



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).

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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–alkyne 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-tetracyanoquinodimethane (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-dibromiodobenzene [41], *N,N*-dihexadecyl-4-iodoaniline [42], 4-ethynyl-*N,N*-dihexadecylaniline [42], 4-[(2-bromophenyl)ethynyl]-*N,N*-dihexadecylaniline (**7**) [43], 4-[(2,5-dibromophenyl)ethynyl]-*N,N*-dihexadecylaniline (**1**) [44], 4-[(2,5-bis(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 quartz 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 computer-controlled 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*-dihexylaniline (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 C₄₆H₇₃Br₂N: 799.41 g·mol⁻¹, found: 800.3 g·mol⁻¹ [MH]⁺; elemental analysis calculated (%) for C₄₆H₇₃Br₂N (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,N*-dihexadecylaniline (**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 (SiO₂, V_{hexane}/V_{DCM} = 10:1) to produce (**2**) (1.00 g, 48%). ¹H NMR (CDCl₃, 500 MHz): δ = 0.27 (m, 18H), 0.89 (m, 6H), 1.28 (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): ν = 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), K₂CO₃ (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): δ = 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): ν = 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-dibromiodobenzene (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): δ = 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): ν = 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 C₁₉H₁₈Br₂: 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 Et₃N/THF

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