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Twistacene contained molecule for optical nonlinearity: Excited-state based negative refraction and optical limiting

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ABSTRACT

Spindle-type molecules containing twisted acenes (**PyBTA-1** & **PyBTA-2**) are designed, synthesized characterized. Picosecond Z-scan experiments under 532 nm show reverse saturable absorption and negative nonlinear refraction, indicating large third-order optical nonlinearity in **PyBTA-1**. The mechanism of the optical nonlinearity is investigated and the results show that the nonlinear absorption and refraction in **PyBTA-1** originates from a charge transfer (CT) state. Furthermore, relatively long lifetime and absorptive cross section of the CT state are measured. Based on the excited state absorption in **PyBTA-1**, strong optical limiting with ~0.3 J/cm^2 thresholds are obtained when excited by picoseconds and nanoseconds pulses. The findings on nonlinear optics suggest **PyBTA-1** a promising material of all optical modulation and laser protection, which enrich the potential applications of these spindle-type molecules. Comparing to the previously reported spindle-type molecules with analogous structures, the introduction of ICT in **PyBTA-1** & **PyBTA-2** dramatically decreases the two-photon absorption while enhances the nonlinear refraction. The results could be used to selectively tailor the optical nonlinearity in such kind of compounds.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) with twisted π-surface have attracted much attention in recent years. Comparing to their original planar structures, twisted acenes have more sterically hindered π-system that could effectively inhibit π-stacking [1,2]. As a result, fluorescence quenching induced via aggregation is suppressed, which is vital for the fabrication of light emitting devices [3]. Novel PAHs containing twisted acenes have been synthesized via different routes and studied in various experiments [4–6]. Superior electronic and optical properties are displayed in these twistacene molecules, make them suitable materials for applications like organic light-emitting diodes (OLEDs) [7,8] and fluorescence imaging [9–11]. In our previous study [12], spindle-type molecule with a central double ethynes π-bridge (**DPDA** in Scheme 1) is designed and synthesized. Broadband reverse saturable absorption under different laser pulses was successfully achieved via two-photon induced excited state absorption. The results indicate that the spindle-type molecules have enormous potential in nonlinear optical applications. To further explore the optical nonlinearity in molecules containing twisted acenes, intramolecular charge transfer (ICT) is employed since a strong connection between ICT and optical nonlinearity in organic molecules is suggested in various reports [13,14].

Following this strategy, two novel molecules (**PyBTA-1** & **PyBTA-2**, shown in Scheme 1) are designed and synthesized. Both compounds have a spindle-type molecular structure with two identical units containing twisted acenes linked by a π-bridge (central group with two ethynes at each side). 2,1,3-benzothiadiazole (usually employed as strong electron acceptor) is substituted at the center of the π-bridge. The ICT induced optical nonlinearity in **PyBTA-1** & **PyBTA-2** are then investigated via transient absorption & refraction methods, which were rarely reported before. Strong negative nonlinear refraction and optical limiting are revealed in **PyBTA-1**, suggesting that the spindle-type molecule could be a superior material in applications such as laser protection and all optical switching.

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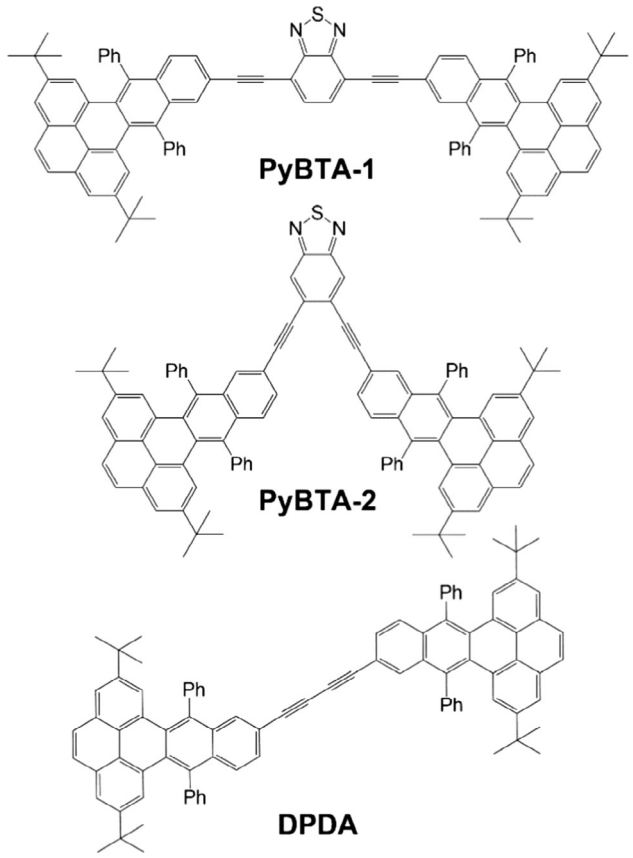


Scheme 1. Chemical structures of molecules PyBTA-1, PyBTA-2 and DPDA.

2. Experimental section

2.1. Synthesis and characterization

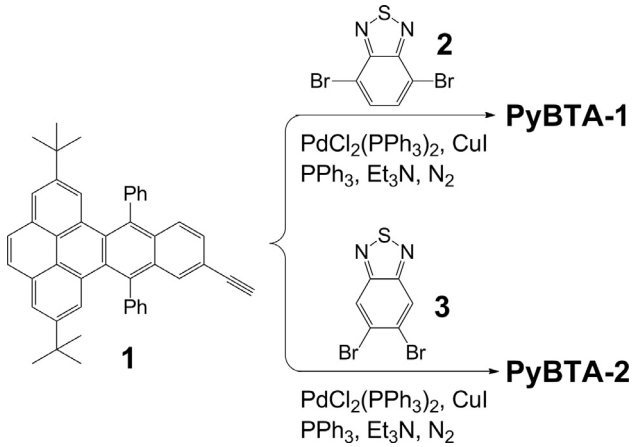
The synthetic procedure is depicted in Scheme 2. The precursor **1** was synthesized according to the method in previous work [3]. Compounds **PyBTA-1** and **PyBTA-2** were obtained via the classical Sonogashira coupling between **1** and 4,7-dibromo-2,1,3-benzothia diazole (**2**)/5,6-dibromo-2,1,3-benzothiadiazole (**3**) in the presence of $PdCl_2(PPh_3)_2$. Both possess good solubility in common organic solvents such as dichloromethane, chloroform, toluene.

PyBTA-1: A mixture of compound **1** (170 mg, 0.29 mmol), 4,7-dibromo-2,1,3benzothiadiazole (**2**, 38 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol), CuI (6 mg, 0.031 mmol) and PPh_3 (16 mg, 0.061 mmol) was dissolved in triethylamine (30 mL) and degassed. Then the reaction mixture was heated to 90 °C and stirred for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. Brine was added. After the solution was extracted with dichloromethane (30 mL) for three times, the collected organic phase was dried with Na_2SO_4. The solvent was evaporated and the residue was purified with petroleum ether/dichloromethane (v/v, 8:1) to give **PyBTA-1** as a solid (142 mg, 83%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K), δ = 8.19 (d, *J* = 1.2 Hz, 2H), 8.17 (d, *J* = 1.8 Hz, 2H), 8.14 (d, *J* = 1.8 Hz, 2H), 7.87–7.84 (m, 10H), 7.76 (s, 2H), 7.66–7.64 (m, 6H), 7.61–7.57 (m, 12H), 7.52–7.48 (m, 4H), 1.14 (s, 36H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K), δ = 154.3, 147.3, 142.3, 142.1, 136.2, 136.0, 132.54, 132.49, 132.41, 131.7, 131.6, 131.0, 130.7, 130.34, 130.32, 129.5, 129.4, 128.0, 127.8, 127.71, 127.66, 127.1, 126.94, 126.91, 123.97, 123.92, 122.6, 122.5, 119.4, 117.1, 98.7, 86.3, 34.8, 31.4. MALDI-TOF (MS): Calc. for $C_{98}H_{76}N_2S$: [m/z] 1313.6, found: [m/z] 1313.7. Details could be found in supplementary materials (Figs. S1, S2).

PyBTA-2: A mixture of compound **1** (170 mg, 0.29 mmol), 5,6-dibromo-2,1,3-benzothiadiazole (**3**, 38 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol), CuI (6 mg, 0.031 mmol) and PPh_3 (16 mg, 0.061 mmol) was dissolved in triethylamine (30 mL) and degassed. Then the reaction mixture was heated to 90 °C and stirred for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. Brine was added. After the solution was extracted with dichloromethane (30 mL) for three times, the collected organic phase was dried with Na_2SO_4. The solvent was evaporated and the residue was purified with petroleum ether/dichloromethane (v/v, 8:1) to give **PyBTA-2** as a solid (78 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$, 298 K), δ = 8.24 (s, 2H), 8.18 (d, *J* = 1.8 Hz, 2H), 8.14 (d, *J* = 1.8 Hz, 2H), 8.01 (d, *J* = 1.8 Hz, 2H), 7.85–7.77 (m, 10H), 7.58–7.56 (m, 4H), 7.54–7.51 (m, 6H), 7.47–7.45 (m, 4H), 7.43–7.41 (m, 2H), 7.25–7.21 (m, 6H), 1.11 (s, 18H), 0.95 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$, 298 K), δ = 154.0, 147.30, 147.29, 142.4, 142.0, 136.1, 136.0, 132.34, 132.29, 131.7, 131.5, 130.9, 130.8, 130.7, 130.34, 130.28, 129.4, 129.34, 129.30, 129.2, 127.8, 127.7, 127.6, 1278.2, 126.91, 126.88, 126.85, 124.3, 124.0, 123.8, 122.6, 122.5, 119.5, 97.4, 88.1, 34.8, 34.6, 31.4, 31.2. MALDI-TOF (MS): Calc. for $C_{98}H_{76}N_2S$: [m/z] 1313.6, found: [m/z] 1313.6. Details could be found in supplementary materials (Figs. S3, S4).



Scheme 2. Synthetic route to compounds PyBTA-1 and PyBTA-2.

2.2. Z-scan experiment

Z-scan experiment [15] was conducted to measure the third-order optical nonlinearity. The light sources included a Q-switched and mode locked Nd: YAG laser (PL2143B, EKSPLA) working at 532 nm pulses with 21 ps pulse width (FWHM); An optical parametric amplifier (OPA) (ORPHEUS, Light Conversion) outputting wavelength tunable 190 fs (FWHM) pulses. The repetition rate was set to 10 Hz to avoid heat accumulation in the sample. The induced laser intensity was tuned to 4.9 GW/cm^2 and 32 GW/cm^2 in picoseconds and femtoseconds Z-scan, respectively. Cuvettes (2 mm) containing sample solution with concentration of 2×10^{-4} M were placed on a translate stage and moved along Z axis. Detectors (Rj-765a, Laser Probe) were used to record the energy data. All systems were controlled through personal computer.

2.3. Phase object pump–probe (POPP)

A Q-switched and mode locked Nd: YAG laser (PL2143B, EKSPLA, 532 nm, 21 ps) is employed as laser source in POPP. The