

Synthesis, optical spectroscopy and laser potential of 2,4,6-triphenylpyrylium chloride

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ABSTRACT

The synthesis, optical spectroscopic properties, and lasing potential of 2,4,6-triphenylpyrylium chloride (PyCl) are reported. The synthesis involves conversion of Py-tosylate (instead of commonly used Py-perchlorate) to a pseudo-base, which is then transformed to PyCl by reacting with HCl. Solutions of the salt in different solvents absorb in the blue-near ultraviolet and emit in the blue-green spectral ranges with fluorescence quantum yield of 0.84 in acetonitrile. Under intense ultrashort laser pumping, salt solutions in acetonitrile, ethanol and methanol demonstrated stimulated emission and laser action with nominal feedback. Two-photon excited fluorescence was also observed.

1. Introduction

Efficient and stable fluorescent dyes [1] continue to be of interest for development of wavelength tunable laser, light emitters such as organic light emitting diodes, solar cells, biomedical imaging, visualization of molecular processes in cells, and study of photochemical reactions and processes [2–8]. More recently, brightly fluorescing small molecules attracted attention as potential building blocks for solid-state photonic materials [9], fluorescent biomarkers for biomedical spectroscopy and contrast agents for optical biomedical imaging [10,11].

Pyrylium salts represent a class of small organic molecules built on a six-membered cationic heterocyclic structure with one positively charged oxygen ion and a variety of counter ions, such as, ClO_4^- , BF_4^- , PF_6^- and OTs^- . While Py-salts with different counter ions have been investigated for various applications including laser action [12–17], to the best of our knowledge, optical spectroscopic properties of PyCl received little attention. It was first synthesized in 1973 for use as an organic precipitant from aqueous solutions for certain anions including iodide, thiocyanate, trichloroacetate, nitrate, ClO_4^- , BF_4^- , permanganate, dichromate, ferrocyanide as well as anionic chloro-complexes of Zn (II), Sn (II), Pb (II), Cd (II), Au (III), and Pt (IV) [18].

Here we report on a safer and less-expensive synthesis route for PyCl than that provided in [18] and present its optical spectroscopic

properties and efficacy as a laser dye in commonly used blue-green laser dye solvents, such as, methanol, ethanol, dichloromethane (DCM) and acetonitrile. We explore its potential as a water-soluble fluorophore. Two-photon absorption (TPA) induced fluorescence characteristics of the salt solutions are investigated to assess its potential application in nonlinear optical microscopy and imaging [11].

The remainder of the article is organized as follows. Section 2 provides an overview of materials, experimental methods, and synthesis procedure. Results are presented and discussed in Section 3. Section 4 summarizes the key results and draws conclusions.

2. Materials and methods

2.1. General information

The chemicals and spectral grade solvents were procured from commercial suppliers, Millipore Sigma Aldrich, and TCI America, 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 the compound in d_6 -DMSO, CDCl_3 , or CD_3CN with tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were recorded using a

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Shimadzu spectrometer (IR Affinity-1) with KBr pellets. Elemental analyses for the salt were obtained from the Atlantic Microlab Inc., Norcross, GA.

The room-temperature fluorescence spectra, excitation spectra and quantum yield of PyCl solutions were measured using the pertinent mode of operation of a PerkinElmer FL 6500 luminescence spectrometer. Fluorescence lifetime and fluorescence spectra of the salt solutions as a function of excitation intensity were measured using a femtosecond Ti: sapphire laser system (Spectra-Physics Spitfire) and a Streak Camera (SC) system (Hamamatsu Streak Scope C4334) coupled with a spectrometer (Imaging Spectrograph G50is). The laser system generated 800-nm, 130-fs duration, 1 kHz repetition-rate pulses. The second harmonic of these pulses at 400-nm was used for linear (one-photon) excitation of the salt solution contained in a quartz cuvette, while the 800-nm beam was used for two-photon excitation experiments. An optical fiber connected with the SC spectrometer collected the sample fluorescence. Temporal resolution of approximately 200 ps and 20 ps resulted when the SC operated in the 20-ns and 2-ns time frames, respectively.

2.2. Synthesis

PyCl was first synthesized [18] with 2,4,6-triphenylpyrylium perchlorate as the starting material which is explosive and hazardous. We first synthesize the safer Py-tosylate, and then convert it to chloride. The Py-tosylate was prepared following a previously reported procedure [16] and converted to PyCl in two steps (Scheme 1).

The first step involved preparation of the pseudobase 1,3,5-triphenyl-2-pentene-1,5-dione from Py-tosylate according to the modified procedure described in [18]. In a typical procedure, Py-tosylate (0.58 g, 1.21 mmol) was dissolved in 10 mL of boiling ethanol on stirring vigorously, and a solution of sodium acetate trihydrate (0.66 g, 4.84 mmol) in 10 mL of boiling distilled water was added in one portion. The product formed immediately, and the reaction mixture was heated on stirring for 30 min. It was cooled to the ambient temperature and then refrigerated overnight. The crude product was collected and washed with water giving white needles (0.31 g, 0.86 mmol, 79 % yield) of the pseudobase. ¹H NMR (CDCl₃, 400 MHz, ppm) δ = 8.08 (2H, d, *J* = 8.0 Hz), 7.99 (2H, d, *J* = 8.0 Hz), 7.56–7.39 (12H, m), 4.87 (2H, s). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ = 196.1, 190.8, 152.7, 142.0, 139.0, 137.0, 133.1, 132.7, 129.3, 128.7, 128.6, 128.5, 128.3, 126.8, 42.9.

In the second step, the pseudobase (0.44 g, 1.35 mmol) was dissolved in 50 mL of boiling ethanol. After dissolution was complete, 2.0 mL of 37 % hydrochloric acid were added with vigorous stirring. The reaction mixture was then continually heated to reflux for 30 min. When the reaction ended, the solution was evaporated to give a crude yellow product. The product was recrystallized from methanol/diethyl ether. It was then dried in vacuum at 80 °C to obtain the pure product (0.40 g, 1.16 mmol, yield 85 %). IR (cm⁻¹): 3066, 1620, 1578, 1493, 1466, 1447, 1420, 1277, 1246, 1192, 1030, 995, 772, 718, 679, 602. ¹H NMR (CD₃OD, 400 MHz, ppm) δ = 9.00 (2H, s), 8.53 (6H, d, *J* = 7.6 Hz), 8.45 (3H, t, *J* = 7.6 Hz), 7.88–7.75 (6H, m). ¹³C NMR (CD₃OD, 100 MHz,

ppm) δ = 171.1, 166.6, 135.0, 134.9, 133.0, 129.9, 129.8, 129.4, 129.2, 128.4, 115.0. Anal. Calculated (Found) for C₂₃H₁₇OCl·0.65H₂O (356.55): C, 77.48 (77.23); H, 5.17 % (4.99 %).

3. Results and discussion

We have successfully adapted the PyCl synthesis approach first introduced by Chadwick [18], and subsequently used by other researchers [19,20] for the preparation of this salt and its derivatives. Our modification of using Py-tosylate as starting material instead of Py-perchlorate makes the synthesis safer and easier to handle. Recently, an alternative one-step approach for the synthesis of 4(4-decyloxyphenyl)-2,6-triphenyl pyrylium chloride by the POCl₃ method was reported [21]. This one-step method for the synthesis of the hydrophobic chloride is feasible probably because the long 10-carbon decyloxy group stabilizes this pyrylium salt to prevent the formation of the corresponding pseudobase and can be isolated. However, isolation of the smaller PyCl molecule using POCl₃ may not be possible because during workup it transforms readily into a pseudobase with water.

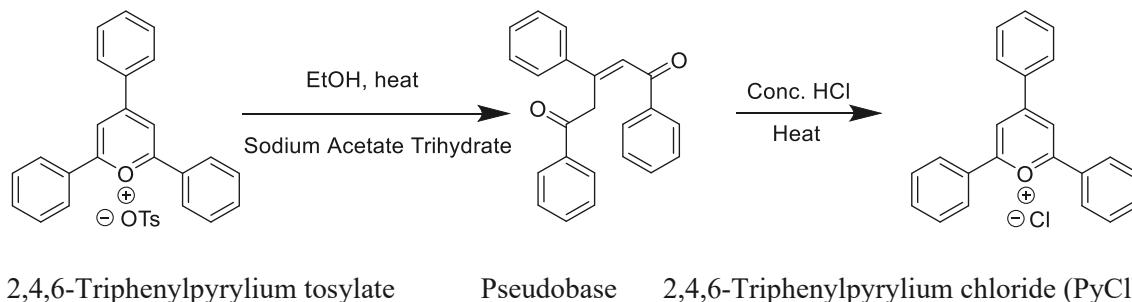
3.1. Physical properties

PyCl is a yellow powder of molecular weight 344.83 g/mol. It is highly soluble in conventional organic solvents, such as, methanol, ethanol, DCM, and acetonitrile. Solutions in these solvents at as high a concentration as (1–4) × 10⁻³ M (commonly used in laser-pumped dye laser operation) are clear and stable. The salt is unstable in water at neutral pH, since it undergoes hydrolytic ring opening to form pseudobase. However, at lower concentrations (~1 × 10⁻⁵ M) it is stable in acidic aqueous solution of pH = 2 that prevents ring opening reaction.

3.2. Optical spectroscopic properties

The emission and excitation spectra of the salt dissolved in acetonitrile, ethanol, methanol, and acidic water (pH = 2) at room temperature are shown in Fig. 1. Corresponding spectra of the DCM solution of the salt appears in Fig. S1 (Supporting Information). Solution in DCM had the lowest fluorescence quantum yield and was not investigated further. The fluorescence spectra obtained by exciting into the lowest-energy absorption band consist of a single broad band from 420 nm to 590 nm with peaks around 465 nm. Identical spectra were obtained for excitation into higher-energy absorption bands. Consequently, the broadband fluorescence is attributed to the transitions from the equilibrated S₁ excited state to the S₀ ground state of PyCl molecule. The salient features of the fluorescence spectra are listed in Table 1.

The excitation spectra indicate that solutions absorbed strongly in the 200–440 nm range with three peaks around 276 nm, 355 nm, and 406 nm. As detailed in Table 1, the solvent-dependent variations in the peak positions were constrained within a few nanometers. We attribute the lowest-energy absorption band to transitions that involve orientations of the transition dipole moment along the long axis passing through the 2- and 6-phenyl group also known as X-chromophore, and



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

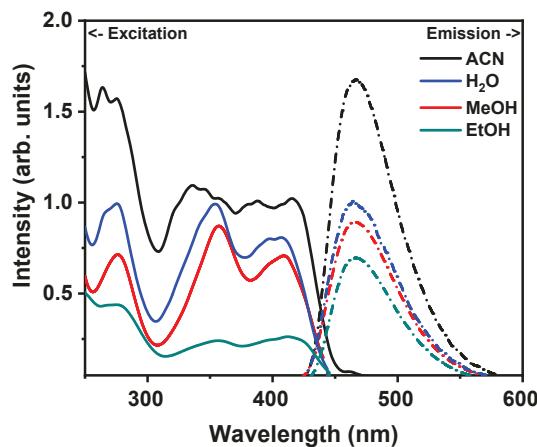


Fig. 1. Room-temperature emission spectra (right, dash-dot curves) and excitation spectra (left, solid curves) of 2,4,6-triphenylpyrylium chloride (PyCl) dissolved in acetonitrile (ACN), ethanol (EtOH), methanol (MeOH), and water (concentration 1.0×10^{-5} M). The emission spectra were measured by exciting the solutions around the lowest-energy absorption peaks. Excitation spectra were recorded by monitoring the fluorescence around the 465-nm peak as the wavelength of the excitation beam was varied.

Table 1
Optical spectroscopic properties of PyCl in different solvents.

Property	Acetonitrile	Ethanol	Methanol	Water (pH = 2)
Peak absorption wavelength (nm)	276, 355, 406	278, 359, 410	276, 357, 406	277, 354, 405
Molar absorptivity ($M^{-1}cm^{-1}$)	$\epsilon_{276} = 18916$ $\epsilon_{355} = 31510$ $\epsilon_{406} = 24396$	$\epsilon_{278} = 16235$ $\epsilon_{359} = 28615$ $\epsilon_{410} = 21560$	$\epsilon_{276} = 16555$ $\epsilon_{357} = 24939$ $\epsilon_{406} = 18414$	$\epsilon_{277} = 16758$ $\epsilon_{354} = 28958$ $\epsilon_{405} = 23286$
Peak emission Wavelength (nm)	465	466	466	464
FWHM emission bandwidth (cm^{-1})	2787	2761	2900	2921
Excited State Energy, (cm^{-1}) ^a	22,805	22,857	22,915	22,957
Stokes shift (cm^{-1}) ^b	3126	2931	3172	3139
Quantum yield, Φ	0.84	0.22	0.25	0.35
Fluorescence lifetime (ps)	1510	1389	1555	950
Free-running laser: Threshold Intensity (W/cm^2)	1.5	4.5	4.5	N/A
Pulse-width (ps)	132	139	73	
Linewidth	14 nm ($603 cm^{-1}$)	14 nm ($603 cm^{-1}$)	11 nm ($478 cm^{-1}$)	

Note: Acidic aqueous solutions with higher dye concentration were subject to hydrolysis at lower pH and fluorescence quenching at higher pH levels. So, the intensity-dependent measurements on sufficiently high concentration solution could not be carried out.

^a Intersection of the absorption and emission spectra is used as estimate of excited state energy in cm^{-1} .

^b Difference between emission maxima and the largest wavelength absorption maxima.

the higher-energy bands to transitions involving orientation of the dipole moment passing through the 4-phenyl group (Y-chromophore) of this salt [22]. The excitation spectra matched with corresponding absorption spectra indicating that the optical spectroscopic properties are intrinsic, not from the impurities.

The absolute fluorescence quantum yield (Φ) of the salt solution was

measured using the integrating sphere protocol of the fluorescence spectrometer (Perkin-Elmer FL 6500) as 0.84, 0.25, 0.22, 0.35 and 0.18 for solutions in acetonitrile, methanol, ethanol, acidic-water, and DCM, respectively. To prevent hydrolysis of PyCl in higher-concentration acidic-aqueous solution, the relative concentration of HCl in the solution needs to be increased, which seem to quench the fluorescence. For example, Φ was measured as 0.15 in ($\sim 1.0 \times 10^{-5}$ M concentration) in 0.1 M hydrochloric acid solution.

3.3. Time-resolved and intensity-dependent emission

Excitation intensity dependent measurements of fluorescence decay dynamics and spectra of PyCl solutions at room temperature were carried out to extract fluorescence lifetime and assess its potential as a laser dye [16,17,23]. Corresponding results for solutions in acetonitrile, methanol and ethanol are presented in Fig. 2, Fig. 3, and Fig. S2, respectively. The upper frame in each figure [labelled (a)] presents the fluorescence decay while the lower frame [labelled (b)] shows the spectral changes.

The salient features of the fluorescence decay profiles and the corresponding spectra are as follows. First, for low average pump intensity [e.g., $0.6 W/cm^2$ in Fig. 2a, $1.1 W/cm^2$ in Fig. 3a, and $1.8 W/cm^2$ in Fig. S2(a)], the fluorescence decayed as a single exponential with time. The fluorescence lifetimes extracted from these measurements are: 1510 ± 5 ps for acetonitrile solution, 1389 ± 5 ps for ethanol solution, 1556 ± 5 ps for methanol solution, and 951 ± 4 ps for acidic-aqueous solution. The full-width-at-half-maximum (FWHM) linewidth of corresponding fluorescence spectra [lowest excitation intensity plots in

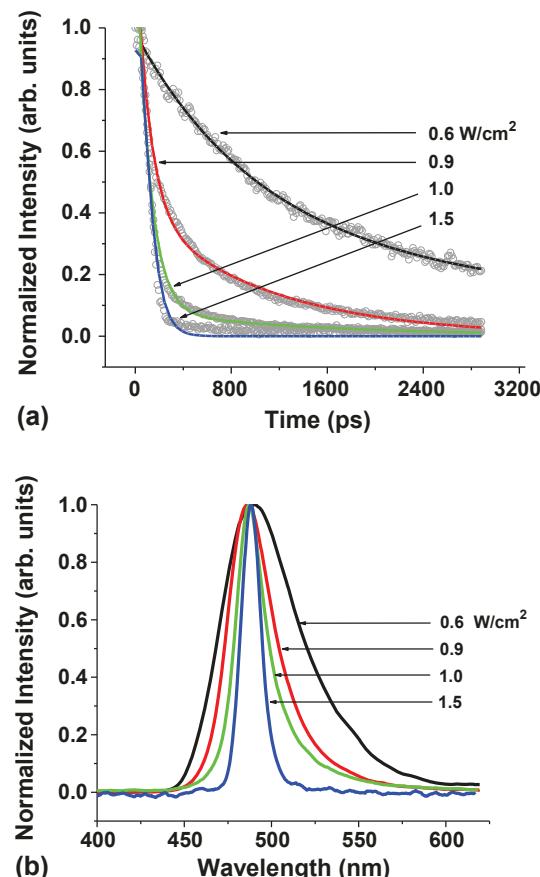


Fig. 2. Excitation intensity dependence of fluorescence (a) lifetime, and (b) spectra, of a 3.5×10^{-3} M solution of the salt in acetonitrile at room temperature. The salt solution in a cuvette was transversely pumped using a cylindrical lens.

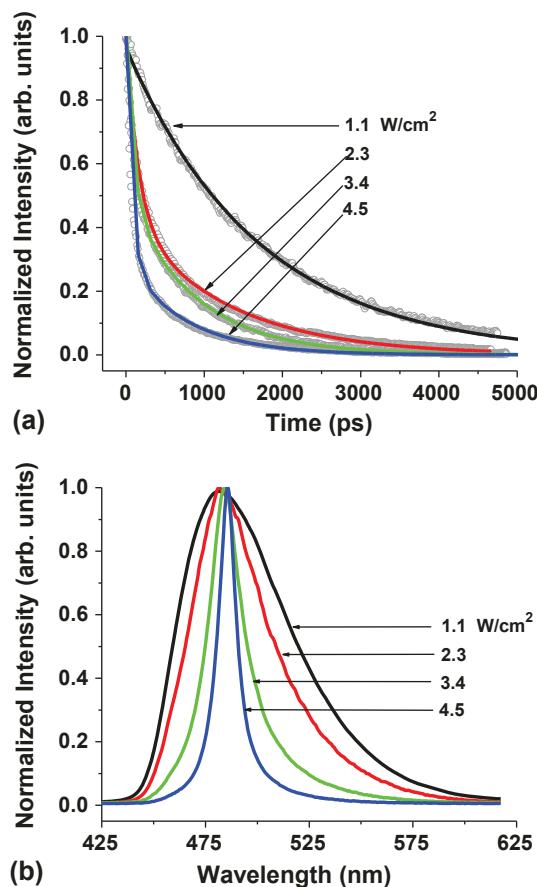


Fig. 3. Pump intensity dependence of fluorescence (a) lifetime, and (b) spectra, of a 3.2×10^{-3} M solution of the salt in methanol at room temperature.

[Fig. 2b, Fig. 3b, and Fig. S2(b)] is around 60 ± 1 nm (2518 ± 41 cm^{-1}), with a solvent-to-solvent variation within 200 cm^{-1} . Second, as the excitation intensity was increased fluorescence decayed faster. A bi-exponential fitting with a shorter decay-time component and a longer decay-time component was needed to reproduce the decay curve. There were corresponding shortenings of the emission linewidth. For example, for the methanol solution of PyCl [Fig. 3(a)] at the average pump intensity of ~ 3.4 W/cm^2 , the decay times were 84 ± 2 ps and 870 ± 4 ps for the faster and the slower components, respectively. The amplitudes of the two components were comparable. The longer fluorescence lifetimes are indicative of spontaneous emission, while shorter lifetimes are consistent with amplified spontaneous emission (ASE) or stimulated emission. For still higher average pump intensities the decay times of both the components shorten further, the amplitude of the slower component reduces and that of the faster component increases, which is indicative of the stimulated emission becoming the dominant relaxation mechanism at higher excitation intensities. At this point when the orientation of the cuvette was slightly adjusted to feedback a fraction of the emission 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 and narrower linewidth. The last row of Table 1 summarizes the key characteristics of the free running laser operation for the dye in three solvents. The broad linewidth (~ 500 – 600 cm^{-1}) is not unexpected since no wavelength selection element was used in the cavity. It further indicates that the optical gain of the salt solution is sufficiently high to support broadband lasing.

PyCl solution in acetonitrile has a fluorescence quantum yield of 0.84 and substantially lower threshold for stimulated emission compared to solutions in methanol and ethanol. It performed better than Py-tosylate

[16], and Py-triflimide [17] salts that we investigated. It compares well with the highest quantum yield laser-active pyrylium and thiopyrylium salts reported by Tripathi et al. [14]. Its lasing wavelength maximum (~ 480 nm) and potential operation range is further to the blue of those for Py-tetrafluoroborates (peaks at 500 nm, 560 nm, and 615 nm) that Fakis, et al. reported [15], and similar to that of Coumarin-480, a commercial laser dye [24]. PyCl is a smaller molecule than other laser-active Py-salts and may serve as a building block for other photonic materials. These results demonstrate the potential of PyCl as a laser dye. A detailed characterization of its laser properties is beyond the scope of this communication.

The room-temperature fluorescence of PyCl solution in acidic water at low concentration (1.0×10^{-5} M) decayed as a single exponential with a decay time of 951 ± 4 ps. Increasing HCl concentration in water enhanced PyCl solubility but the fluorescence efficiency decreased. No excitation intensity dependent lifetime shortening, or spectral narrowing was observed with average excitation intensity in the 1 W/cm^2 to 10 W/cm^2 range, indicating that there had been no onsets of amplified spontaneous emission or stimulated emission. While solubility and emission quenching issues in acidic water precludes laser operation and substantial two-photon-absorption induced fluorescence using PyCl in aqueous solution, it may be a potential contrast agent for one-photon fluorescence-based optical biomedical imaging and visualization of cellular processes. Its small size, low molecular weight and solubility in acidic water are conducive to these applications. However, detailed bio-imaging and cytotoxicity experiments are needed to test these potentials.

3.4. Two-photon absorption induced fluorescence

Two-photon absorption (TPA) is a nonlinear optical process that involves excitation of a higher-energy state through simultaneous absorption of two non-resonant lower-energy photons. The excited state may then relax by emitting a higher-energy photon. Since this TPA-induced fluorescence signal varies as the square of the excitation intensity, the signal is optimal at the focal region of the excitation beam and a much higher spatial resolution and sectioning efficacy is attained using two-photon fluorescence than one-photon fluorescence in microscopy and imaging applications [11,25]. Another salient advantage in biomedical imaging is that much deeper penetration into biological tissues is possible using near-infrared light than the blue-green visible light which suffer strong one-photon absorption by chromophores in tissues. To explore the viability of PyCl as a contrast agent for two-photon imaging and microscopy, we investigated the TPA-induced fluorescence in PyCl solutions, and the results are presented in Fig. 4 and Fig. S3. Fig. 4 displays TPA-induced fluorescence spectra of the acetonitrile solution of PyCl at several excitation intensities. Other than increase in the signal amplitude with increasing average intensity of the 800-nm pump beam, the TP fluorescence spectra had similar shape and spectral range as the OP spectra. The plot of the log (fluorescence intensity) vs log (average pump intensity), shown in the inset, is linear with a slope of 2.1 ± 0.1 , as expected for quadratic dependence on pump power. Solution of the salt in ethanol (Fig. S3) and methanol (not shown) also show similar TPA features.

4. Summary and conclusion

The paper presents a two-step process for synthesis of 2,4,6-triphenylpyrylium chloride from 2,4,6-triphenylpyrylium tosylate. The chemical structure of the salt was established from its ^1H and ^{13}C NMR spectra as well as elemental analysis. The salt is highly soluble in acetonitrile, ethanol and methanol and exhibits some solubility at low concentration in acidic water (pH = 2).

The salt solutions absorb light strongly in the blue-near ultraviolet spectral range (220–420 nm) and fluoresces brilliantly in the blue-green spectral range (400–590 nm) with a quantum yield as high as 0.84 in

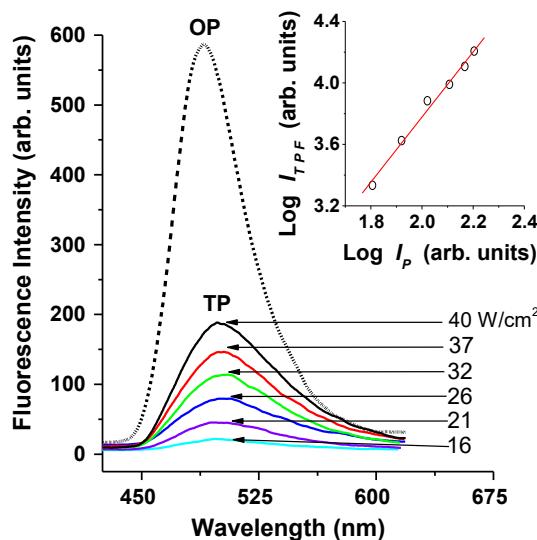


Fig. 4. Two-photon absorption induced fluorescence spectra (TP) of PyCl in acetonitrile (concentration 3.5×10^{-3} M) as a function of 800-nm pump beam intensity. Corresponding one-photon absorption induced fluorescence spectrum (OP) is shown for comparison. Inset is a plot of log (TP fluorescence intensity) vs log (excitation intensity).

acetonitrile. The results demonstrate acetonitrile as the superior solvent for laser operation of the salt.

Under intense pulsed excitation high-concentration ($\sim 10^{-3}$ M) solutions of the salt in acetonitrile, ethanol and methanol demonstrated stimulated emission with accompanied fluorescence lifetime shortening and linewidth narrowing, and broadband free-running laser operation with minimal feedback. The salt is thus highly promising as a laser dye in the blue-green spectral range, with acetonitrile as the optimal solvent. In addition, the salt exhibits potential as a contrast agent for two-photon fluorescence imaging and microscopy applications, and one-photon fluorescence based optical biomedical applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2022.139927>.

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