

Synthesis, Structure of a Symmetrically Substituted Stilbene with Strong Two-photon Absorption and Up-converted Blue Fluorescence

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Abstract: Efficient Ti-catalyzed reductive coupling methodology was first employed to synthesize the symmetrical bis-donor stilbene, trans-4, 4'-bis[diphenyl amino] stilbene (BDPAS). X-ray diffraction analyses reveal that this new crystal belongs to the triclinic crystal system of centro-symmetric P-1 space group. The DBPAS solution, with the linear transmission at wavelength of ≥ 450 nm, possesses large two-photon absorption cross section as high as $39.4 \times 10^{-48} \text{ cm}^4 \cdot \text{s}/\text{photon}$ resulting in strong two-photon induced blue fluorescence of 460 nm, pumped by 740 nm laser irradiation.

Keywords: Symmetrical bis-donor stilbene, synthesis, crystal structure, two-photon absorption, two-photon-induced fluorescence.

Symmetric substituted stilbenes have significantly potential application such as fluorescence microscopy, two-photon photodynamic therapy, optical power limiting, and three-dimensional storage¹⁻². These dyes have strong tendency of symmetric intra-molecular charge transfer under the excited state. As a result, they usually exhibit large two-photon absorptivity (TPA), in the meanwhile emit strong up-converted fluorescence. On the other hand, their solutions generally display linear transmission of $>90\%$ at wavelength of ≥ 500 nm, which is especially suitable for the optical power limiting applied in protecting the eyes of people, sensors and sensitive optical components. Moreover, recently the experimental results³ in our group showed that this type of chromophores have the ability of two-photon initiated polymerizations, which can be further applied in three-dimensional micro-fabrication. Over recent years there has been increasing interest in the search for symmetric molecules with large non-linear optical effects. As reported for synthesizing symmetric substituted stilbenes, the Wittig⁴ and Heck⁵ reactions are considered as the general approaches. However, both of them operate complicatedly and the cost is high. Here we reported an efficient Ti-catalyzed reductive coupling methodology to synthesize the symmetrical substituted stilbenes in “one pot” procedure.

Synthesis and Structure

¹HMR, mass spectrum and elemental analysis were performed on the same methods as reported⁶. X-ray diffraction data of single crystal were collected on a Bruker P4

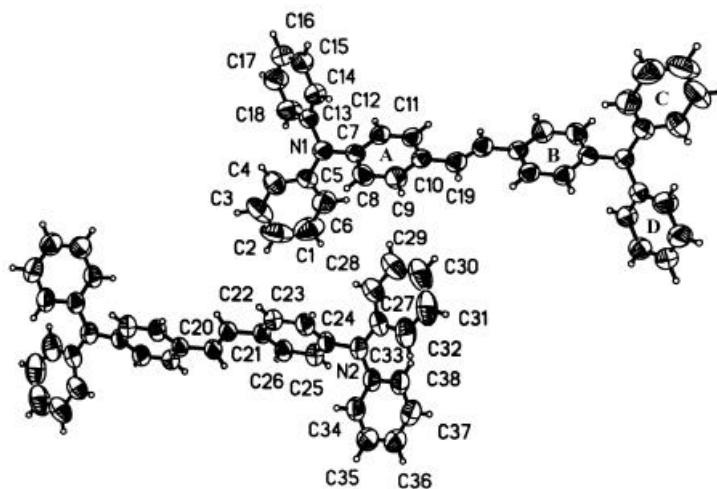
four-circle diffractometer. By using SHELXL-97 programs, the structure was solved by direct method and refined by Full-matrix least-squares on F^2 .

Trans-4,4'-bis[diphenyl amino] stilbene (BDPAS) was synthesized under anhydrous and oxygen-free conditions. A mixture of TiCl_4 (2.2 mL, 20 mmol), zinc (4.4 g, 60 mmol), sodium metal (2.3 g, 100 mmol) and 75 mL of dry tetrahydrofuran (THF) were stirred in the flask at room temperature. After refluxing for one hour, the black mixture was obtained, then cooled to room temperature. A solution of 4(N,N-diethylamino) benzaldehyde⁶ was injected slowly into the flask and further refluxed for 20h. Then cooled, hydrolyzed and neutralized by diluted HCl and sodium hydroxide solution, respectively. The mixture was extracted with chloroform and the organic layer was removed by evaporation. Then purified by column chromatography. The bright yellow slice crystals were obtained with yield of 60% and mp 255.9°C. Mass spectrum, m/z 514 (M^+), 257, 167, 77. Elemental analysis: Calcd.: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.94; H, 5.58; N, 5.36.

Crystal data: $\text{C}_{38}\text{H}_{30}\text{N}_2$, $M=514.64$, triclinic, space group P-1, $a=10.6231(12)$, $b=11.3337(10)$, $c=12.491(3)\text{\AA}$ $\alpha=73.503(9)$, $\beta=89.978(10)$, $\gamma=79.759(8)$ deg., $V=1417.0(4)\text{\AA}^3$, $Z=2$, $\rho_{\text{calcd}}=1.206\text{ Mg}\cdot\text{m}^{-3}$, $\mu=0.070\text{mm}^{-1}$, $F(000)=544$, $T=293(2)\text{K}$. A total of 5951 unique data for $2\theta_{\text{max}}=56^\circ$ was collected of which 4863 were independent. Final R indices [$I>2\sigma(I)$]: $R=0.0562$ and $R_w=0.1245$. The max. and min. residual electron densities were 0.118 and $-0.114\text{ e}\text{\AA}^{-3}$, respectively.

Least-square plane calculations show that the dihedral angle between two benzene rings (A and B rings, shown in **Figure 1**) in stilbene backbone is negligible, and that the dihedral angle between C and D rings is 61.8° , while the dihedral angles between B and C rings, B and D rings are 102.2° , and 106.4° , respectively. That is, the central stilbene backbone possesses perfect planarity, although the two terminal benzene rings (C and D) not only twist each other, but also deviate from the central stilbene backbone (see **Figure 1**). We consider that the better planarity of central stilbene backbone has contribution to high π -conjugation of the whole molecule in the excited state, which is a necessary condition for two-photon absorption and up-converted fluorescence.

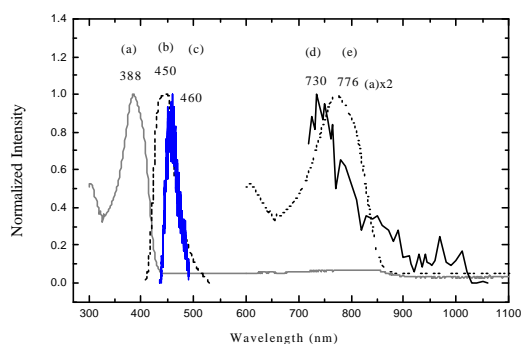
Figure 1 The molecular structures of BDPAS crystals



Linear and nonlinear optical properties

Linear absorption and single-photon fluorescence and two-photon induced fluorescence were recorded on methods as reported⁶. The solvent is DMF.

Figure 2 Linear and nonlinear optical properties of BDPAS



Linear absorption spectrum (a) and one-photon fluorescence (b) at $d_0 = 1 \times 10^{-5}$ M, the two-photon fluorescence (c) and two-photon absorption cross section at $d_0 = 0.005$ M.

Figure 2 shows that the maximum peak of one-photon fluorescence (b) is at 450 nm under the excitation of 390 nm. When pumped by 740 nm laser irradiation, strong two-photon induced up-converted blue fluorescence (c) can be observed with the maximum peak at 460 nm. From **Figure 2** (a), it is can be seen that the linear absorption peak is at 388 nm and there is no linear absorption in the range ≥ 450 nm. It is in the region of one-photon transparency that the nonlinear absorption can occur. Experimental result indicates that the maximum peak of two-photon absorption spectrum is at 730 nm. **Figure 2** (e) is plotted as two times of linear absorption spectrum (a). Comparing with (d) and (e), a relatively good correlation between the linear and nonlinear absorption spectra was observed.

Two-photon absorption spectrum and the cross section were determined by nonlinear transmitted (NLT) technique. An optical parameter amplifier (OPA) pumped by a mode-locked Nd: YAG laser was used as a pumping source which can be turned in the range of 400 nm – 2000 nm. The large TPA cross section for the chromophore BDPAS (39.4×10^{-48} cm⁴·s/photon) open the door for potential applications of this type of chromophores in optical power limiting and two-photon fluorescence imaging applications.

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