Short Communication

Effects on the Two-photon Excited Fluorescence of Thiophene Derivatives

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Abstract

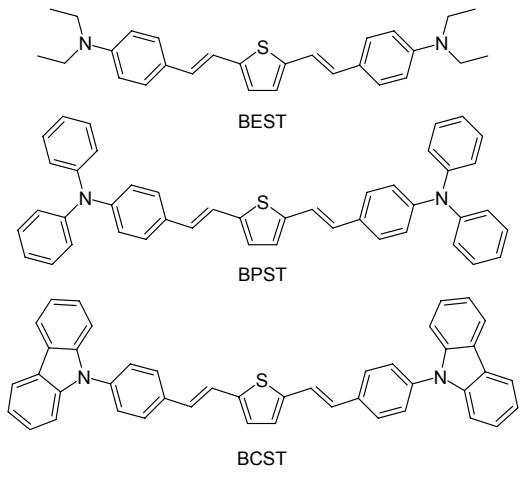
Three new thiophene-based organic luminescence compounds named as 2,5-bis(*p*-*N*,*N*-diethylaminostyryl)thiop hene (BEST), 2,5-bis(*p*-*N*,*N*-diphenylaminostyryl)thiophene (BPST) and 2,5-bis(*p*-*N*-carbazoylstyryl)thiophene (BCST) were synthesized. All of their single-photon excited fluorescence (SPEF) locate in the range of ~530nm with the quantum yield around 40%, and the corresponding lifetime was ~1 ns. The target compounds show strong solvatochromism in their SPEF spectra except BCST. There is no obvious change for the peak wavelength in the linear spectra of BCST in different polar solvent. Excited by a fs laser at 800 nm, strong up-converted fluorescence of target compounds was detected. The profile of two-photon excited fluorescence (TPEF) was likely with that of SPEF. The two-photon absorption (TPA) cross sections of the compounds were determined by TPEF method. All target compounds show large TPA cross section in our experiments. So that thiophene derives may have good TPA properties.

Key words: two-photon absorption, up-converted fluorescence, thiophene derivatives

Introduction

Two-photon excited fluorescence (TPEF), caused by simultaneously absorbing two photons by each molecule, has been attracting more and more research interest for its various nonlinear optical (NLO) applications such as two-photon pumped up-conversion lasing[1] and TPEF microscopy.[2,3] 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. And it also leads better penetrability of the incident light in the material. The absorbance scales quadratically with the intensity of exciting radiation in TPEF process, whereas it scales linearly in SPEF. Then the excitation of materials with high degree of spatial selectivity in three dimensions can be easily done using focused beam in TPEF process while it cannot in SPEF.

In the past few years, various kinds of chromophores were synthesized for TPEF and the main attention has been focused on the nonlinear optical (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.[4,5] Based on these, we synthesized a series of new thiophene derivatives (shown in Scheme 1): 2,5-bis(*p*-*N*,*N*-diethylaminostyryl)thiophene (BEST), 2,5-bis(*p*-*N*,*N*-diphenylaminostyryl)thiophene (BPST) and 2,5-bis(*p*-*N*-carbazoylstyryl)thiophene (BCST), which can emit strong SPEF and TPEF.



Scheme 1. Structures of target compounds.

Results and Discussion

Linear spectral properties

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

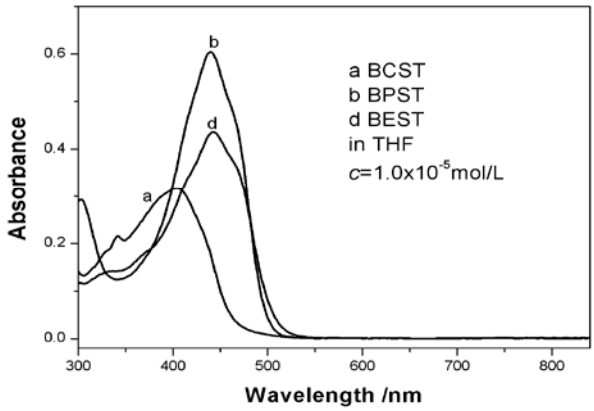


Figure 1. Absorption spectra of BEST, BPST and BCST in THF.

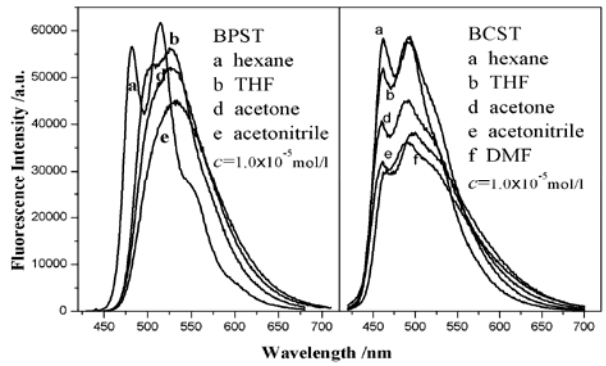


Figure 2. Fluorescence spectra of BPST and BCST in different solvent.

Linear absorption spectra of target compounds

Linear absorption spectra of BEST, BPST and BCST in toluene are shown in Figure 1. Peak absorption of these compounds are located at 442 nm (BEST), 440 nm (BPST) and 404 nm (BCST) respectively, and there are no linear absorption from 550nm to 1000 nm. The peak absorption of BCST has a blue-shift of 38 nm compared to that of BEST. This may be caused by the different electron giving/pulling ability of the donor. The lone pair electrons of nitrogen in BCST are delocalized in a wide range of carbazoyl, and the strong electron pulling ability of nitrogen atom may change the electron giving/pulling ability of the donor/or acceptor,[6] then carbazoyl in BCST shows weak electron pulling ability, while alkyl amino is a strong electron donor in BEST. The adjacent absorption peak position of BEST and BPST show adjacent electron giving ability of the end group of the two target compounds.[7]

Linear fluorescence spectra of target compounds

It is the difference of electron giving/pulling ability of the end groups of the target compounds that lead different solvatochromism in their fluorescence spectra. There are obvious solvatochromism in the fluorescence spectra of BEST and BPST while there isn't in that of BCST (Figure 2 and Table 1). Strong electron giving ability of alkyl amino in BEST and BPST lead severe electron re-distribution, which become more severely in their excited state. The shift of the energy level induced by intra-molecular re-distribution of electron is strongly affected by the solvent polar. The different effect taken by polar solvent between the ground and excited state influence on the fluorescence spectra. Solvatochromism emerged in the fluorescence spectra of BEST and BPST.

In nonpolar solvent hexane the SPEF spectra of BPST obviously split two peaks, one at 482 nm and another at 515nm, which can be attributed to electron transitions form different electronic vibrational levels of a same excited state. In polar solvents the dual peaks is combined as a single peak and with the increasing of solvent polar the emission peaks are red-shifted and the corresponding lifetimes get longer.

In the fluorescence spectra of BCST, there are two peaks in either nonpolar solvent hexane or polar solvent like DMF, and the peaks' position are not changed following the change of the solvent polar. Only the fluorescence intensity is lowered when the solvent polar becomes strong. It is just for the reason that the weak electron pulling ability of carbazoyl in BCST result in poor intramolecular electron re-distribution both at the ground state and the excited state, which make absence of change in the fluorescence spectra of BCST.

Table 1. The SPEF properties of target compounds in different solvent.*

Solvent	BEST			BPST			BCST		
	Peaks (nm)	Stokes shifts	τ (ns)	Peaks (nm)	Stokes shifts	τ (ns)	Peaks (nm)	Stokes shifts	τ (ns)
Toluene	527	91	1.03	515	75	1.02	491	87	1.07
THF	529	93	1.05	525	85	1.10	494	90	1.05
Acetone	532	96	1.09	526	86	1.14	492	88	1.06
Acetonitrile	534	98	1.11	534	94	1.18	489	85	1.09
DMF	540	104	1.15				496	92	1.07

* The SPEF spectra were excited by 450W Xe lamp. Excited wavelength: BEST and are BPST 400nm□BCST is 440nm. Concentrations of all compounds are 1.0×10^{-5} mol/L.

Two-photon excited fluorescence spectral properties

In the measurement of TPEF, a Ti Sapphire fs laser was used as a pump source and the fluorescence signal was recorded by a streak camera system (Hamamastsu model C5680). A barrier filter is put between the sample and the detector system to avoid the scattering light.

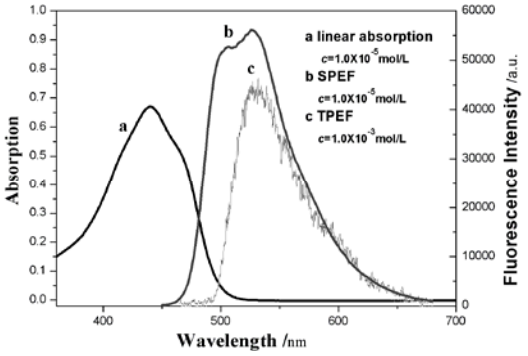


Figure 3. TPEF spectra of BPST in THF.

As shown in Figure 3, the peak wavelength of TPEF spectrum of BPST is located at 530 nm, which is similar to the peak position of SPEF. This may be explained by a presumption that the emission energy level corresponding to TPEF be the same as that to SPEF, even the excited energy of them are different in our experiment (the summation energy of the two photons in TPEF is a little higher than that of the single photon in SPEF).

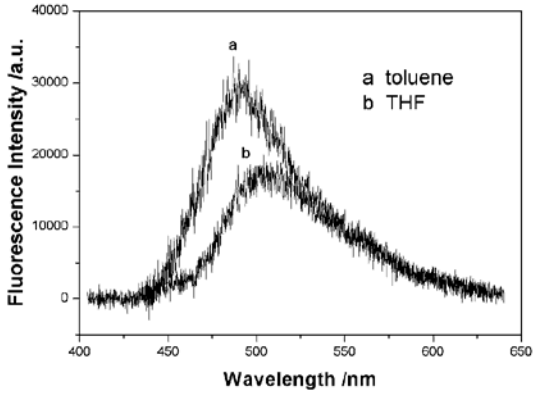


Figure 4. TPEF spectra of BCST in THF and toluene.

The TPEF spectra of BCST in THF and toluene are shown in Figure 4. There are two peaks in the SPEF spectra of BCST in different solvent and there is no obvious solvatochromism. But it is changed in the TPEF spectra. There is only one peak in the spectra in different solvent and solvatochromism seemingly emerge. This may be caused by re-absorption. Measurement of the very weak TPEF needs higher concentration than that for SPEF. On the other hand, the weak TPEF may be severely affected by the re-absorption. Then the profile of TPEF is distinct from that of SPEF.

Two-photon absorption cross-section measurement

The two-photon absorption cross-section σ of the target compounds were measured by the TPEF method[6] and we used Coumarin 307 and fluorescein as standard samples. Under the strictly same condition, we recorded the TPEF spectra of the target compounds, Coumarin 307 in THF and fluorescein in 0.1mol/L NaOH solution (their concentrations in measurement were fixed at 1×10^{-3} mol/L and the power of the laser was 1 W). TPA cross section σ of the target compounds were obtained by comparing their TPEF integral intensities with that of standard compounds according to:

$$\sigma\phi = \sigma_s\phi_s\left(\frac{C_s}{C}\right)\left(\frac{n_s F}{nF_s}\right)$$

where n is the refractive index, C is the concentration and F is the TPEF intensity and the subscript s refers to the standard compounds. In our experiment the TPA cross section of the target compounds BEST, BPST and BCST were measured to be 82, 256 and 25×10^{-50} cm^4 s/photon respectively.

In the measurement of TPA cross-section σ, we found that it is greatly affected by the electron donor/acceptor in the compound molecule. Strong electron giving ability of alkyl amino in BEST and BPST lead better TPA property than those compounds with electron pulling ability group, like BCST, do. Aromatic end group with electron giving ability may do better to the TPA cross-section σ of the compound. For example, BPST have the largest TPA cross-section among the target compound.[7]

Conclusion

A series of novel thiophene derivatives, BEST, BPST and BCST were synthesized. These compounds can emit strong single-photon fluorescence excited by a 450 W Xe lamp and the corresponding lifetimes are around 1.10 ns in THF. Excited by a Ti Sapphire fs laser, strong two-photon fluorescence is obtained. The TPA cross section of the target compounds BEST, BPST and BCST were measured to be 82, 256 and 25×10^{-50} cm^4 s/photon respectively, and it is greatly affected by the electron donor/acceptor in the compound molecule. BPST, with aromatic electron giving ability end group, have the largest TPA cross-section among the target compound. So these compounds may have some potential optical applications such as used to be

two-photon excitation fluorescence microscopy, optical limiting and three-dimensional optical storage.

Experimental section

General methods. The target compounds were synthesized by Wittig reaction and the reaction was conducted under dry N_2 atmosphere. Reagents were used as received from commercial supplier. THF was distilled over sodium and the other solvents were redistilled before use.

Synthesis of 2,5-diformacylthiophene. 8 mL (0.1 mol) thiophene and 250 mL THF were added to a flask under N_2 atmosphere. Then 125 mL 1.6 M *n*-butyllithium in hexane was dropped in and keep stirring for 1 hr at room temperature. 23 mL (0.3 mol) DMF was added dropwise into the flask at –78 °C. 3 hrs later the solution was poured into 500 mL of water, the pH adjusted to 7 by diluted hydrochloric acid, and the product was extracted with $CHCl_3$. After further purified by column chromatography yellow powder was obtained (yield 53%). ^{1}H NMR ($CDCl_3$) δ 9.91 (s, 2H), 7.80 (d, *J* 4.5 Hz, 2H).

Synthesis of dialkylaminobenzaldehyde. Dialky laminobenzaldehydes were synthesized according to reference 6.

Diethylaminobenzaldehyde is pale yellow solid (yield 67%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.69 (s, 1H), 7.68 (d, *J* 8.8 Hz, 2H), 6.65 (d, *J* 8.8 Hz, 2H), 3.41 (q, *J* 7.0 Hz, 4H), 1.19 (t, *J* 7.1 Hz, 6H).

N-Carbazoylbenzaldehyde is yellow solid (yield 48%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.09 (s, 1H), 8.12 (m, 4H), 7.43 (m, 8H).

Synthesis of diphenylaminobenzaldehyde. 10 g (0.041 mol) Triphenylamine dissolved in 6 mL (0.08 mol) of DMF was put into a 250 mL flask with ice water bath. Then 36.8 mL (0.4 mol) phosphorus oxychloride was added dropwise into the flask. The reaction mixture was stirred for 2.5 hr. After hydrolyzed with ice water and purified by column chromatography, yellow solid was obtained (yield 54%). mp 139–142 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.77 (s, 1H), 7.67 (d, *J* 6.8 Hz, 2H), 7.19 (m, 12H).

Synthesis of dialkylaminotoluenyltriphenylphos phoium bromide. 17.7 g (0.1 mol) diethylaminobenza ldehyde, 2.0 g (0.04 mol) KBH_4, 300 mL ethanol were added to a 500 mL flask and refluxed for 4 hrs. The solution was neutralized with dilute hydrochloric acid and product extracted with $CHCl_3$. The product and 41 g (0.1 mol) $HP^+Ph_3Br^-$ were combined in a flask with 300 mL $CHCl_3$, and then refluxed for 3 hrs, distilled, and treated with ether. White solid (diethylaminotoluenyltri phenylphosphoium bromide) was obtained. Yield 98%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (m, 19H), 5.71 (d, *J* 14.6 Hz, 2H), 3.74 (t, *J* 6.8 Hz, 4H), 0.86 (d, *J* 5.8 Hz, 6H).

Diphenylaminotoluenyltriphenylphosphoium bromide was obtained by the same method. Yield 98%.

N-Carbazoyltoluenyltriphenylphosphoium bromide was obtained by the same method. Yield 95%.

Synthesis of 2,5-bis(*p*-*N*,*N*-diethylaminostyryl) thiophene (BEST). Under N_2 atmosphere and at 0 °C, a solution of 0.03 mol t-BuOK in 50 mL THF was added dropwise into a flask containing 0.02 mol diethylaminotoluenyltriphenylphosphoium bromide, 2,5-diformacylthiophene and 200 mL THF. The reaction was kept for 15 h at room temperature. The mixture was poured into 500 mL of water and the pH adjusted to 7 by dilute hydrochloric acid. The product was extracted with $CHCl_3$. After further purification by column chromatography dark-red powder was obtained (yield 38%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (d, *J* 8.8 Hz, 1H), 6.75 (m, 6H), 3.30 (q, *J* 8.8 Hz, 4H), 1.1 (t, *J* 8.0 Hz, 6H). MS (70 eV) m/z (%) 430 (M^+ 100). Anal. Calcd for $C_{28}H_{34}N_2S$ C 78.09, H 7.96, N 6.50. Found C 77.95, H 7.99, N 6.48.

Synthesis of 2,5-bis(*p*-*N*,*N*-diphenylaminostyryl) thiophene (BPST). The same method as for BEST was used to synthesize BPST. Yield 27%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.34 (d, *J* 8.6 Hz, 4H), 7.28 (m, 8H), 7.13 (d, *J* 8.0 Hz, 8H), 7.07 (m, 10H), 6.91 (s, 2H), 6.85 (d, *J* 15.9, 2H). MS (70 eV) m/z (%) 622 (M^+ 100). Anal. Calcd for $C_{44}H_{34}N_2S$: C 84.85, H 5.50, N 4.50. Found C 85.17, H 5.52, N 4.49.

Synthesis of 2,5-bis(*p*-*N*-carbazoylstyryl)bithioph ene (BCST). The same method as for BEST was used to synthesize BCST. Yield 34%. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.87 (m, 4H), 7.35 (m, 8H), 7.29 (d, *J* 8.7 Hz, 8H), 7.15 (m, 10H). MS (70 eV) m/z (%) 618 (M^+ 100). Anal. Calcd for $C_{44}H_{30}N_2S$: C 85.41, H 4.89, N 4.53. Found C 85.19, H 4.92, N 5.16.

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Povzetek

Sintetizirali smo tri nove luminiscentne spojine na osnovi tiofena, 2,5-bis(*p-N,N*-dietilaminostiril)tiofen (BEST), 2,5-bis(*p-N*,*N*-difenilaminostiril)tiofen (BPST) in 2,5-bis(*p-N*-karbazoilstiril)tiofen (BCST). Vse tri pri enofotonskem vzbujanju (SPEF) fluorescirajo v območju ~530nm s kvantnim izkoristkom okrog 40% in življenjsko dobo vzbujenega stanja ~1 ns. Spojine, razen BCST, kažejo v fluorescenčnem spektru močan solvatokromni efekt. Pri vzbujanju s fs laserjem pri 800 nm se je pojavila močna fluorescenca, povzročena z dvofotonskim vzbujanjem (TPEF). Dvofotonski absorpcijski (TPA) presek spojin smo določili z metodo TPEF, pri čemer so vse tri spojine pokazale velik TPA presek. Tiofenski derivati bi torej lahko imeli dobre TPA lastnosti.