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Synthesis, structure and nonlinear optical properties of a two-photon photopolymerization initiator

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The target compound, *Trans*-4-(N-2-hydroxyethyl-N-ethyl amino)-4′-(diethyl amino)stilbene, has been synthesized and characterized. The one-photon fluorescence and its lifetimes, two-photon fluorescence and solvent effects have been studied in detail. X-ray diffraction analyses reveal that it is a highly delocalized π-electron system structure. It belongs to monoclinic system, $P2_1/n$ space group. A two-photon initiating polymerization microfabrication experiment has been carried out and the possible photopolymerization mechanism is also discussed. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Organic materials possessing large two-photon absorption (TPA) cross sections can be used for a variety of technical applications, such as optical power limiting [1, 2], two-photon fluorescence microscopy [3], frequency-upconverted lasing [4], three-dimensional (3D) optical data storage and microfabrication [5–8]. These applications take advantage of the fact that the TPA depends quadratically on the excitation intensity, so under tight-focusing conditions, the absorption at the focus is confined to a volume of order λ^3 (where λ is the excitation wavelength). Although 3D microfabrication has been illustrated using two-photon-initiated polymerization of resins incorporating conventional ultraviolet-absorbing initiators, the TPA cross sections, δ, of most initiators including commercial dyes are typically very small, and as a result they exhibit low two-photon sensitivity. Resins containing these initiators can be patterned only by means of long exposure times and high excitation intensities that frequently result in damage to the structure. At present, effective two-photon photopolymerization initiators are still rare because the photopolymerization mechanism and relationships of structure and property for the initiator remained unclear. Therefore, it is urgently required to make clear the photopolymerization mechanism and relationships of structure/property of the initiator to search for effective and high photosensitive two-photon photopolymerization initiators. Here we report the structure of an initiator whose synthesis had ever been reported [9]. X-ray diffraction analyses reveal that it is a highly delocalized π-electron system structure. The experimental results confirm that the target compound is a good two-photon absorbing chromophore and operative two-photon photopolymerization initiator. A two-photon initiating polymerization microfabrication experiment has been carried out and the possible photopolymerization mechanism is also discussed.

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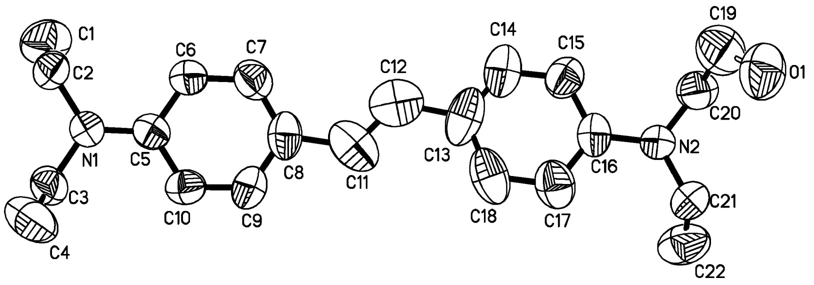

Figure 1 Crystal structure of the title compound.

2. Experimental

2.1. Instruments

The 600 MHz H^1 NMR and ^{13}C NMR spectra are obtained on a Bruker av600 spectrometer. Elemental analysis is performed using PE 2400 elemental analyzer. UV-Vis-near-IR spectra are measured on a Hitachi U-3500 recording spectrophotometer. Melting point is measured on DSC822^e Mettler-Toledo instruments. The steady-state fluorescence spectra measurement is performed using an Edinburgh FLS 920 spectrofluorimeter. A 450 W Xe arc lamp provides the ~400 nm excitation source. Spectra are record between 420 and 700 nm using a photomultiplier tube as detector, which is operated in the single photon counting mode. The spectral resolution is 0.1 nm. The quartz cuvettes used are of 1 cm path length.

2.2. Synthesis

The synthesis of the title compound is according to the reference [9].

The target compound is obtained with yield of 55% and mp127.1°C. The enthalpy is −104.9 mJ/mg. Anal. calcd for $C_{22}H_{30}N_2O$: C 78.11, H 8.87, N 8.28. Found: C 78.53, H 8.95, N 8.36. ^1H NMR, $\delta(CDCl_3$, 600 MHz): 7.30 (q, $J = 6.19$ Hz, 4H); 6.78 (s, 2H); 6.63 (t, $J = 8.36$ Hz, 4H); 4.69 (s, 1H); 3.53, (t, $J = 5.60$ Hz, 2H); 3.34 (m, 8H); 1.08 (t, $J = 6.85$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 600 MHz) [ppm] δ: 148.67, 148.37, 128.98, 128.92, 126.98, 126.95, 125.60, 125.56, 113.61, 113.43, 60.38, 54.08, 46.60, 45.62, 14.47, 14.03.

2.3. Structure

The X-ray diffraction data of single crystal for the target molecule is collected on a Bruker P4 four-cycle diffractometer. Using SHELXL-97 programs [10], the structure is solved by direct methods and refined by full-matrix least-squares on F^2. The crystal structure is shown in Fig. 1. It belongs to monoclinic crystal system, $P2_1$/n space group, $M = 337.47$, $a = 14.283(5)$, $b = 8.144(5)$, $c = 17.063(5)$ Å, $\alpha = 90.000(5)$, $\beta = 92.684(5)$, $\gamma = 90.000(5)$, $V = 1982.6(15)$ Å^3, Z = 4, $T = 293$ (2) K, $D_c = 1.131$ gcm^{-3}, $R_1 = 0.0937$, $R_w = 0.2438$ for $I > 2\sigma(I)$, $F(000) = 736$. The dihedral angle between two benzene rings is 16.2°, which shows that they are almost co-planar. The bond lengths of C8-C11 and C12-C13 are 1.498(6) and 1.510(7) Å, respectively. They are shorter than the typical single bond length of C–C (1.524 Å). The bond lengths of C11-C12 is 1.318 (1) Å which is almost the same as the typical double bond length of C=C (1.317Å). The bond lengths of two benzene rings are all normal aromatic character. The conjugated geometric configuration reveals that the target molecule is a highly delocalized π-electron system.

3. Results and discussion

3.1. Linear and nonlinear optical properties

The photophysical properties of the title compound are summarized in Table I. The one-photon fluorescence spectra and its lifetimes are measured in different solvents with a concentration of $d_0 = 1 \times 10^{-5}$ mol/L. The excited wavelength is 370 nm. Figs 2 and 3 are

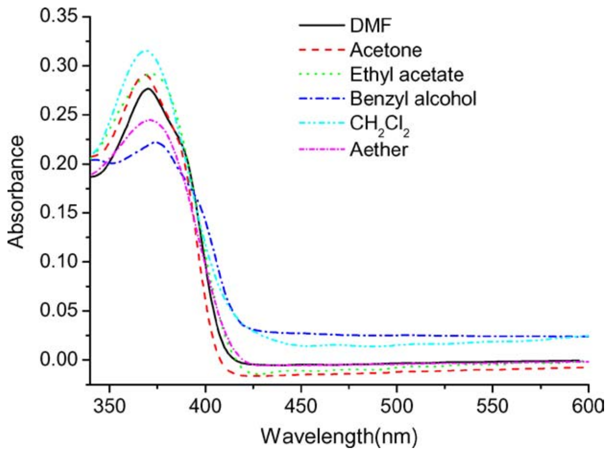

Figure 2 Linear absorption spectra of the title compound in solvents of different polarity at a concentration of 1×10^{-5} mol L^{-1}.

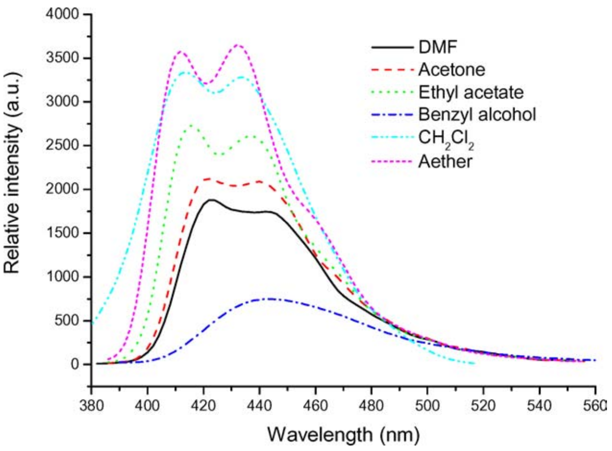

Figure 3 One-photon fluorescence spectra of the title compound in solvents of different polarity at a concentration of 1×10^{-5} mol L^{-1}.

TABLE I The data of absorption, one- and two-photon fluorescence spectra with solvent effects of the title compound

Solvents	ε	$\lambda_{\max}^{(1a)}$(nm)	$\varepsilon_{\mathrm{res}}(10^4)$	$\lambda_{\max}^{(1f)}$ (nm)	τ (ns)	$\lambda_{\max}^{(2f)}$ (nm)
DMF	37.6	370	2.46	422, 442	1.23, 1.28	445
Acetone	20.7	368	2.91	422, 440	1.54, 1.53	443
Ethyl acetate	6.02	372	2.92	416, 436	1.33, 1.41	442
Benzyl alcohol	13.1	374	2.22	444	0.98, 1.09	448
CH_2Cl_2	9.1	369	3.15	414, 434	1.25, 1.26	440
Aether	4.197	371	2.45	412, 432	0.90, 0.93	438

$\lambda_{\max}^{(1a)}$, $\lambda_{\max}^{(1f)}$ and $\lambda_{\max}^{(2f)}$ are one-photon absorption, one-photon fluorescence and two-photon fluorescence maxima peaks, respectively. τ is one-photon fluorescence lifetime. ε is the relative permittivity that was measured at 20°C [11]. $\varepsilon_{\mathrm{res}}$ is the corresponding molar absorption coefficient.

linear absorption and one-photon fluorescence spectra of the title compound, respectively. From Table I can be seen that the maximum absorption peaks show no obviously change rule, while the maximum one-photon fluorescence peaks slightly show a red-shift except for benzyl alcohol with the increase of the polarity of the solvent. As shown in Table I, the polarity of the solvents is reduced gradually from DMF to aether. In aether, the solvent of least polarity (1.15D), the fluorescence peak is at 438 nm. In DMF, the solvent of highest polarity (3.82D), the peak is located at 445 nm, which is red-shifted by 7 nm due to the changed molecular environment. This can be explained by the fact that the excited state of the target compound may possess higher polarity than that of the ground state, for the solvatochromism is associated with the energy level lowering. Increased dipole-dipole interaction between the solute and solvent leads to lowering the energy level greatly [12, 13]. In benzyl alcohol, the absorption and the emission bands are obvious red-shift compared to that of the other solvents. For the case of the benzyl alcohol, we can easily realize the possibility of forming the hydrogen bonding between the solvent and solute molecules that will push the excitation energy lower [14]. By use of Gaussian-98 program [15], the dipole moments of the ground state and the first excited state (namely charge transfer state) of the title compound can be calculated with the time-dependent hybrid density functional theory (B3LYP/6-31G) and the finite field approach. The dipole moments of the ground and the first excited states are respective 0.67 and 0.76 au, which indicates that the excited state possess higher polarity than the ground state.

The two-photon induced emission spectrum can be observed with a 760 nm laser beam from a mode-locked Ti:sapphire laser (Coherent Mira 900F) as the pump source with a pulse duration of 200 fs, a repetition rate of 76 MHz, and a single-scan streak camera (Hamamatsu Model C5680-01) together with a monochromator as the recorder. The two-photon absorption induced emission spectra (see Fig. 4) is measured in different solvents with concentration of 1×10^{-2} mol/L. Fig. 4 shows that the two-photon fluorescence spectrum slightly shows a red-shift with increase in solvent polarity that is in comformity with one-photon fluoresence spectrum. From Table I can be seen that the maximum peak positions of the two-photon fluorescence spectra show slightly a red-shift compared to that of one-photon fluorescence for each solvent. This is attributed to an artefact associated with re-absorption [16] of the emitted light on the blue edge of the spectrum that occurs because the spectrum is collected with a high-concentration optically-dense medium (see Fig. 5).

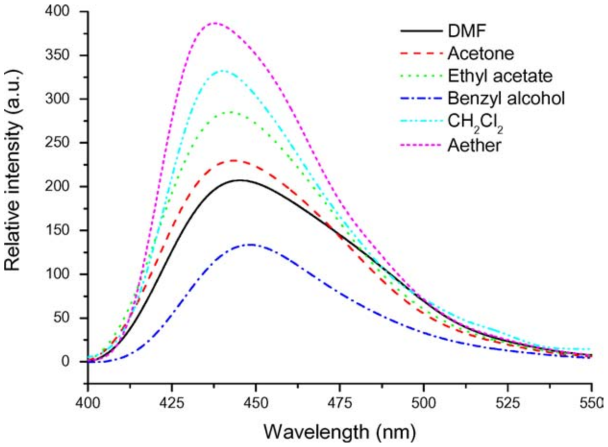

Figure 4 Two-photon fluorescence spectra of the title compound in solvents of different polarity at a concentration of 1×10^{-2} mol L^{-1}.

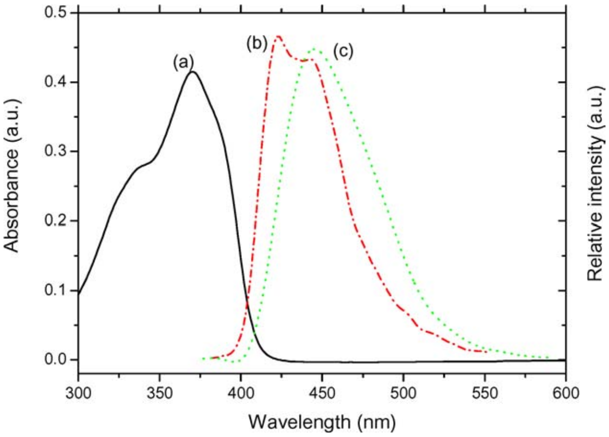

Figure 5 Absorption and fluorescence spectra of the title compound: (a) linear absorption with $c = 1 \times 10^{-5}$ mol/L in DMF, (b) one-photon fluorescence spectra with $c = 1 \times 10^{-5}$ mol/L in DMF, and (c) two-photon fluorescence spectra with $c = 1 \times 10^{-2}$ mol/L in DMF.

3.2. Two-photon photopolymerization

In our two-photon initiation polymerization experiment, a solid skeleton is fabricated with negative resins system, which contains oligomer (bisphenyl A epoxide dimethylacrylate) and 0.5% the target compound as initiator and a little 1,2-dichloroethane (increasing

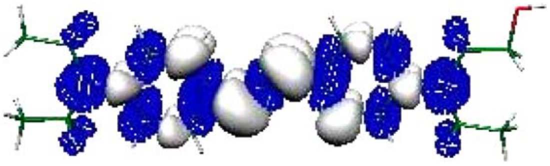

Figure 6 Density difference between the charge-transfer and ground states of the title compound in gas phase. Areas with chickenwire and dots represent the electron loss and gain, respectively, upon the excitation.

the compatibility and controlling the viscosity). A DATACHROOM-5000 nanosecond laser system with pulse width of 10 ns, 15 mJ pulse centers at 600 nm at a repetition rate of 10 Hz and peak value power density of 3.8 GW/cm^2. The 600 nm lasing source is tightly focused *via* an objective lens, and the focal point is focused on the sample film on the *xy*-step. The polymerized solid skeleton is obtained after the unreacted liquid mixture is washed out.

The photopolymerization mechanism of the initiator is still unknown. According to Cumpston *et al.* [5] strong donor substituents would make the conjugated system electron rich, and after one- or two-photon photoexcitation, molecule would be able to transfer an electron even to relatively weak acceptors, and this process could be used to activate the polymerization reaction. In order to demonstrate this process, we try to make a theoretical investigation. Our *ab initio* calculation at time-dependent hybrid density functional theory B3LYP level coded in GAUSSIAN package for the title compound shows that the first excited state is the charge-transfer (CT) state with the excited energy $\lambda = 358$ nm ($\Delta E = 3.4597$ eV, $f = 1.56$). When the target molecule is irradiated by 600 nm laser beam, it can be expected that the molecule will simultaneously absorb two photons and is excited to the first excited state (the CT state). For a better understanding of the charge-transfer process, we have plotted the charge density difference between the ground and the CT states for the target molecule in gas phase (see Fig. 6), which is visualized by use of MOLEKEL program [17]. From Fig. 6 can be seen that upon the excitation, charges are mainly distributed at the D donor side of the molecule indicating that can be give away its electron to its surrounding. This picture seems to support the Cumpston's discussion. However, whether the photoinduced electron-transfer reaction can be energetically feasible needs to be further investigated theoretically.

4. Conclusions

In conclusion, the title compound has been synthesized and characterized, and its crystal structure has been determined by X-ray single crystal diffraction analysis. The one-photon fluorescence emission and their quantum yields, lifetimes and solvent effects are studied in detail. The experimental results confirmed that it is a good two-photon absorbing chromophore and operative two-photon photopolymerization initiator. A two-photon initiating polymerization microfabrication experiment has been carried out and the possible photopolymerization mechanism is also discussed.

Acknowledgements

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