Electronic Supplementary Information (ESI)

New Hyperbranched Polyaryleneethynylene Containing Azo-benzene Chromophores in the Main Chain: Facile Synthesis , Large Optical Nonlinearity and High Thermal Stability

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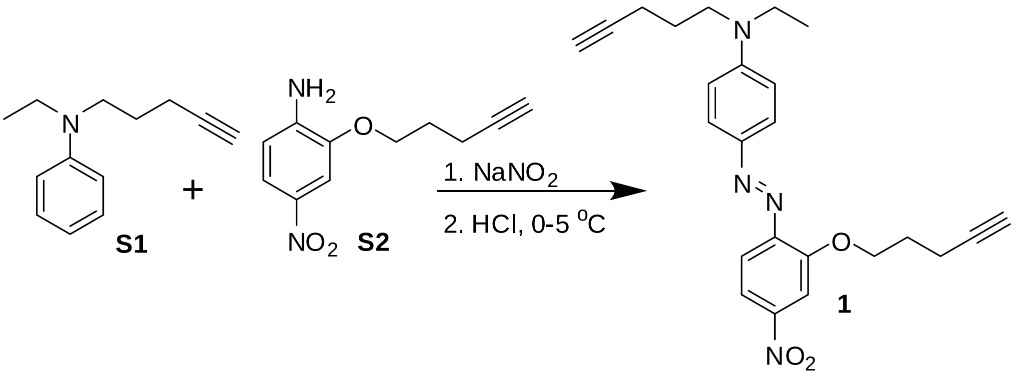
Scheme S1



Experimental Section

Materials

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Triethylamine (Et_3N) was distilled under normal pressure and kept over potassium hydroxide. Compounds **S1** and **S2** were synthesized in our previous work.[1,2] Compounds **2** and **3** were prepared according to the literatures.[3,4] All other reagents were used as received.

Instrumentation.

The ^1H NMR spectra were measured on a Bruker ARX 400 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000-400 cm^{-1} on NaCl pellets. UV-visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

Synthesis of chromophore 1.

Compound **S2** (0.43 g, 1.95 mmol) was dissolved in a water solution of 35% hydrochloric acid. The mixture was cooled to 0-5 °C in an ice bath, and then a solution of sodium nitrite (0.14 g, 2.03 mmol) in water was added to the above cooled solution dropwise. After stirred below 5 °C for 15 min, a solution of compound **S1** (0.31 g, 1.66 mmol) in ethanol was added slowly. The mixture was left in the ice bath for another 1 h, some sodium bicarbonate was added to adjust the pH value to about 7.0. The reaction mixture was stirred for another 0.5 h, the red precipitate was filtered, washed with water. The crude product was purified by recrystallization from ethanol/water to afford deeply red powder (0.57 g, 84.8 %). IR (thin film), υ (cm^{-1}): 3290 (C≡CH), 1516, 1339 ($-NO_2$). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.25 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 1.90 (m, 2H, $-CH_2-$), 2.00 (s, 1H, C≡CH), 2.07 (s, 1H, C≡CH), 2.15 (m, 2H, $-CH_2-$), 2.31 (m, 2H, $-CH_2C-$), 2.51 (m, 2H, $-CH_2C-$), 2.51(t, *J* = 5.1 Hz, 2H, $-CH_2C≡$), 3.52 (m, 4H, $-NCH_2-$), 4.34 (t, *J* = 6.0 Hz, 2H, $-O-CH_2-$), 6.75 (d, *J* = 9.2 Hz, 2H, ArH), 7.67 (d, J = 8.8 Hz, 2H, ArH), 7.91 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.64, 15.39, 16.21, 26.31, 28.33, 45.78, 49.50, 63.50, 69.39, 69.64, 83.40, 83.49, 109.47, 109.65, 111.51116.95, 117.63, 126.57, 144.43, 147.60, 148.26, 151.35, 155.20. MS (EI), m/z [M^+]: 418, calcd: 418. $C_{24}H_{26}N_4O_3$ (EA) (%, found/calcd): C, 68.81/68.88; H, 6.16/6.26; N, 12.88/13.39. UV-Vis (THF, 1.25×10^{-5} mol/L): λ_{max}: 489 nm; ε_{max}: 1.56×10^3 mol^{-1} L cm^{-1}.

Synthesis of hyperbranched polymer P1.

A mixture of chromophore **1** (94 mg, 0.225 mmol), compound **2** (93 mg, 0.150 mmol), copper iodide (CuI) (5 mg, 0.026 mmol), triphenylphosphine (PPh_3) (10 mg, 0.038 mmol), triphenylphosphineandtetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (14 mg, 0.012 mmol) was carefully degassed and charged with nitrogen. THF (2.5 mL)/Et_3N (1 mL) was then added. The reaction was stirred for 3 days at room temperature. The mixture was passing through a cotton filter and dropped into a lot of acetone. The precipitate was collected, further purified by several precipitations of its THF solution into acetone, and dried in a vacuum at 40 °C to a constant weight to yield **P1** as deeply red powder (80 mg, 61.5 %). M_w = 11 100, M_w/M_n = 1.73 (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1505, 1333 (-NO_2). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.0-1.3 (-CH_3), 1.8-2.0 (-CH_2), 2.0-2.2 (-CH_2), 2.4-2.7 (-CH_2C-), 3.3-3.7 (-CH_2N-), 4.2-4.4 (-CH_2O-), 6.6-7.0 (ArH), 7.2 (ArH), 7.4-7.7 (ArH), 7.7-8.0 (ArH). UV-Vis (THF, 0.01 mg/mL): λ_{max}: 488 nm.

Synthesis of linear polymer P2.

A mixture of chromophore **1** (84 mg, 0.200 mmol), compound **3** (103 mg, 0.200 mmol), copper iodide (CuI) (4 mg, 0.02 mmol), triphenylphosphine (PPh_3) (8 mg, 0.030 mmol), triphenylphosphineandtetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (12 mg, 0.010 mmol) was carefully degassed and charged with nitrogen. THF (2 mL)/Et_3N (0.8 mL) was then added. The reaction was stirred for 4 days at room temperature. The mixture was passing through a cotton filter and dropped into a lot of acetone. The precipitate was collected, further purified by several precipitations from its THF solution into acetone, and dried in a vacuum at 40 °C to a constant weight to yield **P2** as deeply red powder (88 mg, 66.7 %). M_w = 11 550, M_w/M_n = 2.54, (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 1516, 1337 ($-NO_2$). ^1H NMR ($CDCl_3$) δ (ppm): 1.1-1.3 ($-CH_3$), 1.8-2.0 ($-CH_2$), 2.0-2.2 ($-CH_2$), 2.3 ($-CH_3$), 2.4-2.6 ($-CH_2C-$), 2.6-2.8 ($-CH_2C-$), 3.3-3.6 ($-CH_2N-$), 4.3-4.4 ($-CH_2O-$), 6.7-6.8 (ArH), 6.8-7.0 (ArH), 7.1 (ArH), 7.2 (ArH), 7.6-7.7 (ArH), 7.8-7.9 (ArH). UV-Vis (THF, 0.01 mg/mL): λ_{max}: 491 nm.

Preparation of Polymer Thin Films.

The polymers were dissolved in THF (concentration ~4 wt %) and the solutions were filtered through syringe filters. Polymer films were spin coated onto indium-tin-oxide (ITO)-coated glass substrates, which were cleaned by *N*, *N*-dimethyformide, acetone, distilled water and THF sequentially in ultrasonic bath before use. Residual solvent was removed by heating the films in a vacuum oven at 40 °C.

NLO Measurement of Poled Films.

The second-order optical nonlinearity of the polymers was determined by in-situ second harmonic generation (SHG) experiment using a closed temperature-controlled oven with optical windows and three needle electrodes. The films were kept at 45° to the incident beam and poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: different for each polymer (Table 2); voltage: 7.8 kV at the needle point; gap distance: 0.8 cm. The SHG measurements were carried out with a Nd:YAG laser operating at a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

References

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(2) Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z. *Macromolecules* **2007**, *40*, 5634-5637.

(3) Kiang, Y. H.; Gardner, G. B.; Lee, S.; Xu, Z.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204-8215.

(4) Plater, M. J.; Jackson, T. *Tetrahedron* **2003**, *59*, 4687-4692.

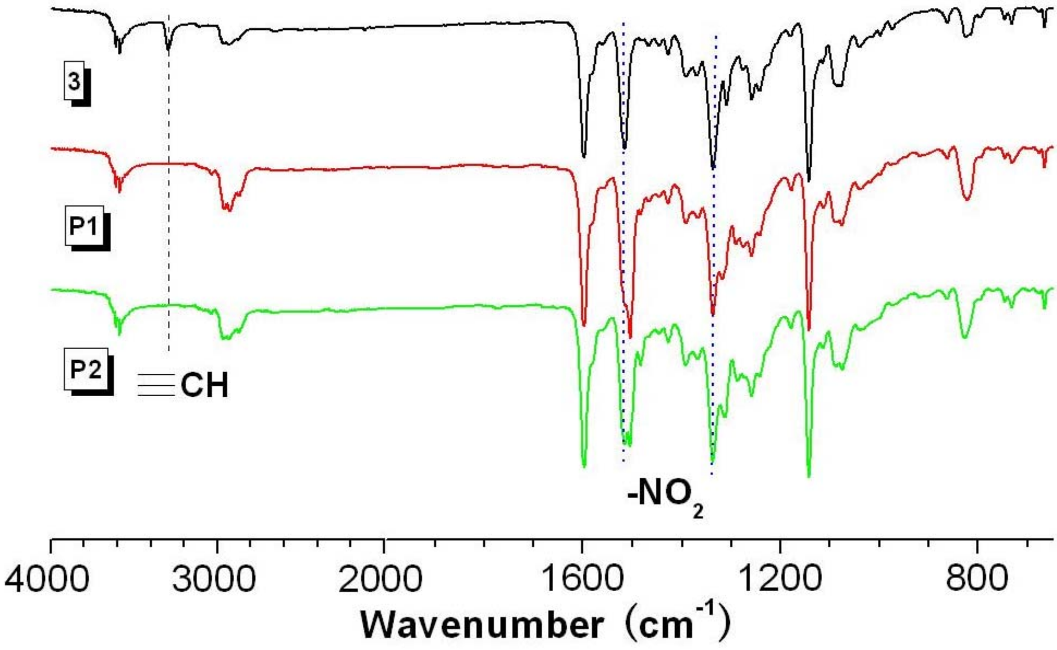

Figure S1. IR spectra of chromophores **3** and polymers **P1**-**P2**.

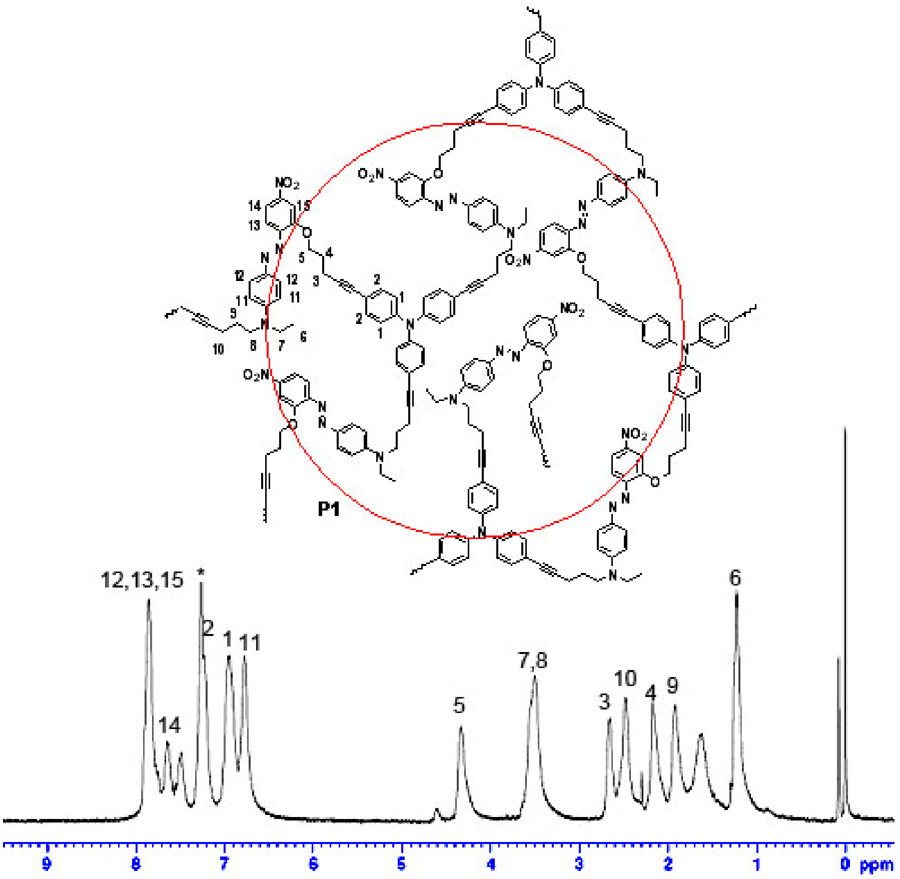

Figure S2. ^{1}H NMR spectrum of **P1** in chloroform-*d*.

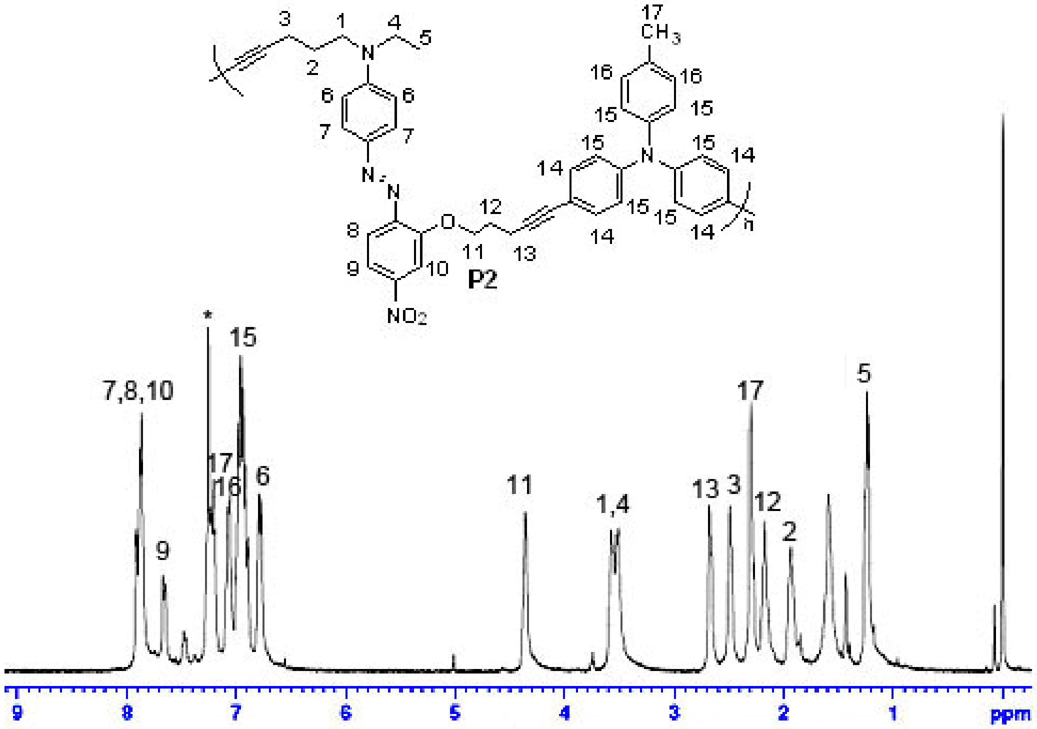

Figure S3. ^{1}H NMR spectrum of **P2** in chloroform-*d*.

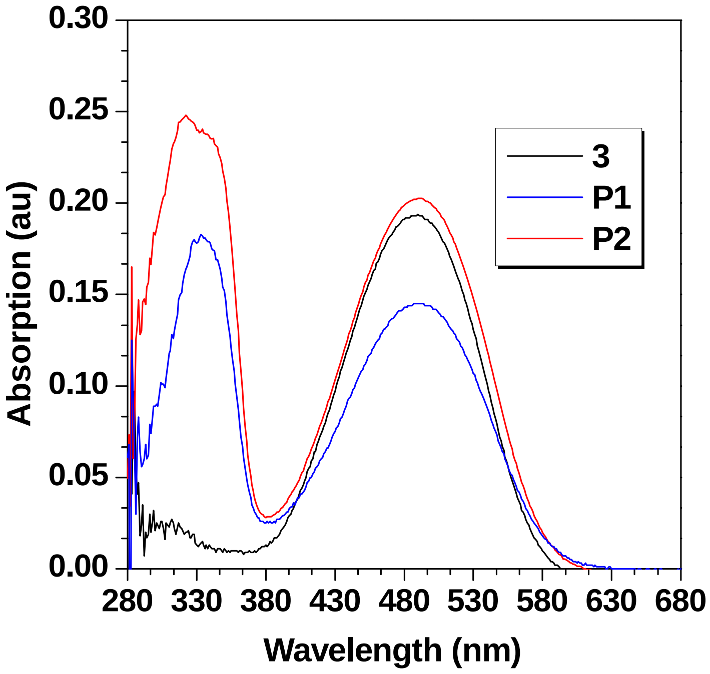

Figure S4. UV-Vis spectra of THF solutions of polymers **P1**-**P2** (0.01 mg/mL) and chromophore **3** (2.5×10^{-5} mol/L).

$$d_{33} = \frac{1}{2} N\beta f^{2\omega} \left(f^{\omega}\right)^2 \left\langle \cos^3 \theta \right\rangle \qquad \text{Equation S1}$$

where N is the number density of the chromophore, β is its first hyperpolarizability, f is the local field factor, 2ω is the double frequency of the laser, ω is its fundamental frequency, and $<\cos^3\theta>$ is the average orientation factor of the poled film.