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Synthesis, Optical, and Thermal Properties of 2,4,6-Tris(4-Substituted Phenyl)Pyrilium Tosylates And Triflimides

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Synthesis, optical, and thermal properties of 2,4,6-tris(4-substituted phenyl)pyrylium tosylates and triflimides

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ABSTRACT

A group of five 2,4,6-tris(4-substituted phenyl)pyrylium tosylates were synthesized in one-pot reaction from para-substituted benzaldehyde and para-substituted acetophenones using tosic acid as a condensing agent. The tosylate salts were converted to the corresponding triflimide salts by metathesis reactions. Chemical structures, as well as optical spectroscopic and thermal properties of these salts were studied using pertinent experimental techniques. Trimethyl- and trihalo-substituted pyrylium salts emitted strong blue light with peaks in the 456 nm–479 nm range and trimethoxy-pyrylium salts emitted intense green light with maxima around 526 nm in acetonitrile solution. Quantum yields of the solutions were rather low, but they were also fluorescent in the solid state. Acetonitrile solution of trichloro-substituted pyrylium triflimide showed significant spectral line narrowing and fluorescence lifetime shortening under intense excitation, and laser action with minimal feedback. The salts have low melting transitions compared to the corresponding $^{-}\text{BF}_4$ salts, and their thermal stability is excellent with decomposition temperature in the 268–402 °C range in nitrogen.

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1. Introduction

Pyrylium salts are an important class of cationic organic molecules having a trivalent oxygen atom in a six-membered heterocyclic aromatic ring. These salts are multifunctional materials with unique properties, and hence drawn attention for various applications in chemistry, physics, and biology [1–19]. They are used as precursors for synthesis of important compounds, such as, substituted furans, pyridines, pyridinium salts and betaine dyes [1–6]. These salts are electron deficient in their molecular structures. So, they are capable of accepting electron from electron rich organic molecules, which make them suitable as sensitizers of photo-induced electron transfer processes [7–9]. Their absorption and fluorescence properties have been exploited to design sensors for cyanide ion [10], amines, amino acid, nitric oxide [11], and proteins [12]. Their multiphoton absorption properties make them useful in applications, such as, three dimensional data storage, photodynamic therapy, optical power limiting, and upconversion lasers [13]. In recent years, pyrylium salts have been reported as photo-oxidants for

the metal-free ring-opening metathesis polymerization reactions of norbornenes—strained bicyclic alkenes and functionalized norbornenes [14–17]. Interestingly enough, they are found to be effective initiators for the both photochemical and thermal cationic polymerization reactions of epoxy resins [18] that has practical implication for three dimensional UV-curing. Additionally, they have been used for the photocatalytic degradation of different pollutants from aqueous environments, which is quite significant for green chemistry [19]. Recently, we reported on the synthesis of four pyrylium salts using tosic acid as a benign, condensing agent and demonstrated the potential of these salts as high-gain laser dyes in the blue-green spectral region [20]. Although tosic acid has previously been used in diverse organic reactions [21–26], the preparation of pyrylium salts using this acid is relatively rare [20]. The representative of commonly used pyrylium salts of diverse chemical structures with different counterions (**I–XXII**), mostly inorganic ions, for various applications is shown in Fig. S1 [20,27].

In this article, we report on a facile synthesis of a series of 2,4,6-tris(4-substituted phenyl)pyrylium tosylates, **PT1–PT5**, and their subsequent transformation to pyrylium triflimides, **PTF1–PTF5**, using metathesis reaction (Scheme 1). As opposed to inorganic counterions, organic counterions of the salts, specifically triflimide counterions, impart good solubility, low melting points and other physical properties including optical properties in the solid states. The chemical structures

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Scheme 1. Synthesis methods of PT1-PT5 and PTF1-PTF5.

of both tosylates and triflimides were characterized using ^1H , ^{13}C NMR spectra (Figs. S2–S11) and elemental analysis. Their optical and thermal properties were examined with the aim of understanding the structure-property relationship and developing this class of pyrylium salts for multi-functional applications.

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 TFA-d , CDCl_3 , or CD_3CN with tetramethylsilane as an internal standard. 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 PerkinElmer LS-55 luminescence spectrometer with a xenon lamp as a light source. Quantum yields were estimated using the following relation:

$$\Phi_X = \Phi_{ST} \left(\frac{\text{Grad}X}{\text{Grad}ST} \right) \left(\frac{\eta^2 X}{\eta^2 ST} \right), \quad (1)$$

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 [28].

thracene) 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 [28].

2.2. Synthesis

PT1-PT5 were prepared using one-pot reaction of para-substituted aldehydes with para-substituted acetophenones in presence of tosic acid in 1,2-dichloroethane on heating to reflux. Pyrylium triflimides, PTF1-PTF5, were prepared using the metathesis reaction of PT1-PT5 with lithium triflimide on heating in acetonitrile (Scheme 1).

2.2.1. General procedure for one-pot synthesis of PT1 and PT3-PT5

To a 50 mL round-bottomed flask, 0.460 g (3.83 mmol) of 4-methylbenzaldehyde, 1.03 g (7.65 mmol) of 4'-methylacetophenone and 1.46 g (7.65 mmol) of tosic acid monohydrate were added. Then 7 mL of 1,2-dichloroethane was added to the flask and heated to reflux for 24 h with stirring. The reaction mixture turned from yellow solution to dark red solution. At the end of the reaction period, the flask was cooled down to room temperature (rt) resulting in yellow-green precipitate product. The product was then transferred to a 150 mL Erlenmeyer flask containing ether and kept on stirring for 30 min to yield bright yellow precipitate. It was then washed with copious amount of water to remove the excess tosic acid and collected by vacuum filtration to give 0.383 g (0.733 mmol, yield = 19%). For analytically pure compound PT1, it was then recrystallized from acetonitrile. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.84 (s, 2H), 8.57 (d, $J = 8.8\text{ Hz}$, 2H), 8.37 (d, $J = 8.4\text{ Hz}$, 4H), 7.96 (d, $J = 6.4\text{ Hz}$, 2H), 7.34 (d, $J = 8.0\text{ Hz}$, 4H), 7.19 (d, $J = 8.0\text{ Hz}$, 2H), 7.06 (d, $J = 8.4\text{ Hz}$, 2H), 2.42 (s, 6H), 2.40 (s, 3H), 2.06 (s, 3H). The solubility of PT1 in CDCl_3 is good enough for ^1H NMR, but not for ^{13}C NMR (carbon signals are very weak). ^{13}C NMR (100 MHz, TFA-d) δ ppm 168.7, 163.8, 146.4, 146.2, 142.1, 128.6, 128.4, 127.3, 126.9, 126.0, 125.2, 123.6, 123.2, 109.8, 17.8, 17.2. Anal. Calculated (found) for $\text{C}_{33}\text{H}_{30}\text{O}_4\text{S}$ (522.65): C, 75.83 (75.56); H,

5.79 (5.76); S, 6.14 (5.96%). Data for **PT3** yield = 21%, recrystallized from tetrachloroethane. ^1H NMR (400 MHz, TFA-*d*) δ ppm 8.53 (s, 2H), 8.38 (dd, $J_{\text{ortho}} = 7.6\text{ Hz}$, $J_{\text{meta}} = 4.8\text{ Hz}$, 4H), 8.25 (dd, $J_{\text{ortho}} = 7.6\text{ Hz}$, $J_{\text{meta}} = 4.8\text{ Hz}$, 2H), 7.79 (d, $J = 7.2\text{ Hz}$, 2H), 7.46–7.40 (m, 6H), 7.30 (d, $J = 7.6\text{ Hz}$, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, TFA-*d*) δ ppm 170.4, 169.0, 166.4, 165.8, 144.3, 131.3, 131.2, 130.5, 130.4, 129.1, 128.4, 125.7, 124.3, 117.6, 113.2, 19.4. Anal. Calculated (found) for $\text{C}_{30}\text{H}_{21}\text{O}_4\text{F}_3\text{S}$ (534.55): C, 67.41 (67.11); H, 3.96 (3.93); S, 6.00 (6.29%). Data for **PT4** yield = 20%, recrystallized from acetic acid. ^1H NMR (400 MHz, TFA-*d*) δ ppm 8.61 (s, 2H), 8.30 (d, $J = 8.8\text{ Hz}$, 4H), 8.16 (d, $J = 8.8\text{ Hz}$, 2H), 7.81 (q, $J = 10.8\text{ Hz}$, 8H), 7.33 (d, $J = 8.0\text{ Hz}$, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, TFA-*d*) δ ppm 181.1, 170.8, 166.2, 144.5, 144.0, 130.7, 130.7, 130.5, 129.8, 129.3, 129.0, 126.4, 125.9, 113.9, 19.6, 18.6. Anal. Calculated (found) for $\text{C}_{30}\text{H}_{21}\text{O}_4\text{SCl}_3$ (583.91): C, 61.71 (67.41); H, 3.63 (3.60); S, 5.49 (5.31%). Data for **PT5** yield = 21%, recrystallized from acetic acid. ^1H NMR (400 MHz, TFA-*d*) δ ppm 8.62 (s, 2H), 8.20 (d, $J = 8.8\text{ Hz}$, 4H), 8.06 (d, $J = 8.8\text{ Hz}$, 2H), 7.95–7.90 (m, 6H), 7.80 (d, $J = 8.4\text{ Hz}$, 2H), 7.33 (d, $J = 8.4\text{ Hz}$, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, TFA-*d*) δ ppm 180.9, 170.9, 166.3, 144.4, 135.9, 133.7, 133.6, 132.3, 132.2, 130.8, 129.5, 129.2, 128.7, 126.7, 125.7, 113.8, 19.5, 18.4. Anal. Calculated (found) for $\text{C}_{30}\text{H}_{21}\text{O}_4\text{SBr}_3$ (717.26): C, 50.24 (50.13); H, 2.95 (2.88); S, 4.47 (4.39%).

2.2.2. Procedure for one-pot synthesis of **PT2**

To a 100 mL three-necked, round-bottomed flask, 0.477 g (3.50 mmol) of 4-methoxybenzaldehyde, 1.05 g (7.00 mmol) of 4'-methoxyacetophenone and 1.33 g (7.00 mmol) of tosic acid monohydrate were added. Then 7 mL of 1,2-dichloroethane was added, and the reaction flask was assembled with a condenser and purged with N_2 . To minimize the impurities generated due to oxidation in air and, hence, to isolate the reaction product **PT2** became easier when the reaction was purged with N_2 . The reaction mixture was heated to reflux for 24 h with stirring. During the reaction, the solution turned from bright red to dark red. After the end of the reaction period, the flask was cooled down to rt resulting in a black tar-like mixture. The contents were transferred to a separatory funnel with enough chloroform to fully dissolve the compound. Water was then added to the funnel and shaken to remove the excess tosic acid. This washing procedure was repeated until excess tosic acid was removed completely as tested with the litmus paper. The organic layer was collected, and solvent was removed by a rotary evaporator, resulting in a sticky dark red crude compound. It was dissolved in a minimum volume of chloroform, and then ether was added to precipitate out the desired compound. It was collected and dried in vacuum to afford 0.348 mg (0.610 mmol) (yield = 17%). For analytically pure **PT2**, it was recrystallized from using a minimum volume of chloroform. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.45 (d, $J = 8.0\text{ Hz}$, 2H), 8.41 (s, 2H), 8.18 (d, $J = 9.2\text{ Hz}$, 4H), 8.00 (d, $J = 8.0\text{ Hz}$, 2H), 7.22 (d, $J = 7.6\text{ Hz}$, 2H), 6.80 (d, $J = 8.8\text{ Hz}$, 4H), 6.61 (d, $J = 9.2\text{ Hz}$, 2H), 3.76 (s, 6H), 3.60 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 166.9, 165.2, 164.5, 161.6, 144.9, 138.8, 133.3, 130.5, 128.5, 126.4, 123.9, 120.8, 115.3, 115.2, 110.4, 55.6, 55.4, 21.3. Anal. Calculated (found) for $\text{C}_{33}\text{H}_{32}\text{O}_8\text{S}$ (588.68): C, 67.33 (67.93); H, 5.48 (5.32); S, 5.45 (5.45%).

2.2.3. General procedure for metathesis reaction for the preparation of **PTF1-PTF5**

An amount of 0.795 g (1.52 mmol) of **PT1** was suspended in 100 mL of acetonitrile into one-necked, round-bottomed flask. In the case of **PTF2**, a solution of **PT2** in 50 mL of acetonitrile was charged into a flask. The clear solution obtained from 0.480 g (1.67 mmol) lithium triflimide dissolved in 5 mL acetonitrile was added dropwise to the flask. A fluffy precipitate appeared immediately, which soon turned into fine crystals. The reaction mixture was then heated to reflux for 24 h. At the

end of the reaction, it was allowed to cool. The solvent from the reaction contents was removed by rotary evaporator. Plenty of water was then added to remove lithium tosylate yielding **PTF1**. It was then collected by vacuum filtration and dried in vacuo to give 0.889 g (1.41 mmol, yield = 93%). ^1H NMR (400 MHz, CD_3CN) δ ppm 8.56 (s, 2H), 8.30 (d, $J = 8.4\text{ Hz}$, 4H), 8.21 (d, $J = 8.0\text{ Hz}$, 2H), 7.60 (d, $J = 8.0\text{ Hz}$, 6H), 2.54 (s, 9H). ^{13}C NMR (100 MHz, CD_3CN) δ ppm 170.5, 165.5, 147.6, 147.5, 131.1, 131.0, 130.3, 129.8, 128.8, 126.6, 117.6, 114.3, 21.3, 21.2. Anal. Calculated (found) for $\text{C}_{28}\text{H}_{23}\text{NO}_5\text{F}_6\text{S}_2$ (631.61): C, 53.25 (53.49); H, 3.67 (3.54); N, 2.22 (2.22); S, 10.15 (9.98%). Data for **PTF2** yield = 92%. ^1H NMR (400 MHz, CD_3CN) δ ppm 8.33–8.27 (m, 8H), 7.25 (d, $J = 9.2\text{ Hz}$, 6H), 3.99 (s, 3H), 3.98 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ ppm 169.0, 166.1, 165.6, 163.0, 132.1, 130.8, 125.0, 121.6, 115.8, 115.7, 111.6, 56.2, 56.1. Anal. Calculated (found) for $\text{C}_{28}\text{H}_{23}\text{NO}_8\text{F}_6\text{S}_2$ (679.61): C, 49.48 (49.64); H, 3.41 (3.40); N, 2.06 (2.09); S, 9.44 (9.55%). Data for **PTF3** yield = 81%. ^1H NMR (400 MHz, CD_3CN) δ ppm 8.63 (s, 2H), 8.50 (dd, $J_{\text{ortho}} = 9.2\text{ Hz}$, $J_{\text{meta}} = 4.0\text{ Hz}$, 4H), 8.41 (dd, $J_{\text{ortho}} = 7.2\text{ Hz}$, $J_{\text{meta}} = 3.6\text{ Hz}$, 2H), 7.56 (dd, $J_{\text{ortho}} = 8.8\text{ Hz}$, $J_{\text{meta}} = 2.0\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ ppm 170.0, 168.5, 165.9, 165.2, 133.0, 132.9, 132.1, 132.0, 129.5, 125.7, 125.7, 115.5. Anal. Calculated (found) for $\text{C}_{25}\text{H}_{14}\text{NO}_5\text{F}_9\text{S}_2$ (643.50): C, 46.66 (46.80); H, 2.19 (2.17); N, 2.18 (2.30); S, 9.97 (9.90%). Data for **PTF4** yield = 92%. ^1H NMR (400 MHz, CD_3CN) δ ppm 9.00 (s, 2H), 8.51 (d, $J = 8.4\text{ Hz}$, 4H), 8.43 (d, $J = 8.8\text{ Hz}$, 2H), 7.82 (dd, $J_{\text{ortho}} = 8.8\text{ Hz}$, $J_{\text{meta}} = 2.0\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ ppm 170.2, 165.4, 142.0, 141.9, 131.5, 130.6, 127.7, 121.8, 117.6, 116.2. Anal. Calculated (found) for $\text{C}_{25}\text{H}_{14}\text{NO}_5\text{F}_6\text{S}_2\text{Cl}_3$ (692.86): C, 43.34 (43.41); H, 2.04 (2.11); N, 2.02 (1.94); S, 9.25 (9.22%). Data for **PTF5** yield = 90%. ^1H NMR (400 MHz, CD_3CN) δ ppm 8.69 (s, 2H), 8.32 (dd, $J_{\text{ortho}} = 8.8\text{ Hz}$, $J_{\text{meta}} = 2.0\text{ Hz}$, 4H), 8.21 (dd, $J_{\text{ortho}} = 8.8\text{ Hz}$, $J_{\text{meta}} = 2.0\text{ Hz}$, 2H), 7.98 (dd, $J_{\text{ortho}} = 8.8\text{ Hz}$, $J_{\text{meta}} = 2.4\text{ Hz}$, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ ppm 170.4, 165.6, 133.6, 132.0, 131.5, 130.8, 130.8, 130.5, 128.1, 116.2. Anal. Calculated (found) for $\text{C}_{25}\text{H}_{14}\text{NO}_5\text{F}_6\text{S}_2\text{Br}_3$ (826.22): C, 36.34 (36.59); H, 1.71 (1.72); N, 1.70 (1.66); S, 7.76 (7.89%).

2.3. Optical spectroscopic measurements

Both steady-state and time-resolved spectroscopic measurements of the acetonitrile solutions of the salts were carried out to investigate the characteristics of the absorption and fluorescence spectra, fluorescence lifetime, and excitation-intensity dependent features of fluorescence spectra and lifetime. Steady-state absorption spectra were measured using a UV-Visible-Near-Infrared spectrophotometer (Varian Cary 50 Bio). Steady-state fluorescence spectra were measured using a PerkinElmer LS-55 luminescence spectrometer with a xenon lamp as the light source.

Time-resolved measurements were carried out on two of the triflimide salt (**PTF2** and **PTF4**) solutions in acetonitrile by exciting the samples with the 400-nm second harmonic output of a Ti: sapphire laser and regenerative amplifier system (Spectra-Physics Spitfire) and monitoring the time evolution of the fluorescence using a streak camera system (Hamamatsu Streak Scope C4334 coupled with a spectrometer (Imaging Spectrograph G50is). The laser system generated 800-nm, 120-fs, 1 kHz repetition rate pulses which were frequency-doubled in a nonlinear optical crystal to generate the 400-nm pulses. The salt solutions were contained in a 10 mm $\times$ 10 mm $\times$ 30 mm rectangular quartz cuvette and intensity-dependent measurements were carried out by using calibrated neutral density filters to control power of the pump beam and adjusting the focusing arrangement. The cuvette was pumped along one of its 10 mm sides (path length 10 mm) and emission was collected from one of the adjacent sides.

3. Results and discussion

3.1. Synthesis of salts

We synthesized **PT1-PT5** salts containing tosylate counterions with reasonable yields (19%, 17%, 21%, 20% and 21%, respectively). The yields of the corresponding $^-BF_4$ salts are (41%, 12%, 40%, 19% and 22%), respectively, reported by Martiny et al. [29]. The yields of trimethoxy-, trichloro- and tribromo-pyrylium salts are comparable with those of corresponding $^-BF_4$ salts, but those of trimethyl- and trifluoro-pyrylium salts are low. Generally, yields of $^-BF_4$ salts are higher than those of the corresponding tosylate salts [20]. Yields for **PTF1-PTF5** following the metathesis reaction were in the 81–93% range. One can usually prepare 2,4,6-triphenyl pyrylium salt from the reaction of *trans*-chalcone with acetophenone, which in turn can be prepared from benzaldehyde and acetophenone in alkaline medium via aldol condensation. It can also be prepared from the dehydrocyclization of 1,3,5-triphenyl-1,5-pentanedione (aka 1,5-diketone), a Michael addition [30] product of acetophenone to a chalcone in alkaline medium. Both

two-step methods usually give better yields of pyrylium salts than the one-step reaction. Mechanistically, in one-step reaction *trans*-chalcone and 1,5-diketone are formed *in situ* in presence of tosic acid that then undergo dehydrocyclization to form pyrylium salt.

3.2. Optical spectroscopic properties

The UV–vis absorption spectra of the both tosylate and triflimide pyrylium salts in acetonitrile at room temperature are shown in Fig. 1. Missing from the figure are spectra of **PT4** and **PT5** because those do not dissolve well in acetonitrile. Solutions of the salts absorbed strongly in the near-ultraviolet-blue (325 nm–450 nm) spectral range, except for salts **PT2** and **PTF2** which absorbed in the violet-blue (360–520 nm) spectral region.

Each salt solution exhibits two overlapping absorption bands with two principal absorption peaks, except **PT2** and **PTF2** that exhibit one principal peak (at 411 nm) along with a shoulder peak (at 455 nm). For comparison, the corresponding perchlorate salt exhibits a principal peak (at 410 nm) and a shoulder (at 450 nm) in acetonitrile. Note here that the parent salt 2,4,6-triphenylpyrylium perchlorate shows two absorption peaks at 355 nm and 405 nm in acetonitrile [31]. The peak absorption wavelengths and corresponding molar absorptivity of these salts are summarized in Table 1. The amplitude and spectral position of these two absorption peaks were dependent on the nature of substituents present in the 2-, 4- and 6- phenyl groups of these pyrylium salts. Along the line of other authors [31,32] we attribute the longer wavelength band to transitions that involve orientation of the transition dipole moment along the long axis passing the positions 2 and 6 ('x-axis'); and the shorter-wavelength band to transitions involving orientation of the dipole moment approximately along the short axis ('y-axis') passing through the 4-position, as shown in the inset of Fig. 1. These salts have relatively large absorption coefficients in the range of 27000–50000 M⁻¹cm⁻¹ as calculated from the respective Beer-Lambert plots (Table 1), which are in good agreement with the results of other pyrylium perchlorates [31]. Note here that the recorded excitation spectra of these salts matched with their UV–vis absorption spectra that provided the compelling evidence for their photoluminescence properties in acetonitrile not from the impurities.

The room temperature fluorescence spectra of **PTF1-PTF5** salt solutions in acetonitrile at various excitation wavelengths are displayed in Fig. 2. The fluorescence spectrum of every salt solution consists of a single broad band in the blue-red spectral range; and together the five

Fig. 1. UV–visible absorption spectra of the solutions of **PT1-PT3** and **PTF1-PTF5** in acetonitrile at room temperature, (concentration: 5×10^{-6} M).

Table 1
Optical spectroscopic properties of **PT1-PT3** and **PTF1-PTF5** in acetonitrile.

Salt	PT1	PTF1	PT2	PTF2	PT3	PTF3	PTF4	PTF5
Peak Absorbance	375, 425	375, 425	411, 445 sh ^a	411, 445 sh ^a	358, 410	358, 410	371, 417	376, 422
λ_{max} (nm)								
Molar Absorptivity (M ⁻¹ cm ⁻¹)	$\epsilon_{425} = 33000$ $\epsilon_{375} = 46000$	$\epsilon_{425} = 33000$ $\epsilon_{375} = 46000$	$\epsilon_{411} = 50,000$	$\epsilon_{411} = 31,000$	$\epsilon_{410} = 27,000$ $\epsilon_{358} = 37,000$	$\epsilon_{410} = 27,000$ $\epsilon_{358} = 37,000$	$\epsilon_{417} = 33,000$ $\epsilon_{371} = 45,000$	$\epsilon_{422} = 30,000$ $\epsilon_{376} = 41,000$
Peak Emission λ_{em} (nm) ^b	473	473	526	526	456	456	471	479
ν (cm ⁻¹)	21,142	21,142	19,011	19,011	21,930	21,930	21,231	20,877
Stokes Shift (cm ⁻¹) ^c	2387	2387	3461	3461	2460	2460	2749	2820
Bandwidth, $\Delta\nu$ (cm ⁻¹) ^d	2693	2693	2431	2431	2752	2752	2807	2758
Quantum Yield (Φ_F) ^e	0.32	0.31	0.24	0.40	0.41	0.39	0.31	0.13

^a Shoulder.

^b All measurements are for salt solutions in acetonitrile (CH₃CN) at room temperature.

^c Difference between emission maximum and the larger wavelength absorption maxima.

^d Bandwidth = Full-width-at-half-maximum.

^e Quantum yield was calculated against diphenyl anthracene as standard ($\Phi_F = 0.9$) [28].

Fig. 2. Room-temperature fluorescence spectra of the solutions of **PTF1**–**PTF5** in acetonitrile at excitation wavelengths listed in the inset.

spectra cover the 410 nm–650 nm spectral range. The peak emission wavelength of the salt solutions lies within the 455 nm–480 nm (blue) range, except for that of **PTF2** which is at 526 nm. The corresponding **PT** salt solutions **PT1**, **PT2**, and **PT3** have emission maxima at 473 nm, 526 nm and 456 nm, respectively (not shown in the figure). The broad-band fluorescence spectrum of all the salt solutions are attributed to the transitions from the equilibrated S_1 state to the ground S_0 state involving the transition dipole moment along the long axis (x -axis). The salient features of the fluorescence spectra are also listed in Table 1.

For comparison, the corresponding perchlorate salt of **PT2** and **PTF2** exhibits λ_{em} peak at 539 nm when excited at 450 nm in acetonitrile. Additionally, the parent salt 2,4,6-triphenylpyrylium perchlorate shows λ_{em} peak at 466 nm when excited at 405 nm in acetonitrile. The λ_{em} peaks of the pyrylium salts depend on the nature of substituents. Trimethoxy-, trichloro- and tribromo-substituents shift bathochromically and trifluoro-substituent shifts hypsochromically (Table 1) when compared with the parent pyrylium perchlorate salt in identical polar solvent. For comparison the parent pyrylium salt and its trimethoxy-substituent variant show Stokes shifts of 61 nm and 89 nm and quantum yields of 0.60 and 0.97, respectively [31]. Salts used in the present study exhibit Stokes shifts in the 46 nm – 81 nm (2387 cm^{-1} – 3461 cm^{-1}) range (Table 1). The emission spectral range of each salt solution had a full-width-at-half-maximum (FWHM) in the 57–67 nm (2431 cm^{-1} – 2807 cm^{-1}) range which resembled that of Coumarin laser dyes that operate in the blue-green spectral range. The quantum yields (Φ_F) of these salts were determined against diphenylanthracene ($\Phi_F = 0.9$) in cyclohexane [31] and were found to be in the range 0.13–0.41. The reason for low quantum yields of these salts is not clear, since many structural factors are responsible for quantum yields. Salt **PTF5** had the lowest quantum yield, as expected, on account of heavy atom (^-Br) induced fluorescence quenching effect [33]. The optical spectroscopic properties of these pyrylium salts are greatly affected by chemical structure modifications with electron donating substituents in the primary chromophore, which is the pyrylium cation. These results also suggest that the emission peaks and quantum yields (with one exception) of these pyrylium salts are independent of organic counterions such as tosylate and triflimide. Generally, the salt or the organic compound that is highly fluorescent in solution, is non-fluorescent in the solid state because aggregation induced fluorescent quenching. Interestingly, the salts **PTF1**–**PTF5** fluoresced in the solid state (Fig. S12). Organic salts with specially designed chemical architectures such as benzobisimidazolium salts are found to be highly lumines-

cent [34]. In this regard, luminescent pyrylium salts can be added to the repertoire of the class of light-emitting organic salts for multifunctional applications.

3.3. Time-resolved and intensity-dependent emission

The time-resolved and pump intensity dependent emission characteristics of a 2,4,6-triphenyl pyrylium tosylate salt has previously been reported by us [20]. We have carried out similar measurements on two triflimides, **PTF2** and **PTF4**, to extract the fluorescence lifetime and assess their potential as active materials for dye lasers [20,35]. The results of measurements on **PTF4** is presented here, and those on **PTF2** are provided in the Supplementary Information (Fig. S13). The time evolution of fluorescence of an acetonitrile solution of **PTF4** salt (concentration $2.3 \times 10^{-3}\text{ M}$) are shown in Fig. 3(a) for different pump intensities. The corresponding fluorescence spectra are displayed in Fig. 3(b). The 400-nm, 100-fs, 1 kHz repetition-rate pump beam was the second harmonic of an amplified Ti: sapphire laser output. Measurement were made at other intermediate pump powers as well, however, those are not shown to reduce overcrowding of data and curves that compromises clarity.

The salient features of the fluorescence decay curves and the corresponding spectra are as follows. For low pump intensity (1.25 W/cm^2) and the fluorescence (Curve 1 in Fig. 3(a)) decayed as a single exponential with a decay time of $2.4 \pm 0.1\text{ ns}$. The corresponding emission spectrum (Curve 1 in Fig. 3(b)) has a FWHM linewidth of $62 \pm 1\text{ nm}$ ($2720 \pm 46\text{ cm}^{-1}$). As the pump intensity was increased, fluorescence decay became faster with a corresponding shortening of the emission linewidth. As a typical example, for the average pump intensity of 5.0 W/cm^2 (Curve 3 in Fig. 3(a)), the decay time reduced to $456 \pm 28\text{ ps}$. The corresponding spectrum (Curve 3 in Fig. 3(b)) has a narrower linewidth of $27.7 \pm 0.8\text{ nm}$ ($1260 \pm 21\text{ cm}^{-1}$).

The longer fluorescence lifetimes are indicative of spontaneous emission, while shorter lifetimes are consistent with amplified spontaneous emission (ASE) or stimulated emission. For a still higher pump intensity of 7.5 W/cm^2 substantial further shortening of fluorescence lifetime and spectral linewidth were observed, which were indicative of stimulated emission. At this point when the orientation of the cuvette was slightly adjusted so that a fraction of the emission was reflected by the sidewalls through the pumped volume, free-running laser action was observed. The spot size of the emission tightened and became intense and significantly directional with concomitant shorter pulse width of $190 \pm 10\text{ ps}$ [Fig. 3(a), curve 4] and linewidth of $19.4 \pm 0.6\text{ nm}$ ($879 \pm 14\text{ cm}^{-1}$) [Fig. 3(b), curve 4]. The linewidth of laser emission is rather broad, which is expected since the output was multi-modal, no wavelength selection element was used in the cavity and gain of the salt solution, like organic dyes, is high. This initial experiment demonstrates the potential of **PTF4** as a laser dye, a detailed characterization of its laser properties is beyond the scope of this study.

Acetonitrile solution (concentration $2.3 \times 10^{-3}\text{ M}$) of the salt **PTF2** also exhibited similar pump intensity dependent fluorescence lifetime and linewidth characteristics as presented in the Supplementary Information section (Fig. S13). However, the **PTF2** solution did not seem to be as efficient a laser material as the **PTF4** solution. The fluorescence lifetime at low pump intensity (1.25 W/cm^2) was $4.7 \pm 0.1\text{ ns}$, and the linewidth was $67.7 \pm 1.0\text{ nm}$. At higher pump intensities a double exponential decay with a shorter lifetime (few tenths of an ns) and a longer lifetime ($\sim 4\text{ ns}$) were observed. Linewidth narrowing was not also as prominent as in **PTF4** solution, which together with double exponential decay of fluorescence is indicative of both spontaneous and stimulated emission processes being operative and stimulated emission being not as efficient as in **PTF4** solution.

Fig. 3. Pump intensity dependence of fluorescence (a) lifetime, and (b) spectra, of a 2.3×10^{-3} M solution of PTF4 salt in acetonitrile at room temperature. The average pump intensity for curves 1–4 in both (a) and (b) are: Curve 1: 1.25 W/cm^2 , Curve 2: 2.5 W/cm^2 , Curve 3: 5.0 W/cm^2 , and Curve 4: 7.5 W/cm^2 . The emission was recorded through a side window of the cuvette in a direction orthogonal to the pump direction. Curves were obtained by pumping the cuvette transversely using a cylindrical lens. Curve 4 (in both figures) was obtained by adjusting the orientation of the cuvette so that a fraction of the reflections go back through the pumped volume. Since the solution had high gain even this small feedback led to laser oscillation, as evident from shortest pulse width and linewidth of Curve 4 in Fig. 3(a) and (b), respectively.

3.4. Thermal properties

The thermal properties of salts **PT1-3** and **PTF1-5** were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and their results are compiled in Table 2. The TGA results (Fig. S14) revealed that all of them had excellent thermal stability in the temperature range of $268\text{--}402^\circ\text{C}$, the temperature at which the loss of 5 wt% of each of these salts occurred at a heating rate of 10°C/min in nitrogen. Salts containing triflimide counterion had better thermal stabilities than those containing tosylate counterion. This characteristic trend may be justified for non-nucleophilicity of triflimide counterion when compared with tosylate counterion [4]. They had lower melting transitions than the corresponding tetrafluoroborate salts as expected.

Table 2
Thermal properties of **PT1-5** and **PTF1-5** as determined by DSC and TGA.

Salt	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_d ($^\circ\text{C}$)	Salt $^{29} T_m$ ($^\circ\text{C}$)
PT1		228^a (decomp.)	268	TriMePyBF ₄ 312
PT2	(79) ^c	206^b (amorphous)	303	TriMeOPyBF ₄ 347
PT3	(72)	276 (234)	321	TriFPyBF ₄ 244–246
PT4		250 (decomp.)	305	TriClPyBF ₄ 308–310
PT5		274 (decomp.)	294	TriBrPyBF ₄ 296
PTF1		229 (227)	335	
PTF2		253^d (253)	353	
PTF3		191^e (191)	402	
PTF4		262 (261)	401	
PTF5		291 (290)	386	

^a One endotherm (Cr–Cr transition) prior to melting in the first heating cycle.

^b The melting transition of monohydrate salt which then formed an amorphous phase.

^c Datum in parenthesis obtained from the second heating cycle of DSC thermogram.

^d Multiple endotherms (Cr–Cr transitions) prior to the melting transition both in the first and second heating cycles.

^e One endotherm (Cr–Cr transition) prior to melting in both first and second heating cycles.

Two of the salts exhibited one crystal-crystal transition prior to melting transition. The salt **PTF2** exhibited several crystal-crystal transitions prior to the melting transition that appeared in both heating and cooling cycles (Fig. S15), which potentially indicative of plastic crystalline property [36]. This polymorphism phenomenon is quite common in many ionic liquids as well as ionic liquid crystals [37–39]. One additional comment on the salt **PT2** is that it was obtained as monohydrate. Its melting transition at 206°C obtained from the first heating cycle. Subsequent heating and cooling cycles there were no endotherm and exotherm, respectively, but only showed T_g suggesting it was amorphous.

4. Conclusions

In this work, we have presented a facile synthetic one-step procedure for the synthesis of five 2,4,6-tris(4-substitutedphenyl)pyrylium tosylates by using tosic acid as a condensing agent. The tosylates salts were then converted to triflimide salts by a metathesis reaction. Their chemical structures were established from their ^1H and ^{13}C NMR spectra as well as elemental analysis. Their optical and thermal properties were examined. Acetonitrile solutions of a majority of the salts emitted blue light (peak emission in $456\text{--}479 \text{ nm}$ range), while two salts emitted green light (emission peak at 526 nm). Their solution quantum yields were in the range of $0.13\text{--}0.41$. Interestingly, they exhibited fluorescent properties in the solid state. One of the salts (**PTF4**) exhibited stimulated emission under sufficiently intense optical pumping and free-running laser action with a small feedback. The salts have low melting transitions when compared with the corresponding BF_4 salts and excellent thermal stability in the temperature range of $268\text{--}402^\circ\text{C}$ in nitrogen. These luminescent organic salts have potential for multifunctional applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2019.127325>.

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