

## Synthesis and Study of Two-Photon Induced Fluorescence of Novel Dyes

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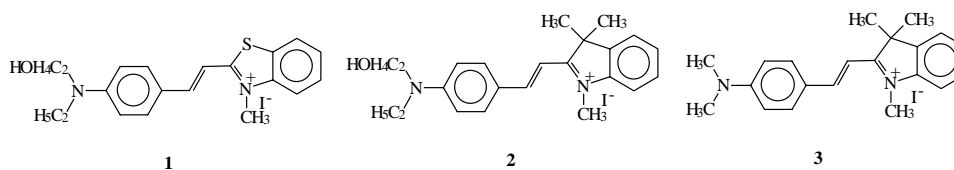
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**Abstract:** The synthesis and upconverted fluorescent properties of three novel organic compounds with the structure: donor/bridge/acceptor are reported. The dyes show strong upconverted fluorescence.

**Keywords:** Two-photon, upconverted fluorescence, synthesis of new dyes.

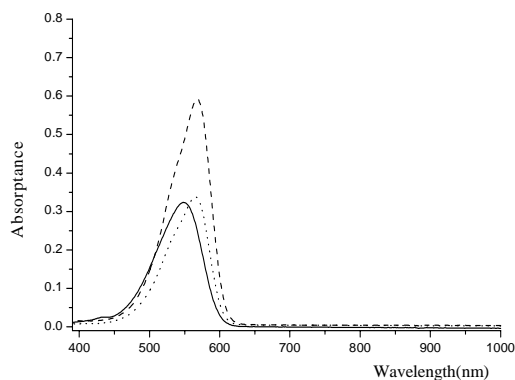
More recently, the synthesis of new dyes with large upconverted fluorescence becomes the focus of the research and has opened up a myriad of applications. The applications include two-photon induced lasing<sup>1</sup>, two-photon optical power limiting<sup>2</sup>, three-dimensional optical data storage<sup>3</sup>, and photodynamic therapy<sup>4</sup>. Nevertheless, this technique has never reached its full potential due to the lack of dyes which exhibit high upconverted fluorescent intensity. This report describes the synthesis and properties of two-photon induced fluorescence dyes which are specifically designed for excitation at 1064 nm. The novel dyes have the following structures:



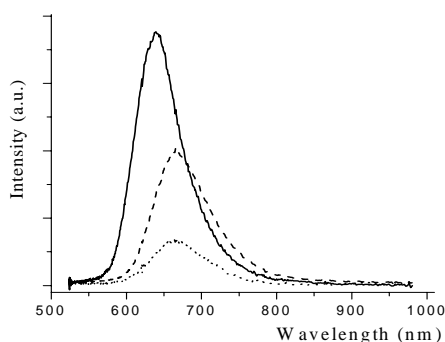
The dyes, *trans*-2-[*p*-(*N*-ethyl-*N*-hydroxyethylamino)styryl]-*N*-methylbenzothiazolium iodide **1**, *trans*-2-[*p*-(*N*-ethyl-*N*-hydroxyethylamino)styryl]-1',3',3'-trimethylindolium iodide **2**, and *trans*-2-[*p*-(*N,N*-dimethylamino)styryl]-1',3',3'-trimethylindolium iodide **3**, are dark red crystals which have a high solubility and photostability in benzyl alcohol, cyclopentanone and *N,N*-dimethylformamide (DMF). **Figure 1** shows the UV absorption spectra of **1**, **2** and **3** recorded at a concentration of  $1 \times 10^{-5}$  mol/L. Evidently, **1**, **2** and **3** have their maximum absorption at 548, 567 and 565 nm, respectively. Significantly, no absorption in the range from 650 to 1100 nm was detected. Thus, any emission upon excitation with a laser at 1064 nm must be attributed to a two-photon absorption process.

**Figure 2** shows the two-photon pumped fluorescence spectra of **1**, **2**, and **3** in benzyl alcohol, measured *via* a single sweep streak camera (Hamamatsu Model 1587) connected to a polychromator. The excitation wavelength for all measurements is 1064 nm. The concentration of **1** was 0.035 mol/L. While those of **2** and **3** were 0.07 mol/L. The maximum emission wavelength for **1**, **2**, and **3** are 639, 666, 665 nm, respectively. As shown in **Figure 2**, **1** shows the strongest two-photon induced fluorescence in the studied three dyes.

**Figure 1:** The UV spectra of the dye **1**(—), **2**(---)and **3**(.....) in benzyl alcohol. the concentration of the samples is  $1 \times 10^{-5}$  mol/L.



**Figure 2.** The upconverted fluorescence spectra of the dye **1**(—), **2**(---) and **3**(.....) in benzyl alcohol.



The synthesis of three dyes is depicted in **Scheme I**

*4-(N-ethyl-N-hydroxyethylamino)benzaldehyde* (**A**) The compound was synthesized according to the procedure described in the reference<sup>5</sup> with the yield of 58%. <sup>1</sup>HNMR (CDCl<sub>3</sub>) δ 1.22 (t, 3H), 1.85 (s, 1H), 3.53 (q, 2H), 3.60 (t, 2H), 3.86 (t, 3H), 6.78 (d, 2H), 7.7 (d, 2H), 9.7 (s, 1H) ppm.

*1,2-dimethylbenzothiazolium iodide* (**B**) A mixture of 2-methylbenzothiazole (1.15 g, 0.01 mol) and methyl iodide ( 2.0 g, 0.014 mol) dissolved in 10 ml trichloromethane was magnetically stirred at 60 °C in an one-neck flask equipped with a condenser for 24 hours. After cooling to room temperature, the solution was filtered and the solid product was washed with acetone, then it was recrystallized twice from ethanol to give 1.42 g (49% yield) of **B**. <sup>1</sup>HNMR (D<sub>2</sub>O) δ 3.17 (s, 3H), 3.43 (s, 3H), 7.8 (t, 1H), 7.88 (t, 1H), 8.1 (d, 1H), 8.18 (d, 1H) ppm.

*1,2,3,3-tetramethylindolium iodide* (**C**) The compound was synthesized according to the procedure described above, using 2,3,3-trimethylindolenine instead of 2-methylbenzothiazole. Yield 70%. <sup>1</sup>HNMR (D<sub>2</sub>O) δ 1.55 (s, 6H), 2.75 (s, 3H), 4.0 (s, 3H), 7.62 (m, 2H), 7.72 (m, 2H) ppm.

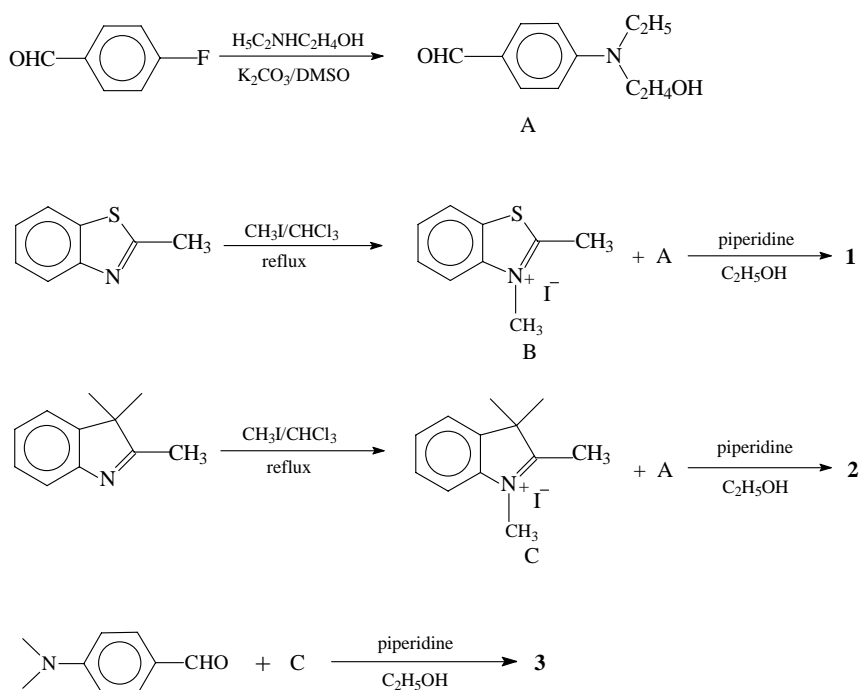
*Trans-4-[p-(N-ethyl-N-(hydroxyethylamino)styryl)-N-methylbenzothiazolium iodide* (**1**) To a 50-ml one-neck flask equipped with a magnetic stirrer and a condenser were added 0.4 g (0.0021 mol) of compound **A**, 0.58 g (0.002 mol) of **B** and one drop of piperidine in 20ml absolute ethanol. The solution was refluxed for 12 hours. After

cooling to room temperature, it was placed in a refrigerator overnight. Then the solution was filtered and the solid was washed with absolute ethanol and cool water, yield 0.38g (40.8%). MS:  $m/z$  466( $M^+$ ).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  1.15 (t, 3H), 3.45-3.60 (m, 6H), 4.18 (s, 3H), 6.86 (d, 2H), 7.58 (d, 1H), 7.66 (t, 1H), 7.76 (t, 1H), 7.86 (d, 2H), 8.02 (d, 1H), 8.08 (d, 1H), 8.28 (d, 2H) ppm. Anal. Calcd for  $\text{C}_{20}\text{H}_{23}\text{N}_2\text{SOI}$ : C, 51.50; H, 4.94; N, 6.01. Found: C, 52.38; H, 5.18; N, 6.13.

*Trans-4-[p-(N-ethyl-N-(hydroxethylamino)styryl)-1',3'3'-trimethylindolium iodide (2)* **2** was synthesized according to the procedure of **1** by using **C** as the starting material instead of **B**. Yield 72.9%. MS:  $m/z$  476( $M^+$ ), 349( $M-I$ ).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  1.15 (t, 3H), 1.73 (s, 6H), 3.50-3.65 (m, 6H), 3.93 (s, 3H), 6.90 (d, 2H), 7.24 (t, 1H), 7.47 (t, 1H), 7.54 (t, 1H), 7.69 (d, 1H), 7.76 (d, 1H), 8.06 (d, 2H), 8.29 (d, 1H) ppm. Anal. Calcd. for  $\text{C}_{23}\text{H}_{29}\text{N}_2\text{OI}$ : C, 57.98; H, 6.09; N, 5.88. Found: C, 55.65; H, 5.99; N, 5.43.

*Trans-4-[p-(N,N-dimethylamino)styryl]-1',3'3'-trimethylindolium iodide (3)* **3** was synthesized according to the procedure of **2** by using N,N-dimethylaminobenzaldehyde instead of **A**. Yield 57%. MS:  $m/z$  432( $M^+$ ), 305 ( $M-I$ ).  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ )  $\delta$  1.73 (s, 6H), 3.15 (s, 6H), 3.95 (s, 3H), 6.87 (d, 2H), 7.24 (d, 1H), 7.47 (t, 1H), 7.54 (t, 1H), 7.69 (d, 1H), 7.76 (d, 1H), 8.06 (d, 2H), 8.29 (d, 1H) ppm.

Scheme 1



### Acknowledgments

The authors would like to thank the Ministry of State Science and Technology of China for financial support (Major Key Research Project).

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Received 22 July 1999