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New Thiophene Derivatives with Two-photon Excited Fluorescence

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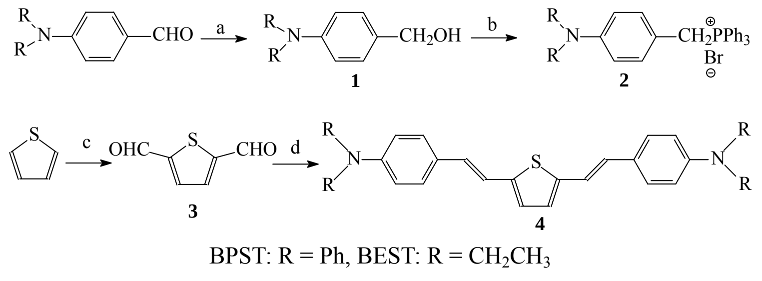
Abstract: Two new compounds involving a thiophene moiety named as 2,5-bis[4-(N,N- diphenylamino)styryl]thiophene (BPST) and 2,5-bis[4-(N,N-diethylamino)styryl]thiophene (BEST) have been synthesized. The two-photon absorption cross section of BPST was measured as large as 256×10^{-50} $cm^4 \cdot s$/photon, when it was excited by 800 nm femtosecond laser.

Keywords: Thiophene, two-photon absorption, two-photon excited fluorescence.

Organic molecules that can simultaneously absorb two or more photons in reaching their excited states have recently been the subject in various photon-electronic fields. To meet the criteria for various nonlinear optical applications, such as three-dimensional optical storage[1] and up-converted lasing[2], molecules with large two-photon absorption (TPA) cross-section σ are required and have been synthesized. These dyes generally belong to the structural modes of D-π-D, A-π-A[3] or D-π-A, where D is an electron-donating group, A is an electron-acceptor group, and π is a conjugating linker. Recently, we have synthesized a series of D-π-D type of organic dyes with thiophene rings in the center of π conjugating linker. We herein report two compounds named BPST and BEST.

Synthesis

Scheme 1 Synthesis outline of BPST and BEST



BPST: R = Ph, BEST: R = CH_2CH_3

a) KBH_4, C_2H_5OH b) $PPh_3 \cdot HBr$, CH_3Cl c) BuLi, DMF, -78 ℃ d) BuOK, THF

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As shown in **Scheme 1**, the target compounds BPST and BEST were synthesized by Wittig reaction. The starting benzaldehyde, which was prepared according to a literature procedure, was reduced by KBH_4 to afford the corresponding benzalcohol. Refluxing the $CHCl_3$ solution of equivalent amount of benzalcohol and $Ph_3\cdot HBr$, the phosphonium salt (compound **2**) can be obtained. The 2,5-diformyl thiophene was formylated by DMF in strong base condition. At 0ºC under N_2, the THF solution of *t*-BuOK was added dropwise into the mixture of **2** and **3** (the molar ratio of **2** and **3** was 2:1). The reaction mixture was refluxed for further 15 hours and then poured into ice-water. The crude products were extracted with chloroform and purified by column chromatography. The target compounds BPST and BEST were obtained as orange-red powders. BPST: elemental analysis: calcd. (%) for $C_{44}H_{34}N_2S$: C 84.89, H 5.47, N 4.50; found: C 84.22, H5.73, N 4.71; ^{1}HNMR (600 MHz, $CDCl_3$, δ ppm) 6.85 (d, 2H, J = 15.9 Hz), 6.91 (s, 2H), 7.04 - 7.09 (m, 10H), 7.13 (d, 8H, J = 8.0 Hz), 7.27 - 7.29 (m, 8H), 7.34 (d, 4H, J = 8.6 Hz); MS: *m/z* (%) 622(M^+ 100); mp 199-201 ºC.

BEST: elemental analysis: calcd. (%) for $C_{28}H_{34}N_2S$: C 78.14, H 7.90, N 6.50, found C 76.49, H 7.74, N 6.83. ^{1}HNMR (90 MHz, $CDCl_3$, δ ppm) 1.11 (t, 12H, J = 6.8 Hz), 3.30 (q, 8H, J = 7.0 Hz), 6.52-6.82 (m, 10H), 7.25 (d, 4H, J = 8.8 Hz). MS: *m/z* (%) 430 (M^+ 100); mp 209-210 ºC.

Single and two-photon excited fluorescence properties

Linear absorption spectra were recorded on a PE lambda 35 UV-Vis spectrophotometer, single-photon excited fluorescence (SPEF) spectra were measured on an Edinburgh FLS920 fluorescence spectrometer, two-photon excited fluorescence (TPEF) were excited by a Ti:Sapphire fs laser at 800 nm and detected by a Hamamastsu model C5680 streak camera.

As shown in **Figure 1**, in non-polar hexane solvent the SPEF spectrum of BPST obviously splits into two peaks, one at 482 nm and the other at 515 nm. In polar solvents the dual peaks are combined into a single peak. The dual peaks can be attributed to the transition from the same excited state to two different vibrational levels of a same electronic ground state, for the fluorescence lifetimes at 482 and 515 nm are nearly the same (shown in **Table 1**). With the increase of polarity of the solvents, the emission peaks are red-shifted and the corresponding lifetimes get longer.

Figure 1 SPEF spectra of BPST in different solvents

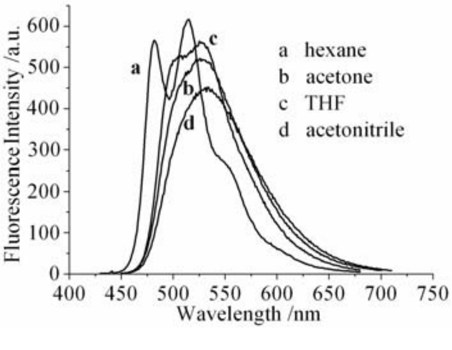


Table 1 The SPEF properties of BPST in different solvents

Solvent	hexane	THF	acetone	acetonitrile
Absorption peak position (nm)	435	440	437	435
SPEF peak position (nm)	482, 515	525	526	534
Fluorescence lifetime (ns)	0.99, 1.02	1.10	1.14	1.18
Fluorescence quantum yield (at 410 nm)	0.22	0.26	0.22	0.20

Figure 2 Absorbance, SPEF and TPEF spectra of BPST in THF

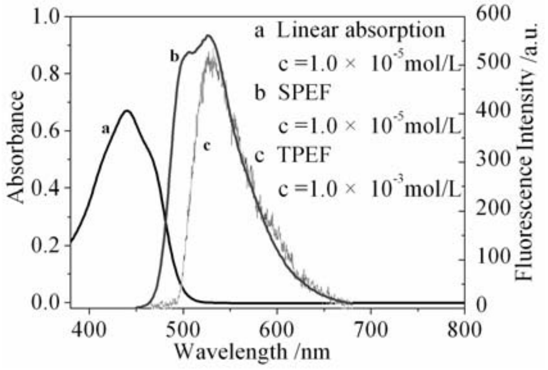
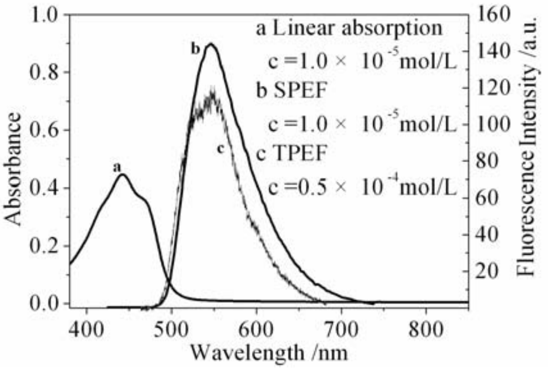


Figure 3 Absorbance, SPEF and TPEF spectra of BEST in THF



As shown in **Figure 2,** the peak wavelength of TPEF spectrum of BPST is located at 530 nm, which is similar to that of SPEF. This may be explained by a presumption that the emission energy level corresponding to TPEF and that corresponding to SPEF are the same. The SPEF and TPEF spectra of BEST in THF (shown in **Figure 3**) are similar to those of BPST.

The TPA cross sections σ of target compounds were measured by TPEF method. Coumarin 307 and fluorescein were used as standard samples for BPST and BEST, respectively. Under the same condition, the streak camera recorded the TPEF spectra of BPST and that of coumarin 307 in THF respectively (their concentrations were fixed at

1.0×10^{-3} mol/L). Then we can calculate TPA cross section σ of the BPST according to this equation [4].

$$\sigma = \sigma_{\mathbf{ref}} \frac{\Phi_{\mathbf{ref}}}{\Phi} \frac{C_{\mathbf{ref}}}{C} \frac{n_{\mathbf{ref}}}{n} \frac{F}{F_{\mathbf{ref}}}$$

In the above equation, n is the refractive index, C is the concentration and F is the integral intensity of TPEF and the subscript *ref* refers to the standard sample. The TPA cross section σ of BPST was measured to be 256×10^{-50} cm^4·s/photon in THF at 1.0×10^{-3} mol/L, and the σ value of BEST to be 199×10^{-50} cm^4·s/photon in THF at 5.0×10^{-4} mol/L. Compared with BEST, BPST has a much larger TPA cross section. This result indicates that the diphenylamino group in BPST is an excellent fluorophore, both for SPEF and TPEF [5].

In conclusion, we have synthesized two new thiophene derivatives which can emit strong two-photon fluorescence and exhibit large TPA cross sections σ. Taking BPST for example, it shows a strong green TPEF with the peak position at 525 nm and has the measured σ value of 256×10^{-50} cm^4·s/photon in THF. These thiophene derivatives may have some potential applications in photon-electronic materials.

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