

Several Organic Salts with High Two-Photon Active

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Several organic salts with D-A molecular structure and different counterion have been prepared and experimentally investigated. The two-photon induced frequency-upconverted spectra and two-photon pumped lasing are measured for the organic salt solutions in various solvents. The results indicate that counterions have influence on their stability and lasing property.

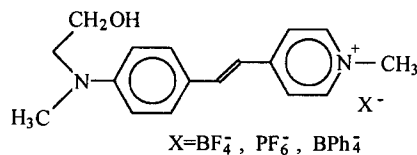
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Introduction

There is considerable interest in the synthesis of new materials with a large two-photon absorption (TPA) cross section and intense upconverted fluorescence.¹ Related experimental² and theoretical^{1,3} studies were also reported due to its opening up a myriad of new applications. These new applications include two-photon upconverted lasing,⁴ two-photon optical power limiting,⁵ three-dimensional optical data storage,⁶ and photodynamic therapy.⁷ Another application which has, unlike the others, received a reasonable amount of attention is three-dimensional imaging using two-photon laser scanning confocal microscopy.⁸ The potential of these new materials for applications is hard to overestimate. Progress has been made in the field, especially two-photon-pumped lasing material of several organic chromophores.⁹⁻¹¹

As we know, the similar compound, ASPI, has high lasing efficiency in cavity laser.¹² However, to our

knowledge, iodide ion in the molecule is unfavourable for its lasing and stable property due to heavy atom effect and being oxidized. In this paper, we focus on the synthesis of several organic salts with different counterions. The organic salts have good solubility in common organic solvents. Changing counterion will make them easier to crystallize and more stable, which also has an influence on their spectral properties. The organic salts have the following structure:



Experimental

Materials and measurements

Elemental analysis data were obtained using a Perkin-Elmer 240 analyzer. Infrared spectra were recorded from KBr discs in the range 4000—400 cm⁻¹ on a Nicolet FT-IR-170SX instrument. Electronic absorption spectra were obtained on a Hitachi 340 spectrophotometer in DMF solution (1.0 × 10⁻⁴ mol/L). The electrospray mass spectra (ES-MS) were determined on a Finnigan LCQ mass spectrograph, the concentration of the samples was about 1.0 mmol/L. The diluted solution

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was electrospayed at a flow rate of 5×10^{-6} L/min with a needle voltage of + 4.5 kV. The mobile phase was an aqueous solution of methanol (V/V, 1:1). The samples were run in the positive-ion mode. In our experimental setup, the up-conversion fluorescence experiments were performed with a passively mode-locked Nd:YAG laser as a pump source, and a single sweep streak camera (Hamamatsu Model C1587) connected to a polychromator as a recorder. The pulse duration of the passively mode-locked Nd:YAG laser is 50 ps. The efficiency of two-photon-pumped lasing was measured with a single pulse mode-locked Nd:YAG picosecond laser and a Q switch Nd:YAG nanosecond laser (Spectra-Physics GCR Series) as pump source and a laser energy meter (Laser

Precision, Model Rj-7200) with a double detector as a recorder. One detector was used as a monitor of pump energy and the other was used to detect the upconverted amplified spontaneous emission (ASE) energy. As the pump laser was focused into dye cell by a lens, the up-converted ASE emitted from the dye cell in the direction of pump laser and with a duration as the same as the pump pulse. For detecting the ASE energy, the detector faced the direction of ASE, and a filter for cutting pump light was inserted between the cell and the detector. In the measurement of two-photon-induced fluorescence, the dye solutions were excited closed to the surface of the cell. The experimental setup for the nonlinear absorption measurements is shown in Fig. 1.

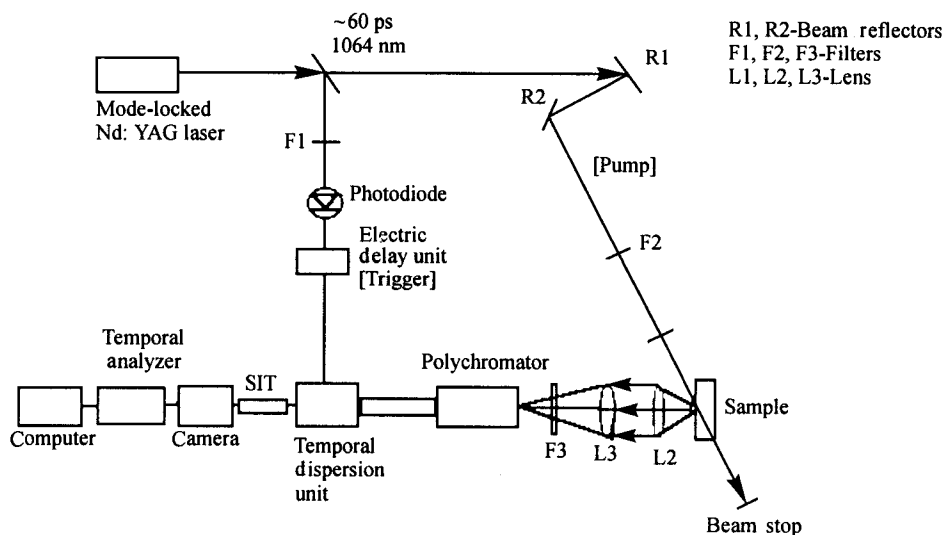


Fig. 1 Experimental setup for the nonlinear absorption measurements.

Preparations

4-(*N*-Methyl-*N*-(hydroxyethyl) amino) benzaldehyde (1) According to the literature method¹³ compound 1 was obtained as a pale yellow oil, yield 65%.

4-Methyl-*N*-methylpyridinium iodide (2) 9.3 g (0.1 mol) of 4-picoline and 21.6 g (0.11 mol) of methyl iodide were mixed in 50 mL of absolute ethanol. The solution was stirred at room temperature for 4 h and then refluxed for 30 min. After cooling, colorless crystals appeared and was filtered. The colorless crystals were washed with ethyl ether and dried under vacuum.

Trans-4-[*p*-(*N*-methyl-*N*-(hydroxyethyl) amino)-styryl]-*N*-methylpyridinium tetrafluoroborate (abbreviated as MAPBF₄) 3.6 g (20 mol) of compound 1,

4.4 g (20 mol) of compound 2 and 60 mL of absolute methanol were mixed. Five drops of piperidine were added into the mixture. Then the solution was heated to reflux overnight. When the solution was kept warm and filtered into a methanol solution of silver nitrate with stirring, precipitate appeared. The solution was filtered into another methanol solution of sodium tetrafluoroborate, and the formed red solid was washed with methanol three times, and dried over vacuum, yield 3.9 g (55%). Anal. C₁₇H₂₁N₂OBF₄. Calcd: C, 57.30; H, 5.90; N, 7.87. Found: C, 57.44; H, 5.78; N, 7.67.

Trans-4-[*p*-(*N*-methyl-*N*-(hydroxyethyl) amino)-styryl]-*N*-methylpyridinium hexafluorophosphate (abbreviated as MAPPF₆) The synthetic procedure is

similar to that of MAPBF₄, yield 5.2 g (63%). Anal. C₁₇H₂₁N₂OPF₆. Calcd: C, 49.28; H, 5.07; N, 6.76. Found: C, 49.44; H, 5.23; N, 6.67.

Trans-4-[p-(N-ethyl-N-(hydroxyethyl)amino)-styryl]-N-methylpyridinium tetraphenylborate (abbreviated as MAPBPh₄). The synthetic procedure is similar to that of MAPBF₄, yield 7.5 g (62%). Anal. C₄₁H₄₁N₂BO. Calcd: C, 83.67; H, 6.97; N, 4.76. Found: C, 83.69; H, 6.98; N, 4.44.

Crystal determination for MAPBPh₄

The relevant crystal data and structure parameters are summarized in Table 1. A red-black prismatic crystal with dimensions of 0.35 × 0.30 × 0.25 mm was mounted on a Bruker P4 four-circle diffractometer with monochromated Mo K_α (λ = 0.071073 nm) radiation using the θ-2θ scan mode with a variable scan speed 3.0—30.0°/min in ω. A total of 7028 reflections were collected and 5714 unique reflections were found. The data corrected for Lorentz and polarization effects during data reduction using XSCANS. The structure was solved by direct methods and refined on F² by full-matrix least-

Table 1 Crystal data and details of the structure determination for MAPBPh₄

Formula	C ₄₁ H ₄₁ N ₂ OB
Formula weight	588.57
Color	Red
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (nm)	1.8677(2)
b (nm)	1.0792(2)
c (nm)	1.7406(2)
β (deg)	111.13(1)
V (nm ³)	3.273(1)
Z	4
Density (g/cm ³)	1.195
F(000)	1256
μ (Mo K _α) (cm ⁻¹)	10
Crystal size (mm)	0.30 × 0.35 × 0.25
Temperature (K)	293(2)
λ (nm)	0.071073
Total, Uniq. Data, R(int)	7028, 5714, 0.081
Observed data [I > 2.0σ(I)]	1185
R, R _w	0.0789, 0.1435
S	0.89
Δρ _{min} , Δρ _{max} (e/nm ³)	-260, 230

$$w = 1/[S^2(F_o^2) + (0.0010P)^2], \text{ where } P = (F_o^2 + 2F_c^2)/3$$

squares methods using SHELXTL (version 5.1). All the non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions. Final R was 0.0789 for 1185 observed reflections with I > 2σ(I).

Results and discussion

Characterizations

The IR spectra of three organic salts of MAP are similar and show one band around 3360 cm⁻¹ due to the O—H group stretching frequency. The regions of the bands at 1580 cm⁻¹ and 1120 cm⁻¹ are attributed to the vibrations of ν(C=C) and ν(C—N), respectively. Those bands shift to lower frequencies due to high delocalization in the system. The relative new technique of electrospray mass spectrometry (ES-MS) allows pre-existing ions in solution to be transferred very gently into the gas phase with minimal fragmentation.¹⁴ Fig. 2 shows the positive-ion ES mass spectrum of a solution of the organic salt MAPBF₄ in methanol solution. The other mass spectra for MAPPF₆ and MAPBPh₄ are very similar to it. The mass spectrum was determined by the peak at m/z 269, which is due to the same part of positive ion (MAP⁺) in the organic salts. No fragmentation peaks of the MAP⁺ were observed. It showed that the organic salts were rather stable in methanol solution.

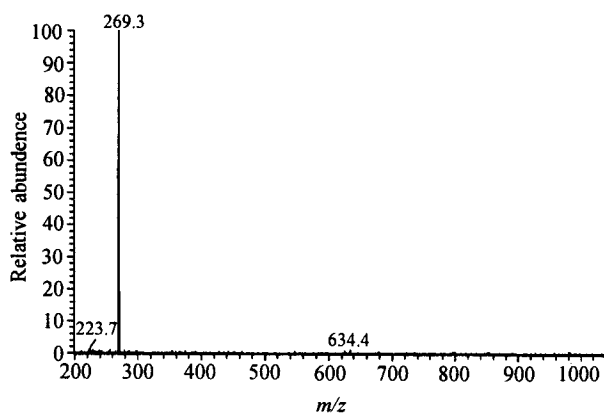


Fig. 2 ES mass spectrum of MAPBF₄ in methanol.

The data of selected bond lengths and angles for MAPBPh₄ were listed in Table 2. Its molecular structure is shown in Fig. 3. It can be seen that the molecule almost lies in one plane, and the hydroxyethyl group is

perpendicular to the plane. The planar configuration of MAP⁺ shows that there is a high electron delocalization in the donor-acceptor system, which is similar to other

cyanine dyes.¹⁵ However, no two-photon fluorescence was observed in these cyanine compounds under our experimental condition.

Table 2 Selected bond lengths (nm) and angles (°) for MAPBP₄

Bond distance			
N(1)—C(1)	0.149(1)	N(1)—C(2)	0.136(1)
N(1)—C(6)	0.135(1)	N(2)—C(12)	0.137(1)
N(2)—C(15)	0.145(0)	C(2)—C(3)	0.137(1)
N(2)—C(16)	0.147(1)	C(3)—C(4)	0.134(1)
C(4)—C(5)	0.137(1)	C(4)—C(7)	0.161(1)
C(5)—C(6)	0.135(1)	C(7)—C(8)	0.116(1)
C(8)—C(9)	0.160(1)	C(9)—C(14)	0.139(1)
C(9)—C(10)	0.142(1)	C(10)—C(11)	0.134(1)
C(11)—C(12)	0.140(1)	C(12)—C(13)	0.139(1)
C(13)—C(14)	0.137(1)	C(16)—C(17)	0.175(1)
Bond angle			
C(1)—N(1)—C(2)	122.1(7)	C(1)—N(1)—C(6)	119.7(7)
C(12)—N(2)—C(15)	121.3(6)	C(12)—N(2)—C(16)	123.0(6)
C(15)—N(2)—C(16)	114.9(6)	C(4)—C(7)—C(8)	113.9(10)
C(7)—C(8)—C(9)	117.6(10)	N(2)—C(12)—C(11)	120.3(7)

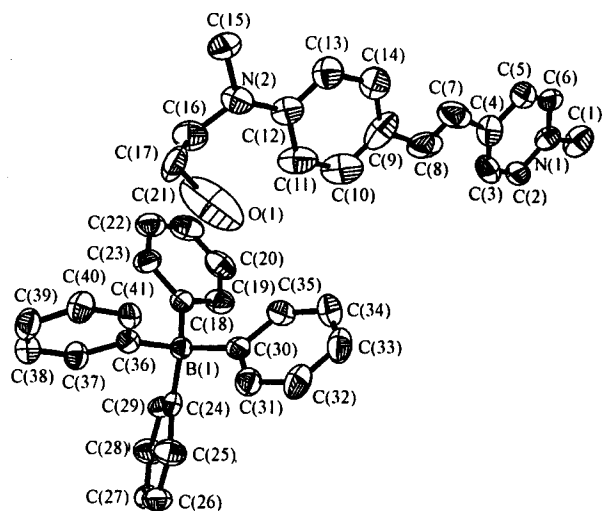


Fig. 3 Molecular structure of MAPBP₄.

Based on analysis of the bond lengths, one can find that the C—C bonds [C(2)—C(3), C(5)—C(6), C(10)—C(11), C(13)—C(14)] in phenyl ring along the molecular axis exhibit more double bond character than the other bonds [C(3)—C(4), C(4)—C(5), C(9)—C(10), C(11)—C(12)]. So do the C—N bonds. The fact supports the conclusion that there is de-

localization in the molecular system. Also, on the basis of quantum chemical calculations, Fromherz¹⁶ recently reported that the positive charge of the chromophoric in zwitterionic hemicyanine dyes is displaced upon excitation from the pyridinium moiety toward the amino moiety. The change in bond lengths can be explained by the oscillation model,¹⁶ which is consistent with the crystal determination. The structural characters of the molecule maybe result in nonlinear optical response.

The organic salts in this study show excellent solubility in many common solvents such as benzene, toluene, tetrahydrofuran, chlorobenzene, and benzyl alcohol. The linear absorption spectra of the organic salts were obtained with a scanning spectrophotometer (Hitachi 340) in DMF solution at concentration of $C = 1 \times 10^{-5}$ mol/L. The spectra of the three organic salts exhibit very similar linear absorption spectra. There is one strong absorption band with a peak wavelength at ~ 480 nm.

Single-photon excited fluorescence

In order to investigate solvent influence on emission behavior further, the relative single-photon excited emission spectra of MAPPF₆ solution in seven different polar

solvents are shown in Fig. 4. One can see from the figure that there are considerable differences in both the relative fluorescence intensity and the emission wavelength positions among the measured samples. For the samples in seven different solvents MAPPF₆ in benzene gave the strongest emission with a shortest peak wavelength position, while MAPPF₆ in acetonitrile gave the weakest emission. Similar fluorescence behavior of the ASPT and ASPI dye solutions in different solvents were reported recently.¹² For the ASPT and ASPI solution, the strong dependence of the fluorescence intensity and peak position on the solvent polarity can be explained by the twisted intramolecular charge transfer (TICT) process.¹⁷ As shown in Fig. 4, our experimental results of MAPPF₆ solution samples are basically in agreement with the prediction of the TICT model. However, no obvious rule was observed for the fluorescence spectra of MAPBF₄ and MAPBPh₄ (Fig. 5, MAPBF₄ as an example) with increasing solvent polarity and the TICT process no longer played a role in the two organic salts solutions. Interestingly, MAPPF₆ in both benzene and benzyl alcohol gave strong emission, whereas MAPBF₄ and MAPBPh₄ in the same solvents gave the weakest emission.

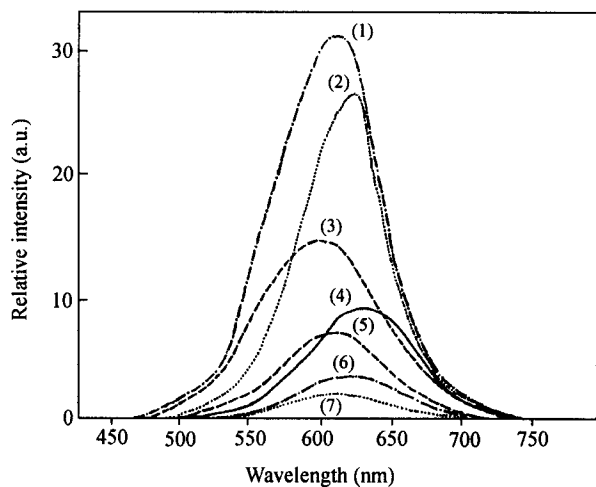


Fig. 4 Single-photon-excited fluorescence of the organic salt MAPPF₆ solution in different solvents with the same concentration of $C = 1 \times 10^{-5}$ mol/L. (1) MAPPF₆ in benzene, (2) MAPPF₆ in toluene, (3) MAPPF₆ in benzyl alcohol, (4) MAPPF₆ in chlorobenzene, (5) MAPPF₆ in tetrahydrofuran, (6) MAPPF₆ in DMF, (7) MAPPF₆ in acetonitrile.

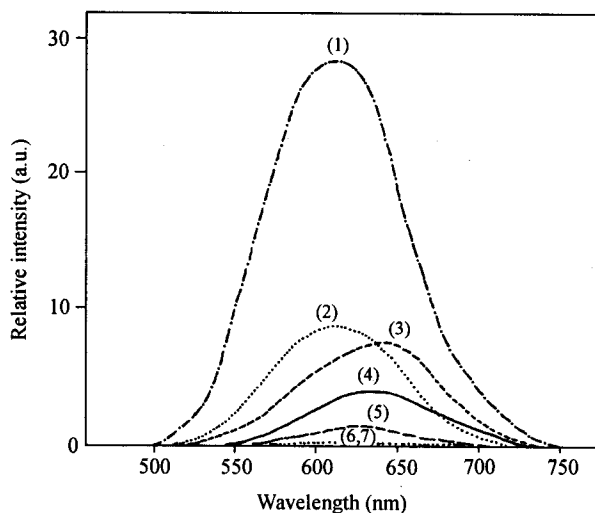


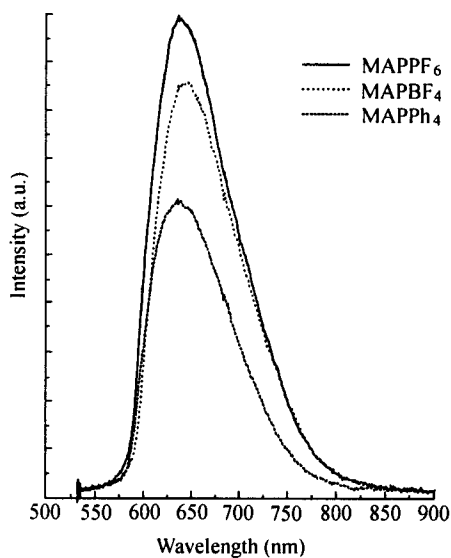
Fig. 5 Single-photon-excited fluorescence of the organic salt MAPBF₄ solution in different solvents with the same concentration of $C = 1 \times 10^{-5}$ mol/L. (1) MAPBF₄ in toluene, (2) MAPBF₄ in chlorobenzene, (3) MAPBF₄ in tetrahydrofuran, (4) MAPBF₄ in DMF, (5) MAPBF₄ in acetonitrile, (6) MAPBF₄ in benzene, (7) MAPBF₄ in benzyl alcohol.

Two-photon fluorescence and energy conversion properties

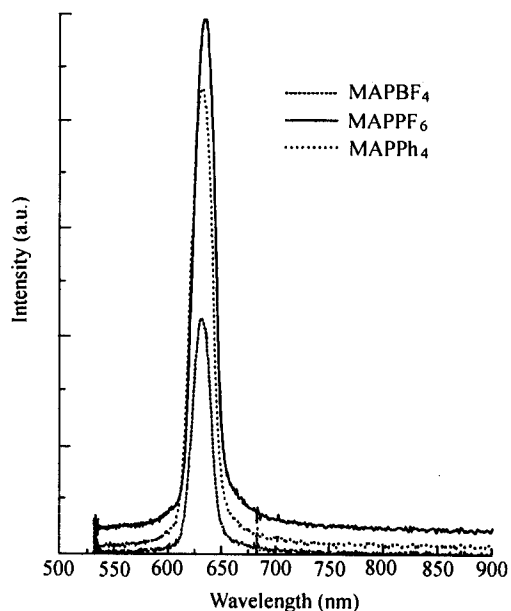
The series of organic salts in this paper have strong linear absorption around 480 nm, but no absorption in the spectra ranging from 580 to 1100 nm. Upon irradiation with a laser at 1064 nm, there should be no linear absorption induced fluorescence. The two-photon energy of 1064 nm IR radiation falls in the strong absorption band of all solutions of the organic salts. Very strong frequency upconverted fluorescence can be easily observed from the solutions excited with mode-locked Nd:YAG laser beam at the wavelength mentioned above (Fig. 6). This indicated that quite strong two-photon absorption process was occurring for the samples. The conversion efficiencies of two-photon-pumped ASE in Table 3 were calculated by $\eta = (E_{up}/E_p)100\%$ in which E_{up} is the energy of upconverted ASE in red wavelength, and E_p is the energy of the pump laser rather than the absorbed energy. The pump laser is a pulse laser of 0.6 mJ pulse energy, 38 ps pulse duration, and 1064 nm wavelength. The normalized spectral distributions of the two-photon pumped lasing spectra for organic salts are shown in Fig. 7.

Table 3 Comparative features of several two-photon fluorescence and two-photon-pumped lasing properties

MAPBF ₄	Solution (mol/L)	Width (nm)	Peak position (nm)	η (%)
Lasing	0.1 (DMF)	16	629	3.1
	0.1 (cyclopentanone)	15	625	2.3
Fluorescence	0.1 (DMF)	73	651	
	0.1 (cyclopentanone)	68	648	
MAPPF₆				
Lasing	0.1 (DMF)	17	627	5.3
	0.05 (cyclopentanone)	13	621	2.1
Fluorescence	0.1 (DMF)	75	641	
	0.05 (cyclopentanone)	87	643	
MAPBPh₄				
Lasing	0.1 (DMF)	20	629	2.5
	0.075 (cyclopentanone)	16	624	3.2
Fluorescence	0.1 (DMF)	67	650	
	0.075 (cyclopentanone)	71	645	

**Fig. 6** Two-photon excited fluorescence spectra of the organic salts in DMF solution with concentration of 0.01 mol/L.

From the determination results above, several significant features can be obtained. i) The fluorescence and lasing properties are related with solvents and concentration. There are obvious solvent effects in the sample solutions. High two-photon fluorescence and two-photon pumped (TPP) lasing of the organic salts can be obtained by the measurements in different solvents. In order to reach a higher two-photon absorption (TPA) and a subsequent TPP gain, the concentration of the organic salts should be kept at $C \geq 0.005$ mol/L. For salts

**Fig. 7** Two-photon induced lasing spectra of the organic salts in DMF solution with concentration of 0.01 mol/L.

having low solubility in those solvents such as, toluene, chlorobenzene and tetrahydrofuran, no TPP lasing was observed in those solutions. ii) From the results in Table 3, it is easy to find that red-shift takes place with increasing the solvent polarity. Fluorescence spectral wavelength position in DMF of the three salts is longer than that in cyclopentanone. iii) The fluorescence peak position is about 650 nm while the lasing peak is blue-shifted by about 20 nm, whereas in most cases, the TPP

lasing spectra are red-shifted due to the residual reabsorption in solution.¹⁸⁻²¹ iv) It is very obvious that the lasing spectral width (~ 16 nm) is much narrower than the fluorescence spectral width (70 nm) even without using any intracavity dispersion elements. v) One can see that at low and moderate pump levels the high concentration sample provided a higher overall energy conversion efficiency. The energy conversion efficiency for sample MAPPF₆ is much higher than that of ASPI under the exactly same conditions.¹² vi) There are different selection rules between one-photon fluorescence and two-photon fluorescence. For example, the one-photon fluorescence of sample MAPBF₄ was quenched in benzyl alcohol while obvious two-photon fluorescence behavior was observed. vii) The unconverted fluorescent lifetime of the series of compounds excited by two-photon is about 90 ps, which is much shorter than that of Rh6G. The unconverted fluorescent lifetime of Rh6G is 5300 ps. η of Rh6G was measured under the same experimental condition for comparison, and the largest η of Rh6G was only 0.4%. It is postulated that η of the compounds are correlated to their lifetimes. viii) We kept the solution of the compounds in our laboratory for 16 months; the lasing properties of the solutions did not change. The result demonstrates that the organic salts in this report are very stable unconverted emission compounds. As a conclusion, compared to known similar molecules (SAPI and ASPT),¹² the organic salts have good lasing property and are more stable, which are important characters for their application.

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