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Effects of symmetric intramolecular charge transfer and molecular coplanarity on two-photon polymerization

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Three nonlinear chromophores of stilbene derivatives, 4,4´-bis(diphenylamino-trans-styryl)biphenyl (*BPSBP*), 4,4´-bis(diethylamino-trans-styryl)biphenyl (*BESBP*) and 4,4´-bis(9-carbazyl-trans-styryl)biphenyl (*BCSBP*) have been synthesized, which possess symmetric D-π-D molecular structure and different extended coplanar conjugation. Two-photon absorption (TPA) cross- sections, 892 GM, 617 GM and 483 GM respectively, were measured by up-converted fluorescence technique. One- and two-photon induced photophysical properties show that symmetric intramolecular charge transfer based on molecular coplanarity played an important role in TPA behaviors, which was further demonstrated by the results of two-photon induced polymerization (TPIP) using these chromophores as TPIP photoinitiators.

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1. Introduction

Two-photon absorption (TPA) plays an important role in modern nonlinear optics and opto-electronics for its widely potential applications in frequency up-converted laser, three-dimensional (3D) microfabrication, optical power limiting, biologic fluorescence imaging and photodynamic therapy [1-5]. However, two-photon absorption, especially TPIP, has limited applications at present due to the small TPA cross-sections of common materials. Organic nonlinear optical materials are promising in TPA fields for their short response time and easily tailored molecular structure which could be designed to respond to a certain range of laser wavelengths. Thus development of organic molecular materials with large TPA cross-section has been a subject of great interest in recent years. One of the current works is to synthesize stable molecules with large TPA cross-section and to further explore the structure and property relationships for large TPA cross-section, which is of great importance to the corresponding TPA induced applications.

S. Marder *et al* [17] correlated the enhancement of TPA cross-section in bis-donor substituted compounds with intramolecular charge transfer from the terminal donor groups to the π-center comparing to those of the corresponding unsubstituted molecules [6,7]. The magnitude of TPA cross-section could thus be controlled through the modification of the molecular structure in such a way as to affect the amount of intramolecular charge transfer. B. Reinhardt *et al* indicated in the aromatic bridges, planarity seems to be critical in obtaining high values of the TPA cross-section [8]. Donors need to have relatvely strong donating activity to maximize TPA cross-section because the polarizability brought about by the rigid and planar molecular structure will contribute a great deal to the reduction of electronic band gap and the extended π-electron delocalization.

From the theoretical structure-property predictions of nonlinear organic materials, the delocalization of π-electrons occurring in the conjugated molecules can lead to significant enhancement of the third-order optical nonlinearities. Theoretical investigations also have revealed that major contribution to the static value of the third-order polarizability originates from the transition dipole term that involves the difference between the dipole moments in the ground state and in the lowest excited state [9]. The large intramolecular charge transfer in excited state will induce effective charge redistribution which can increase the transition dipole term.

In this paper, we synthesized a series of nonlinear chromophores with extended conjugated structure of D-π-D (D denotes the electron donor) and different coplanarity, which enable symmetric intramolecular charge transfer from strong donor groups to π-center on excitation. In the D-π-D molecular motif, π-center is biphenyl and D denotes different terminal donor groups which were connected by conjugated bridge of styryl with π-center. These chromophores show excellent TPA/third-order response to the femtosecond laser pulse at 800 nm and large TPA cross-sections were obtained by using two-photon induced upconverted fluorescence method. The application of two-photon induced polymerization was also carried out using the same femtosecond laser source. The results of TPA cross-section and the behaviors of two-photon induced polymerization show close relationship with the molecular coplanarity and the strength of charge transfer in molecules. The possible mechanism of two-photon polymerization also indicates good coplanarity of TPA photoinitiators will facilitate the process of electron-transfer to the monomers to initiate the radical polymerization reaction.

2. Experimental

2.1. Chemicals and synthesis

All chemicals were of analytical reagent (A.R.) grade and used without further purification. The solvents for synthesis and measurements were purified according to conventional methods. IR spectra were obtained on a Nicolet NEXUS 870 spectrometer (KBr pellets). Nuclear magnetic resonance (NMR) was performed on a Bruker-Avance300 (300MHz) spectrometer in $CDCl_3$ (TMS as internal standard). The elemental analysis was obtained on a Elementar-VARIO ELβ elemental analyzer. All synthetic processes and characterizations were described in detail elsewhere [10].

The synthetic route is illustrated in Fig. 1. Molecular π-electron conjugated system was enlarged by forming –CH=CH– group through Wittig condensation reaction under moderate conditions in a facile and convenient way. The terminal donor groups such as diphenylanimo, diethylanimo and carbazyl were introduced at the ends of the molecules which extended the conjugated length and enhanced the molecular photostability. As shown in Fig. 1, in *N, N*-dimethylformamide (DMF) and exccessive amount of triphenylphosphine, 4, 4′-dichloromethylenebiphenyl can be converted quantitatively to bis-phosphonium salt **1** which has strong electron-donating ability and good solubility in most organic solvents. **2** was prepared from triphenylamine by selective formylation of Vilsmeier reagents to produce single substituted triphenylamine. **3** was achieved by the copper-catalyzed Ullmann arylation procedure to obtain the same product yield as the reaction of *p*-chlorobenzaldehyde with carbazole catalyzed by Pd/P(*t*-Bu_3) [11]. **1** could be converted to bisphosphonium "ylide" in ethanol solution of sodium ethoxide and then reacted with **2,** 4-(*N, N*-diethylamino)benzaldehyde and **3** by Wittig condensation method to obtain target compounds **4**, **5**, and **6** with high yields (>90%).

2.2. Instruments and measurements

The linear absorption and one-photon excited fluorescence spectra were measured on Shimadzu UV-2401 UV-Vis recording spectrophotometer and Shimadzu RF5301pc spectrofluoriphotometer, respectively. The quantum-yield Φ was measured by the standard comparison method [15] using 0.05M sulfuric acid/quinine sulfate as the reference standard.

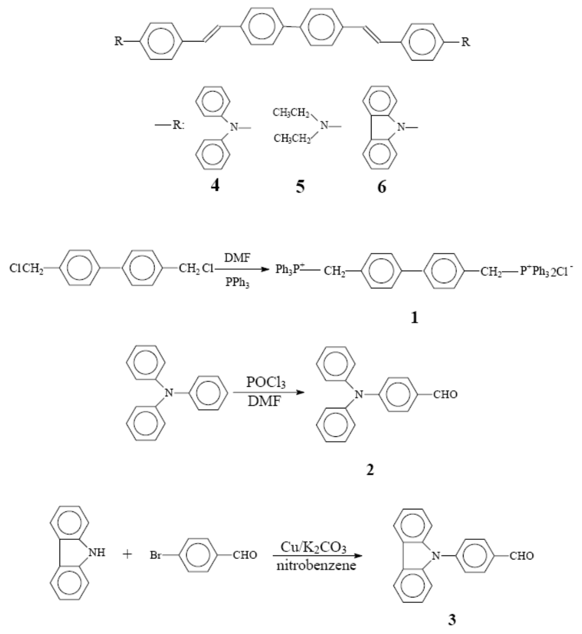


Fig. 1. Structures and synthetic route of the studied molecules.

TPA cross-sections (δ) of three chromophores at 800 nm were determined through the two-photon induced up-converted fluorescence method by using Rhodamine B as the standard in chloroform at the concentration of 1×10^{-3} mol/L. Parameters of mode-locked femtosecond laser include the pulse width of 80 femtosecond, the central wavelength of 800 nm and the repetition frequency of 80 MHz. Femtosecond laser firstly passed through a couple of Nicol's prisms, which were used as an attenuator to obtain a tunable excitation intensity, then the laser was split into two beams. The weaker one was used as a reference beam, which entered directly into the detector of a power meter in order to monitor the intensity of the excitation beam. The intense beam was focused into the sample by a lens. The fluorescence was collected at the direction perpendicular to the pump beam. To minimize reabsorption effect, the excitation beam was focused as close to the front wall of the quartz cell as possible. Two-photon induced fluorescence was recorded by an optical multi-channel analyzer. TPA cross-section δ was determined by comparing its two-photon fluorescence to that of Rhodamine B according to the literatures [13, 14]

$$\delta_2 = \delta_1 \frac{F_2 \Phi_1 c_1}{F_1 \Phi_2 c_2} \tag{1}$$

where c is the solution concentration, Φ is the fluorescence quantum yield and F is the time-averaged fluorescence. The subscript of 1 refers to the standard reference solution and 2 corresponds to the sample solution.

3. Results and discussion

3.1. Structural and photophysical properties

In order to obtain the molecular three-dimensional illustrations, we used Chem3D Ultra 7.0 software package and MM2 method as the energy minimization algorithm. These results can help us to interpret the observed spectroscopic properties. Fig. 2 shows the optimized equilibrium geometry of the three two-photon chromophores. Two important features can be seen: first, the whole molecular motif is nearly coplanar indicating high rigidity of the molecules; and second, the chromophores have extended conjugation along the molecular chains which were encapped with strong donor groups. The two features would enable effective symmetric intramolecular charge transfer on excitation to induce great change of dipole moment during the transition from ground state to excited state.

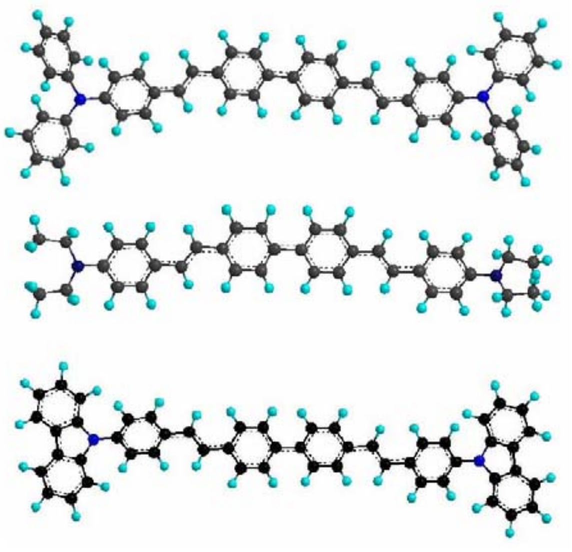
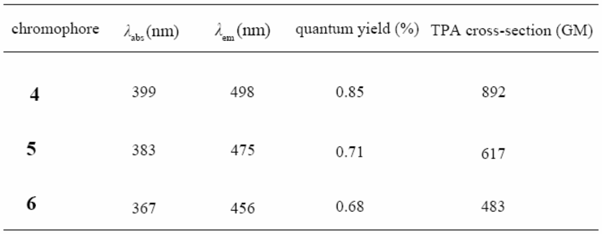


*Fig. 2. The optimized equilibrium geometry of the three two-photon chromophores.(From top: chromophore **4**, **5** and **6**, respectively).*

$$\delta_2 = \delta_1 \frac{F_2 \Phi_1 c_1}{F_1 \Phi_2 c_2} \tag{2}$$

Basic photophysical properties of the three two-photon chromophores in chloroform at the concentration of 1×10^{-5} mol/L are listed in Table 1. The influences of the quartz cell and the solvents have been subtracted. Strong linear absorption bands vary from 354 nm to 399 nm for these chromophores. There is no linear absorption above the wavelength of 500 nm in the absorption spectra (not shown) which means the solutions are transparent to the pump light at 800 nm used in the measurements of molecular TPA cross-section. The maximum absorption appears at 399 nm for chromophore **4** (corresponding molar absorption coefficient ε_{max}=63800), 383 nm for **5** (ε_{max}=72800), and 367 nm for **6** (ε_{max}=55800) in chloroform, respectively. The redshift at absorption peak of chromophore **6**, **5** and **4** shows a decrease of energy levels between the ground state and the first low-lying excited state and an increase of electron-donating ability from carbazyl group, diethylanimo group to diphenylanimo group.

Table 1 Photophysical properties of three two-photon chromophores in chloroform.



chromophore	λ_{abs}(nm)	λ_{em}(nm)	quantum yield (%)	TPA cross-section (GM)
4	399	498	0.85	892
5	383	475	0.71	617
6	367	456	0.68	483

*(1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1})

Emission spectra were recorded using the maximum wavelengths in the absorption spectra as excitation wavelengths. The peaks of the fluorescent spectra and their fluorescent quantum yields are also listed in Table 1. The energy of two photons at 800 nm falls into the strong linear absorption bands of these chromophores. Therefore two-photon absorption in these chromophores can be expected when pumped with a pulsed laser at 800 nm. The TPA cross-section values of these chromophores have also been measured and listed in Table 1 and the big δ values at 800 nm indicate large charge-transfer dipole moment originating from highly rigid coplanarity of the molecules and the extended conjugation. As shown in Table 1, chromophore **4** has the largest TPA cross-section (892 GM), because it has the largest strength of charge-transfer dipole moment. In molecule **4**, the strongest donors of diphenylanimo will induce symmetric charge transfer from end groups to π-center along the extended and coplanar conjugation on excitation.

Chromophore **5** has relative weaker donors at the ends of the molecule and shorter molecular conjugation comparing with chromophore **4**. Therefore the values of quantum yield and TPA cross-section are smaller than those of chromophore **4**. However, chromophore **6** has the smallest values of quantum yield and TPA cross-section, which was correlated with the distorted character of molecular structure. Though carbazyl group is an excellent electron-donating group, the size of the group and spatial hindrance causes the molecular motif a little distortion around the C-N single bond and thus the coplanarity of the whole molecule becomes weaker in contrast with the other two chromophores. The decrease in molecular coplanarity weakened symmetric charge transfer from end groups to π-center and molecular effective conjugation, which resulted in the smallest values of quantum yield and TPA cross-section.

3.2. Two-photon microfabrication

As the TPA cross-sections are large for these chromophores, two-photon induced polymerization could be explored for the application of microdevices through two-photon microfabrication technology. Two-photon induced polymerization experiments were carried out with the same femtosecond laser source that was used in the measurements of TPA cross-section. A 3D scanner driven by PZT (P-537.CL) is used to control three-dimensional movements of the sample. The fabrication process can be real-time monitored with a CCD camera system. The focused laser beam penetrates into the volume of the sample through a numerical aperture objective of 40×, 0.65 NA.

In the two-photon microfabrication, the three chromophores were used as TPA photoinitiators with the concentration of 8 μmol/g for the fabrication of microdevices, and multifunctional resin of pentaerythritoltriacrylate (PETA) as polymerizable monomer. A little solvent of tetrahydrofuran (THF) was added to make the mixture homogeneous. A 20-μm thick film was prepared on clean glass substrate by spin-coating method. The diameter (φ) of focused laser beam was evaluated by Rayleigh criterion $\varphi=1.22\lambda/NA$ and the exposure time was 10 ms for each polymerized dot.

Table 2 Parameters of two-photon photopolymerization.

chromophore	polymerization power (mW)	polymerization threshold ($\times 10^6$ mJ cm^{-2})
4	4.7	2.3
5	7.8	3.8
6	13.7	6.7

It was found that the photopolymerization did not occur until the incident laser power increased to 4.7, 7.8 and 13.7mW for chromophores **4**, **5** and **6**, respectively as shown in Table 2. The TPA photopolymerization thresholds (TPA_{TH}) for these chromophores at the wavelength of 800 nm were calculated to be 2.3×10^6, 3.8×10^6 and 6.7×10^6 mJ cm^{-2} respectively according to the literature [15]. These values are much lower than the TPA_{TH} value of 1.8×10^{12} mJ cm^{-2} for the resin of SCR-500 produced by Synthetic Rubber Co. Ltd., Japan [16]. This indicates that these chromophores have high TPA photosensitivity at the wavelength of 800 nm. Fig. 3 demonstrates scanning electron microscope image of a microgear with double-layer structure using chromophore **4** as two-photon photoinitiator with the laser power of 5 mW. The polymerized solid skeleton was obtained after any unreacted liquid mixture had been washed out.

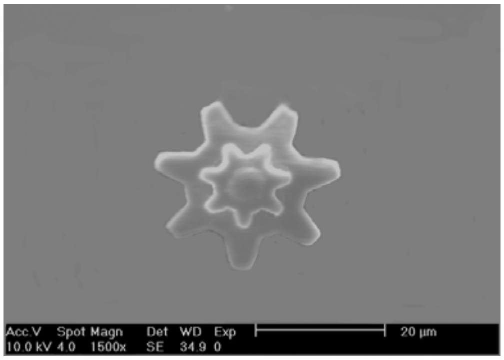


*Fig. 3. SEM image of microgear using chromophore **4** as two-photon photoinitiator.*

The photopolymerization mechanism of these photoinitiators is still unknown. According to Cumpston et al. [17], strong electron-donating substituents would make the conjugated system electron rich, and after one- or two-photon photoexcitation, these chromophores would be able to transfer an electron even to relatively weak acceptors (monomers), and this process could be used to activate the radical polymerization reaction. Chromophore **4**, **5** and **6** possess strong electron-donating substituents at the ends of the molecules and the extended and coplanar conjugation, which makes the molecular conjugated system electron rich. The chromophores also have the virtue of excellent electron delocalizataion upon excitation, which is believed to be another necessary condition for them to easily initiate a two-photon radical photopolymerization reaction. As the TPA cross-section values of these chromophores are large enough, two-photon excitation induced electron transfer between the electron-donating chromophores and the electron-drawing monomers should be efficient. Among the chromophores, Chromophore **4** and **5** have the more planar molecular motifs than that of chromophore **6**, which benefited the electron rich on excitation. And the distorted molecular structure of chromophore **6** prohibited the electron delocalizataion at a certain extent. So the TPA cross-section of chromophore **6** is the smallest among them, and meanwhile TPA photopolymerization threshold is far bigger than those of the other two.

4. Conclusions

In conclusion, a series of nonlinear chromophores with large TPA cross-section have been designed and synthesized. The symmetric D-π-D structure and extended and coplanar conjugated motifs help to enhance third-order response to the femtosecond laser pulse at 800 nm. It is found molecular coplanarity would induce more effective symmetric intramolecualr charge transfer from the analysis of structure-property relationship and the results of two-photon polymerization, which resulted from greater change of dipole moments during the transition from ground state to excited state. Molecular coplanarity and extended conjugation of two-photon chromopores is a promising guideline for designing TPA materials with large photosensitivity.

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