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# Two-photon Pumped Up-conversion Lasing Properties of A Series of Organic Salts with Different Side-chains

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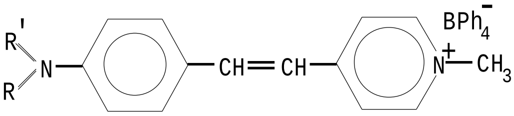
**Abstract:** The synthesis and upconverted fluorescent properties of a series of organic compounds with the structure: donor/bridge/acceptor, and different side-chains are reported. The results show that the compounds with different side-chains exhibit different two-photon induced fluorescent properties, although they have the same main donor/bridge/acceptor structure.

**Keywords:** Two-photon, upconverted fluorescence, side chain.

Two-photon processes, perceived until recently to be of only academic interest, are now receiving a great deal of interest for their many potential technological applications[1-3], This area offers numerous opportunities both for fundamental research and for new application development. From the fundamental research point of view, there are numerous challenges for computational and synthetic chemists. In exploring strong TPA (two-photon absorption) compounds, Albota *et al*. have focused on symmetric intramolecular charge transfer organic molecules[1] and Baur *et al*. have emphasized the asymmetric intramolecular charge transfer organic molecules[4]. Up till now, the correlation between structure and TPA properties has not been well understood. On the other hand, as a rule of thumb, most TPP (two-photon pumped) lasing molecules are large polar $\pi$-conjugated systems with excellent planar molecular configuration and donor-acceptor substituents. These structural characteristics are similar to those of second order nonlinear optically active molecules. Obviously, the electron delocalization in these molecules contributes to the enhancement of the TPA cross section. However, few report focused on the effects of the amino (donor group) with different pendent chains in the same $\pi$-conjugated system.

This report describes the synthesis and properties of two-photon induced fluorescence dyes with amine group (donor group) having different pendent chains in the same $\pi$-conjugated system. The reported compounds have the general structure as following:



**1** R = R′ = $CH_3$—; **2** R = R′ = $CH_3CH_2$—;
**3** R = $CH_3$—, R′ = $HOCH_2CH_2$—; **4** R = $CH_3CH_2$—, R′ =$HOCH_2CH_2$—;
**5** R = R’ = $HOCH_2CH_2$—

## Experimental

The compound **1**, *trans*-4′-dimethylamino-N-methyl-4-stibenazolium tetraphenyl borate, was synthesized by Meredith[5], which possessed an enormous nonlinearity. The compounds **3** and **4** were synthesized according to literature methods[6]. The similar synthetic methods for 4 -diethylaminobenzaldehyd were described in our previous paper[7].

*Trans*-4′-diethylamino-N-methyl-4-stibenazolium tetraphenyl borate **2**. 3.6 g (20 mmol) 4-diethylaminobenzaldehyde, 4.4 g (20 mmol) 4-methyl-N-methylpyridinium iodide[6] and 60 mL of absolute methanol were mixed. Five drops of piperidine were added into the mixture. Then the solution was refluxed overnight. When the solution was kept warm and filtered into a methanol solution of silver nitrate with stirring. Precipitate appeared. The suspension was filtered. The filtrate was added into another methanol solution of sodium tetraphenyl borate. The red solid was formed and washed with methanol for three times, and dried in vacuum, yield 3.9 g (55%). Elemental analysis, Calcd: C, 88.42; H, 7.54; N, 4.91. Found: C, 88.64; H, 7.78; N, 4.67.

*Trans*-4′-dimethylamino-N-methyl-4-stibenazolium tetraphenyl borate **5**. The synthesis procedure is similar to that of **2**, yield 63%. Elemental analysis. Calcd: C, 83.72; H, 7.14; N, 4.65. Found: C, 83.44; H, 7.23; N, 4.67.

## Results and discussion

The TPP fluorescence spectra of the compounds in DMF measured *via* a single sweep streak camera (Humanatsu Model 1587) connected to a polychromator. The excitation wavelength for all measurements is 1064 nm. The concentration of the solutions was 0.07 mol/L. No TPP fluorescence was observed for **1**. The TPP fluorescent properties for **3** and **4** have been reported by Prasad[8]. The maximum emission wavelengths for **2** and **5** are 645 and 624 nm, respectively. The narrow lasing peak is at 627 nm with a width at half maximum of 17 nm, which is blue-shifted by ~18 nm compared to its corresponding two-photon-excited fluorescence peak. The overall energy conversion efficiency is 10.5 for **2** (output/input energy), which is larger than that of **3** and **4**[8]. However, no TPP lasing was observed for **5**.

The compounds above have very similar main structure, the same counterion $BPh_4^-$, but with different side chain to amino group. By comparing their spectra, including UV spectra, two-photon induced fluorescence spectra and TPP lasing spectra, we found that compound **5** has very week absorption at *ca*. 480 nm (**Figure 1**). Although, compounds **1**~**4** have similar absorption spectra, they have different two-photon induced fluorescence properties. It is very difficult to observe two-photon fluorescence for compound **1**. After the methyl was substituted by ethyl in the side chain, the compound **2** has strong TPP fluorescence and good lasing properties (**Figure 2**). After the one side chain of **1** or **2** was substituted by hydroxyethyl to get compound **3** or **4**, which has good TPP fluorescence and lasing properties reported by Prasad[8]. However, after two side chains of **1** or **2** were substituted by hydroxyethyl, compounds **5** has very poor TPP fluorescence and without any TPP lasing properties. Based on our determination results, we believe that the side chains have also some influence on two-photon process. Further study is underway.

**Figure 1** The UV spectra of the compounds **1**~**5** in DMF ($1\times10^{-5}$ mol/L)

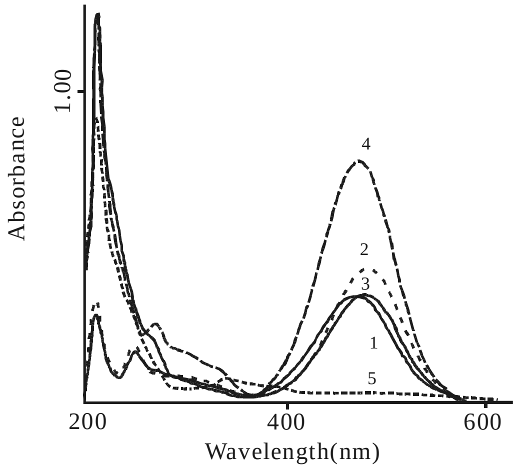
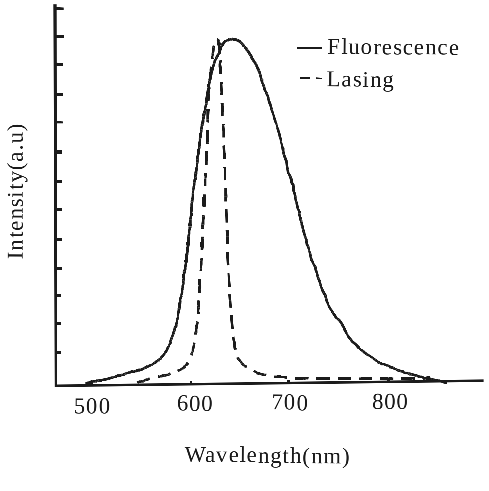


**Figure 2** Two-photon (by 1064 nm laser pulses) excited fluorescence and TPP lasing spectra of DMF solution of **2** (0.07mol/L)



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## References

1. M. Albota, D. Beljonne, J. L. Bredas, *et al*., *Science*, **1998**, *281*, 1653.
2. B. H. Cumpston, S. P. Ananthavel, S. Barlow, *et al*., *Nature*, **1999**, *398*, 51.
3. G. S. He, J. Swiatkiewicz, Y. Jiang, P. N. Prasad, *J. Phys. Chem.* A, **2000**, *104*, 4805.
4. J. W. Baur, M. D. Alexander Jr., *et al*., *Chem. Mater*., **1999**, *11*, 2899.
5. G. R. Meredith, D. J. William, S. N. Fishman, *J. Phys. Chem*., **1983**, *87*, 1697.
6. C. F. Zhao, G. S. He, J. D. Bhawalkar, *Chem. Mater*., **1995**, *7*, 1979.
7. Y. Ren, Q. Fang, Y. P. Tian, M. H. Jiang, *J. Mater. Chem*., **2000**, *11*, 2052.
8. G. S. He, L. X. Yuan, Y. P. Cui, P. N. Prasad, *J. Appl. Phys*., **1997**, *81*, 2529.

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