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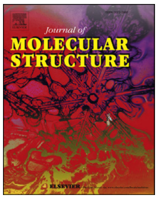

Synthesis, optical spectroscopy and laser potential of pyrylium tosylates

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ABSTRACT

Safe and inexpensive methods for synthesis of a series of four substituted 2,4,6-triphenylyrylium 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, ^{1}H and ^{13}C 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.

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 ClO_4^- or BF_4^- 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 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 °C/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 °C/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:

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

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)

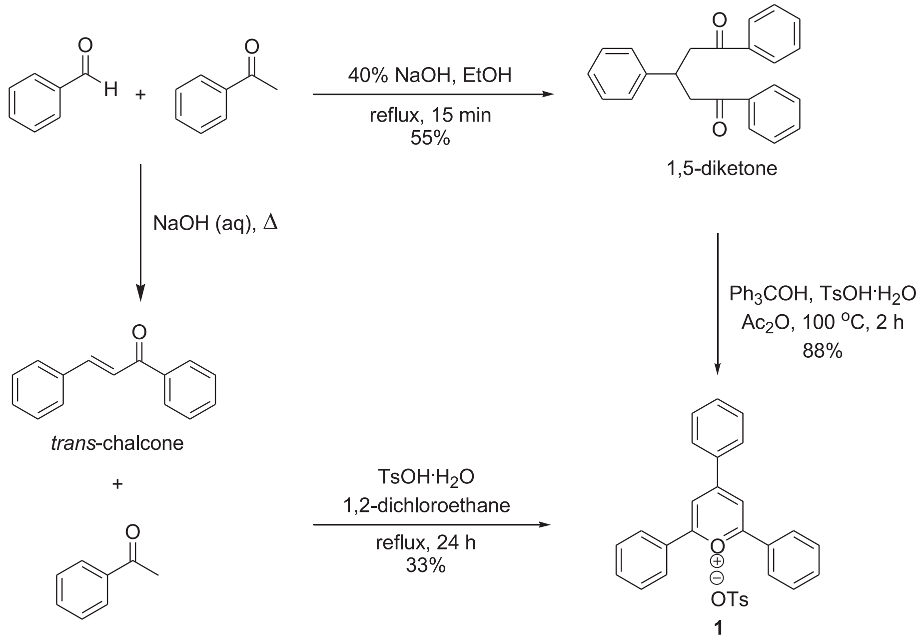
This procedure is an improved modification of that described by Dimroth [24]. The *p*-toluenesulfonic acid monohydrate (9.49 g, 49.9 mmol) was slowly added into a solution of *trans*-chalcone (10.4 g, 49.9 mmol), acetophenone (3.00 g, 25.0 mmol), and 20 mL of 1,2- dichloroethane while keeping the temperature 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)

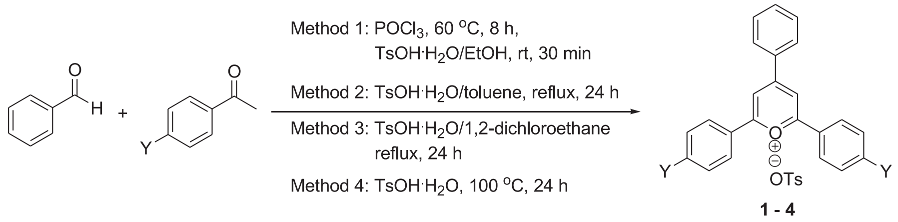
1,3,5-Triphenyl-1,5-pentanedione was prepared first by following a modified procedure of that described by Hirsch and Bailey [21]. The *p*-toluenesulfonic acid monohydrate (1.45 g, 7.61 mmol) was slowly added to a mixture of 1,3,5-triphenyl-1,5-pentanedione (1.00 g, 3.05 mmol) and triphenylmethanol (1.98 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



Scheme 1. Synthesis of 2,4,6-triphenylpyrylium tosylate.



Product	Y	Isolated Yield (%)			
		Method 1	Method 2	Method 3	Method 4
1	H	54	26	28	28
2	CH_3	32	16	19	18
3	Br	36	25	23	27
4	OCH_3	32	–[a]	11	–[a]

[a] Desired product was not obtained from the crude mixture.

Scheme 2. Synthesis of pyrylium tosylates **1**–**4**.

resulting a black viscous solution, and yellow precipitate was obtained followed by addition of diethyl ether. The precipitate was collected and washed to remove excess *p*-toluenesulfonic acid monohydrate. The identical purification procedure was followed as described in *trans*-chalcone method (*vide supra*) to yield 22.6 g (47.0 mmol, 54% yield) of the pure product **1.** Similarly, salts **2**–**4** were prepared by using benzaldehyde and the corresponding substituted acetophenones with the lower yields than that of **1** as shown in Scheme 2.

2.2.4. Method 2 (Scheme 2)

This procedure is an improved modification of that described by Bello and Kotra [23] for the corresponding tetrafluoroborate salt. A mixture of benzaldehyde (0.883 g, 8.33 mmol), acetophenone (2.00 g, 16.7 mmol), and *p*-toluenesulfonic acid monohydrate (3.17 g, 16.7 mmol) in 5 mL toluene was heated to reflux for 24 h. The reaction flask was cooled to room temperature and the black viscous solution was poured into diethyl ether. The yellow precipitate was collected and washed with water to remove excess *p*-toluenesulfonic acid monohydrate. The identical purification procedure was followed as Route 1 to yield 1.04 g (2.17 mmol, 26% yield) of the pure product.

2.2.5. Method 3 (Scheme 2)

The identical synthetic procedure was followed as in Method 2 using 5 mL of 1,2-dichloroethane instead of toluene to yield 1.10 g (2.29 mmol, 28% yield) of the pure product [24].

2.2.6. Method 4 (Scheme 2)

The identical synthetic procedure was followed as Method 2 without a solvent at 100 °C to yield 1.13 g (2.35 mmol, 28% yield) of the pure product [15]. IR (cm^{-1}): 3066, 2914, 1624, 1500, 1448, 1199, 1122, 1033, 767.^{1}H NMR (DMSO-d_6, 400 MHz, ppm) $\delta = 9.18$ (2H, s), 8.61 (6H, d, $J = 7.2$ Hz), 7.89 (3H, t, $J = 7.6$ Hz), 7.80–7.77 (6H, m), 7.48 (2H, d, $J = 6.4$ Hz), 7.11 (2H, d, $J = 8.0$ Hz), 2.28 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) $\delta = 170.5, 165.5, 146.3, 137.9, 135.6, 135.4,$

132.9, 130.5, 130.3, 130.2, 129.5, 129.2, 128.4, 125.9, 115.6, 21.2. Anal. Calculated (Found) for $C_{30}H_{24}O_4S$ (%): C, 74.98 (74.87); H, 5.03 (5.16); S, 6.67 (6.54).

2.3. *Synthesis of 2,6-bis(4-methylphenyl)-4-phenylpyrylium tosylate **(salt 2)***

The identical synthetic procedures from Methods 2–4 were followed by using 4′-methylacetophenone instead of acetophenone for the preparation of salt **2** [25]. Its yields from three different methods were given in Scheme 2. IR (cm^{-1}): 3061, 2914, 1620, 1500, 1193, 1120, 1033, 773.^{1}H NMR (DMSO-d_6, 400 MHz, ppm) $\delta = 9.05$ (2H, s), 8.57 (2H, d, $J = 7.2$ Hz), 8.49 (4H, d, $J = 8.4$ Hz), 7.87 (1H, t, $J = 7.6$ Hz), 7.78 (2H, t, $J = 8.0$ Hz), 7.60 (4H, d, $J = 8.4$ Hz), 7.48 (2H, d, $J = 8.0$ Hz), 7.11 (2H, d, $J = 8.0$ Hz), 2.50 (6H, overlap with the solvent residual peak), 2.28 (3H, s). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) $\delta = 170.2$, 164.8, 146.6, 146.3, 137.9, 135.3, 133.0, 130.9, 130.3, 130.1, 129.1, 128.4, 126.9, 125.9, 114.7, 21.9, 21.2. Anal. Calculated (Found) for $C_{32}H_{28}O_4S$ (%): C, 75.56 (75.28); H, 5.55 (5.62); S, 6.30 (6.09).

2.4. *Synthesis of 2,6-bis(4-bromophenyl)-4-phenylpyrylium tosylate **(salt 3)***

The identical synthesis procedures from Methods 2–4 were followed by using 4′-bromoacetophenone instead of acetophenone for the preparation of salt **3** [25]. Its yields from three different methods were also given in Scheme 2. IR (cm^{-1}): 3061, 2914, 1622, 1489, 1215, 1120, 1033, 767, 489.^{1}H NMR (DMSO-d_6, 400 MHz, ppm) $\delta = 9.18$ (2H, s), 8.61 (2H, d, $J = 7.6$ Hz), 8.52 (4H, d, $J = 8.8$ Hz), 7.98 (4H, d, $J = 8.4$ Hz), 7.88 (1H, t, $J = 7.2$ Hz), 7.77 (2H, t, $J = 8.0$ Hz), 7.49 (2H, d, $J = 8.0$ Hz), 7.11 (2H, d, $J = 8.0$ Hz), 2.28 (3H, s). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) $\delta = 169.6$, 165.6, 146.0, 138.0, 135.8, 133.3, 132.7, 131.0, 130.6, 130.2, 129.9, 128.6, 128.4, 125.9, 115.9, 21.2. Anal. Calculated (Found) for $C_{30}H_{22}Br_2O_4S$ (%): C, 56.44 (56.42); H, 3.47 (3.51); S, 5.02 (4.88).

2.5. *Synthesis of 2,6-bis(4-methoxyphenyl)-4-phenylpyrylium tosylate **(salt 4)***

The identical synthetic procedure from Method 3 was followed by using 4′-methoxyacetophenone instead of acetophenone for the synthesis of salt **4** [25,26]. At the end of the reaction, the solution was concentrated under vacuum. The minimum amount of acetonitrile was added to the flask to dissolve the dark viscous solution, and dark orange solid was precipitated out by addition of ice. The crude product was collected and recrystallized from chloroform to yield 537 mg (11%, 0.99 mmol). IR (cm^{-1}): 3061, 2937, 1622, 1602, 1491, 1263, 1120, 1031, 773.^{1}H NMR (DMSO-d_6, 400 MHz, ppm) $\delta = 8.88$ (2H, s), 8.55 (6H, m), 7.82 (1H, t, $J = 7.2$ Hz), 7.76 (2H, t, $J = 7.2$ Hz), 7.49 (2H, d, $J = 8.0$ Hz), 7.31 (4H, d, $J = 9.2$ Hz), 7.11 (2H, d, $J = 8.0$ Hz), 3.97 (6H, s), 2.28 (3H, s). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) $\delta = 169.3$, 165.2, 163.6, 146.2, 137.9, 134.9, 133.1, 131.4, 130.1, 130.0, 128.4, 125.9, 121.8, 115.8, 113.1, 56.5, 21.2. Anal. Calculated (Found) for $C_{32}H_{28}O_6S$ (%): C, 71.09 (70.52); H, 5.22 (5.25); S, 5.93 (5.79).

3. Results and discussion

3.1. *Synthesis*

Salt **1** was synthesized from both *trans*-chalcone [20] and 1,5-diketone [21] in a one-step procedure using tosic acid as shown in Scheme 1 in relatively high yields of 33 and 88%, respectively. In Scheme 2, the salt **1** was directly synthesized from benzaldehyde with acetophenone in 1:2 mol ratio in a one-step procedure using tosic acid in four different methods. Method 1 using $POCl_3$ generated in situ 2,4,6-triphenylpyrylium salt with chloride as a counterion, and subsequently it was isolated as tosylate salt with the addition of tosic acid. This method gave the highest yield (54%) of **1,** but comparable yields of **2**–**4** when compared with that perchlorate of a pyrylium salt (29%) reported by Moghimi et al. [22]. These results suggest that the yields of pyrylium salts are highly dependent on the substituents present in 2-, 4- and 6-phenyl groups. Salts **2**–**4** were also prepared from the reaction of benzaldehyde and corresponding substituted acetophenone in 1:2 mol ratio in a one-step procedure with tosic acid in different methods and conditions. We also explored the synthesis of pyrylium salts in the melts without solvents [16]. The reaction conditions and yields are compiled in Scheme 2. *Trans*-chalcone and 1,5-diketone methods gave higher yields of pyrylium salts than the direct method, that is, from the reactions of benzaldehyde or substituted benzaldehydes with acetophenone or substituted acetophenones. The FTIR, ^{1}H, and ^{13}C NMR spectra of salts **1**–**4** along with their elemental analysis data were consistent with the chemical structures of desired salts.

3.2. *Thermal properties*

The thermal properties of salts **1**–**4** were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The results are presented Table 1 and compared with the corresponding tetrafluoroborates [25,27] and perchlorates [26,28]. The melting transitions of the salts were lower than those of pyrylium salts both containing perchlorates, and tetrafluoroborates. This is expected, since bulky organic anion such as tosylate lowers the melting point of organic salts than compared to that done by inorganic counterions. Salt **4** did not show any crystallization exotherm either in the first cooling cycle or in the second, it had a tendency to form an amorphous phase. Additionally, it showed a T_g at 72 °C (Table 1 and Fig. S1).

3.3. *Solubility in organic solvents*

In general, highly rigid materials that consist of aromatic rings have limited solubility [29,30], but all of the pyrylium salts herein except the salt **3** had relatively good solubility in common organic solvents. They were dissolved both in low polarity solvents such as chloroform, dichloromethane, and THF as well as high polarity solvents such as methanol, acetonitrile, and DMSO.

Table 1
Thermal properties of **1**–**4** as determined by DSC and TGA.

Salt	T_g[a] (°C)	T_m[b] (°C)	T_d[c] (°C)
1, 1BF_4, **1**ClO_4		222 (215)[d], 255 [25], 273 [28]	316
2, 2BF_4		219[e] (decomp.), 311 [25] and 268–269 [27]	281
3, 3BF_4		268[e] (decomp.), 356 [25]	293
4, 4ClO_4	(72)	218[f] (209), 274–275 [26]	291

[a] T_g is the glass transition temperature.

[b] T_m is the melting transition as determined by DSC obtained at heating and cooling rates of 10 °C/min in nitrogen.

[c] T_d is the decomposition temperature at which 5% weight loss of salt occurred obtained at a heating rate of 10 °C/min in nitrogen.

[d] Value in the parentheses obtained from the second heating cycle of DSC thermogram.

[e] Obtained from the first heating cycle of DSC thermogram.

[f] Overlapped endotherms (crystal-crystal transitions) prior to melting transition in the first heating cycle only.

3.4. Optical spectroscopic properties

Among the various solvents, acetonitrile (CH_3CN) was chosen for investigating the optical spectroscopic properties since salt **3** showed very limited solubility in the other organic solvents.

The room-temperature optical absorption spectra of all four pyrylium salts dissolved in CH_3CN with the concentration of 4×10^{-6} M are displayed in Fig. 1. Solutions of all four salts absorbed strongly in the blue-near ultraviolet spectral range, except for salt **4** which absorbed in the blue-green in addition to blue-near-UV range. Each salt solution exhibits three principal absorption peaks in the above-mentioned spectral range. The peak absorption wavelengths and corresponding molar absorptivity, along with other optical spectroscopic properties such as photoluminescence spectra and quantum yields in acetonitrile (CH_3CN) are summarized in Table 2. According to the previously reported studies of 2,4,6-triphenylpyrylium perchlorate, two absorption peaks at 417 nm and 369 nm are observed in CH_2Cl_2 [7,32]. The absorption spectrum of salt **1** in CH_3CN (Fig. 1) is similar in appearance to that of the 2,4,6-triphenylpyrylium perchlorate in CH_2Cl_2, but its peak absorption (λ_{max}) exhibited hypsochromic shifts caused by the increased solvent polarity. Similarly, salts **2**–**4** also showed hypsochromic shifts in acetonitrile when compared with those in CH_2Cl_2 [32]. In salt **2** small bathochromic shifts of 12 nm and 6 nm in the shorter wavelengths and large bathochromic shift of 25 nm in the longer wavelength were observed when compared with those in salt **1.** Similarly, salt **3** showed small bathochromic shifts of 12 nm and 11 nm in the shorter wavelengths and large bathochromic shift of 16 nm in the longer wavelength. Salt **4** contains two methoxy groups (strong donor strength) bearing in 2- and 6-phenyl rings and showed significant bathochromic shifts of 44 nm and 21 nm at the shorter wavelength and 66 nm at the longer wavelength since the 2,6-diphenylpyrylium substructure is responsible for the absorption at the longer wavelength. These results confirmed that the strong electron-donating substituent such as methoxy group caused significant changes in the longer wavelength absorption in the 2,4,6-triphenylpyrylium cation, because the primary chromophore is only available in the cation. These salts have relatively large absorption coefficients in the range of 19000–40000 $M^{-1}cm^{-1}$ in acetonitrile as calculated from the respective Beer-Lambert law plots (Table 2, Fig. S2-S5), which are in good agreement with the results of corresponding pyrylium perchlorates [32]. It is to be noted here that the recorded excitation spectra of these salts were similar to their UV–visible absorption spectra that provided the compelling evidence for the photoluminescence properties of the salts not the impurities in acetonitrile. The fluorescence spectra of salts **1**–**4** in CH_3CN are shown in Fig. 2, which also indicate the respective excitation wavelengths. Salts **1**–**3** emitted in the blue-green spectral region with emission peaks in the 450–478 nm range when excited at various wavelengths of light, and these values indicate that the variation of the substituents in 2- and 6-phenyl rings had an effect on the light emission properties. However, salt **4** showed a significant bathochromic shift and emitted green light with λ_{max} at 536 nm when excited at 375 nm (Fig. 2). Fig. 3 also displays the fluorescence of **1**–**4** in acetonitrile when excited at hand-held UV lamp (365 nm). The excited state energies of these salts in acetonitrile as calculated from the intersections of absorption spectra and emission spectra (Figs. S6-S9) were found to be 2.89 eV, 2.66 eV, 2.78 eV, and 2.46 eV, respectively. The excited state energies for the two corresponding perchlorates in acetonitrile are reported to be 2.83 eV and 2.70 eV [33]. Their wavelengths of light emission were hypsochromically shifted in acetonitrile when compared with those of the corresponding perchlorate salts; and they showed Stokes shift of 2530, 2390, 2668 and 2520 cm^{-1}, respectively. The peak emission wavelengths of the corresponding perchlorates in acetonitrile are 466 nm, 490 nm, and 546 nm and their Stokes shifts are 3232, 2956, and 3052 cm^{-1}, respectively [32]. The emission spectral range of each salt solution had a full-width-at-half-maximum (FWHM) in the 2448-2829 cm^{-1} range which resembled that of Coumarin laser dyes that operate in the blue-green spectral range. The single emission peak and the magnitude of FWHM are indicative of a single chromophore being responsible for the fluorescence. The quantum yields (Φ_F) of salts **1**–**4** were determined against diphenylanthracene (Φ_F) in cyclohexane and were found to be in the range 0.27–0.56. Salt **3** had the lowest quantum yield, as expected, due to heavy atom effect [34]. The corresponding perchlorate salts are reported [32] to have quantum yields of 0.60–0.82. The optical spectroscopic properties of the pyrylium salts are greatly affected by chemical structure modifications with electron donating substituents in its primary chromophore, which is the cationic moiety. These results suggested that the optical properties of these pyrylium salts can be tuned with the variation of organic counterions such as tosylate.

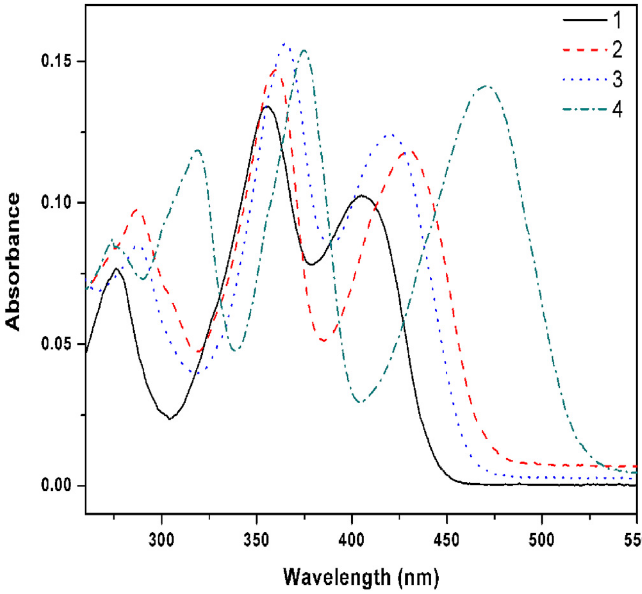


Fig. 1. UV–visible spectra of the solutions of salts **1**–**4** in CH_3CN (concentration of 4×10^{-6} M).

3.5. Time-resolved and intensity-dependent emission

Steady-state fluorescence measurements revealed that salt **1** has the highest quantum yield of 0.56 among the four, and hence was further explored using time-resolved and pump intensity-dependent measurements to assess its potential as an active material for a dye laser [35]. The time-evolution of fluorescence of an acetonitrile solution of the salt (concentration 2×10^{-3} M) is shown in Fig. 4(b) for different pump intensity levels. The corresponding emission spectra are presented in Fig. 4(a). The solution was contained in a 10 mm × 10 mm x 30 mm rectangular quartz cuvette and was excited using the 400 nm, 130 fs, 1 kHz repetition rate pulses from the Ti: sapphire laser system mentioned in Section 2. The average beam power was maintained at 10 mW, but the spot size and hence the intensity were changed using different focusing conditions. The salient features of the fluorescence decay curves and the corresponding emission spectra are as follows. When the pump beam was focused to a 2 mm diameter spot (average pump intensity of 0.032 W/cm^2) and the emission was collected from the

Table 2
Optical spectroscopic properties of salts **1**–**4**.

Entry	salt 1	salt 2	salt 3	salt 4
Peak absorption Wavelength, λ_{max} (nm)	275, 354, 404	287, 360, 429	287, 365, 420	319, 375, 470
Molar absorptivity ($M^{-1}cm^{-1}$)	å$_{275}$ = 19000	å$_{287}$ = 24000	å$_{287}$ = 21000	å$_{319}$ = 28000
	å$_{354}$ = 34000	å$_{360}$ = 36000	å$_{365}$ = 40000	å$_{375}$ = 37000
	å$_{404}$ = 26000	å$_{429}$ = 29000	å$_{420}$ = 32000	å$_{470}$ = 34000
Peak Emission Wavelength (nm)[a]	450	478	473	536
Excited State Energy (eV)[b] (cm^{-1})[b]	2.89 (23310)	2.73 (22026)	2.78 (22422)	2.46 (19881)
Stokes shift (cm^{-1})[c]	2530	2390	2668	2520
FWHM (cm^{-1})	2677	2814	2829	2448
Ô$_F$[d]	0.56	0.47	0.27	0.33

[a] All measurements are for salt solutions in CH_3CN.

[b] Intersection of the absorption and emission spectra (Fig. S6-S9) is used as estimate of excited state energy in eV (cm^{-1}).

[c] Difference between emission maxima and the largest wavelength absorption maxima.

[d] Quantum yield was calculated against diphenyl anthracene as standard ($\Phi_F = 0.9$) [19,31].

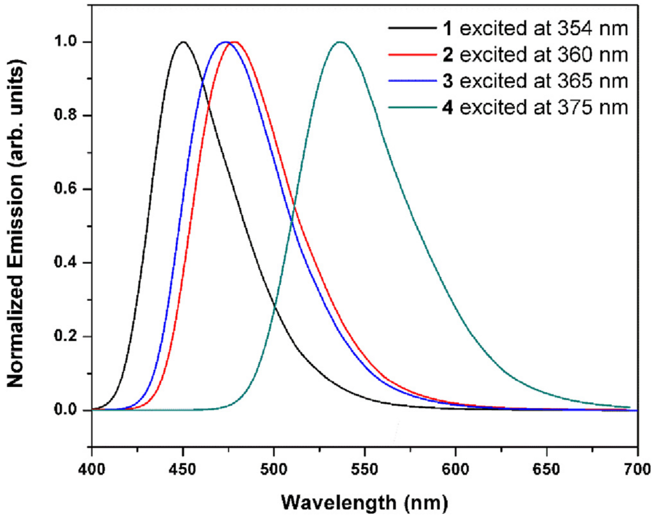


Fig. 2. Emission spectra of salts **1**–**4** recorded in CH_3CN at various excitation wavelengths.

front surface at an angle with respect to the incident direction, the fluorescence decayed as a single exponential with a fluorescence lifetime of 4.6 ± 0.1 ns (Curve 1 in Fig. 4(b)) and the FWHM linewidth was 77 ± 1 nm (Curve 1 in Fig. 4(a)). Similar lifetime and linewidth were obtained (not shown in the figure) for much lower concentrations (10^{-5} M and 10^{-6} M) solutions, as well. As the pump intensity was increased (spot size 0.2 mm, average intensity 3.2 W/cm^2) the lifetime shortened 3.5 ± 0.1 ns and the linewidth narrowed 71 ± 1 nm, for similar collection geometry (Curve 2 in both figures). The longer fluorescence lifetimes are indicative of spontaneous emission, while shorter lifetimes are consistent with amplified spontaneous emission (ASE) or stimulated emission. When more intense transverse pumping using a cylindrical lens was employed generating a narrow excited stripe (0.02 mm width and 5 mm length) across the cuvette, stimulated emission was observed from the two sides of the cuvette at a direction perpendicular to the pump beam. This emission had substantial directionality, a much reduced lifetime of 615 ps and a significantly narrow linewidth of 21.5 ± 0.5 nm, as seen in curve 3 of Fig. 4(b) and Fig. 4(a), respectively. The directionality, lifetime shortening and linewidth reduction are indications of stimulated emission [35,36]. What was even more interesting, when the orientation of the cuvette was adjusted so that a fraction of the emission reflected from its side walls could pass through the excited region, the output from the side resembled a symmetric pulse of FWHM width 247 ± 5 ps [Fig. 4(b) Curve 4] and linewidth 7.5 ± 0.5 nm [Fig. 4(b) Curve 4] indicative of laser action. The onset of stimulated emission and laser action were observed with the higher-concentration solution (concentration 2×10^{-3} M), while with the lower-concentration solution (concentrations 1×10^{-4} M or lower) only the spontaneous emission was observed. A detailed systematic

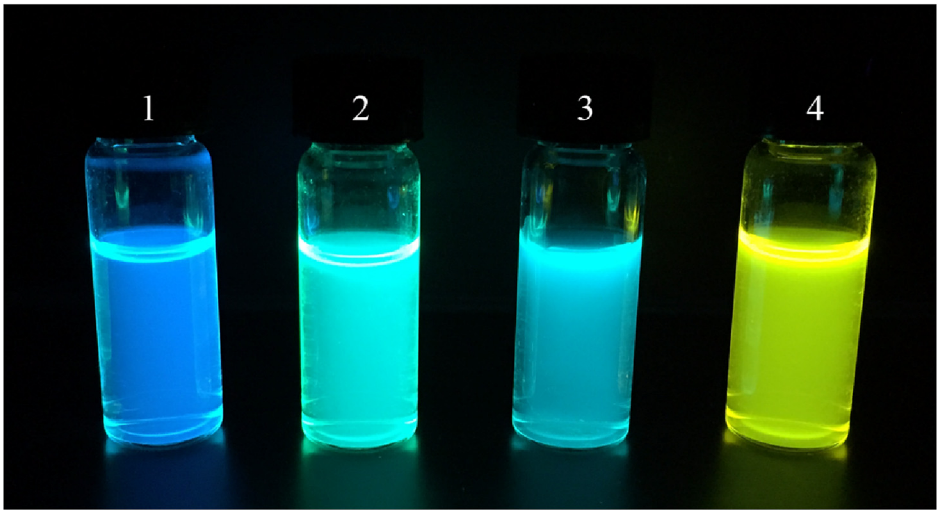


Fig. 3. Salts **1**–**4** in CH_3CN under hand-held UV lamp (365 nm) exhibiting fluorescence.

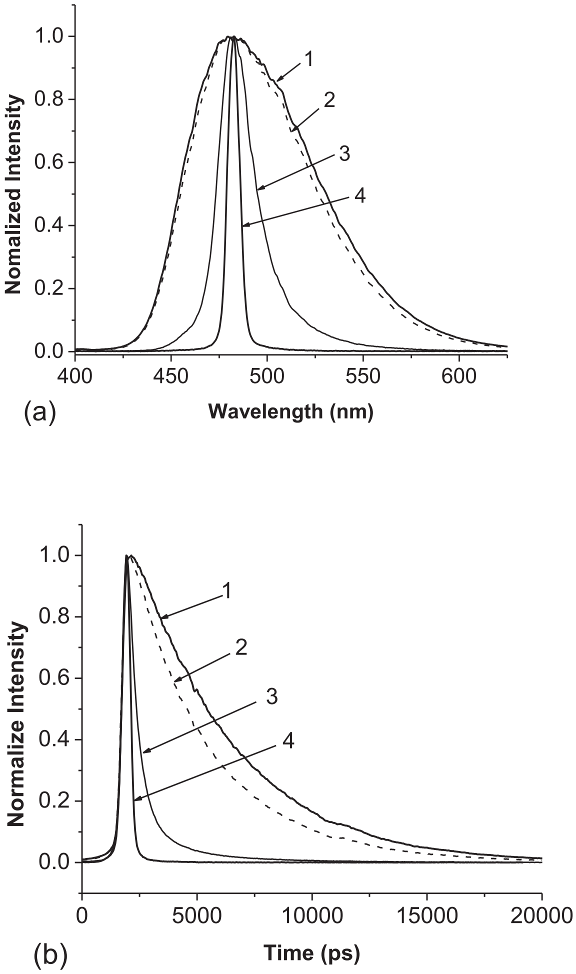


Fig. 4. Pump intensity dependence of (a) fluorescence spectra, and (b) fluorescence lifetime of a 2.0×10^{-3} M solution of 2, 4, 6-triphenylpyrylium tosylate (salt 1) in acetonitrile at room temperature. Curve 1 and Curve 2 in both Fig. 4(a) and Fig. 4(b) were recorded for longitudinal pumping into the cuvette containing the dye solution. The spot size and average intensity of the pump beam were 2.0 mm and 0.032 W/cm^2 (for Curve 1); 0.2 mm and 3.20 W/cm^2 (for Curve 2). Curve 3 and Curve 4 in both Fig. 4(a) and (b) were recorded for transverse pumping of the dye solution in the cuvette using a cylindrical lens. The beam was focused to a 0.02 mm × 5 mm line and the average intensity was 4.02 W/cm^2. Curve 3 (in both figures) was recorded without making any effort to feed the reflected fluorescence from cuvette walls back through the pumped volume of the dye, while Curve 4 (in both figures) was obtained by adjusting the orientation of the cuvette so that a significant fraction of the reflections go back and forth through the pumped volume. Since the solution had high gain even this small feedback led to laser oscillation, as evident from shortest linewidth and pulse width, as well as, symmetric line shape and pulse shape of Curve 4 in Fig. 4(a) and (b), respectively.

concentration-dependent study is required to determine optimal concentration for efficient laser action. Both the center wavelength of stimulated emission and laser spectra coincided with the peak of the fluorescence spectrum, where the gain is maximum. The laser action was obtained with reflection from the cuvette side walls (approximately 8% from each surface), which is an indication of the high optical gain of the salt **1** solution. The laser linewidth was rather broad and multimodal since no wavelength selection element was used in the cavity. The results on laser action presented here culminate from an exploratory experiment, which demonstrates the potential of the salt as a high-gain laser dye in the blue-green spectral region. However, the detailed quantum electronic characterization of the salt as a laser dye will require determining optimal concentration, design and incorporation of an adequate optical cavity with a wavelength tuning element, and careful measurements of lasing threshold, laser linewidth, output power, tuning range, slope efficiency and other laser parameters, all of which are planned to be pursued in a future study.

4. Conclusions

This study described various methods for the synthesis of several 2,4,6-triphenylpyrylium tosylate salts via dehydrocyclization reaction using *p*-toluenesulfonic acid, which provides significantly safe reaction condition than the conventional acids as condensing agents. The chemical structures were fully characterized from their FTIR, ^{1}H, ^{13}C NMR spectra and elemental analysis. They have good solubility in various common organic solvents, and their thermal stabilities were at the temperatures ca. 300 °C. Given the organic salts, their thermal stabilities are considered to be excellent. Salt **4** showed an amorphous phase as evident from thermal analyses with DSC measurements. Due to the presence of chromophores, they exhibited photoluminescence properties in solution. Salts **1**–**3** emitted intense light in the blue range (450–478 nm) and **4** emitted intense light in the green range (536 nm). In an exploratory experiment, salt **1** with the highest quantum yield demonstrated stimulated emission and free-running laser action with only nominal feedback from cuvette walls, which is indicative of the potential of the salt as the active material for an efficient dye laser operating in the blue-green spectral range. The optical spectroscopic properties of pyrylium salts were dependent on the chemical structures of not only cations but also anions. Their properties can be further tuned by structural modification to suit their multitude applications. Additionally, they can be useful for the synthesis of various heterocyclic molecules. To sum up, the synthesis of these pyrylium salts using safer and inexpensive routes open up possibility of their wide use as light emitters, sensitizers, lasers, and other nonlinear optical and biophotonic applications.

Supplementary information

DSC thermograms of **4,** Beer-Lambert law plots and absorption and emission spectra of **1**–**4** are available.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2018.06.025.

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