



Synthesis, optical spectroscopy and laser potential of pyrylium tosylates



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ABSTRACT

Safe and inexpensive methods for synthesis of a series of four substituted 2,4,6-triphenylpyrylium tosylate salts with different substituents are reported. The synthesis methods use *p*-toluenesulfonic acid monohydrate instead of conventional acid catalysts including perchloric acid or boron trifluoride diethyl etherate that pose explosion danger and difficult storage problems, respectively. The chemical structures of these salts were established using FTIR, ¹H and ¹³C NMR spectroscopic techniques and elemental analysis. Thermogravimetric analysis (TGA) showed that these salts have good thermal stability, and differential scanning calorimetry (DSC) analysis showed that they have lower melting transitions than the corresponding tetrafluoroborate and perchlorate salts. Solutions of the salts in organic solvents (such as acetonitrile and methanol) absorbed strongly in the blue-near-ultraviolet spectral range and emitted efficiently in the blue-green spectral range depending on the substituents in 2- and 6-positions of phenyl groups. The fluorescence quantum yields of the salts ranged from 0.33 to 0.56. Under intense ultrashort laser pumping, an acetonitrile solution of the salt, 2,4,6-triphenylpyrylium tosylate, the salt with the highest quantum yield, demonstrated stimulated emission and laser action with only nominal feedback.

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1. Introduction

The interest in developing safe and inexpensive synthetic methods for pyrylium salts derives from their many potential applications in photochemistry, photobiology and beyond. First, these heterocyclic compounds are used as versatile precursors in a variety of synthetic applications including substituted furan, pyridine, pyridinium salts, and betaine dyes [1–6]. Second, their electron accepting properties make them suitable as sensitizers for photo-induced electron transfer processes in chemical transformations [7]. Third, their strong light emission properties are indicative of potential applications as active materials for dye lasers operating in the blue-green spectral region [7]. Furthermore, their two- and three-photon absorption properties may be useful for diverse applications, such as, three-dimensional optical data storage, photodynamic therapy, upconversion lasers, optical power limiting, as well as micro- and nano-fabrications [8]. Recently, the absorption,

fluorescence and electron acceptor properties of these salts have been explored to design sensors for cyanide ion [9], amines, amino acids, nitric oxide [10], and proteins [11].

In general, perchloric acid and boron trifluoride diethyl etherate are used as common acid catalysts to synthesize pyrylium salts of diverse chemical structures with ClO₄⁻ or BF₄⁻ as counterions [12]. However, perchloric acid poses explosion danger, and boron trifluoride diethyl etherate requires difficult handling, problematic storage, and higher cost. To develop safer, inexpensive and efficient synthesis routes for this important class of compounds, we explored the use of *p*-toluenesulfonic acid (tosic acid) monohydrate which is a solid, relatively safe to handle, and an inexpensive reagent. Although tosic acid has previously been used in many diverse organic transformations [13–18], it has not yet been explored for the synthesis of pyrylium salts of diverse architectures with tosylate counterions. This work explored the use of tosic acid for synthesis of pyrylium salts employing several synthetic pathways under different reaction conditions including solvent-free green synthetic approach. Four 2,4,6-triarylpyrylium tosylates were synthesized and their chemical, thermal, optical

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spectroscopic, and quantum electronic properties were studied. The synthesized salts include: 2,4,6-triphenylpyrylium tosylate (salt **1**), 2,6-bis(4-methylphenyl)-4-phenylpyrylium tosylate (salt **2**), 2,6-bis(4-bromophenyl)-4-phenylpyrylium tosylate (salt **3**), and 2,6-bis(4-methoxyphenyl)-4-phenylpyrylium tosylate (salt **4**). It is also of significant interest to examine the physical properties of these salts such as solubility in various organic solvents when compared with those with ClO_4^- or BF_4^- as counterions. The latter salts have limited solubility in organic solvents, but provide relative ease of their isolation because of high crystallinity of inorganic ions.

The thermal properties and stability of the salts were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. Their optical spectroscopic properties (both in solution and in solid state) were studied using UV–Visible absorption spectroscopy, fluorescence spectroscopy, and time-resolved fluorescence spectroscopy techniques. Introduction of electron donating substituents in para-positions of 2- and 6-phenyl rings of pyrylium salts showed that the substituents influence the optical spectroscopic properties of the salts in solution as well as thermal properties.

2. Materials and methods

2.1. General information

All chemicals including spectral grade solvents were purchased from commercial suppliers and used without further purification. The ^1H and ^{13}C NMR spectra were recorded using a Varian NMR 400 MHz spectrometer equipped with two radiofrequency (RF) channels at room temperature. The NMR sample solutions were prepared by dissolving 10 mg of respective compounds in $\text{DMSO-}d_6$ with tetramethylsilane as an internal standard. FTIR spectra were recorded with Shimadzu spectrometer (IR Affinity-1) using KBr pellets. Elemental analyses for the salts were obtained from the Atlantic Microlab Inc., Norcross, GA.

The phase transition temperature of ionic compounds were studied using TA differential scanning calorimetry (DSC) Q200 series in nitrogen at heating and cooling rates of $10^\circ\text{C}/\text{min}$. The temperature axis of the DSC thermograms was calibrated with reference standards of high purity of indium and tin. The thermal stability of each compound was analyzed using TA TGA Q50 in nitrogen at a rate of $10^\circ\text{C}/\text{min}$ operated in the temperature range between 30 and 800°C .

The UV–Vis absorption spectra of the salts dissolved in acetonitrile were recorded using Varian Cary 50 Bio UV–visible spectrophotometer in quartz cuvettes at room temperature. Photoluminescence spectra of the salts in solution were recorded using a Perkin-Elmer LS-55 luminescence spectrometer with a xenon lamp as a light source. Quantum yields were estimated using the following relation:

$$\Phi_X = \Phi_{ST} \left(\frac{\text{Grad}_X}{\text{Grad}_{ST}} \right) \left(\frac{\eta_X^2}{\eta_{ST}^2} \right) \quad (1)$$

where the subscripts ST and X denote the standard (9,10-diphenylanthracene) and the unknown, respectively, Φ is the fluorescence quantum yield, η is the refractive index of the solvent, and Grad is the gradient from the plot of integrated fluorescence intensity vs. absorbance of the minimum of five solutions prepared by serial dilution [19].

Time-evolution of fluorescence and pump-power dependence of the fluorescence spectra and fluorescence lifetime of the salt with the highest fluorescence quantum yield were measured using a Ti: sapphire laser and regenerative amplifier system (Spectra-Physics Spitfire) and a Streak Camera system (Hamamatsu streak

scope C4334) coupled with a spectrometer (Imaging Spectrograph G50is). The laser system generated 800-nm light pulses of 130 fs full-width-at-half-maximum (FWHM) duration, at a repetition rate of 1 kHz. The second harmonic of this laser output at 400-nm was used to excite into the first absorption band of the salt solution in acetonitrile contained in a quartz cuvette. The fluorescence from the sample was collected by an optical fiber connected with the streak camera spectrometer. Since typical dyes have fluorescence lifetimes of a few nanoseconds, the streak camera was used in the 20-ns time frame with a corresponding temporal resolution of approximately 200 ps. It can provide a temporal resolution of ~ 20 ps when used in the 1-ns time frame.

2.2. Synthesis of 2,4,6-triphenylpyrylium tosylate (salt **1**)

The 2,4,6-triphenylpyrylium tosylate (salt **1**) was prepared by one-step method from both *trans*-chalcone [20], and 1,5-diketone [21] by using tosic acid in accordance of the identical procedures [22–24] that were used for the preparation of the corresponding ClO_4^- and BF_4^- salts with modifications (Scheme 1). It was also prepared by one-step method from benzaldehyde and acetophenone in four different methods as shown in Scheme 2.

2.2.1. *Trans*-chalcone method (Scheme 1)

This procedure is an improved modification of that described by Dimroth [24]. The *p*-toluenesulfonic acid monohydrate (9.49 g, 49.9 mmol) was slowly added into a solution of *trans*-chalcone (10.4 g, 49.9 mmol), acetophenone (3.00 g, 25.0 mmol), and 20 mL of 1,2-dichloroethane while keeping the temperature at 50°C . The mixture was heated to reflux on stirring for 24 h. After the reaction was completed, the solution was concentrated by a rotary evaporator. The concentrated solution was poured into diethyl ether, and the crude product was collected by filtration and washed with diethyl ether. The crude product was purified by dissolving in the minimum amount of dichloromethane and precipitated in diethyl ether, and the final product was dried under vacuum oven to yield 3.96 g (8.24 mmol, 33% yield) of dark yellow solid.

2.2.2. 1,5-Diketone method (Scheme 1)

1,3,5-Triphenyl-1,5-pentanedione was prepared first by following a modified procedure of that described by Hirsch and Bailey [21]. The *p*-toluenesulfonic acid monohydrate (1.45 g, 7.61 mmol) was slowly added to a mixture of 1,3,5-triphenyl-1,5-pentanedione (1.00 g, 3.05 mmol) and triphenylmethanol (1.98 g, 7.61 mmol) in 20 mL of acetic anhydride. After the mixture was kept at 100°C for 2 h, it was cooled to room temperature and yellow precipitate was obtained by addition of 60 mL of water into the flask. The yellow solid was collected and washed with water to remove any residual acid from the reaction. The identical purification procedure was followed as described in *trans*-chalcone method (*vide supra*) to yield 1.30 g (2.71 mmol, 88% yield) of the pure product [16].

2.2.3. Method 1 (Scheme 2)

This procedure is a modification of the method that described by Moghimi et al. [22] for the corresponding perchlorate salt. The POCl_3 (23.9 g, 103 mmol) was added slowly to a solution of benzaldehyde (9.23 g, 87.0 mmol) and acetophenone (26.1 g, 218 mmol) in an ice bath. Then the solution was stirred and kept at 60°C for 8 h. After cooling down, the solution was concentrated by a rotary evaporator to remove excess POCl_3 , and the viscous solution was dissolved in ethanol. The *p*-toluenesulfonic acid monohydrate (20.7 g, 109 mmol) was slowly added to the solution over a period of 5 min at room temperature and kept on stirring for 30 min at identical temperature. The ethanol was removed under vacuum

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