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Structure and Two-photon Excited Blue Fluorescence of an Asymmetrical Substituted Stilbene

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Abstract: The single & two photon excited fluorescence property and crystal structure of a substituted stilbene-type compound *trans*-4-diethylamino-4′-bromostilbene (DEABS) has been reported. The results indicate that this compound has strong two photon excited blue fluorescence at 440 nm when the 700 nm laser was used as the pump source.

Keywords: DEABS, two-photon absorption, up-converted blue fluorescence.

In common fluorescence process, molecular excitation is caused by the absorption of at least a single photon with shorter wavelength. When certain laser is used as the pump source, some compounds can be excited by simultaneous absorption of at least two photons and then the emission of up-converted fluorescence may occur. This process is called two-photon excited fluorescence (TPEF)[1,2]. Because of several advantages of TPEF, including intrinsic high three-dimensional resolution and the penetrating ability, it has attracted great research interest and acquired several applications such as the technique of two-photon laser scanning fluorescence microscopy[3, 4]. It is clear that the development of various TPEF based techniques would greatly depend on the designing and synthesizing of various novel fluorophores with low threshold of laser intensity and/or less fluorophore concentration needed. Among the reported TPEF effective asymmetrical compounds, most of them are orange-red light emitters[5] and a few have the green light emission[6]. As we know, the reports of asymmetric organic TPEF blue emitters are few. In this letter, we report the synthesis and structural characterization of a compound *trans*-4-diethylamino-4′-bromo-stilbene (DEABS), **3**, which shows bright blue TPEF, when the 700 nm laser was used as the exciting light.

Synthesis and Structure

3 was synthesized by Wittig reaction procedure (shown in **Scheme 1**). In a 250 mL

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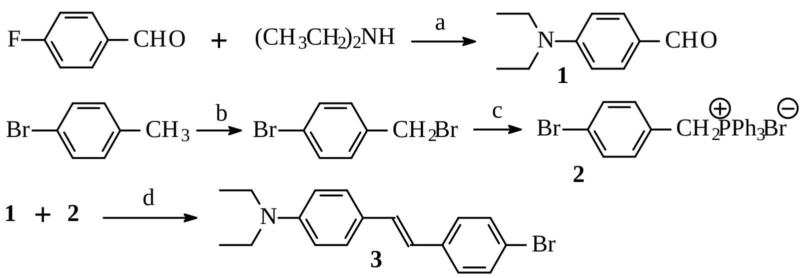
three-neck flask with a magnetic stirrer, 5.12 g (0.01 mol) 4′-bromobenzyl- triphenylphosphonium bromide **2** and 1.77 g (0.01 mol) 4-diethylaminobenzaldehyde **1** was dissolved in 80 mL anhydrous THF. Under dry N_2 and at a constant temperature of 0°C, 30 mL solution of potassium tert-butoxide (1.20 g, 0.011 mol) in tert-butyl alcohol was then dropped into the above flask slowly. After a further 20 h′s stirring, the mixture was poured into ice water, and extracted by chloroform. The organic layer was concentrated and further purified by column chromatography (the eluent is petroleum ether: $CHCl_3$=9:1). The bright yellow micro-crystal was obtained after removing most of the solvent. Yield 78%. m.p. 153-154°C. Bright yellow slice form crystals, which can be served for structure determination, were obtained by recrystallization from THF. Elemental analysis: calcd for $C_{18}H_{20}BrN$: C, 65.40; H, 6.06; N,4.24 ; Found: C, 65.42; H, 6.11; N,4.22. ^{1}H NMR data δ_H($CDCl_3$, δppm), 1.18 (t, 6H, J=6.82Hz), 3.38 (q, 4H, J=6.82Hz), 6.67 (s, 2H), 6.9 (d, 2H, J=7.80Hz), 7.38 (m, 6H, J=6.82Hz).

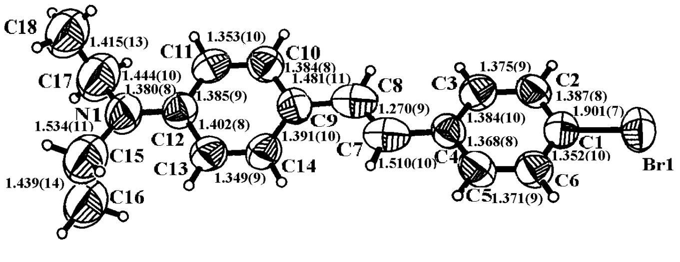
Scheme 1



a) DMSO, K_2CO_3, 72h; b) NBS, CCl_4; c) PPh_3, toluene; d) THF, BuOK, 0°C, 24h, 78%

X-ray diffraction data of the single crystal were collected on a Bruker P4 four-circle diffractometer by MoKα radication. By SHELXL-97 program, the structure was resolved by direct method and refined by Full-matrix least-squares method on F^2. A total of 5945 unique data for $4.32 \leq 2\theta \leq 50.00$ was collected, of which 5009 are independent. DEASB belong to P-1 space group, a=9.774(3)Å, b=12.8307(16) Å, c=13.4964(14) Å, α=82.427(8)°, β=88.146(16)°, γ=75.151(17)°, V=1621.7(6) Å^3, Z=4 , D_c=1.353 g·cm^{-3}, F(000)=680. Final R indices [I>2σ(I)]: R=0.0630, R_w=0.1752. The max and min residual electron densities are 0.726 and -0.458 e·Å^{-3} respectively.

Figure 1 The molecule structure of DEABS

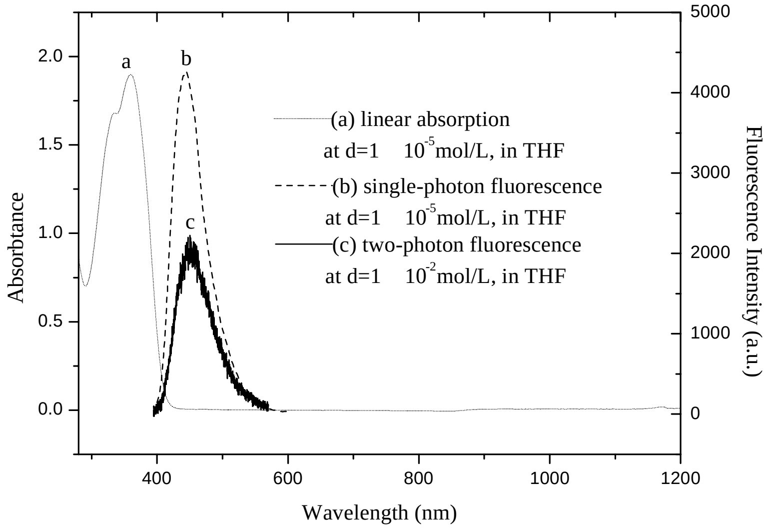


As shown in **Figure 1**, two planar benzene rings slightly twisted by a dihedral angle of 13.5°. The bridge between the two benzene rings consists of two single bonds of C4-C7(1.510 Å), C8-C9(1.481 Å) and one double bond of C7=C8 (1.270 Å). So the planarity of DEABS in crystalline state is fairly good but not perfectly strict.

Single and two-photon excited fluorescence property

Linear absorption and single-photon fluorescence were measured on a Hitachi U-3500 UV-VIS-IR spectrophotometer and on an Edinburgh FLS920 fluorescence spectrometer respectively. To get the two-photon excited fluorescence, an optical parameter amplifier (OPA) pumped by a passively mode-locked Nd: YAG laser with pulse duration of 40 ps was used as a pump source, and a streak camera (Hamamastsu Model C5680) was used as a recorder.

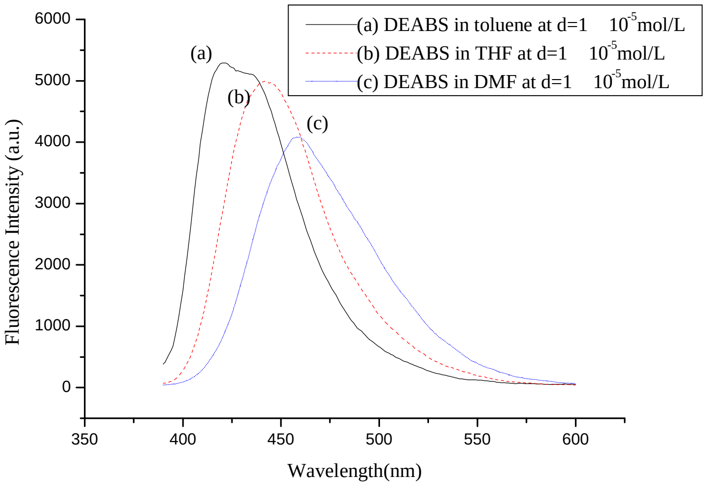
Figure 2 Linear and nonlinear optical properties of DEABS



As shown in **Figure 2**a, the maximum linear absorption is at 360 nm. Excited at this wavelength, the single photon excited emission spectrum shows its peak position at 440 nm and the corresponding lifetime has been measured to be 1.55 ns. From 400 nm to 1200 nm there are not any measurable linear absorption. So, the TPEF spectrum (**Figure 2**c) excited by 700 nm laser can be attributed to the nonlinear two-photon absorption mechanism via so-called virtual state[2]. The emission peak of TPEF is also at 440 nm. This means that the energy levels for both single-photon and two-photon excited emission are the same.

In addition, one can see from **Figure 3** that the emission spectra of DEABS in different solvents have dramatic difference in the peak positions. With the increase of the polarity of solvent, from toluene to THF and DMF, the peak positions are obviously red-shifted. This phenomena definitely indicates that the DEABS in excited state is more polar than in ground state. For the increase of the polarity of the solvent, the energy level which corresponds to a more polar molecular conformation will be more intensively lowered. The excited geometry conformation of DEABS may be suit for the model of twisted intramolecular charge transfer (TICT)[7]. According to the TICT model, the excited molecules initially form a moderately nonpolar state with a geometry similar to that in the ground state. Subsequently, charge transfer from the donor to the acceptor will take place, accompanied by the twist of the molecular plane.

Figure 3 Fluorescence of DEABS in different solvents



In summary, the two-photon excited blue fluorescence of the synthesized compound **3**, which has the asymmetrical near planar X-ray structure, has been reported.

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