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Ultrafast third-order nonlinear optical response of pyrene derivatives



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ABSTRACT

Two mono-substituted pyrene derivatives with delocalized electron system 1-(pyren-1-yl)-3-(4-Methyl thiophene-2-yl) acrylic ketone (13#) and 1-(pyren-1-yl)-3-(4-bromo thiophene-2-yl) acrylic ketone (15#) were successfully synthesized. The resultant compounds were characterized by nuclear magnetic resonance (NMR), infrared spectroscopy (IR), high resolution mass spectrum (HR-MS), and UV–vis spectra. The third-order nonlinear optical properties of the compounds were investigated using Z-scan technique with femtosecond laser pulses at 500 nm and 700 nm, respectively. Both of the compounds showed a decrease in transmittance about the focus, which are typical of two-photon absorption. It was found that the two-photon absorption behavior of the pyrene derivatives were modified by substituents on thiophene ring. These results indicate that both compounds can be promising candidates for future optoelectronic and bio-imaging applications.

1. Introduction

In recent years, organic nonlinear optical (NLO) materials have attracted considerable attentions due to their potential applications in a variety of optoelectronic and photonic fields. Owing to the nonlinear dependence on the excitation power, organic NLO materials enable many innovative applications including optical data storage, photonic switches, bio-imaging, optical power limiting, etc [1–3]. Among various conjugated organic materials, several representative organic molecules have been intensively investigated for third-order NLO applications, including phthalocyanines [4], naphthalocyanines [5], organic salts [6], chalcones [7] and squaraines [8]. Pervious results revealed that the NLO response of conjugated organic materials are closely related to the molecular architecture, such as the efficiency of intra-molecular charge transfer and the size of π -conjugation. Nonetheless, although various perspective materials have been demonstrated, the full understanding on the structure-properties relationships of the organic compounds are still incomplete. It is evidently desirable to further improving the NLO response of organic materials with optimized molecular structure.

Pyrene and its derivatives belong to the family of polyaromatic hydrocarbons (PAHs), which have been reported to be by far the most frequently used dye in fluorescence studies of labeled polymers [9,10]. Due to its planar and highly π -conjugated system, pyrene also exhibit excellent NLO response which is promising for optical limiting and bio-

imaging applications [11–18]. However, almost all substituted pyrene derivatives developed to date have been synthesized in a “symmetric” manner, i.e., a pyrene core with D- π -A or A- π -A structure. The NLO response of asymmetric pyrene derivatives, in particular those containing electron donor (D) and/or electron acceptor (A) moieties, are extremely scarce except for a few examples [11,19]. In our previous work, we found that the nonlinear optical properties of mono-substituted pyrene can be improved by modifying the main nonlinear group possession ratio occupied in frontier molecular orbitals [20]. Following this line of research, we attempt to evaluate the impact of peripheral substituent on the NLO activities of pyrene derivatives. To our knowledge no attempts have been made to evaluate the NLO response of a fixed pyrene architecture by changing the peripheral group on the thiophene ring.

In this paper, we successfully synthesized two pyrene derivatives 1-(pyren-1-yl)-3-(4-Methyl thiophene-2-yl) acrylic ketone (13#) and 1-(pyren-1-yl)-3-(4-bromo thiophene-2-yl) acrylic ketone (15#) from the condensation reaction of 1-acetyl pyrene (AP). The structure of 13# and 15# were characterized via various techniques. And the ultrafast NLO properties of the two compounds were investigated using Z-scan techniques with femtosecond laser pulses. The results demonstrate that both compounds have strong two-photon absorption at 500 and 700 nm. In addition, it is observed that the variation of peripheral group on thiophene ring is sufficient to modify the nonlinear response of pyrene core. Our study concludes that these asymmetric pyrene

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derivatives are promising candidates for two-photon absorption applications in the femtosecond regime.

2. Experimental

2.1. Instruments and reagents

Melting points were determined on an WRS-1B digital melting point apparatus and are uncorrected. IR spectra were recorded on a FT-IR-8400 infrared spectrometer. NMR spectra were recorded on a Bruker Advanced III HD NMR (600 MHz) spectrometer with tetramethylsilane (TMS) as internal standard. HRMS data were measured on a Bruker Daltonics APEX-QE spectrometer. The differential thermal analyses were measured on DCS-200-F3 differential scanning calorimeter. All chemicals used in the study were of analytical grade available in the market.

2.2. The preparation of 1-acetyl pyrene(AP) [21]

At ice water bath, acetyl chloride (4.5 mL, 62 mmol) in CH_2Cl_2 (100 mL) was added drop-wise to a mixture solution of pyrene (10.1 g, 50 mmol) and AlCl_3 (7.0 g, 52 mmol) in CH_2Cl_2 (400 mL) within 2 h. Then the mixture was stirred at room temperature under N_2 atmosphere for 12 h. After which it was cooled, diluted with cooled water. The mixture was extracted with CH_2Cl_2 (3×50 mL), and the organic layer was washed with brine and dried with absolute MgSO_4 . Then, the solvent was removed under reduced pressure. The residue was chromatographed with petroleum ether and CH_2Cl_2 (3:1), yielding 1-acetyl pyrene (9.3 g, 76.2%) with m.p. 86–87 °C.

2.3. Syntheses of 13# and 15#

The synthetic scheme of 13# and 15# was showed in Fig. 1. 1-acetyl pyrene (0.244 g, 10 mmol) was dissolved in 1,4-dioxane (20 mL), small amount of sodium hydroxide solution (20%, 1 mL) and 4-bromo-2-thiophenecarboxaldehyde (0.191 g, 10 mmol) were added drop-wise in sequence. Then the mixture was stirred at 60 °C for 7 h during which Thin-layer chromatography (TLC) was used to detect the reaction process. After 80% of the 1,4-dioxane was evaporated under reduced pressure, the mixture was cooled, diluted with cooled water, filtered and washed by pure water until to pH 7. Then the crude product was recrystallized from ethanol yielding 15# (0.33 g, 79%) as yellow powder. m.p.137.9 °C. ^1H NMR(600 MHz, $\text{DMSO}-d_6$) δ /ppm: 8.624–8.609 (d, 1 H, $J=9.0$, Pyr-H), 8.456–8.284 (m,7 H, Pyr-H), 8.178–8.152 (t, 1 H, $J=7.8$, Pyr-H), 7.923 (s, 1 H, Th-H), 7.785–7.759(d, 1 H, $J=15.6$ Hz, olefinic-H), 7.743 (s, 1 H, Th-H), 7.508–7.482 (d, 1 H, $J=15.6$, olefinic-H). ^{13}C NMR(150 MHz, $\text{DMSO}-d_6$) δ /ppm: 194.25, 141.17, 136.90, 134.28, 133.44, 133.35, 131.15, 130.54, 129.80, 129.66, 129.13, 128.27, 127.73, 127.29, 127.25, 127.00, 126.94, 126.59, 124.96, 124.79, 124.47, 124.01, 110.78. HR-MS m/z: found, 415.98645(Calcd. for $\text{C}_{23}\text{H}_{13}\text{OSBr}$, 415.9865).

The compound 13# was similarly obtained as a yellow solid in 72%

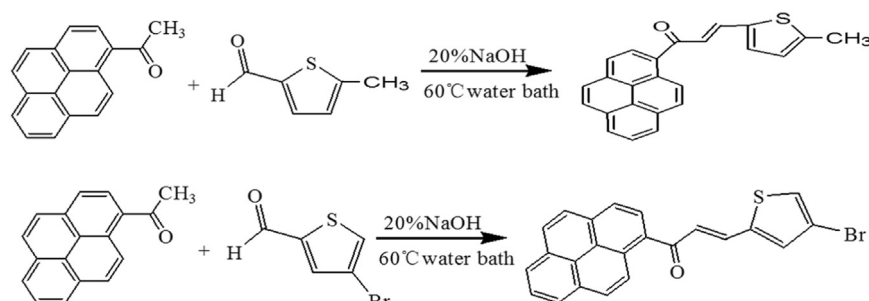


Fig. 1. Synthetic scheme of 1-(pyren-1-yl)-3-(4-Methyl thiophene-2-yl) acryloyl ketone (13#) and 1-(pyren-1-yl)-3-(4-bromo thiophene-2-yl) acryloyl ketone (15#).

yield. m.p.145.1 °C. ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ /ppm: 8.537–8.522(d, 1 H, $J=9.0$ Hz, Pyr-H),8.242–8.284(m, 7 H, Pyr-H), 8.176–8.151(t,1 H, $J=7.5$ Hz, Pyr-H), 7.724–7.699 (d, 1 H, $J=15.0$ Hz, olefinic-H), 7.444–7.439 (d, 1 H, $J=3.0$ Hz, Th-H), 7.186–7.160(d, 1 H, $J=15.6$ Hz, olefinic-H), 6.906–6.901 (d, 1 H, $J=3.0$ Hz, Th-H). ^{13}C NMR(150 MHz, $\text{DMSO}-d_6$) δ /ppm: 194.69, 145.84, 139.16, 137.91, 134.73, 134.05, 133.09, 131.18, 130.58, 129.55, 129.43, 128.89, 128.05, 127.75, 127.26, 126.80, 126.48, 125.00, 124.83, 124.81, 124.46, 124.07, 16.04. HR-MS m/z: found, 352.09165 (Calcd. for $\text{C}_{24}\text{H}_{16}\text{OS}$, 352.0916).

Both 13# and 15# were soluble in common polar solvents such as DMF and DMSO.

2.4. Nonlinear optical measurement

Z-scan measurements were performed at 700 nm and 500 nm using ~200 fs (FWHM) pulses with a repetition rate of 20 Hz from TOPAS (Light Conversion) pumped with a mode-locked Yb: KGW-based femtosecond laser (Pharos SP). The experimental apparatus was analogous to that described in Ref. [20]. A quartz cuvette (2 mm thick) containing the sample solution was traversed in the focusing geometry by a lens of 300 mm focal length. The beam waist at focal plane was estimated to be 30 μm with a corresponding Rayleigh range of ~3 mm. The transmitted power through the sample was measured as a function of sample distance z from the waist plane of laser beam. The studied samples were dissolved in DMSO with concentrations of 0.01 M. The solvent DMSO does not show any third-order nonlinearity under our experimental conditions. The fits to the data were performed using standard two photon absorption (TPA) equations that described in Ref. [22].

3. Results and discussion

3.1. Characterization

The ^1H NMR and ^{13}C NMR spectra of the 13# and 15# compounds are shown in Fig. S1~ Fig.S4. In which, the ^1H NMR peak of methyl group for 13# compound is immersed by the solvent absorption, while the corresponding ^{13}C NMR peak could be observed at 16.04 ppm, which clearly confirms the presence of the methyl group. The types and number of ^1H observed from the ^1H NMR spectrum of 15# compound is perfectly consistent with those of ^{13}C from the corresponding ^{13}C NMR. The HR-MS spectra of the 13# and 15# compounds are shown in Fig. S5~Fig.S6, with a resolution less than 0.00005, which further confirm the structures of the 13# and 15# compounds mentioned in the text. The thermal stability of the 13# and 15# compound are reflected in Fig. S7~ Fig.S8. In which, the respective melting peak show the corresponding melting point.

3.2. Ultraviolet spectra

The UV–vis spectra of the 13# and 15# compounds are shown in

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