

## Two-photon Excited Fluorescence of Bithiophene Derivatives

Guang Ming XIA<sup>1,2</sup>, Qi FANG<sup>1\*</sup>, Xin Guang XU<sup>1</sup>, Gui Bao XU<sup>1</sup>, Wei WANG<sup>1</sup>,  
Zhi Qiang LIU<sup>1</sup>, Gui Lan SONG<sup>2</sup>, Yong Jie WU<sup>2</sup>

<sup>1</sup>State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100

<sup>2</sup>School of Chemical Engineering, Jinan University, Ji'nan 250022

**Abstract:** Two new bithiophene derivatives named as 5, 5'-bis(*p*-N,N-dimethylaminostyryl)-2, 2'-bithiophene (BMSBT), and 5, 5'-bis(*p*-N,N-diethylaminostyryl)-2, 2'-bithiophene (BESBT) have been synthesized. Both compounds can emit strong single-photon excited fluorescence (SPEF) and two-photon excited fluorescence (TPEF) with the emission peaks around ~560 nm and with the lifetime of ~1ns.

**Keywords:** Two-photon absorption, two-photon excited fluorescence, bithiophene.

Two-photon excited fluorescence (TPEF), which is caused by simultaneously absorbing two photons by each fluorophore molecule, has been attracting more and more research interest for its various nonlinear optical (NLO) applications such as two-photon pumped up-conversion lasing<sup>1</sup> and TPEF microscopy<sup>2,3</sup>. Compared to the common single photon excited fluorescence (SPEF), the excited wavelength of TPEF is usually doubled. Obviously, under such a large red-shifted incident light most organic materials are more photostable. In the past few years, various kinds of chromophores were synthesized for TPEF and the main attention has been focused on the NLO active molecules with vinyl or phenyl as conjugated electron relays. Thiophene-based chromophores may be another choice for the electron relay, for thiophene has lower resonance energy compared to benzene<sup>4,5</sup>. Based on this idea, we synthesized two new bithiophene derivatives: 5,5'-bis(*p*-N,N-dimethylaminostyryl)-2,2'-bithiophene (BMSBT), and 5, 5'-bis(*p*-N,N-diethylaminostyryl)-2,2'-bithiophene (BESBT), which can emit strong SPEF and TPEF.

### Synthesis

The target compounds were synthesized by Wittig reaction and the intermediate bithiophene by Grignard reaction (shown in **Scheme 1**). 8.0 g (0.33 mol) magnesium was put in a flask containing 30 mL dry THF, then 26 mL (0.27 mol) 2-bromothiophene dissolved in 120 mL THF was dropped in. 1 hr later, the solution was transferred to another flask containing 22 mL (0.23 mol) 2-bromothiophene, 1.3 g NiCl<sub>2</sub>-dppp and 200 mL THF in ice-water bath. Then the solution was stirred for 24 hrs and the crude

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\*E-mail: fangqi@icm.sdu.edu.cn

product of bithiophene was purified by column chromatography. Under  $N_2$  and at  $0^\circ C$ , a solution of 0.03 mol *t*-BuOK in 50 mL THF was dropped into a flask containing 0.02 mol dialkylaminotoluenyldiphenylphosphonium bromide (compound **2**) and 200 mL THF, then 0.01 mol compound **1** in 50 mL THF was dropped in the flask slowly. After purification by column chromatography, dark-red powders of the target compounds were obtained. Elemental analysis (calculated) for BMSBT: C, 73.15(73.64); H, 6.88(6.18); N, 6.13(6.14); S, 13.84(14.04); BESBT: C, 74.16(74.96); H, 7.48(7.08); N, 5.46(5.46); S, 12.9(12.5).  $^1H$ NMR ( $CDCl_3$ ), BMSBT:  $\delta$  7.4(d, 2H,  $J=8.8$  Hz) 7.0(m, 6H) 3.0(s, 6H); BESBT:  $\delta$  7.25(d, 2H,  $J=9.1$  Hz) 6.88(m, 2H) 2.62(t, 2H,  $J=7.6$  Hz) 1.57 (d, 3H,  $J=8.7$  Hz). MS:  $m/z$ (%) BMSBT, 456 ( $M^+$  100). BESBT, 512 ( $M^+$  100).

Scheme 1

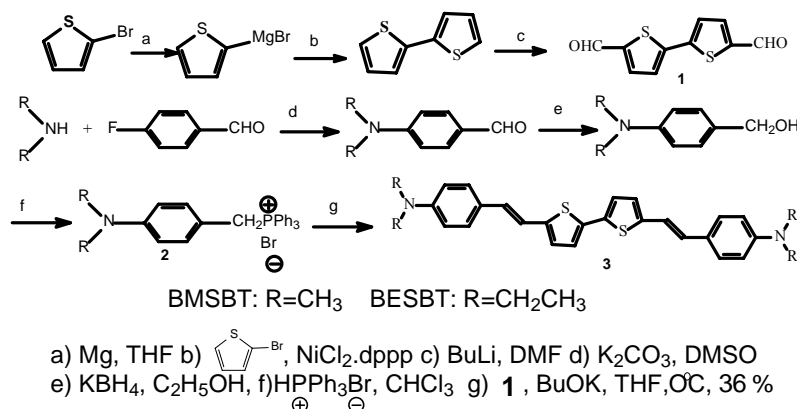
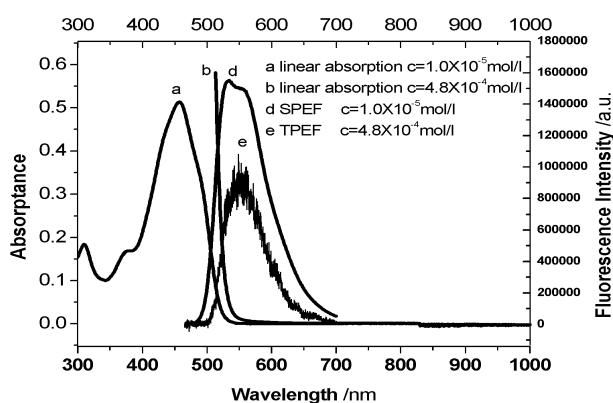


Figure 1 Optical properties of BMSBT in THF

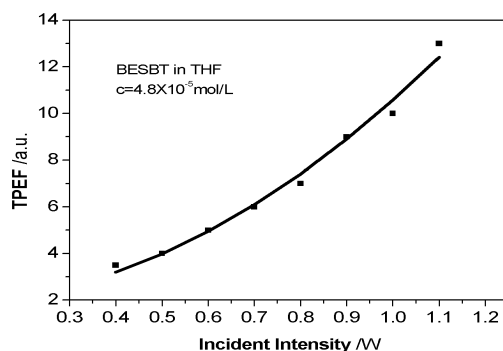


### Spectral characteristics of BMSBT and BESBT

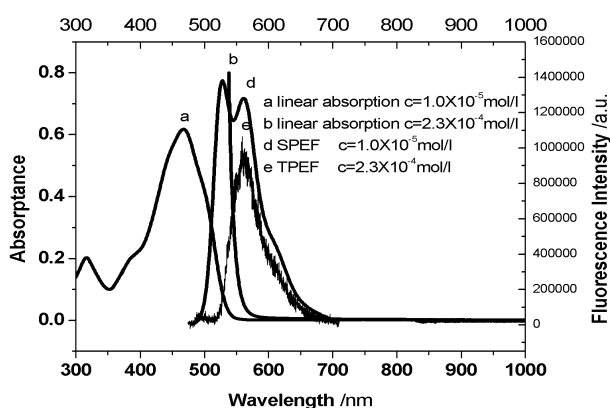
As shown in **Figure 1**, the peak position of absorption spectrum of BMSBT in THF is at 457 nm and there is no linear absorption from 580 nm to 1000 nm even at concentration of  $4.8 \times 10^{-4}$  mol/L. Excited by a 450 W Xe lamp at 457 nm the SPEF spectra were

recorded on an Edinburgh FLS920 fluorescence spectrometer and the corresponding lifetime is 1.08 ns. The TPEF spectra was excited by a Ti:Sapphire fs laser at 800 nm, and the fluorescence signal was recorded by a streak camera (Hamamatsu model C5680). This kind of frequency up-converting should be produced *via* a two-photon absorption (TPA) process and can be definitely attributed to the mechanism of two-photon excited fluorescence. The dependence of the TPEF intensity of BESBT in  $4.8 \times 10^{-4}$  mol/L THF on the incident intensity, which is nearly a perfect quadratic (see **Figure 2**), also indicates that the TPEF is induced by TPA. The peak wavelength of the TPEF spectrum of BMSBT is located at 554 nm, which is just the same position as that of the SPEF spectrum. This may be explained by a presumption that the emission energy level corresponding to TPEF be the same as the one corresponding to SPEF.

**Figure 2** The dependence of the TPEF of BESBT in THF on the incident intensity



**Figure 3** Optical properties of BESBT in toluene



The spectral characteristics of BESBT are basically the same as that of BMSBT with its fluorescence lifetime 1.10 ns in THF. The spectra of linear absorption, SPEF and TPEF of BESBT in toluene are shown in **Figure 3**. The maximum absorption is at 467 nm and there is no linear absorption from 590 nm to 1000 nm even with concentration of  $2.3 \times 10^{-4}$  mol/L. In the less polar solvent, toluene, the SPEF emission obviously split

into two peaks, one at 528 nm and another at 563 nm. But the spectra profile of the TPEF is a single peak. This may be explained by re-absorption. The absorption at 528 nm with the concentration  $2.3 \times 10^{-4}$  mol/L in toluene can not be neglectable, so the supposed emission peak of TPEF at this wavelength may be absorbed. The reserved emission peak is located at 563 nm, the same wavelength as one of the SPEF.

### TPA cross section measurement

The two-photon cross sections  $\sigma$  of BMSBT and BESBT were obtained by the TPEF method<sup>6</sup>. The 800 nm laser beam was introduced into the sample in toluene and a barrier filter was put between the sample and the detector to avoid the scattering light. The  $\sigma$  values of the two compounds were determined by comparing their TPEF intensities with that of fluorescein in 0.1 mol/L NaOH solution (all the concentrations in measurement were fixed at  $5 \times 10^{-4}$  mol/L) according to<sup>6</sup>

$$\sigma \phi = \sigma_{flu} \phi_{flu} (n_{flu} F / n F_{flu}).$$

Where  $n$  is the refractive index and  $F$  is the TPEF intensity. The subscript *flu* refers to the standard fluorescein. In our experiment, the TPA cross sections  $\sigma$  of BMSBT and BESBT were measured to be  $54 \times 10^{-50}$  (cm<sup>4</sup>s)/photon and  $102 \times 10^{-50}$  (cm<sup>4</sup>s)/photon separately.

In conclusion, two new chromophores, BMSBT and BESBT, were synthesized. Both the two compounds can emit strong SPEF and TPEF with the emission peaks around ~560 nm and with the lifetime of 1ns. The TPA cross sections of them are detected to be  $54 \times 10^{-50}$  (cm<sup>4</sup>s)/photon and  $102 \times 10^{-50}$  (cm<sup>4</sup>s)/photon separately. They may be good candidates for some optical application such as two-photon excitation fluorescence microscopy.

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