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Spectroscopic Properties and Three-photon Absorption Induced Optical Limiting of Series of Novel Nonlinear Chromophores

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Three novel nonlinear chromophores with symmetric D- π -D molecular structure and extended conjugated length were synthesized. Solvatochromism analysis shows great symmetric intramolecular charge transfer occurring in chromophores by the enhancement in the dipole moment between the ground and excited states. The properties of optical power limiting induced by three-photon absorption (3PA) are demonstrated. Large 3PA coefficients and the corresponding molecular cross sections as high as 10^{-74} cm⁶s² were obtained for nanosecond laser pulses at 1.06 μ m from nonlinear transmission measurements.

Key words: Nonlinear chromophores, Solvatochromism, Three-photon absorption, Optical limiting

I. INTRODUCTION

Multiphoton absorption plays an important role in modern nonlinear optics and opto-electronics because of its wide potential applications in frequency upconversion laser, three-dimensional (3D) fabrication, optical power limiting, biologic fluorescence imaging, and photodynamic therapy [1-12]. In the last decade, considerable work has been focused on the design, synthesis and application of highly sensitive two-photon chromophores with large two-photon absorption (TPA) cross section [13-17]. However, limited work has been done on three-photon absorption (3PA) due to the small values of 3PA cross section in ordinary nonlinear chromophores [18,19]. In a three-photon process, the cubic dependence of three-photon absorption on the incident light intensity and the utilization of longer excitation wavelength with greater penetration ability can provide a stronger spatial confinement than in a two-photon process. These advantages suggest opportunities for a three-photon process in frequency upconversion lasing, infrared (IR) short-pulse optical communications, high-resolution imaging in deep biological tissues, and optical power limiting.

As a fifth-order nonlinear effect, three-photon absorption has limited applications at present. It is essential to explore the chemical structure-nonlinear optical property relationship for this optical process which is fundamental to provide the basis for molecular engineering to maximize the strength of 3PA cross sections and is the

key to the practical applications of 3PA technology. Organic nonlinear optical materials are promising for their short response time and easily tailored structures which can be designed to respond to a certain range of laser wavelengths. From the structure-property relationship 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 have revealed that a 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 [20]. The large intramolecular charge transfer in excited state will induce effective charge redistribution which can increase the transition dipole term. In this work, we synthesized a series of nonlinear chromophores with extended conjugated structure, D- π -D motif, and symmetric charge transfer from strong donor groups to π -center on excitation. In the D- π -D molecular motif, the π motif is a biphenyl and D denotes different terminal donor groups which were connected by a conjugated bridge of styryl with π -center. These chromophores show excellent 3PA/fifth-order response to nanosecond laser pulse at 1.06 μ m and large 3PA cross sections were obtained by using nonlinear transmission measurements. The properties of optical power limiting induced by three-photon absorption are also demonstrated.

II. EXPERIMENTS

A. Chemicals and synthesis

All chemicals were of analytical reagent (A.R.) grade and used without further purification. The solvents for

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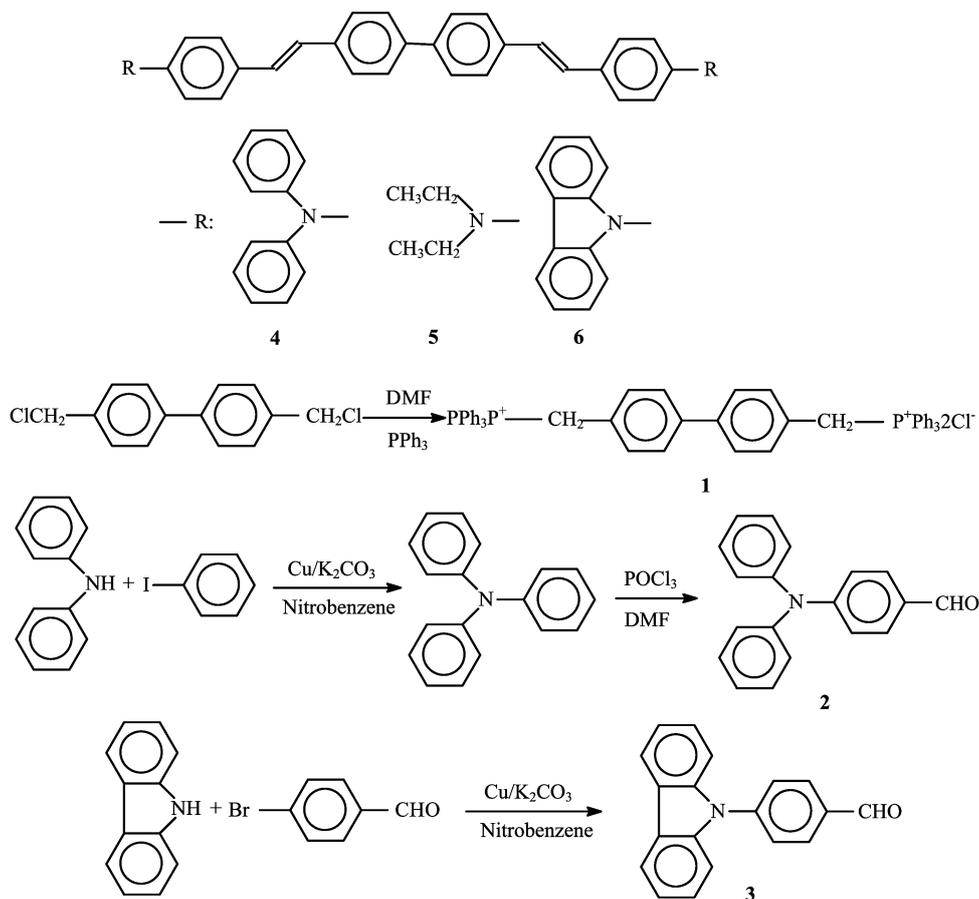


FIG. 1 Structures and synthetic route of the studied chromophores.

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 (300 MHz) spectrometer in CDCl_3 (TMS as internal standard). The elemental analysis was obtained on a Elementar-VARIO ELIII elemental analyzer. All synthetic processes and characterizations were described in detail elsewhere [21].

The synthetic route is illustrated in Fig.1. A molecular π -electron conjugated system was enlarged by forming $-\text{CH}=\text{CH}-$ with Wittig condensation reaction under moderate conditions in a facile and convenient way. The terminal donor groups such as diphenylamino, diethylamino and carbazolyl 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 excessive amount of triphenylphosphine, 4,4'-dichloromethylbiphenyl 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 formulation 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 $\text{Pd}/\text{P}(t\text{-Bu}_3)$ [22]. **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%).

B. Instruments and measurements

Linear absorption spectra and one-photon induced fluorescence spectra for all chromophores in five different polar solvents were measured on a Shimadzu UV-365 UV-Vis-NIR recording spectrophotometer and a Shimadzu RF5301pc spectrofluorimeter, respectively. The solution concentration was 10^{-5} mol/L.

A Q-switched Nd:YAG laser provided pulsed incident light source at $1.06 \mu\text{m}$. The laser pulse has a Gaussian spatial and temporal profile. The laser worked at TEM_{00} mode with a pulse width of 10 ns and a repetition rate of 10 Hz. The laser beam was separated into two beams by the beam splitter (BS). The weaker beam,

TABLE I Photophysical properties of three chromophores in five different polar solvents

Solvent	n	$\varepsilon(20\text{ }^\circ\text{C})$	Δf	4/5/6		
				$\lambda_{\text{max-abs}}/\text{nm}$	$\lambda_{\text{max-em}}/\text{nm}$	Stokes' shift/ cm^{-1}
Cyclohexane	1.426	2.02	0	393/372/354	441/438/409	2769/4051/3798
Toluene	1.494	2.38	0.0140	399/392/367	451/456/423	2890/3580/3606
THF	1.404	7.58	0.2107	398/390/364	472/483/452	3940/4937/5348
Chloroform	1.444	4.81	0.1487	399/383/367	468/475/456	3695/5058/5318
DMF	1.359	37.6	0.2760	399/394/370	496/510/478	4902/5772/6107

$\lambda_{\text{max-abs}}$ is linear absorption peak, $\lambda_{\text{max-em}}$ is one-photon fluorescence peak.

detected by one of the photodiodes of a two-channel energy meter (EPM 2000, Moletron), was used to monitor the incident laser energy. The stronger beam was focused by a 15 cm focal-length lens into a 1 cm long quartz cell containing the solution of the chromophores in 0.01 mol/L chloroform. The incident energy was adjusted by a pair of Glan prisms in the nonlinear transmission measurements. The entire transmitted intensities through the sample were completely collected by a 10 cm focal-length lens to relay to the other photodiode of the energy meter. The signals from the photodiodes were averaged by a Boxcar (EG&G4420). The three-photon induced fluorescence signal was measured in the direction perpendicular to the optical path of the laser beam with a spectrofluorimeter (USB2000-FLG). A 700 nm short pass filter was used to filter the 3PA induced fluorescence to rule out the effect of fluorescence on the transmitted intensity.

III. RESULTS AND DISCUSSION

A. Photophysical properties

Basic photophysical properties of three chromophores in five different polar solvents at the concentration of 10 $\mu\text{mol/L}$ are listed in Table I. 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 1.06 μm used in the nonlinear transmission measurements. For example the maximum absorption appears at 399 nm for **4** (corresponding molar absorption coefficient $\varepsilon_{\text{max}}=63800$), 383 nm for **5** ($\varepsilon_{\text{max}}=72800$), and 367 nm for **6** ($\varepsilon_{\text{max}}=55800$) in chloroform, respectively. Emission spectra were recorded using the maximum wavelengths in the absorption spectra as excitation wavelengths. At the same time two-photon absorption at 1.06 μm , which corresponds to the linear absorption at 532 nm, could not occur. Thus a direct two-photon absorption or single-photon absorption process can be ruled out at the working wavelength of

1.06 μm . The energy of three photons at 1.06 μm falls into the strong linear absorption bands of these chromophores. Therefore three-photon absorption in these chromophores can be expected when pumped with a pulsed laser at 1.06 μm .

It is obvious from Table I that the absorption spectra are not sensitive to solvent polarity. Smaller shifts in the absorption peaks with increasing solvent polarity implies that the ground state is not affected to a greater extent due to the less polar nature of the chromophores in the ground state rather than the excited state. However, solvent polarity strongly influenced the peaks of the emission spectra with a large shift in the range of 441-496 nm for **4**, 438-510 nm for **5** and 409-478 nm for **6**. The peaks of emission spectra in different polar solvents show larger shift compared to those of absorption spectra with the Stokes' shift values varying from 2769 cm^{-1} to 4902 cm^{-1} for **4**, from 4051 cm^{-1} to 5772 cm^{-1} for **5** and from 3798 cm^{-1} to 6107 cm^{-1} for **6**. The increase in the value of Stokes' shift with increasing solvent polarity reveals an increase in the dipole moment on excitation.

In order to further demonstrate the influence of solvents on fluorescence properties, the solvatochromic method has been used for the determination of the difference in the dipole moment between the ground and excited states. The Stokes' shift is defined as the loss of energy between absorption and reemission of light, which is a result of several dynamic processes. These processes include energy losses due to dissipation of vibrational energy, redistribution of electrons in the surrounding solvent molecules induced by the altered dipole moment of the excited chromophore, reorientation of the solvent molecules around the excited state dipole, and specific interactions between the fluorophore and the solvent or solutes. The Lippert equation is the most widely-used equation to describe the effects of the physical properties of the solvent polarity on the emission spectra of chromophores [23]

$$\nu_{\text{abs}} - \nu_{\text{em}} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + \text{const} \quad (1)$$

In this equation, h is Planck's constant and c is the speed of light. The Onsager cavity radius a is the radius of the cavity in which the chromophore resides.

The values of ν_{abs} and ν_{em} (in cm^{-1}) are the wavenumbers of the absorption and emission peaks respectively. The orientation polarizability, Δf , is a solvent polarity parameter for each solvent which is a function of dielectric constant ε and refractive index n .

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

The values of $|\mu_e - \mu_g|$ were obtained from the slope of the plots of $(\nu_{\text{abs}} - \nu_{\text{em}})$ versus Δf given in Fig.2. The Onsager cavity radius was calculated from molecular mechanical method in the Chemoffice software package assuming molecular geometry of the chromophore with the lowest energy. Based on Eq.(1), Eq.(2), and Fig.2, one can evaluate the charge separation of these chromophores upon excitation. Assuming that the cavity radius is 10.2 Å for **4**, 8.7 Å for **5**, and 10.1 Å for **6**, the difference in the calculated dipole moment between the ground and excited states in solution is 28.0, 25.7, and 30.9 Debye, respectively. The symmetric D- π -D molecular structure and the extended conjugated length of these chromophores should be responsible for the large values of $|\mu_e - \mu_g|$. The strong electron-donating terminal groups and the extended conjugated structure of D- π -D led to symmetric intramolecular charge transfer from terminal groups to π -center of the chromophores when excited. The great change in dipole moment or quadrupole moment would enable large nonlinear absorption. Thus these chromophores could be expected in enhancing molecular 3PA coefficients and cross sections.

B. Optical power limiting behavior induced by three-photon absorption

According to the nonlinear absorption theory [24], the intensity change of an excitation beam along the optical propagation path z in the nonlinear materials is given by

$$\frac{dI(z)}{dz} + \alpha I + \beta I^2 + \gamma I^3 = 0 \quad (3)$$

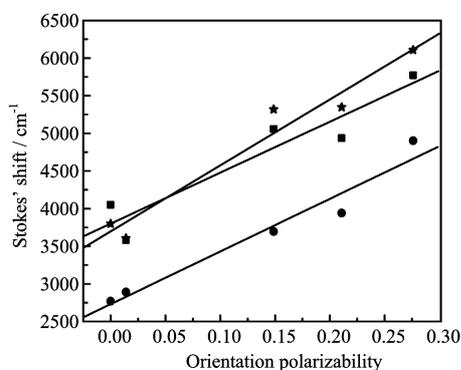


FIG. 2 Stokes' shift of three chromophores (**4** circle, **5** square, and **6** pentacle) in various solvents versus orientation polarizability of the solvents.

Because a direct two-photon absorption and linear absorption for the studied chromophores can be ruled out at the laser wavelength of 1.06 μm , the transmitted beam intensity I_z through the sample in solution is expressed as

$$\frac{dI(z)}{dz} = -\gamma I^3 \quad (4)$$

where γ , 3PA coefficient (in the units of cm^3/W^2), is a constant for the given nonlinear materials and excitation wavelength. The solution of Eq.(4) can be simply obtained as

$$I(z) = \frac{I_0}{\sqrt{1 + 2\gamma z I_0^2}} \quad (5)$$

where I_0 is the incident intensity of the excitation beam and z is the optical propagation distance in the sample. From the relationship between $I(z)$ and I_0 , the 3PA coefficient γ can easily be measured.

For the solution of a given chromophore, the molecular 3PA cross section σ_3 (in the units of cm^6s^2) can be determined by [25]

$$\sigma_3 = \frac{\gamma(h\nu)^2}{N_A d_0} \times 10^{-3} \quad (6)$$

where N_A is the Avogadro number, $h\nu$ is the photon energy of the incident laser beam, and d_0 is the concentration of the sample in solution in the units of mol/L.

Figure 3 shows nonlinear absorption behavior of the chromophores from intensity-dependent transmission measurements in 0.01 mol/L chloroform. The square symbols represent the linear transmission curve of pure chloroform in 1 cm long quartz cell while the other three curves demonstrate a remarkable optical power limiting behavior. In the measurements, the value of each point is an average of 100 data to minimize the fluctuation of laser pulses and the influence of the quartz

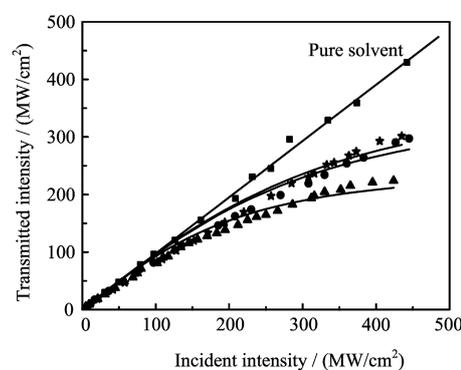


FIG. 3 Transmitted intensity as a nonlinear function of incident intensity demonstrating optical power limiting behavior of three chromophores in 0.01 mol/L chloroform (**4** circle, **5** star, and **6** triangle). The solid lines are the theoretically best fitted curves.

cell has been subtracted. In Fig.3, there is a good linear relationship between incident intensity and transmitted intensity below 100 MW/cm² for all the chromophores and above this value transmitted intensity begins to increase in nonlinearity indicating the effects of three-photon absorption due to higher irradiation energy. For a laser pulse with top-hat spatial and temporal profile, Eq.(5) can be used to estimate transmitted intensity $I(z)$. The solid lines in Fig.3 are the theoretically best fitted curves given by Eq.(5). The best-fit parameters, corresponding to 3PA coefficient γ , are 3.74×10^{-18} , 3.59×10^{-18} , and 8.80×10^{-18} cm³/W² for **4**, **5**, and **6**, respectively.

The molecular intrinsic property, 3PA cross section σ_3 , can be calculated from Eq.(6) based on the known γ values with the concentration dependence. As shown in Table II, three chromophores have large 3PA cross sections as high as the order of 10^{-74} cm⁶s². The values of σ_3 are about two or three orders larger than those obtained for nanoseconds in previous works [26,27]. The large 3PA cross sections for the chromophores are the outcome of the large π -conjugation systems and electron delocalization induced by symmetric intramolecular charge transfer on excitation. From these values, σ_3 value for **6** is more than twice those for **4** and **5**. This can be explained from two aspects. First, **6** has the largest $|\mu_e - \mu_g|$ value which means a stronger symmetric charge transfer in the extended conjugation chain than the other two chromophores. Second, σ_3 value varies in a range of IR excitation wavelengths whose energy of three photons covers the linear absorption spectrum. The biggest σ_3 value will be obtained in the three-photon spectra when the excitation energy of three incident photons coincides with the maximum linear absorption. In the above case, the energy of three incident photons at 1.06 μm , equal to the excitation wavelength at 355 nm, is closer to maximum absorption of **6** other than **4** or **5**. For the same two reasons, σ_3 value for **4** is only a little larger than that for **5**.

TABLE II The measured three-photon absorption data of three chromophores in chloroform pumped with nanosecond laser beam

Chromophores	$\gamma/(10^{-18}\text{cm}^3/\text{W}^2)$	$\sigma_3/(10^{-74}\text{cm}^6\text{s}^2)$
4	3.74	2.17
5	3.59	2.08
6	8.80	5.10

In order to validate the mechanism of the nonlinear behavior induced by three-photon absorption, upconversion fluorescence intensity as a function of IR incident intensity at 1.06 μm for the same solutions was recorded. As shown in Fig.4, the solid curve is the best fit of measured data of **6** based on the relationship of $y=a+bx^n$ with $n=2.88$, where the value of n is less than the cubic dependence due to the occurrence of the decay processes other than the fluorescence emission, such as

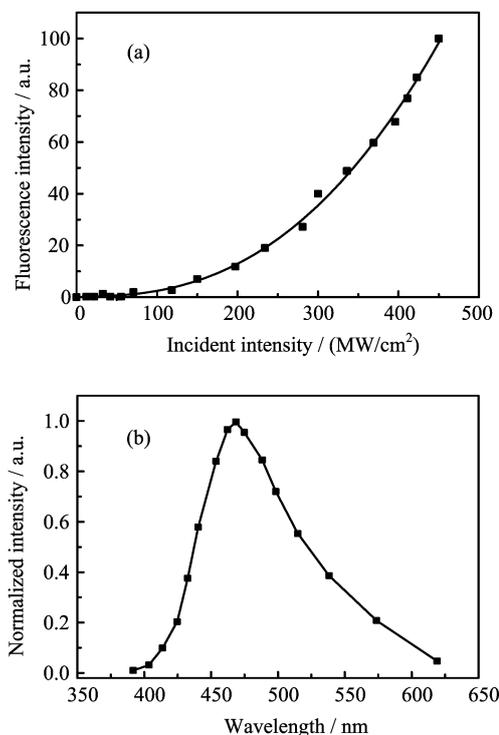


FIG. 4 (a) Upconversion fluorescence intensity as a function of input intensity at 1.06 μm of **6** in 0.01 mol/L chloroform. (b) A normalized spectrum of upconversion fluorescence induced by three-photon absorption. The solid line is the best fitted curve based on the relationship of $y=a+bx^n$ with $n=2.88$.

the excited state absorption or nonradiative transitions. The peak of upconversion fluorescence in Fig.4(b) appears at 468 nm with a red shift of 12 nm comparing with that of one-photon induced fluorescence. This is a result of the reabsorption upon IR excitation in a more concentrated solution of **6**. Similar results were also obtained from the 0.01 mol/L chloroform solutions of **4** and **5**. Based on the cubic law of fluorescence emission dependence on the incident intensity, one can conclude that the nonlinear transmission change and the observed upconversion fluorescence are indeed induced by the three-photon processes.

IV. CONCLUSION

In conclusion, a series of nonlinear chromophores with symmetric D- π -D structure and extended conjugated length were designed and synthesized. Symmetric intramolecular charge transfer based on solvatochromism analysis provides a strategy to enhance 3PA nonlinear absorption in the extended conjugated D- π -D molecules with strong electron-donating terminal groups. Large 3PA coefficients and cross sections were determined from nonlinear transmission measurements. The properties of 3PA induced nonlinear absorption show it is a

promising kind of optical power limiting material.

V. ACKNOWLEDGMENT

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