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Synthesis and Third-Order Nonlinear Optical Properties of Triphenylene Derivatives Modified by Click Chemistry

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A series of asymmetric triphenylene derivatives containing typical D- π -A structures is successfully synthesized by means of [2+2] cycloaddition-cycloreversion click reactions. The photophysical and electrochemical properties, as well as the click reactions, are characterized by means of UV/Vis absorption spectroscopy, cyclic voltammetry, and DFT modulations. In addition, the third-order nonlinear properties, including the nonlinear

1. Introduction

Organic conjugated compounds are widely used in the fields of electronics and optoelectronics. Many organic molecules exhibiting highly efficient nonlinear optical (NLO) properties have attracted considerable attention because of their potential applications in optical communication, optical data storage, photodynamic therapies, three-dimensional memories, and photonic devices such as optical switches.^[1] In particular, organic π -conjugated third-order NLO materials have been extensively studied because of their large second hyperpolarizabilities and their fast response times.^[2] Moreover, much work on optimizing the third-order NLO responses has been performed, revealing that the amplitude and sign of the γ value can be adjusted by changing the bond length alternation, the strength of the donor/acceptor substituents, the charge and the size of the π conjugation.^[3]

Many papers have been reported on investigations of the third-order NLO properties of molecules with *p*-conjugation systems, such as porphyrins, phthalocyanines, azobenzene, and so on.^[4, 5] Triphenylene (TP) has been traditionally chosen as a building block for the fabrication of photoelectric materials, such as liquid crystals (LCs).^[6] It has shown good performance in electronic devices, such as thin film transistors, organic light emitting diodes, and organic solar cells.^[7] TP has been extensively employed as the central core of discotic conjugated molecules, which have shown to be rather promising in optoelectronic applications. However, studies on TP derivatives used in NLO have been rarely reported.

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absorption and the nonlinear susceptibilities, are investigated by using Z-scan techniques. A typical reverse saturable absorption-saturable absorption behavior is observed for the thirdorder nonlinear absorption, with the third-order nonlinear susceptibilities of the compounds being 1.05×10^{-12} , -1.50×10^{-12} , and -0.52×10^{-12} esu, respectively.

One reason that accounts for the disadvantage of TP derivatives as promising NLO materials is that it is costly and timeconsuming to modify the TP derivatives with strong electron donors and acceptors due to the required tedious chemosynthesis and purification processes. Formal [2+2] cycloadditioncycloreversion (CA-CR) reactions between electron alkynes and electron-deficient alkenes, such as tetracyanoethene (TCNE) or 7,7,8,8-tetracyano-p-quinodi- methane (TCNQ), have been developed as a convenient and robust method for preparing nonplanar, π -conjugated, donor-acceptor chromophores that exhibit intense, low-energy, intramolecular charge transfer (CT) and high third-order optical nonlinearities.^[8] These features render 1,3-butadiene CA-CR products that are attractive for NLO applications.^[9] The transformations are generally fast, high-yielding, catalyst-free, and 100% atom-economic, and the resulting products can be easily purified by precipitation or washing.

In the present work, [2+2] CA–CR click reactions were selected to synthesize a novel series of asymmetric TP derivatives with typical D– π –A structures. The physical properties, especially the third-order nonlinear properties of the pre-click and after-click compounds, were fully studied and compared. Our approach opens a new platform for the synthesis of multi-D– π –A TP derivatives to be used in appropriate photonic applications.

2. Results and Discussion

2.1. Synthesis

Scheme 1 shows the molecular structures and synthetic routes of compounds **ATP1**, **CATP1**, and **CATP2**. At first, a carbonyl group was connected to the TP discotic cores through a Friedel–Crafts acylation procedure to obtain the asymmetric TP derivative **1** and introduce a strong electron acceptor, the carbonyl group. By means of bromination and Hagihara–Sonoga-



Scheme 1. Molecular structures of ATP, CATP1, CATP2, and their synthetic routes.

shira cross-coupling, N,N-didodecylanilino substituents were introduced as strong electron donors in **1** to give a typical $D-\pi$ -A structure product, namely, ATP. The asymmetric TP derivative was evidenced by typical peaks at 2960, 2874, 2150, and 1605 cm⁻¹, which could be attributed to the vibration absorptions of methyl and methylene, the carbon-carbon triple bond, and the carbonyl group, respectively. Nuclear magnetic resonance (¹HNMR and ¹³CNMR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), differential scanning calorimetry (DSC), and elemental analysis (EA) results were further used to fully characterize the products. In the ¹HNMR spectra, the hydrogen atoms of the aromatic cores of **ATP** showed chemical shifts (δ) at 6.60~8.98 and the alkyl chains showed relevant shifts at 0.96~3.29. The ¹³CNMR spectra showed the numbers of carbon atoms that had different chemical shifts and the DSC curves showed that the compound has a melting point of 141 °C.

Formal [2+2] cycloaddition of strong electron acceptors of TCNE and TCNQ to electron-rich alkynes, followed by retroelectrocyclization, provides efficient access to nonplanar pushpull chromophores featuring intense intramolecular charge transfer (CT) and high third-order optical nonlinearities.^[10] **CATP1** and **CATP2** were obtained through [2+2] cycloaddition-cycloreversion reactions between ATP and TCNE, TCNQ with relatively high yielding, as was in Scheme 1. TCNE and TCNQ were stepwise added to the side chain alkynes of ATP undergoing a click chemistry-type addition reaction via a [2+ 2] cycloaddition followed by a cycloreversion process. With the introduction of the strong electron-withdrawing cyano groups in TCNE and TCNQ, more complicated D- π -A structured systems had been formed. Both products were evidenced by means of Fourier-transformed infrared (FTIR) spectroscopy for the appearances of peaks at 2216 cm⁻¹ of cyano groups and the disappearances of peaks at 2150 cm⁻¹ of carbon-carbon triple bonds. The ¹HNMR spectra of the click-reaction products showed a low chemical shift at 8.25~6.60 for the H atoms in the aromatics cores, and the DSC curves showed that CATP1 and CATP2 have melting points of 185 and 198°C, respectively. The final products were fully characterized by using ¹³C NMR and MALDI-TOF-MS spectroscopy.

In addition, the [2+2] click-type reaction was characterized by UV/Vis spectroscopic titration of **CATP1**. Quantitative TCNE was added to the dichlorobenzene solution of **ATP**, and the obtained absorption spectra are shown in Figure 1, as well as



Figure 1. a) Reaction of **ATP** with quantitative TCNE to prepare **CATP1.** b) Changes in the UV/Vis absorption spectral shape upon addition of 0 to 2 equiv. TCNE in dichloromethane.

the reaction equation. Upon addition of quantitative TCNE, the spectra of the reaction showed an obvious increment in the CT band intensities in the wavelength region near 300 nm and bathchromical shifts in the near-infrared region. Additionally, the occurrence of an isoabsorptive point at 423 nm indicated no side reactions in the [2+2] click-type reaction.

2.2. UV/Vis Spectra

Figure 2 shows the characteristic UV/Vis absorption spectra of the products ATP, CATP1, and CATP2 in dichloromethane at a concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$. As shown in Figure 2, all the products exhibit intensive absorption bands in the wavelength region between 300 and 415 nm, which correspond to $S_{o}\text{-}CT$ transitions (where S_{o} is the singlet state and CT is the charge-transfer state).^[11] Compared to ATP, the click-type reaction product CATP1 showed two additional absorption bands at 481 (shoulder) and 654 nm, whereas CATP2 showed new broad absorption bands in the 450-1100 nm region. In addition, the end absorption peaks (λ_{end}) of the products bathochromically shifted from ATP (500 nm) to CATP1 (875 nm) and CATP2 (1095 nm), which could be reflected by the photography of products in Figure 2. The absorption spectra indicate that after the addition of an electron-acceptor (cyano) group by means of click-type reactions, CATP1 and CATP2 showed new broad absorption ranges, and the λ_{end} of the CATP1 and



Figure 2. UV/Vis absorption spectra and photos of solutions of the products ATP, CATP1, and CATP2 in dichloromethane.

CATP2 systems showed a bathochromic shift compared to **ATP.** This was due to the electron-donor and electron-acceptor substituents in the synthesized click-type reaction products **CATP1** and **CATP2**, which increased the charge-transfer character.^[12] The fact that the **CATP2** system exhibits a maximum absorption at the longest wavelength (750 nm) among the investigated compounds reflects the highest charge-transfer interactions occurring between the electron-donor (amino) and the electron-acceptor (cyano) groups. This enhancement of the charge-transfer efficiency, if compared to **CATP1**, could be attributed to an increment of the π -conjugated range by the quinone groups.^[13]

2.3. HOMO-LUMO Energy Gap

Electron delocalization was one of the three main factors affecting the third-nonlinear polarizabilities of organic molecules, and the charge delocalized on the molecules varied with the different HOMO/LUMO (highest occupied molecular orbital/ lowest unoccupied molecular orbital) energy levels.^[14] Molecules having delocalized π -electrons and compounds consisting of π -conjugated molecules showed a much larger thirdnonlinear susceptibility. To characterize the electron delocalization of the studied compounds, cyclic voltammetry (CV) and DFT simulations were carried out, and the electrochemical properties of the products are given in Table 1. The HOMO and LUMO energies of ATP, CATP1, and CATP2 were -4.95 and -3.12, -5.53 and -4.15, and -5.05 and -4.59 eV, respectively, and the calculated energy gaps were 1.83 eV for ATP, 1.38 eV for CATP1, and 0.46 eV for CATP2, showing the lowering of HOMO-LUMO energy gaps, which is in good agreement with the energy-gap trends obtained from the onset wavelengths of UV/Vis absorption shown in Table 1. This can be mainly attributed to increments in the charge-transfer character of both π - π transitions and donor-acceptor transitions in these typical $D-\pi-A$ compounds.

Three-dimensional plots of the HOMO and LUMO levels of ATP, CTAP1, and CATP2, calculated by DFT modulations, are

Table 1. Electrochemical properties of ATP, CATP1, and CATP2.									
Sample	E _{onset} ^{ox[a]}	E _{onset} red[b]	HOMO	LUMO	<i>E</i> g ^[c]	$\lambda_{\text{onset}}^{[d]}$	Eg ^{optical[e]}		
	[V]	[V]	[eV]	[eV]	[eV]	[nm]	[eV]		
ATP	0.15	1.68	-4.95	-3.12	1.83	509	2.43		
CATP1	0.73	0.65	-5.53	v4.15	1.38	830	1.49		
CATP2	0.25	0.21	-5.05	-4.59	0.46	1037	1.20		
[a] Onset oxidation potentials determined from cyclic voltammograms in CH_2Cl_2/Bu_4NPF_6 at a scan rate of 40 mV s ⁻¹ . [b] Onset reduction potentials determined from cyclic voltammograms in CH_2Cl_2/Bu_4NPF_6 at a scan rate of 40 mV s ⁻¹ . [c] Band gaps estimated from the onset potentials. [d] Onset wavelength of optical absorption in a dichloromethane solution. [e] Band gaps estimated from the onset potential absorption in a di-									

shown in Figure 3. The electron cloud movements through π conjugated frameworks from electron-donor to electron-acceptor groups and the charge delocalized on the molecule varied with the different HOMO and LUMO energy levels. The HOMO and LUMO energies of **ATP**, **CATP1**, and **CATP2** were -5.63 and -1.75, -5.97 and -3.89, and -5.96 and -3.34 eV, respectively, at the DFT level. The DFT-calculated energy gaps of 3.88 eV for **ATP**, 2.08 eV for **CATP1**, and 2.62 eV for **CATP2** also showed the lowering of energy gaps and reflected the third-order NLO activities of the molecules.^[15]

2.4. Z-Scan Curves

chloromethane solution.

The NLO responses of **ATP**, **CATP1**, and **CATP2** were measured by the "open aperture" Z-scan technique; several recordings were acquired. All the samples were studied from a 10^{-6} M solution in tetrahydrofuran (THF) spectrum pure (SP) and the solvent itself did not show any third-order nonlinearities under the experimental conditions. The nonlinear absorption coefficient β was determined using Equation (1) and the imaginary parts of the third-order nonlinear susceptibility could be calculated using Equation (2) (see Experimental Section).

Figure 4 shows the "open aperture" Z-scan data and the normalized transmittance curves of all the products, which could be perfectly fitted to Equation (1). In Figure 4a, a profound transmittance valley could be seen around the focal plane, which is characteristic of the reverse saturable absorption (RSA)-type behavior of ATP. Materials showing RSA become more opaque on exposure to high photon fluxes due to the high absorption from the excited state, and this property has been exploited in the field of optical limiting for laser protection. Figure 4b shows the typical transmittance peaks of the click-reaction products CATP1 and CATP2, which exhibit saturable absorption (SA)-type behaviors. It could be shown that compared to ATP, the click-reaction products CATP1 and CATP2 exhibit a clearly reverse saturable absorption-saturable absorption (RSA-SA) transition, which is achieved by click-type reactions in the organic molecules.

From a plethora of recordings, the $Im\chi^{(3)}$ value of **ATP** has been determined according to Equations (1) and (2) (see Experimental Section) and was found to be $Im\chi^{(3)} = 1.05 \times 10^{-11}$ esu, which corresponds to a nonlinear absorption coefficient of $\beta =$

 $-4.66 \times 10^{-12} \text{ m w}^{-1}$. The $\text{Im}\chi^{(3)}$ values of **CATP1** and **CATP2** were -1.50×10^{-12} and -0.52×10^{-12} esu, while the nonlinear absorption coefficients β were -6.66×10^{-12} and $-2.31 \times$ 10^{-12} m w⁻¹, respectively. Compared to other organic molecules measured by Z-scan, the third-order nonlinear values of our compounds were relatively good.^[16,17] CATP1 shows a larger $Im\chi^{(3)}$ value compared to **ATP**, which can be ascribed to the introduction of electron-acceptor (cyano) groups from TCNE and may help increase the third-order nonlinear susceptibility of the compound by modifying charge transfer within the molecule.^[18] In addition, CATP2 shows a lower $Im\chi^{(3)}$ value compared to CATP1, which can be attributed to an increment of the π -conjugated ranges in CATP2 and could have an influence on the charge transfer, hinering the polarizabilities of the molecule.^[19] The properties of these products are important for the synthesis of new molecules to be used in NLO applications.

3. Conclusions

Novel asymmetric TP derivatives, having large conjugated systems as well as strong D– π –A structures, were synthesized by means of [2+2] click procedures. Investigations of the photophysical and electrochemical properties of the products by using UV/Vis spectroscopy and CV showed that the CT character of the D– π –A structures plays a key role in the absorptionpeak shifts and the HOMO–LUMO energy levels. Most importantly, upon the introduction of electron acceptors, the third-order nonlinear absorption of the products showed a typical RSA–SA transition and the third-order nonlinear susceptibilities increased. This approach combines the possibility to vary the structures of the conjugated system with third-order optical nonlinearities, opening new perspectives to utilize the system in a variety of photoelectric applications.

Experimental Section

General Methods

¹HNMR and ¹³CNMR spectra of the samples were recorded with a Varian 400 MHz instrument, MALDI-TOF-MS spectra were determined on a Shimadzu AXIMA-CFR mass spectrometer. DSC analyses were performed on a PerkinElmer Pyris 6 instrument at a heating/ cooling rate of 10 °C min⁻¹. All UV/Vis spectra were recorded on a HITACHI U-3010 spectrophotometer, and FTIR spectra were recorded on a PerkinElmer LR-64912C spectrophotometer. Elemental analyses were performed at the Institute of Chemistry of the Chinese Academy of Sciences using a Flash EA 1112 instrument.

Synthesis of phenyl(triphenylen-2-yl)methanone (1). Triphenylene (5.00 g, 21.9 mmol, 1 equiv) and benzoyl chloride (3.08 g, 21.9 mmol, 1 equiv) were dissolved in dichloromethane (60 mL) and then the reactor was cooled to 0 °C. After the portionwise addition of AlCl₃ (4.17 g, 31.3 mmol), the reaction mixture was heated under reflux for 10 h and then poured into ice-water. The resulting mixture was stirred until the color of the organic phase turned from black to yellow and the layers were separated in which the aqueous phase was extracted with dichloromethane and dried with anhydrous MgSO₄. After evaporation of the solvent in high vacuum, the residue was purified by column chromatography

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Figure 3. Electron densities in the HOMOs (bottom) and LUMOs (top) of ATP, CATP1, and CATP2. The atoms are color coded as follows: carbon, gray; nitrogen, blue; oxygen, red; hydrogen, white.

(silica gel, dichloromethane/petroleum ether=3/2, v/v) to afford the pure 1 (5.11 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ =9.10 (1 H, s), 8.79 (1 H, d, J=8.0 Hz), 8.71 (3 H, m), 8.60 (1 H, d, J=8.0 Hz), 8.06 (1 H, d, J=8.0 Hz), 7.91 (2 H, m), 7.68 (5 H, m), 7.54 ppm (2 H, m). FT-IR (KBr): $\tilde{\nu}$ =1654, 1596, 1264, 812 cm⁻¹. MALDI-TOF-MS (dithranol): *m*/*z*: calcd for C₂₅H₁₆O: 332.12 gmol⁻¹, found: 332.4 gmol⁻¹ [*M*H]⁺.

Synthesis of (6,10-dibromotriphenylen-2-yl)(phenyl)methane (2): Compound 1 (1.00 g, 3.01 mmol, 1 equiv) was dissolved in nitrobenzene (20 mL). Bromine (2.37 g, 15.0 mmol, more than 2 equiv) was then added slowly under vigorous stirring. After complete addition, the temperature was heated to 140 °C and maintained for 8 h. The cooled reaction suspension was poured into acetone and the precipitate filtered off. Further drying of the precipitate under high-vacuum conditions gave the crude product **2** (1.18 g, 80%), which was used without further purification because of the bad solubility in common organic solvents. FTIR (KBr): $\tilde{\nu} = 1648$, 1606, 1271, 955, 757 cm⁻¹.

Synthesis of (6,10-bis((4-(dibutylamino)phenyl)ethynyl)triphenylen-2-yl)(phenyl)methanone (ATP): Compound 2 (0.50 g, 1.02 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 2.05 mmol), and Cul (7.81 mg, 4.10 mmol) were added to a degassed solution of TEA (15 mL) and THF (15 mL) under argon. While stirring, the reaction

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Figure 4. Open-aperture Z-scans measured in a THF solution of: a) **ATP** and b) **CATP1**, **CATP2**. As seen from the figures, the optical transmission is a function of the sample option (Z=0 is the beam focus). T_{norm} is the measured transmission normalized by the linear transmission of the sample. The solid curves correspond to numerical fits to the data.

ether = 1/4, v/v) to give the pure CATP2 (0.20 g, 87%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.25$ (14 H, m), 7.53 (4H, d, J=8.0 Hz), 6.64 (12H, m), 3.32 (8H, m), 1.23 (16H, m), 0.91 ppm (12 H, m). $^{13}CNMR$ (100 MHz, CDCl₃): $\delta = 195.4$, 167.4, 153.7, 153.3, 151.4, 150.8, 136.7, 135.6, 134.6, 134.0, 132.8, 132.0, 131.7, 131.2, 130.6, 129.8, 129.3, 128.5, 128.3, 126.1, 125.0, 123.0, 122.8, 114.6, 113.1, 112.4, 111.9, 93.3, 65.2, 50.8, 31.6, 30.2, 29.3, 29.1, 19.9, 18.8, 13.5, 13.4 ppm. FT-IR (KBr): $\tilde{\nu} = 2927$, 2867, 2216, 1660, 1485, 1186, 833 cm⁻¹

mixture was heated to 70°C and N,N-dibuty-4-ethynylaniline (0.47 g, 2.04 mmol, 2 equiv) was injected. After 15 min of stirring at this temperature, the reaction was continually heated to 80 °C and stirred for 8 h under argon atmosphere. The cooled reaction mixture was diluted with CH₂Cl₂ and extracted with water. The organic phase was dried with MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 1/4, v/ v) to give **ATP** (0.52 g, 65%). ¹HNMR (400 MHz, CDCl₃): $\delta = 8.98$ (1 H, s), 8.71 (2 H, s), 8.10 (11 H, m), 7.65 (4 H, d, J=8.0 Hz), 6.60 (4 H, d, J=8.0 Hz), 3.29 (8 H, m), 1.30 (16 H, m), 0.96 ppm (12 H, m). $^{13}\text{C}\,\text{NMR}$ (100 MHz, CDCl_3): $\delta\!=\!$ 195.6, 137.1, 132.9, 132.4, 131.0, 130.6, 129.8, 128.2, 127.9, 127.5, 126.3, 125.9, 125.1, 124.4, 124.2, 122.9, 121.9, 111.0, 50.4, 29.4, 29.1, 20.0, 13.7 ppm. FTIR (KBr): $\tilde{\nu} =$ 2960, 2874, 2150, 1605, 1514, 1365, 1178, 860, 818 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd. for $C_{57}H_{58}N_2O$: 786.45 g mol⁻¹, found: 787.1 g mol⁻¹ [MH]⁺. Elemental analysis calcd. (%) for C₅₇H₅₈N₂O (787.08): C 86.97, H 7.37, N 3.55; found: C 86.98, H 7.43, N 3.56. MP: 141 °C.

Synthesis of 3, 3'-(10-benzoyltriphenylene-2,6-diyl)bis(2-(4-(dibutylamino)phenyl)buta-1,3-di-ene-1,1,4,4-tetracarbonitrile)

(CATP1): ATP (0.15 g, 0.20 mmol, 1 equiv) and TCNE (51.2 mg, 0.40 mmol, 2 equiv) were mixed in dichloromethane (10 mL). After stirring for several minutes, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/4, v/ v) to give the final click-type reaction product CATP1 (0.18 g, 89%). ¹HNMR (400 MHz, CDCl₃): δ = 8.23 (14 H, m), 7.47 (4 H, d, J = 8.0 Hz), 6.60 (4H, d, J=8.0 Hz), 3.29 (8H, m), 1.36 (16H, m), 0.96 ppm (12 H, m). ¹³C NMR (100 MHz, CDCl₃): $\delta = 195.7$, 167.6, 153.9, 153.4, 151.6, 150.9, 136.9, 135.7, 134.8, 134.1, 133.9, 133.0, 130.2, 131.2, 130.6, 128.8, 128.3, 126.1, 125.0, 123.0, 122.8, 114.6, $113.1,\ 112.1,\ 111.9,\ 93.3,\ 65.2,\ 51.3,\ 31.6,\ 30.2,\ 29.8,\ 29.5,\ 20.4,$ 14.0 ppm. FTIR (KBr): $\tilde{\nu} = 2927$, 2867, 2216, 1660, 1485, 1186, 818 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd. for C₆₉H₅₈N₁₀O: 1042.48 g mol⁻¹, found: 1043.3 g mol⁻¹ $[MH]^+$. Elemental analysis calcd. (%) for C₆₉H₅₈N₁₀O (1043.27): C 79.36, H 5.56, N 13.42; found: C 79.44, H 5.60, N 13.43. MP: 185 °C.

Synthesis of 2,2'-(2,2'-(10-benzoyltriphenylene-2,6-diyl)bis(1-(4-(dibutylamino)phenyl)-2-(4-(dicyanomethylene) cyclohexa-2,5-dienylidene)ethan-2-yl-1-ylidene))dimalononi trile (CATP2): ATP (0.15 g, 0.20 mmol, 1 equiv) and TCNQ (0.08 g, 0.40 mmol, 2 equiv) were dissolved in dichlorobenzene (10 mL). Under stirring, the reactor was heated to 140 °C and maintained for 1 h. The solvent of the cooled reaction mixture was removed under reduced pressure and the crude product was purified by column chromatography

Nonlinear Optical Studies: Z-Scan Measurement

In our experiments, to investigate the third-order nonlinearities of the products, Z-scan measurements were performed using a 20 ps mode-locked Nd:YAG laser at 532 nm. "Open aperture" Z-scan measurements were carried out to separately determine the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$ and the nonlinear absorption coefficient β , which is related to the nonlinear absorption of the samples. Additionally, the advantage of the Z-scan measurements is that apart from the magnitude, they can also provide the sign of $Im\chi^{(3)}$, where the latter is directly related to the nonlinear absorption type [saturable absorption (SA) or reverse saturable absorption (RSA)].

Details of the experimental techniques, as well as the procedure to analyze the experimental data, are only briefly described here. Extended information can be found in the literature. Here, a laser beam is focused using a lens and passed through the sample. The beam's propagation direction is taken as the z axis, and the focal point is taken as Z=0. The beam will have a maximum energy density at the focus, which will symmetrically reduce toward either side for the positive and negative values of Z. In our experiments, THF solutions of the samples were taken in 1 mm cuvettes and the measurements were performed by placing the samples in the beam at different positions with respect to the focus (different values of z) and measuring the corresponding light transmission. The graph plotted between the samples T (norm) (transmission normalized to the linear transmission of the sample) is known as the Z-scan curve. From the "open aperture" Z-scan curves, the nonlinear absorption coefficient β was determined using Equation (1):

$$\beta(\mathsf{m}\,\mathsf{w}^{-1}) = \frac{2\sqrt{2}[1 - T(Z=\mathbf{0})]}{l_0 L_{\text{eff}}} \tag{1}$$

where *T* is the normalized transmittance, $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, α_0 is the linear absorption coefficient of the sample at the laser excitation wavelength, *L* is the sample thickness, and l_0 is the on-axis irradiance at the focus. The beam waist ω_0 at the Z=0 was 12.6 µm, the parameter Z_0 was 0.94, the pulse repetition rate of the laser was 10 Hz, and the l_0 intensity was 3.11 GW cm⁻². From the nonlinear absorption coefficient, the imaginary part of the third-order nonlinear susceptibility

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was determined using Equation (2):

$$Im\chi^{(3)}(esu) = \frac{c^2 n_0^2 \beta}{240 \, \pi^2 \omega} \tag{2}$$

where *c* is the speed of light in cm s⁻¹, n_0 is the linear refractive index, and $\omega = \frac{2\pi c}{\lambda}$ is the fundamental frequency in cycles s⁻¹.

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