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Exploration of Optical Properties of Novel Pyrene Derivatives Modified by Click Functionalization

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Abstract: A simple synthetic method was designed, in which the Sonogashira coupling reaction and [2+2] cycloaddition click reaction with high yield were performed on 1-bromopyrene to obtain several novel pyrene derivatives. The structure of each sample was characterized by Nuclear Magnetic Resonance (NMR), Mass Spectrometry (MS), Fourier transform infrared (FTIR) and elemental analysis. The characterization of the products by Ultraviolet-visible (UV-vis) and Photoluminescence (PL) spectroscopy proves that the addition of click groups has an important effect on the optoelectronic properties of pyrene derivatives. The Z-scan technique was used to test the third-order nonlinear optical (NLO) properties of the samples, and it could be found that the NLO properties of the products were improved and the transition of saturable absorption and reverse saturable absorption occurred with the addition of click reagent. These factors indicate that the click-modified pyrene derivatives have potential applications in areas such as optical limiting.

Keywords: pyrene derivatives; click chemistry; nonlinear optics

1. Introduction

Nonlinear optics has been developed for half a century since its introduction, and the development of nonlinear optics has been significant in various fields [1,2], including optical communication [3], laser protection [4], optical switching [5,6], and three-dimensional (3D) micro- and nano-manufacturing [7]. Various nonlinear optical materials are constantly being developed and progressed. Organic nonlinear optical materials are attracting the interest of scientists due to their excellent chemical stability, easy modification and processing, and strong NLO responsiveness [8–12].

Click chemistry has a wide and universal application in the synthesis of organic molecules, especially in the field of biopharmaceuticals [13–16]. Thiol–alkene reaction and Diels–Alder reaction are all classical click reactions discovered by scientists. Click chemistry is popular in organic synthesis because of its high yield, mild reaction conditions, and no byproducts [17]. The [2+2] cycloaddition click reactions can react click reagents such as ethene-1,1,2,2-tetracarbonitrile (TCNE), 2,2′-(cyclohexa-2,5-diene-1,4-diylidene)dimalononitrile (TCNQ) with alkyne structures to form larger conjugated structures [18–21], which have great potential for the design and synthesis of third-order NLO molecules. In the previous reports, materials such as fullerenes [22] and porphyrins [23] were modified by [2+2] cycloaddition click chemistry, which significantly improved their third-order nonlinear properties [24–27].

Pyrene is an aromatic compound with a large, conjugated structure, which has excellent fluorescence properties and good chemical stability [28–31]. Because of their excellent chemical properties and low cost, various compounds of pyrene structure have many applications in nonlinear optics [32,33], photoluminescence [34,35] and other fields. The use of click reactions on pyrene derivatives has also led to a broader application of this type of compound [36,37].

In this paper, several novel monosubstituted pyrene derivatives were prepared by [2+2] cycloaddition click chemistry and the Sonogashira coupling reaction. The synthesis method of pyrene derivatives using the click reaction is simple, convenient, and efficient. Moreover, the conjugated structure of pyrene derivatives is enlarged by the click chemical modification, which is beneficial to the electron energy transition, thus improving its nonlinear optical properties. They were confirmed to be the target products by NMR, MS, FTIR, and elemental analysis; the samples were tested by UV-vis spectroscopy, PL spectroscopy, and Z-scan technology, and their properties were also in line with expectations. Click-modified pyrene derivatives may be applied to various fields in the future to benefit people's daily life.

2. Materials and Methods

2.1. Preparation Method

The synthetic route of pyrene derivatives is shown in Figure 1, and PY-C16 and its click-modified products PY-C16-TCNE and PY-C16-TCNQ were prepared. It can be seen that monobromopyrene derivatives are linked to triple bonds by the Sonogashira coupling reaction [38], and the triple bond is protected by a silicon group [39]. After the removal of the edge protecting silicon group, the product was subjected to the same cross-coupling reaction to attach the R group. Finally, PY-C16 was modified by the click reagents TCNE and TCNQ to obtain the click products PY-C16-TCNE and PY-C16-TCNQ. The whole reaction process is not only simple, but also very efficient. What is more, almost no by-products were generated during the reaction. Only simple column chromatography was required to obtain the final product with high purity.
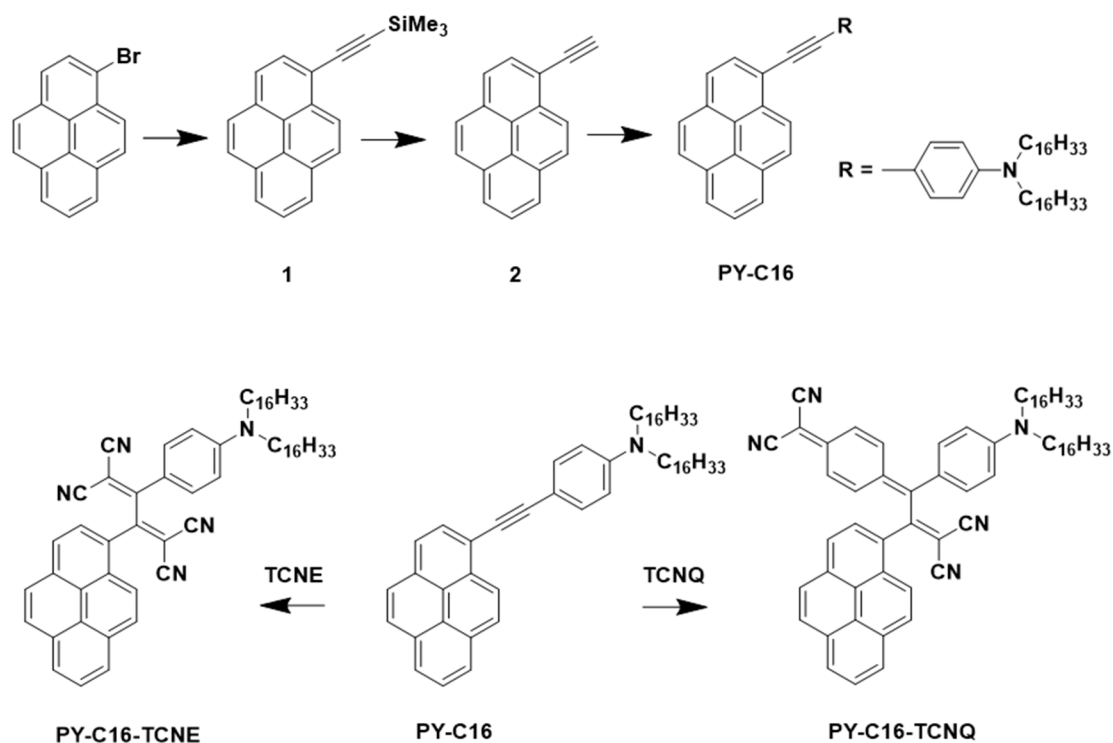

Figure 1. Synthetic route of pyrene derivatives.

2.2. Experimental Method

Reagents that were all bought from commercial sources (Energy chemical, Aladdin) for preparation were used without any further purification. In the experimental process, BRUKER AVANCE III HD NMR 400 MHZ at 20 °C was used to measure ^{1}H NMR, Perkin Elmer LR-64912C tests the FTIR spectra of the samples, and JASCO V-570 tests the UV-vis spectra of the products. MALDI-TOF-MS (Time-of-Flight Mass Spectrometry) continuums were measured by Shimadzu AXIMA-CFR spectrometers. The NLO properties of the materials were tested by the Z-scan technology (20 ps/532 nm).

2.2.1. Synthesis of Trimethyl(pyren-1-ylethynyl) Silane (**1**)

In total, 6 mL of tetrahydrofuran (THF) and 6 mL of triethylamine (TEA) were mixed, then 280 mg of 1-bromopyrene (98%, 1.00 mmol) were added, argon was bubbled and deoxygenated by ultrasonic for 50 min. Then 46.0 mg of Pd(PPh$_3$)$_4$ (98%, 0.04 mmol), 15.0 mg of CuI (98%, 0.08 mmol) and 490 mg of ethynyltrimethylsilane (TMSA, 5.00 mmol) were added to the system. The temperature of the entire reaction system was kept at 80 °C, oxygen was isolated, and the reaction was magnetically stirred for 8h. Dichloromethane (DCM) was poured into the cooled reactor, the insoluble solids was removed by suction filtration, and the liquid was removed by spin evaporation. Then using the chromatographic column (SiO$_2$, $V_{DCM}/V_{petroleum\ ether\ (PE)}$ = 1/8) to purify again, the solid compound Trimethyl(pyren-1-ylethynyl)silane (compound 1 in Figure 1) was obtained. Yield: 0.25 g (81%). Yield: 0.25 g (81%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.70 (1H, d), 8.20 (8H, m), 0.9 (9H, m) ppm. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{21}$H$_{18}$Si: 298.12 g mol^{-1}, found: 299.23 g mol^{-1} [MH]$^+$. Elemental analysis calcd (%) for C$_{21}$H$_{18}$Si: C 84.51, H 6.08, Si 9.41; found: C 84.50, H 6.09, Si 9.41.

2.2.2. Synthesis of 1-Ethynylpyrene (**2**)

Trimethyl(pyren-1-ylethynyl)silane (250 mg, 0.81 mmol) was placed in a flask containing 5 mL of THF and 3 mL of methanol (MeOH), followed by K$_2$CO$_3$ (336 mg, 2.44 mmol). The temperature of the entire reaction system was kept at 25 °C; the reaction was magnetically stirred for 3h and protected from light. After removing the insoluble K$_2$CO$_3$, the system was spin-distilled. The chromatographic column (SiO$_2$, DCM) and spin evaporation were employed to obtain solid compound 1-ethynylpyrene (compound 2 in Figure 1). Yield: 0.16 g (88%). Yield: 0.16 g (88%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.70 (1H, d), 8.20 (8H, m), 3.50 (1H, s) ppm. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{18}$H$_{10}$: 226.08 g mol^{-1}, found: 227.09 g mol^{-1} [MH]$^+$. Elemental analysis calcd (%) for C$_{18}$H$_{10}$: C 95.55 H, 4.45; found: C 95.56 H, 4.44.

2.2.3. Synthesis of N,N-Dihexadecyl-4-(pyren-1-ylethynyl)aniline (PY-C16)

In total, 20 mL of THF was mixed with 20 mL of TEA, then 1-ethynylpyrene (200 mg, 0.80 mmol) and N,N-hexadecyl-4-iodoaniline (2.40 g, 3.60 mmol) were put into the flask. The system was deoxygenated by sonication for 45 min in argon atmosphere. CuI (19.0 mg, 0.10 mmol) and Pd(PPh$_3$)$_4$ (55.0 mg, 0.05 mmol) were added to the reaction vessel. The temperature of the entire reaction system was kept at 80 °C, oxygen was isolated, and the reaction was magnetically stirred for 8h. Dichloromethane (DCM) was poured into the cooled reactor, the insoluble solids were removed by suction filtration, and the liquid was removed by spin evaporation. Then using the chromatographic column (SiO$_2$, V_{DCM}/V_{PE} = 1/8) to purify again, the solid product PY-C16 was obtained. Yield: 0.63 g (79%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.70 (1H, d), 8.20 (8H, m), 7.58 (2H, d), 6.68 (2H, d), 3.34 (4H, m), 1.20 (56H, m), 0.90 (6H, m) ppm. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{56}$H$_{79}$N: 765.62 g mol^{-1}, found: 766.63 g mol^{-1} [MH]$^+$. FT-IR (KBr): 2931, 2866, 2201, 1609, 1463, 1372, 1016, 852, 790 cm-1. Elemental analysis calcd (%) for C$_{56}$H$_{79}$N: C 87.78, H 10.39, N 1.83; found: C 87.79, H 10.40, N 1.81.

2.2.4. Synthesis of 2-(4-(Dihexadecylamino)phenyl)-3-(pyren-1-yl)buta-1,3-diene-1,1,4,4-tetracarbo Nitrile (PY-C16-TCNE)

Compound PY-C16 (100 mg, 0.08 mmol) and ethene-1,1,2,2-tetracarbonitrile (TCNE) (9.60 mg, 0.08 mmol) were transferred to a reaction vessel containing 10 mL of DCM. The temperature of the entire reaction system was kept at 25 °C, the reaction was magnetically stirred for 30min, and the solvent was distilled off under reduced pressure. Then the chromatographic column (SiO$_2$, V$_{DCM}$/V$_{PE}$ = 1/1) was used to purify, and finally the solid click reaction product PY-C16-TCNE was obtained. Yield: 60.7mg (85%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.37 (1H, d), 8.21 (8H, m), 7.90 (2H, d), 6.72 (2H, d), 3.40 (4H, d), 1.28 (56H, m), 0.90 (6H, m) ppm. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{62}$H$_{79}$N$_5$: 893.63 g mol^{-1}, found: 894.65 g mol^{-1} [MH]$^+$. FT-IR (KBr): 2921, 2857, 2216, 2192, 1597, 1465, 1365, 1182, 809 cm^{-1}. Elemental analysis calcd (%) for C$_{62}$H$_{79}$N$_5$: C 83.27, H 8.90, N 7.83; found: C 83.28, H 8.90, N 7.82.

2.2.5. Synthesis of 2-(4-(3,3-Dicyano-1-(4-(dihexadecylamino)phenyl)-2-(pyren-1-yl)allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (PY-C16-TCNQ)

Compound PY-C16 (100 mg, 0.08 mmol) and 2,2′-(cyclohexa-2,5-diene-1,4-diylidene) dimalononitrile (TCNQ) (11.80 mg, 0.08 mmol) were transferred to a reaction vessel containing 12 mL of DCM. The temperature of the entire reaction system was kept at 25 °C, and the reaction was magnetically stirred for 2 h. Then the chromatographic column (SiO$_2$, V$_{DCM}$/V$_{PE}$ = 1/1) was used to purify, and finally the solid click reaction product PY-C16-TCNQ was obtained. Yield: 62.1 mg (80%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.15 (8H, m), 7.99 (1H, d), 7.46 (1H, d), 7.38 (2H, d), 7.24 (2H, d), 7.09 (1H, d), 6.63 (2H, d), 3.33 (4H, d), 1.27 (56H, m), 0.89(6H, m) ppm. MALDI-TOF-MS (dithranol): m/z: calcd for C$_{68}$H$_{83}$N$_5$: 969.66 g mol^{-1}, found: 970.69 g mol^{-1} [MH]$^+$. FT-IR (KBr): 2921, 2857, 2216, 2192, 1597, 1465, 1365, 1182, 809 cm^{-1}. Elemental analysis calcd (%) for C$_{68}$H$_{83}$N$_5$: C 84.16, H 8.62, N 7.22; found: C 84.16, H 8.63, N 7.21.

3. Results and Discussion

3.1. UV-Vis and PL Spectroscopy

Figure 2 shows the UV-vis absorption spectra of pyrene derivatives (PY-C16) and their click reaction products (PY-C16-TCNE, PY-C16-TCNQ) in dichloromethane solution. It can be clearly seen that the maximum absorption peak of PY-C16 is around 400 nm, which is related to the π-π* transition absorption of the pyrene conjugated group of the molecule [40]. Compared with PY-C16 before the click reaction, the maximum absorption peaks of PY-C16-TCNE and PY-C16-TCNQ after the click reaction were red-shifted to around 500 nm and 780 nm, respectively. The red-shift of the absorption peak is mainly due to the strong electron withdrawing group (cyano group) in the click reagent. The introduction of the cyano group in the click reagents (TCNE and TCNQ) will reduce the density of the π electron cloud in the molecule, and the molecular π-π* transition energy will decrease. In addition, the same comparison between PY-C16-TCNE and PY-C16-TCNQ can be drawn, due to the existence of the quinoid conjugated structure in TCNQ. But because the π-conjugated structure of PY-C16-TCNQ is larger, the π-π* transition energy is thus further reduced, and the absorption peak is more red-shifted.

In order to characterize the reaction characteristics of the click reaction, UV-vis titration tracking experiment was carried out for the click reaction. As shown in Figure 3, as TCNE was gradually added dropwise to PY-C16, the original strong absorption peak near 400 nm in the UV-Vis absorption curve of PY-C16 decreased, and an absorption peak was generated near 500 nm, which also accorded with to the UV-Vis absorption curve of PY-C16-TCNE. When the reaction was completed, the curve at this time was completely consistent with the PY-C16-TCNE curve, which proves that the reaction is an efficient chemical modification method without side reactions.
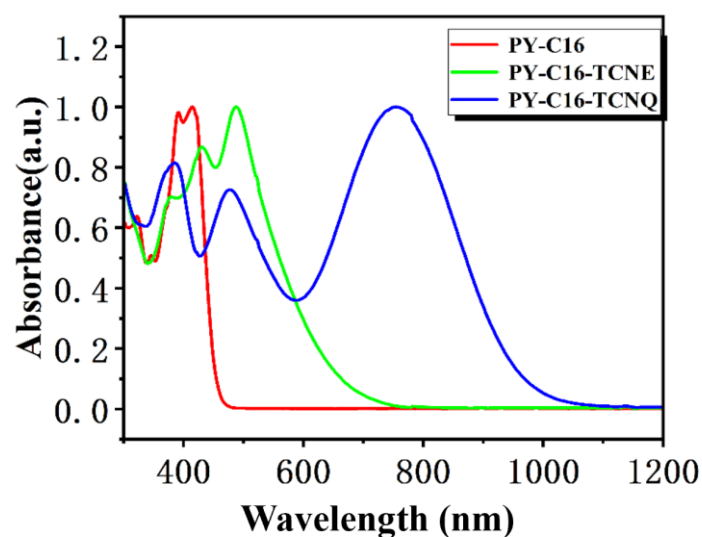
Figure 2. Normalized UV-vis absorption spectra of compound PY-C16 and click products PY-C16-TCNE, PY-C16-TCNQ measured in dichloromethane solution with a concentration of 10^{-5} M.
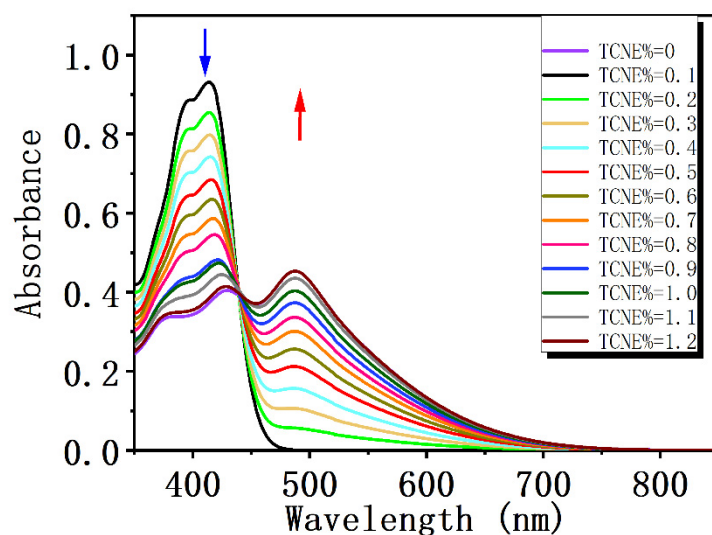

Figure 3. Normalized UV-vis spectral changes of PY-C16 during the TCNE titration in dichloromethane.

The UV-vis absorption and PL spectra of PY-C16 in different solvents are shown in Figures 4 and 5 and Table 1 shows the highest peaks of the UV absorption spectrum and the photoluminescence spectrum of PY-C16 in various solvents. As shown in Figure 4, with the increase in solvent polarity, there is no obvious red shift or blue shift in the sample, which indicates that solvents with different polarities have little influence on the absorption capacity of ground-state compounds [41]. However, in the fluorescence emission spectrum shown in Figure 5, with the increase in the polarity of the solvent, the emission peak of the sample is obviously red-shifted. When the solvent is DMF, the emission peak reaches 130nm, which is a typical positive solvent effect. The reason for this phenomenon is that the interaction between the molecular excited state of the compound and different solvents is different, which leads to the change of emission peak position. The fluorescence properties of pyrene derivatives almost disappeared after the click chemical modification, which may be because the introduction of strong electron withdrawing groups in the click reagents changed the conjugated structure of PY-C16, while the strong π-π* interaction favors electron transfer, which leads to the phenomenon of photoluminescence quenching [42,43].

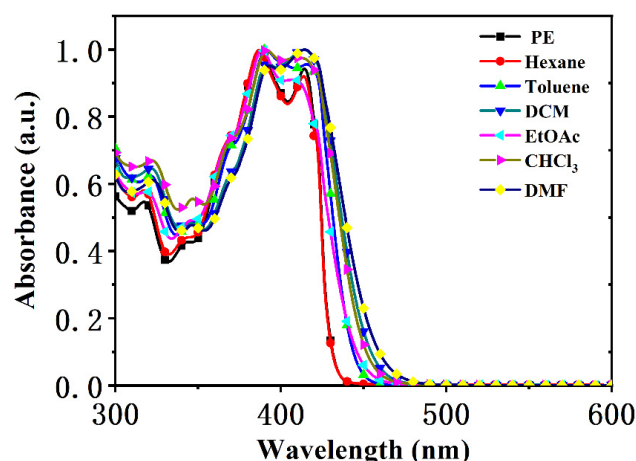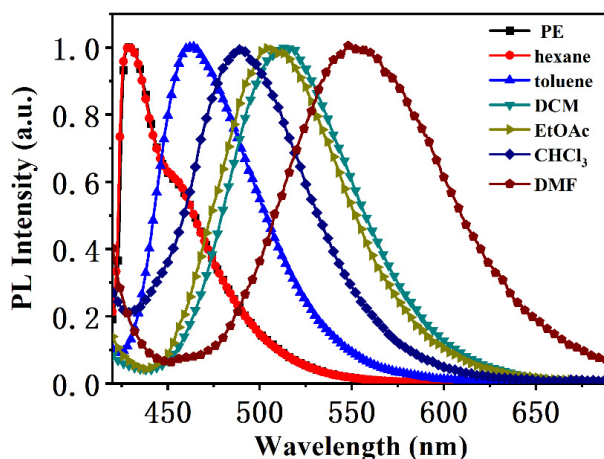**Figure 4.** Normalized UV-vis absorption spectra of PY-C16 in different solvents.

Figure 5. Normalized photoluminescence spectra of PY-C16 in different solvents.

Table 1. The positions of the highest peaks of PY-C16 absorption and emission spectra in different solvents.

Solvent	$\lambda_{abs,1}$ (max/nm)	$\lambda_{abs,2}$ (max/nm)	λ_{em} (max/nm)	Stokes Shift (cm^{-1})
petroleum ether(PE)	414	388	430	898
hexane	414	386	430	898
toluene	416	392	470	2761
dichloromethane (DCM)	414	392	515	4737
EtOAc	408	388	500	4509
CHCl₃	412	392	490	3863
N,N-Dimethylformamide (DMF)	414	388	555	6136

3.2. Z-Scan Experiments

To determine the NLO properties of the above three pyrene derivatives, Z-scan measurements were performed using a nanosecond pulsed laser at 532 nm. The curves measured by the Z-scan method not only allowed the sign of the NLO coefficient of the material to be determined, but also the NLO refractive index and NLO absorption coefficient of the material were able to be obtained by further calculations [44,45].

Figure 6 is the open aperture Z-scan traces of this series of pyrene derivatives. It can be seen from Figure 6a that with the increase in the incident laser light intensity, the light absorption intensity of the compound PY-C16 decreases, which is a typical saturable absorption (SA) characteristic. On the contrary, in the scanning curves of Figure 6b,c, it can be seen that the transmittance of PY-C16-TCNE and PY-C16-TCNQ gradually decreases with the increase in incident laser intensity, which is the characteristic of typical reverse saturated absorption (RSA). It can be concluded that the NLO absorption property of the material is changed by the click chemical modification of TCNE and TCNQ, and the transition from saturable absorption to reverse saturable absorption occurs. The modification of the click reagents TCNE and TCNQ improves the excited state absorption capacity of the pyrene derivative PY-C16 [44].
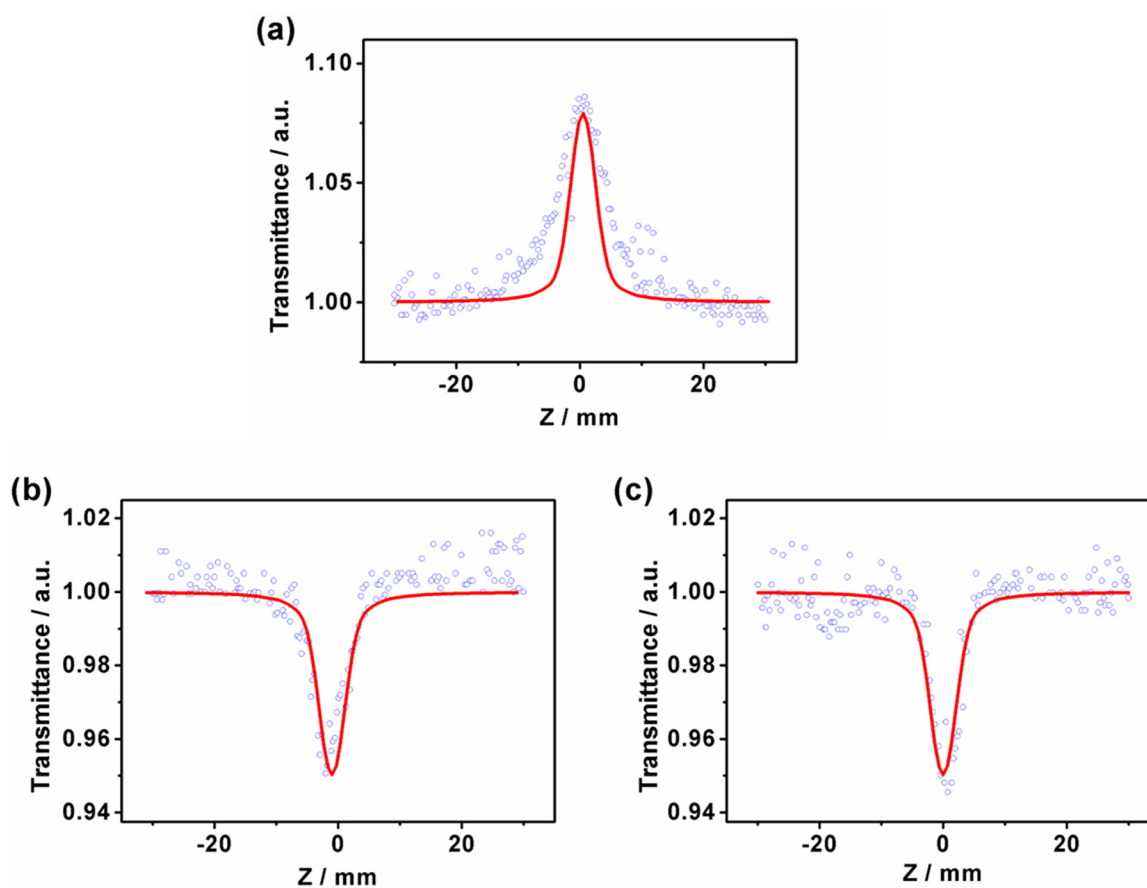

Figure 6. Open-aperture Z-scan curves of compound (**a**) PY-C16, (**b**) PY-C16-TCNE and (**c**) PY-C16-TCNQ.

The normalized close aperture Z-scan trace of compound PY-C16 is shown in Figure 7. Moreover, there is no regular nonlinear refraction curve of the product modified by the click reaction. It can be confirmed that PY-C16 has the characteristic of NLO negative refraction according to the Z scan trajectory of the first wave peak and then the wave trough. The close aperture Z-scan trace reflects the NLO refraction effect of the product, but the products PY-C16-TCNE and PY-C16-TCNQ after the click modification have no obvious NLO refraction effect. This may be due to the fact that different substituents have different effects on the NLO refraction effect of different materials.
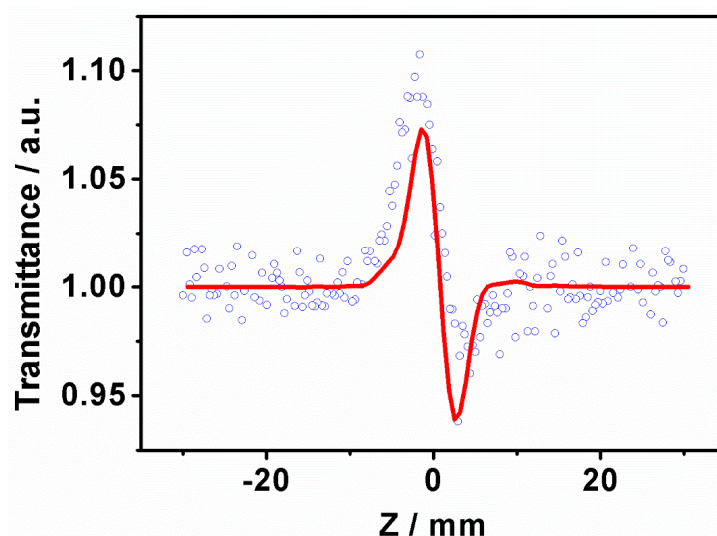
Figure 7. Closed-aperture Z-scan curve of compound PY-C16.

The calculated nonlinear optical coefficients of the samples are shown in Table 2, where β is the NLO absorption coefficient, n_2 is the NLO refractive index, and $\chi^{(3)}$ is the third-order nonlinear polarizability. As can be seen from Table 2, compared with the absorption coefficient of NLO, the third-order nonlinear refractive index of PY-C16 is much smaller. It can be seen that the anti-saturable absorption performance of PY-C16-TCNQ is stronger than that of PY-C16-TCNE, because the former obtains a larger conjugated structure after clicking [1–4,45]. Compared with some other novel NLO organic materials that have been reported, the NLO absorption coefficients of these samples can also reach the same order of magnitude [22,23,27].

Table 2. Third-order nonlinear parameters of compounds.

Samples	$B \times 10^{-12}$ (m/W)	$n_2 \times 10^{-19}$ (m²/W)	$\chi^{(3)} \times 10^{-13}$ (esu)
PY-C16	−2.1	−1.7	4.8
PY-C16-TCNE	0.8	—	1.8
PY-C16-TCNQ	1.4	—	3.1

4. Conclusions

In summary, three materials were obtained by preparing a monosubstituted pyrene derivative and modifying it by click chemistry. The test results of UV-vis spectroscopy and photoluminescence spectroscopy indicated that the click reagent was successfully attached to the monosubstituted pyrene product. The access of TCNE and TCNQ of the click reagent increases the conjugated structure of the product, which affects the electron transfer and energy transition of the product, and the product has a broader absorption in the near-infrared and visible regions. The application of Z-scan technology confirms that the use of click chemistry makes the pyrene derivative undergo a transition from saturable absorption to reverse saturable absorption, and the increase in the conjugated structure after the click modification improved the third-order NLO absorption coefficient of the material. Click-modified conjugated organic molecules provide a promising result for the development and preparation of organic materials for NLO applications.

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