



A new free and immobilized pyrylogen electron transfer sensitizer

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ABSTRACT

The synthesis, photophysical, and electrochemical characterization of *N*-allyl-2,6-diphenyl-4,4'-pyrylogen bis tetrafluoroborate is reported. The pyrylogen is reduced under dissolving metal reduction conditions with formation of the radical cation. In addition, it can be copolymerized with styrene and divinylbenzene to generate a polymer bound reagent that facilitates its separation from photochemically induced electron-transfer reaction mixtures.

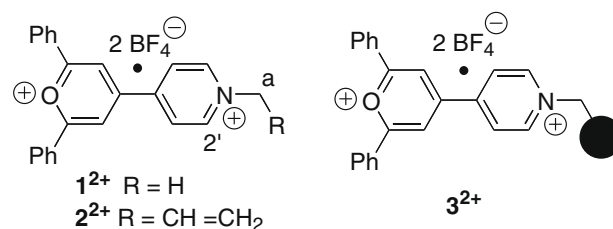
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Charge shift (CS) electron-transfer reactions that lead to formation of neutral radical/radical-cation pairs that lack a coulombic barrier for diffusive separation have been employed for many years to improve the efficiencies of photoinduced electron-transfer (PET) reactions.¹ Measurements of the quantum yields for the separation of the radical/radical-cation pair have shown that this strategy is reasonably effective.² However, there is room for improvement and as a consequence pyrylogen, **1**²⁺, (Scheme 1) has recently been introduced as a new charge shift electron-transfer sensitizer.³ The charge shift in the critical electron-transfer step with this PET sensitizer generates a repulsive radical-cation/radical-cation pair. The rapid electrostatically assisted separation of these radical cations competes with energy wasting return electron transfer and results in a more efficient 'green' photoinduced electron-transfer (PET) reaction.⁴

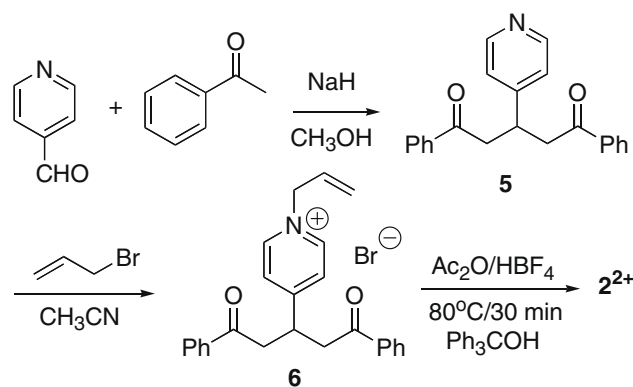
In this Letter we report the synthesis of a new pyrylogen, **2**²⁺, and its characterization that provides additional insight into the photochemical behavior of this new class of charge shift electron-transfer sensitizers. In addition, we report the synthesis of the first polymer-bound pyrylogen, **3**²⁺, in order to take advantage of all the desirable features, including enhanced stability of the sensitizer,⁵ reported for other insoluble polymer-bound reagents/dyes such as Rose Bengal,⁶ fullerene C₆₀,⁷ and pyrylium salts.⁸

The synthesis of **2**²⁺ was accomplished by the three-step procedure shown in Scheme 2. In this reaction two moles of acetophenone are allowed to react with pyridine-4-carboxaldehyde to give a 1,5-diketone, **5**. Allylation to give **6** followed by oxidative ring closure generated the purified pyrylogen product in an overall yield of 28%.

The structure of pyrylogen **2**²⁺ was confirmed using standard spectroscopic techniques. The electrospray mass spectrum (see



Scheme 1. Pyrylogens.



Scheme 2. Synthesis of pyrylogen **2**²⁺.

Supplementary data) exhibits a peak at 351.13 *m/z* consistent with formation of the radical cation, a peak for the (**2**²⁺ + methoxy adduct) at 382.20 *m/z*, and a peak at 310.33 *m/z* for the loss of the allylic cation. The ¹H and ¹³C NMR spectra of both **1**²⁺ and **2**²⁺ in CD₃CN were significantly broadened. It is possible that CD₃CN is acting as a reducing agent to produce a small amount of paramagnetic radical cation that is responsible for the broadening. The

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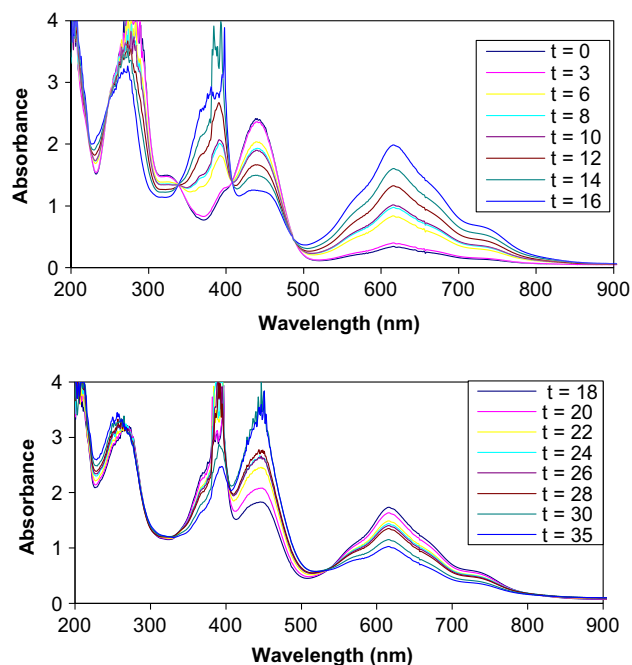


Figure 1. UV-vis spectra of Zn reduction of 2^{2+} in CH_3CN . Top; Increase in absorbance at 616 nm as a function of time (min). Bottom; Decrease in absorbance at 616 nm as a function of time (min).

ability of CH_3CN to act as a reducing agent in reactions with tetracyanoethylene and iodine has previously been reported.⁹ The electron transfer in these reactions is induced by irradiation into a weak charge transfer band. Indeed, this conjecture is also supported in our case by the appearance of a small peak at 620 nm in the UV-vis spectrum of an acetonitrile solution of 2^{2+} that was irradiated with either a conventional lamp (350 nm) or with a Nd:YAG laser at 355 nm. We have verified that this peak is the radical cation by independently synthesizing both 1^+ and 2^+ by Zn metal reduction under a vacuum atmosphere in CH_3CN . The solution of 1^+ and 2^+ are intense in color and absorb at 620 nm and 616 nm, respectively (Fig. 1). The behavior of 2^{2+} is in sharp contrast to the laser flash photolysis of 1^{2+} in the less polar 1,2-dichloroethane that preferentially leads to the observation of a transient absorbance at 570 nm that is quenched by oxygen and is characteristic of the triplet.³ Finally, broadening of the NMR spectra is not observed in CDCl_3 in the presence of approximately 33% trifluoroacetic acid added to increase solubility.

Table 1
Photophysical and electrochemical data for pyrylogens 1^{2+} and 2^{2+}

	1^{2+}	2^{2+}
$E_{1/2}(1)^a$	0.17	0.17
$E_{1/2}(2)^a$	-0.35	-0.34
λ_F^b	533	536
λ_P^c	565	590
τ_F^d	3.42 ± 0.23	
τ_P^e	35.6 ± 0.2	30.4 ± 1
$E(S_1)^f$	59	58
$E(T_1)^f$	54	53
Φ_F^g	0.18 ± 0.01	0.33 ± 0.09

^a In volts versus SCE.

^b In nanometers (nm) in CH_3CN at 298 K.

^c In nanometer nm in EtOH/HCl(g) at 77 K.

^d In nanoseconds (ns).

^e In milliseconds (ms) at 77 K in EtOH/HCl(g).

^f In kcal/mol.

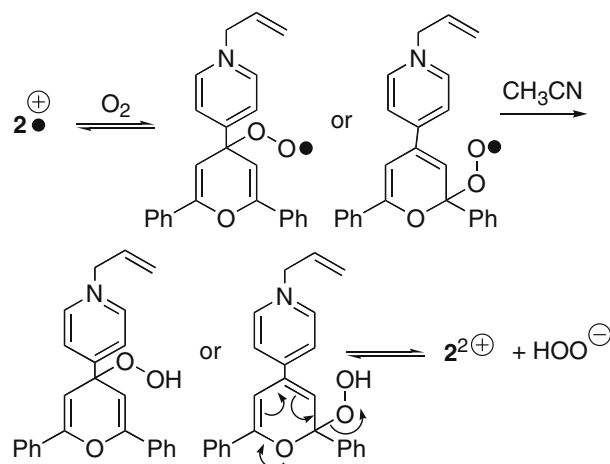
^g Fluorescence quantum yield in CH_3CN .

Formation of 2^+ begins almost immediately upon addition of a degassed solution of 2^{2+} to zinc and the green color continues to intensify to reach a maximum after approximately 16 min (Fig. 1 top). Remarkably, at this point the concentration of 2^+ begins to decrease concomitantly with the apparent/possible increase of the dication, 2^{2+} concentration (Fig. 1 bottom). Oxidation of 2^+ by adventitious oxygen to form superoxide can be ruled out as a mechanism for this process since it is thermodynamically uphill (Table 1) by more than 10 kcal/mol.¹⁰ A disproportionation mechanism to simultaneously form a reduced and oxidized product ($2^{2+} + 2^0 \rightarrow 2 \cdot 2^+$) can also be eliminated by consideration of its electrochemical behavior. In particular, pyrylogen 2^{2+} is reduced in two chemically reversible and electrochemically quasireversible steps to the radical cation and neutral redox partners (Table 1). The equilibrium constant for disproportionation, $K_{\text{eq}} = [2^+]^2 / ([2^{2+}][2^0])$, which can be calculated¹¹ from the difference between the first and second reduction potentials of 2^{2+} ($\log K_{\text{eq}} = [0.17 - (-0.34)] / 0.059$) is far too large (4.4×10^8) to account for the extent of disappearance of 2^+ or amount of 2^{2+} formed (Fig. 1 bottom).

The radical cation, 2^+ , is unreactive with oxygen even at the 100 mV/s time scale of a cyclic voltammetry experiment. However, the radical cation clearly does react with oxygen on the laboratory time scale. Consequently, it is tempting to suggest that the formation of the dication, 2^{2+} , from the radical cation, 2^+ , occurs by reaction with adventitious oxygen via the mechanism depicted in Scheme 3. The fact that not all of 2^{2+} is recovered reflects an equilibrium established in the last step, or potentially competitive reductive decompositions of the hydroperoxides.

The UV-vis spectrum of 2^{2+} (Fig. 1; $t = 0$) exhibits three absorption maxima at $\lambda_{\text{MAX}}(\epsilon) = 282 \text{ nm}$ ($40,000 \text{ M}^{-1} \text{ cm}^{-1}$), 325 nm ($11,000 \text{ M}^{-1} \text{ cm}^{-1}$), and 441 nm ($23,000 \text{ M}^{-1} \text{ cm}^{-1}$). Time dependent density functional theory calculations on the B3LYP/6-311+G(d) geometry minimum of 2^{2+} reveals that the lowest energy absorption band corresponds exclusively to the HOMO \rightarrow LUMO transition. This transition involves a significant charge transfer from the pyrylium to the pyridinium ring (Fig. 2). Pyrylogen 2^{2+} also fluoresces and phosphoresces allowing determination of approximate singlet and triplet energies (Table 1). In addition, at 77 K the phosphorescence spectrum of 2^{2+} exhibited a second peak that could be eliminated at longer delay times indicative of delayed fluorescence (See Supplementary data).

Two minimum energy conformations of 2^{2+} can be located with the B3LYP/6-311+G(d) computational model (Fig. 3). The two conformations differ primarily by the orientation of the allyl group. In the lowest energy conformation the vinyl- C_3 - $\text{N}-\text{C}_2$ dihedral angle is 46° and vinyl group is eclipsed with an allylic C-H bond. In the



Scheme 3. Potential mechanism for the formation of 2^{2+} from 2^+ .

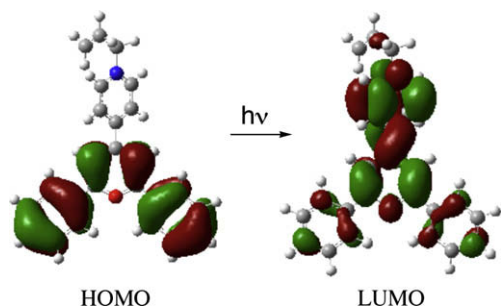


Figure 2. HOMO–LUMO transition in 2^{2+} .

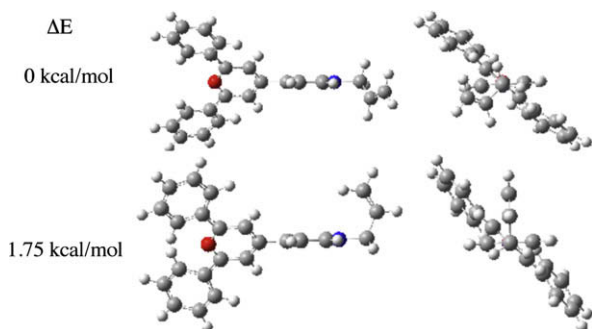


Figure 3. Two views of the B3LYP/6-311+G(d) minima for 2^{2+} .

higher energy conformation (1.75 kcal/mol), the vinyl- C_a - N - C_2 dihedral angle is 89.4° and the vinyl group is eclipsed with the N -allylic carbon bond placing the vinyl group over the plane of the pyridinium ring. In both conformations the pyrylium and pyridinium rings are twisted with an inter-ring dihedral angle of approximately 45° .

Pyrylogen 2^{2+} is also readily incorporated into a polymer backbone to create the first heterogeneous PET dicationic sensitizer. In the polymerization reaction styrene, divinyl benzene, 2^{2+} , and AIBN, were mixed in toluene and heated to 80°C for 12 h. The polymer was then precipitated by the addition of methanol to the cooled solution to give a 33% yield of the heterogeneous sensitizer. The incorporation of 2^{2+} into the polymer backbone was confirmed by recording the fluorescence spectrum of the polymer ($\lambda_F = 538\text{ nm}$) which is nearly identical to the free pyrylogen (Table 1). Determination of the polymer molecular weight and the molecular weight distribution (PDI) was achieved by gel per-

meation chromatography (GPC) using polystyrene standards. The polymer was found to have a weight average molecular weight (M_W) = 20,089 and a number average molecular weight (M_n) = 9818 and hence a polydispersity (PDI) of 2.046.

In summary, we have reported the synthesis and the electrochemical and photophysical characteristics of a new pyrylogen; the first that replaces the N -methyl group with another substituent. We have also demonstrated that this pyrylogen can be incorporated into a heterogeneous catalyst. The utility of this new catalyst in electron-transfer reactions will be reported in the future.

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Supplementary data

Supplementary data (synthetic procedures, polymerization procedure, structural, photophysical, electrochemical and computational characterization) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.102.

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