

Synthesis, as well as linear and nonlinear fluorescence properties of 5,5'-bis(4-*N*-carbazolylstyryl)-2,2'-bithiophene

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(Received 28 July, revised 16 December 2003)

Abstract: A new bithiophene-based organic luminescence material, named 5,5'-bis(4-*N*-carbazolylstyryl)-2,2'-bithiophene (BCSBT), was synthesized. Its single-photon excited fluorescence band is located in the range of 520–530 nm, with a quantum yield of around 10 %. The compound emits strong two-photon-excited fluorescence when excited by 200 fs laser pulses. The two-photon absorption cross section of BCSBT was found to be $124 \times 10^{-50} \text{ cm}^4 \text{ s}$ by the two-photon-excited fluorescence method.

Keywords: two-photon absorption, up-converted fluorescence, bithiophene derivatives.

INTRODUCTION

Under ordinary experimental condition, molecular fluorescence emission obeys the Stark-Einstein law, *i.e.*, the fluorescence is caused by a single photon absorption process. When a laser acts as the excitation source, the law may not be strictly abided to because of the high energy of the excitation beam. Some molecules can absorb two photons simultaneously, which leads to two-photon excited fluorescence (TPEF). TPEF has advantages over single-photon excited fluorescence (SPEF). Firstly, excitation wavelength for TPEF is usually twice that for SPEF. Obviously, under red-shifted incident light, most organic materials are photostable. Secondly, the large red-shift of the incident light leads to a better penetrability of the material. Finally, the absorbance is quadratic with the intensity of the excitation radiation in the TPEF process, whereas it is linear in SPEF. Therefore, excitation of materials with a high degree of spatial selectivity in three dimensions can be easily performed using a focused beam in a TPEF process while this is not the case in a SPEF process. So molecules with large two-photon absorption (TPA) cross sections are in demand for a variety of applications, such as

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two-photon excited up-converted lasers,¹ two-photon fluorescence microscopy,^{2,3} three-dimensional optical memory⁴ and photodynamic therapy.⁵

In recent years, most compounds with a strong TPEF are π -conjugated molecules based on polyvinyl or styryl moieties. Thiophene has a lower resonance energy compared to benzene and a better coplanar conformation to polyenes.^{6,7} Compounds based on thiophene as an electron relay may have better TPEF characteristics than those based on styrene or polyene. So a new compound derived from 2,2'-bithiophene, named 5,5'-bis(4-*N*-carbazolylstyryl)-2,2'-bithiophene (BCSBT) (the structure is shown in Fig. 1) was synthesized. It can emit strong SPEF and TPEF.

RESULTS AND DISCUSSION

Linear spectral properties

The absorption spectra were recorded on a Hitachi U-3500 spectrophotometer and the SPEF spectra on an Edinburgh FLS920 fluorescence spectrometer.

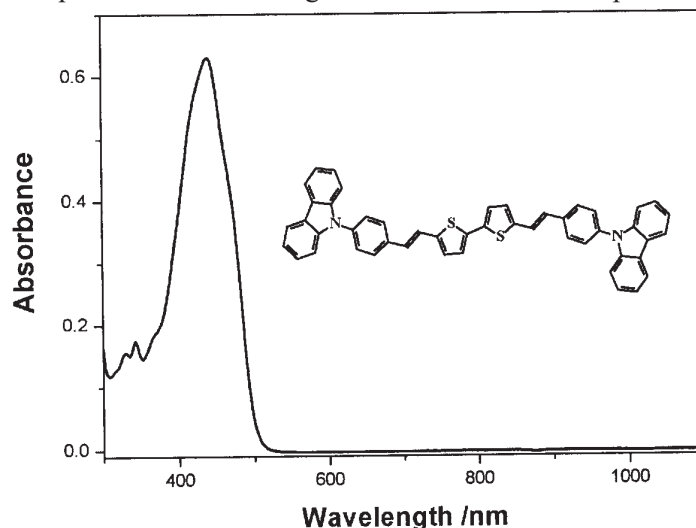


Fig. 1. Absorption spectra of BCSBT in toluene.

The linear absorption spectrum of BCSBT in toluene ($c = 1.0 \times 10^{-5}$ mol/L) is shown in Fig. 1. As can be seen the peak absorption of the target compound is located at 437 nm and there is no linear absorption from 550 nm to 1000 nm.

The SPEF of the target compound in different solvents (all concentrations were 1.0×10^{-5} mol/L) were recorded using the 420 nm band of a 450 W Xe lamp as the excitation source. The SPEF spectrum of BCSBT in tetrahydrofuran (THF) is shown in Fig. 2. It is evident that the fluorescence peak is split into two peaks, one at 497 nm and the other at 528 nm. The two split peaks may be caused by different vibrational energy levels. In different solvents, the SPEF spectra of BCSBT are almost the same. The emission peaks are all located at about 528 nm, the quantum

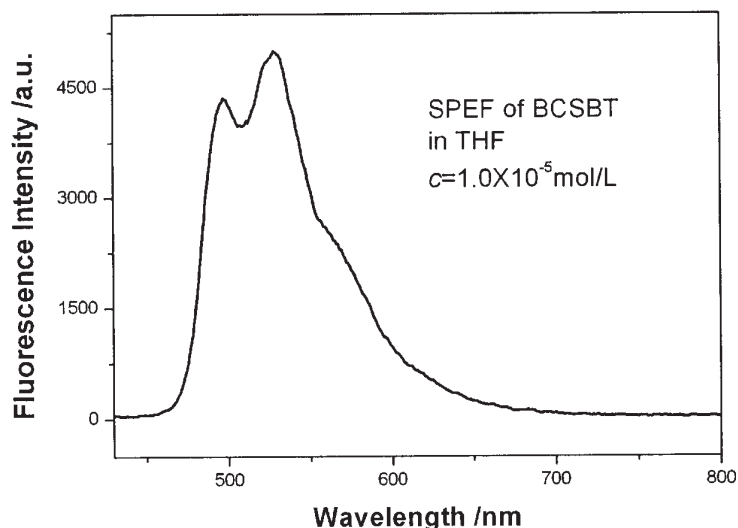


Fig. 2. Fluorescence spectra of BCSBT in THF.

yields are about 0.10 and the lifetimes about 1.06 ns in toluene, THF, acetone, acetonitrile and DMF. The molecular structure of BCSBT is symmetrical. Because of the good electron delocalization, the electron donating ability of the carbazoyl group is very low. Hence, intra-molecular electron transfer in BCSBT is very weak. The whole molecule may have a well conjugated structure and the polarization is weak. Thus, the SPEF spectra of BCSBT show little solvatochromism.

Two-photon excited luminescence spectral properties

For the measurement of the TPEF, a Ti:Sapphire fs laser was used as a source and the fluorescence signals were recorded using a streak camera system (Hamamatsu model C5680). A barrier filter was situated between the sample and the detector system to avoid scattered light.

Before measurement of the TPEF, the absorption spectra of the target compound at a high concentration (the same concentration as the one used for the TPEF measurements) was recorded (curve b in Fig. 3). The peak absorption is very strong at this concentration, but there is still no linear absorption in the wavelength range from 590 nm to 1000 nm. Hence, the luminescence observed on excitation by the 800 nm laser can be attributed to TPEF.

The spectra of linear absorption, SPEF and TPEF of BCSBT in toluene are shown in Fig. 3. The maximum absorption is at 437 nm and there is no absorption between 590 nm and 1000 nm, even at a concentration of 5.0×10^{-4} mol/L. In the low polar solvent, toluene, the SPEF emission obviously splits into two peaks, one at 499 nm and another at 532 nm (curve d in Fig. 3). But the spectral profile of the TPEF is a single peak. This may be explained by re-absorption. The absorption at 499 nm at a concentration of 5.0×10^{-4} mol/L in toluene cannot be neglected, so the

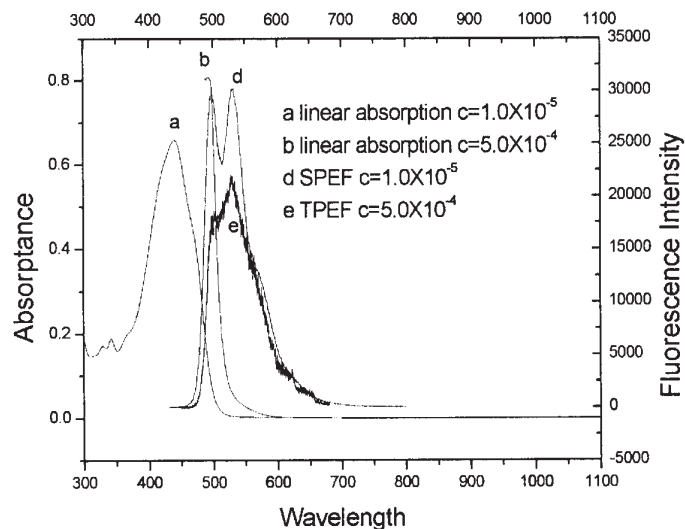


Fig. 3. Optical properties of BCSBT in toluene.

TPEF emission peak expected at this wavelength may be absorbed. The observed emission peak is located at 532 nm, the same wavelength as the one for SPEF.

Different TPEF spectra are likely in different solvents (Fig. 4). The molecular structure of BCSBT is symmetrical, so the luminescence in the nonpolar solvent, toluene, is greater than that in the polar solvent, THF.

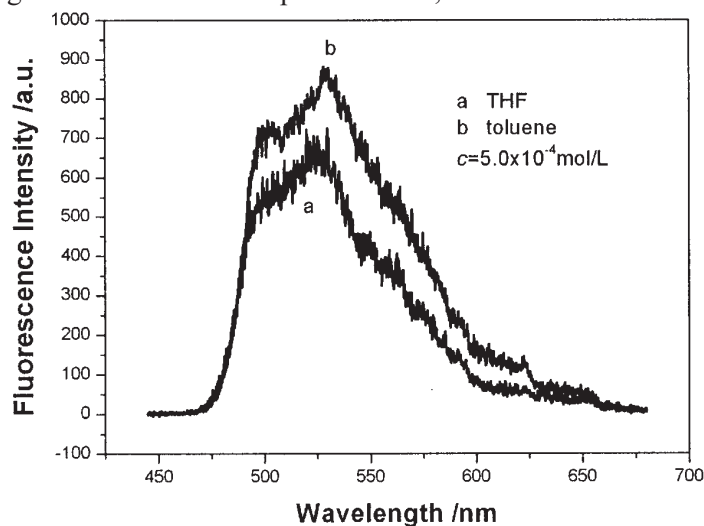


Fig. 4. TPEF properties of BCSBT in toluene and THF.

TPA cross section measurement

Two-photon absorption (TPA) cross section σ of the target compound BCSBT was obtained by the TPEF method.⁸ Using strictly the same experimental condi-

tions, the TPEF spectra of BCSBT in toluene and that of fluorescein in 0.1 mol/L NaOH solution were recorded (the concentrations of the solutions were both fixed at 5.0×10^{-4} mol/L). The σ value of BCSBT was determined by comparing its TPEF integral intensity with that of fluorescein according to:⁸

$$\sigma\phi = \sigma_{\text{flu}}\phi_{\text{flu}} (C_{\text{flu}}/C)(n_{\text{flu}}F/nF_{\text{flu}})$$

where ϕ , C , n and F are fluorescence quantum yield, concentration, refractive index and the TPEF intensity, respectively. The subscript flu refers to the standard fluorescein. In the present experiments, the wavelength of the incident laser was 800 nm. The TPA cross section σ of fluorescein σ_{flu} is 36×10^{-50} (cm⁴ s)/photon,⁹ and its fluorescence quantum yield ϕ_{flu} is 0.9.⁸ As all the concentrations measured were the same, the effect of concentration on the TPA cross section σ can be neglected. The TPA cross section σ of BCSBT was found to be 124×10^{-50} cm⁴ s.

CONCLUSION

A new compound derived from bithiophene, named BCSBT, was synthesized. The compound shows good linear fluorescence properties. The emission peaks are located at about 530 nm and the corresponding lifetimes are about 1 ns in different solvent. The fluorescence spectra of BCSBT exhibit little solvatochromism.

The target compound emits strong up-converted fluorescence when excited by an 800 nm laser. The TPA cross section σ of BCSBT was found by the TPEF method to be 124×10^{-50} cm⁴ s. Hence BCSBT may be considered a good TPA and TPEF material.

EXPERIMENTAL

General methods

The target compound was synthesized by the Wittig reaction and the intermediate bithiophene by the Grignard reaction. All reactions were conducted under a dry N₂ atmosphere. The reactants were used as received from a commercial supplier. THF was distilled over sodium and the other solvents were redistilled before use.

Synthesis of 2,2'-bithiophene

To 8.0 g (0.33 mol) magnesium in a flask containing 150 mL dry THF, 26 mL (0.27 mol) 2-bromothiophene was added dropwise under N₂. After 1 h, the solution was transferred dropwise to another flask containing 22 mL 2-bromothiophene, 1.3 g NiCl₂.dppp and 200 mL THF in an ice-water bath. Then the solution was stirred for 24 h at room temperature. The crude product was purified by column chromatography. A pale purple solid (58.1 g) was obtained (yield, 58 %; m.p. 32–33 °C). ¹H-NMR (CDCl₃) δ 7.19 ppm (*q*, $J = 4.5$ Hz, 4H), 7.01 ppm (*t*, $J = 4.2$ Hz, 2H).

Synthesis of 5,5'-diformyl-2,2'-bithiophene

To 16.6 g (0.1 mol) 2,2'-bithiophene and 250 mL THF in a flask under a N₂ atmosphere was added dropwise under stirring 125 mL 1.6 M *n*-butyllithium in hexane. After stirring for 1 h at room temperature, the mixture was cooled to -78 °C and 23 mL (0.3 mol) DMF was added dropwise. After 3 h, the solution was poured into 500 mL water and the pH adjusted to 7 with dilute hydrochloric

acid, and the product was extracted with CHCl_3 . After further purification by column chromatography, 11.0 g of powder was obtained (yield 48 %). $^1\text{H-NMR}$ (CDCl_3) δ 9.91 ppm (*s*, 2H), 7.72 ppm (*d*, $J = 6.1$ Hz, 2H), 7.42 ppm (*d*, $J = 3.9$ Hz, 2H).

Synthesis of 4-*N*-carbazolylbenzaldehyde

4-*N*-Carbazolylbenzaldehyde was synthesized according to Ref. 10. A pale-yellow solid (yield 48 %) was obtained. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz), δ 10.09 ppm (*s*, 1H), 8.12 ppm (*m*, 4H), 7.43 ppm (*m*, 8H).

Synthesis of 4-*N*-carbazolylbenzyltriphenylphosphonium bromide

A mixture of 27.1 g (0.1 mol) 4-*N*-carbazolylbenzaldehyde, 2.0 g (0.04 mol) KBH_4 and 300 mL ethanol in a 500 mL flask were refluxed for 4 h. The solution was neutralized with dilute hydrochloric acid, and the product extracted with CHCl_3 . The product and 41 g (0.1 mol) $\text{HP}^+\text{Ph}_3\text{Br}^-$ were added to a flask containing 300 mL CHCl_3 , and then refluxed for 3 h, distilled, and subsequently treated with ether. A white solid (4-*N*-carbazolylbenzyltriphenylphosphonium bromide) was obtained. Yield 95 %.

Synthesis of 5,5'-bis(4-*N*-carbazolylstyryl)-2,2'-bithiophene (BCSBT)

Under N_2 , a solution of 0.03 mol *t*-BuOK in 50 mL THF was added dropwise to a flask containing 0.02 mol 4-*N*-carbazolylbenzyltriphenylphosphonium bromide, 5,5'-diformyl-2,2'-bithiophene and 200 mL THF at 0 °C. The reaction was allowed to proceed for 15 h at room temperature. The mixture was poured into 500 mL water and the pH adjusted to 7 with dilute hydrochloric acid, and the product extracted with CHCl_3 . After further purification by column chromatography, a dark-yellow powder was obtained. Yield 34 %. MS (70 eV) m/z (%) 700 (M^+ 50) 350 ($\text{M}^+/2$ 36). Anal. Calcd. for $\text{C}_{48}\text{H}_{32}\text{N}_2\text{S}_2$: C, 82.25; H, 4.60; N, 4.00; S, 9.15, found C, 81.54; H, 4.79; N, 3.48; S, 9.50.

ИЗВОД

SINTEZA I LINEARNE I NELINEARNE FLUORESCENTNE OSOBINE 5,5'-BIS(4-*N*-KARBAZOLILSTIRIL)-2,2'-BITIOFENA

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Синтетисан је нов, на основи битиофена заснован, органски лиминисцентан материјал, 5,5'-бис(4-*N*-карбазоллстирил)-2,2'-битиофен (BCSBT). Флуоресцентна трака ексцитована једним електроном налази се у области 520–530 nm са квантним приносом од око 10 %. Једињење емитује јаку двофотонску луминисценцију када се побуђује ласерским пулсима од 200 fs. Нађено је коришћењем методе двоелектронске флуоресцентне екситације да је попречни пресек двоелектронске апсорпције BCSBT $124 \times 10^{-50} \text{ cm}^4 \text{ s}$.

(Примљено 28. јула, ревидирано 16. децембра 2003)

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