboxylates in methanolic solution.[5] Thus, it was necessary to establish that ensemble **I** would in fact form under simple equilibrium mixing conditions. To this end, standard ^{1}H NMR binding titrations were carried out (cf., for example, Figure 1); these confirmed the expected 1:1 stoichiometry and established a K_a for ensemble **I** of $(2.6 \pm 0.5) \times 10^3$ M^{-1} in CD_2Cl_2.[10]

Once this predicative molecular recognition work was complete, a variety of time-resolved fluorescence measurements were made in an effort to characterize the intraensemble energy transfer dynamics of system **I**. In the case of the porphyrin

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(1) (a) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, *355*, 796. (b) Beratan, D. N.; Onuchic, J. N.; Winkler, J.; Gray, H. *Science* **1992**, *258*, 1740. (c) Baum, R. M. *Chem. Eng. News* **1993** (Feb 22), 20. (d) Pelletier, H.; Kraut, J. *Science* **1992**, *258*, 1748.

(2) (a) Ojadi, E.; Selzer, R.; Linschitz, H. *J. Am. Chem. Soc.* **1985**, *107*, 7783. (b) Hofstra, U.; Koehorst, R. B. M.; Schaafsma, T. *J. Chem. Phys. Lett.* **1986**, *130*, 555. (c) Hugerat, M.; Levanon, H.; Ojadi, E.; Biczok, L.; Linschitz, H. *Chem. Phys. Lett.* **1991**, *181*, 400. (d) Segawa, H.; Takehara, C.; Hondo, K.; Shimidzu, T.; Asahi, T.; Mataga, N. *J. Phys. Chem.* **1992**, *96*, 503.

(3) An electrostatic, salt-bridge type approach to stabilizing side-by-side donor−acceptor orientations has recently been reported: Kirby, J. P.; van Dantzig, N. A.; Chang, C. K.; Nocera, D. G. *Tetrahedron Lett.* **1995**, *36*, 3477−3480.

(4) Perpendicular binding geometries have been stabilized by metal-based ligation approaches, a strategy that necessarily differs from the *metal-free* one presented here. For representative examples, see: (a) Anderson, H. L.; Hunter, C. A.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 226. (b) Hunter, C.; Sanders, J.; Beddard, G.; Evans, S. *J. Chem. Soc., Chem. Commun.* **1989**, 1765. (c) Kimura, A.; Funatsu, K.; Imamura, T.; Kido, H.; Sasaki, Y. *Chem. Lett.* **1995**, 207.

(5) The anion binding characteristics of the protonated sapphyrins are now well documented. In fact, single-crystal X-ray diffraction structures are available for many adducts, including the bis(diphenylphosphate) and bis(*p*-tosylate) complexes; both show a near-perpendicular anion-to-sapphyrin orientation (Král, V.; Lynch, V.; Sessler, J. L. Unpublished results). (a) Shionoya, M.; Furuta, H.; Lynch, V.; Harriman, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 5714. (b) Sessler, J. L.; Furuta, H.; Král, V. *Supramol. Chem.* **1993**, *1*, 209. (c) Iverson, B. L.; Shreder, K.; Král, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 11022−11023. (d) Král, V.; Andrievsky, A.; Sessler J. L. *J. Am. Chem. Soc.* **1995**, *117*, 2953.

(6) Excited state energy levels were calculated from the intersection between the absorbance and fluorescence spectra. The one-electron reduction potential of monohydrochloride salt of sapphyrin is −0.53 V vs Ag/AgCl. The one-electron oxidation potential of **2** is 1.23 V vs Ag/AgCl, and its excitation energy, taken from the intersection between absorption and fluorescence spectra, is 2.0 eV. Therefore, unidirectional photoinduced energy transfer from the porphyrin excited singlet state to sapphyrin is expected to be thermodynamically favorable by ca. 0.24 V. See also ref 7.

(7) Sessler, J. L.; Brucker, E.; Kral, V.; Harriman, A. *Supramol. Chem.* **1994**, *4*, 35.

(8) Porphyrin **2** was prepared from the mixed condensation of benzaldehyde, 4-carboxybenzaldehyde, and bis(3-butyl-4-methyl-2-pyrryl)methane. See the supporting information for characterization data.

(9) Hoehner, M.; Sessler, J. L. Unpublished result.

(10) Binding constants (K_a) and stoichiometries were determined from either ^{1}H or ^{2}D NMR titrations carried out in accord with the general methods reported earlier;[5d] in all cases, the change in chemical shift of the signals ascribed to the benzoic acid portion of the molecule were monitored as a function of increasing concentration of free-base sapphyrin. In these titrations, the free-base form of **1** was added to CD_2Cl_2 solutions of **2** (as its free acid). Because of the manner in which it was recorded, this K_a value reflects only electrostatic binding contributions. See footnote 18.

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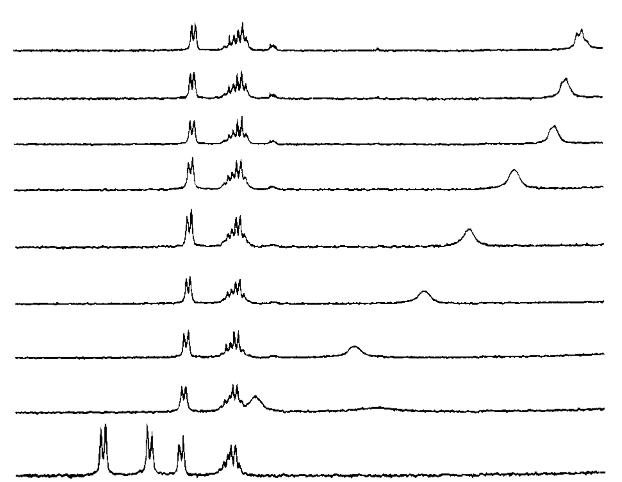
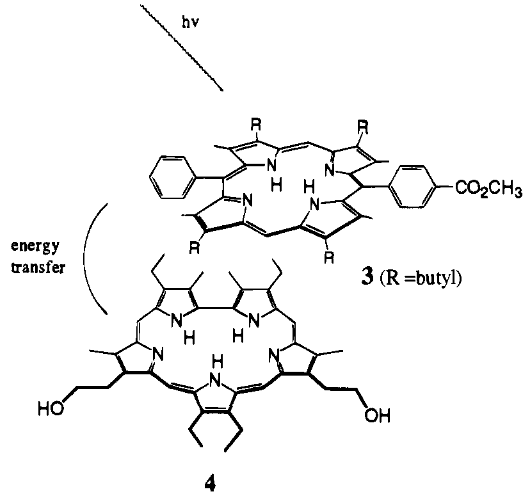


Figure 1. ^{1}H NMR spectroscopic titration of free-acid **2** with free-base **1** in CD_2Cl_2. The initial concentration of porphyrin acid **2** is 1.72 × 10^{-3} M, and the stacked plots show the effect of adding up to 4.0 equiv of free-base sapphyrin **1** to this solution. The observed upfield shifts of the *m*-carboxyphenyl proton resonances of **2** are consistent with the formation of ensemble **I** upon addition of **1**; see text.

acid corresponding to **2**, such analyses, carried out in dry CH_2Cl_2, yielded a monoexponential decay with a lifetime of 12.3 ns, with similar dynamic behavior being recorded for the anion of **2** itself (studied as the pyridinium salt).[11] Addition of sapphyrin **1** (as the free base; 0–600 μM) to **2** (in its free-acid form) then produced a biexponential fluorescence decay which could be analyzed in terms of two components, a long component with a 12.3 ± 0.8 ns lifetime and a short component with a lifetime of 500 ± 60 ps. The fractional amplitude of the shorter lived component increased with increasing sapphyrin concentration, but the lifetime remained essentially unchanged.[12] The fractional contribution of the shorter lived component increased from 0 to 88% in the presence of 6.0 × 10^4 M sapphyrin.[13] The shorter lived component is attributed to unidirectional singlet–singlet energy transfer[14] from **2** to **1** within the anion-chelation-based complex, while the longer lived component is attributed to uncomplexed **2**. The photoinduced energy transfer rate from **2** to **1** is $(1.8 \pm 0.2) \times 10^9$ s^{-1} with a quantum yield of $\Phi = 0.96$.[15] This rate is consistent with the rate constant calculated from Förster theory.[16] There was no observable deuterium isotope effect on the rate of photoinduced singlet–singlet energy transfer, which is also consistent with a dipole–dipole mechanism.

As a control, the porphyrin ester **3** (1.9 × 10^4 M in CH_2Cl_2) was also studied in the presence of free-base sapphyrin. (6.0 × 10^4 M in CH_2Cl_2). In this case, ca. 23% fluorescence quenching was observed. The time-resolved fluorescence decay was biphasic under these conditions with both long lived (12 ns) and shorter lived components ($\leq$300 ps) being observed. While the first of these could be assigned to the uncomplexed porphyrin **3**, the latter was rationalized in terms of an intrasubunit energy transfer process taking place within a π–π stacked, face-to-face porphyrin–sapphyrin dimer (complex **II**),[17] an interpretation supported both by the low K_a value recorded for **II** in CD_2Cl_2 ($(4.0 \pm 0.3) \times 10^2$ M^{-1})[18] and by salt-bridge disrupting solvent mixing studies. The latter studies involved adding methanol (6% v/v) to a 4:1 ratio of **1** and **2** (combined as the respective free base and free acid). Under these conditions, the fractional amplitude of the shorter lifetime decreased from 90 to 30%. However, when a similar quantity of methanol was added to a 3.2:1 ratio of free-base sapphyrin **4** and porphyrin ester **3** (cf. structure **II**), the fractional amplitude of the short lifetime was found to remain unchanged. Taken together, these findings are consistent with the methanol serving to disrupt the salt bridge in **I** but not the π–π stacking interactions present in **II**. Thus, while control **II** is not as "clean" as one might like, it nonetheless serves to support the critical finding that electrostatic, salt-bridge-like interactions are the dominant binding force present in the photoactive ensemble **I**.



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II

In summary, we have described here what appears to be a unique approach to noncovalent electron and energy transfer that is based on anion chelation. Extensions of this approach involving, say, the binding of sulfate or phosphate species could, conceivably, be used to construct higher order multichromophoric arrays wherein a greater number of donors and/or acceptors are held together within a single supramolecular assembly.

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Supporting Information Available: Text describing NMR spectral characterization of complexes **I** and **II** (including curve fitting analyses), table giving mass spectrometric data for complex **I**, and figures displaying visible absorbance spectra for complexes **I** and **II**, time resolved emission decay profiles for compound **2** and complex **I**, and solvent mixing results for complexes **I** and **II** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[11] The free-base form of porphyrin **2**, and independently its pyridinium salt, was photoexcited at 573 nm using a Rhodamine 6G mode-locked, synchronously pumped cavity dumped dye laser, with the monitored emissions being analyzed at several different wavelengths and over a range of time domains.

[12] The emission was monitored at ~630 nm, where there is no emission for free-base sapphyrin or the monohydrochloride salt of sapphyrin.

[13] At the highest concentration of sapphyrin (600 μM), the relative amplitude of the shorter lived component is expected to be ca. 55–60% on the basis of a K_a of $(2.6 + 0.5) \times 10^3$ M^{-1}. However, π-stacking interactions, for which $K_a = (4.0 \pm 0.3) \times 10^2$ M^{-1}, are expected to raise this by ca. 20%. The resulting "mismatch", 75–80% shorter lived component calculated *versus* 88% observed, is ascribed to experimental error.

[14] The quenching is ascribed to energy transfer, as opposed to electron transfer on the basis of the observed sapphyrin-based fluorescence (at 715 nm); such emission would not be expected from the kinds of radical species one might expect to obtain as the result of an electron transfer process. See also ref 7.

[15] The lifetimes were measured by time-correlated single photon counting and the rate constant was derived as $k_{ss} = 1/\tau_2 - 1/\tau_1$.

[16] Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

[17] On the basis of studies with covalent systems, the rate of porphyrin-to-sapphyrin energy transfer in a π–π associated face-to-face pseudo-dimer is expected to be very fast; cf. ref 7.

[18] Determined by ^{1}H NMR titrations carried out in a manner analogous to those made in the case of **I**. In these titrations, no shifts in the carboxyl-bearing phenyl signals were observed. This means that, in the case of **I**, the changes associated with these latter provide a direct measure of salt-bridge binding (only). In other words, the K_a value of $(2.6 \pm 0.5) \times 10^3$ M^{-1} cited for **I** contains no π–π stacking contribution.