

# Synthesis and ultrafast optical absorption response of novel d- $\pi$ -a pyrene chalcone derivatives

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**Abstract.** Two chalcone derivatives 1-(2,5-dimethoxy phenyl)-3-(pyren-1-yl) acrylic ketone (a) and 1-(3,4-dimethoxyphenyl)-3-(pyren-1-yl) acrylic ketone (b) were designed and synthesized. The structures were characterized by IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR and LC-MS. The ultraviolet (UV) and fluorescence (FL) spectra of the compounds were determined. The theoretical calculation and thermal characteristics of a and b are studied, and the relationship between structure and performance was explained. The electronic structures of a and b were optimized at B3LYP/6-311 + G (d, p) level. Frontier molecular orbitals analysis demonstrated that the energy gap of a and b are 3.24 and 3.08 eV. Femtosecond Z-scan measurements showed that the two molecules exhibited reverse saturation absorption (RSA) at 515 and 532 nm. The thermal properties, the theoretical calculations and the experimental results consistently indicate that the compound b has a good application prospect in nonlinear optics materials.

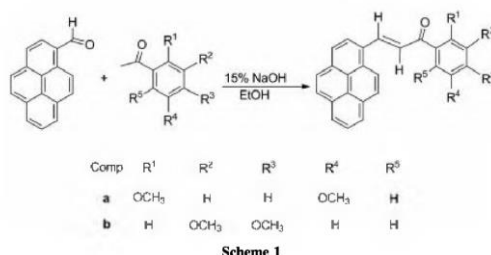
**Keywords.** Chalcone, third-order nonlinear optical absorption, theoretical calculation, ultrafast optical response, synthesis, front track, reverse saturation absorption.

Since the 1960s, scientists have discovered such optical phenomena as photoelectric effect, optical rectification effect, and two-photon absorption, which has laid the foundation for the birth of nonlinear optics. With the rapid progress of the information era and the development of sciences and technologies, nonlinear optical materials are also created accordingly. Nonlinear optical materials are those whose frequency, phase, amplitude and other aspects change under the action of external optical field, electric field and strain electric field, thereby causing changes to such aspects as the refractive index, light absorption and light scattering, showing great application potential in image processing, optical switch, optical storage, memory system and other fields. Nonlinear optical materials are capable of light wave frequency conversion and optical signal processing, and, as a kind of photoelectric materials, have a wide application prospect in high-speed optical communication, optical information processing, optical storage and other fields [1].

The most remarkable feature of nonlinear optical materials is that they have a high nonlinear optical coefficient. In particular, organic nonlinear optical materials, due to their large conjugated systems, strong electrical responsivity, fast response time and good optical performance within a wide frequency range, being easy to design and cut and change into a device, low cost, low dielectric constant and other advantages, have become a research hotspot in the field of nonlinear optics and materials [2-3]. At present, nonlinear optical materials have entered their practical stage, and second- and third-order organic nonlinear optical effects have attracted much attention of researchers [4].

Large conjugated organic compounds show good nonlinear optical properties since the charges move easily due to the delocalization of the  $\pi$  electrons in the backbone. In the chalcone compounds (Ar-CH = CH-CO-Ar'), the carbonyl group (C = O) acts the electron-withdrawing group (A), and the electron-rich substituent group on the benzene ring acts as the electron-donating group (D), thus forming the D- $\pi$ -A molecule, a kind of nonlinear optical cross conjugated chromogen, which displays good second-harmonic generation (SHG) efficiency and transparency, and is easy to crystallize [5]. Pyrene, as an extended  $\pi$  aromatic conjugated system compound with a two-dimensional conjugated structure, has its derivatives with good a good third-order nonlinear optical effect [6-7], and pyrene compounds can generally be used as strong electron donors or receptors, which are assembled with other molecules by conjugated bridge and thus obtain compounds with excellent properties and novel configurations [8]. SHI et al. found [9-10] that pyrene chalcone derivatives showed good third-order nonlinear optical properties. Owing to the high selectivity and sensitivity and excellent luminescence properties, pyrene and its derivatives have been widely used in the field of fluorescence labeling and application. However, they are an organic fluorescent material, and an increasingly number of people improve their properties by adding asymmetric or dendritic groups [11-15], so as to obtain nonlinear optical materials with better properties.

Taking pyrenecarboxaldehyde and two dimethoxyacetophenones as raw materials, this research group synthesized two compounds with delocalized  $\pi$  electron conjugated system structure by condensation reaction: 1-(2,5-dimethoxy phenyl)-3-(pyren-1-yl) acrylic ketone (a) and 1-(3,4-dimethoxy phenyl)-3-(pyren-1-yl) acrylic ketone (b, Scheme 1), and studied the linear optical properties, nonlinear optical absorption properties, thermal properties and other aspects of the two compounds.



## 1. Experiment

### 1.1. Instruments and reagents

UV-2550 ultraviolet spectrometer (wavelength range: 190–900 nm, resolution: 0.1 nm, Shimadzu, Japan); F-4600 fluorescence spectrometer (resolution: 1.0 nm, Hitachi, Japan); Bruker Advanced III nuclear magnetic resonance spectrometer (600 MHz, DMSO-*d*<sub>6</sub> is the solvent, TMS is the internal standard, frequency resolution: better than 0.005 Hz, phase resolution: better than 0.01°, Bruker, Switzerland); IRAffinity-1S Fourier transform infrared spectrometer (KBr tableting, resolution: at least better than 0.5 cm<sup>-1</sup>, Shimadzu, Japan); LCMS-8030 liquid chromatograph mass spectrometer (LC-MS) (ESI ion source, resolution: 0.6 amu, Shimadzu, Japan); NETZSCH STA 449 F5 integrated thermal analyzer (rt–1 600°C, resolution: 0.1 µg, Netzsch, Germany); Nd: YAG (NT 342B) tunable laser (wavelength: 515 and 532 nm, pulse width: 190 fs, EKSPALA, Lithuania).

All reagents used were analytically pure.

### 1.2. Synthesis [16-17]

A total of 3 mmol (0.69 g) of pyrenecarboxaldehyde was placed in a 250 mL round-bottom flask, added with 50 mL of anhydrous ethanol, and mixed to dissolve it; another 3 mmol of dimethoxyacetophenone was added in the reaction flask, and after the raw materials were completely dissolved, 3 mL of 15% NaOH solution was added in the flask and stirred to make it react for 10 h at room temperature; the temperature was controlled at 50–60°C, and the reaction continued for 5 h. The reaction process was followed by TLC during the reaction (developers:  $V_{\text{ethyl acetate}}/V_{\text{petroleum ether}} = 1/3$ ). The reaction mixture was transferred to a 500 mL flask when it was hot, kept still until it was cool, and sucked and filtered by reducing pressure, the filter cake was recrystallized with hot anhydrous ethanol, and then crystal was dried in vacuum to obtain the products.

1-(2,5-dimethoxy phenyl)-3-(pyren-1-yl) acrylic ketone (a): 0.92 g of orange powdery crystal, with the yield of 78.2%, m. p. 147.4°C; IR (KBr)  $\nu$ : 3045.6, 2964.6, 2839.2, 1647.2 (C = O), 1585.5, 1492.9, 1431.2 (benzene ring) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$ : 8.671–8.646 (d,  $J = 15.0$  Hz, 1H, olefin-H), 8.551–8.513 (d,  $J = 22.8$  Hz, 2H, benzene-H), 8.366–8.348 (d,  $J = 10.8$  Hz, 4H, pyrene-H), 8.271–8.236 (d,  $J = 15.0$  Hz, 2H, pyrene-H), 8.125 (s, 1H, benzene-H), 7.753–7.729 (d,  $J = 14.4$  Hz, 1H, olefin-H), 7.184 (s, 3H, pyrene-H), 3.890 (s, 3H, -OCH<sub>3</sub>), 3.792 (s, 3H, -OCH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$ : 191.70, 153.61, 152.64, 138.87, 132.79, 131.32, 130.66, 129.91, 129.82, 129.55, 129.35, 129.13, 128.78, 127.86, 127.16, 127.72, 126.46, 125.90, 125.22, 124.57, 124.22, 122.71, 119.37, 114.60, 114.48, 56.93, 56.09; LC-MS(ESI)  $m/z$ : calcd for C<sub>27</sub>H<sub>21</sub>O<sub>3</sub>{[M + H]<sup>+</sup>}393.1492, found 393.15.

1-(3,4-dimethoxy phenyl)-3-(pyren-1-yl) acrylic ketone (b): 0.94 g of orange powdery crystal, with the yield of 79.9%, m. p. 181.1°C; IR  $\nu$  (KBr): 1649.1 (C = O); 1579.7, 1512.2 (benzene ring); <sup>1</sup>H NMR (600 MHz, DMSO-*d*)  $\delta$ : 8.883 (s, 1H, benzene-H), 8.859–8.845 (d,  $J = 8.4$  Hz, 1H, benzene-H), 8.645–8.629 (d,  $J = 9.6$  Hz, 1H, olefin-H), 8.409–8.365 (m, 4H, pyrene-H), 8.309–8.260 (m, 3H, pyrene-H), 8.154–8.129 (t, 1H,  $J = 7.5$  Hz, pyrene-H), 8.057–8.039 (q, 1H,  $J = 3.6$  Hz, pyrene-H), 7.732–7.729 (d,  $J = 1.8$  Hz, 1H, benzene-H), 7.176–7.162 (d,  $J = 8.4$  Hz, 1H, olefin-H), 3.913 (s, 3H, -OCH<sub>3</sub>), 3.910 (s, 3H, -OCH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*)  $\delta$ : 187.70, 153.80, 149.34, 139.26, 132.82, 131.34, 131.09, 130.70, 130.03, 129.31, 129.09, 128.92, 127.90, 127.15, 126.69, 126.44, 125.75, 125.56, 124.69, 124.60, 124.29, 124.04, 122.83, 111.46, 111.34, 56.30, 56.14; LC-MS (ESI)  $m/z$ : calcd for C<sub>27</sub>H<sub>21</sub>O<sub>3</sub>{[M + H]<sup>+</sup>}393.1492, found 393.15.

## 2. Results and discussion

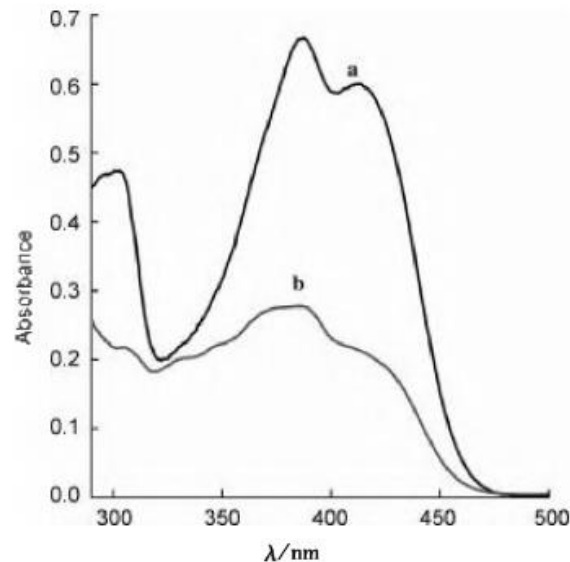
### 2.1. Representation

According to the analysis of infrared spectra, H-NMR spectra, C-NMR spectra and high resolution mass spectra (figures were omitted) of compounds a and b, the type and number of protons, and the number of carbon atom species of the two compounds fitted with the molecules; the LC-MS spectra showed that the absolute error of molecular mass was 0.0008, and the relative error was  $2.0 \times 10^{-6}$ ; based on various representation data, it could be concluded that the synthesized products were consistent with the target compounds.

### 2.2. Linear spectral properties

The UV-visible spectra ( $1 \times 10^{-5}$  mol/L, CH<sub>2</sub>Cl<sub>2</sub>) and fluorescence emission spectra ( $1 \times 10^{-6}$  mol/L, CH<sub>2</sub>Cl<sub>2</sub>; 5 nm/5 nm) of compounds a and b are seen in Fig. 1 and Fig. 2. According to Fig. 1, the maximum UV absorption wavelength of a is 387 nm, the absorbance is 0.45, and the molar absorption coefficient  $\epsilon$  is  $4.5 \times 10^4$  L·mol<sup>-1</sup>·cm<sup>-1</sup>. The maximum UV absorption wavelength of b is 386 nm, the absorbance is 0.27, and the molar absorption coefficient  $\epsilon$  is  $2.7 \times 10^4$  L·mol<sup>-1</sup>·cm<sup>-1</sup>. From Fig. 2, the maximum fluorescence emission wavelength of a is 501.6 nm, and the fluorescence intensity is 510.3, showing relatively weak fluorescence. The maximum fluorescence emission wavelength of b is 495 nm, and the fluorescence intensity is 2742. The methoxy group on the benzene ring has a great influence on the absorption wavelength of chalcone derivatives, because its participation in the conjugation of the system strengthens the electron delocalization of the conjugated system, causing the red shift of the absorption spectra; in terms of the fluorescence emission spectra, the unsubstituted parent chalcone of the benzene ring is not fluorescent, then several methoxy electron-donating groups

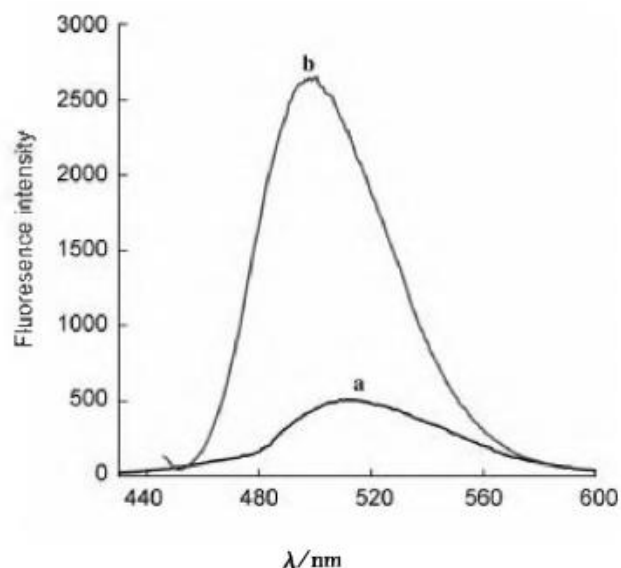
are introduced to benzene rings at both ends to make a and b have the characteristic intramolecular charge transfer, and intense molecular polarization occurs at optical excitation, making the electron clouds gather at both ends of the molecule to increase fluorescence quantum yield of chalcone and make it show strong fluorescence characteristic [18]. The experiment suggested that the fluorescence characteristic of b is stronger than a, the contribution of 3,4-methoxy group to the fluorescence intensity was greater than 2,5-methoxy group, due to the high molecular polarization intensity. Based on the linear spectra of a and b, they were relatively close in the UV absorption wavelength and the fluorescence emission wavelength, but different in the corresponding absorbance and fluorescence intensity. The UV absorption wavelength at 386 nm signified that the conjugated systems in the two isomer compounds a and b molecules were large, indicating the existence of intramolecular charge transfer and high polarizability. This is well confirmed by theoretical calculation.



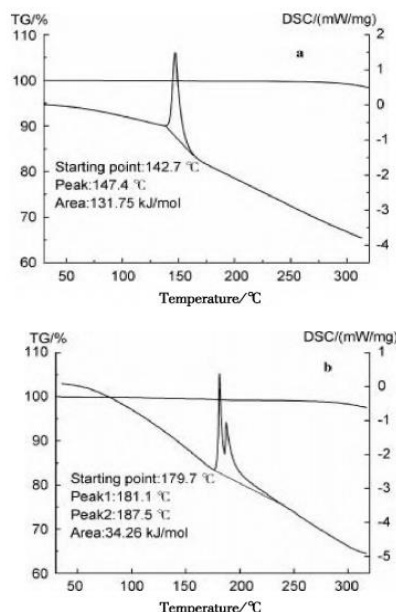
**Figure 1.** Uv-Vis absorption of **a** and **b**

### 2.3. Thermal properties

The DSC/TG curves of compounds a and b were determined by differential scanning calorimetry (DSC), with the temperature of 30–250°C, and the temperature rate of 5°C/min (Fig. 3). According to Fig. 3, the DSC curves show that the melting point of a is 147.4°C, and the enthalpy is 131.75 kJ/mol; the melting point of b is 181.1°C, and the enthalpy is 34.26 kJ/mol, and there may be two different crystal forms. The TG curves show that weight loss occur in a and b at 300°C, with the weight loss ratios of 1.48% and 2.49%, respectively, both of which are less than 5.0%, indicating good thermal stability. Neither compounds interacts with water, so they can be used as nonlinear optical materials.



**Figure 2.** Fluorescence emission spectra of **a** and **b**

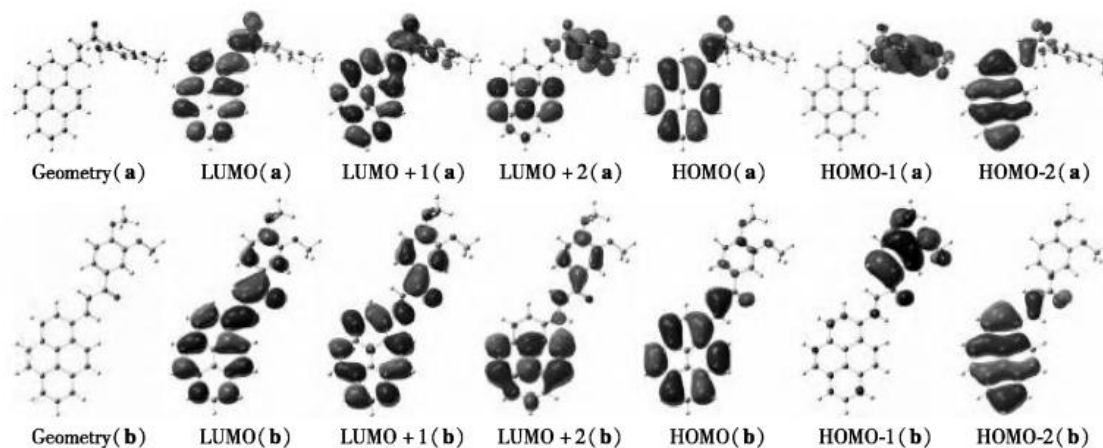


**Figure 3.** DSC/TG curves of **a** and **b**

#### 2.4. Theoretical calculation

The Gaussian 09 quantum chemistry program package [19] was used for structural optimal calculation of compounds **a** and **b** at the theoretical level of B3LYP/6-311 + G (d, p) [20-21], the geometric structure, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and other nearby Kohn-Sham orbital compositions of BTAB were given (Fig. 4), and the energy gap and polarizability between the molecular orbital energy, HOMO and LUMO of **a** and **b** were obtained (Table 2).

From the distribution of electron clouds on molecular orbitals of **a** and **b** in Fig. 4, it can be seen that electron clouds are mainly distributed on the pyrene ring, carbon-carbon double bond and carbonyl group in HOMO and HOMO-2, and on the dimethoxy phenyl group and carbonyl group in HOMO-1; in LUMO, LUMO+1 and LUMO+2, they are mainly distributed on the pyrenyl group, carbon-carbon double bond and carbonyl group. However, since the methoxy group of **a** molecule is inside the benzene ring and the structure is distorted, electron clouds in the middle of LUMO+2 are sparse and move to both ends, thus the energy of LUMO (**a**) is higher than that of LUMO (**b**), making the energy of HOMO (**a**) lower than that of HOMO (**b**) in the ground state. It can be seen from the distribution of electron clouds in the above orbitals, electrons in **a** and **b** molecules can transit from one end to the other, indicating that the degree of resonance polarization of the  $\pi$  electron system is large and there is intramolecular charge transfer, which makes molecules show the nonlinear optical properties. In addition, from the frontier molecular orbital figure obtained by quantum chemistry calculation, it can be seen that pyrenyl groups of the two molecules have  $\pi$  electrons on HOMO and LUMO, showing obvious  $\pi$ - $\pi^*$  transition characteristic [22]. Therefore, during the transition of HOMO-LUMO, the intramolecular charge transfer and  $\pi$ - $\pi^*$  transition of chalcone derivatives **a** and **b** occur simultaneously. In Table 1, the energy gap between LUMO and HOMO is small, and that of **b** molecular is smaller than that of **a** molecule, and the electron clouds can be polarized more easily, indicating that electron transition is more likely to occur and show greater polarizability (11421.71 eV). For D- $\pi$ -A molecules, the intramolecular charge transfer is more likely to occur with higher polarizability.



**Figure 4.** Geometric structure and molecular orbital composition of **a** and **b**

**Table 1.** Molecular orbital energy and polarization of **a** and **b**

Compound	HOMO/eV	LUMO/eV	$\Delta E_{\text{LUMO-HOMO}}$ /eV	Polarizability/eV
<b>a</b>	-5.74	-2.50	3.24	10310.40
<b>b</b>	-5.70	-2.62	3.08	11421.71

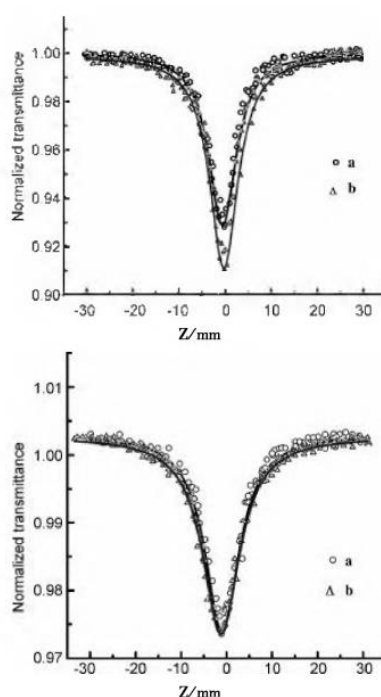
**Table 2.** Third-order nonlinear absorption coefficients of **a** and **b** under different conditions

Compound	$\beta/m \cdot W^{-1}$	$\beta/m \cdot W^{-1}$
	(515 nm, 100 nj, 190 fs)	(532 nm, 100 nj, 190 fs)
<b>a</b>	$2.05 \times 10^{-13}$	$1.05 \times 10^{-13}$
<b>b</b>	$2.55 \times 10^{-13}$	$1.05 \times 10^{-13}$

## 2.5. Nonlinear optical properties

The NLO absorption properties of **a** and **b** were determined by femtosecond z-scanning technology. The reverse saturation absorption curves of samples were measured by transient absorption experiment at 515 nm, 100 nj and 0.5 mg/mL (DMSO) and 532 nm, 100 nj and 0.5 mg/mL (DMSO), under the pulse condition of 190 fs (Fig. 5, the small circles and triangles indicate experimental data, and the solid lines are the theoretical fitted curves). That is, the normalized transmittance decreases with the increase of the light intensity incident on the sample, and the third-order nonlinear absorption coefficient is obtained by fitting (Table 2), showing ultrafast optical response.

Fig. 5 shows that under the same laser pulse condition, the nonlinear absorption intensities of compounds **a** and **b** at 515 nm and 532 nm are different. According to the third-order nonlinear absorption coefficients in Table 2, the absorption is intense at 515 nm,  $\beta_a = 2.05 \times 10^{-13}$  m/W,  $\beta_b = 2.55 \times 10^{-13}$  m/W, and the third-order nonlinear absorption coefficient of **b** is 1.2 times that of **a**, indicating better nonlinear absorption characteristics; as the tested wavelength increases, the nonlinear absorption coefficients of **a** and **b** decrease to  $1.05 \times 10^{-13}$  m/W. Compared with the three isomer pyrene chalcone derivatives ( $\beta_{3a} = 0.6 \times 10^{-13}$ ,  $\beta_{3b} = 1.4 \times 10^{-13}$ ,  $\beta_{3c} = 1.6 \times 10^{-13}$  m/W, 180 fs, 532 nm) of 1-(pyren-1-yl)-3-pyridyl-2-acrylic-1-ketone [17], the nonlinear absorption intensities of **a** and **b** increase; compared with 2-(pyren-1-yl)-1,8 naphthyridine ( $\beta = 9.0 \times 10^{-14}$  m/W) [23], the nonlinear absorption coefficients of **a** and **b** increase by about one order of magnitude; this suggests that the contribution of polymethoxyphenyl group to nonlinear absorption coefficients is greater than pyridyl group and naphthyridine group. In pyrene chalcone derivatives, since the location of carbonyl group is different, there are two pyrene chalcone derivatives in the structure: one is the connection of pyrenyl group and carbonyl group, the other is the connection of pyrenyl group and carbon-carbon double bond. This slight difference leads to large differences in the third-order nonlinear optical absorption properties of molecules. It was found in the experiment that the difference in the molecular structure of the three compounds is that the location of carbonyl groups and the number of methoxy groups connected on the benzene ring are different, where the carbonyl groups in **a** and **b** molecules are connected to the benzene ring at the right end and have two methoxy groups, and those in the **p** molecules are connected to the pyrenyl group at the left end and have only one methoxy group on the benzene ring; but the third-order nonlinear optical absorption coefficient of **p** is four orders of magnitude larger than that of **a** and **b**, suggesting that the location of carbonyl groups has great impact on the third-order nonlinear optical absorption coefficient of materials. This provides important information for the molecular design during the synthesis of such materials.


**Figure 5.** Open-aperture Z-scan curves of **a** and **b**

### 3. Conclusion

Two novel pyrene chalcone derivatives a and b were synthesized. These compounds contain polycyclic aromatic extended  $\pi$  electron conjugated system structures, and are bonded with covalent, showing good chemical and thermal stability; the theoretical calculation suggested that due to the high delocalization of  $\pi$  electrons on the backbone, the charge is easy to move and there is obvious intramolecular charge transfer. In a certain medium, less time is needed for ion polarization to produce electric dipoles, that is, there is ultrafast optical response. In addition, owing to the interaction between the electro-donating group and the electron-withdrawing group in the large conjugated system, the nonlinear polarizability can be increased, so it shows good third-order nonlinear optical effect, and can be used as an alternative material for the nonlinear optical application.

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