Synthesis and Characterization of a Novel Charge Transfer Compound with Large Three-Photon Absorption Cross Section

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A new intramolecular charge transfer compound containing diethylamino group as electronic donor and oxadiazole group as electronic acceptor has been synthesized using Wittig–Horner reaction. This long conjugated molecule has large three-photon absorption cross section excited at 1.06 μm lasing.

There has recently been a considerable amount of interest in frequency up-conversion process because of their potential applications to frequency-upconverted lasing,[1] optical power limiting,[2] frequency-upconverted fluorescence microscopy,[3] photorefractive effect in organic materials,[4] three dimensional optical data storage,[5] and two-photon photodynamic therapy.[6] A major impetus to this application has been provided by reports of molecules with large nonlinear absorption cross sections.[7]

The delocalization of π-electrons occurring in the conjugated molecules can lead to significant enhancement of the high-order optical nonlinearity. Recently theoretical investigations[8] reveal that the major contribution to the static value of the third-order polarizabilities originates from the transition dipole term that involves the difference between the dipole moments in the ground state and in the lowest charge transfer excited state. The effective charge transfer can increase the transition dipole term. Those reported molecules, which are specially designed for multi-photon process, could be mainly divided into two types. One is the symmetric types[9] whose charges transfer from the end to the middle in the molecule chains or versa; the other is push–pull asymmetric types[10] whose charges transfer from one end to another. In our present work, we designed a donor–acceptor–donor system, in which charge transfer may be more effective from the end to the middle than that of popular donor–conjugated bridge–donor system.

In this letter we report the synthetic route of that new intramolecular charge transfer compound named 2,5-bis[4-(4-*N*,*N*-diethylaminostyryl)phenyl]oxadiazole (BASDO). We also use intensity dependent transmission measurement to obtain the three-photon absorption cross section of BASDO at 1.06 μm pumped with nanosecond laser.

The molecular structure of BASDO is presented in Figure 1. BASDO was synthesized by Wittig–Horner reaction (Figure 1). The detailed synthetic steps are depicted as follows: Polyphospharic acid (50 mL) was added to 50% hydrazine hydrate (5 g, 0.05 mol) at 50 °C under N_2. The mixture was heated to 80 °C. *p*-Toluic acid (13.6 g, 0.1 mol) was added. The resulting mixture was heated to 130 °C and stirred for 10 h. After cooling, the mixture was poured into water. The solid was filtered and washed with 5% Na_2CO_3 aqueous solution (2 × 200 mL) and water (2 × 200 mL) to give 12.6 g of product **1** (mp 243–245 °C). ^{1}H NMR (DMSO-d_6, ppm) δ 2.35 (s, 6H, –CH_3), 7.32 (d, 4H, ArH), 7.81 (d, 4H, ArH), 10.35 (s, 2H, –NH).

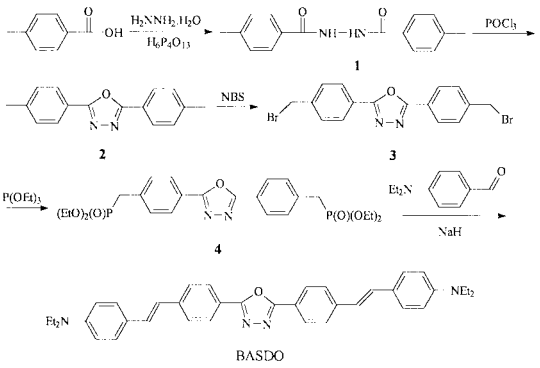

Figure 1. Synthetic route of BASDO.

A mixture of compound **1** (12.5 g, 46.64 mmol) and $POCl_3$ (250 mL) was refluxed under N_2 for 7 h. The excess $POCl_3$ was distilled out and the residue was poured into water. The filtered solid was purified by recrystallization from $CHCl_3$/methanol to give compound **2** (mp 172–173 °C). ^{1}H NMR ($CDCl_3$, ppm) δ 2.43 (s, 6H, –CH_3), 7.32 (d, 4H, ArH), 8.05 (d, 4H, ArH).

A mixture of compound **2** (3 g, 12 mmol), *N*-bromosuccinimide (NBS) (4.7 g, 26 mmol), benzoxy peroxide (0.05 g), and CCl_4 (60 mL) was refluxed for 6 h. The mixture was filtered while it was still hot. The solid was washed with hot chloroform. The residual solid was recrystallized from THF/methanol to give product **3** (mp 226–227 °C). ^{1}H NMR (DMSO-d_6, ppm) δ 4.80 (s, 4H, –CH_2Br), 7.72 (d, 4H,ArH), 8.15 (d, 4H, ArH).

A mixture of compound **3** (2.0 g, 4.90 mmol) and $P(OEt)_3$ (5 mL) was stirred at 150 °C for 5 h. The excess $P(OEt)_3$ was distilled out. The residual solid was recrystallized from THF/hexane to give product **4** (mp 113–115 °C). ^{1}H NMR (DMSO-d_6, ppm) δ 1.18 (t, 12H, –CH_3), 3.45 (d, 4H, –CH_2P), 3.95 (m, 8H, –OCH_2–), 7.50 (d, 4H, ArH), 8.10 (d, 4H, ArH).

NaH (0.136 g, 5.65 mmol) was added into a solution of 4-diethylaminobenzaldehyde (0.678 g, 3.83 mmol) in 10 mL of diethene glycol dimethyl ether (DME) under N_2. The resulting suspension was stirred for 5 min and was then added dropwise to a solution of compound **4** (1.000 g, 1.91 mmol) in DME at room temperature. The resulting solution was stirred at 80 °C overnight and then poured into methanol. The filtered solid was purified by silica gel column to give BASDO (mp 156–159 °C) ^{1}H NMR ($CDCl_3$, ppm) δ 1.23 (t, 12H, –CH_3), 3.44 (d, 8H,–NCH_2–), 6.90 (m, 4H, –CH=CH–), 7.49 (d, 4H, ArH), 7.72 (d, 4H, ArH), 8.07–8.10 (d, 8H, ArH).

The linear absorption single peak of BASDO in $CHCl_3$ at 1.0×10^{-5} M/L was located around 347 nm (Figure 2), where is the three-photon energy region of the 1.06 μm incident lasing. So the three-photon absorption in this long conjugated com-

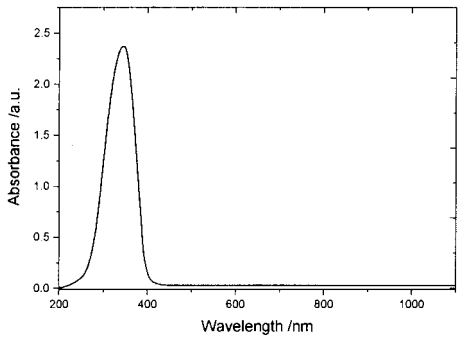

Figure 2. One-photon absorption spectrum of BASDO in the solvent of $CHCl_3$ at the concentration of 1×10^{-5} M/L.

pound may be expected excited by 1.06 μm lasing. It also can be seen from Figure 2 there is no linear absorption at the one-photon energy or the two-photon energy of 1.06 μm radiation.

In the measurement of nonlinear transmission, the incident 1.06 μm lasing was provided by a Q-switched Nd:YAG laser (continuum, Surelite II) with pulse duration of 8 ns. The pump energy was controlled by rotating a half-wave plate (HWP) between two polarizers. The energies of the incident and transmitted beams were measured using two large-area silicon photodiodes connected to a Boxcar averagor.

In an optical event if simultaneous absorption of three-photon is the only process involved, the intensity change of an excitation beam along the optical propagation path z is given by: $-dI(z)/dz = \gamma I^3(z)$ (1) where γ is the three-photon absorption coefficient of the given sample medium. The solution of eq (1) can be simply obtained as[11] $I(z) = I_0(1 + 2\gamma a I_0^2)^{-1/2}$ (2) where I_0 is the incident intensity of the excitation beam and a is the sample thickness. From the relationship between $I(z)$ and I_0, the three-photon absorption coefficient γ can be easily deduced.

Figure 3 shows the transmitted intensity as a function of the incident intensity of BASDO in $CHCl_3$ at 2.0×10^{-2} M/L. Each datum was an average of 128 laser pumps. During the experiments, we eliminate the influence from the cell walls and the solvent. In Figure 3 the solid curve is given by eq (2) by using the value $\gamma = 2.2\times10^{-17}$ cm^3/W^2 (a macroscopic parameter). One can see that the theoretical curve agreed with the measured data. The corresponding three-photon absorption cross section

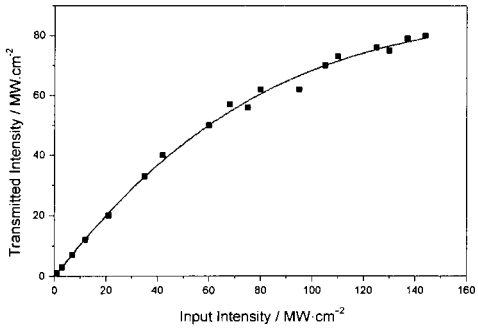

Figure 3. Transmitted intensity versus input intensity of BASDO in $CHCl_3$ at 2.0×10^{-2} M/L pumped by nanosecond laser (8 ns, 1.06 μm). The solid line is the theoretical best-fit curve with the parameter of $\gamma = 2.2\times10^{-17}$ cm^3/W^2.

σ_3 of the solute molecule (a molecular property) can be determined by using the following relationship: $\gamma = \sigma_3 N_A d_0 \times 10^3/(h\nu)^2$ where $N_A = 6.023\times10^{23}$ is Avogadro number and $h\nu$ is the photon energy of the excitation beam. For the BASDO solution in $CHCl_3$, the experimentally estimated value of three-photon absorption cross section is $\sigma_3 = 6.4\times10^{-74}$ cm^6/s^2.

The three-photon cross-section of BASDO is about two orders of magnitude larger than that obtained by He et al.[11] from BBTDOT molecule pumped at 1.06 μm. It can be explained from two aspects: (1) the longer conjugated chains in BASDO; (2) more effective charge transfer. In BASDO molecule, the two diethylamino groups at the each end of the molecule are good electron donors and the oxadiazole group at the middle of the molecule is an electron acceptor. So the BASDO molecule is a donor–acceptor–donor system. This structure may facilitate the charge transfer in the long conjugated chain, and thus increases the three-photon absorption cross-section.

It should be pointed out that, instead of direct three-photon absorption, another mechanism is also possible that is based on two-photon absorption followed by excited one-photon absorption. This may lead to the same transmission relationship. From Figure 2, one can see that there is no real energy level to correspond the two-photon energy of our 1.06 μm incident lasing. Furthermore, the absence of significant pulse width dependence of our result for both 8 ns and 40 ps pulses makes a two-step process less likely there.[12] In addition, some other mechanisms (such as thermal effect, self-scattering, etc.) may increase the measured data. In order to distinguish the possible contributions from other effects, we also use 40 ps pulse duration in our experiment. The resulting three-photon absorption coefficient is comparable to that of ns pulse duration. So the transmission curve is indeed mainly induced by three-photon absorption.

In summary, we reported here the synthetic route of a charge transfer compound with the largest three-photon absorption cross section in the reported literatures[11] to our best knowledge. The three-photon absorption cross section was deduced by intensity dependent transmission measurement.

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