

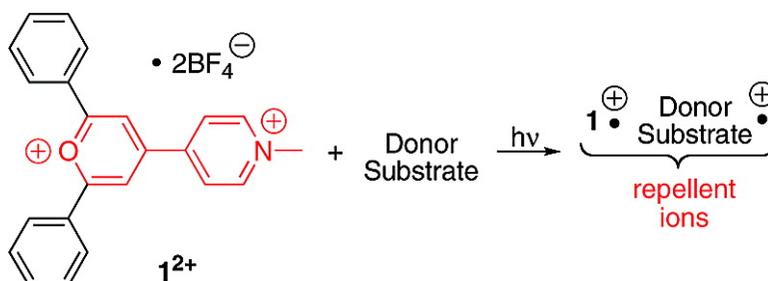
Communication

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Pyrylogens: Synthesis, Structural, Electrochemical, and Photophysical Characterization of a New Class of Electron Transfer Sensitizers

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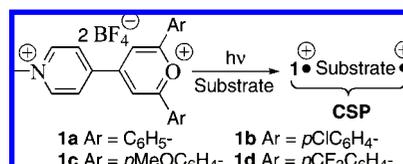
The past 25 years has seen the development of a remarkable array of photochemical electron transfer (PET) reactions with significant synthetic potential.¹ Unfortunately, this potential is often not realized because return electron transfer (RET) limits the efficiencies of these reactions and in the worst case scenarios allows detrimental side reactions to dominate. Consequently, it is not surprising that considerable effort has been expended to prevent energy-wasting RET.² These efforts include (1) thermodynamic manipulations of the energetics of return electron transfer to put the system deep in the Marcus inverted region where RET is too slow to compete with the chemical reaction of interest;³ (2) the use of steric effects in either the substrate or sensitizer to increase substrate–sensitizer distance in the ion pair intermediate decreasing the electronic coupling matrix element for RET;⁴ (3) the generation of triplet ion pair intermediates in which RET is spin-forbidden;⁵ (4) amplification of the quantum yields by design of electron transfer chain reactions;⁶ (5) the use of cosensitizers;^{2a} and (6) the use of charge-shift reactions that eliminate Coulombic attraction between the reduced sensitizer and substrate radical cation thereby enhancing their diffusive separation.^{2b}

In this Communication we report the synthesis and properties of a new class of sensitizers, pyrylogens **1a–d** (Scheme 1), that are formally hybrids of pyrylium cations and viologens. These compounds were fabricated to extend the charge shift concept from cationic to dicationic sensitizers. The diaryl-pyrylium chromophores in the pyrylogens impart desirable optical properties while the pyridinium ring provides a residual positive charge on the sensitizer in the charge shift product (CSP) that is designed to repel the substrate radical cation and competitively inhibit RET.

The key step in the synthesis of the pyrylogens⁷ (Scheme 2) is oxidative cyclization of a 1,5-dione patterned after the most popular method to generate triarylpyrylium salts.⁸ Triphenyl carbenium ion⁹ is preferred to benzalacetophenone as a hydride acceptor because a small amount of retro-Michael addition in the 1,5-diketone can lead to formation of trace amounts of a triarylpyrylium cation contaminant. The structures of the pyrylogens were confirmed by standard structural characterization methods (see Supporting Information) and in the case of **1a** by metathesis with $\text{KB}(\text{C}_6\text{F}_6)_4$ to form crystals suitable for X-ray diffraction. In the solid state the pyrylogen is sandwiched in between the two counterions and is characterized by rotation of the pyridinium ring 53° out of the plane of the pyrylium core.

The pyrylogens, **1a–d**, are reduced by cyclic voltammetry (CV) in two one-electron chemically reversible and electrochemically quasireversible steps (Table 1). The reduction potentials for formation of both the radical cation (slope = 0.34; $R^2 = 0.9988$) and the neutral (slope = 0.12; $R^2 = 0.97$) redox partners are linearly related to the Hammett substituent constant σ^+ . Replacement of the 4-phenyl ring in 2,4,6-triphenylpyrylium tetrafluoroborate, **2**⁺, with the methyl-pyridinium ring in **1a** increases the ease of reduction by over 500 mV. The pyrylogen radical cations, in stark

Scheme 1. Pyrylogens and the Repulsive CSP



Scheme 2. Synthesis of Pyrylogens

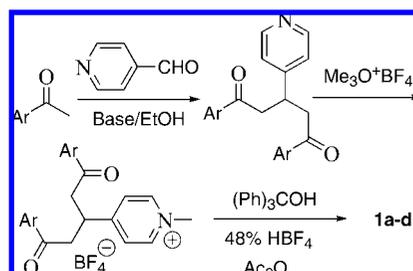


Table 1. Photophysical and Electrochemical Data for **1a–d** and **2**⁺

	1a	1b	1c	1d	2 ⁺
$E_{1/2}(1)^a$	0.17	0.19	0.05	0.37	−0.35
$E_{1/2}(2)^a$	−0.35	−0.35	−0.42	−0.27	−1.53
λ_F^b	533	556	659	494	465
λ_P^c	565	588	665	546	520
τ_F^d	3.42 ± 0.23			2.1 ± 0.21	4.1(2.9) ^e
τ_P^e	35.6 ± 0.2	38.3 ± 1	25.4 ± 0.6	33.9 ± 0.2	225 ± 3
$E(S_1)^f$	59	56	48	63	65 ⁱ
$E(T_1)^f$	54	53	48	57	53 ⁱ
Φ_F^g	0.18 ± 0.01	0.43 ± 0.01	<i>h</i>	0.24 ± 0.01	0.60 ⁱ
Φ_T	0.03 ± 0.02				

^a In volts versus SCE. ^b In nanometers (nm) at 298K. ^c In nm in EtOH/HCl(g) at 77K. ^d In nanoseconds (ns). ^e In milliseconds (ms) at 77K in EtOH/HCl(g). ^f In kcal/mol. ^g Fluorescence quantum yield in CH₃CN. ^h Too small to measure. ⁱ Miranda, M. A.; García, H. *Chem. Rev.* **1994**, *94*, 1063–1069. ^j Haucke, G.; Czerney, P.; Cebulla, F. Absorption and Fluorescence of Pyrylium Salts. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 880–886. CH₃CN(CH₂Cl₂).

contrast to **2**⁺, do not react with oxygen even at 50 mV/sec scan rates. We attribute this reluctance to react with oxygen to the greater positive charge in the pyrylogen radical cations and to their more delocalized spin density in comparison to **2**⁺. Neither **2**⁺ nor **1**⁺**a–d** are thermodynamically capable of producing superoxide. Furthermore, irradiations of pyrylogens **1a–d** at 355 nm, where all the pyrylogens absorb (vide infra) did not produce emission at 1270 nm consistent with their inability to sensitize formation of singlet oxygen (¹Δ_g).

The UV–vis spectra for the pyrylogens and **2**⁺ are compared in Figure 1. The two lowest energy bands in **2**⁺ at 401 and 355 nm have been interpreted as two perpendicular chromophores polarized in the *X* and *Y* directions, respectively.¹⁰ This assignment is

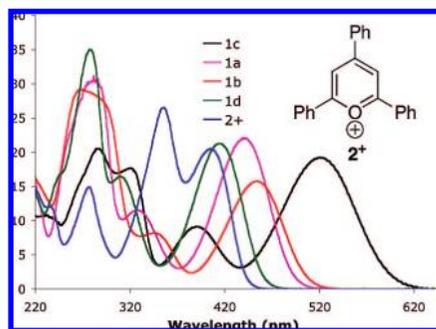


Figure 1. UV-visible spectra of **1a–d** and **2** in CH_3CN .

confirmed by time dependent DFT calculations on the B3LYP/6-31G(d) structure of 2^+ as shown in the Supporting Information. The UV-vis spectra of **1a–d** are qualitatively similar (Figure 1) but the Y-band, which is a charge-transfer band from the 4-aryl ring to the pyrylium core, is missing in the pyrylogens as a result of the electron poor character of the 4-pyridinium ring and has been replaced by a weaker intensity band that is essentially a charge shift from the 2,6-aryl rings to the pyridinium ring.

All of the pyrylogens also fluoresce and phosphoresce at the wavelengths shown in Table 1. The significantly smaller quantum yields of fluorescence for the pyrylogens in comparison to 2^+ is consistent with a previous suggestion that the Y chromophore, which is missing in the pyrylogens, is the predominant fluorophore in 2^+ .¹¹ The crossing point of the normalized absorption and fluorescence spectra were used to calculate the S_1 energies and the onset of the phosphorescence spectra were used to estimate the T_1 energies. These energies coupled with the reduction potentials suggest that the ionization potentials of the S_1 states increase in the order **1c** (2.13 eV) < 2^+ (2.47 eV) < **1b** (2.62 eV) < **1a** (2.73 eV) < **1d** (3.10 eV) and the T_1 states in the order 2^+ (1.95 eV) < **1c** (2.13 eV) < **1b** (2.49 eV) < **1a** (2.51 eV) < **1d** (2.84 eV).¹² These data suggest that S_1 and T_1 of all the pyrylogens, with the exception of electron rich S_1 -**1c**, are more potent oxidants than the popular pyrylium sensitizer, 2^+ .

Laser flash photolysis (LFP) of **1a** in 1,2-dichloroethane resulted in observation of two peaks at 370 and 560 nm (Supporting Information). Both peaks decay at the same rate suggesting that they arise from a common transient species. We have identified this transient as the triplet based upon the ability of oxygen to quench both the 370 and 560 nm peaks and on our previous observation that the pyrylogen radical cations do not react with oxygen even on the much longer time scale of a CV experiment. In addition, an independently generated radical cation of **1a** absorbs strongly at 614 nm (Figure 2).

The triplet-triplet absorbance spectrum of **1a** is dramatically enhanced and its fluorescence quenched by the addition of 1-bromobutane. This allowed measurement of the quantum yield for triplet formation using the method of Wilkinson.¹³ This accurate

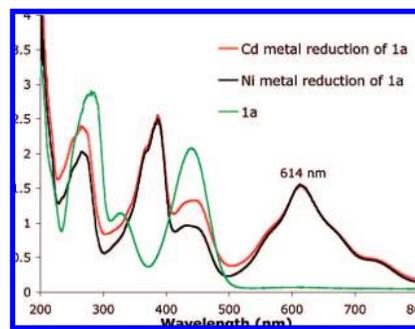


Figure 2. A comparison of the UV-vis spectrum of **1a** and its radical cation.

method, which only requires experimental ratios Φ_T/Φ_T^0 from LFP and Φ_f^0/Φ_f from Stern Volmer studies with 1-bromobutane, gives a value of 0.03 ± 0.02 for Φ_T^0 (Table 1).

Finally, we have also demonstrated that these pyrylogens act as sensitizers in the cleavage of *r*-1-, *c*-2-, *t*-3-, *t*-4-tetraphenylcyclobutane to form *trans*-stilbene.¹⁴ Work to establish the mechanism and to maximize and measure absolute efficiencies of these reactions are in progress.

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Supporting Information Available: Synthesis of **1a–d** and X-ray data for **1a**·**2B(C₆F₅)₄**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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