Accepted Manuscript

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PII: S0040-4020(16)30420-3

DOI: 10.1016/j.tet.2016.05.035

Reference: TET 27762

To appear in: Tetrahedron

Received Date: 29 February 2016

Revised Date: 12 May 2016

Accepted Date: 13 May 2016

Please cite this article as: Miao Z, Han H, Wang D, Gao H, Gu J, Hu H, Nonlinear optical and energy-level modulation of organic alkynes by click chemistry, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.05.035.

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Nonlinear optical and energy-level modulation of organic alkynes by click chemistry

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ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Nonlinear optical Energy-level modulation Click chemistry Near infrared absorption

ABSTRACT

A series of novel donor-acceptor chromophores have been successfully synthesized in excellent yield by metal-free [2+2] click chemistry, which was effective in the energy-level modulation of organic the π -conjugation aniline derivatives. Meanwhile, structures of all products were fully characterized by NMR, IR, and MS. UV-vis spectra were enlarged with end-absorptions into the near infrared region in varying degrees by introducing TCNE, TCNQ, F4-TCNQ click reagents and correspondingly electrochemical tests revealed that the energy levels of HOMO and LUMO were effectively tuned. The third order nonlinear optical properties studied at 532/1064 nm with picosecond Z-scan techniques indicated that almost all products exhibited the high NLO properties, especially, for dye c_5 , exhibiting third-order susceptibility $\chi^{(3)}$ =1.83×10⁻⁷ esu under laser beam at 1064 nm.

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1. Introduction

The nonlinear optical organic materials have received wide attention in material science due to their possible applications in electronic and optoelectronic devices[1-11]. The organic materials, which were gaining considerable interest as a promising class of materials, were being used in optical limiting, optical switching, electronic devices, and nonlinear optical media[12-15], because of their large nonlinear optical (NLO) response, chemical stability and process ability. Donor-acceptor conjugated organic materials containing both electron rich and electron deficient moieties along the molecule backbone were known to exhibit the enhanced third-order NLO properties due to the increase in effective π electron delocalization. Design and synthesis of the excellent performance of the three order NLO materials was a hot research topic in recent years. To date, many kinds of organic NLO materials have been synthesized, such as D-A push-pull structure of azo compounds, squaric acid, heterocyclic compounds, tetrathiafulvalene derivatives, schiff base complex, phthalocyanine compounds and ferrocene derivatives[16-26]. Among them, complexes with potential NLO properties, good thermal and photochemical stability, and redox switching abilities have caused considerable interests. These studies had focused on the important role of substituents enhancing third-order NLO properties of such materials.

Both increasing the light absorption intensity and expanding the light absorption range, which were important to improve third-order NLO properties, were still the important task. Fortunately, we found a simple and efficient method for the synthesis of organic benzene derivatives with great potential applications for photoelectric materials which can be achieved by the thermal [2+2] cycloaddition followed by the ring-opening of click chemistry[27-31]. This approach through linking click reagent to the π -conjugation bridge of the compound extending the photo absorption to longer wavelength, and obtaining higher molar extinction coefficients access to the better third-order NLO properties[32-35].

Here, we designed and synthesized a family of organic conjugated molecules with great potential applications for photoelectric materials. Meanwhile, the novel click chemistry allowed us to efficiently modulate the HOMO-LUMO energy band gap, leading top-conjugated molecules with tunable electrochemical properties as well as excellent solubility, which was beneficial for processing. The differences of the NLO performance had also been analyzed based on the chemical structures of the compounds.

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2. Experimental section

2.1. Instrumental characterization equipments

¹H NMR spectra were measured on a Bruker AV 500 NMR spectrometer (500 MHz) at 20 °C. Chemical shifts were reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. FT-IR was recorded on a Perkin Elmer LR-64912C Fourier transform infrared spectrometer. All MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer. UV-vis spectra were recorded in a quartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out on a computercontrolled CHI 660C instrument at RT. Both the first oxidation potentials (E_{ox}) corresponding to the HOMO levels of the compounds and the first reduction potentials (E_{red}) relating to the LUMO levels of the compounds were measured by cyclic voltammetry (CV) in CH2Cl2 solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte, glassy carbon as working electrode, Ag/AgCl as the reference electrode, Pt as the counter electrode and a standard ferrocene/ferrocenium redox system as the internal standard. The third order NLO properties such as nonlinear index of refraction n_2 and nonlinear absorption coefficient β can be measured with high accuracy by a singlebeam Z-scan technique. Test conditions of Z scanning platform were as follows: for the 532-band laser, DMSO acts a standard sample and pulse width of 21 ps was applied. The conditions of focal length, energy and light hole diameter were 400 mm, 0.39 uj and 4.8 mm, respectively. Additionally, for the 1064-band laser, the standard sample of Silicon sheet was used and pulse energy decreases from 0.39 uj to 1.2 uj. Moreover, transmission was reduced from 58 percent to 10 percent, which other parameters were not changed comparing with the 532-band laser. Elemental analyses were performed at Flash EA 1112 instrument.

2.2. Synthesis routes

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Materials were synthesized via the synthetic route presented in **Scheme 1**. $\mathbf{a}_2 - \mathbf{a}_4$, \mathbf{b}_1 , \mathbf{c}_3 , \mathbf{b}_2 , \mathbf{c}_6 were synthesized according to the corresponding literature methods[27-31]. Notice: DMF: dimethyl-formamide, THF: tetrahydrofuran, TEA: triethylamine, TMSA: trimethylsilylacetylene, TCNE: tetracyanoethylene, TCNQ: 2,2'-(cyclohexa-2,5-diene-1,4-diylidene) dimalononitrile, F₄-TCNQ: 2,2'-(perfluoroc-yclohexa-2,5-diene-1,4-diylidene) dimalono nitrile.



Scheme 1. Synthesis routes of compounds, Reagents and conditions: (i) DMF, C_4H_9Br , 130 °C, 20 h; (ii) THF, TEA, Pd(PPh₃)₄, CuI, TMSA, 40 °C, 12 h; (iii) THF, methanol, K_2CO_3 , 40 °C, 3 h; (iv) THF, TEA, Pd(PPh₃)₄, CuI, 80 °C, 8 h; (v) N,N,N',N'-tetraethylethylenediamine, toluene, CuCl, 60 °C, 24 h.



	b ₁ (78%)	$\mathbf{b}_{2}(60\%)$	b ₃ (70%)	b ₄ (95%)
TCNE	c ₁ (91%)	$c_4 (89\%)$	c ₇ (93%)	c ₁₀ (92%)
TCNQ	c ₂ (92%)	c ₅ (95%)	c ₈ (83%)	c ₁₁ (96%)
F4-TCNQ	c ₃ (97%)	$c_6 (98\%)$	c ₉ (93%)	c ₁₂ (89%)

Scheme 2. Synthesis routes of click reaction and yield, Reagents and conditions: (i) THF, TCNE/TCNQ/F₄-TCNQ, 40 °C, 2 h.

2.3. Materials synthesis

4,4'-(Ethyne-1,2-diyl)bis(N,N-dibutylaniline) (**b**₁).

 a_2 (0.166 g, 0.5 mmol) and a_4 (0.137 g, 0.6 mmol) were dissolved in the mixed solvent of TEA (150 mL) and THF (150 mL). The Pd(PPh₃)₄ (20.8 mg, 0.018 mmol) and CuI (5.7 mg, 0.03 mmol) were added into the solution after flushing with bubbling Ar gas for 30 min. The reaction mixture was then stirred at 40 °C for 10 h under Ar atmosphere. The resulting mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo, and the product was purified by column chromatography (SiO₂, petroleum ether/CH₂Cl₂=4:1) to give $\mathbf{b_1}$ (0.155 g, 78%) as a colorless solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.99 (m, 12H), 1.38 (m, 8H), 1.62 (m, 8H), 3.31 (m, 8H), 6.59 (d, J=8.5Hz, 4H), 7.36 (d, J=8.5Hz, 4H) ppm. FT-IR (KBr): v=2947, 2874, 2200, 1587, 1527, 1441, 1367, 1024, 914, 804, 621, 523 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₀H₄₄N₂: 432.35 g/mol, found: 433.3 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₀H₄₄N₂ (432.69): C 83.28, H 10.25, N 6.47; found: C 83.27, H 10.26, N 6.47.

2,3-bis(4-(dibutylamino)phenyl)buta-1,3-diene-1,1,4,4-tetra carbonitrile (c_1).

b₁ (43.2 mg, 0.1 mmol) and click reagent TCNE (12.8 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₁ (51.0 mg, 91%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.98 (m, 12H), 1.39 (m, 8H), 1.64 (m, 8H), 3.39 (m, 8H), 6.67 (d, J=9.0 Hz, 4H), 7.80 (d, J=8.5 Hz, 4H) ppm. FT-IR (KBr): v=2922, 2836, 2200, 1649, 1607, 1464, 1343, 1184, 914, 621 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₆H₄₄N₆: 560.36 g/mol, found: 561.2 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₆H₄₄N₆: C 77.10, H 7.91, N 14.99; found: C 77.08, H 7.92, N15.00.

2-(1,2-bis(4-(dibutylamino)phenyl)-2-(4-(dicyanomethylene) cyclohexa-2,5-dien-1-ylidene)ethylidene)malononitrile (**c**₂).

b₁ (43.2 mg, 0.1 mmol) and click reagent TCNQ (20.4 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₂ (58.3 mg, 92%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.99 (m, 12H), 1.42 (m, 8H), 1.63 (m, 8H), 3.38 (m, 8H), 6.61 (d, J=9.0 Hz, 2H), 6.72 (d, J=9.0 Hz, 2H), 6.98 (d, J=9.0 Hz, 1H), 7.12 (d, J=9.5 Hz, 1H), 7.27 (d, J=9.5 Hz, 1H), 7.35 (d, J=9.0 Hz, 2H), 7.58 (d,

J=9.5 Hz, 1H), 7.75 (d, J=8.5 Hz, 2H) ppm. FT-IR (KBr): M ν =2922, 2833, 1575, 1477, 1391, 1331, 1160, 890, 816, 719 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₄₂H₄₈N₆: 636.39 g/mol, found: 636.0 g/mol [M]. Elemental analysis calcd (%) for C₄₂H₄₈N₆: C 79.21, H 7.60, N 13.20; found: C 79.20, H 7.62, N 13.18.

2-(2-(4-(Dibutylamino)phenyl)-2-(4-(dicyanomethylene)-2,3,5,6tetrafluorocyclohexa-2,5-dien-1-ylidene)-1-(4nitrophenyl)ethylidene)malononitrile (**c**₃).

b₁ (120 mg, 0.361 mmol) and F₄-TCNQ (0.090 g, 0.360 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar atmosphere. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₃ (0.213 g, 97%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.94 (m, 6H), 1.00 (m, 6H), 1.44 (m, 4H), 1.51 (m, 4H), 1.66 (m, 4H), 1.78 (m, 4H), 3.57 (m, 4H), 3.61 (m, 4H), 6.62 (d, J=9.0 Hz, 2H), 6.83 (d, J=9.5 Hz, 2H), 7.41 (d, J=9.0 Hz, 2H), 7.56 (d, J=9.0 Hz, 2H) ppm. FT-IR (KBr): v=2947, 2874, 2187, 1587, 1527, 1441, 1367, 1024, 914, 804, 621, 523 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₄₂H₄₄N₆F₄: 708.84 g/mol, found: 709.6 g/mol [MH]⁺. Elemental analysis calcd (%) for C₄₂H₄₄N₆F₄ (708.84): C 71.17, H 6.26, N 11.86; found: C 71.19, H 6.28, N 11.87.

N,*N*-*dibutyl*-4-((4-*pentylphenyl*)*ethynyl*)*aniline* (**b**₂).

 \mathbf{a}_4 (0.137 g, 0.6 mmol) and 1-bromo-4-pentylbenzene (0.113 g, 0.5 mmol) were dissolved in the mixed solvent of TEA (150 mL) and THF (150 mL). The solution was flushed with bubbling Ar gas for 30 min. Then the Pd(PPh₃)₄ (20.8 mg, 0.018 mmol) and CuI (5.7 mg, 0.03 mmol) were added. The reaction mixture was then stirred at 80 °C for 10 h under Ar atmosphere. The resulting mixture was concentrated, rediluted with CH2Cl2, and filtered through a plug of silica gel. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, petroleum ether/CH₂Cl₂=7:1) to give \mathbf{b}_2 (0.135 mg, 60%) as a yellow oil liquid. ¹H NMR (CDCl₃, 500 MHz): δ=0.94 (m, 3H), 1.00 (m, 6H), 1.39 (m, 8H), 1.68 (m, 6H), 2.65 (m, 2H), 3.33 (m, 4H), 6.62 (d, J=9.0 Hz, 2H), 7.17 (d, J=7.5 Hz, 2H), 7.40 (d, J=9.0 Hz, 2H), 7.45 (d, J=7.5 Hz, 2H) ppm. FT-IR (KBr): v=2935, 2850, 2200, 1601, 1503, 1367, 1184, 112, 792, 731, 535 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{27}H_{37}N$: 375.29 g/mol, found: 376.2 g/mol [MH]⁺. Elemental analysis calcd (%) for C₂₇H₃₇N (375.29): C 86.34, H 9.93, N 3.73; found: C 86.35, H 9.94, N 3.74.

$2-(4-(dibutylamino)phenyl)-3-(4pentylphenyl)buta-1,3-diene-1,1,4,4tetracar-bonitrile (<math>c_4$).

b₂ (37.5 mg, 0.1 mmol) and click reagent TCNE (12.8 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₄ (44.8 mg, 89%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.92 (m, 3H), 1.04 (m, 6H), 1.36 (m, 4H), 1.43 (m, 4H), 1.63 (m, 2H), 1.67 (m, 4H), 2.70 (m, 2H), 3.40 (m, 4H), 6.69 (d, J=9.0 Hz, 2H), 7.35 (d, J=8.0 Hz, 2H), 7.70 (d, J=8.0 Hz, 2H), 7.80 (d, J=9.0 Hz, 2H) ppm. FT-IR (KBr): v=2935, 2850, 2187, 1613, 1477, 1343, 1184, 816 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₃H₃₇N₅: 503.30 g/mol, found: 504.2 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₃H₃₇N₅: C 78.69, H 7.40, N 13.90; found: C 78.68, H 7.43, N 13.89.

 $2-(2-(4-(dibutylamino)phenyl)-2-(4-(dicyanomethylene) cyclohexa-2,5-dien-1-ylidene)-1-(4-pentylphenyl) ethylidene)malononitrile (<math>c_5$).

A b₂ (37.5 mg, 0.1 mmol) and click reagent TCNQ (20.4 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₅ (55.0 mg, 95%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.92 (m, 3H), 1.02 (m, 6H), 1.37 (m, 4H), 1.43 (m, 4H), 1.67 (m, 6H), 2.66 (m, 2H), 3.40 (m, 4H), 6.71 (d, J=9.0 Hz, 2H), 6.94 (d, J=9.5 Hz, 2H), 7.14 (d, J=9.5 Hz, 2H), 7.30 (d, J=7.0 Hz, 2H), 7.54 (d, J=9.5 Hz, 2H), 7.63 (d, J=7.0 Hz, 2H) ppm. FT-IR (KBr): v=2910, 2850, 2187, 1575, 1391, 1331, 1172, 914, 719, 645 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₉H₄₁N₅: 579.34 g/mol, found: 579.60 g/mol [M]. Elemental analysis calcd (%) for C₃₉H₄₁N₅: C 80.79, H 7.13, N 12.08; found: C 80.77, H 7.14, N 12.09.

 $2-(2-(4-(Dibutylamino)phenyl)-2-(4-(dicyanomethylene)-2,3,5,6-tetrafluorocyclohexa-2,5-dien-1-ylidene)-1-(4-pentylphenyl)ethylidene)malononitrile (<math>c_6$).

b₂ (112 mg, 0.3 mmol) and F₄-TCNQ (0.082 g, 0.30 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar atmosphere. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₆ (0.19 g, 98%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.92 (m, 3H), 1.04 (m, 6H), 1.36 (m, 4H), 1.48 (m, 4H), 1.67 (m, 2H), 1.75 (m, 4H), 3.68 (m, 2H), 3.60 (m, 4H), 6.86 (d, J=9 Hz, 2H), 7.33 (d, J=8 Hz, 2H), 7.38 (d, J=9 Hz, 2H), 7.53 (d, J=8 Hz, 2H) ppm. FT-IR (KBr): v=2935, 2850, 2200, 1601, 1379, 1012, 816, 645, 559 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₉H₃₇F₄N₅: 651.30 g/mol, found: 652.4 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₉H₃₇F₄N₅ (651.30): C 71.87, H 5.72, N 10.75; found: C 71.89, H 5.71, N 10.74.

N,*N*-dibutyl-4-((4-nitrophenyl)ethynyl)aniline (**b**₃).

 \mathbf{a}_4 (229.2 mg, 1.0 mmol) and 1-bromo-4-nitrobenzene (200.9 mg, 1.0 mmol) were dissolved in the mixed solvent of 25 mL TEA and 25 mL THF. After the solution was flushed with bubbling Ar for 30 min, Pd(PPh₃)₄ (23.1 mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol) were added. The reaction mixture was then stirred at 80 °C for 12 h under an Ar atmosphere. The resulting mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo and the product was purified by column chromatography (SiO₂, petroleum ether/CH₂Cl₂=4:1) to give b₃ (245.0 mg, 70%) as a red solid. ¹H NMR (CDCl₃, 500 MHz): δ=0.97 (m, 6H), 1.37 (m, 4H), 1.56 (m, 4H), 3.29 (m, 4H), 6.58 (d, J=11.0 Hz, 2H), 7.38 (d, J=11.0 Hz, 2H), 7.58 (d, J=11.0 Hz, 2H), 8.17 (d, J=11.0 Hz, 2H) ppm. FT-IR (KBr): v=2960, 2850, 2187, 1587, 1489, 1331, 1190, 809, 731, 509 cm⁻¹.MALDI-TOF-MS (dithranol): m/z: calcd for C₂₂H₂₆O₂N₂: 350.20 g/mol, found: 351.1 g/mol [MH]⁺. Elemental analysis calcd (%) for C₂₂H₂₆O₂N₂: C 75.40, H 7.48, N 7.99; found: C75.39, H 7.50, N 7.99.

$2-(4-(dibutylamino)phenyl)-3-(4-nitrophenyl)buta-1,3-diene-1,1,4,4-tetr-acarbonitrile (<math>c_7$).

b₃ (35.0 mg, 0.1 mmol) and click reagent TCNE (12.8 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₇ (44.5 mg, 93%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =1.02 (m, 6H), 1.43 (m, 4H), 1.66 (m, 4H), 3.45 (m, 4H), 6.74 (d, J=9.0 Hz, 2H), 7.79 (d, J=9.0 Hz, 2H), 7.89 (d, J=8.5 Hz, 2H), 8.39 (d, J=8.5 Hz, 2H) ppm. FT-IR (KBr): v=2922, 2862, 2200, 1587, 1477, 1331, 1172, 902, 719 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₂₈H₂₆ N₆O₂: 478.21 g/mol, found: 478.9 g/mol [MH]⁺.

Elemental analysis calcd (%) for $C_{28}H_{26}N_6O_2$: C 70.28, H 5.48, M A160, J 184, 1098, 926, 790, 523 cm⁻¹. MALDI-TOF-MS N 17.56; found: C 70.25, H 5.49, N 17.53. (dithranol): m/z: calcd for $C_{38}H_{44}N_6$: 584.36 g/mol, found: 584.6

2-(2-(4-(dibutylamino)phenyl)-2-(4-(dicyanomethylene)cyclohexa -2,5-dien-1-ylidene)-1-(4-nitrophenyl)ethylidene)malononitrile (c₈).

b₃ (35.0 mg, 0.1 mmol) and click reagent TCNQ (20.4 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₈ (47.1 mg, 83%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ=1.00 (m, 6H), 1.43 (m, 4H), 1.63 (m, 4H), 3.39 (m, 4H), 6.69 (d, J=8.5 Hz, 2H), 6.98 (d, J=10.0 Hz, 2H), 7.22 (d, J=9.0 Hz, 2H), 7.24 (d, J=7.0 Hz, 2H), 7.32 (d, J=9.5 Hz, 2H), 7.51 (d, J=10.0 Hz, 2H), 7.81 (d, J=8.5 Hz, 2H), 8.32 (d, J=8.5 Hz, 2H) ppm. FT-IR (KBr): v=2922, 2850, 2187, 1575, 1503, 1379, 1331, 890, 707 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₄H₃₀N₆O₂: 554.24 g/mol, found: 555.1 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₄H₃₀N₆O₂ (555.1): C 73.63, H 5.45, N 15.15; found: C 73.60, H 5.47, N 15.14.

2-(2-(4-(dibutylamino)phenyl)-2-(4-(dicyanomethylene)-2,3,5,6tetrafluorocy-clohexa-2,5-dien-1-ylidene)-1-(4-nitrophenyl) ethylidene)malononitrile (**c**₉).

b₃ (35.0 mg, 0.1 mmol) and click reagent F₄-TCNQ (27.6 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₉ (58.2 mg, 93%) as a black red solid. ¹H NMR (CDCl₃, 500 MHz): δ =1.02 (m, 6H), 1.44 (m, 4H), 1.73 (m, 4H), 3.59 (m, 4H), 6.85 (d, J=12 Hz, 2H), 7.31 (d, J=11.5 Hz, 2H), 7.77 (d, J=10.5 Hz, 2H), 8.33 (d, J=11.0 Hz, 2H) ppm. FT-IR (KBr): v=2935, 2850, 2175, 1379, 1330, 1170, 1024, 950, 840, 755 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₄H₂₆F₄N₆O₂: 626.21 g/mol, found: 627.10 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₄H₂₆F₄ N₆O₂: C 65.17, H 4.18, N 13.41; found: C 65.15, H 4.18, N 13.40.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-dibutylaniline) (**b**₄).

To a solution of \mathbf{a}_4 (458.4 mg, 2.0 mmol) in toluene (3 mL), CuCl (97.9 mg, 1.0 mmol) and N, N, N', N'tetramethylethylenediamine (0.8 mL, 5.5 mmol) was added, and the mixture was stirred at 60 °C for 24 h. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in *vacuo*, and the resulting product was purified by column chromatography (SiO₂, petroleum ether/CH₂Cl₂=4:1) to give \mathbf{b}_4 (424.4 mg, 93%) as a yellow solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.98 (m, 12H), 1.38 (m, 8H), 1.58 (m, 8H), 3.29 (m, 8H), 6.55 (d, J=6.5 Hz, 4H), 7.36 (d, J=9.0 Hz, 4H) ppm. FT-IR (KBr): v=2972, 2862, 2187, 2139, 1601, 1539, 1367, 1184, 1098, 926, 719, 743 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₃₂H₄₄N₂: 456.35 g/mol, found: 457.6 g/mol [MH]⁺. Elemental analysis calcd (%) for C₃₂H₄₄N₂: C 84.16, H 9.71, N 6.13; found: C 84.17, H 9.70, N 6.14.

2-(4-(*dibutylamino*)phenyl)-3-((4-(*dibutylamino*)phenyl)ethynyl) buta-1,3diene-1,1,4,4-tetracarbonitrile (**c**₁₀).

b₄ (45.6 mg, 0.1 mmol) and click reagent TCNE (12.8 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₁₀ (53.7 mg, 92%) as a black solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.99 (m, 12H), 1.42 (m, 8H), 1.67 (m, 8H), 3.41 (m, 8H), 6.62 (d, J=9.0 Hz, 4H), 6.69 (d, J=9.0 Hz, 4H), 7.47 (d, J=8.5 Hz, 4H), 7.82 (d, J=9.0 Hz, 4H) ppm. FT-IR (KBr): v=2922, 2836, 2223, 2127, 1587, 1515, 1343,

4160, 1184, 1098, 926, 790, 523 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{38}H_{44}N_6$: 584.36 g/mol, found: 584.6 g/mol [M]. Elemental analysis calcd (%) for $C_{38}H_{44}N_6$: C 78.05, H 7.58, N 14.37; found: C 78.06, H 7.59, N 14.35.

2-(1,4-bis(4-(dibutylamino)phenyl)-1-(4-(dicyanomethylene) cyclohexa-2,5-dien-1-ylidene)but-3-yn-2-ylidene)malononitrile (**c**₁₁).

b₄ (45.6 mg, 0.1 mmol) and click reagent TCNQ (20.4 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₁₁ (63.4 mg, 96%) as a black solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.99 (m, 12H), 1.43 (m, 8H), 1.60 (m, 4H), 1.65 (m, 4H), 3.36 (m, 4H), 3.43 (s, 4H), 6.60 (d, J=8.5 Hz, 2H), 6.74 (d, J=9.0 Hz, 2H), 7.26 (m, 2H), 7.41 (d, J=9.0 Hz, 4H), 7.41 (m, 2H) ppm. FT-IR (KBr): υ=2919, 2850, 2187, 2120, 1575, 1391, 1331, 1172, 1098, 890 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₄₄H₄₈N₆: 660.39 g/mol, found: 660.1 g/mol [M]. Elemental analysis calcd (%) for C₄₄H₄₈N₆: C 79.96, H 7.32, N 12.72. found: C 79.98, H 7.32, N 12.70.

$2-(1,4-bis(4-(dibutylamino)phenyl)-1-(4-(dicyanomethylene)-2,3,5,6-tetrafluor-ocyclohexa-2,5-dien-1-ylidene)but-3-yn-2-ylidene)malononitrile (<math>c_{12}$).

b₄ (45.6 mg, 0.1 mmol) and click reagent F₄-TCNQ (27.6 mg, 0.1 mmol) were dissolved in THF (2 mL). After the reaction mixture was then stirred at 40 °C for 2 h under Ar. The solvent was removed in *vacuo*, and the product was purified by column chromatography (SiO₂, CH₂Cl₂) to give **c**₁₂ (64.4 mg, 89%) as a black solid. ¹H NMR (CDCl₃, 500 MHz): δ =0.99 (m, 6H), 1.04 (m, 6H), 1.40 (m, 4H), 1.46 (m, 4H), 1.61 (m, 4H), 1.75 (m, 4H), 3.37 (m, 4H), 3.59 (m, 4H), 6.61 (d, J=9.0 Hz, 2H), 6.82 (d, J=8.5 Hz, 2H), 7.36 (d, J=8.5 Hz, 2H), 7.45 (d, J=6 Hz, 2H) ppm. FT-IR (KBr): v=2972, 2862, 2187, 2139, 1601, 1539, 1367, 1184, 1098, 926, 719, 743 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calcd for C₄₄H₄₄F₄N₆: 732.36 g/mol, found: 733.5 g/mol [MH]⁺. Elemental analysis calcd (%) for C₄₄H₄₄F₄N₆: C 72.11, H 6.05, N 11.47; found: C 72.09, H 6.06, N 11.46.

3. Results and discussion

The reacting aromalkyne molecules \mathbf{b}_1 - \mathbf{b}_4 were shown in Scheme 1, were synthesized according to the literature methods[27]. All the compounds were fully characterized by NMR, IR, and MS spectra from which the chemical structures were verified. Compounds $(\mathbf{b_1}$ - $\mathbf{b_4})$ have good solubility in common organic solvents. Synthesis of donor-acceptor chromophores c_1 - c_{12} was achieved through introducing in aminesubstituted aromatic precursors by the high-yielding [2+2] click reactions using TCNE, TCNQ, and F₄-TCNQ as acceptor molecules. As it was shown in Scheme 2, the click reaction was high yield from 83% to 95%, could be fulfilled under ambient temperature, and enhancement of temperature to 40 °C was just for higher efficiency. In the previous studies[31-35], it has been proved that the [2+2] click reaction has high yield and near to 100%. In this paper, the equimolar mixtures of alkynyl and click reagent were used, but a certain kind of compound should be residual. Here we selected the column chromatography to purify the products and to remove the trace amount of residual compounds. However, losing parts of products in purified process influence on the data of yields, and all the yields would be lower than 100%. In addition, \mathbf{b}_4 has the diacetylene and it was difference from $b_1 - b_3$. In the reference [36-43], it was proved that only one alkyne in the diacetylene can be reacted with the electron-withdrawing click reagents. In this paper, because it was symmetrical chemical structure for b4, any one of

alkyne groups was reacted with the click reagents, the products would be same. All the newly prepared products were in high purity, which was confirmed by NMR, IR, and MS spectra. Moreover, they were stable at ambient temperature under air and reasonably soluble in common organic solvents, such as CH₂Cl₂, acetone, and acetonitrile, which was beneficial for processing. Furthermore, no special purification process was necessary because of the absence of byproducts. Therefore, this kind of reaction satisfied most of the requirements of click chemistry, and it could be classified as a new metal-free click chemistry that further improved optoelectronic properties of organic materials.

3.1. UV-vis absorption

The normalized UV-vis absorption spectra were shown in Fig. 1. The spectral shapes and positions were very similar to the reported click products[27-35]. Most of the prepared products showed intense CT bands with end-absorptions reaching into the near infrared region. Aromoalkyne \mathbf{b}_1 - \mathbf{b}_4 reacting with different click reagents TCNE, TCNQ, and F₄-TCNQ yielded click compounds c_1 - c_{12} , respectively (Scheme 2). Throughout the click reaction, the colors of compounds were changed, and the images of solution samples were shown in Fig. 1. For example, the color was nearly colorless for b_1 solution, was red for c_1 solution (with TCNE moiety), was black red for c_2 solution (with TCNQ moiety), and was black brown for c_3 solution (with F₄-TCNQ moiety). The color got darker from b₁, c₁, c₂, and c₃, and it was suggested that the UV-vis absorption spectra would be different obviously. For example, the maximum absorption of b_1 was 341 nm, and was red-shifted significantly to 480 nm, 684 nm and 830 nm for c_1 , c_2 , and c_3 . For the other series, the similar phenomena were observed and the results were shown in Fig.1 (b-d). The reasons were dramatically facilitated by the elongation of conjugation lengths of molecular backbones and enhancement of electron affinities via introduction of strong electron-withdrawing substitutes[31].

Table 1. Optical properties of all products

Mate rial	λ_{max}^{a} (nm)	ϵ^{b} (10 ⁻³ M ⁻ ¹ cm ⁻¹)	E_{g}^{c} (eV)	Mate rial	λ_{max}^{a} (nm)	ϵ^{b} (10 ⁻³ M ⁻ ¹ cm ⁻¹)	$E_{\rm g}^{\rm c}$ (eV)
b ₁	341	1.8	3.16	b ₃	430	1.6	2.13
c ₁	480	3.1	1.95	c ₇	469	2.5	1.64
\mathbf{c}_2	686	3.2	1.33	c ₈	723	2.9	1.13
c ₃	832	3.5	1.06	C9	890	3.6	0.91
\mathbf{b}_2	342	1.2	3.23	\mathbf{b}_4	357	2.1	2.93
c_4	480	1.4	1.93	c ₁₀	534	2.2	1.60
c ₅	696	1.6	1.24	c ₁₁	706	2.4	1.20
c ₆	863	3.3	1.00	c ₁₂	856	2.6	0.95
9							

^aAbsorption spectra were measured in CH_2Cl_2 solution (5×10⁻⁷ M).

 ${}^{b}\varepsilon$ was the molar extinction coefficient at the absorption peak of λ_{max} with maximum wavelength).

^cBand gap estimated from the onset wavelength of optical absorption in CH_2Cl_2 solution.

For the \mathbf{c}_3 , \mathbf{c}_6 , \mathbf{c}_9 , and \mathbf{c}_{12} , the same click reagent (F₄-TCNQ) was used, and the main difference was the substituted group, such as R₁. The UV-vis absorption spectra were shown in Fig. 1 (e), and it can be proved that the spectra were influenced by the substituted group. The red-shifted order was \mathbf{c}_3 , \mathbf{c}_{12} , \mathbf{c}_6 , and \mathbf{c}_9 . Although the substituted group was similar for \mathbf{c}_3 , and \mathbf{c}_{12} , the conjugation length of \mathbf{c}_{12} was larger than that of \mathbf{c}_3 , and the intramolecular charge transferred over a longer conjugation length along the molecular backbones, so the CT bands were red shifted form 832 nm to 856 nm. The introduction of the weak electron donating group (-C₅H₁₁) broke molecular symmetry and make electronic adjacent circulating ability easier, so compared with \mathbf{c}_{12} the maximum absorption peak of \mathbf{c}_6 were red-shifted

significantly to larger value. In addition, the introduction of the strong electron-withdrawing group $(-NO_2)$ managed to extend photo absorption to a longer wavelength region and the maximum absorption was red-shifted significantly to larger value comparing with other compounds under the same conditions.



Fig. 1. UV-vis absorption spectra of compounds in CH_2Cl_2 at RT (the inset photographs were the images of solutions).

To evaluate the possibility of electron transfer, the CV of compounds were tested, and some CV curves were shown in Fig. 2 (a). The data were listed in Table 1, such as onset oxidation/reduction potentials, band gaps, LUMO and HOMO levels. According to the data, it was clear that the band gaps and energy levels were affected by the chemical structures, such as the substituted groups and clicked moieties. It was suggested that the parental choice would be increased, such as the band gaps (from 0.9 to 3.1). For the band gaps, some interesting phenomena can also be observed from Fig. 2 (b). If the compounds have the same substituted groups and different clicked moieties, the band gaps became smaller with the introduction of click reagent (TCNE, TCNQ, F₄-TCNQ) for all the series. The reasons were dramatically facilitated by the elongation of conjugation lengths of molecular backbones and enhancement of electron affinities via introduction of strong electron-withdrawing substitutes[31]. If the compounds have the same clicked moieties and different substituted groups, a broadly decreasing trend for band gap was - $N(C_4H_9)_2$, $-C_5H_{11}$, $-NO_2$. The introduction of the weak electron donating group (-C5H11) broke molecular symmetry and make electronic adjacent circulating ability easier, and the introduction of the strong electron-withdrawing group (-NO₂) managed to decrease the band gaps too. In short, depending on the difference click reagent and the difference of the terminal group, both the HOMO levels and the LUMO levels were regulated in varying degrees, which was in result of the enlargement of the absorption spectrum and the corresponding CT bands strongly bathochromically shifted with an end-absorption, and photoelectric properties of organic materials further was improved.



Fig. 2. Cycle voltammograms of clicked derivatives c_1 , c_4 , c_7 and c_{10} at RT.

Tetrah	edron					
ED M	1AN G SCF	0.35	-0.45	-5.15	-4.35	0.80
X 7 C	b ₂		-1.23		-3.57	
V of	c ₄	0.78	-0.98	-5.58	-3.82	1.76
n Fig.	c ₅	0.31	-0.65	-5.11	-4.15	0.96
onset	C ₆	0.4	-0.33	-5.20	-4.47	0.73
OMO	b ₃		-1.25		-3.55	
s and	c ₇	0.84	-0.7	-5.64	-4.10	1.54
d that	c ₈	0.31	-0.6	-5.11	-4.20	0.91
gane	C9	0.4	-0.27	-5.20	-4.53	0.67
mena	\mathbf{b}_4		-1.23		-3.57	
ncha ze the	c ₁₀	0.9	-0.75	-5.70	-4.05	1.65
band	c ₁₁	0.31	-0.58	-5.11	-4.22	0.89
agent	c ₁₂	0.4	-0.3	-5.20	-4.50	0.70

^aOnset potentials determined from cyclic voltammograms in CH_2Cl_2/Bu_4NPF_6 at a scan rate of 40 mV/s.

^bBand gap calculated from the energy level of cyclic voltammograms.

3.3. Nonlinear optics Properties

Z-scan experiments were utilized to evaluate the applications of NLO enhancements via fictionalization of click reagents and the results were shown in Fig. 3. The NLO parameters were summarized in Table 2, which included with nonlinear absorption coefficient (β), nonlinear index (n) and third-order nonlinear susceptibility. The study indicated that the compounds without clicked moieties did not exhibit any NLO response. After the clicked functional methods, the compounds have strong thirdorder NLO properties through modification of the different click chemistry. The third-order NLO properties relied on strong partnerships with chemical structures. When using 532 pulses, materials, having end group of the amyl $(-C_5H_{11})$, showed a prominent nonlinear properties comparing with other compounds, which non-linear absorption coefficient of c_5 shows higher magnitude of 10^{-11} and nonlinear index value was 100 times that of other materials under the same conditions. To our surprise, the NLO properties of \mathbf{b}_2 derivatives were better than those of other compounds. Comparing to \mathbf{b}_1 , \mathbf{b}_2 lacks a strong electron donating group. Comparing to \mathbf{b}_3 , \mathbf{b}_2 lacks a strong electron withdrawing group. Comparing to b₄, b₂ has the shorter conjugated structure. Usually, the strong electron donating/withdrawing and the conjugated structures are the key factors for enhancing NLO properties. We suspect that the unusual phenomenon may be due to electronic cloud distribution. The abilities of π -electron delocalization and intramolecular charge transfer are the foundation for enhancing NLO properties. The strong electron donating/withdrawing could improve abilities of π -electron delocalization, but hinder transfer abilities. When using 1064 pulses, it was attractive that these material, functionalized by click reagent of F4-TCNQ, had pretty high nonlinear absorption coefficient (10^{-7}) and nonlinear index (10^{-13}) , and that of these numbers were obviously larger than that of these irradiated by 532 pulses. Automatically, comparing with using 532 pulses, these materials also showed amazing thirdorder nonlinear susceptibility when using 1064 pulses. From the UV-vis absorption spectra, the products with F₄-TCNQ moieties were potentially facilitated at long wavelength. It was suggested that the existence of strong electron-withdrawing substitutes caused that the negative charge located on the click moieties, and the products were easier excitated using 1064 pulses.

Table 3. NLO properties of all the products

Table 2. Ele	ctrochem	cal proper	ties of an pro	baucts								
	E_{aa}^{a}	E_{a}^{a}	Energy	Energy level	$E_{\rm b}^{\rm b}$		NLO (532 nm)			NLO (1064 nm)		
Material	(eV)	(eV)	$E_{\rm HOMO}^{a}$	E _{LUMO} ^a	(eV)	Mate rial	β 10 ⁻¹²	N 10 ⁻¹⁹	$\chi^{(3)}_{10^{-13}}$	$\beta_{10^{-13}}$	N 10 ⁻⁷	$\chi^{(3)}_{10^{-7}}$
b ₁		-1.28		-3.52		IIui	m/W	m^2/W	esu	m/W	m^2/W	esu
c ₁	0.72	-1.08	-5.52	-3.72	1.80	b 1						
c ₂	0.29	-0.71	-5.09	-4.09	1.00	c ₁	-1.8	-7.0	4.02			

c ₂	0.3	1.5	0.86		ACCE	PTED]
c3	1.3	1.7	1.31	-3.3	5.5	1.83
\mathbf{b}_2						
c_4	-8.5	-10.5	10.5			
c ₅	20.5	128.5	72.64			
c ₆	9.1	0	6.64	10-5	10-5	5×10^{-6}
b ₃						
c ₇	-1.1	-3.2	1.96			
c ₈	-0.6	1.7	1.04			
C9	-1.1	1.7	1.24	-3.3	-2.3	1.69
\mathbf{b}_4						
c ₁₀	-5.2		3.8	0	0.9	0.12
c ₁₁	-1.0	1.6	1.13			
c ₁₂	-0.5		0.37		1.5	0.20



Fig. 3. Z-scan results in CH₂Cl₂. The half-open circles represent the Z-scan experimental data, and the solid lines were the theoretical fitting curves: (a)/(c)/(e) data collected under the open-aperture configuration; (b)/(d)/(f) data collected under the closed-aperture configuration; (a)/(b) NLO properties of c_4 under condition of 532 pulses; (c)/(d) NLO properties of c_5 under condition of 532 pulses; (e)/(f) NLO properties of c_9 under condition of 1064 pulses.

4. Conclusions

We addressed the significance of third-order NLO properties in the compounds obtained by click chemistry. It was found that the introduction of the click reagents improved optical performance can make the electron cloud arrange, renewably, which UV-vis spectra were enlarged with end-absorptions into the near infrared region in varying degrees and energy level has been adjusted appropriately. Z-scan measurements to evaluate the third-order NLO properties found that that almost all of the derivative compounds modulated by click reagents have excellent NLO properties. It was the most wonderful result that the excellent NLO properties at 1064 nm were proved, and these findings should inspire a new approach toward the future design of the third-order NLO materials.

Acknowledgments

This work was supported by the National Key Basic Research Program of China (No. 2014CB931804), Natural Science Basic Research Plan in Shaanxi Province of China (No. 2013JQ8043).

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