Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

Synthesis, characterization and third-order nonlinear optical behaviour of three novel ethyne-linked donor/acceptor chromophores

Yuehua Yuan^a, Wenfa Zhou^b, Maozhong Tian^{a,*}, Jiangtao Song^a, Yunfeng Bai^a, Feng Feng^{a,**}, Yinglin Song^{b,***}

^a School of Chemistry and Chemical Engineering, Shanxi Datong University, Datong, 037009, China
^b Department of Physics, Harbin Institute of Technology, Harbin, 150001, China

ARTICLE INFO

Keywords: Ethyne-linked chromophores Third-order nonlinear optical properties Z-Scan Transient absorption spectra Excited-state dynamics

ABSTRACT

Three novel ethyne-linked donor/acceptor chromophores, **BAB**, **BAS** and **SAS** were synthesized. The results of **BAB** in femtosecond and nanosecond Z-scan at 532 nm reveal that the transition from saturable absorption (SA) to reverse saturable absorption (RSA), while that of **BAS** and **SAS** display RSA. The femtosecond Z-scan results for all compounds at 600 nm–800 nm indicate the obvious RSA, which can be mainly attributed to the two-photon absorption (TPA). The TA results demonstrate that all compounds display strong excited-state absorption and long lifetime, and the evolution of TA spectra for these compounds reveals the relaxation process from the local excited-state (LE) to charge transfer state (CTS). With different conjugation extent and intramolecular charge transfer (ICT), the nonlinear response and excited-state dynamics of these chromophores could be dramatically modulated. The threshold of **BAS**/DCM solution excited at 532 nm with nanosecond pulse was 0.631 J/cm². The results indicate that these compounds may be the potential candidates for future application in optical limiting.

1. Introduction

Nonlinear optical (NLO) materials have stimulated great enthusiasm of many researchers around the world in recent years owing to their diverse applications in optical switching [1–3], signal processing [4,5], optical communication [6,7], optical sensing [8,9], and optical computing [10,11], and so forth. Compared to their inorganic counterparts, organic materials are more suitable NLO material owing to their fast nonlinear optical responses [12-14], large third-order optical nonlinearities [15-17], their relatively low cost, ease of fabrication, and more flexible to optimize the required nonlinear optical property by altering the functional groups on the organic molecules [18–21]. Thus, nonlinear optical properties in organic systems are under active study [22-27]. It has been found that strong nonlinearities in organic materials usually arise from intensive π -electron delocalization and asymmetric polarizability in this kind of material [28]. In general, the strength of donor and acceptor, nature of the π -conjugated spacers have significant effects on the nonlinear properties of the molecules [29].

Recently π -conjugated molecules bearing the 2,1,3-benzothiadiazole

unit as an intensive acceptor have received great deal of interest because of their high nonlinearities when linked to some donors [30-32]. On the other hand, thiophene is one of the most widely used electron donors for π -conjugated systems due to their electrical properties, environmental stability, and non-linear optical properties [33-35]. Motivated by this, we synthesized three new molecules based on thiophene and 2,1,3-benzothiadiazole, in which the donor moieties consisted of the ((2-ethylhexyl)oxy)benzene and thiophene units, while the benzothiadiazole acted as the electron acceptor. In this paper, three new molecules were fabricated, which can be easily obtained via Sonogashira crosscoupling and protection/deprotection technique of functional groups such as a terminal ethyne. The characterization of three new compounds and their photophysical properties were analyzed. Their nonlinear absorption (NLA) responses were investigated by means of femtosecond and nanosecond open aperture Z-scan. The evolutions of their excited-state dynamics for these compounds were analyzed via the femtosecond transient absorption (TA) measurements. The threshold of BAS/DCM solution was obtained through the optical limiting (OL) experiment. Our results indicate that all compounds are excellent NLO materials and the

https://doi.org/10.1016/j.dyepig.2021.109235

Received 13 December 2020; Received in revised form 3 February 2021; Accepted 9 February 2021 Available online 16 February 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.





^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: tmzhong2002@163.com (M. Tian), feng-feng64@263.net (F. Feng), ylsong@hit.edu.cn (Y. Song).

conjugation extent and/or intramolecular charge transfer (ICT) can modulate their NLO response.

2. Experimental

2.1. Materials and instruments

All reagents were obtained from commercial suppliers, and were of analytical reagent grade, and used without further purification. Solvents were distilled by using standard methods. All reactions were performed under an argon atmosphere. TLC analysis was performed on silica gel plates and flash column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals.

NMR spectra in CDCl₃ solution were recorded on Bruker ARX400 spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C. Tetramethylsilane (TMS) was used as the internal standard and chemical shifts (δ) are given in ppm relative to TMS. Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry was performed on a BrukerBiflex III mass spectrometer. Fluorescence emission spectra were recorded at room temperature with a HITACHI F2500 spectrophotometer with a 1 cm standard quartz cell. UV–vis absorption spectra were obtained on PerkinElmer Lambda 35 UV/Vis spectrophotometer.

2.2. Synthesis and characterization

Compound **1** [36], compound **2** [37], compound **4** [38] and compound **7** [39] were synthesized according to the literature. All physical data agreed with reported literature values.

Synthesis of compound 5. A mixture of compound 2 (3.6 g, 12.5 mmol), toluene (100 mL) and potassium hydroxide (700 mg, 12.5 mmol) was heated under argon in an oil bath held at 110 °C for 30 min. The mixture was allowed to cool to room temperature and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane: light petroleum (1:80) mixtures as eluent to give compound 3 as an oil (2.3 g, 80%). A mixture of compound 3 (1.2 g, 5.0 mmol), compound 4 (1.5 g, 5.0 mmol), Pd(PPh₃)₂Cl₂ (50 mg, 17.4 mmol), and cuprous iodide (25 mg, 0.11 mmol) was suspended in dry tetrahydrofuran (30 mL) and triethylamine (30 mL), and the resulting solution was stirred and heated at 60 °C for 10 h. The solvent was evaporated and the crude product was separated by column chromatography with elution in dichloromethane/light petroleum (1:100) to afford a yellow solid 5 (1.5 g, 70%). ¹H NMR (400 M, CDCl₃, 298K) δ 7.69 (d, J = 7.4 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.87 (d, J = 6.1 Hz, 2H), 3.01 (s, 1H), 1.68-1.78 (s, 7H), 1.55-1.38 (m, 4H), 1.28-1.36 (m, 4H), 1.00-0.86 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ160.3, 154.5, 154.4, 133.6, 132.7, 131.9, 117.9, 116.1, 114.8, 114.3, 102.0, 98.2, 84.2, 78.2, 70.8, 65.8, 39.4, 31.5, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. MALDI-TOF Calcd for C27H30N2O2S [M] 446.2028; Found 446.2034.

Synthesis of compound **6**. A mixture of compound **5** (1.2 g, 2.7 mmol), toluene (50 mL) and potassium hydroxide (151.2 mg, 2.7 mmol) was heated under argon in an oil bath held at 110 °C for 30 min. The mixture was allowed to cool to room temperature and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane: light petroleum (1:60) mixtures as eluent to give **6** as a light brown oil (873 mg, 87%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.87 (d, *J* = 6.0 Hz, 2H), 3.66 (s, 1H), 1.72–1.75 (m, 1H), 1.56–1.38 (m, 4H), 1.38–1.23 (m, 4H), 0.89–0.95 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 160.4, 154.7, 154.3, 133.7, 131.7, 118.8, 115.3, 114.8, 114.2, 98.6, 84.8, 84.1, 79.4, 70.8, 39.4, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. MALDI-TOF Calcd for C₂₄H₂₄N₂OS [M] 388.1609; Found 388.1603.

Synthesis of compound 9. A mixture of 2-(trimethylsilyl)ethynyl-5-

bromothiophene (1.29 g, 5.0 mmol), compound 3 (1.2 g, 5.0 mmol), Pd (PPh₃)₂Cl₂ (50 mg, 17.4 mmol), and cuprous iodide (25 mg, 0.11 mmol) was suspended in dry tetrahydrofuran (30 mL) and triethylamine (30 mL), and the resulting solution was stirred and heated at 60 °C for 10 h. The solvent was evaporated and the crude product chromatographed directly with dichloromethane: light petroleum (1:80), affording a yellow solid 8 (1.43 g, 73%). To a solution of compound 8 (1.43 g, 3.6 mmol) in the mixture of THF and methanol was added 497 mg of K₂CO₃. The reaction mixture was stirred for 1 h at room temperature and the solvent and K₂CO₃ were removed. The residue was purified by column chromatography over silica using dichloromethane: light petroleum (1:80) mixtures as eluent to give compound 9 (956 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 3.8 Hz, 1H), 7.08 (d, J = 3.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 3.97–3.77 (m, 2H), 3.38 (s, 1H), 1.75 (m, 1H), 1.58-1.39 (m, 4H), 1.38-1.31 (m, 4H), 0.95–0.91 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 133.1, 133.1, 131.0, 125.8, 122.7, 114.8, 114.2, 94.4, 82.1, 80.8, 77.5, 70.7, 39.4, 30.6, 29.2, 23.9, 23.2, 14.2, 11.2. MALDI-TOF Calcd for C22H24OS [M] 336.1548; Found 336.1544.

Synthesis of compound BAB. A mixture of compound 6 (400 mg, 1.03 mol), PdCl₂(PPh₃)₂ (30 mg, 0.042 mmol) and CuI (15 mg, 0.079 mmol) was suspended in dry tetrahydrofuran (20 mL) and triethylamine (20 mL). The resulting mixture was stirred for 8 h and worked up. The solvent was evaporated and the crude product was purified by column chromatography over silica using light petroleum:EtOAc (10:1) mixtures as eluent to give pure **BAB** as a red solid (263 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.4 Hz, 2H), 7.74 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 8.6 Hz, 4H), 6.92 (d, J = 8.6 Hz, 4H), 3.89 (d, J = 5.8 Hz, 4H), 1.74 (dd, J = 12.0, 5.8 Hz, 2H), 1.57–1.38 (m, 8H), 1.36–1.33 (m, 8H), 0.96–0.90 (m, 12H). 13 C NMR (100 MHz, CDCl₃) δ 160.5, 154.8, 154.4, 134.5, 133.8, 131.8, 119.4, 114.9, 114.2, 99.6, 84.5, 81.30, 80.5, 70.8, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.2. FT-IR (thin film on KCl, cm⁻¹): 3444, 2963, 2926, 2856, 2195, 1598, 1535, 1510, 1460, 1365, 1290, 1251, 1162, 1030, 886, 827, 631, 536. MALDI-TOF Calcd for C48H46N4O2S2, [M] 774.3062; found 774.3063.

Synthesis of compound BAS. To a solution of compound 6 (400 mg, 1.03 mmol) in acetone (20 mL) was added NBS (195 mg, 1.1 mmol) and AgNO₃ (30 mg, 0.18 mmol) at room temperature with magnetic stirring. After 2 h, the reaction mixture was diluted with hexanes (20 mL) and filtered off the crystals formed. The filtrate was concentrated under reduced pressure and passed through a pad of silica gel using hexane as an eluent. The filtrate was collected and evaporated under reduced pressure to afford a pure compound 10 (393 mg, 82%). To a stirred solution of compound 10 (300 mg, 0.64 mmol) and compound 9 (215 mg, 0.64 mmol) in tetrahydrofuran (20 mL) and Et₃N (20 mL) were added PdCl₂(PPh₃)₂ (30 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol) under an argon flow at room temperature. The solution was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the mixture was purified by column chromatography over silica with light petroleum:EtOAc (6:1) mixtures as eluent to obtain pure **BAS** as a brown solid (133 mg, 29%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.8 Hz, 4H), 7.24 (d, *J* = 3.8 Hz, 2H), 7.11 (d, *J* = 3.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 4H), 3.87 (d, J = 5.9 Hz, 4H), 1.81–1.75 (m, 2H), 1.57–1.39 (m, 16H), 1.02–0.99 (m, 12H). $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) δ 160.4, 160.0, 154.7, 154.3, 134.7, 133.9, 133.6, 133.1, 131.7, 131.2, 127.4, 122.1, 119.0, 114.9, 114.7, 114.1, 114.0, 99.4, 95.4, 84.3, 81.2, 80.7, 79.9, 78.7, 77.8, 70.7, 39.3, 30.5, 29.1, 23.9, 23.0, 14.1, 11.1. FT-IR (thin film on KCl, cm⁻¹): 3444, 3083, 3038, 2964, 2926, 2856, 2540, 2209, 2142, 1889, 1787, 1604, 1567, 1529, 1501, 1460, 1388, 1295, 1251, 1174, 1141, 1105, 1036, 998, 833, 732, 682, 612, 534. MALDI-TOF Calcd for C₄₆H₄₆N₂O₂S₂, [M] 722.3001; found 722.3001.

Synthesis of compound **SAS**. A mixture of compound **9** (400 mg, 1.19 mmol), $PdCl_2(PPh_3)_2$ (30 mg, 0.042 mmol) and CuI (15 mg, 0.079 mmol) was suspended in dry tetrahydrofuran (20 mL) and triethylamine (20 mL). The resulting mixture was stirred for 8 h and worked up. The solvent was evaporated and the crude product was purified by column



Scheme 1. Synthesis of intermediates. Reagents and conditions: (a) K₂CO₃, ACN, 2-ethyl-1-bromohexane, reflux, 91% yield; (b), (d) 2-methylbut-3-yn-2-ol, PdCl₂(PPh₃)₂, THF/Et₃N, CuI. Compound **2**: 53% yield. Compound **4**: 35% yield; (c) and (f) KOH, toluene, reflux. Compound **3**: 80% yield. Compound **6**: 87% yield; (e) PdCl₂(PPh₃)₂, THF/Et₃N, CuI, 70% yield.

chromatography over silica using light petroleum:EtOAc (8:1) mixtures as eluent to offer pure **SAS** as a yellow green solid (313 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.7 Hz, 4H), 7.21 (d, J = 3.8 Hz, 2H), 7.08 (d, J = 3.8 Hz, 2H), 6.87 (d, J = 8.7 Hz, 4H), 3.86 (d, J = 5.8 Hz, 4H), 1.76–1.70 (m, 2H), 1.56–1.24 (m, 16H), 1.01–0.80 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 134.5, 133.1, 131.2, 127.1, 122.3, 114.7, 114.0, 95.3, 80.8, 78.6, 70.7, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1. FT-IR (thin film on KCl, cm⁻¹): 3437, 3096, 2952, 2926, 2856, 2540, 2206, 2135, 1889, 1781, 1604, 1566, 1522, 1503, 1383, 1295, 1250, 1174, 1143, 1104, 1029, 998, 833, 801, 732, 682, 612, 543. MALDI-TOF Calcd for C₄₄H₄₆O₂S₂, [M] 670.2939; found 670.2944.

2.3. Nonlinear optical experiments

The NLAs were measured by open aperture Z-scan method [40] with multiple laser sources: an optical parametric amplifier (OPA, Light Conversion, ORPHEUS) pumped by a mode-locked Yb: KGW-based fiber laser (1030 nm, 190 fs, 20 Hz). The excitation wavelengths were tuned from 532 nm to 800 nm 4 ns (FWHM) pulse of 532 nm were extracted from a Q-switched Nd: YAG laser (Surelite II, Continuum). The low repetition rate (10 Hz in nanosecond pulse) can effectively eliminate the influence of thermally induced nonlinearities. The spatial and temporal distributions of the pulses were all nearly Gaussian profiles. These compounds dissolved in dichloromethane (DCM) solvent were contained in 2 mm quartz cell for measurement, respectively. The concentration of BAS/DCM and SAS/DCM was 6.92 \times 10^{-4} mol/L and 7.45 \times 10^{-4} mol/L, respectively, while that of BAB/DCM was 3.23 \times 10^{-4} mol/L. The experimental setup used for OL measurement was same as that for Z-scan. The sample with concentration of 3.46×10^{-4} mol/L in 5 mm quartz cell was placed at focus position for measurement. The linear transmittance of BAS/DCM in OL experiment was 72%.

Since the TA spectrum experiment records the evolution of absorptive spectrum of samples within 1.7 ns delay time after excitation, the ultrafast relaxing processes of the samples could be revealed. The laser source used in this experiment is same as that used in femtosecond openaperture Z-scan. A supercontinuum white light generating from fundamental frequency (1030 nm) passing through sapphire crystal was used as probe beam while the output wavelength from OPA was used as pump beam. The repetition rate of laser pulse was 6 kHz. The instrument response function was estimated to be around 250 fs. The wavelength of pump beam was tuned to 400 nm.2.4. *DFT calculation*.

All the density functional theory (DFT) calculations were performed with the Gaussian 16 program [41] package with Becke's three-parameter hybrid functional and Lee-Yang-Part's gradient corrected correlation functional (B3LYP) level of theory using the 6-311G basis set.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes of intermediates and target compounds are shown in Schemes 1 and Scheme 2. Sonogashira crosscoupling were carried out to offer **BAB**, **BAS**, and **SAS** in a yield of 66%, 29%, 79%, respectively (see Experimental section for details). These new compounds were characterized by the ¹H NMR, ¹³C NMR (see Supplementary data) and mass spectrometry.

3.2. Photophysical properties

The UV–vis absorption and fluorescence emission spectra of **BAB**, **BAS** and **SAS** are shown in Fig. 1 (a) and (b), respectively. The concentration of compounds **BAB**, **BAS** and **SAS** are all fixed at 1×10^{-6} mol/L in DCM. As depicted in Fig. 1 (a), the main absorption peaks of **BAB** are located at 315 and 462 nm, respectively. The **BAS** exhibited three distinct absorption peaks in the range of 301–338, 338–396 and 396–540 nm. Wherein higher energy peaks observed at 315 nm for **BAB** and at 328 and 358 nm for **BAS**, correspond to the π – π * electronic transitions in the molecules, while a band at lower energy region (358–552 nm) for **BAB** and a band (396–540 nm) for **BAS** correspond to the ICT, leading to the extension of π –conjugation. In the case of molecule **SAS** the observed peak at 392 nm could be attributed to π – π * electronic excitations.

As shown in Fig. 1 (b), the fluorescence spectra of **BAB**, **BAS** and **SAS** showed emission bands at about 534 nm, 558 nm and 530 nm respectively when they were selectively excited at 460 nm, and the peak of the spectrum of **BAS** also has a red shift compared with that of **SAS** corresponding the UV–vis absorption spectrum of them.



Scheme 2. Synthesis of compounds BAB, BAS and SAS. Reagents and conditions: (a) PdCl₂(PPh₃)₂, trimethylsilylacetylene, Et₃N, CuI, 29% yield; (b) Compound 3, PdCl₂(PPh₃)₂, Et₃N, CuI, 73% yield; (c) K₂CO₃, MeOH/THF, 78% yield; (d) NBS, AgNO₃ and acetone, 82% yield; (e), (f), (g) PdCl₂(PPh₃)₂, Et₃N, CuI. **BAB**: 66% yield, **BAS**: 29% yield, **SAS**: 79% yield.

3.3. Femtosecond open aperture Z-scan and transient absorption spectrum

Femtosecond open aperture Z-scan was conducted to investigate the ultrafast NLA of three compounds. The excitation wavelengths were tuned from 532 nm to 800 nm. The linear transmittances for **BAS** and **BAB** at 532 nm are 72% and 73%, respectively, while they exhibit high linear transmittance (**BAS** \geq 97%, **BAB** \geq 97%) at 600 nm–800 nm. **SAS** displays high linear transmittance (**SAS** \geq 98%) at all measurement wavelengths. It is widely known that when sample excited by laser pulses displays a unimodal curve with its peak locates at zero position (focus point), it means the transmittance of the sample increases when

the input intensity increases. This phenomenon is commonly referred to as the saturable absorption (SA). On the contrary, when sample excited by laser pulses displays a unimodal curve with its valley locates at zero position (focus point), it means the transmittance of the sample decreases when the input intensity increases. This phenomenon is commonly referred to as the reverse saturable absorption (RSA). The observed NLA of compounds was evaluated to originate from the solution molecule because the pure solvent displayed no NLA in the experimental conditions.

The experimental results of 532 nm for three compounds are discussed first, as shown in Fig. 2. With the increase of input intensity, it



Fig. 1. (a) UV–Vis absorption spectra of compounds BAB, BAS and SAS in DCM. (b) The fluorescence spectra of compounds BAB, BAS and SAS in DCM. [BAB] = [BAS] = [SAS] = 1 \mu M.



Fig. 2. Open aperture Z-scan curves of BAB/DCM (a), BAS/DCM (b) and SAS/DCM (c) at 532 nm under 190 fs excitation. The circles are the experimental results. The solid lines are the theoretical fitting curves.

Table 1	
Parameters of femtosecond open-aperture Z-scan experiments at 532 nm.	

Sample	Wavelength (nm)	I_0 (GW/cm ²)	$I_{\rm s}$ (GW/cm ²)	$\alpha_2(10^{-2} \text{ cm/GW})$
BAB	532	$\begin{array}{c} 4.05 \pm 0.42 \\ 20.2 \pm 1.5 \\ 40.5 \pm 2.1 \end{array}$	$\textbf{6.1} \pm \textbf{0.4}$	$0 \\ 12.8 \pm 1.3 \\ 12.2 \pm 1.1$
BAS		40.5 ± 2.1 20.2 ± 1.5 40.5 ± 2.1	/	13.2 ± 1.1 7.42 ± 0.63 8.16 ± 0.79
SAS		$\begin{array}{c} 20.2\pm1.5\\ 40.5\pm2.1 \end{array}$	/	$\begin{array}{c} 5.34 \pm 0.54 \\ 6.74 \pm 0.65 \end{array}$

can be seen that the NLA of **SAS** and **BAS** display RSA while the NLA of **BAB** exhibits the characteristic of transforming from SA to RSA. When excited by femtosecond pulse, two-photon absorption (TPA) and excited-state absorption (ESA) are commonly mentioned as the causes of

RSA. When excited at 532 nm (2.33 eV), electrons in the ground state will be excited to the excited state. The transition energies (between S_0 and S_1) of the three compounds (**BAB**, **BAS**, **SAS**) were calculated to be 2.275, 2.271, and 2.64 eV. Hence, we consider that TPA is the main mechanism for **SAS** at 532 nm. However, since 532 nm locates at the edge of the absorption band of **BAB** and **BAS** (see UV–Vis), one-photon induced excited-state absorption is considered as the mechanism of nonlinear absorption for them. The transition from SA to RSA of **BAB**/DCM could be modeled via saturable intensity (I_s) and effective nonlinear absorptive coefficient (α_2), respectively [42]. The total absorption (α) of the sample could be expressed as:

$$\alpha = \alpha_0 \frac{1}{1 + I/I_s} + \alpha_2 I$$

Where α_0 represents linear absorptive coefficient and *I* is the input



Fig. 3. Z-scan open aperture curves of BAB/DCM (a), BAS/DCM (b) and SAS/DCM (c) at various wavelengths under 190 fs excitation. The circles are the experimental data. The solid lines are the theoretical fitting.

Table 2

Parameters of NLA at different wavelengths extracted from femtosecond openaperture Z-scan.

Wavelength	I0 (GW/	BAB	BAS	SAS
(nm)	cm²)	$\alpha_2(10^{-2} \text{ cm/})$ GW)	$a_2(10^{-2} \text{ cm/} \text{GW})$	$\alpha_2(10^{-2} \text{ cm/})$ GW)
600	$\begin{array}{c} 47.8 \pm \\ 2.6 \end{array}$	$\textbf{3.92} \pm \textbf{0.36}$	$\textbf{3.28} \pm \textbf{0.29}$	1.93 ± 0.18
	$\begin{array}{c} 63.7 \pm \\ 3.3 \end{array}$	$\textbf{4.74} \pm \textbf{0.49}$	3.86 ± 0.37	$\textbf{2.33} \pm \textbf{0.22}$
700	$\begin{array}{c} 46.8 \pm \\ 2.4 \end{array}$	1.52 ± 0.16	1.33 ± 0.15	1.45 + 0.17
	$\begin{array}{c} 70.2 \pm \\ 3.5 \end{array}$	1.94 ± 0.19	1.84 ± 0.18	1.77 ± 0.19
800	$\begin{array}{c} 53.7 \pm \\ 2.7 \end{array}$	1.86 ± 0.18	1.58 ± 0.17	/
	$\begin{array}{c} 71.6 \pm \\ 3.5 \end{array}$	2.01 ± 0.22	1.64 ± 0.16	/

intensity. The results of **BAS**/DCM and **BAB**/DCM can be fitted by Sheik Bahae's theory [40]. The numerical fitting results of open aperture Z-scan at 532 nm are list in Table 1.

As shown in Fig. 3, all compounds exhibit obvious RSA at 600 nm–800 nm. The photon energies of excitation were calculated to be 2.067, 1.771, and 1.55 eV, respectively. Electrons in the ground state will be excited to the excited state, which has the closest energy when simultaneously absorbing two or more photons. The transition energies (between S_0 and S_1) of the three compounds (**BAB**, **BAS**, **SAS**) were calculated to be 2.275, 2.271, and 2.695 eV, respectively. So, it can be confirmed that TPA dominates the RSA at 600–800 nm. In addition, high

linear transmittance was measured at 600 nm–800 nm and the femtosecond laser pulse was used as light source. As such, the measured NLA is mainly related to TPA. The experimental results are fitted by Sheik Bahae's theory [40]. The parameters are summarized in Table 2. The experimental error was about 10%.

It is known that organic molecules may exhibit both TPA and TPA induced ESA processes under off-resonant excitation [43,44]. Herein, the TA measurement was conducted to further interpret the TA dynamic changes of the molecules under femtosecond laser excitation. The evolution associated difference spectra (EADS) for compounds are plotted in Fig. 4. The changes in the absorption intensity at specific wavelengths obtained from transient absorption spectra experiments are represented by changes in optical density (Δ OD), which can be expressed as follows:

$\Delta OD = -\lg(T/T_0)$

Here, *T* is the transmittance of the sample after pumping, and T_0 is the linear transmittance of the sample. The positive signal represents RSA, and the negative signal represents SA. For **BAB**/DCM (Fig. 4(a)& (d)), two signal bands appear near the zero delay, namely, a negative signal band centered at 500 nm and a positive signal band between 560 nm and 755 nm. Then the amplitude of spectra gradually increases. The positive signal reaches its maximum value near 0.5 ps. The absorption spectrum evolves into a negative signal band of 470 nm–595 nm and a positive signal band of 595 nm–755 nm. As the delay time become longer , The amplitude of the positive signal band of the absorption spectrum decreases while the amplitude of the negative signal band increases. In addition, the absorption bands exhibit the red shift. After more than a dozen of picosecond, the spectrum evolves into a negative signal band in the range



Fig. 4. The TA spectrum of (a) BAB/DCM, (b) BAS/DCM and (c) SAS/DCM. Several absorptive spectra of (d) BAB/DCM, (e) BAS/DCM and (f) SAS/DCM at selected delay time are displayed.

Y. Yuan et al.



Fig. 5. The kinetic traces of several selected wavelengths for (a) BAB/DCM, (b) BAS/DCM and (c) SAS/DCM following femtosecond laser excitation at 400 nm. Inset graphs show early stage dynamics of the same (within the first 20 ps). Circles are experimental data. The solid lines represent theoretical fitting.

from 625 nm to 755 nm. Finally , the amplitude of spectra for BAB/ DCM attenuated according to this waveform. The negative signal band ranging from 470 nm to 625 nm can be attributed to ground state bleaching (centering at 470 nm) and stimulated emission (SE) (centering at 560 nm). The evolution processes of the absorption spectra for BAB/ DCM show that the particles under photoexcitation have different relaxation processes. Through global analysis [45] (see Fig. 5(a)), we obtain four dynamic processes and the lifetimes are about 0.25 ps. 2.1 ps, ~587.8 ps and ~7.8 ns, respectively. As will be discussed below regarding the quantum chemical calculations, the HOMO-LUMO transitions of all molecules are clearly accompanied by ICT, which is expected to activate the NLO response. We consider that the optical nonlinearity originates from the layout of the excited-state particles to the charge-transfer state (CTS) [46]. The first content is unable to be distinguished as the time resolution of our experiment is 0.25 ps. So we assign the ultrafast process of 0.25 ps to the internal conversion in the local excited state (LE). The next component with a 2.1 ps lifetime corresponds to the vibrational relaxation of LE. The last two lifetimes are the ICT process of particles from LE to the CTS (~587.8 ps) and the process of relaxation from CTS to the ground state (~7.8 ns).

For **BAS**/DCM(Fig. 4(b)&(e)), a negative signal band centered at 480 nm and a positive signal band centered at 650 nm appear near zero delay. Then the amplitude of the absorption spectrum gradually increases, and the absorption peak displays red-shifted. The amplitude of the absorption spectrum reaches the maximum near 0.5 ps. The absorption spectrum evolves into a negative signal band in the range from 470 nm to 585 nm and a positive signal in the range from 585 nm to 755

nm band. After that, the amplitude of spectra for BAS/DCM attenuated according to this waveform. After dozens of picoseconds, it evolves into a negative signal band in the range of 470 nm-495 nm and a positive signal band centered at 520 nm, 610 nm and greater than 755 nm, respectively. As the increase of delay time, the amplitude of the absorption spectrum gradually increases. The absorption spectrum evolves into a negative signal band of 470 nm-495 nm and a positive signal band centered at 590 nm near 1700 ps. Due to the limitation of experimental conditions, the change of absorption spectrum with a delay time greater than 1700 ps cannot be accurately measured. The spectral changes of BAS/DCM mean that ESA does not originated from the same excitedstate [47,48]. The negative signal before 500 nm can be owing to ground state bleaching while the generation and disappearance of the negative signal ranging from 500 nm to 590 nm could be caused by the combination of SE and ESA. Through global analysis (see Fig. 5(b)), we obtain four similar dynamic processes and the lifetimes are about 0.25 ps, 5.6 ps, ~956.8 ps and ~12 ns, respectively.

For **SAS**/DCM (As shown in Fig. 4(c)&(f)), a negative signal band of 470 nm–500 nm and a positive signal band of 500 nm–755 nm appear near zero delay time. As the delay time increases, the amplitude of the absorption spectrum gradually increases. Near 0.3 ps, the amplitude of absorption spectrum is stable, which evolved into a negative signal band centered at 485 nm and a positive signal band centered at 745 nm. The amplitude of spectra for **SAS** attenuated according to this waveform. But the spectral form changes after dozens of picoseconds, evolving into a positive signal band centered at 675 nm and 745 nm while the negative signal band gradually weakens. The absorption peak of positive signal



Fig. 6. Open aperture Z-scan curves of BAB/DCM (a), BAS/DCM (b) and SAS/DCM (c) at 532 nm under 4 ns excitation. The circles are the experimental data. The solid lines are the theoretical fitting.

Table 3 Open aperture Z-scan data of 4 ns for BAB/DCM, BAS/DCM and SAS/DCM solutions.

Sample	Wavelength (nm)	$I_0 (10^{-2} \text{ GW}/\text{cm}^2)$	$I_{\rm s}~(10^{-2}~{\rm GW}/{\rm cm}^2)$	$\alpha_2(10^2 \text{ cm}/\text{GW})$
BAB	532	1.4 ± 0.20	1.6 ± 0.3	0
		26.5 ± 2.12		0.323 ± 0.33
BAS		1.4 ± 0.20	/	3.68 ± 0.52
		26.5 ± 2.12		$\textbf{2.42} \pm \textbf{0.25}$
SAS		$\textbf{26.5} \pm \textbf{2.12}$	/	/

band stabilizes at 670 nm near 100 ps, and the negative signal band disappears. Finally, the amplitude of spectra for SAS/DCM attenuated according to this waveform. Similarly, the generation and disappearance of the negative signal is caused by the combination of ground state bleaching and ESA. Through global analysis (see Fig. 5 (c)), four similar dynamic processes are obtained and the lifetimes are about 0.25 ps, 1.3 ps, ~40.5 ps and ~5.8 ns, respectively. Unlike BAB/DCM and BAS/DCM, there is no SE in the TA spectrum of SAS/DCM, and the intensity of ESA of ASA/DCM is greater than that of BAB/DCM and BAS/DCM in the visible range. However, the lifetime of excited-state for BAS/DCM is the longest among the three samples. Obviously, the results of TA spectra for three derivatives imply that the excited-state relaxation processes change dramatically with the molecule structure change, which may be

relevant to the conjugation extent and ICT.

3.4. Nanosecond open aperture Z-scan

To investigate the NLO properties about three samples under different pulse excitation, we perform Z-scan experiments using 4 ns laser pulses at 532 nm to evaluate the NLA response of three compounds. The Z-scan curves of the three compounds at different incident intensities are shown in Fig. 6. The results of nonlinear absorption parameters measured are summarized in Table 3. It can be seen that there is no obvious response found in Z-scan for SAS/DCM under 4 ns experiments indicates neglectable nonlinear absorption at 532 nm while the NLA of BAB/DCM display the transition from SA to RSA and that of BAS/DCM exhibit RSA. As discussed in femtosecond Z-scan, the mechanism of RSA for BAB/DCM and BAS/DCM was one-photon induced excited-state absorption while that for SAS/DCM was mainly TPA. When excited with nanosecond laser, ground state electrons are continuously promoted to excited state during the nanoseconds laser pulse, more electrons are maintained in excited-state comparing to femtosecond case, thereby ESA is enhanced. It should be noted that TPA needs certain intensity to occur, which may be the reasonable explanation that SAS/ DCM has no obvious nonlinear response. Since the samples used in experiments are solutions and the solution is uniformly distributed as well as the molecules are chaotic, they have no directionality. Under the excitation of low repetition (10 Hz) laser without external force (such as



Fig. 7. DFT optimized structure and distribution of frontier molecular orbitals in BAB, BAB and SAS (in the ball-and-stick representation, carbon, oxygen, nitrogen and sulfur atoms are colored in gray, red, blue and yellow, respectively).



Fig. 8. The OL performance of **BAS**/DCM as the function of the input fluence at 532 nm with nanosecond excitation.

a magnetic field, electric field, etc), the orientation of the molecule cannot be induced. As the result, the contribution of thermal effect can be neglected in the above results.

3.5. Quantum chemical calculation

In order to obtain further insight into the differences of the photophysical properties of compounds **BAB**, **BAS** and **SAS**, quantum chemical calculation of density functional theory (DFT) at b3lyp/6–311+g(d, p) level has been performed for them. The frontier molecular orbitals distributions along with optimized structures of **BAB**, **BAS** and **SAS** were displayed in Fig. 7.

Obviously, the distribution of the highest occupied molecular orbital (HOMO) is highly localized on the molecular backbone connected by the alkyne group for three compounds, while that of lowest unoccupied molecular orbital (LUMO) is mainly drifted toward the benzothiazole moiety for **BAB** and **BAS**, and drifted toward the thiophene for **SAS**. This reflects that the ICT comes from the ((2-ethylhexyl)oxy)benzene subunit to benzothiazole one via the alkyne bridge. The HOMO-LUMO gap (2.29 eV) of compound **BAB** and that (2.33 eV) of compound **BAB** and BAS exhibit larger conjugation extent than **SAS**. The charge-transfer interactions between donor and acceptor moieties are relatively strong and has higher hyperpolarizabilities [13]. This is consistent with the above Z-Scan experimental results and interprets that the remarkable NLO responses under photoexcitation may be related to the conjugation extent and the excited absorption from charge transfer for **BAB** and **BAS**.

3.6. Optical limiting

From above analysis, **BAS**/DCM exhibits superior RSA in nanosecond pulse, which means it may display excellent OL response. To evaluate the OL property of **BAS**/DCM, its OL experiments was conducted under the excitation of nanosecond pulse. Fig. 8 displays the variation of the transmittance of **BAS**/DCM as a function of the input laser fluence at excitation wavelength of 532 nm, and the transmittance of **BAS**/DCM decrease with increasing input fluence. The threshold of OL defined as the input fluence when the transmittance decreases to half of the initial value is one of properties of the materials. The OL threshold of **BAS**/DCM is 0.631 J/cm², which is superior to reported materials [49–51]. The results are summarized in Table 4. Based on analysis in Z-scan, the OL property of **BAS**/DCM can be attributed to one-photon induced

Table 4

Comparison with rep	orted optical	limiting materials.
---------------------	---------------	---------------------

Sample	Pulse	Wavelength (nm)	T ₀ (%)	Threshold (J/cm ²)	Ref.
BAS/DCM	4 ns	532	72	0.631	This work
0.2 wt% c-dot doped LC	7 ns	532	-	1.23	49
GO with silver NPs	5 ns	532	-	1.56	50
H-shaped Thiophene-based oligomers	7 ns	532	70–74	>3.14	51

excited-state absorption.

4. Conclusions

In summary, three ethyne-linked donor/acceptor compounds, **BAB**, **BAS** and **SAS**, were designed and synthesized based on the large nonlinear response of chromophores and the effective electron transfer of structure. Their third-order nonlinear optical properties were investigated using Z-scan technique and transient absorption spectra at femtosecond regime. Results show that the NLA of **BAB** exhibits the characteristic of transforming from SA to RSA , while that of **SAS** and **BAS** only display RSA. The excited-state relaxation processes change dramatically with the molecule structure change, which may be relevant to the conjugation extent and ICT. In nanosecond pulse, the threshold of BAS/DCM was 0.631 J/cm². These results illustrate that these chromophores may be potential candidates for future application in optical limiting.

Author statement

Under supervision by Maozhong Tian, Yinglin Song, and Feng Feng, Yuehua Yuan, Jiangtao Song and Maozhong Tian performed the synthesis of all compounds and data analysis. Wenfa Zhou and Yinglin Song investigated nonlinear optical (NLO) properties of three compounds and analysis. Yunfeng Bai performed UV–vis absorption and fluorescence emission spectra. Feng Feng performed *DFT* calculation. All authors read and contributed to the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank the financial support of 1331 project of Shanxi Province, the Applied basic Research Program of Shanxi Province (No.201801D121039), Key Research and Development Project of Datong (No. 2019019), the Science Research Foundation of Shanxi Datong University (No.2018K1). Research topic of postgraduate education reform (No.2020YJJ299 for Shanxi Province, 20JG03 for Shanxi Datong University).

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109235.

References

 Biswal BP, Valligatla S, Wang M, Banerjee T, Saad NA, Mariserla BMK, et al. Nonlinear optical switching in regioregular porphyrin covalent organic frameworks. Angew Chem Int Ed 2019;58(21):6896–900.

Y. Yuan et al.

- [2] Hansel M, Barta C, Rietze C, Utecht M, Ruck-Braun K, Saalfrank P, et al. Twodimensional nonlinear optical switching materials: molecular engineering toward high nonlinear optical contrasts. J Phys Chem C 2018;122(44):25555–64.
- [3] Zhai YL, Xu WJ, Meng XR, Hou HW. Adjusting the third-order nonlinear optical switch performance based on azobenzene derivatives. Hua Hsueh Hsueh Pao 2020; 78(3):256–62.
- [4] Song YF, Chen YX, Jiang XT, Liang WY, Wang K, Liang ZM, et al. Nonlinear fewlayer antimonene-based all-optical signal processing: ultrafast optical switching and high-speed wavelength conversion. Adv Opt Mater 2018;6(13).
- [5] Wang J, Hu X. Recent advances in graphene-assisted nonlinear optical signal processing. J Nanotechnol 2016:1–18.
- [6] Gaiarin S, Perego AM, da Silva EP, Da Ros F, Zibar D. Dual-polarization nonlinear Fourier transform-based optical communication system. Optica 2018;5(3):263–70.
 [7] Zhao ZH, Xin HY, Liu T. Nonlinear effect measurement based on high-speed optical
- transmission communication system. Microw Opt Technol Lett 2020;62(4):1471–6. [8] Felscia UR, Rajkumar BJM, Sankar P, Philip R, Mary MB. Theoretical and
- experimental investigations of nitropyrene on silver for nonlinear optical and metal ion sensing applications. Mater Chem Phys 2020:243.
- [9] Ray PC. Size and shape dependent second order nonlinear optical properties of nanomaterials and their application in biological and chemical sensing. Chem Rev 2010;110(9):5332–65.
- [10] Rashed ANZ, Mohammed AA, Zaky WF, Amiri IS, Yupapin P. The switching of optoelectronics to full optical computing operations based on nonlinear metamaterials. Results Phys 2019;13:102152.
- [11] Smolyaninov II. Nonlinear optics of photonic hyper-crystals: optical limiting and hyper-computing. J Opt Soc Am B 2019;36(6):1629–36.
- [12] Ashcroft CM, Cole JM, Boardman EA, Lin TC, Perez-Moreno J, Clays K. Molecular origins of the nonlinear optical responses of a series of alpha-(X-2-Pyridylamino)-ocresol chromophores from concerted X-ray diffraction, hyper-Rayleigh scattering, and ab lnitio calculations. J Phys Chem C 2019;123(1):665–76.
- [13] Wen LF, Fang Y, Yang JY, Han YB, Song YL. Third-order nonlinear optical properties and ultrafast excited-state dynamics of benzothiazolium salts: transition in absorption and refraction under different time regimesl. Dyes Pigments 2018; 156:26–32.
- [14] Xiao ZG, Ge JF, Sun R, Fang Y, She YC, Li ZG, et al. Impact of electronegative character on ultrafast nonlinear optical absorption of azine derivatives. Opt Mater 2018;83:300–5.
- [15] Vinaya PP, Prabhu AN, Bhat KS, Upadhyaya V. Synthesis, growth and characterization of a long-chain pi-conjugation based methoxy chalcone derivative single crystal; a third order nonlinear optical material for optical limiting applications. Opt Mater 2019;89:419–29.
- [16] Zongo S, Sanusi K, Britton J, Mthunzi P, Nyokong T, Maaza M, et al. Nonlinear optical properties of natural laccaic acid dye studied using Z-scan technique. Opt Mater 2015;46:270–5.
- [17] Iliopoulos K, Czaplicki R, El Ouazzani H, Balandier JY, Chas M, Goeb S, et al. Physical origin of the third order nonlinear optical response of orthogonal pyrrolotetrathiafulvalene derivatives. Appl Phys Lett 2010;97(10):101104 (1-3).
- [18] Bredas JL, Adant C, Tackx P, Persoons A, Pierce BM. 3rd-order nonlinear-optical response in organic materials-theoretical and experimental aspects. Chem Rev 1994;94(1):243–78.
- [19] Iliopoulos K, Guezguez I, Kerasidou AP, El-Ghayoury A, Branzea D, Nita G, et al. Effect of metal cation complexation on the nonlinear optical response of an electroactive bisiminopyridine ligand. Dyes Pigments 2014;101:229–33.
- [20] Kulyk B, Waszkowska K, Busseau A, Villegas C, Hudhomme P, Dabos-Seignon S, et al. Penta(zinc porphyrin)[60]fullerenes: strong reverse saturable absorption for optical limiting applications. Appl Surf Sci 2020;533:147468.
- [21] Kulyk B, Guichaoua D, Ayadi A, El-Ghayoury A, Sahraoui B. Functionalized azobased iminopyridine rhenium complexes for nonlinear optical performance. Dyes Pigments 2017;145:256–62.
- [22] Jiang D, Chen SH, Xue Z, Li YJ, Liu HB, Yang WS, et al. Donor-acceptor molecules based on benzothiadiazole: synthesis, X-ray crystal structures, linear and thirdorder nonlinear optical properties. Dyes Pigments 2016;125:100–5.
- [23] Samal M, Valligatla S, Saad NA, Rao MV, Rao DN, Sahu R, et al. A thiazolo 5,4d thiazole-bridged porphyrin organic framework as a promising nonlinear optical material. Chem Commun 2019;55(74):11025–8.
- [24] Karthick S, Thirupugalmani K, Krishnakumar M, Kannan V, Vinitha G, Brahadeeswaran S. Synthesis, structural, dielectric, laser damage threshold, third order nonlinear optical and quantum chemical investigations on a novel organic crystalline material: pyrrolidin-1-ium 2-chloro-4-nitrobenzoate 2-chloro-4nitrobenzoic acid for opto-electronic applications. Optic Laser Technol 2020;122: 105849.
- [25] Thirumurugan R, Babu B, Anitha K, Chandrasekaran J. Synthesis, growth, characterization and quantum chemical investigations of a promising organic nonlinear optical material: thiourea-glutaric acid. J Mol Struct 2018;1171:915–25.

- [26] Suresh A, Manikandan N, Jauhar RM, Murugakoothan P, Vinitha G. Growth and characterizaion of urea p-nitrophenol crystal: an organic nonlinear optical material for optoelectronic device application. Appl Phys A-Mater 2018;124(6):419.
- [27] Zhu WG, Zhu LY, Sun LJ, Zhen YG, Dong HL, Wei ZX, et al. Uncovering the intramolecular emission and tuning the nonlinear optical properties of organic materials by cocrystallization. Angew Chem Int Ed 2016;55(45):14023–7.
- [28] Boyd RW. Nonlinear optics. third ed. Oxford: Elsevier Ltd; 2008.
- [29] Li YJ, Liu TF, Liu HB, Tian MZ, Li YL. Self-assembly of intramolecular chargetransfer compounds into functional molecular systems. Acc Chem Res 2014;47(4): 1186–98.
- [30] Chen SH, Qin ZH, Liu TF, Wu XZ, Li YJ, Liu HB, et al. Aggregation-induced emission on benzothiadiazole dyads with large third-order optical nonlinearity. Phys Chem Chem Phys 2013;15(30):12660–6.
- [31] Narayanan S, Raghunathan SP, Poulose AC, Mathew S, Sreekumar K, Kartha CS, et al. Third-order nonlinear optical properties of 3,4-ethylenedioxythiophene copolymers with chalcogenadiazole acceptors. New J Chem 2015;39(4):2795–806.
- [32] Jia JH, Li T, Cui YH, Li YZ, Wang WB, Han L, et al. Study on the synthesis and third-order nonlinear optical properties of D-A poly-quinacridone optical materials. Dyes Pigments 2019;162:26–35.
- [33] Xu QY, Li ZG, Liu NC, Jia JD, Yang JY, Song YL. Third order nonlinear optical properties and transient dynamics of thiophene-contained pyrene derivatives: effect of peripheral substituent group. Optic Laser Technol 2019;109:666–70.
- [34] Zaitri LK, Mekelleche SM. Computational study of linear and nonlinear optical properties of substituted thiophene imino dyes using long-range corrected hybrid DFT methods. Mol Phys 2020;118(4):1618508.
- [35] Anandan S, Manoharan S, Narendran NKS, Girisun TCS, Asiri AM. Donor-acceptor substituted thiophene dyes for enhanced nonlinear optical limiting. Opt Mater 2018;85:18–25.
- [36] Arakawa Y, Nakajima S, Ishige R, Uchimura M, Kang S, Konishi G-i, et al. Synthesis of diphenyl-diacetylene-based nematic liquid crystals and their high birefringence properties. J Mater Chem 2012;22(17):8394–8.
- [37] Lo S-C, Harding RE, Brightman E, Burn PL, Samuel IDW. The development of phenylethylene dendrons for blue phosphorescent emitters. J Mater Chem 2009;19 (20):3213–27.
- [38] Kitamura C, Saito K, Nakagawa M, Ouchi M, Yoneda A, Yamashita Y. Synthesis and properties of a new ethyne-linked donor/acceptor pentamer. Tetrahedron Lett 2002;43(18):3373–6.
- [39] Huang C, Zhen C-G, Su SP, Loh KP, Chen Z-K. Solution-processable polyphenylphenyl dendron bearing molecules for highly efficient blue lightemitting diodes. Org Lett 2005;7(3):391–4.
- [40] Sheikbahae M, Said AA, Wei TH, Hagan DJ, Vanstryland EW. Sensitive measurement of optical nonlinearities using a single beam. IEEE J Quant Electron 1990;26(4):760–9.
- [41] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 16, revision A03. Wallingford CT: Gaussian, Inc; 2016.
- [42] Gao YC, Zhang XR, Li YL, Liu HF, Wang YX, Chang Q, et al. Saturable absorption and reverse saturable absorption in platinum nanoparticles. Optic Commun 2005; 251(4–6):429–33.
- [43] Delysse S, Filloux P, Dumarcher V, Fiorini C, Nunzi JM. Multiphoton absorption in organic dye solutions. Opt Mater 1998;9(1–4):347–51.
- [44] Sutherland RL, Brant MC, Heinrichs J, Rogers JE, Slagle JE, McLean DG, et al. Excited-state characterization and effective three-photon absorption model of twophoton-induced excited-state absorption in organic push-pull charge-transfer chromophores. J Opt Soc Am B 2005;22(9):1939–48.
- [45] van Stokkum IHM, Larsen DS, van Grondelle R. Global and target analysis of timeresolved spectra. BBA- Bioenergetics 2004;1658(2–3):82–104.
- [46] Niu R, Wang Y, Wu X, Chen S, Zhang X, Song Y. D-π-A type pyrene derivatives with different push-pull properties: broadband Absorption response and transient dynamic analysis. J Phys Chem C 2020;124(9):5345–52.
- [47] Sung J, Kim P, Lee YO, Kim JS, Kim D. Characterization of ultrafast intramolecular charge transfer dynamics in pyrenyl derivatives: systematic change of the number of peripheral N,N-dimethyaniline substituents. J Phys Chem Lett 2011;2(7): 818–23.
- [48] Carlotti B, Elisei F, Mazzucato U, Spalletti A. Unusual high fluorescence of two nitro-distyrylbenzene-like compounds induced by CT processes affecting the fluorescence/intersystem-crossing competition. Phys Chem Chem Phys 2015;17 (22):14740–9.
- [49] Praseetha KP, Chandrasekharan K, Varghese S. Optical behaviour of nematic liquid crystal doped with carbon dot in the nonlinear optical regime. Optic Laser Technol 2020;130:106367.
- [50] Cai SG, Zheng C, Xiao XQ, Li W, Chen WZ. Graphene-based hierarchical sandwichtype hybrid nanostructures for optical limiters. Opt Mater 2019;98:109453.
- [51] Kakekochi V, Nikhil PP, Chandrasekharan K. Impact of donor–acceptor alternation on optical power limiting behavior of H–Shaped thiophene–imidazo[2,1- b] [1,3,4]thiadiazole flanked conjugated oligomers. Dyes Pigments 2020;175: 108181.