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Energy-level tuning of poly(p-phenylenebutadiynylene) derivatives by click chemistry-type postfunctionalization of side-chain alkynes



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ABSTRACT

A series of poly(p-phenylenebutadiynylene) polymers substituted with electron-rich alkynes as the side chain were synthesized by homocoupling polymerization of asymmetric bifunctional monomers. The electron-rich alkynes underwent "click chemistry" with tetracyanoethylene (TCNE) to produce donor-acceptor chromophores. Optical and electrochemical characterizations clearly indicated that the energy level and band gap of P2 could be precisely controlled by the addition of acceptor molecules. One of the most important conclusions of this study is that a linear relationship between the lowest occupied molecular orbital (LOMO) and the amount of TCNE was observed. From the Z-scan measurement, all the compounds exhibited very special nonlinear optical properties, which suggested a tendency to transfer from saturable absorption (SA) to reverse saturable absorption (RSA). © 2016 Published by Elsevier B.V.

1. Introduction

Conjugated organic molecules and polymers play a primary role in the development of a new generation of optical and electronic materials [1–6]. In particular, conjugated polymers are now of significant commercial importance for the construction of organic light-emitting diodes (OLEDs), thin-film transistors (TFTs), and field effect transistors (FETs), which are finding applications in computing hardware and electronic appliances [7–16].

In order to achieve an appreciable device performance, it is important to design polymer structures with energy levels suitable for a specific application. One of the most direct and promising approaches is the modification of the side-chain groups of the polymer [17,18]. The introduction of electron-donating or electron-accepting groups directly or *via* a π -spacer into the polymer side chain dramatically altered the energy levels. Tuning of the electronic highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) levels is crucial in enhancing the optoelectronic properties of organic materials. Designing new donor-acceptor-type π -conjugated molecules is one solution, because through-bond interactions between donor and acceptor moieties result in narrow band gaps originating from the elevated HOMO and lowered LUMO levels.

Click chemistry provides efficient, reliable, and selective reactions for synthesizing new compounds and generating combinatorial libraries [19]. Click chemistry can be defined as a highly efficient addition reaction, essentially yielding no by-product [19]. At present, the most famous and well-studied click reaction is the copper(I)-catalyzed azide-alkyne cycloaddition reaction (CuAAC), forming a triazole ring, which has been widely used for the preparation of functional materials [20–25]. Nevertheless, one drawback of these 1.3-dipolar azide-alkvne reactions is the little effect on the conjugation and energy level, which are commonly used for nonlinear optical (NLO) properties [26,27]. This may hinder their general applicability for optical polymers, such as NLO. In order to solve this problem, other click-type reactions have simultaneously been developed [28-33]. For introducing strong electron-withdrawing groups for NLO application, the typically thermal [2 + 2] cycloadditions, followed by *retro*-electrocyclization of tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethanel (TCNQ), were linked to "electronically confused" alkynes [34–40]. By using this reaction, the polymer energy levels and thermal stability were significantly controlled.

In this study, novel poly(p-phenylenebutadiynylene)s (PPBs) containing full conjugated main chain and postfunctionalized side groups were designed and synthesized. Because of the conjugated relationship between main chain and side groups, the postfunctionalized reaction affects the electronic cloud distribution of not only the side groups but also the whole main chain. It could be assumed that the energy levels

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of polymers are precisely controlled by the extent of postfunctionalized reaction. It is interesting to note that the selection of [2 + 2] click chemistry method has resulted in the accurate quantification of the amount of click moieties. It was for precisely tuning energy levels, at the same time, the NLO properties may be challenged to control the postfunctionalized reaction.

2. Experimental

2.1. Materials

Chemicals purchased from TCI, J&K, Alfa Aesar, and Aldrich were used as received. 2,5-dibromoiodobenzene [41], *N*,*N*-dihexadecyl-4iodoaniline [42], 4-ethynyl-*N*,*N*-dihexadecylaniline [42], 4-[(2bromophenyl)ethynyl]-*N*,*N*-dihexadecylaniline (7) [43], 4-((2,5dibromophenyl)ethynyl)-*N*,*N*-dihexadecylaniline (1) [44], 4-((2,5bis((trimethylsilyl)ethynyl)phenyl)ethynyl)-*N*,*N*-dihexadecylaniline (2) [44], and 4-((2,5-diethynylphenyl)ethynyl)-*N*,*N*-dihexadecylaniline (3) [44] were synthesized according to the methods described in the literature.

2.2. General measurements

¹H nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV300 NMR spectrometer (300 MHz) at 20 °C. Chemical shifts are reported in parts per million downfield from SiMe₄, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. All matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating potential of 20 kV by a linear positive-ion mode with dithranol as a matrix. Gel permeation chromatography (GPC) was measured on a Shodex system equipped with polystyrene gel columns using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. Relative molecular weights were determined by comparison with the calibrated standard polystyrenes. Thermogravimetric analysis (TGA) was carried out on a Seiko SII TG 6220 under nitrogen flow at a scanning rate of 10 °C/min. Ultraviolet-visible (UV-Vis) spectra were recorded in a guartz cuvette on a JASCO V-570 spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using glassy carbon working electrodes of diameter 2 mm, a platinum wire counterelectrode, and an Ag/Ag⁺/CH₃CN/Bu₄NPF₆ reference electrode on a computercontrolled CHI 660C instrument at room temperature (rt). All potentials were referenced to the ferricinium/ferrocene (Fc/Fc⁺) couple used as an internal standard. The NLO response was measured by Z-scan technique, using 21-ps laser pulses at 532 nm delivered by a mode-locked Nd:YAG laser. Elemental analyses were conducted using the Flash EA 1112 instrument.

2.3. Synthesis of monomers

2.3.1. 4-((2,5-dibromophenyl)ethynyl)-N,N-dihexadecylaniline (1)

To a degassed solution of 4-ethynyl-*N*,*N*-diihexylaniline (3.00 g, 5.31 mmol) and 1,4-dibromo-2-iodobenzene (2.30 g, 6.37 mmol) in triethylamine (TEA) (40 mL) and THF (40 mL), bis(triphenylphosphine) palladium(II) dichloride (PdCl₂(PPh₃)₂) (0.22 g, 0.32 mmol) and cuprous iodide (CuI) (0.12 g, 0.64 mmol) were added under Ar atmosphere. The mixture was stirred at 40 °C for 15 h. After removal of the precipitated salt, evaporation and column chromatography (SiO₂, V_{hexane}/V_{dichloromethane(DCM)} = 20:1) afforded the desired product (1) (2.62 g, 62%). ¹H NMR (CDCl₃, 500 MHz): δ = 0.90 (m, 6H), 1.29 (s, 52H), 1.58 (m, 4H), 3.30 (m, 4H), 6.60 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 8.5 Hz, 1H), 7.65 (s, 1H) ppm. Fourier transform infrared spectra (FT-IR) (KBr): ν =

2925, 2854, 2203, 2156, 1604, 1550, 1532, 1519, 1466, 1405, 1369, 1249, 1188, 1140, 1097, 1029, 952, 860, 843, 812, 760 cm⁻¹. MALDI-TOF-MS (dithranol): *m/z*: calculated for $C_{46}H_{73}Br_2N$: 799.41 g·mol⁻¹, found: 800.3 g·mol⁻¹ [MH]⁺; elemental analysis calculated (%) for $C_{46}H_{73}Br_2N$ (799.41): C 69.11, H 9.48, N 1.70. found: C 69.10, H 9.49, N 1.69.

2.3.2. 4-((2,5-bis((trimethylsilyl)ethynyl)phenyl)ethynyl)-N,Ndihexadecylaniline (2)

Compound (1) (2.00 g, 2.51 mmol) and (triisopropylsilyl)acetylene (TMSA) (0.74 g, 7.53 mmol) were dissolved in TEA/THF (V_{TEA} : V_{THF} = 1:1, 40 mL). After the solution was purged with bubbling Ar for 30 min, PdCl₂(PPh₃)₂ (0.11 g, 0.15 mmol) and CuI (0.06 g, 0.30 mmol) were added. The reaction mixture was then stirred at 80 °C for 12 h under Ar atmosphere. The mixture was concentrated, rediluted with DCM, and filtered through a plug of silica gel. The solvent was removed in vacuo and the crude product was purified by column chromatography $(SiO_2, V_{hexane}/V_{DCM} = 10:1)$ to produce (2) (1.00 g, 48%). ¹H NMR $(CDCl_3, 500 \text{ MHz}): \delta = 0.27 \text{ (m, 18H)}, 0.89 \text{ (m, 6H)}, 1.28 \text{ (m, 52H)},$ 1.58 (m, 4H), 3.29 (m, 4H), 6.58 (d, J = 9.0 Hz, 2H), 7.28 (s, 1H), 7.40 (m, 3H), 7.60 (s, 1H) ppm. FT-IR (KBr): v = 2916, 2851, 2206, 1604,1515, 1472, 1402, 1369, 1198, 1122, 1078, 1029, 878, 808, 715 cm⁻¹. MALDI-TOF-MS (dithranol): m/z: calculated for C₅₆H₉₁Br₂NSi₂: 833.70 g·mol⁻¹, found: 834.8 g·mol⁻¹ [MH]⁺; elemental analysis calculated (%) for C₅₆H₉₁Br₂NSi₂ (833.70): C 80.37, H 11.01, N 1.72. found: C 80.34, H 11.03, N 1.71.

2.3.3. 4-((2,5-diethynylphenyl)ethynyl)-N,N-dihexadecylaniline (3)

To a 100-mL flask, (**2**) (1.00 g, 1.20 mmol), K_2CO_3 (0.50 g, 3.60 mmol), and MeOH (15 mL) were added, and the mixture was stirred at 20 °C for 3 h. The mixture was diluted with DCM and the organic phase was washed thrice with water. After drying over Na₂SO₄, the solution was filtered. Removal of the solvent *in vacuo* and column chromatography (SiO₂, $V_{hexane}/V_{DCM} = 10:1$) yielded the desired product (**3**) (0.70 g, 85%). ¹H NMR (CDCl₃, 500 MHz): $\delta = 0.86$ (m, 6H), 1.26 (m, 52H), 1.55 (m, 4H), 3.13 (s, 1H), 3.25 (m, 4H), 3.39 (s, 1H), 6.54 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 10.0 Hz, 1H), 7.36 (d, J = 10.5 Hz, 2H), 7.42 (d, J = 5.5 Hz, 1H), 7.59 (s, 1H) ppm; FT-IR (KBr): $\nu = 3340, 2918, 2853, 2166, 1604, 1515, 1472, 1402, 1369, 1198, 1122, 1078, 1029, 865, 715 cm⁻¹. MALDI-TOF-MS (dithranol):$ *m/z*: calculated for C₅₀H₇₅N: 689.62 g•mol⁻¹, found: 690.8 g•mol⁻¹ [MH]⁺; elemental analysis calculated (%) for C₅₀H₇₅N (689.62): C 87.16, H 10.80, N 2.04. found: C 87.15, H 10.82, N 2.03.

2.3.4. 1,4-dibromo-2-((4-pentylphenyl)ethynyl)benzene (4)

In a 250-mL round-bottom flask, 2,5-dibromoiodobenzene (3.60 g, 10.0 mmol) and 1-ethynyl-4-pentylbenzene (1.89 g, 11.0 mmol) were dissolved in Et₃N (TEA)/THF 1:1 (80 mL). After the solution was purged with bubbling Ar for 40 min, Pd(PPh₃)₄ (347 mg, 0.30 mmol) and CuI (114 mg, 0.60 mmol) were added. The reaction mixture was then stirred at 40 °C for 12 h under Ar atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 10:1) to produce 4 (3.27 g, 81%) as a yellow liquid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.92$ (m, 3H), 1.36 (m, 4H), 1.63 (m, 2H), 2.65 (m, 2H), 7.21 (d, J = 4.5 Hz, 2H), 7.31 (d, J = 4.8 Hz, 1H), 7.48 (d, J = 5.1 Hz, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.70 (s, 1H) ppm. FT-IR (KBr): $\nu = 2920$, 2848, 2205, 1606, 1553, 1519, 1466, 1405, 1370, 1248, 1136, 1095, 1029, 952, 862, 844, 762 cm⁻¹. MALDI-TOF-MS (dithranol) m/z: calculated for $C_{19}H_{18}Br_2$: 403.98 g•mol⁻¹, found: 405.1 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 56.19, H 4.47; found: C 56.15, H 4.49.

2.3.5. 1,4-bis((trimethylsilyl)ethynyl)-2-((4-pentylphenyl)ethynyl)benzene (5)

Compound **4** (2.02 g, 5.0 mmol) was cross-coupled with (trimethylsilyl)ethyne (1.47 g, 15.0 mmol) and dissolved in Et_3N/THF

1:1 (40 mL). After the solution was purged with bubbling Ar for 40 min, Pd (PPh₃)₄ (231 mg, 0.20 mmol) and CuI (76 mg, 0.40 mmol) were added. The reaction mixture was then stirred at 40 °C for 12 h under Ar atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 20:1) to produce **5** (1.28 g, 58%) as a yellow solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.29$ (m, 18H), 0.93 (m, 3H), 1.35(s, 4H), 1.65 (m, 2H), 2.64 (m, 2H), 7.19 (d, J = 4.8 Hz, 2H), 7.34 (d, J = 5.1 Hz, 1H), 7.45 (d, J = 5.1 Hz, 1H), 7.48 (d, J = 4.8 Hz, 2H), 7.64 (s, 1H) ppm. FT-IR (KBr): $\nu = 2913, 2853, 2202, 1611, 1505, 1468, 1411, 1342, 1178, 1121, 1075, 1030, 867, 841, 710 cm⁻¹. MALDI-TOF-MS (dithranol)$ *m/z*: calculated for C₂₉H₃₆Si₂: 440.24 g•mol⁻¹, found: 441.1 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 78.92, H 8.28; found: C 78.97, H 8.26.

2.3.6. 1,4-diethynyl-2-((4-pentylphenyl)ethynyl)benzene (6)

Compound **5** (0.88 g, 2.0 mmol) in THF (10 mL) was added to tetra*n*-butylammonium fluoride (TBAF) (4 M in THF 20 mL). The reaction mixture was stirred at rt for 30 min. Then, the mixture was diluted with CH₂Cl₂, washed with H₂O, dried (MgSO₄), and concentrated *in vacuo*. In general, the resultant terminal alkyne was then used with no further purification. A yellow liquid (monomer **6**) was obtained (53 mg, 90%) as the product. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.96$ (m, 3H), 1.39 (s, 4H), 1.67 (m, 2H), 2.66 (m, 2H), 3.23 (s, 1H), 3.50 (s, 1H), 7.22 (d, J = 4.8 Hz, 2H), 7.41 (d, J = 4.8 Hz, 1H), 7.52 (d, J = 5.4 Hz, 1H), 7.54 (d, J = 4.8 Hz, 2H), 7.72 (s, 1H) ppm. FT-IR (KBr): v = 3315, 2912, 2850, 2148, 1603, 1512, 1468, 1401, 1369, 1198, 1122, 1078, 1029, 878, 808, 714 cm⁻¹. MALDI-TOF-MS (dithranol) *m/z*: calculated for C₂₃H₂₀: 296.16 g•mol⁻¹, found: 297.3 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 93.20, H 6.80; found: C 93.18, H 6.82.

2.3.7. **P1**

To a solution of monomer **3** (0.41 g, 0.60 mmol) in toluene (2 mL), CuCl (30 mg, 0.3 mmol) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (250 μ L, 1.68 mmol) were added. The mixture was stirred at 60 °C for 24 h, Then, the reaction mixture was poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol twice, and dried under vacuum to yield an orange solid as the product (0.36 g, 87%). FT-IR (KBr): v = 2922, 2851, 2194, 1606, 1536, 1518, 1466, 1401, 1397, 1363, 1185, 1140, 1029, 888, 811, 720 cm⁻¹.

2.3.8. **P2** (x = 1)

To a solution of **P1** (100 mg, 0.145 mmol) in 1,2-dichloroethane (10 mL), TCNE (18.68 mg, 0.145 mmol) was added, and the mixture was stirred at 25 °C for 1 h. Removal of the solvent *in vacuo* yielded a brown solid **P2** (x = 1; 118 mg, 99%). FT-IR (KBr): v = 2922, 2851, 2214, 1602, 1485, 1415, 1401, 1338, 1182, 805, 720 cm⁻¹.

2.3.9. **P3**

To a solution of monomer **6** (177 mg, 0.60 mmol) in toluene (2 mL), CuCl (30 mg, 0.3 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (250 μ L, 1.68 mmol) were added. The mixture was stirred at 60 °C for 24 h, and the reaction mixture was poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol twice, and dried under vacuum to yield an orange solid as the product (150 mg, 85%). FT-IR (KBr): $\nu = 2923$, 2846, 2204, 1605, 1558, 1519, 1403, 1378, 1245, 1136, 1029, 952, 862, 846, 760 cm⁻¹.

2.3.10. N,N-dihexadecyl-4-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)aniline (8)

The compound **7** (1.44 g, 2.0 mmol) was cross-coupled with (trimethylsilyl)ethyne (0.246 g, 2.5 mmol) and dissolved in Et₃N/ THF1:1 (30 mL). After the solution was purged with bubbling Ar for 40 min, Pd (PPh₃)₄ (69 mg, 0.06 mmol) and CuI (23 mg, 0.12 mmol) were added. The reaction mixture was then stirred at 80 °C for 12 h under Ar atmosphere. The mixture was concentrated, rediluted with CH₂Cl₂, and filtered through a plug of silica gel. The solvent was removed in vacuo, and the crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂ 20:1) to produce **8** (1.06 g, 72%) as an orange solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.34$ (m, 9H), 0.93 (m, 6H), 1.33 (s, 52H), 1.62 (m, 4H), 3.31 (m, 4H), 6.61 (d, J = 5.4 Hz, 2H), 7.21 (m, 1H), 7.27 (m, 1H), 7.43 (d, J = 5.1 Hz, 2H), 7.52 (d, J = 5.1 Hz, 1H), 7.61 (d, J = 5.4 Hz, 1H) ppm. FT-IR (KBr): v = 2916, 2851, 2206, 1604, 1515, 1472, 1402, 1369, 1198, 1122, 1078, 1029, 878, 808, 715 cm⁻¹. MALDI-TOF-MS (dithranol) m/z: calculated for C₅₁H₈₃NSi: 737.63 g•mol⁻¹, found: 738.5 g•mol⁻¹ [MH]⁺. Elemental



Scheme 1. Synthesis routes of monomers (3 and 6). (a) NaNO2, KI, HCl/H2O; (b) Pd(PPh3)4, Cul, Et3N/THF, rt; (c) Pd(PPh3)4, Cul, Et3N/THF, 80 °C; (d) TBAF, THF, 0 °C.



Scheme 2. Synthesis routes of all the polymers and the postfunctionalization by TCNE addition. (a) CuCl, N,N,N',N'-tetramethylethylenediamine, toluene, 60 °C; (b) TCNE, dichlorobenzene, 100 °C.

analysis calculated (%) for: C 82.97, H 11.33, N 1.90; found: C 82.92, H 11.36, N 1.91.

2.3.11. 4-((2-Ethynylphenyl)ethynyl)-N,N-dihexadecylaniline (9)

Compound **8** (0.74 g, 1.0 mmol) in THF (10 mL) was added to TBAF (2 M in THF 10 mL). The reaction mixture was stirred at rt for 30 min. Then, the mixture was diluted with CH_2Cl_2 , washed with H_2O , dried (MgSO₄), and concentrated *in vacuo*. In general, the resultant terminal alkyne was then used with no further purification. An orange liquid

(compound **9**) was obtained (0.61 g, 92%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.93$ (m, 6H), 1.32 (s, 52H), 1.62 (m, 4H), 3.31 (m, 4H), 6.62 (d, J = 5.4 Hz, 2H), 7.24 (m, 1H), 7.27 (m, 1H), 7.46 (d, J = 5.4 Hz, 2H), 7.56 (d, J = 5.1 Hz, 1H), 7.65 (d, J = 5.1 Hz, 1H) ppm. FT-IR (KBr): $\nu = 3290, 2921, 2853, 2196, 1606, 1516, 1470, 1400, 1368, 1190, 1078, 878, 808, 713 cm⁻¹. MALDI-TOF-MS (dithranol)$ *m/z*: calculated for C₄₈H₇₅N: 665.59 g•mol⁻¹, found: 666.7 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 86.55, H 11.35, N 2.10; found: C 86.50, H 11.37, N 2.12.



Scheme 3. Synthesis routes of model compounds. (a) TMSA, Pd(PPh₃)₄, Cul, Et₃N/THF, 80 °C; (b) TBAF, THF, 0 °C; (c) CuCl, N,N,N',N'- tetramethylethylenediamine, toluene, 60 °C; (d) TCNE, dichlorobenzene, rt.

2.3.12. 4.4'-((buta-1,3-diyne-1,4-diylbis(2,1-phenylene))bis(ethyne-2,1divl))bis(N,N-dihexadecylaniline) (M)

To a solution of compound **9** (0.40 g, 0.60 mmol) in toluene (2 mL), CuCl (30 mg, 0.3 mmol) and N,N,N',N'-tetramethylethylenediamine (250 µL, 1.68 mmol) were 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 crude product was purified by column chromatography (SiO_2 , hexane/CH₂Cl₂ 20:1) to produce **M** (1.06 g, 72%) as an orange solid. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.90$ (m, 12H), 1.28 (s, 104H), 1.58 (m, 8H), 3.23 (m, 8H), 6.52 (d, J = 5.4 Hz, 4H), 7.22 (m, 1H), 7.33 (m, 1H), 7.45 (d, J = 5.4 Hz, 4H), 7.51 (d, J = 4.5 Hz, 2H), 7.57 (d, J = 4.5 Hz, 2H) ppm. FT-IR (KBr): v = 2922, 2853, 2206, 1607, 1520, 1298, 1190, 808, 753 cm⁻¹. MALDI-TOF-MS (dithranol) m/z: calculated for C₉₆H₁₄8N₂: 1329.6 g•mol⁻¹, found: 1330.5 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 86.68, H 12.21, N 2.11; found: C 86.62, H 12.25, N 2.13.

2.3.13. M-TCNE

To a solution of **M** (66 mg, 0.05 mmol) in 1,2-dichloroethane (5 mL), TCNE (12.80 mg, 0.10 mmol) was added, and the mixture was stirred at 25 °C for 1 h. Removal of the solvent in vacuo yielded the brown solid M-**TCNE** (78 mg, 91%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.92$ (m, 12H), 1.28 (s, 104H), 1.59 (m, 8H), 3.33 (m, 8H), 6.55 (d, J = 5.1 Hz, 4H), 7.32 (m, 1H), 7.39 (m, 1H), 7.48 (d, J = 4.5 Hz, 2H), 7.54 (d, J = 5.4 Hz, 4H), 7.59 (d, J = 5.1 Hz, 2H) ppm. FT-IR (KBr): v = 2924, 2853, 2215, 1733, 1603,1492, 1467, 1416, 1367, 1342, 1184, 823, 758 cm⁻¹. MALDI-TOF-MS (dithranol) m/z: calculated for $C_{108}H_{148}N_{10}$: 1585.19 g•mol⁻¹, found: 1586.3 g•mol⁻¹ [MH]⁺. Elemental analysis calculated (%) for: C 81.77, H 9.40, N 8.83; found: C 81.75, H 9.44, N 8.81.

3. Results and discussion

Both asymmetric bifunctional monomers with various alkyne substituents were synthesized by the sequential Sonogashira crosscoupling and silvl deprotection protocol. Starting from 2,5dibromoiodobenzene, selective introduction of one equivalent of alkyne groups into the iodo positions resulted in 1 or 4, respectively (Scheme 1). Compounds 2 or 5 were synthesized by Sonogashira coupling with (trimethylsilyl)ethyne and compounds 1 or 4. Subsequent silyl deprotection of compounds 2 or 5 with TBAF afforded the asymmetric monomers **3** or **6**. All the compounds were characterized by NMR, IR, and MS spectra. Monomers **3** and **6** were used in a acetylenic



Fig. 1. UV-Vis NIR spectral change of P1 with TCNE addition reaction to the electron-rich alkyne at the polymer side chain. Inset: Plots of TCNE addition amount vs. absorbance increase at 570 nm.



Fig. 2. FT-IR spectra of **P1** before "click" and **P2** (x = 1) after reaction.

oxidative coupling polymerization in the presence of catalytic CuCl and *N*,*N*,*N*',*N*'-tetramethylethylenediamine under air at 60 °C, and the crude materials of PPBs (P1 and P3) were produced (Scheme 2). The corresponding polymers P1 and P3 were precipitated by slow addition of the reaction mixture into a large volume of well-stirred methanol. The precipitates were washed and collected, and the pure polymers P1 and P3 were obtained. These polymers are soluble in common organic solvents such as THF, DCM, chloroform, and benzene, because of the presence of long alkyl chains. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of P1 and P3 were determined by GPC (eluent: THF). As the polymerization results were reproducible, there were no significant side reactions in this case.

The development of a unique class of nonplanar push-pull chromophores by means of [2+2] cycloaddition, followed by cycloreversion, of electron-deficient olefins, such as TCNE, TCNO, and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) has been studied [45, 46]. The high-yielding, click chemistry-type transformation always affords electron sinks capable of multiple electron uptake with a narrow potential range. In this study, the unexpected results are that only P1 can be reacted with click reagents, and the clicked products exhibit poor solubility. Only **P2** with TCNE moieties can be dissolved in general solvents such as THF, DCM, chloroform, and benzene. In this case, P3 cannot be clicked by TCNE, but P1 can be. It was suggested that TCNE can only react with electron-rich alkyne groups (see Schemes 2 and 3) and generated the chromophore group (1,1,4,4-tetracyanobuta-1,3diene (TCBD)).

The addition of TCNE solution in 1,2-dichloroethane to the precursor polymer in o-dichlorobenzene at rt resulted in a color change from yellow to dark red, together with a gradual increase in a charge transfer (CT) band around 570 nm (Fig. 1). The presence of isosbestic points

Table 1	
Summary of the polymerization	results and thermal properties.

Polymer	$Mn^{a} (10^{4})$	Mw^{a} (10 ⁴)	$(Mw/Mn)^{a}$	$Td_{5\%}(^{\circ}C)^{b}$	$Td_{10\%}(^{\circ}C)^{b}$
P1	3.66	7.72	2.11	360	390
P2 ($x = 0.25$)	4.01	8.38	2.09	352	377
P2 ($x = 0.5$)	4.16	7.88	1.89	347	374
P2 ($x = 0.75$)	4.31	9.10	2.11	325	357
P2 ($x = 1$)	4.52	8.75	1.94	261	316
P3	0.29	0.71	2.45	190	220

^a Molecular weights determined by GPC (eluent: THF, calibrated by polystyrene

standards). ^b The 5% and 10% weight loss temperatures determined by TGA at the heating rate of 10 °C/min



Fig. 3. Normalized UV–Vis spectra of monomer 3, P1, P2 $\left(x=1\right)$ and P3 in dichloromethane.

(311 and 416 nm) in the UV-Vis spectral change indicates the absence of undesired side reactions. In order to reveal the quantitative yield of the polymer reaction, the full TCNE adduct (TCNE: alkyne in polymer = 1:1) was prepared and unambiguously characterized. The inset of Fig. 1 shows the linear relationship between the amount of TCNE added and absorbance at 570 nm. It was suggested that a quantitative reaction occurred between the alkyne groups of P1 and TCNE. In the IR spectra (Fig. 2), the precursor polymer **P1** displayed a peak at 2194 cm^{-1} , which was attributed to the alkyne vibration of the side chains. After the addition of TCNE, the peak (alkyne) completely disappeared and became equivocal due to overlap with a new and strong cyano vibrational peak. The TCNEadducted polymer **P2** (x = 1) showed a new and stronger peak attributed to the cyano vibration at 2214 cm⁻¹. After TCNE addition, the position and intensity of these peaks were consistent with previous reports [47,48]. GPC showed an appreciable increase in molecular weight (M_n) , as shown in Table 1.

In contrast to the previous report that the [2 + 2] click reaction sometimes enhances the thermal stability of polymers, in this study, 5% and 10% decomposition temperatures (Td_{5%} and Td_{10%}) of polymer **P2** series were lower than those of the corresponding precursor polymer **P1** (Table 1 and Fig. S1) [42,48–50]. However, both the obtained polymers were thermally stable without any decomposition at least up to 260 °C. The result may be derived from reduced individual bond energy by introducing strong acceptor cyano groups.

3.1. UV-Vis spectroscopy

The normalized UV–Vis absorption spectra are shown in Figs. 3 and S2. Compared to the UV spectra of monomer **3**, **P1** and **P3** show double absorption peaks because of the presence of both intramolecular CT

Table	e 2
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Optical andelectrochemica	l properties	of monomers and	d polymers
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Fig. 4. Relationship between the amount of TCNE and the LOMO and HOMO levels, determined by the E^{red}_{on} and E^{ox}_{on} the solid lines show a fit of the data.

transitions and π - π^* transition of full conjugated main chain in them. A comparison of model monomeric compound **M** and monomer **3** shows that the intensification of conjugation was much larger and the intramolecular charge transferred over a longer conjugation length along the molecular backbones. **M-TCNE** significantly lowered the energy of the CT bands compared with **M**, because of the introduction of the electron-withdrawing group CN. The λ_{end} of **P1** measured in THF was 575 nm (2.16 eV), while **P2** (x = 1) displayed the bathochromically shifted λ_{end} value at 822 nm (1.50 eV). This result suggested that the formation of donor-acceptor chromophores in the side chains by the postfunctionalization lowered the polymer band gap. All the compounds showed complicated absorption behaviors in UV–Vis absorption spectra, and only the λ_{max} values are not as highly regular as the onset wavelength of optical absorption.

3.2. Electrochemistry

In order to verify the optical band gaps and determine the absolute energy levels, the cyclic voltammograms (CVs) were measured in CH₃CN with 0.1 M Bu₄NPF₆ at 20 °C for the polymer thin films cast on a glassy carbon electrode. Several postfunctionalized polymers **P2** with different acceptor addition amounts were prepared to elucidate the relationship between the added acceptor amount (x) and the absolute energy levels. CVs of **P1** and **P2** (x = 1) are shown in Fig. S3 and the peak top values are summarized in Table 2. **P1** showed the first oxidation peak potential (E^{ox}_{on}) at 0.54 eV (*vs.* Fc/Fc⁺), which was attributed to the *N*,*N*-dihexadecylaniline moieties. From the CV curves, **P1** did not exhibit any clear reduction peak in the potential range. A stepwise TCNE addition to **P1** gradually changed reduction potential, but oxidation

1	1 1	1 5					
Materials	$\lambda_{max} \left(nm \right)$	$E^{ox}_{on}{}^{a}(V)$	$E^{red}_{on}{}^{a}(V)$	HOMO (eV)	LOMO (eV)	Eg ^b (eV)	Eg ^c (eV)
P1	364	0.54	_	-5.13	_	_	2.16
P2 (x = 0.25)	364	0.53	-0.46	-5.12	-4.13	0.99	1.55
P2 ($x = 0.5$)	364	0.52	-0.42	-5.11	-4.17	0.94	1.53
P2 (x = 0.75)	395	0.53	-0.39	-5.12	-4.20	0.92	1.52
P2(x = 1)	395	0.52	-0.37	-5.11	-4.22	0.89	1.50
P3	398	0.64	-	- 5.23	-	_	2.42
Μ	329	0.51	- 1.25	-5.10	-3.34	1.76	1.86
M-TCNE	295	0.53	-0.87	-5.12	-3.72	1.40	1.35

^a Onset potentials determined from cyclic voltammograms in CH₃CN with 0.1 M Bu₀NPF₆ at a scan rate of 100 mV/s.

^b Band gap calculated from the energy level of cyclic voltammograms.

^c Band gap estimated from the onset wavelength of optical absorption in THF solution.



Fig. 5. Z-scan results of dichloromethane. (a) Data collected under the open-aperture configuration; (b) data collected under the closed-aperture configuration.

potential remains unchanged. For example, **P2** (x = 0.25) and **P2** (x = 0.50) displayed *N*,*N*-dihexadecylaniline-centered E^{ox}_{on} at 0.53 and 0.52 V, respectively. In contrast to the oxidation peaks, the origin of the first reduction peak potential (E^{red}_{on}) was changed from the polymer main chain to the TCBD moieties when TCNE was added to **P1**. Thus, the reduction potential of **P1** was facilitated as more TCNE was added. The E^{red}_{on} of **P1** bathochromically shifted to -0.45, -0.42, -0.39, and -0.36 V for **P2** with x = 0.25, 0.50, 0.75, and 1, respectively.

The HOMO and LUMO energy levels of all the polymers were calculated from the E^{ox}_{on} and E^{red}_{on} values, respectively, based on the assumption of Fc/Fc⁺ [51–53]. The energy levels were plotted against the amount of TCNE (x; Fig. 4). The data clearly indicated that the HOMO remained unchanged and LUMO levels decreased as more acceptor molecules were added (Table 2). The fitting line of LOMO shows a linear relationship between LOMO and the amount of TCNE. It was suggested that the energy levels of conjugated polymers be accurately adjusted by the postfunctionalization method. Accordingly, the electrochemical band gaps, calculated from the difference between the HOMO and LUMO levels, considerably decreased after postfunctionalization. The electrochemical properties have been studied by CVs, indicating

T	a	b	le	3	

Third-order NLO parameters of all the compounds.

Samples	P1	P2 ($x = 0.5$)	P2 (x = 1.0)	М	M-TCNE
$\beta \times 10^{-11} (m \cdot w^{-1})$ Im $\gamma^{(3)} \times 10^{-18} (esu)$	2.6	11.0 -2.7	- 0.51 -	_	-3.6 -2.4

a good agreement between the electrochemical and optical band gaps determined by the end absorption.

3.3. Nonlinear optics

The NLO responses of **P1** and **P2** were measured by the Z-scan technique, and Fig. 5 displayed the nonlinear absorptive and refractive behaviors of **P1** and **P2**. A good fit was achieved between the experimental data and the theoretical curves, and the NLO data are shown in Table 3.

In Fig. 5, a profound transmittance valley could be seen around the focal plane for P1, which was characteristic of reverse saturable absorption (RSA)-type behavior of P1. Materials with RSA became more opaque on exposure to high photon fluxes due to the high absorption from the excited state, and the properties had been exploited in the field of optical limiting for laser protection. For **P2** (x = 0.5), a similar RSA-type behavior was observed, and the NLO response was reduced by click reaction. However, Fig. 5 showed typical transmittance peaks of click reaction products **P2** (x = 1.0), which exhibited saturable absorption (SA)-type behaviors. Compared to **P1** without click moieties. the clicked products exhibited clearly RSA-SA transition, and the transition was achieved by click-type reactions in organic molecules. Threshold intensity was the reason behind conversion from RSA to SA phenomenon [38,39,54], which was determined by parameters such as absorption cross section, level lifetime and decline of saturation intensity. Once the incident light intensity crossed the threshold intensity, conversion from RSA to SA happened. Comparing with curves in Fig. 5a, the same phenomenon was observed in Fig. S4(a) for the model compounds. The model compound M did not show the NLO response because of the short conjugated length. The M-TCNE exhibited SA-type behaviors because of the introduced clicked moieties. From all the figures and data in Table 3, it can be proved that the click addition was the most important factor to affect the NLO properties. 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 [38,39,54].

4. Conclusions

A series of PPB derivatives were prepared by the [2 + 2] cycloaddition of TCNE to donor-substituted alkynes in excellent yields and full characterization. The data suggested that a careful selection of the species and amount of the added acceptor molecules enables good control of the polymer energy levels. The data clearly indicated that a linear relationship between LOMO and the amount of TCNE was an objectively existing rule. These results provide a promising prospect for applying this methodology to other conjugated polymers. Z-scan measurements to investigate the third-order NLO properties confirmed that the click reaction was key factor for the typical RSA–SA reverses.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.reactfunctpolym.2016.06.001.

References

- C.D. Simpson, J.S. Wu, M.D. Watson, K. M
 ülen, From graphite molecules to columnar superstructures - an exercise in nanoscience, J. Mater. Chem. 14 (2004) 494–504.
- [2] H. Kang, G. Evrenenko, P. Dutta, K. Clays, K. Song, T.J. Marks, X-shaped electro-optic chromophore with remarkably blue-shifted optical absorption. Synthesis, characterization, linear/nonlinear optical properties, self-assembly, and thin film microstructural characteristics, J. Am. Chem. Soc. 128 (2006) 6194–6205.
- [3] G. Hughes, M.R. Bryce, Electron-transporting materials for organic electroluminescent and electrophosphorescent devices, J. Mater. Chem. 15 (2005) 94–107.
- [4] M. Van der Auweraer, F.C. De Schryver, Organic electronics: supra solutions, Nat. Mater. 3 (2004) 507–508.
- [5] M. Li, S.L. Li, H. Chen, R. Hu, L.B. Liu, F.T. Lv, S. Wang, Preparation of conjugated polymer grafted with H₂O₂-sensitive prodrug for cell imaging and tumor cell killing, ACS Appl. Mater. Interfaces 8 (2016) 42–46.
- [6] J.J. Yao, C.M. Yu, Z.T. Liu, H.W. Luo, Y. Yang, G.X. Zhang, D.Q. Zhang, Significant improvement of semiconducting performance of the diketopyrrolopyrrolequaterthiophene conjugated polymer through side-chain engineering via hydrogenbonding, J. Am. Chem. Soc. 138 (2015) 173–185.
- [7] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions, Science 270 (1995) 1789–1791.
- [8] H. Sirringhaus, N. Tessler, R.H. Friend, Integrated optoelectronic devices based on conjugated polymers, Science 280 (1998) 1741–1744.
- [9] L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones, D.L. Allara, J.M. Tour, P.S. Weiss, Are single molecular wires conducting? Science 271 (1996) 1705–1707.
- [10] S.W. Thomas III, G.D. Joly, T.M. Swager, Chemical sensors based on amplifying fluorescent conjugated polymers, Chem. Rev. 107 (2007) 1339–1386.
- [11] A. Babel, S.A. Jenekhe, High electron mobility in ladder polymer field-effect transistors, J. Am. Chem. Soc. 125 (2003) 13656–13657.
- [12] G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, Flexible lightemitting diodes made from soluble conducting polymers, Nature 357 (1992) 477–479.
- [13] D.T. McQuade, A.E. Pullen, T.M. Swager, Conjugated polymer-based chemical sensors, Chem. Rev. 100 (2000) 2537–2574.
- [14] M. Gross, D.C. Müller, H.G. Nothofer, U. Scherf, D. Neher, C. Bräuchle, K. Merrholz, Improving the performance of doped pi-conjugated polymers for use in organic light-emitting diodes, Nature 405 (2000) 661–665.
- [15] T. Miteva, L. Palmer, L. Kloppenburg, D. Neher, U.H.F. Bunz, Interplay of thermochromicity and liquid crystalline behavior in poly(p-phenyleneethynylene)s: pi-pi interactions or planarization of the conjugated backbone, Macromolecules 33 (2000) 652–654.
- [16] M.D. Watson, A. Fechtenkötter, K. Müllen, Big is beautiful "Aromaticity" revisited from the viewpoint of macromolecular and supramolecular benzene chemistry, Chem. Rev. 101 (2001) 1267–1300.
- [17] J. Choi, C.R. Ruiz, E.E. Nesterov, Temperature-induced control of conformation and conjugation length in water-soluble fluorescent polythiophenes, Macromolecules 43 (2010) 1964–1974.
- [18] K. Wagner, L.L. Crow, P. Wagner, S. Gambhir, A.C. Partridge, J.C. Earles, T.M. Clarke, K.C. Gordon, D.L. Officer, Indanedione-substituted poly(terthiophene)s: processable conducting polymers with intramolecular charge transfer interactions, Macromolecules 43 (2010) 3817–3827.
- [19] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click chemistry: diverse chemical function from a few good reactions, Angew. Chem. Int. Ed. 40 (2001) 2004–2021.
- [20] H. Nandivada, X. Jiang, J. Lahann, Click chemistry: versatility and control in the hands of materials scientists, Adv. Mater. 19 (2007) 2197–2208.
- [21] J.F. Lutz, 1,3-dipolar cycloadditions of azides and alkynes: a universal ligation tool in polymer and materials science, Angew. Chem. Int. Ed. 46 (2007) 1018–1025.
- [22] D. Fournier, R. Hoogenboom, U.S. Schubert, Clicking polymers: a straightforward approach to novel macromolecular architectures, Chem. Soc. Rev. 36 (2007) 1369–1380.
- [23] B.Z. Tang, Construction of functional polymers from acetylenic triple-bond building blocks, Macromol. Chem. Phys. 209 (2008) 1304–1307.
- [24] E. Demirel, H. Durmaz, G. Hizal, U. Tunca, A route toward multifunctional polyurethanes using triple click reactions, J. Polym. Sci. A Polym. Chem. 54 (2016) 480–486.
- [25] C. Zhou, V.X. Truong, Y. Qu, T. Lithgow, G.D. Fu, J.S. Forsythe, Antibacterial poly(ethylene glycol) hydrogels from combined epoxy-amine and thiol-ene click reaction, J. Polym. Sci. A Polym. Chem. 54 (2016) 656–667.
- [26] D.J.V.C. van Steenis, O.R.P. David, G.P.F. van Strijdonck, J.H. van Maarseveen, J.N.H. Reek, Click-chemistry as an efficient synthetic tool for the preparation of novel conjugated polymers, Chem. Commun. 34 (2005) 4333–4335.
- [27] S. Bakbak, P.J. Leech, B.E. Carson, S. Saxena, W.P. King, U.H.F. Bunz, 1,3-dipolar cycloaddition for the generation of nanostructured semiconductors by heated probe tips, Macromolecules 39 (2006) 6793–6795.
- [28] N.V. Tsarevsky, K.V. Bernaerts, B. Dufour, F.E.D. Prez, K. Matyjaszewski, Well-defined (Co)polymers with 5-vinyltetrazole units via combination of atom transfer radical (Co)polymerization of acrylonitrile and "click chemistry"-type postpolymerization modification, Macromolecules 37 (2004) 9308–9313.

- [29] T.D. Kim, J. Luo, Y. Tian, J.W. Ka, N.M. Tucker, M. Haller, J.W. Kang, A.K.Y. Jen, Diels-Alder "click chemistry" for highly efficient electrooptic polymers, Macromolecules 39 (2006) 1676–1680.
- [30] K.L Killops, L.M. Campos, C.J. Hawker, Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "Click" chemistry, J. Am. Chem. Soc. 130 (2008) 5062.
- [31] B.C. Yao, J. Mei, J. Li, J. Wang, H.Q. Wu, J.Z. Sun, A.J. Qin, B.Z. Tang, Catalyst-free thiolyne click polymerization: a powerful and facile tool for preparation of functional poly(vinylene sulfide)s, Macromolecules 47 (2014) 1325–1333.
- [32] Y.R. Zhang, G. Chen, Y.L. Lin, L.F. Zhao, W.Z. Yuan, P. Lu, C.K.W. Jim, Y.M. Zhang, B.Z. Tang, Thiol-bromo click polymerization for multifunctional polymers: synthesis, light refraction, aggregation-induced emission and explosive detection, Polym. Chem. 6 (2015) 97–105.
- [33] B.C. Yao, T. Hu, H.K. Zhang, J. Li, J.Z. Sun, A.J. Qin, B.Z. Tang, Multi-functional hyperbranched poly(vinylene sulfide)s constructed via spontaneous thiol-yne click polymerization, Macromolecules 48 (2015) 7782–7791.
- [34] A.P. Xu, H.H. Han, J. Lu, P.P. Yang, Y.J. Gao, H.W. An, D. Zhanng, L.Z. Li, J.P. Zhang, D. Wang, L. Wang, H. Wang, Charge transfer NIR dyes for improved photoacoustic effect, Dyes Pigments 125 (2016) 392–398.
- [35] Y.S. Mi, P.X. Liang, Z. Yang, D. Wang, H. Cao, W.L. He, H. Yang, Effects of donor and acceptor on optoelectronic performance for porphyrin derivatives: nonlinear optical properties and dye-sensitized solar cells, Chem. Res. Chin. Univ. 31 (2015) 992–996.
- [36] P.X. Liang, Z.C. Du, D. Wang, Z. Yang, H.Y. Sheng, S.Q. Liang, H. Cao, W.L. He, H. Yang, Optoelectronic and self-assembly properties of porphyrin derivatives with click chemistry modification, ChemPhysChem 15 (2014) 3523–3529.
- [37] D. Wang, X.K. Wang, Y.Z. Zhao, H. Gao, Y. Xing, H. Yang, Ladder-type poly(benzopentalene) derivatives with tunable energy levels by "click" reaction, Polym. Chem. 3 (2012) 914–919.
- [38] Y.S. Mi, P.X. Liang, Z.K. Jin, D. Wang, Z. Yang, Synthesis and third-order nonlinear optical properties of triphenylene derivatives modified by click chemistry, ChemPhysChem 14 (2013) 4102–4108.
- [39] Z.K. Jin, D. Wang, X.K. Wang, P.X. Liang, Y.S. Mi, H. Yang, Efficient modification of pyrene-derivative featuring third-order nonlinear optics via the click postfunctionalization, Tetrahedron Lett. 54 (2013) 4859–4864.
- [40] D. Wang, W.S. Zhang, Y. Xing, H. Gao, X.K. Wang, Y.Z. Zhao, H. Yang, Energy-level modulation of organic alkynes by click chemistry, Tetrahedron 69 (2013) 895–901.
- [41] B.B. Xu, M. Lu, J.H. Kang, D. Wang, J. Brown, Z.H. Peng, Synthesis and optical properties of conjugated polymers containing polyoxometalate clusters as side-chain pendants, Chem. Mater. 17 (2005) 2841–2851.
- [42] Y.R. Li, T. Michinobu, Sequential double click reactions: a highly efficient postfunctionalization method for optoelectronic polymers, Polym. Chem. 1 (2010) 72–74.
- [43] D. Wang, T. Michinobu, One-step synthesis of ladder-type fused poly(benzopentalene) derivatives with tunable energy levels by variable substituents, J. Polym. Sci. A Polym. Chem. 49 (2011) 72–81.
- [44] D. Wang, Q.S. Guo, H. Gao, Z. Yang, Y. Xing, H. Cao, W.L. He, H.H. Wang, J.M. Gu, H.Y. Hu, The application of double click in the third-order nonlinear polymer containing donor-acceptor chromophores, Polym. Chem. (2016), http://dx.doi.org/10.1039/ c6py00106h.
- [45] M. Kivala, C. Boudon, J.P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, Charge-transfer chromophores by cycloaddition-Retro-electrocyclization: multivalent systems and cascade reactions, Angew. Chem. Int. Ed. 46 (2007) 6357–6360.
- [46] A.D. Payne, G. Bojase, M.N. PaddonRow, M.S. Sherburn, Practical synthesis of the dendralene family reveals alternation in behavior, Angew. Chem. Int. Ed. 48 (2009) 4836–4839.
- [47] T. Michinobu, H. Kumazawa, K. Noguchi, K. Shigehara, One- step synthesis of donor-acceptor type conjugated polymers from ferrocene-containing poly(aryleneethynylene)s, Macromolecules 42 (2009) 5903–5905.
- [48] Y.R. Li, K. Tsuboi, T. Michinobu, Double click synthesis and second-order nonlinearities of polystyrenes bearing donor-acceptor chromophores, Macromolecules 43 (2010) 5277–5286.
- [49] T. Michinobu, Click synthesis of donor-acceptor-type aromatic polymers, Pure Appl. Chem. 82 (2010) 1001–1009.
- [50] W.Y. Huang, H.Y. Chen, Synthesis and characterization of a low-bandgap poly(arylene ethynylene) having donor-acceptor type chromophores in the side chain, Macromolecules 46 (2013) 2032–2037.
- [51] T. Michinobu, H. Kumazawa, E. Otsuki, H. Usui, K. Shigehara, Synthesis and properties of nitrogen-linked poly(2,7-carbazole)s as hole-transport material for organic light emitting diodes, J. Polym. Sci. A Polym. Chem. 47 (2009) 3880–3891.
- [52] T. Michinobu, F. Kato, J. Inui, H. Nishide, Two-dimensionally extended aromatic polyamines for optimization of charge-transporting properties by partial oxidation, J. Polym. Sci. A Polym. Chem. 47 (2009) 4577–4586.
- [53] T. Michinobu, H. Osako, K. Shigehara, Synthesis and properties of conjugated poly(1,8-carbazole)s, Macromolecules 42 (2009) 8172–8180.
- [54] W.S. Zhang, D. Wang, H. Cao, H. Yang, Energy level tunable pre-click functionalization of [60]fullerene for nonlinear optics, Tetrahedron 70 (2014) 573–577.