



## Full length article

# Third order nonlinear optical properties and transient dynamics of thiophene-contained pyrene derivatives: Effect of peripheral substituent group



Qianyan Xu<sup>a</sup>, Zhongguo Li<sup>b,c,\*</sup>, Nanchun Liu<sup>a</sup>, Jidong Jia<sup>a</sup>, Junyi Yang<sup>a</sup>, Yinglin Song<sup>a,\*</sup>

<sup>a</sup> College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215123, China

<sup>b</sup> College of Physics & Electronic Engineering, Changshu Institute of Technology, Changshu 215500, China

<sup>c</sup> Key Lab of Modern Optical Technologies, Soochow University, Suzhou 215006, China

## HIGHLIGHTS

- Two  $\pi$ -conjugated pyrene derivatives were synthesized successfully.
- The benzene peripheral substituent enhance the third-order optical nonlinearity.
- The difference phenomenon for excited-state lifetime between both compounds.
- Detailing description on transient absorption to interpret the dynamic process.

## ARTICLE INFO

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## ABSTRACT

In this work, two pyrene derivatives with delocalized  $\pi$ -electron system 1-(pyren-1-yl)–3-(5-Chlorothiophene-2-yl)acrylic ketone (**1612**) and 1-(pyren-1-yl)–3-(5-Phenylthiophene-2-yl) acrylic ketone (**1613**) were synthesized. The third-order nonlinear optical (NLO) response of these compounds dissolved in DMSO were investigated using Z-scan technique with 190 fs laser pulses at 532 nm. Large two-photon absorption was found for the two compounds, while the NLO response of **1613** was larger than **1612**. The femtosecond transient absorption (TA) results demonstrate that both compounds have broad TA absorption band over the visible regime. Compared to **1612**, the TA band of **1613** exhibit a 15-nm blue shift of its peak while its UV–Vis absorption peak have 50 nm red-shift. Meanwhile, the TA decay curve also show that the excited-state lifetime of **1613** is longer, indicating the substituent group functionalization also has a significant impact on the excited-state relaxation processes. Our results show that both the NLO response and photo-physical dynamics of pyrene chromophores are readily tunable via peripheral substituent group, which is essential for the development of novel NLO materials based on this conjugated molecules.

## 1. Introduction

Over the past two decades, organic  $\pi$  conjugated molecule have attracted considerable attentions in optoelectronic and photonic fields. Owing to their excellent structure tunability and large nonlinear optical (NLO) response, organic materials have been widely used in optical data storage, all-optical switching, optical power limiting, etc. [1–10]. Previous results revealed that the extending of  $\pi$  conjugated system and the intra-molecular charge transfer play a significant role in the nonlinear optical response of organic molecule [11,12]. However, although considerable effects have been devoted to improve the NLO response of

$\pi$  conjugated molecule, the full understanding on the structure-properties relationship of organic NLO materials remains largely unknown. Therefore, it is essential to study the NLO response of novel organic  $\pi$  conjugated molecule for optimizing their NLO response.

Pyrene and its derivations have been widely employed to many areas such as organic light-emitting diodes (OLEDs) [13,14], micro-environment sensors [15], laser dyes [16] and biological probes [17]. Recently, the optical nonlinearity of pyrene derivatives are also studied due to their delocalized  $\pi$  electron system [18,19]. It was found that the charge transfer from donor to acceptor group via the core pyrene chromophore plays a key role in the nonlinear absorption of the

\* Corresponding authors.

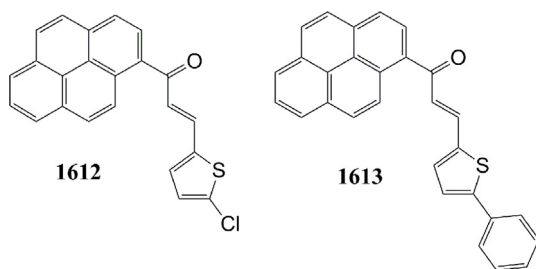
E-mail addresses: [zgli@csig.edu.cn](mailto:zgli@csig.edu.cn) (Z. Li), [ylsong@hit.edu.cn](mailto:ylsong@hit.edu.cn) (Y. Song).

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**Scheme 1.** Chemical structures of 1-(pyren-1-yl)-3-(5-Chlorothiophene-2-yl) acrylic ketone (**1612**) and 1-(pyren-1-yl)-3-(5-Phenylthiophene-2-yl) acrylic ketone (**1613**).

compound. Importantly, Jin et al. reported that the strong donor-acceptor interaction conjugation improved push-pull functionalization and forcefully enhanced third-order optical nonlinearities of the pyrene derivative [20]. On the other hand, it was reported that thiophene as versatile units have been widely utilized to improve the transport properties [21] which not only act as donor but also acceptor with functional variation in specific molecules [22,23]. However, to the best of our knowledge, there is no report concerning the effect of peripheral substituent of thiophene terminal on the photo-physical properties of pyrene derivatives. Herein, we choose pyrene as the skeleton and attempt to evaluate the impact of peripheral substituent of thiophene terminal on the NLO activities. Following this idea, we synthesized successfully two pyrene derivatives: 1-(pyren-1-yl)-3-(5-Chlorothiophene-2-yl)acrylic ketone (**1612**) and 1-(pyren-1-yl)-3-(5-Phenylthiophene-2-yl) acrylic ketone (**1613**) (Scheme 1). Their NLO response were investigated using femtosecond Z-scan technique with 190 fs laser pulse at 532 nm. And the ultrafast excited-state dynamics of these two compounds were also studied via femtosecond transient absorption measurements. Our results show that the peripheral substituent group could effectively modify both the NLO response and dynamics of pyrene derivatives.

## 2. Experimental section

### 2.1. Synthesis and characterization of 1612 and 1613

**Synthesis of 1612.** 1-acetyl pyrene (0.61 g, 2.5 mmol) was dissolved in absolute ethyl alcohol (60 mL), 5-Chlorothiophene-2-formaldehyde (0.373 g, 3.5 mmol) and sodium hydroxide solution (10%, 3 mL) were stirred together at room temperature for 20 h, during which Thin-layer chromatography (TLC) was used to detect the reaction process. Then 5-Chlorothiophene-2-formaldehyde was evaporated under reduced pressure, the mixture was filtered and washed by absolute ethyl alcohol until the 1-acetyl pyrene was gone, then vacuum dried for 4 h. The crude product was recrystallized from ethanol yielding **1612** (0.80 g, 85.82%) as yellow powder.  $^1\text{H}$  NMR (600 MHz, DMSO-*d*)  $\delta$ /ppm: 8.594–8.578 (d, 1H,  $J = 9.6$  Hz, Pyr-H), 8.410–8.330 (m, 6H, Pyr-H), 8.305–8.290 (d, 1H,  $J = 9.0$  Hz, Pyr-H), 8.182–8.157 (t, 1H,  $J = 7.5$  Hz, Pyr-H), 7.753–7.727 (d, 1H,  $J = 15.6$  Hz, Olefinic-H), 7.558–7.552 (d, 1H,  $J = 3.6$  Hz, Thi-H), 7.356–7.330 (d, 1H,  $J = 15.6$  Hz, Olefinic-H), 7.246–7.240 (d, 1H,  $J = 3.6$  Hz, Thi-H);  $^{13}\text{C}$  NMR (150 MHz, DMSO-*d*)  $\delta$ /ppm: 194.38, 139.20, 137.80, 133.73, 133.50, 133.34, 132.90, 131.16, 130.56, 129.74, 129.61, 129.22, 129.06, 127.74, 127.29, 127.13, 126.91, 126.57, 126.37, 124.97, 124.78, 124.46, 124.02. LC-MS  $m/z$ : found, 373.00, calcd. for C<sub>23</sub>H<sub>14</sub>O<sub>2</sub>Cl ([M+H]<sup>+</sup>), 373.0455. See support information Figs. S1–S2–S5.

**Synthesis of 1613.** 1-acetyl pyrene (0.732 g, 3 mmol) was dissolved in absolute ethyl alcohol (90 mL), 5-phenylthiophene-2-formaldehyde (0.752 g, 4 mmol) were stirred together at suitable temperature for 10 minutes until the reactants were completely dissolved, then sodium hydroxide solution (10%, 3 mL) was injected and stirred together at room temperature for 20 h, during which Thin-layer chromatography

(TLC) was used to detect the reaction process. Then 5-phenylthiophene-2-formaldehyde was evaporated under reduced pressure, the mixture was filtered and washed by absolute ethyl alcohol until the 1-acetyl pyrene was gone, then vacuum dried. The crude product was recrystallized from ethanol yielding **1613** (1.2084 g, 96.1%) as orange-yellow powder.  $^1\text{H}$  NMR (600 MHz, DMSO-*d*)  $\delta$ /ppm: 8.601–8.586 (d, 1H,  $J = 9.0$  Hz), 8.453–8.402 (m, 4H), 8.366–8.337 (t, 2H,  $J = 8.7$  Hz), 8.316–8.302 (d, 1H,  $J = 8.4$  Hz), 8.187–8.161 (t, 1H,  $J = 7.8$  Hz), 7.829–7.803 (d, 1H,  $J = 15.6$  Hz, Olefinic-H), 7.760–7.747 (d, 2H,  $J = 7.8$  Hz, Ar-H), 7.682–7.676 (d, 1H,  $J = 3.6$  Hz, Thi-H), 7.642–7.636 (d, 1H,  $J = 3.6$  Hz, Thi-H), 7.487–7.462 (t, 2H,  $J = 7.5$  Hz, Ar-H), 7.406–7.394 (d, 1H,  $J = 7.2$  Hz, Ar-H), 7.381–7.354 (d, 1H,  $J = 16.2$  Hz, Olefinic-H).  $^{13}\text{C}$  NMR (150 MHz, DMSO-*d*)  $\delta$ /ppm: 195.16, 148.31, 139.26, 138.30, 133.87, 133.56, 133.45, 133.20, 131.13, 130.67, 129.32, 129.14, 129.05, 128.57, 127.18, 126.07, 125.78, 124.89, 124.73, 124.41, 124.26, 124.10, 77.23, 77.02, 76.81. LC-MS (ESI)  $m/z$ : found, 415.80; calcd. for C<sub>29</sub>H<sub>18</sub>O<sub>2</sub>([M+H]<sup>+</sup>), 415.1158. See support information Figs. S3–S4–S6.

### 2.2. Quantum chemical calculations

The significant of structural changes on the frontier molecular orbitals involved in the two lowest-energy optical transitions was evaluated by density functional theory (DFT) calculations. The Gaussian 09 program package [24] with DFT was implemented with B3LYP/6-31G(d,p) model to invest electron cloud distribution of the frontier molecular orbitals.

### 2.3. Open aperture Z-scan experiment

The nonlinear optical response of the pyrenes were studied using open aperture Z-scan experiment. The detailed experimental setup can be found in Ref. [25]. The light source was an optical parametric amplifier (OPA, Light Conversion ORPHEUS) which generated 190 fs laser pulses with repetition rate of 20 Hz. The low repetition rate was aimed to prevent the accumulation effect of thermally-induced nonlinearities. The output wavelength of OPA was tuned to 532 nm. The sample solution with concentration of  $6.0 \times 10^{-3}$  mol/L was put in a glass cuvette of 2 mm, which was moved along the z-axis of laser beam by a moving stage. The input laser beam was focused by a convex lens with focal length of 400 mm, the radius of laser beam at the focal plane was around  $2.1 \times 10^{-2}$  mm. We adopt the benchmark ZnSe to calibrate our experiment systems at room temperature.

### 2.4. Transient absorption spectrum experiment

The transient absorption measurement was performed by a regenerative amplified Yb:KGW fiber laser system (Light Conversion, PHAROSSP) which can produce 1 mJ pulses with a repetition rate of 6 kHz and 190 fs (FWHM). The results of experiment were recorded under the excitation of 400 nm for **1613** and 350 nm for **1612**, respectively. The white light supercontinuum probe was produced by focusing the laser beam to a 2 mm thick sapphire plate, the probe wavelength was between 478 and 780 nm. The probe waist ( $\sim 22 \mu\text{m}$ ) was much smaller than the pump waist radius which is  $152 \mu\text{m}$  was aimed to ensure that the probe beam could present a uniformly excited region of samples. The angle between pump and probe beams was magic angle which can avoid anisotropic effect.

## 3. Results and discussion

### 3.1. UV-Vis absorption spectrum

The UV-Vis absorption spectra of compounds **1612** and **1613** are shown in Fig. 1. The concentration of compounds **1612** and **1613** diluted dimethylsulfoxide (DMSO) were on the order of  $10^{-4}$  mol/L.

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