

Single & Two-photon Excited Fluorescence of Two New Compounds with 2-Benzothiazolyl as Electron Acceptor

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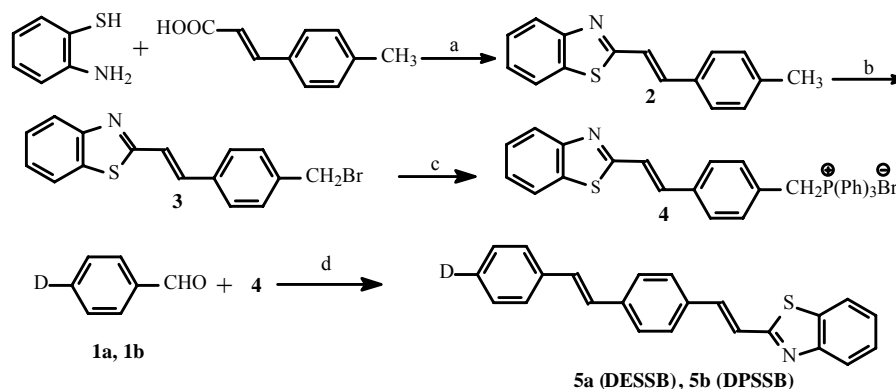
Abstract: Two new D- π -A type compounds, where electron-donor D is tertiary amino group, electron-acceptor A is 2-benzothiazolyl and π is two conjugated styryl units, have been synthesized. They are named as *trans*, *trans*-2-{4-[4-(N, N-diethylamino)styryl]styryl}-1, 3-benzothiazole and *trans*, *trans*-2-{4-[4-(N, N-diphenylamino)styryl]styryl}-1, 3-benzothiazole. Both compounds show strong two-photon excited fluorescence in yellow-orange region when excited by a femtosecond laser at 800 nm.

Keywords: Benzothiazole derivatives, two-photon excited fluorescence, nonlinear optical compounds.

When certain lasers are used as pump source, some organic molecules can simultaneously absorb two photons to reach one of their excited states and subsequently frequency up-converted fluorescence emission may follow^{1,2}. Compared with common single-photon excited fluorescence (SPEF), this two-photon excited fluorescence (TPEF) is characterized by its excitation process of two-photon absorption (TPA) that presents several advantages including high three-dimensional resolution as well as low photo-damage³. In recent years, TPEF and TPA have given rise to series of new techniques such as two-photon fluorescence microscopy and three-dimensional optical data storage, and considerable research interests have been aroused to synthesize strong TPEF active compounds. D- π -A type compounds have been recognized to satisfy the necessary structural conditions of molecular engineering for TPEF, thus we designed and synthesized two title D- π -A type compounds adopting 2-benzothiazolyl as an electron-acceptor (A), tertiary amino group as an electron-donor (D) and two conjugated styryl units as π -bridge. 2-Benzothiazolyl group has been chosen because it exhibits significant electron-withdrawing ability and benzothiazole derivatives have comparatively better chemical, thermal and photochemical stabilities⁴. In this letter, after briefly describing the synthesis, we mainly report the SPEF and TPEF properties of these two benzothiazole-based compounds.

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Scheme 1



(a) POCl₃; (b) NBS, CCl₄, (C₆H₅CO)₂O₂; (c) P(Ph)₃, toluene; (d) *t*-BuOK, THF
D = diethylamino (a), diphenylamino (b)

Experimental

As outlined in **Scheme 1**, we synthesized the two title compounds by cyclization, bromination and subsequently modified Wittig reaction.

trans, trans-2-{4-[4-(N, N-diethylamino)styryl]styryl}-1, 3-benzothiazole (**DESSB**, **5a**): Red powders with yield 40%. *m p* 227-230°C, ¹H NMR (CDCl₃), δ (ppm): 1.19 (t, 6 H, J = 6.9 Hz), 3.39 (q, 4H, J = 6.9 Hz), 6.72-7.52 (m, 14 H), 7.86 (d, 1 H, J = 7.8 Hz), 7.99 (d, 1 H, J = 8.1 Hz). MS: *m/z* 410 (M⁺, 100%), 395 (M-CH₃, 89%). Elemental analysis: Calcd: C, 78.99; H, 6.38; N, 6.82; S, 7.81. Found: C, 78.68; H, 6.31; N, 6.65; S, 7.69.

Trans, trans-2-{4-[4-(N, N-diphenylamino)styryl]styryl}-1, 3-benzothiazole (**DPSSB**, **5b**): Yellow powders with yield 42%. *m p* 277-278°C, ¹H NMR (CDCl₃), δ (ppm): 6.97-7.60 (m, 24 H), 7.87 (d, 1H, J = 8.1 Hz), 8.03 (d, 1 H, J = 7.8 Hz). MS: *m/z* 506 (M⁺, 100%), 253 (M²⁺, 24%). Elemental analysis: Calcd: C, 82.97; H, 5.17 N, 5.53; S, 6.33. Found: C, 82.39; H, 5.07; N, 5.31; S, 6.49.

Linear absorption spectra with $C = 5 \times 10^{-6}$ mol/L were recorded on a Hitachi U-3500 UV-VIS-IR spectrophotometer. Steady state and time-resolved SPEF spectra with $C = 5 \times 10^{-6}$ mol/L were measured on an Edinburgh FLS920 fluorescence spectrometer. TPEF experiments with $C = 1 \times 10^{-3}$ mol/L were performed with a Mira 900 femtosecond Ti:Sapphire laser as pump source and a streak camera (Hamamatsu, model: C5680) in conjunction with an imaging spectrograph (Hamamatsu, model: C5094) as recorder. The pulse width and repetition rate of the laser are 200 fs and 76 MHz respectively.

Results and Discussion

The SPEF and TPEF properties are summarized in **Table 1**. Linear absorption and SPEF spectra of **DPSSB** are shown in **Figure 1**. There is no detectable linear

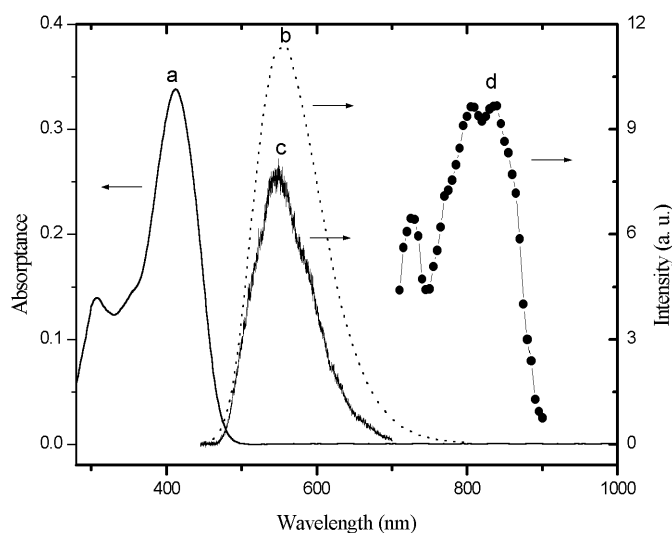
absorption in the wavelength range from 550 nm to 1000 nm, thus the excitation by the tunable laser from 710 nm to 900 nm in our TPEF experiments must be attributed to multiphoton absorption process. Replacement of the terminal diethylamino group by diphenylamino group will result in obvious blue shifts of absorption maximum and fluorescence peak.

Our detailed experiments demonstrated that TPEF peak positions of these two compounds are independent of the excitation wavelength in the range of 710 ~ 900 nm, but their TPEF intensities will be obviously influenced by the excitation wavelength. By varying pump wavelength step by step from 710 nm to 900 nm at fixed excitation power and then recording the TPEF intensities, two-photon excitation (TPE) spectra of **DESSP** and **DPSSB** were obtained. From the TPE spectrum of **DPSSB** shown in **Figure 1**, we can see that the profile is quite similar to that of linear absorption spectrum except that the wavelengths are doubled. We can also see that the TPEF peak position is very close to that of SPEF for same compound. Thus either single-photon excited initial state or two-photon excited initial state may quickly relax to the same fluorescence emission state.

From TPEF intensity data, TPEF cross-section σ_e can be determined according to the following equation^{6,7}:

$$\sigma_e = \sigma_{e,r}(F n_r) / (F_r n)$$

Figure 1 Linear and nonlinear optical properties of **DPSSB** in THF solution



- (a) Linear absorption with $C = 5 \times 10^{-6}$ mol/L; (b) SPEF spectrum with $C = 5 \times 10^{-6}$ mol/L;
 (c) TPEF spectrum with $C = 1 \times 10^{-3}$ mol/L; (d) TPE spectrum with $C = 1 \times 10^{-3}$ mol/L.

Table 1 Photo-physical properties of the title compounds in THF solution

	Linear absorption	SPEF properties			TPEF properties		
	λ_{\max} (nm)	λ_{\max} (nm)	Φ^a	τ (ns)	λ_{\max} (nm)	σ (GM) ^{b, c}	σ_e^d
DESSB	425	590	0.43	2.3	590	359	4.76
DPSSB	412	552	0.60	2.0	551	360	6.67

^a Determined using fluorescein as a standard ($\Phi = 0.9$)⁵. ^b Fluorescein (36GM at 800 nm) as reference⁶. ^c 1GM = $1 \times 10^{-50} \text{cm}^4 \text{s/photon}$. ^d Relative TPEF cross-section by assigning that of fluorescein at 800 nm equals to 1.

In above expression, the subscript r means reference, F is the integral intensity of TPEF and n is the refractive index of the sample. By assigning σ_e of fluorescein equals to 1, then the relative σ_e values were obtained and shown in the last column of **Table 1**, both compounds have much larger σ_e than that of fluorescein.

The TPEF cross-section is supposed to be linearly dependent on the two-photon absorption cross-section σ , with TPEF quantum yield Φ_2 as the coefficient: $\sigma_e = \sigma \Phi_2^6$.

In most previous reported works, SPEF quantum yield Φ was adopted instead of Φ_2 . In this way, we obtained the σ (shown in **Table 1**), which is one of the most important parameters in two-photon optics. Both compounds possess significantly large σ values, about one order of magnitude higher than that of fluorescein.

In summary, two benzothiazole-based compounds with various tertiary amino donor groups have been synthesized. Pumped by 800 nm lasers, **DESSB** and **DPSSB** exhibit strong up-converted orange ($\lambda_{\max} = 590 \text{ nm}$) and yellow ($\lambda_{\max} = 551 \text{ nm}$) TPEF in THF solution.

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