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Highly Broadband NLO Response of Acceptor-Donor-Acceptor Material with Planar Conformation

Yulin Huang,ab Wenfa Zhou,c,d Xiaofang Li, b Li Jiang*ae and Yinglin Song*c,d

The third-order nonlinear optical properties of A-D-A structural molecule which originally used as acceptor in organic photovoltaics (OPV) devices were investigated in the form of solution and film to deeply understand molecular conformation-properties relationship. Firstly, planar structure [O-IDTBR] bearing indacenodithiophene (ID) core and twisted molecule (IDFBR) comprising indenofluorene (IF) core, which possess identical acceptor units were chosen to be measured by Z-scan technique at near-infrared region in toluene solution. O-IDTBR exhibits more superior TPA cross section than IDFBR in the range of 800~1030 nm (ca. 1497-8811 GM). Especially, the TPA cross section of planar configuration is 8811 GM, over 4 times relative to that of twisted molecule at 800 nm. Secondly, their corresponding spin-coating films are investigated via 4f coherent imaging experiment at 532 nm. It’s noticeable that the nonlinear refractive index of planar molecule is up to 2.09-2.15×10-15 m2/W, which is nearly 5 times than that of IDFBR. The dynamic processes and morphologies of films are systematically characterized by transient absorption spectrum and AFM. The investigations present a better understanding of structure-properties relationship of the A-D-A conjugated materials which are believed to be promising NLO application in the future.

Introduction

Nonlinear optical (NLO) materials have giant potential application in optical limiting, data storage, optical-controllable switching.1-3 Therefore, the materials have attracted considerable attention in recent years. Owing to their advantages of low cost, architectural flexibility and fast response speed, organic nonlinear optical materials are believed to be potentially applicable nonlinear optical materials.4,6 Generally, the nonlinear optical properties are regulated by multiple factors, including conjugated length, the intramolecular charge transfer (ICT) and molecular conformation.7-9 Thus, diverse strategies were performed to optimize NLO performance through synthesizing molecules with various donor and acceptor groups.10-12 The A-D-A type molecules have emerged as outstanding electron acceptors in the organic photovoltaics (OPV) with high power conversion efficiency (PCE). Additionally, due to highly conjugated system, strong intramolecular charge transfer (ICT) and high electron mobility, the A-D-A type molecules are expected to show large NLO response. Recently, a series of quadrupolar A-D-A (A-π-D-π-A) chromophores in which 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (INCN) while indacene- and thieno[3,2-b]thiophene (TT)-based cores being donor units exhibited large nondegenerate two-photon absorption (NDTPA) cross-sections (ca. 6-27×1013 GM) in the near-infrared region.13 However, the study on NLO properties of A-D-A as mentioned above mainly focus on increasing the number of rings to modify conjugated length and changing terminal group to regulate the ICT. More factors, such as the influence of molecular conformation on NLO performance remain unknown. Moreover, the ICT properties of compounds are governed not only by the inherent features of their component moieties but also by their molecular packing.14 Therefore, molecular configuration should be another important factor to enhance NLO performance in theory. The fully comprehensive understanding of structure-properties relationship of A-D-A type materials is undoubtedly necessary. In this context, planar A-D-A molecule (O-IDTBR and EH-IDTBR) and twisted conformation molecule (IDFBR) were chosen to perform contrast study15,16 of which chemical structure are displayed in Figure 1. Due to a steric clash was generated between the IDF and BT units, a more twisted conformation with a dihedral angle of 33° for IDFBR was calculated by density functional theory (DFT) methods.17 By contrast, O-IDTBR was essentially planar due to the increased quinoidal character of the phenyl-thiényl bond reduced steric twisting and enhanced the planarity compared to the phenyl-phenyl bond.15 The O-IDTBR and IDFBR are investigated by broadband femtosecond Z-scan

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a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: jiangli@iccas.ac.cn
b Key Laboratory of Theoretical Organic Chemistry and Functional Molecules, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 412001, China
c Department of Physics, Harbin Institute of Technology, Harbin 150001, China
d School of Optoelectronic Science and Engineering, Soochow University, Suzhou 215006, China. E-mail: ylsong@hit.edu.cn
e University of Chinese Academy of Sciences, Beijing 100049, China
measurement in toluene solvent. Meanwhile, the nonlinear optical properties of spin coating films are fully performed by the coherent imaging technique at solid state. The morphology and excited-state dynamics of films were comprehensively studied by atomic force microscopy (AFM) and femtosecond transient absorption spectrum.

Results and discussion

UV-vis absorption and fluorescence spectroscopy

As shown in Figure 2a, the maximum absorption peak of IDFBR is 502 nm while O-IDTBR and EH-IDTBR are 642 nm. The lower-energy peak, resulting from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) transition, has obviously redshifted (140 nm) for O-IDTBR and EH-IDTBR, which is due to their more electron-rich core as well as a more planar molecular structure. The emission peaks of IDFBR, O-IDTBR and EH-IDTBR locate at 637 nm, 745 nm and 738 nm in CH$_2$Cl$_2$ solution when the excited wavelength is set to excitation wavelength, respectively. Pronounced positive solvatochromic effect is observed in different polarity solvents (Figure S1). With increasing solvent polarity, the fluorescence maxima peak in emission spectra shows a bathochromic shift accompanied by a decrease of fluorescence intensity, which clearly indicates the existence of ICT process. Additionally, the absorption of O-IDTBR and EH-IDTBR films exhibit a shoulder peak compared with IDFBR, which is attributed to the aggregation of indacenodithiophene-benzothiadiazole (IDT-BT). The maximum emission peaks of IDFBR, O-IDTBR and EH-IDTBR are at 622 nm, 784 nm and 766 nm at solid film state and maximum absorption wavelength is set to excitation wavelength.

The morphology of film images

AFM is one of the most effective methods to observe the surface morphology of spin-coating films. As shown in the AFM images in Figure 3 and the corresponding 3D images in Figure S2, IDFBR film (Figure 3a) takes on amorphous surface while O-IDTBR (Figure 3b) and EH-IDTBR (Figure 3c) show more well-ordered crystallinity morphology. The well-order crystallization of O-IDTBR and EH-IDTBR should result from planar backbone to allow effective π-stacking in the solid state, while twisted IDFBR obviously make against stacking as well as crystallinity and consequently displays an amorphous surface. The side chain will great impact on intermolecular packing to make O-IDTBR film and EH-IDTBR film arrange in different ways, which LH-IDTBR displays a closed morphology while O-IDTBR shows a loose morphology as shown in AFM images.

Z-scan experiment

To determine the nonlinear optical properties, femtosecond Z-scan experiment was conducted. The output wavelength of Z-
scan was tuned to 800 nm, 900 nm, and 1030 nm to characterize the NLO response in the toluene solvent. As shown in Figure 4, it is obvious that the samples show deep valley at zero position, which is characteristic of reverse saturated absorption (RSA). Moreover, the O-IDTBR exhibit much deeper valley compared to IDFBR, indicating O-IDTBR has stronger NLO response than IDFBR at given wavelengths. Considering the extremely high transmittance (up to 93%) and off-resonant excitation in open-aperture Z-scan experiment, two-photon absorption (TPA) is believed to be the major mechanism of nonlinear absorption. Unfortunately, the nonlinear refractive index is too weak to be observed in closed aperture Z-scan measurement. Through numerical simulations, the nonlinear absorption coefficient $\beta$ is extracted with equation (1), where $\beta$ is nonlinear absorption coefficient, $L_{\text{eff}} = \frac{1 - e^{-\alpha_L}}{\alpha_0}$ is the effective interaction length with the sample thickness of L, and $\alpha_0$ represents linear absorption coefficient. The third-order optical nonlinear susceptibilities $\chi^3$ are also obtained from equation (2), the TPA cross section $\sigma_{\text{TPA}}$ is calculated through equation (3) and molecular second hyperpolarizability $\gamma$ is acquired with following equation (4).

All parameters are summarized in table 1.

| sample    | wavelength (nm) | $\beta_{\text{lin}}$ ($\times 10^{-13}$ m/W) | $\sigma_{\text{TPA}}$ (GM) | $\chi^3$ ($\times 10^{-15}$ esu) | $\gamma$ ($\times 10^{-33}$ esu) |
|-----------|----------------|---------------------------------------------|-----------------------------|---------------------------------|---------------------------------|
| O-IDTBR   | 800            | 20                                          | 8811                        | 58.1                            | 32.10                           |
|           | 900            | 6                                           | 1713                        | 14.3                            | 7.90                            |
|           | 1030           | 4.7                                         | 1497                        | 1.6                             | 9.04                            |
| IDFBR     | 800            | 3.5                                         | 1902                        | 12.7                            | 6.93                            |
|           | 900            | 2.3                                         | 580                         | 4.9                             | 2.67                            |
|           | 1030           | 1.3                                         | 633                         | 7.0                             | 3.82                            |

From the fitting results, we can find that both IDFBR and O-IDTBR possess broadband NLO response and large TPA cross section at near infrared (NIR) region. It is worth noting that the efficient nonlinear absorption coefficient ($\beta_{\text{lin}}$) of O-IDTBR (up to $20 \times 10^{-13}$ m/W) is almost 6 times higher than that of IDFBR ($3.5 \times 10^{-13}$ m/W). Meanwhile, the TPA cross section of O-IDTBR is 8811 GM, which is over 4 times as much as IDFBR (1902 GM) at 800 nm. Due to O-IDTBR exhibits better NLO property, it can be ascribed to the combination of ICT and coplanar molecular conformation. However, as the literature reported, the more twisted IDFBR has more localized HOMO and LUMO wavefunctions, leading to stronger charge transfer (CT)-like character compared to O-IDTBR. Briefly, IDFBR possesses stronger ICT character than O-IDTBR while O-IDTBR exhibits outstanding NLO performance. Therefore, the better NLO properties of O-IDTBR should mainly originate from its more planar conformation. Moreover, the $\sigma_{\text{TPA}}$ of A-D-A structure in the present study are large than NLO materials reported (table 2).

| wavelength       | $\sigma_{\text{TPA}}$ (GM) | sample   |
|------------------|-----------------------------|----------|
| 800 nm           | 8811                        | this work|
| 900 nm           | 1902                        | ref\textsuperscript{27} |
| 1030 nm          | 203                         | ref\textsuperscript{28} |
| 3.5 x 10\textsuperscript{-13} m/W | 434-1115 | ref\textsuperscript{29} |
| 3.5 x 10\textsuperscript{-13} m/W | 420   | ref\textsuperscript{30} |
| 800-900 nm       | 130-300                     | ref\textsuperscript{31} |
4f coherent imaging system

The 4f coherent images are obtained at the wavelength of 532 nm with laser duration of 190 fs, a repetition rate of 20 Hz. As shown in Figure 5, a, b and c are linear images of films, which are achieved at low laser intensity by placing neutral density filters (ND) before the sample. The transmitted intensity of central areas (PO) is similar to the outside annular. In contrast, nonlinear images (d-f) are obtained at high excitation intensity. It’s obvious that the PO region exhibits higher irradiance than corresponding spherical surfaces, revealing they have positive nonlinear refractive index ($n_2 > 0$) which means self-focusing effect.

Table 3 Third-order NLO parameters of thin films at 532 nm

| sample       | $\beta$ ($10^{-9}$ m/W) | $n_2$ ($10^{-16}$ m²/W) | thickness (nm) |
|--------------|-------------------------|--------------------------|----------------|
| O-IDTBR      | 2.77                    | 20.9                     | 27             |
| EH-IDTBR     | -3.83                   | 21.5                     | 23             |
| IDFBR        | -4.77                   | 4.97                     | 38             |

Considering the 532 nm is in the resonant region of IDFBR, The SA behaviour is attributed to the ground state bleaching (GSB). All nonlinear absorption curves of EH-IDTBR exhibit RSA in toluene solution (Figure S3) while SA in the film, revealing molecular packing can significantly modulate the signal of NLO response. Moreover, the side chain great impact on intermolecular packing. EH-IDTBR displays a closed morphology while O-IDTBR shows a loose morphology as shown in AFM images. Consequently, The SA behaviour of EH-IDTBR is mainly ascribed to different molecular packing in solid film status compared to O-IDTBR. It’s remarkable that $n_2$ of planar molecule (O-IDTBR and EH-IDTBR) is over 4 times relative to twisted structure (IDFBR). It’s believed to planar structure enable effective π-π stacking and form well-order morphology. The well-order arrangement would be conducive to enhance intermolecular π-π interaction, favouring the electron more delocalized in solid states to improve the NLO properties. The transient absorption spectra

The TA spectra of O-IDTBR and EH-IDTBR films were recorded in the visible region under pump excitation of 700 nm laser, while the pumped wavelength is set at 500 nm for IDFBR as shown in Figure 6. In Figure 6b-c, positive signal from 440 to 550 nm are observed in planar molecule (O-IDTBR and EH-IDTBR) films, which are attributed to the excited-state absorption (ESA) originating from promptly photoinduced exciton (EX) or charge transfer (CT) in neat films. In the first 0.45 ps, planar molecules have weak hypsochromic shift while IDFBR (Figure 6a) exhibit weak blue shift in first 0.35 ps.
According to the linear absorption of sample film, the negative features can be assigned to ground state bleaching (GSB). Noting that the maxima fluorescence emission peak of O-IDTBR and EH-IDTBR films is located at 784 nm and 766 nm, which is beyond the probe window. Meanwhile, negative signal of IDFBR from 450 to 600 nm can be attributed to GSB, which causes the SA of IDFBR at 532 nm. The stimulated radiation (SR) of IDFBR in the 620 nm region gradually shifts to an ESA feature, it may be originated from CT state or the pre-existing ESA dominating the SR.

In order to extract the decay dynamic of TA spectra, the global and target analysis with the software (carpetView) was conducted. Four dynamic processes are achieved by fitting the temporal dynamics at representative wavelengths and dynamic trace as shown in Figure S4. The lifetimes of samples are listed in Table 4. EH-IDTBR and O-IDTBR are deduced to possess similar dynamic processes because of their similar profile. The shortest lifetime corresponds to vibrational cooling in the locally excited (LE) state. Due to the time resolution of the TA spectroscopy is approximately 250 fs, it is impossible to distinguish processes with a lifetime of fewer than 250 fs. The second component with 3.3 ps lifetime is the radiative transition in the emissive state. The third component with 53 ps lifetime represents the process of charge transfer from S1 to CT. The last component with 1.7 ns lifetime corresponds to the attenuation of CT states. Additionally, since the process of the radiative transition is much faster than that of CT states, stimulated emission is dominant and steady-state fluorescence is observed. The proposed dynamic process is displayed in Figure S5.

Conclusions

In summary, the influence of planar and twisted conformation on third-order NLO properties of a series of A-D-A chromophores has been investigated in solution and at solid state. The Z-scan analysis reveals that both planar molecule and twisted molecule exhibit broadband RSA and large the two-photon absorption (TPA) cross section in solution. Especially, the TPA cross section of planar molecule (O-IDTBR) is over 4 times to that of twisted structure (IDFBR) at 800 nm. Through numerical simulations, 4f coherent imaging measurement demonstrates that all samples display self-focusing effect and the nonlinear refractive index n2 of planar molecule is nearly 5 times than that of twisted molecule. The dynamic processes and morphologies of films are systematically characterized by transient absorption spectrum and AFM. Our results present a better understanding of structure-properties relationship of A-D-A chromophores and provide significant guidance for the development of designing excellent NLO materials in the future.

Experimental

Material and instrumentation
All the commercial reagents were used without further purification, the A-D-A molecules (O-IDTBR, EH-IDTBR and IDFBR) were purchased from 1-Material. The UV-VIS absorption spectrum was recorded by HITACHI UV/Vis/NIR Spectrometer UH4150 with the concentration of $10^{-6} \text{M}$ and the fluorescence spectrum was collected by F-7100 of HITACHI with the concentration of $10^{-5} \text{M}$ at room temperature. The morphology of films was characterized by atomic force microscopy (AFM) with standard tapping mode probes (Bruker, RTESP-300) on silica wafer.

The fabrication of solid film

Firstly, quartz substrates were cleaned with piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 3:1$) in an ultrasonic bath for 1h. After washing by deionized water, it was rapidly dried under high purity nitrogen. The samples are dissolved in CHCl$_3$ and the solution is filtered with 0.22 μm filter to remove large particles before use. Samples were prepared by spin-coating from the solution directly into pan at 3500 rpm for 30s at room temperature, allowing the solvent to evaporate under air. The thickness of films was determined by a profile step scanner (Bruker Dektak XT).

Z-scan measurement

In Z-scan experiment, an optical parametric amplifier (OPA, ORPHEUS, Light Conversion) pumped via a Yb:KGW based fiber laser (PHAROS, Light Conversion) is employed as light source. The light source can generate laser pulses with tunable wavelengths, here in Z-scan with laser duration of 190 fs, a repetition rate of 20 Hz and laser pulses are tuned to 1030 nm. To minimize the influence of thermal lens effect, low repetition rate is used to avoid the accumulation of heat in samples. The laser pulse in Z-scan experiment has a Gaussian profile. IDFBR, O-IDTBR were dissolved in toluene solvent and the concentration was $7.6 \times 10^{-4} \text{M}$, $7.5 \times 10^{-4} \text{M}$. Solutions were placed in 2 mm thickness quartz cells and the influence of solvent was removed from the experiment data. A schematic diagram of Z-scan is shown in Figure S6.

4f coherent imaging technique

The 4f coherent imaging technique with phase object (NIT-PO) method was used to simultaneously investigate the nonlinear absorption coefficient $\beta$ and nonlinear refractive index $n_2$ through recording the fluence distribution of laser profiles, the schematic of 4f coherent imaging technique is shown in Figure S7. The experiment details were reported in the previous work.\textsuperscript{31, 40} The light source of 4f system is same as Z-scan and the laser beam passes through a phase object (PO) which is placed in the input plane. The radius of PO is 0.5 mm and the circular aperture is 1.7 mm. Since the radius of input laser beam is larger than that of circular aperture, a top-hat beam profile is obtained. A phase retardation of $\phi_1=0.5\pi$ at 532 nm is introduced to the central part of the beam when passing through the PO. After the PO, the laser separates into two parts. One passes through the sample which is placed at focal plane to investigate NLO properties, another is used as reference. Lastly, the output laser beam is recorded by a CCD camera that is arranged at output plane in 4f system experiment. The radius of beam is 57 μm at focal plane with Rayleigh length (19 mm), which is thicker than the thickness of films. Among various method of Z-scan techniques, the 4f coherent imaging system as a new measurement to determine third-order NLO properties has many advantages such as single laser shot, no sample movement, lower sensitivity to statistical fluctuations of the laser beam and higher sensitivity to characterize the uneven surface of thin films.\textsuperscript{41} Due to its advantages mentioned above, 4f coherent imaging system is suitable to measure the third-order NLO properties of nano-films.

Femtosecond time-resolved transient absorption

To further investigate the dynamic process of the films after photoexcitation, the femtosecond transient absorption experiment was conducted. The light source is same as Z-scan. The pump wavelength is set to 500 nm and 700 nm while the spectral window of probe is tuned in visible region. The basic description of transient absorption technique was available on previous report.\textsuperscript{42, 43}

Conflicts of interest

There are no conflicts to declare.

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