Synthesis, Characterization, Photophysics and Photochemistry of Pyrylogen Electron Transfer Sensitizers[†]

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ABSTRACT

A series of new dicationic sensitizers that are hybrids of pyrylium salts and viologens has been synthesized. The electrochemical and photophysical properties of these "pyrylogen" sensitizers are reported in sufficient detail to allow rationale design of new photoinduced electron transfer reactions. The range of their reduction potentials (+0.37-+0.05 V vs SCE) coupled with their range of singlet (48-63 kcal mol⁻¹) and triplet (48–57 kcal mol⁻¹) energies demonstrate that they are potent oxidizing agents in both their singlet and triplet excited states, thermodynamically capable of oxidizing substrates with oxidation potentials as high as 3.1 eV. The pyrylogens are synthesized in three steps from readily available starting materials in modest overall 11.4-22.3% yields. These sensitizers have the added advantages that: (1) their radical cations do not react on the CV timescale with oxygen bypassing the need to run reactions under nitrogen or argon and (2) have long wavelength absorptions between 413 and 523 nm well out of the range where competitive absorbance by most substrates would cause a problem. These new sensitizers do react with water requiring special precautions to operate in a dry reaction environment.

INTRODUCTION

The ostensibly minor modification of an organic substrate that occurs by addition or removal of an electron can open new reaction channels leading to remarkable bonding changes that are difficult or impossible to achieve by other methods. Consequently, these reactions have received considerable attention from both physical organic and synthetic organic chemists (1). Photoinduced electron transfer (PET) (2) potentially provides a convenient and green method to initiate these reactions since they can be engineered in favorable cases to bypass the use of stoichiometric methods employing chemical or photochemical oxidants or reductants whose remnants need to be separated from the desired reaction product at the end of the reaction. The green variant of the PET reaction requires regeneration of the electron-transfer photocatalyst (CAT) concomitant with product formation as illustrated in Scheme 1a. Photocatalysts (3,4) can either donate or remove an electron from a suitable substrate since upon promotion to an excited state they generate a hole that can potentially

act as the oxidant and an energetic electron that can function as a reductant.

The efficiency of green PET reactions critically depend upon the photocatalyst regeneration partition ratio ($\kappa_{\text{Reg}} = N_{\text{P}^{\oplus \bullet}}/N_{\text{R}^{\oplus \bullet}}$), where $N_{\text{P}^{\oplus \bullet}}$ and $N_{\text{R}^{\oplus \bullet}}$ are, for the reaction shown in Scheme 1, the number of product radical cations ($P^{\oplus \bullet}$) and reactant radical cations ($R^{\oplus \bullet}$), respectively, that oxidize CAT⁻⁻ to regenerate the photocatalyst CAT. Unfortunately, a significant number of the oxidations of CAT⁻⁻ by the reactant radical cation occur in a tight radical-cation/radical-anion pair ($R^{\oplus \bullet} \parallel \text{CAT}^{--}$) that forms in the initial electron transfer event. This nondiffusive return electron transfer (RET) is entropically favored with respect to oxidation with $P^{\oplus \bullet}$ and, as a consequence, is a major source of reaction inefficiency in many PET reactions.

In order to realize the full synthetic potential of PET reactions a significant amount of effort has been expended to minimize energy wasting RET in the tight ion pair ($R^{\oplus \bullet} \parallel CAT^{--}$). Several clever methods have been devised to discriminate against RET including the use of cosensitizers (5), the generation of triplet tight ion pairs where RET is spin forbidden (6), the use of substituent effects in order to place the RET deep in the Marcus inverted region where the rate constants are diminishingly small (7), and the use of charge shift (CS) reactions (8). Unfortunately, none of these methods are universally applicable and they have all generated mixed results. For example, the quantum yield of ion pair separation in the PET reaction of biphenyl (Scheme 2) exhibited only a modest increase from 0.18 to 0.33 as the attractive interaction in ion pair I was decreased by forming the nonattractive CS pair II (9) (Scheme 2).

In this manuscript, we describe in detail our synthesis, characterization, electrochemical and photophysical studies of new **pyry**lium-cation/vio**logen** hybrid CS sensitizers, the pyrylogens, **XPY**²⁺ (Scheme 1b) (10). These new photocatalysts were designed in anticipation that the repulsive interaction in the initially formed CS radical-cation/radical-cation pair would enhance k_{SEP} (Scheme 2) above that observed in ion pair I and CS pair II and completely inhibit RET (k_{RET} in Scheme 2).

MATERIALS AND METHODS

General aspects. 4-Pyridine carbaldehyde, acetophenone, *p*-chloroacetophenone, *p*-methoxyacetophenone, *p*-(trifluoromethyl)acetophenone, triphenyl carbinol, methyl iodide, trifluoroacetic acid, boron trifluoride dietherate, trimethyloxonium tetrafluoroborate, sodium hydride, and 2,4,6-triphenylpyrylium tetrafluoroborate were all obtained from Sigma-Aldrich and used without further purification. Tetra-*n*-butyl ammonium perchlorate was obtained from Fluka and recrystallized twice from

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Scheme 1. (a) Catalyzed photoinduced electron-transfer reactions. (b) Structures of pyrylogen photoinduced electron transfer catalysts.



Scheme 2. Photoinduced electron transfer reactions of biphenyl and structures of electron transfer initiated tight ion pairs.

ethanol and then dried at 40°C in a vacuum oven. Potassium tetrakis(pentafluorophenyl)borate was obtained from Boulder Scientific Company and used as received. 1-Iodobutane was obtained from Sigma-Aldrich and purified by passing it through a column of activated alumina. HPLC Grade acetonitrile was purified by refluxing with a small amount of CaH₂ for a few hours followed by distillation. THF was first distilled after refluxing with sodium for 2 h then redistilled from sodium/benzophenone ketyl. Methylene chloride was shaken with several portions of sulfuric acid until the acid layer remained colorless, then washed with water, 5% aqueous sodium bicarbonate, sodium hydroxide and finally with water. It was then predried with anhydrous calcium chloride and distilled from calcium hydride. Chloroform was washed with water to remove the ethanol stabilizer, dried over calcium chloride and distilled from P₂O₅. Tetra-*n*-butyl ammonium perchlorate is recrystallized from absolute ethanol and dried in vacuo at 75°C.

IR spectra were recorded on a Nicolet Nexus 470 FT-IR using OMNIC ESP 5.2 software. ElectroSpray Ionization mass spectra and MS/MS spectra were obtained with a Thermo-Finnigan LCQ mass spectrometer. The samples were prepared by addition of the compound of interest to methanol. UV–Visible spectra were collected on either an Agilent 8453 or on a Cary 50 spectrometer. Fluorescence and phosphores cence spectra were collected on a Cary Eclipse using concentrations that had less than 0.1 absorbance at the excitation wavelength. Cyclic Voltammetry was done with a CH Instruments Inc. CHI 900 electrochemical analyzer. Nanosecond laser flash photolysis was done using a Luzchem

miniaturized laser flash photolysis system coupled to a Spectra-Physics 10 Hz pulsed Nd:YAG laser. A Bruker EMX EPR spectrometer was used to acquire electron spin resonance (ESR) spectra. Proton and carbon NMR were obtained on a Bruker 400 MHz NMR and referenced to either the solvent or TMS.

Fluorescence lifetimes. Time resolved fluorescence lifetime measurements were made using a time-correlated single photon counting apparatus. The samples were irradiated at 400 or 420 nm obtained by frequency-doubling the 800 or 840 nm output of a Ti:Sapphire laser (Spectra Physics, Tsunami 3941) operating at a repetition rate of 80 MHz. Fluorescence was detected over 60-90 s intervals at the emission maximum (5 nm slit widths) and the traces were deconvoluted from the detector response function using the CFS_LS program. The detector response function was recorded using a piece of glass to direct some of the laser beam onto the detector and recording the subsequent signal at 405 and 425 nm using a slit width of 1 nm.

Cyclic voltammetry. All CV experiments were done in a three-electrode cell using glassy carbon as the working electrode, Ag/AgNO₃ (0.01 $\,\text{M}$ in CH₃CN) as a nonaqueous reference electrode, and a platinum wire as the counter electrode. Samples were 2×10^{-3} M in the substrate and ferrocene, which was used as an internal standard, and 0.1 M in the supporting electrolyte, Bu₄N⁺ ClO₄⁻. Samples were run at a variety of scan rates in both argon and oxygen atmospheres.

Computational chemistry. Geometry optimizations were performed with the Gaussian 03 program using the Becke/Stephens three parameter Lee–Yang–Parr correlation hybrid functional B3LYP in conjunction with the 6-311+G(2d,p) basis set. Frequency calculations were used to verify location of energy minima. The absence of spin contamination was verified in each calculation by examination of $\langle S^2 \rangle$ that showed values acceptably close to 0 for all singlets and to 0.75 for all doublets. TD-DFT calculations were done with the Gaussian 09 program using 6-311+G(2d,p) optimized geometries as input (11).

1,5-Diphenyl-3-(4-pyridyl)pentane-1,5-dione 1 (X = H). Sodium hydride (0.15 g; 6.00 mmol) was added to 15 mL of vigorously stirred methanol at 0°C followed by 5.0 g (41.7 mmol) of acetophenone. Pyridine-4-carbaldehyde (2.0 g; 19.0 mmol) was then added slowly in order to maintain the temperature between 0°C and 10°C. After addition was complete water was then added dropwise until the solution turns milky. A viscous oil settles to the bottom of the flask after stirring for 4 h. This mixture was then stored at 0°C for 12 h and the resulting solid filtered and recrystallized from 95% ethanol to afford 3.11 g (50% yield) of creamy white crystals. m.p. 125–126°C. ¹H NMR (CDCl₃) δ 3.4(dd, J = 7.3, 17.2 Hz, 2H), 3.53(dd, J = 6.7, 17.2 Hz, 2H), 3.89(tt, J = 6.7, 17.4 Hz, 1H), 7.36(m, 2H), 7.52(m, 4H), 7.65(m, 2H), 7.95(m, 4H), 8.41 (m, 2H). ¹³C NMR (CDCl₃) δ 36.2, 43.9, 123.8, 128.4, 129.2, 133.8, 137, 150, 153.7, 198.7.

3-(1-Methylpyridium-4-yl)-1, 5-diphenylpentane-1, 5-dione Iodide 2 (X = H). Methyl iodide (1.0 g; 0.0068 mol) was added to a solution of 2.78 g (0.00850 mol) of 1, 5-diphenyl-3-(4-pyridyl) pentane-1, 5-dione in 5 mL of chloroform. The solution is stirred for half an hour at room temperature. After evaporation of chloroform at 20 mmHg, the green oil is triturated with diethyl ether and the yellow crystals are recrystallized from ethanol. Yield(1 g, 30%), m.p. 180–182°C. ¹H NMR (CF₃COOH/CDCl₃ (1:2)) δ 3.45(dd, *J* = 7.8, 17.3 Hz, 2H), 3.52(dd, *J* = 6.3, 17.3 Hz, 2H), 4.28(s, 3H), 4.25(quintet, *J* = 6.5 Hz, 1H), 7.45(m, 4H), 7.65(m, 2H), 7.95(m, 4H), 8.25(m, 2H), 8.95(m, 2H). ¹³C NMR (CF₃COOH/CDCl₃ (1:2)) δ 36.4, 43.6, 47.6, 127.5, 128.4, 129.3, 134.0, 136.6, 145.1, 164.9, 198.0.

4-(2,6-Diphenylpyrylium-4-yl)-1-methylpyridinium bistetrafluoroborate. (HPY²⁺) Boron trifluoride (10 mL) is added dropwise with stirring to a solution of benzalacetophenone(0.5 g) and 3-(1-methyl-4-yl)-1,5-diphenylpentane-1,5-dione iodide (0.84 g, 0.0020 mol) in 5 mL of hot acetic acid. The mixture is refluxed for 12 h. After cooling to room temperature and addition of diethyl ether (20 mL), crystallization occurred. Recrystallization from acetic acid/acetonitrile afforded yellow crystals. Yield: 0.66 g, 76%. ¹H NMR (CF₃COOH/CDCl₃ (1:2)) δ 4.58 (3H, s), 7.8(t, J = 8.4 Hz, 4H), 7.9(t, J = 7.6 Hz, 2H), 8.45(d, J = 7.5 Hz, 4H), 8.71(d, J = 6.8 Hz, 2H), 8.81(s, 2H), 9.02(d, J = 6.8 Hz, 2H). ¹³C NMR (CD₃CN) δ 50.0, 119, 128.4, 129.6, 130.4, 8.71(d, J = 6.8 Hz, 2H), 8.81(s, 2H), 9.02(d,131.4, 137.6, 147.9, 149.4, 161, 174.0. Elemental analysis: Found (C, 53.7; H, 4.0; N, 2.8%), Calculated for $C_{23}H_{19}B_2F_8NO$ (C, 55.4; H 3.8; N, 2.8), Calculated for C₂₃H₁₉B₂F₈NO·H₂O (C, 53.4; H, 4.1; N, 2.7%). IR (KBr) 3090, 1630, 1520, 1430, 1270, 1210, 1090 cm⁻¹. ESI-MS *m/z* (%): 356.4 ($M^{++} + CH_3O^-$, 100). ESI-MSMS m/z (%): 325.4(M^{++} , 100).

1,5-Di-4-methoxyphenyl-3-(4-pyridyl)pentane-1,5-dione 1 (X = MeO). Pyridine-4-carbaldehyde (0.75 mL) was added to a warm solution of *p*-methoxy acetophenone (3.125 g) in 80% EtOH (12.5 mL) containing potassium hydroxide (0.375 g). The solution turns dark immediately and was heated under reflux (80°C) for 6 h. The solid product, which separated upon cooling, was recrystallized twice from EtOH to give white crystals. Yield: 1.3 g, 43%. ¹H NMR (CD₃CN) δ 3.31(dd, *J* = 7.4, 16.9 Hz, 2H), 3.46(dd, *J* = 8, 16.9 Hz, 2H), 3.87(s, 6H), 4.06(quintet, *J* = 7 Hz, 1H), 6.91–6.94(m, 4H), 7.25–7.27(m, 2H), 7.91–7.94(m, 4H), 8.49–8.50(m, 2H).

3-(1-Methylpyridium-4-yl)-1, 5- di-4-methoxyphenylpentane-1, 5-dione Iodide 2 (X = MeO). To a solution of 0.595 g (0.00850 mol) of 1, 5-di-4methoxyphenyl-3-(4-pyridyl) pentane-1, 5-dione in chloroform (1 mL), 0.22 g (0.0068 mol) of methyl iodide was added. The solution is stirred for half an hour at room temperature. After evaporation of chloroform at 20 mmHg, the red oil is triturated with diethyl ether and the crystals recrystallized from ethanol. Yield: (0.53 g, 90%). ¹H NMR (CD₃CN) δ 3.61– 3.62(m, 4H), 3.88(s, 6H), 4.21(small quintet under one big singlet, 4H), 7.00–7.03(m, 4H), 7.94–7.96(m, 2H), 8.03–8.05(m, 4H), 8.48–8.50(m, 2H).

4-(2,6-Di-4-methoxyphenyl pyrylium-4-yl)-1-methylpyridinium bistetrafluoroborate (MeOPY²⁺). Prepared by the method used to prepare **HPY²⁺** (*vide supra*). Yield: 0.3 g, 55%. ¹H NMR (CD₃CN) δ 4.01 (s, 6H), 4.45 (s, 3H), 7.28–7.31 (d, J = 9.1 Hz, 4H), 8.41–8.43(d, J = 9.1 Hz, 4H), 8.47 (s, 2H), 8.57–8.59(d, J = 6.8 Hz, 2H), 8.94–8.95 (d, J = 6.8 Hz, 2H). ¹³C NMR (CD₃CN) δ 49.9(q, J = 146 Hz), 57.3(q, J = 146 Hz), 116.0(d, J = 176 Hz), 117.1(d, J = 164 Hz), 121.9(s), 128.0(d, J = 176 Hz), 132.9(d, J = 164 Hz), 147.8(d, J = 194 Hz), 156 (s), 158.3(s), 167.8(s), 172.3(s). Elemental analysis: Found (C, 52.0; H, 4.22; N, 2.43), Calculated for C₂₅H₂₃B₂F₈NO₃ (C, 53.7; H, 4.1; N, 2.5), Calculated for C₂₅H₂₃B₂F₈NO₃ H₂O (C, 52.03; H, 4.36; N, 2.43). IR (KBr): 3125, 3086, 1606, 1626, 1415–1507, 1375, 1120–1270 cm⁻¹. ESI-MS m/z (%): 416.5 (M⁺ + CH₃O⁻, 100). ESI-MSMS m/z (%): 385.5 (M⁺, 100).

1, 5-Di-*p*-chlorophenyl-3-(4-pyridyl) pentane-1, 5-dione 1(X = Cl). *p*-Chloroacetophenone (3.2 g, 21 mmol) was added to a solution of 0.15 g sodium hydride in 15 mL of anhydrous methanol at 0°C. The cloudy solution is stirred vigorously. Pyridine-4-carbaldehyde 1.50 g (14.2 mmol) is added slowly maintaining the temperature at 0–10°C. Water was added dropwise until the solution became milky. After stirring the solution for one hour, white crystals were formed. The solution was placed in ice for one hour and the resulting crystals were filtered and recrystallized from 90% ethanol. After being dried in a vacuum oven at room temperature, white crystals were obtained (1.24 g, 55%), m.p. 163–165°C. ¹H NMR (CDCl₃) δ 3.35(dd, J = 11, 7 Hz, 2H), 3.49(dd, J = 11, 7 Hz, 2H), 4.03(m, 1H), 7.2(d, J = 5 Hz, 2H), 7.4(dd, J = 5, 2 Hz, 4H), 8.5(d, J = 5 Hz, 2H). ¹³C NMR (CDCl₃) δ 3.6.5, 43.4, 128.4, 129.3, 129.8, 134.5, 140.3, 144.3, 165.8, 196.5.

3-(1-Methylpyridinium-4-yl)-1,5-di-*p*-chlorophenylpentane-1,5-dione tetrafluoroborate 2(X = Cl). 1,5-di-*p*-Chlorophenyl-3-(4-pyridyl) pentane-1,5-dione (1.5 g, 3.8 mmol) was dissolved in 30 mL of chloroform. Trimethyloxonium tetrafluoroborate (0.59 g, 4.0 mmol) was added to the mixture and stirred for 30 min. The solvent was evaporated *in vacuo*. Ethanol (95%) was added and gently heated in order to dissolve the entire residue. The cooled solution was refrigerated for 25 min inducing precipitation of white crystals. The crystals were filtered and dried in a vacuum oven at room temperature to afford 1.25 g, 65.8% yield of product. m.p. 107–108°C. ¹H NMR (CDCl₃) δ 8.5(d, J = 7 Hz, 2H), 8.1(d, J = 7 Hz, 2H) 7.85(dd, J = 9, 8 Hz, 4H), 7.35(dd, J = 9, 8 Hz, 4H), 4.25(s, 3H), 4.10(m, 1H), 3.65(dd, J = 10, 7 Hz, 2H), 3.55(dd, J = 10, 7 Hz, 2H) ¹³C NMR (CDCl₃) δ 36.5, 43.4, 48.0, 128.4, 129.3, 129.8, 134.5, 140.3, 144.3, 165.8, 196.5.

4-(1-Methylpyridinium-4-yl)-2,6-di-p-chlorophenylpyrylium bistetrafluoroborate (CIPY²⁺). Triphenyl methanol (1.3 g, 5.0 mmol) was added to a 40 mL solution of 1.0 g (2.0 mmol) of 3-(1-methylpyridium-4-yl)-1,5-dip-chlorophenylpentane-1,5-dione tetrafluoroborate (1.0 g, 2.0 mmol) in acetic anhydride. A 50% HBF₄ solution, prepared by adding HBF₄ dropwise to cold acetic anhydride, was then added dropwise to the stirred dione solution. The mixture was then allowed to stir at 50°C for an additional 30 min. Diethyl ether was added to the cooled solution to induce formation of a precipitate. The precipitate was filtered and recrystallized from glacial acetic acid. After drying, it afforded orange crystal (0.56 g, 46% yield). m.p. 303-305°C. Elemental Analysis: Found (C, 48.35; H, 3.1; N, 2.5), Calculated for $C_{23}H_{17}B_2F_8NOCl_2$, (C, 48.64; H, 3.0; N, 2.5). ¹H NMR (CDCl₃/CF₃COOH) δ 4.6(s, 3H), 7.7(d, J = 9 Hz, 4H), 8.3(d, J = 9 Hz, 4H), 8.7(d, J = 7 Hz, 2H), 8.8(s, 2H), 9.0(d, J = 6 Hz, 2H). ¹³C NMR $(CDCl_3/CF_3COOH)$ 49.4(q, J = 147 Hz), 117.7(d, J = 177 Hz), 126.6(s), 128.3(d, J = 176 Hz), 130.7(d, J = 165 Hz), 131.8(d, J = 171 Hz), 146 (s), 147.3(d, J = 194 Hz), 149.6(s), 160.9(s), 173.5(s). IR (KBr) 3428, 1629, 1591, 1513, 1468, 1272, and 1088 cm⁻¹. UV–Vis λ_{max} 270, 345 and 455 nm. ESI-MS m/z (%): 424.1(M⁺⁺ + CH₃O⁻, 100), 426.1 (63), 427.1 (18), 393.2. ESI-MSMS m/z (%): 393.1(M⁺⁺, 100), 395.1(63), 394.1(25).

1,5-Di-4-trifluoromethylphenyl-3-(4-pyridyl)pentane-1,5-dione 1 (X = CF₃). Sodium hydride (0.2 g, 6 mmol) was added to 20 mL of vigorously stirred methanol at 0°C followed by 0.7 g of 4-trifluoromethyl acetophenone. Pyridine-4-carbaldehyde (0.535 g) is then added slowly maintaining the temperature at 0–10°C. Water was added dropwise until the solution became milky. The solution was kept stirring at room temperature overnight and a solid precipitated out during the reaction. The solution was filter and the filtrate was discarded. Crude product was purified by precipitation with MeOH/H₂O to give a creamy soft powder (0.3 g, 50%). ¹H NMR (CDCl₃) δ 3.42(dd, *J* = 6.8, 17.5 Hz, 2H), 3.56 (dd, *J* = 6.9, 17.5 Hz, 2H), 4.09(quintet, *J* = 6.8 Hz, 1H), 7.24(d, *J* = 6 Hz, 2H), 7.74(d, *J* = 8.1 Hz, 4H), 8.05(d, *J* = 8.1 Hz, 4H), 8.54(d, *J* = 6 Hz, 2H).

3-(1-Methylpyridium-4-yl)-1, 5- di-4-trifluoromethylphenyl -1, 5-dione tetrafluoroborate 2 (X = CF₃). A mixture of 1,5-di-4-trifluoromethylphenyl-3-(4-pyridyl)pentane-1,5-dione (320 mg, 0.688 mmol) and trimethyloxonium tetrafluoroborate (101 mg, 0.688 mmol) in 20 mL

anhydrous CH₂Cl₂ is stirred overnight at room temperature. After the removal of the solvent, the crude product is used directly in the next step (purity >95%). (360 mg, 95% yield). ¹H NMR (CD₃CN) δ 3.66(dd, J = 18.7, 8.0 Hz, 2H), 3.73(dd, J = 18.8, 5.4 Hz, 2H), 4.19(s, 3H), 4.22 (quintet, J = 5.8 Hz, 1H), 7.83(d, J = 8.3 Hz, 4H), 8.00(d, J = 6.6 Hz, 4H), 8.08(d, J = 8.3 Hz, 2H), 8.46(d, J = 6.8 Hz, 2H).

4-(2,6-Di-4-trifluoromethylphenyl pyrylium-4-yl)-1- methyl- pyridini-um bistetrafluoroborate (CF_3PY^{2+}). 3-(1-Methylpyridium-4-yl)-1,5-di-ptrifluoro-methylphenylpentane-1,5-dione tetrafluoroborate (0.38 g. 0.67 mmol) is dissolved in 10 mL of acetic anhydride and 0.436 g of triphenyl methanol (1.67 mmol) is added to the solution. A 50% HBF₄ solution, which was prepared by slowly adding 48% HBF₄ in H₂O to 10 mL of cold acetic anhydride, was then added dropwise to the rapidly stirred dione solution. The mixture was kept at 80°C for half an hour followed by addition of 100 mL diethyl ether to the cooled solution to induce precipitate formation. The precipitate was filtered and dried under vacuum at 100°C. (200 mg, 47% yield). ¹H NMR (CDCl₃/CF₃COOH) δ 4.59(s, 3H), 8.05(d, J = 8.4 Hz, 4H), 8.49(d, J = 8.4 Hz, 4H), 8.74(d, J = 6.4 Hz, 2H), 8.99(s, 2H), 9.00(d, J = 6.4 Hz, 2H). ¹³C NMR (CDCl₃/CF₃COOH;decoupled and gated coupled data) δ 49.4(q, J = 146 Hz), 119.6(d, J = 178 Hz), 123.3(q, 273 Hz), 128(d, J = 169 Hz, ${}^{3}J_{CF} = 3$ Hz), 128.2(d, J = 167 Hz), 130(d, J = 166 Hz), 131(s), 138.9(q, J = 34 Hz), 147.1(d, J = 195 Hz), 149(s), 162.4(s), 173.7(s). Elemental analysis: found (C, 46.7; H, 2.95; N, 2.16), Calc. for C₂₅H₁₇B₂F₁₄NO (C, 47.3; H, 2.7; N, 2.5), Calc. for C₂₅H₁₇B₂F₁₄NO·H₂O (C, 45.98; H, 2.93; N, 2.14). IR(KBr): 3124, 1631, 1528, 1322 cm⁻¹. ESI-MS m/z (%): 492.1 (M⁺⁺ + CH₃O⁻, 100). ESI-MSMS m/z (%): 461.1(100)

3-(1-methylpyridium-4-yl)-1, 5- diphenylpent-2-ene -1, 5-dione tetrafluoroborate. An aqueous solution of 10^{-4} M NaOH was added to a stirred mixture of **PY**²⁺ until the pH reaches 6. The mixture is then stirred for an additional 0.5 h and the pale yellow precipitate was filtered and recrystallized twice in hot water to give very low yield (15%) of the **PY**²⁺-H₂O-adduct. 1H NMR (CD₃CN) δ 8.63(d, 2H, J = 6.7 Hz), 8.17 (d, 2H, J = 6.7 Hz), 8.05–8.01(m, 4H), 7.77(s, 1H), 7.71–7.65(m, 2H), 7.59–7.53(m, 4H), 4.77(s, 2H), 4.29(s, 3H). 13C NMR (CD₃CN; decoupled and gated coupled data) δ 197.33(s), 191.87(s), 158.33(s), 146.43(d, J = 192 Hz), 145.93(s), 138.61(s), 137.44(s), 135.02(d, J = 162 Hz), 134.87(d, J = 162 Hz), 132.11(d, J = 159 Hz), 130.03(d, J = 164 Hz), 130.00(d, J = 164 Hz), 129.77(d, J = 161 Hz), 129.32(d, J = 161 Hz), 126.54(d, J = 173 Hz), 48.90(q, J = 145 Hz), 42.15(t, J = 130 Hz). Elemental analysis: C₂₃H₂₀BF₄NO₂, (C, 64.36%; H, 4.70%; N, 3.26%), Found: (C, 64.35%; H, 4.65%; N: 3.22%).

General sensitized irradiation conditions. Acetonitrile solutions containing between 5×10^{-4} and 1×10^{-3} M of $HPY^{2+}BF_4^{--}$ and 0.1 to 0.02 M substrate (see Fig. 7) were placed in pyrex flasks open to the atmosphere. These flasks were then irradiated with UVA lamps, tungsten halogen lamps, or medium-pressure Hanovia lamps, through 1 cm of a 75% aqueous NaNO₂ solution to insure elimination of all photons higher in energy than 420 nm. The reactions were then monitored by thin layer chromatography, gas chromatography, or NMR and generally were complete within 10 min to an hour. Preparative reactions were worked up by first washing with water to remove the charged hydrolysis product of the sensitizer. Then the organic layer was dried (MgSO₄) and removed by rotovap to give the products that were characterized by standard analytical techniques.

RESULTS AND DISCUSSION

Synthesis and structural characterization

We initially adapted a method used extensively for the synthesis of pyrylium cations, as shown in Scheme 3, for the construction of HPY^{2+} (12). The reaction is initiated by a base catalyzed condensation between acetophenone and pyridine-4-carbaldehyde to give an α -, β -unsaturated ketone that immediately undergoes a Michael addition with a second equivalent of acetophenone to give 1,5-diketone 1 (Scheme 3). Alkylation of this ketone with methyl iodide gives a pyridinium cation, **2**, that is subsequently oxidatively cyclized to give the pyrylogen.

Benzalacetophenone, 3, in the cyclization step shown in Scheme 3 functions as a hydride acceptor (oxidant) that is necessary in order to convert a 2H-pyran, or possibly 4H-pyran, intermediate into the pyrylium ring found in HPY²⁺. When this reaction was utilized to make MeOPY²⁺ a peak at 460 nm in the fluorescence spectrum that accompanied the emission of MeOPY²⁺ at 653 nm was observed. We tentatively identify this spurious emission to 2,4,6-triphenylpyrylium tetrafluoroborate $(\lambda_{em} = 465 \text{ nm})$ (13) that presumably forms by Michael addition of acetophenone to benzalacetophenone followed by oxidative cyclization. Apparently traces of acetophenone, only detectable in the emission and not NMR spectrum, formed under the reaction conditions by a minor background hydrolysis of benzalacetophenone, 3. On the other hand, a peak at approximately 540 nm was not observed for 2,4-diphenyl-6-(p-methoxyphenyl) pyrylium tetrafluoroborate ($\lambda_{em} = 538$ nm) (13) even though p-methoxyacetophenone is a potential product of retro-Michael addition of either the 1,5-diketone or alkylated 1,5-diketone intermediate in the formation of MeOPY²⁺. In order to prevent formation of 2,4,6-triphenylpyrylium tetrafluoroborate we replaced benzalacetophenone, 3, with trityl cation (Ph₃C \oplus) as the hydride acceptor for all the studies that required spectroscopically pure pyrylogen. The trityl cation was generated in situ by treatment of triphenylcarbinol with HBF4 during the last (oxidative cyclization) step (14). This strategy completely eliminated the emission peak at 460 nm and provided verification of its tentative assignment to 2,4,6-triphenylpyrylium tetrafluoroborate. Another advantage of this oxidative cyclization procedure is that it is readily adaptable to form pyrylogens with perchlorate (HClO₄/Ph₃COH) or hexafluorophosphate (HPF₆/Ph₃COH) counterions.

The structure of **HPY**²⁺ was confirmed with a crystal structure of its bis-tetra-perfluorophenyl borate, $(C_6F_5)_4B^-$ salt (Fig. 1). This counterion was used since repeated attempts to get X-ray quality crystals of **HPY**²⁺·2**BF**₄⁻ failed. The tetra-perfluorophenyl borate counterion was not incorporated in the pyrylogen during the oxidative cyclization step as described above. Instead, an ion exchange process that takes advantage of the enhanced solubility of the $(C_5F_6)_4B^-$ pyrylogens was used. When a mixture of



Scheme 3. Synthesis of pyrylogens.

the insoluble salts, $HPY^{2+} \cdot 2BF_4^-$ and $(C_5F_6)_4B^-K^+$, was stirred under a blanket of CH_2Cl_2 the methylene chloride gradually turned yellow as ion exchange occurred. Simple filtering of the KBF₄ and removal of the methylene chloride then gave pure $HPY^{2+} \cdot 2(C_6F_5)_4B^-$.

The dication is nonplanar with a pyridinium-pyrylium ring dihedral angle of 53.2° and phenyl-pyrylium ring dihedral angles of 10.2° . The two counterions sandwich the dication (Fig. 1) and exhibit close contact distances of 2.66 and 2.68 Å between the hydrogen on C₂, and 2.78 Å between the hydrogens on C₅, and fluorines on the perfluorophenyl rings. A similar geometry of the ion pair may also exist in solution since it is the hydrogens on C_2 (8.28 ppm) and C_5 (8.36 Å) that exhibit the largest ¹H NMR upfield shifts of 0.52 and 0.24 ppm when the BF_4^- counterion is replaced by $(C_6F_5)_4B^-$. The crystal structure geometry is remarkably well reproduced by density functional theory (DFT) calculations (15) using the B3LYP/6-311+G(2d,p) basis set with the exceptions of the pyridinium- (43.1°) and phenyl-pyrylium (16.2° and 16.7°) ring dihedral angles. The barrier for twisting around the single bond connecting the pyridinium and pyrylium rings at the B3LYP/6-31G(d) computational level is only about 2.1 kcal mol^{-1} and as a consequence the electronically preferred intra-ring dihedral angles could easily be sacrificed for favorable crystal packing energy. (see Supplementary Material for complete computational details).

Pyrylogen redox couple

In analogy to the isoelectronic viologens it was anticipated that pyrylogens would exist in three readily accessible redox states (Scheme 4). This contention is supported by computational studies at the B3LYP/6-311+G(2d,p) level that located the dication, radical cation and neutral redox partners. In the computed **HPY^x** structures the bond connecting the pyridinium and pyrylium rings decreases in length from 1.486 to 1.432 to 1.383 Å and the pyridinium–pyrylium ring dihedral angle decreased from 43.1° to 3.2° to 0.4° along the sequence dication-radical-cation-neutral as expected from the Lewis structures shown in Scheme 4.

The reduction potentials for the pyrylogens, XPY^{2+} , were determined in acetonitrile at a glassy carbon electrode relative to

the ferrocene-ferrocenium (16) ion redox couple (17). The first reduction potentials spanned a range of nearly one-third of a volt increasing in the following order $MeOPY^{2+}$ (+0.05 V) < HPY^{2+} $(+0.17 \text{ V}) < \text{CIPY}^{2+} (+0.19 \text{ V}) < \text{CF3PY}^{2+} (+0.37 \text{ V})$ all versus the standard calomel electrode (SCE). Remarkably, in dramatic contrast to the reduction to the radical-cation, the second reduction to the neutral redox couple was nearly insensitive to the substituent effect and only spanned a range of 0.15 V increasing in the order $MeOPY^{2+}$ (-0.42 V) < HPY^{2+} (-0.35 V) $CIPY^{2+}$ $(-0.35 \text{ V}) < \text{CF3PY}^{2+}$ (-0.27C) all versus SCE. These results, and for comparison, a series of substituted 2,6-diphenyl-4-X-phenyl-pyrylium salts, **XTPP⁺** can be viewed quantitatively by relating them to the substituent constants σ_{n+} as shown in Fig. 2. The effect of substituents on the reductions of **XTPP⁺** and **XPY**²⁺·**2BF**₄ is similar ($\rho^+ = 0.13$ and 0.16) but more than twice as large as that observed for reduction of **XPY**⁺. ($\rho^+ = 0.061$). The reduced effect of substituents on the reduction potentials of XPY^{+} in comparison to those observed for the dication, XPY^{2+} , is consistent with a Mulliken population analysis that reveals that the pyrylium ring in the dication bears a much greater positive charge than in the radical-cation (vide infra). It is also instructive to compare the reduction potentials of $XTPP^+$ (X = H; -0.35 V) to **HPY²⁺** (+0.17 V), which demonstrates that replacement of a phenyl ring with a pyridinium ring increases the ease of reduction by over 0. 5 V.

The radical cation formed during reduction of $\mathbf{HPY}^{2+} \cdot \mathbf{2BF_4}^$ did not react with oxygen on the CV time scale (50–500 mV s⁻¹) in contrast to the rapid reaction of the radical formed upon reduction of 2,4,6-triphenylpyrylium tetrafluoroborate. This is most likely a result of the enhanced electrophilic character of \mathbf{HPY}^+ in comparison to **XTPP**[•] (X = H).

Insight into the electronic character and potential reactivity of all three redox partners was obtained by partitioning the charge or charge/spin on the pyrylogens between the diarylpyrylium (red in Scheme 4) and *N*-methylpyridinium (blue in Scheme 4) functional groups using Mulliken population analysis and the B3LYP/6-311+G(2d,p) minimized geometries. In all the dications, **XPY²⁺**, the positive charge is greater on the diarylpyrylium (+1.239 \pm 0.083) than on the *N*-methylpyridinium (+0.760 \pm 0.083) groups. This is consistent with the enhanced



Figure 1. View of $[C_{23}H_{19}NO]$ 2 $[B(C_6F_{5})_4]$. Thermal ellipsoids are draw at 30% probability. Hydrogen atoms are omitted for clarity.



Scheme 4. Pyrylogen dication, radical-cation and neutral redox states.



Figure 2. Reduction potentials as a function of $\Sigma \sigma_{p+}$.

opportunity to delocalize the positive charge when placed on the diarylpyrylium (resonance structures A, B and C; Scheme 5) in comparison to the N-methylpyridinium (resonance structure D; Scheme 5) groups. In all the radical cations, **XPY**⁺, the charge is greater on the N-methylpyridinium (+0.748 \pm 0.056) than on the diarylpyrylium (+0.252 \pm 0.056) group but the spin is greater on the diarylpyrylium (0.558 \pm 0.045) than on the Nmethylpyridinium (0.442 \pm 0.045) group. This is consistent with the greater importance of resonance structure E than F in the overall electronic description of XPY+. In all the neutral redox partners, **XPY⁰**, polarization occurs to place a negative -0.284 ± 0.063 charge on the diarylpyrylium and a positive $+0.284 \pm 0.063$ charge on the *N*-methylpyridinium group. This Mulliken population analysis reflects the greater contribution of resonance structure G (Scheme 5) than resonance structure H to the description of the neutral redox partner. This CS (polarization) is consistent with lower electronegativity of nitrogen than oxygen and its ability to accommodate a positive charge.

Photophysical properties

The UV–Vis spectra for the pyrylogens, $XPY^{2+} \cdot 2BF_4^-$ are compared to the closely related 2,4,6-triphenylpyrylium

tetrafluoroborate, $TPP^+ \cdot BF_4^-$ (13), in Fig. 3 and Table 1. All the XPY^{2+} spectra, and for comparison TPP^+ were taken in CH₃CN since XPY^{2+} had limited solubility in less polar solvents. In order to explore the effect of solvent on the XPY^{2+} absorption spectra the BF_4^- counterions had to be exchanged to give $XPY^{2+} \cdot 2[B(C_6F_4)_4]^-$. For example, $HPY^{2+} \cdot 2[B(C_6F_4)_4]^-$ is soluble in CH₂Cl₂ and absorbs at 476 nm but shifts to 441 nm when dissolved in the more polar CH₃CN. This hypsochromic shift with increased solvent polarity is consistent with stabilization of a more polar ground state in preference to a less polar excited state.

The absorption spectra of alkyl- and aryl-substituted pyrylium cations were first examined in detail by Balaban *et al.* in 1960 (18). This study and several subsequent studies (19) that focused on the effect of substituents (20) on the appearance of the absorption spectra (21) came to two key conclusions (22): (1) The absorption spectra of pyrylium cations can be characterized by two chromophores one with its transition dipole oriented along the pseudo-*x*-axis passing through carbons 2 and 6 and the other lying along the C₂ axis passing through the aryl group on carbon 4 and the oxygen atom (23); (Scheme 6) and (2) Both of these transitions are charge transfer transitions involving migration of electron density from the aryl rings to the pyrylium core.



Scheme 5. Resonance structure rationalization of Mulliken charge and charge/spin distributions.

Examples of how substituent effects can provide evidence for these two conclusions are illustrated in Scheme 6.

The x-band (chromophore) is the lowest energy absorbance in **TPP**⁺ appearing at 404 nm in acetonitrile (Fig. 3) and at 421 nm in methylene chloride. The y-band is more intense and appears at 357 nm in acetonitrile and 371 nm in methylene chloride. Addition of the electron donating dimethylamino group to the paracarbon of the 2-phenyl group to generate 2-NMe₂TPP⁺ raises the 2-chromophore orbital energy and reduces the HOMO-LUMO gap shifting the x-band by 156 nm from 421 to 577 nm (24). The y-band experiences a much smaller hypsochromic shift from 371 to 359 nm. The bathochromic shift of the x-band is magnified when a 2nd dimethylamino group is added to the 2-chromophore to generate 2,6-[NMe₂]TPP⁺ (Scheme 6). On the other hand, addition of a nitro group to the 2-phenyl ring to generate NO₂TPP⁺, has the opposite effect of lowering the HOMO energy and increasing the HOMO-LUMO gap and shifting the xband hypsochromically to 410 nm (25). Addition of an electrondonating group to the y-chromophore also has the anticipated effect of raising the y-chromophore energy and shifting the y-band to lower energy (26). This effect is modest when a

methoxy group is added to 2,6-[NMe2]2TPP+ (477-482 nm) to give 4-MeO-2,6-[NMe2]2TPP+ because the electronic demand for charge transfer to the pyrylium core is significantly diminished by the strong electron donating aryl groups at the 2,6-positions. On the other hand, when there are no electron donating groups appended to the 2-chromophore addition of the potent electron donating dimethylamino group to the 4-phenyl of TPP⁺ to generate 4-NMe₂TPP⁺ generates an enormous 181 nm bathochromic shift to 552 nm so that the y-band now becomes the lowest energy band in the UV-Vis spectrum. Addition of two less potent electron-donating p-methoxy groups to the 2-chromophore of 4-NMe₂TPP⁺ generates a 61 nm bathochromic shift of the x-band and a 9 nm hypsochromic shift of the y-band but (see 2,6-diMeO-4-NMe2TPP+) but does not reverse the assignment of the lowest energy absorbance to the y-chromophore. (Scheme 6).

In the pyrylogens, XPY^{2+} , the donor part of the *y*-chromophore in **TPP**⁺, the 4-phenyl ring, has been replaced with an electron poor *N*-methylpyridinum group. Consequently, we anticipated that the low energy band in XPY^{2+} would correspond to an *x*-chromophore transition and that a *y*-band would be either at



Figure 3. UV–Vis spectra for TPP⁺ (dotted line) and XPY²⁺ (solid lines) in CH₃CN.

much higher energy or absent. This speculation was confirmed by time domain density functional calculations (TD-DFT) in acetonitrile using B3LYP/6-311+G(2d,p) calculations in conjunction with the polarization continuum model as shown in Scheme 7. This model chemistry does an excellent job of reproducing the experimental absorption spectra of **TPP**⁺. The HOMO \rightarrow LUMO transition in **TPP**⁺ is responsible for the low energy absorption at 410 nm (404 nm experimentally) and is clearly an *x*-band transition involving charge transfer from the 2,6-arylrings to the pyrylogen core. The HOMO-1 \rightarrow LUMO (*y*-band) transition is responsible for the peak at 370 nm (357 nm experimentally) and involves charge transfer from the 4-phenyl ring to the pyrylium ring. In **HPY**²⁺, the low energy band at 467 nm (441 nm experimentally) is also the HOMO \rightarrow LUMO transition and an *x*-band. In fact, no low energy *y*-band was detected computationally. Two bands with low oscillator strengths (f = 0.0034, 0.0111) appearing at approximately 400 nm and a band with modest oscillator strength (f = 0.1896) at 361 nm are both *x*-band transitions. The agreement between the computed and observed wavelength of the low energy *x*-band, Δ_{nm} , is much better for **TPP**⁺ ($\Delta_{nm} = 6$ nm) than for **HPY**²⁺ ($\Delta_{nm} = 26$ nm). We believe this reflects the much greater charge transfer observed from the 2,6-phenyl-rings to the dicationic pyrylogen than mono-cationic pyrylium core. It is well established that charge transfer bands are poorly predicted with TD-DFT as a result of their incorrect long-range form of the exchange potential (27). Despite this problem we do believe that the TD-DFT calculations for **HPY**²⁺

Table 1. Photophysical data for $XPY^{2+} \cdot 2BF_4^-$ and TPP^+ .

	HPY ²⁺	ClPY ²⁺	CF ₃ PY ²⁺	MeOPY ²⁺	TPP ⁺
λ_{MAX}^*	441	454	413	523	401
					355
<i>ε</i> *	21 010	24 030	21 770	20 640	24 920
					31 700
λ_{MAX} †	467	500	440	575	410
					370
ſ†	0.4156	0.5186	0.4989	0.4225	0.4790
					0.6415
$\lambda_{\rm F}$ ‡	533	556	494	659	465
$\lambda_{\mathbf{P}}$ §	578 (565)	588 (588)	552 (546)	658 (665)	520
Stokes shift	92	102	81	136	64
$\tau_{\rm F}$	3.42 ± 0.23	_	2.1 ± 0.21	_	4.1 (2.9)††
$\tau_{\rm P}$	35.6 ± 0.2	38.3 ± 1	33.9 ± 0.2	25.4 ± 0.6	225 ± 311
	(91 ± 4)	(109 ± 3)	(214 ± 57)	(55 ± 1)	
E(S1)#	59	56	63	48	65‡‡
E(T1)#	54	53	57	48	53‡‡
Φ_F^{**}	0.18 ± 0.01	0.43 ± 0.01	0.24 ± 0.01	\$\$	0.60
$\Phi_{\rm T} \ \ $	0.03 ± 0.02	-	-	_	_

*Experimental absorption spectrum in CH₃CN; ε mol⁻¹ L⁻¹ cm⁻¹. †TD-DFT B3LYP/6-311+G(2d,p) calculations in CH₃CN; f-oscillator strength. ‡In nanometers (nm) at 298 K. §In nm in EtOH/HCl(g) and in parenthesis nPrCN/HCl(g) at 77 K. ||In nanoseconds (ns). ¶In milliseconds (ms) at 77 K in EtOH/HCl(g) and in parenthesis nPrCN/HCl(g). #In kcal mol⁻¹. **Fluorescence quantum yield in CH₃CN. ††Haucke, G., P. Czerney, F. Cebulla (1992) Absorption and Fluorescence of Pyrylium Salts. *Ber. Bunsenges. Phys. Chem.*, 96, 880–886. CH₃CN(CH₂Cl₂). ‡‡Miranda, M. A., H. García (1994) 2,4,6-Triphenylpyrylium Tetrafluoroborate as an Electron-Transfer Photosensitizer *Chem. Rev.*, 94, 1063–1089. §§Too small to be measured accurately. ||||Triplet quantum yield.



Scheme 6. Effect of substituents on positions of pyrylium cation x- and y-bands.

The calculation successfully predicts the substituent induced shift in the *x*-band and a plot of the observed (*x*-axis) versus the TD-DFT calculated (*y*-axis) *x*-band wavelength gives a straight line (slope = 1.23; $R^2 = 0.98604$).

The fluorescence of all the pyrylogens, **XPY²⁺**, at room temperature in acetonitrile is characterized by a single peak devoid of any fine structure at the wavelengths depicted in Table 1. The fluorescence quantum yields are much smaller (Table 1) than the 0.60 reported for TPP⁺. It is tempting to suggest that the low fluorescence quantum yields are due to the absence of the y-chromophore in XPY²⁺. This speculation is based on a very novel study of TPP⁺ which demonstrated that incarceration in the supramolecular host cucurbit[8]uril restricted the motion of the 2,6-phenyl groups in the x-chromophore and allowed simultaneous observation of fluorescence and room temperature phosphorescence (28). Furthermore, irradiation into the y-band increased, and irradiation into the x-band decreased, the room temperature $\Phi_{\rm E}/\Phi_{\rm P}$ ratio. On the other hand, intramolecular charge transfer (ICT) quenching of the fluorescent state, especially in MeOPY²⁺, cannot be unambiguously ruled out. The formation of an unusual radicalcation/cation state, (CT-MeOPY²⁺)* with a near planar geometry (Scheme 8) reminiscent of pyrylogen radical-cations (vide supra) could explain both the unusually small $\Phi_{\rm F}$ and unusually large Stokes shift observed for MeOPY²⁺ (Table 1).

The fluorescence peak for HPY^{2+} in an EtOH/HCl matrix shifted bathochromically by 36 nm as the temperature was

increased from 77 to 202 K. We attribute this shift to comparable rate constants for emission and solvent reorganization leading to emission from a continuum of slightly divergent solvated excited states; an explanation that was previously utilized (29) to explain a similar spectral shift that had been observed for **TPP**⁺ (30). Emission from a Franck–Condon state at low temperature and a relaxed excited state at higher temperatures is not a viable explanation for this phenomenon since the peak width at half height and the excitation spectrum did not change between 77 and 202 K.

The emission wavelength for **XPY**²⁺·**2**[**B**(**C**₆**F**₄)₄]⁻ also shifted bathochromically by ~30 nm as the solvent polarity was decreased from acetonitrile to 1,2-dichloroethane. Unfortunately, **XPY**²⁺·**2**[**B**(**C**₆**F**₄)₄]⁻ does not exhibit sufficient solubility in the widespread range of solvents necessary to construct a statistically meaningful (31) Lippert–Mataga plot (32). Nevertheless, the bathochromic shift with decreasing solvent polarity is consistent with the previous conclusion from absorption spectra (*vide supra*) that the dipole moment of pyrylogen excited states are smaller than the dipole moment of their ground state.

Phosphorescence was observed at 77 K for $XPY^{2+}BF_4^-$ in a variety of low temperature glasses including butyronitrile/HCl(g) and EtOH/HCl(g) (Table 1). The acid was added to decrease the nucleophilic character of the medium. The stability of the prylogens under these conditions was demonstrated by UV–Vis spectroscopy. Identical phosphorescence wavelengths were observed for $CIPY^{2+}BF_4^-$ in both glasses while minor environmental effects





Scheme 8. Electronic distribution in the intramolecular charge transfer (ICT) state.

were observed for the other pyrylogens (Table 1). On the other hand, triplet lifetimes were dramatically different and systematically longer in butyronitrile than in EtOH (Table 1) suggesting that the nucleophilic reaction of ethanol (*vide infra*) with the pyrylogens was not completely suppressed by the addition of HCl. The triplet energies in Table 1 were determined from the onset of the phosphorescence and were identical within ± 0.2 kcal mol⁻¹ in the two glasses. Formation of the triplet was independently verified during a nanosecond laser flash photolysis study of $HPY^{2+}BF_4^{-1}$ in 1,2-dichloroethane. Irradiation with 10 mJ 355 nm pulses from a Nd/YAG laser generated bleaching of the pyrylogen and observation of a transient absorption at 570 nm (Fig. 4). The absence of

reactivity of the pyrylogen radical cation with oxygen on the much longer time scale of a CV experiment eliminates it as a candidate for the peak at 570 nm. Instead, the transient signal was assigned to the triplet–triplet absorption spectrum based upon its dramatic quenching with oxygen (inset in Fig. 4).

Reactions

The pyrylogens are potent oxidants in both the S₁ and T₁ excited states. The reduction potentials of the excited states suggest that the ease of oxidation of a substrate, M, $[\Delta G^{\circ} = E^{0}(M/M^{+}) - E^{0}(XPY^{2+}/XPY^{++}) - E(S_{1} \text{ or } T_{1})]$ by the S₁ or T₁ excited state will



Figure 4. Laser flash photolysis of 1.1×10^{-4} M HPY²⁺ in 1,2-dichloroethane. Inset: Effect of oxygen on the decay of the peak at 570 nm.



Scheme 9. Hydrolytic ring opening of HPY²⁺.

increase in the order ³(**TPP**⁺)* [1.95 eV] < ^{1.3}(**MeOPY**²⁺)* [2.13 eV] < ¹(**TPP**⁺)*[2.47 eV] < ³(**CIPY**²⁺)*[2.49 eV] < ³(**HPY**²⁺)* [2.51 eV] < ¹(**CIPY**²⁺)* [2.62 eV] < ¹(**HPY**²⁺)* [2.73 eV] < ³(**CF3PY**²⁺)* [2.84 eV] < ¹(**CF**₃**PY**²⁺)* [3.10 eV]. The ground states, S_o, of the pyrylogens are also very electron deficient and reactive, consequently, it is important to be aware of potential reactions of S_o when designing PET reactions using these sensitizers. For example, **HPY**²⁺ reacts rapidly with water at the pyrylium ring to generate a ring-opened water adduct (Scheme 9) and care must be expended to scrupulously dry PET reaction solvents.

Pyrylogens also form charge transfer complexes (33) (CT) that could potentially function as precursors to an electron transfer event (34). Upon addition of 1,4-dimethoxybenzene (PDMB) to a solution of CF_3PY^{2+} a new peak was observed at 595 nm that increased in intensity with increasing concentration of PDMB (Fig. 5). Charge transfer complexes of the other pyrylogens with PDMB are not as readily apparent and are only observed as a broad shoulder on the long wavelength side of the pyrylogen UV-Vis spectrum. This hypsochromic shift with decreasing thermodynamic stability of the complex is a well-established phenomenon and serves as confirmation for the assignment of these bands to CT complexes (35). The long-wavelength edges of the CT bands in conjunction with a Benesi-Hildebrand analysis (36) demonstrates that these are weak complexes $(0.2 < K_{eq} < 1)$. The K_{eq} value for CF₃PY²⁺...PDMB (0.63 ± 0.09) is larger than that measured for the CT complexes of HPY²⁺ (0.47 \pm 0.02), CIPY²⁺ (0.40 \pm 0.05), or MeOPY²⁺ (0.56 \pm 0.02) and is probably more accurate (37), despite its larger error limits (38), because it forms a well defined peak clearly separated from the CF_3PY^{2+} absorbance (39).



Figure 5. Charge transfer band formation between CF3PY²⁺ and PDMB.



Figure 6. Reduction of HPY²⁺ with Cd and Ni in acetonitrile.

Pyrylogens will also react with several different chemical reducing agents. For example, when an acetonitrile solution of $HPY^{2+} \cdot 2BF_4^{-}$ is allowed to stir over metallic nickel or cadium a new peak appears in the UV–Vis spectrum at 614 nm (Fig. 6).



Figure 7. Photoinduced electron transfer reactions catalyzed by HPY²⁺.

We assign this peak to the radical cation, HPY^{+} , based upon several pieces of evidence: (1) the same peak is formed during a coulometric reduction of $HPY^{2+}2BF_4^{-}$; (2) a single broad peak is observed in the ESR spectrum of solutions containing the peak at 614 nm; (3) the closely related dimethyl viologen radical cation appears at 620 nm (40); and (4) a time dependent density functional theory calculation for HPY^{+} at the B3LYP/6-311+G (2d,p) computational level predict a peak at 594 nm with an oscillator strength of 0.4049. Parenthetically, the appearance of this peak at 614 nm provides additional evidence for the veracity of the assignment of the peak at 570 nm in the laser flash photolysis study as the triplet–triplet absorption.

Finally, we did a brief study of a series of well-established PET reactions in order to determine if HPY^{2+} could function as a catalyst as shown in Fig. 7. The reaction of the 1,3-dithiane, **4** (41), and adamantane adamantylidene, **5** (42), are both electron transfer oxygenation reactions that gave only the products indicated along with unreacted starting material. These reactions were also accompanied by extensive decomposition of the pyrylogen sensitizer. On the other hand the cycloaddition of 1,3-cyclohexadiene (43) occurred with 95% conversion in one-hour with less than 5% decomposition of the pyrylogen sensitizer. The formation of transient HPY^{+} and stilbene radical cations were directly confirmed by UV–Visible spectroscopy and by laser flash photolysis in the 1,3-cyclohexadiene cycloaddition and the cyclobutane cycloreversion reactions (44), respectively.

Mechanistic tools

Both spectral identification of the pyrylogen radical cation and triplet formation provides mechanistic tools that can be used to follow pyrylogen sensitized reactions. For example, both 1-bro-mobutane and bromobenzene quench the fluorescence of **HPY²⁺**, however, in the nanosecond time-resolved emission spectra

enhanced triplet-triplet absorption of ${}^{3}(\mathbf{HPY^{2+}})^{*}$ at 570 nm is observed in the presence of 1-bromobutane but only radical cation (**HPY**⁺) formation, at ~620 nm, is observed in the presence of bromobenzene. This suggests that 1-bromobutane promotes singlet-triplet intersystem crossing ${}^{1}(\mathbf{HPY^{2+}})^{*} \rightarrow {}^{3}(\mathbf{HPY^{2+}})^{*}$ while bromobenzene undergoes an PET reaction.

Furthermore, the ability of 1-bromobutane to promote intersystem crossing provides us with an additional mechanistic tool to measure the quantum yield of triplet formation, Φ_{T} . This method, first used by Horrocks et al. (45), compares the ability of 1-bromobutane to quench S_1 to its enhancement of triplet formation as shown in Eq (1). The virtue of this method is that absolute quantum yields do not need to be measured but only the ratios of the amount of triplet formed in the presence and absence of 1-bromobutane, Φ_T / Φ_T^0 , and the quenching ratios in Stern–Volmer experiments, Φ_f^0/Φ_f , are needed to plot the quantity $[\Phi_f^0/\Phi_f - 1]$ versus the term in the parenthesis on the left side of equation 1 to determine Φ_T^0 . The ratio Φ_T/Φ_T^0 is conveniently determined by taking the ratio of integrated triplet-triplet absorption decay curves at 570 nm in the laser flash photolysis experiment in the presence and absence of the different concentrations of 1-bromobutane. In the case of HPY²⁺, the quantum yield of triplet formation, $\Phi_{\rm T}^0 = 0.033 \pm 0.02$, is significantly smaller than that reported for **TPP**⁺, $\Phi_{\rm T}^0 = 0.48$ (12).

$$\left[\frac{\Phi_T}{\Phi_T^0} x \frac{\Phi_f^0}{\Phi_f} - 1\right] \Phi_T^0 = \frac{\Phi_f^0}{\Phi_f} - 1 \tag{1}$$

CONCLUSION

The synthesis of a series of pyrylogen sensitizers and preliminary evidence that they catalyze PET reactions has been presented. These promising results along with electrochemical and photophysical characterizations of the pyrylogens should enhance design of PET reactions using these new sensitizers. In addition, several mechanistic tools that have been introduced should assist in the analysis and optimization of new PET reactions using these sensitizers.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Data S1: Supplementary Material Computational Results: Table S1. B3LYP/6-311+G(2d,p) Structural Parameters for 4,4'-Pyrylogen Dications.; Table S2. B3LYP/6-311+G(2d,p) Structural Parameters for 4,4'-Pyrylogen Radical Cations.; Table S3. B3LYP/6-311+G(2d,p) Structural Parameters for Neutral 4,4'-Pyrylogens.; TD-DFT Results.

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