

Supplementary Information for

**Synthesis and electrochromic property of polyamines containing 4,4'-
diaminotriphenylamine-*N,N'*-diyl unit in the polymer backbone: Ru-catalyzed N–H
insertion polycondensation of 1,4-phenylenebis(diazoacetate) with 4,4'-
diaminotriphenylamine derivatives**

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Experimental section

Materials.

Monomers **1**,¹ **2a**,² and **2b**³ were prepared according to the literatures. Dichloro(*p*-cymene)ruthenium(II) dimer ([RuCl₂(*p*-cymene)]₂; Sigma-Aldrich), CaH₂ (Nacalai Tesque, >99.0%), MgSO₄ (FUJIFILM Wako Pure Chemical, >98.0%) were used as received. 1,2-dichloroethane (FUJIFILM Wako Pure Chemical, Guaranteed Reagent) were dried over CaH₂ and used without further purification.

Polymer Synthesis.

P3-CN (polymerization of **1** with **2b**). Under a N₂ atmosphere, a 1,2-dichloroethane solution (0.85 mL) of **1** (60.5 mg, 0.200 mmol) and **2b** (60.1 mg, 0.200 mmol) were placed in a Schlenk tube. At room temperature, a 1,2-dichloroethane solution (0.4 mL) of [RuCl₂(*p*-cymene)]₂ [3.1 mg, 0.0050 mmol (0.010 mmol of Ru)] was added to the solution, and the mixture was stirred at 30 °C for 12 h. Then, CHCl₃ (15 mL) was added, and the resulting mixture was transferred to a separatory funnel, where the organic layer was washed with water (15 mL) and brine (15 mL). The organic layer was dried over MgSO₄, and the volatiles were removed under reduced pressure. The residual crude product was subjected to purification with preparative recycling SEC using CHCl₃ as an eluent to afford **P3-CN** (49 mg, 43%).

¹H NMR (500 MHz, CDCl₃, δ): 7.47 [s, 4*n*H, Ar-*H* (derived from **1**)], 7.2 [br, 2*n*H, Ar-*H* (derived from **2b**)], 6.9 [br, 4*n*H, Ar-*H* (derived from **2b**)], 6.7 [br, 2*n*H, Ar-*H* (derived from **2b**)], 6.5 [br, 4*n*H, Ar-*H* (derived from **2b**)], 5.00 (s, 2*n*H, CH), 4.9 (br, 2*n*H, NH), 4.0–4.3 (m, 4*n*H, OCH₂), 1.2 (m, 6*n*H, CH₃).

¹³C NMR (126 MHz, CDCl₃, δ): 171.5 (C=O), 152.5 [Ar, quaternary (q.)], 144.0 (Ar, q.), 137.8 (Ar, q.), 136.3 (Ar, q.), 133.0 [Ar (C-H)], 128.0 [Ar (C-H)], 127.7 [Ar (C-H)], 120.4 (CN), 116.3 [Ar (C-H)], 114.3 [Ar (C-H)], 99.6 (Ar, q.), 62.0 (OCH₂), 60.8 (CH-NH), 14.1 (CH₃).

Anal. Calcd for [C₃₃H₃₀N₄O₄ · H₂O]_{*n*}: C, 70.20; H, 5.71; N, 9.92. Found: C, 70.56; H, 6.30; N, 8.92.

P3-OMe was prepared in a similar manner by the polymerization of **1** with **2a**.

¹H NMR (500 MHz, CDCl₃, δ): 7.45 [s, 4*n*H, Ar-*H* (derived from **1**)], 6.9–6.7 [m, 2*n*H × 2 + 4*n*H, Ar-*H* (derived from **2a**)], 6.4 [br, 4*n*H, Ar-*H* (derived from **2a**)], 5.0 (br, 2*n*H, CH), 4.2–4.1 (m, 4*n*H, OCH₂), 3.71 (s, 3*n*H, OCH₃), 1.2–1.1 (m, 6*n*H, CH₃).

¹³C NMR (126 MHz, CDCl₃, δ): 171.1 (C=O), 150–110 (Ar), 61.8 (OCH₂), 60.9 (CH-NH), 55.5 (OCH₃), 14.1 (CH₃). Because of the very broad appearance and overlapping, the signals for aromatic carbons of **P3-OMe** cannot be precisely assigned.

Anal. Calcd for [C₃₃H₃₃N₃O₅]_{*n*}: C, 71.85; H, 6.03; N, 7.62. Found: C, 71.05; H, 6.14; N, 7.30.

Fabrication of the Electrochromic Films and Devices

For polymer films in the electrochemical measurements, 10 mg polymer samples were first dissolved into 5 mL DMAc. After the samples dissolved, the polymer solution was filtered through 0.22 μm PTFE filters and dropped onto the indium-tin-oxide (ITO)-coated glasses (6 mm × 30 mm). The specimen was dried under vacuum at room temperature until most of the solvent was removed and then heated at 80 °C for 4 hours and 160 °C for 8 hours.

As for devices, the polyamine was drop-coated onto ITO-coated glass substrates (25 mm × 30 mm). Then, confined the gap to 120 μm between two pieces of ITO-coated glass substrates by using a full-auto dispenser to coat thermoset adhesive with a 20 × 20 mm² active area under 120 °C for 6 hours and retained a tiny hole to inject gel solution into the device using vacuum encapsulating method. After injection of gel electrolytes, sealed the tiny hole with UV-curing adhesive, and the device would cure under 75 °C for 2 hours. The polymer gel was made of 7.6 mg of poly(MMA-HEMA), 1.65 mg (0.1 M) of tetrabutylammonium tetrafluoroborate (TBABF₄), 0.40 mg (0.015 M) of HV, 0.63 mg of aliphatic polyisocyanate (Desmodur® N3200), 0.01 mg of catalyst dibutyltin diacetate, and 0.048 mL of propylene carbonate (PC).

Measurements.

The polymers' molar mass distributions were measured via SEC in THF at 40 °C on polystyrene gel columns (Waters Styragel HR4 and HR2 with molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively; column size = 300 mm × 7.8 mm i.d.; average particle size = 5 μm, flow rate = 1.0 mL/min) connected to a pump (JASCO, PU-4180), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (JASCO, UV-4075), and a refractive index detector (JASCO, RI-2031 Plus). The number-average molar mass (M_n) and dispersity [D ; weight-average molar mass/number-average molar mass (M_w/M_n)] were calculated from the chromatographs based on six poly(methyl methacrylate) (PMMA) standards (Shodex M-75; M_p = 2400–212000, $D < 1.1$) and dibutyl sebacate (molar mass = 314.5). Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of JAIGEL-3H and JAIGEL-2H (Japan Analytical Industry; molar mass exclusion limit = 70 kDa and 5 kDa for polystyrene, respectively; column size = 600 mm × 20 mm i.d.) using chloroform as eluent at a flow rate of 3.8 mL/min at room temperature.

¹H (500 MHz) and ¹³C (126 MHz) NMR spectra were recorded on a Bruker Avance III HD 500 spectrometer in CDCl₃ at room temperature or at 50 °C.

FT-IR spectra were recorded on Perkin-Elmer Spectrum Two system using KBr pellets.

Elemental analyses were performed on a YANAKO CHN Corder MT-5.

The glass transition temperature (T_g) of polymers was determined by differential scanning calorimetry (DSC; Seiko Instruments Inc., EXSTAR DSC6000) in the range from −100 °C to 200 °C for product polymers. The heating and cooling rates were 10 °C/min. The T_g of the polymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. Thermogravimetric analysis was performed with Exstar TG/DTA6200 (Seiko Instruments). The experiments were carried out with about 5 mg of a sample under a nitrogen atmosphere at a heating rate of 10 °C/min.

Electrochemical properties, including cyclic voltammetry (CV) and differential pulse voltammograms (DPV), were conducted through CH Instruments 6122E Electrochemical Analyzer under a three-electrode system consisting of polymer film coated on a 6 mm by 30 mm ITO glass as a working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode in 3 mL PC with 0.1 M TBABF₄ as supporting electrolyte. An Ailgent UV-vis spectrophotometer recorded the spectroelectrochemical spectra.

Supplementary Figures

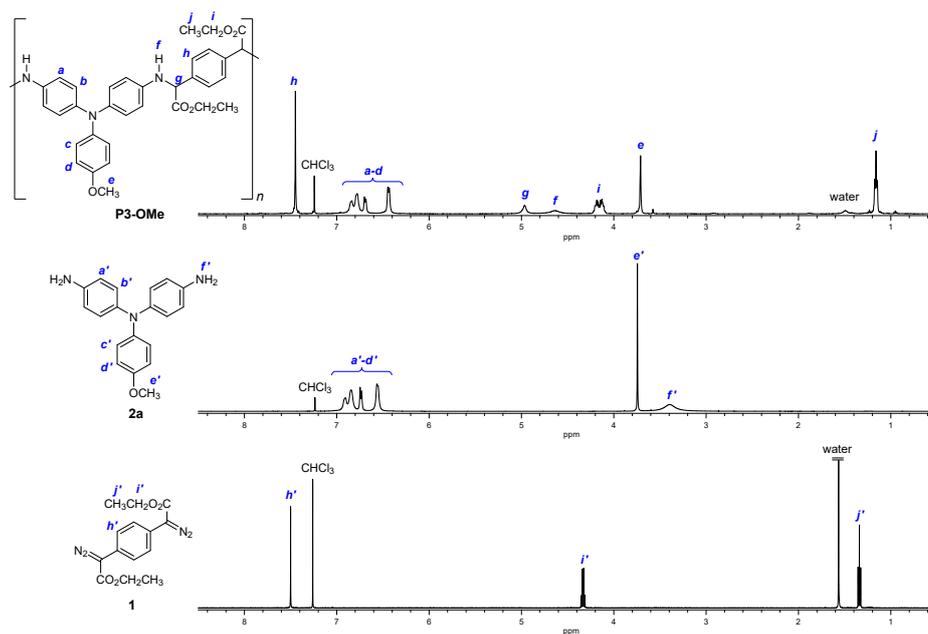


Figure S1. ^1H NMR spectra of **P3-OMe** ($M_n = 7700$, $D = 1.44$), **2a**, and **1**.

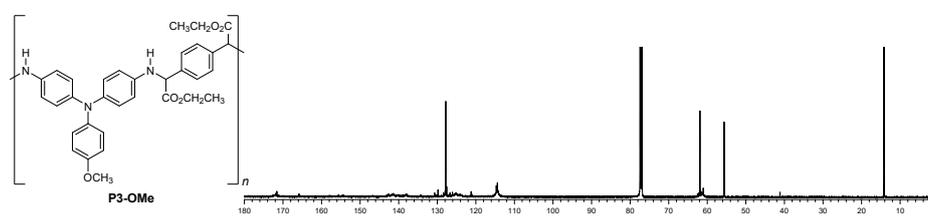


Figure S2. ^{13}C NMR spectra of **P3-OMe** ($M_n = 4000$, $D = 2.10$).

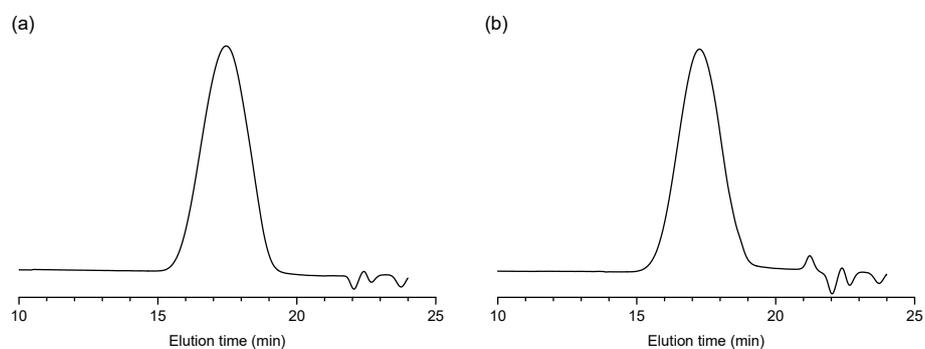


Figure S3. SEC charts of (a) **P3-OMe** ($M_n = 7700$, $D = 1.44$) and (b) **P3-CN** ($M_n = 8700$, $D = 1.40$).

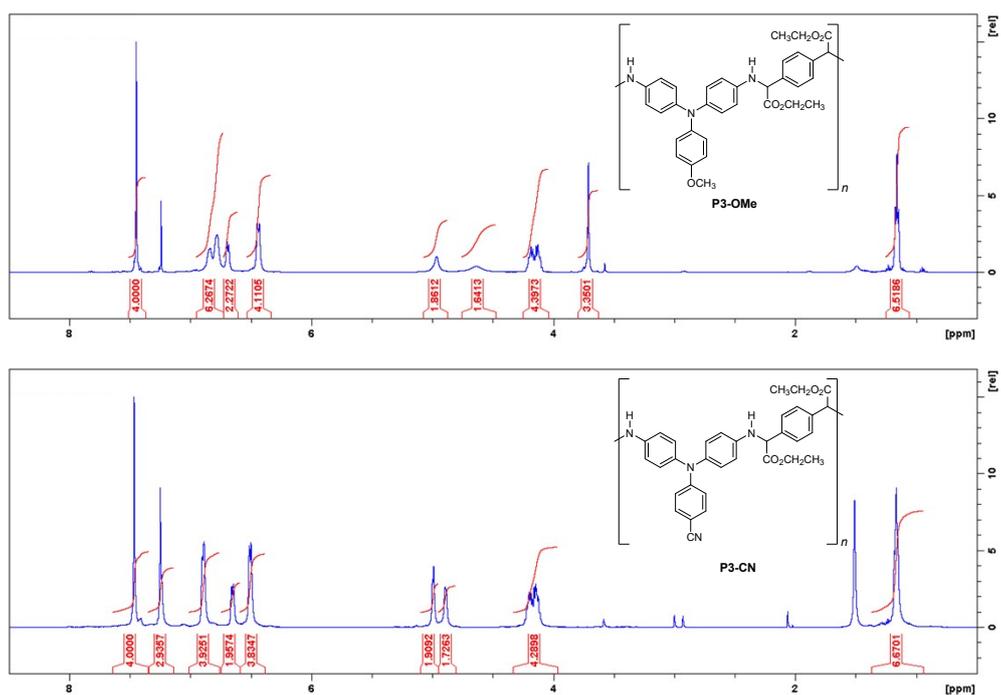


Figure S4. ¹H NMR spectra of **P3-OMe** (upper; $M_n = 14000$, $D = 1.42$) and **P3-CN** (lower; $M_n = 7700$, $D = 1.44$) with the intensities of signals.

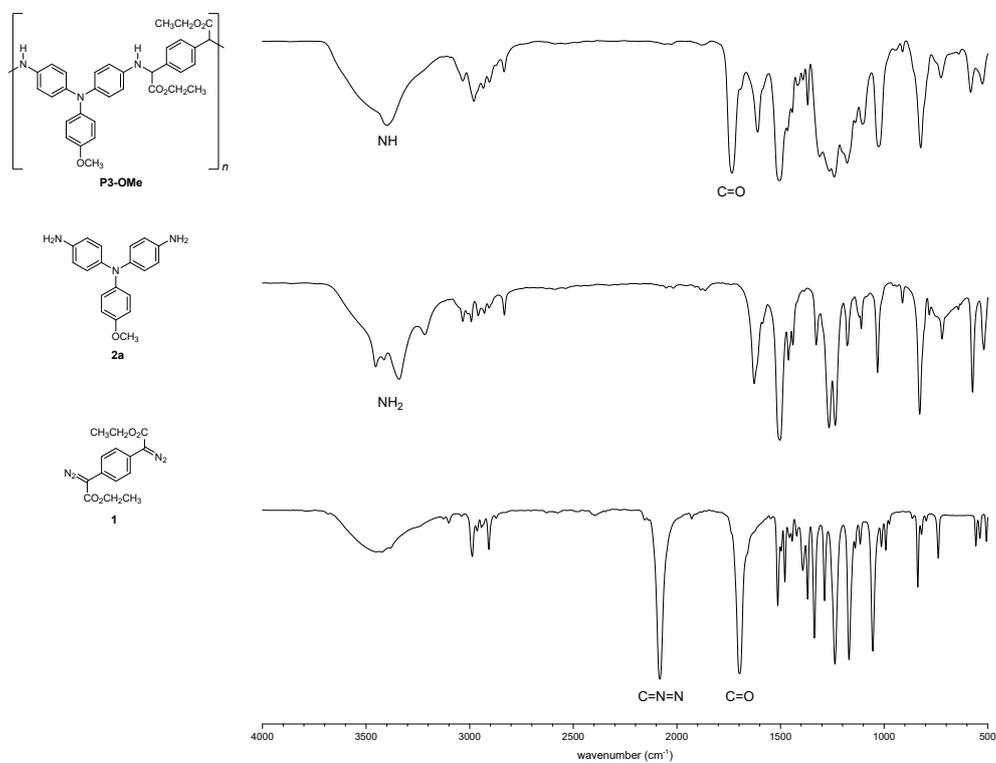


Figure S5. FT-IR spectra of **P3-OMe** ($M_n = 7700$, $D = 1.44$), **2a**, and **1**.

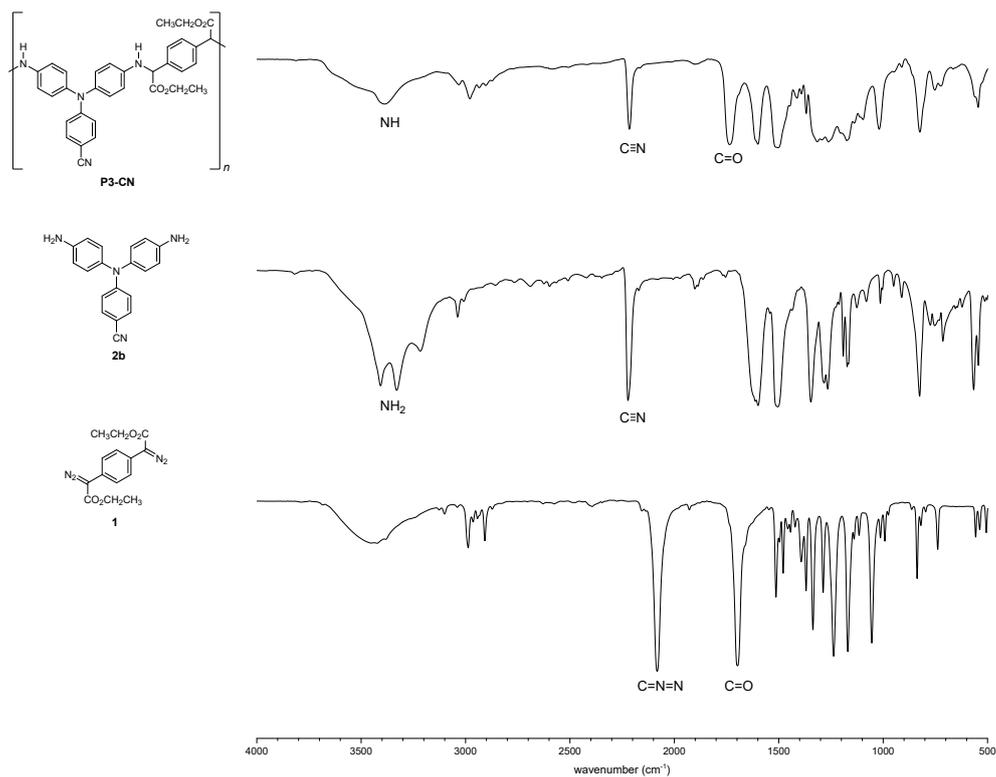


Figure S6. FT-IR spectra of **P3-CN** ($M_n = 14000$, $\bar{D} = 1.42$), **2b**, and **1**.

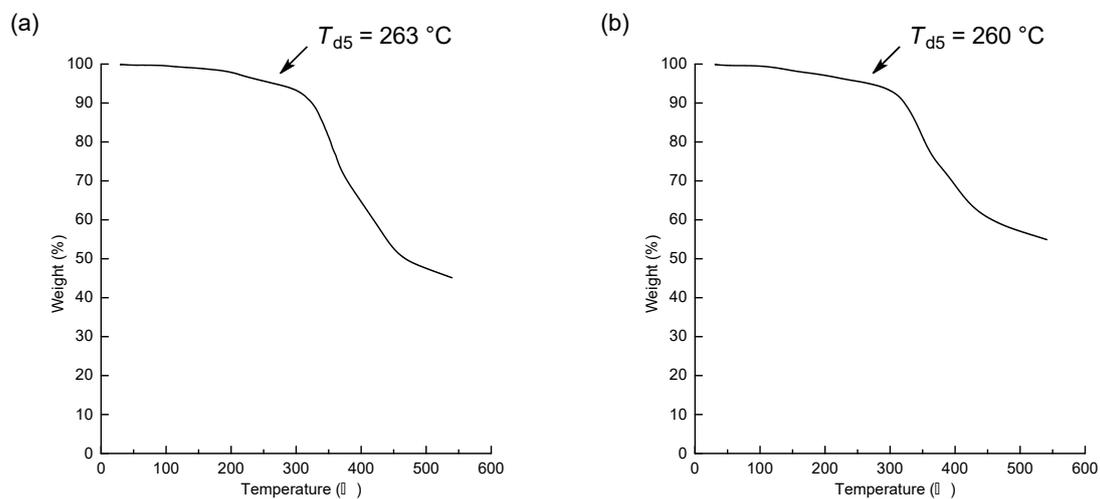


Figure S7. Thermogravimetric analysis results of (a) **P3-OMe** ($M_n = 7100$, $\bar{D} = 1.64$) and (b) **P3-CN** ($M_n = 9800$, $\bar{D} = 1.40$).

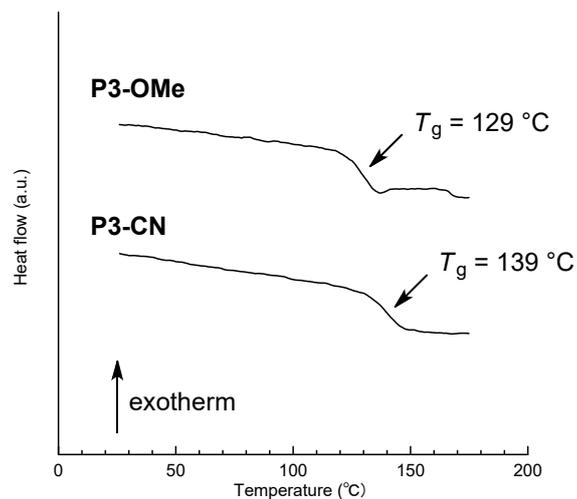


Figure S8. DSC thermograms of **P3-OMe** ($M_n = 7100$, $D = 1.64$) and **P3-CN** ($M_n = 9800$, $D = 1.40$).

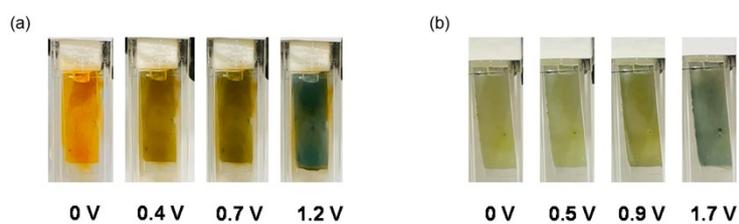


Figure S9. Photographs of (a) **P3-OMe** (thickness: $500 \pm 10\text{ nm}$) and (b) **P3-CN** (thickness: $500 \pm 40\text{ nm}$) in TBABF₄/PC at the neutral state and three oxidation states.

References

1. H. Shimomoto, H. Mukai, H. Bekku, T. Itoh and E. Ihara, *Macromolecules*, 2017, **50**, 9233–9238.
2. C.-W. Chang, G.-S. Liou and S.-H. Hsiao, *J. Mater. Chem.*, 2007. **17**, 1007–1015.
3. H.-J. Yen, C.-J. Chen and G.-S. Liou, *Chem. Comm.*, 2013. **49**, 630–632.