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Supporting Information

Chemically Controlled Volatile and Nonvolatile Resistive Memory Characteristics of Novel Oxygen-Based Polymers

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Materials and Synthesis

Poly(ethylene-*alt*-dibenzyl maleate) (PEM-Bz). PEM (200 mg, 1.59 mmol of anhydride moiety) was mixed with benzyl alcohol (0.821 ml, 7.93 mmol) in dry DMF (30 mL). EDC (912.1 mg, 4.76 mmol), DMAP (581.3 mg, 4.76 mmol), and triethylamine (TEA: 0.221 mL, 1.59 mmol) were then added to the mixture (Scheme 1). The mixture was stirred in room temperature for 72 h. The dry DMF was then removed from the reaction flask through evaporation and the remaining contents were dissolved with dichloromethane (CH₂Cl₂). The reaction mixture in CH₂Cl₂ was then precipitated into cold methanol (MeOH) to yield white powder. The cold precipitation step was repeated three times to yield the final product (466.4 mg). Yield: 90.7%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.22 (br, aromatic), 4.91 (br, -OCH₂-benzyl), 2.80–0.95 (m, -CH₂-CH₂-CH(COO-benzyl)-CH(COO-benzyl)-). $M_{n,SEC} = 168.0$ kDa (DMF); $D = 2.85$.

Poly(ethylene-*alt*-di(4-methylbenzyl) maleate) (PEM-BzMe). PEM-BzMe was synthesized from PEM (200 mg, 1.59 mmol of anhydride moiety) and 4-methylbenzyl alcohol (7.93 mmol) in the same manner as PEM-Bz was prepared above (Scheme 1). Yield: 67.4%. ¹H NMR (400

MHz, deuterated chloroform (CDCl₃): δ (ppm) 7.08–7.04 (br, aromatic), 4.86 (br, –OCH₂–(4-methylbenzyl)), 2.23 (br, CH₃–), 2.80–0.95 (m, –CH₂–CH₂–CH(COO–(4-methylbenzyl))–CH(COO–(4-methylbenzyl))–). $M_{n,SEC} = 307.0$ kDa (DMF); $D = 3.23$.

Poly(ethylene-*alt*-di(3-methoxybenzyl) maleate) (PEM-BzOMe). In the same manner, PEM-BzOMe was synthesized from PEM (200 mg, 1.59 mmol of anhydride moiety) and 4-methoxybenzyl alcohol (7.93 mmol) (Scheme 1). Yield: 80.2%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.15, 6.77 (br, aromatic), 4.88 (br, –OCH₂–(3-methoxybenzyl)), 3.68 (br, CH₃–O–), 2.80–0.95 (m, –CH₂–CH₂–CH(COO–(3-methoxybenzyl))–CH(COO–(3-methoxybenzyl))–). $M_{n,SEC} = 233.0$ kDa (DMF); $D = 4.80$.

Poly(ethylene-*alt*-di(3,5-dimethoxybenzyl) maleate) (PEM-BzOMe₂). In the same manner, PEM-BzOMe₂ was synthesized from PEM (200 mg, 1.59 mmol of anhydride moiety) and 3,5-dimethoxybenzyl alcohol (7.93 mmol) (Scheme 1). Yield: 74.5%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.35, 6.28 (br, aromatic), 4.83 (br, –OCH₂–(3,5-dimethoxybenzyl)), 3.65 (br, CH₃–O–), 2.80–0.95 (m, –CH₂–CH₂–CH(COO–(3,5-dimethoxybenzyl))–CH(COO–(3,5-dimethoxybenzyl))–). $M_{n,SEC} = 312.5$ kDa (DMF); $D = 4.34$.

Poly(ethylene-*alt*-dipiperonyl maleate) (PEM-BzO₂C). In the same manner, PEM-BzO₂C was synthesized from PEM (200 mg, 1.59 mmol of anhydride moiety) and piperonyl alcohol (7.93 mmol) (Scheme 1). Yield: 85.3%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.69 (br, aromatic), 5.85 (br, methylenedioxy), 4.84 (br, –OCH₂–piperonyl), 2.80–0.95 (m, –CH₂–CH₂–CH(COO–piperonyl)–CH(COO–piperonyl)–). $M_{n,SEC} = 334.0$ kDa (DMF); $D = 3.77$.

Poly[ethylene-*alt*-di(3,4,5-trimethoxybenzyl) maleate] (PEM-BzOMe₃). In the same manner, PEM-BzOMe₃ was synthesized from PEM (200 mg, 1.59 mmol of anhydride moiety) and 3,4,5-trimethoxybenzyl alcohol (7.93 mmol) (Scheme 1). Yield: 73.0%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.45 (br, aromatic), 4.81 (br, –OCH₂–(3,4,5-trimethoxybenzyl)), 3.75 (br, CH₃–O–), 2.80–0.95 (m, –CH₂–CH₂–CH(COO–(3,4,5-trimethoxybenzyl))–CH(COO–(3,4,5-trimethoxybenzyl))–). $M_{n,SEC} = 312.0$ kDa (DMF); $D = 4.29$.

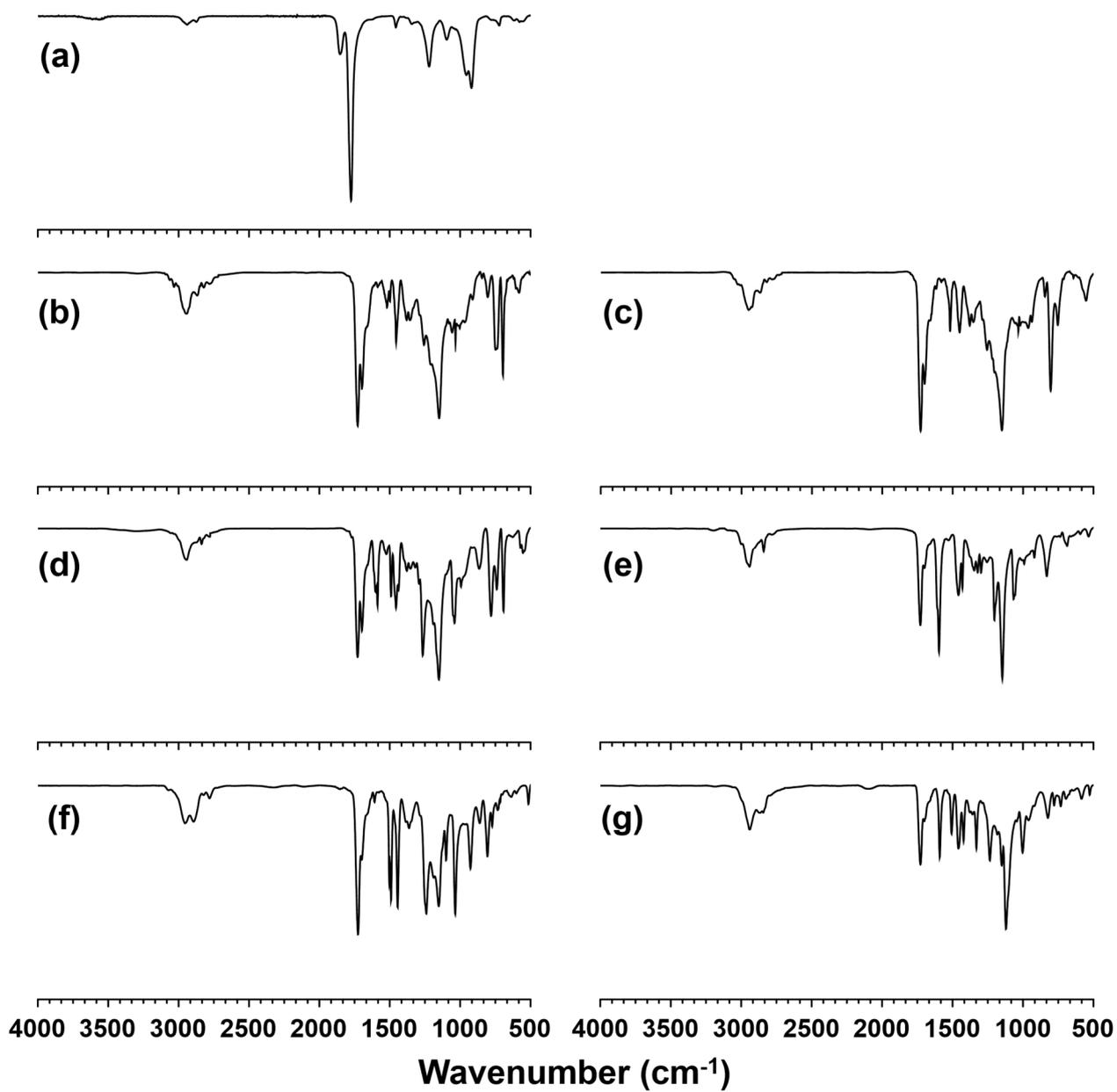


Figure S1. FTIR spectra: (a) PEM; (b) PEM-Bz; (c) PEM-BzMe; (d) PEM-BzOMe; (e) PEM-BzOMe₂; (f) PEM-BzO₂C; (g) PEM-BzOMe₃.

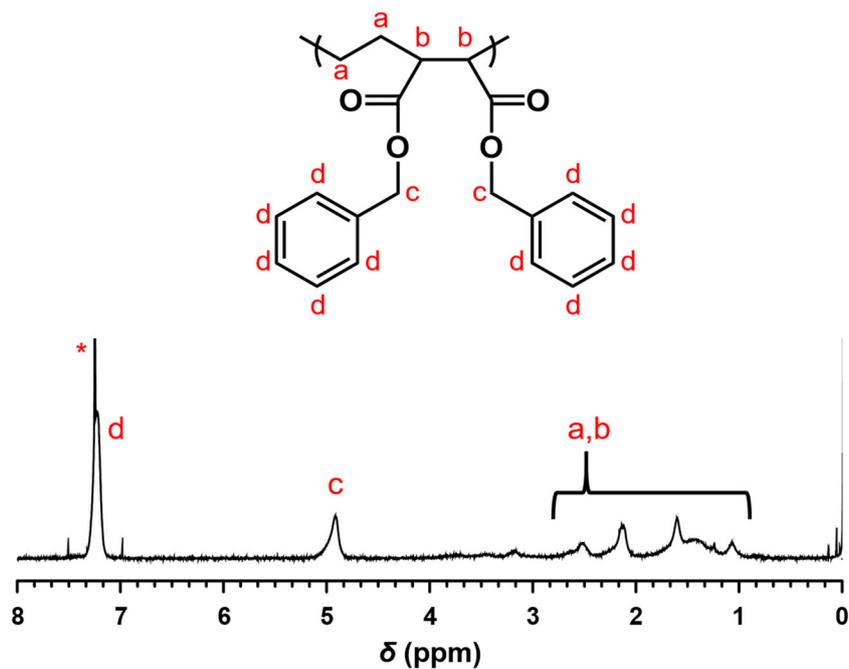


Figure S2. ^1H NMR spectrum of PEM-Bz in CDCl_3 (400 MHz). The chemical shift of the solvent used is marked with asterisk.

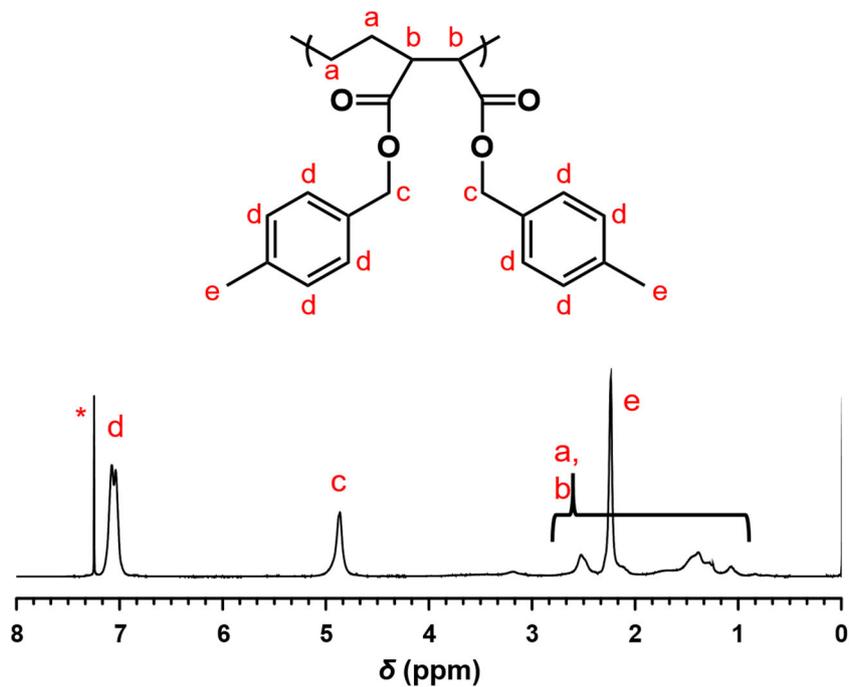


Figure S3. ^1H NMR spectrum of PEM-BzMe in CDCl_3 (400 MHz). The chemical shift of the solvent used is marked with asterisk.

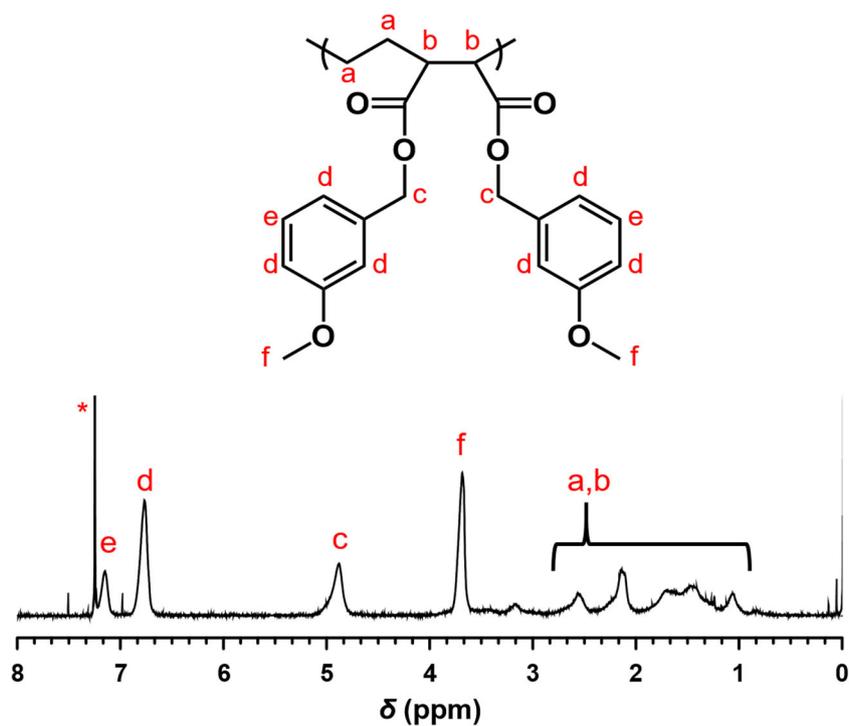


Figure S4. ¹H NMR spectrum of PEM-BzOMe in CDCl₃ (400 MHz). The chemical shift of the solvent used is marked with asterisk.

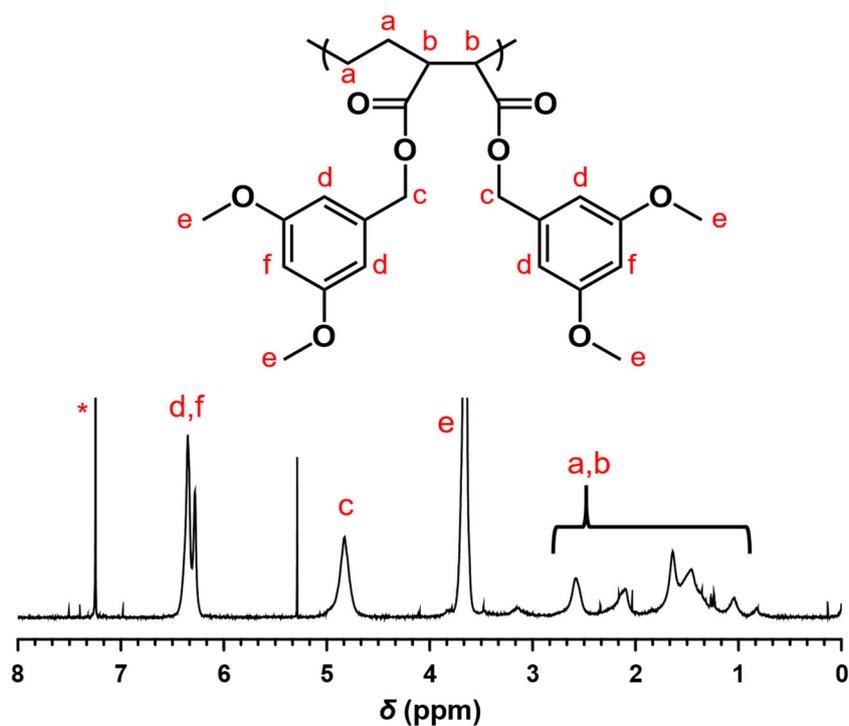


Figure S5. ¹H NMR spectrum of PEM-BzOMe₂ in CDCl₃ (400 MHz). The chemical shift of the solvent used is marked with asterisk.

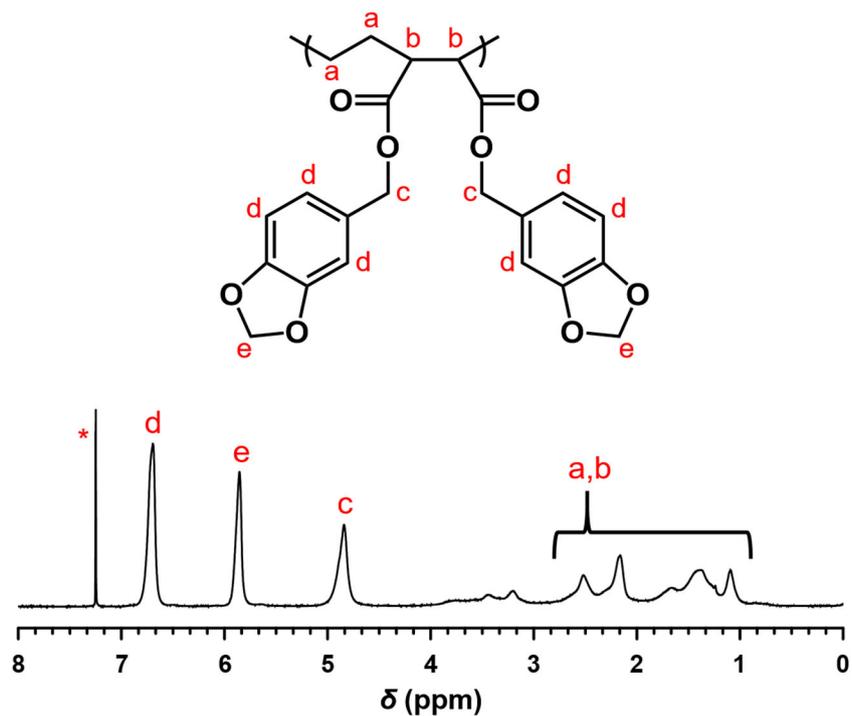


Figure S6. ^1H NMR spectrum of PEM-BzO₂C in CDCl₃ (400 MHz). The chemical shift of the solvent used is marked with asterisk.

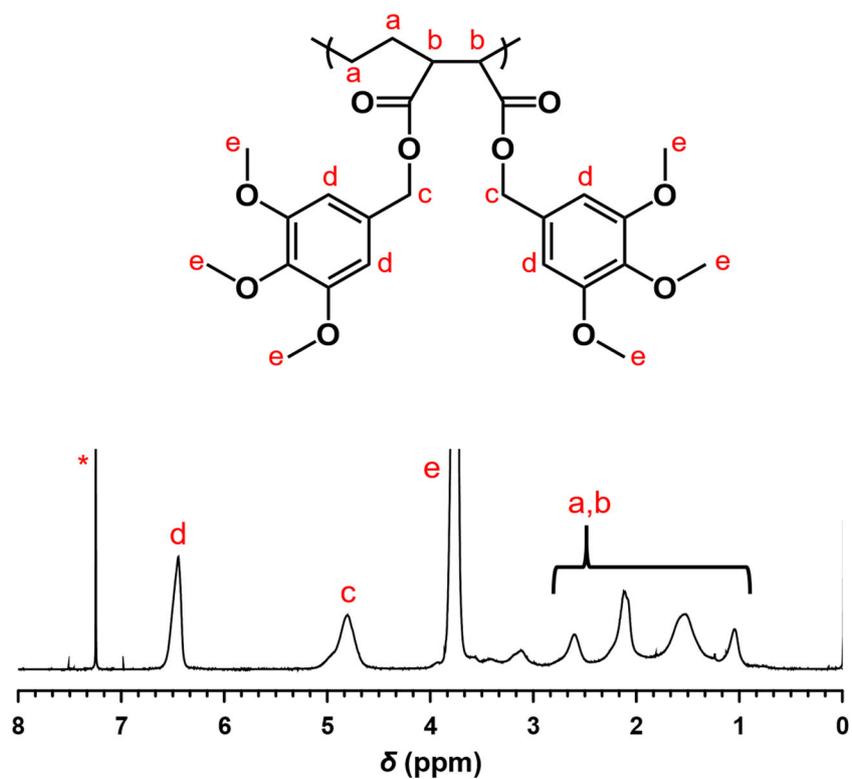


Figure S7. ^1H NMR spectrum of PEM-BzOMe₃ in CDCl₃ (400 MHz). The chemical shift of the solvent used is marked with asterisk.

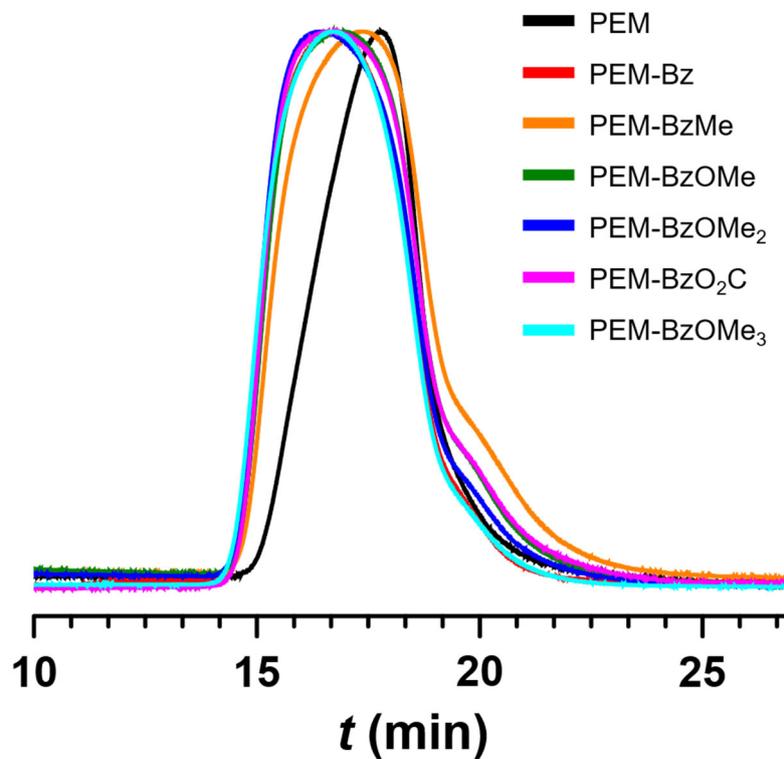


Figure S8. SEC traces of polymers: (black line), PEM; (red line), PEM-Bz; (orange line), PEM-BzMe; (green line), PEM-BzOMe; (blue line), PEM-BzOMe₂; (pink line), PEM-BzO₂C; (sky blue line), PEM-BzOMe₃. Dry DMF was used as the eluent. The SEC system was calibrated by using PMMA standards.

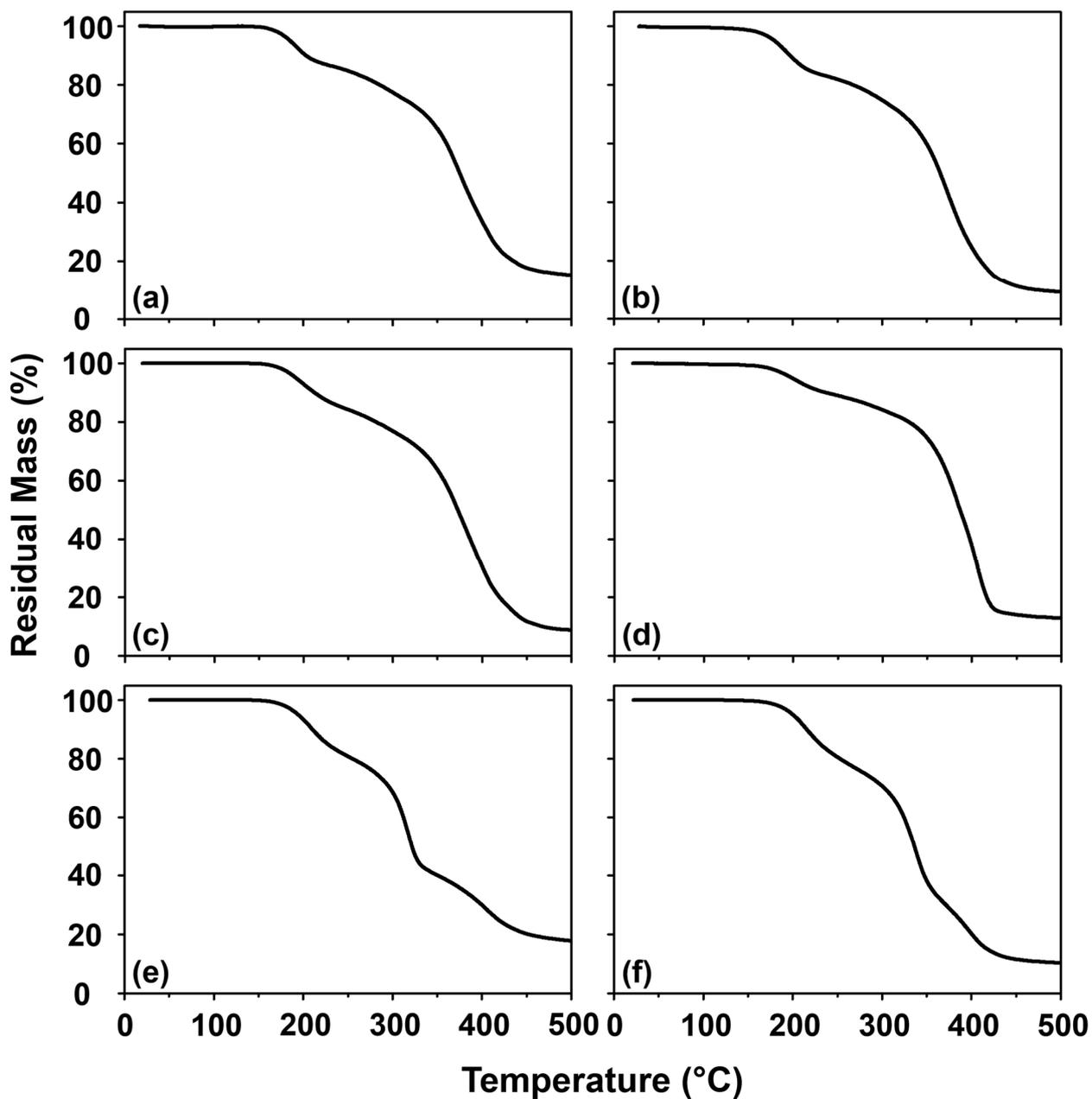


Figure S9. TGA thermograms measured with a rate of 10.0 °C/min in a nitrogen atmosphere: (a) PEM-Bz; (b) PEM-BzMe; (c) PEM-BzOMe; (d) PEM-BzOMe₂; (e) PEM-BzO₂C; (f) PEM-BzOMe₃.

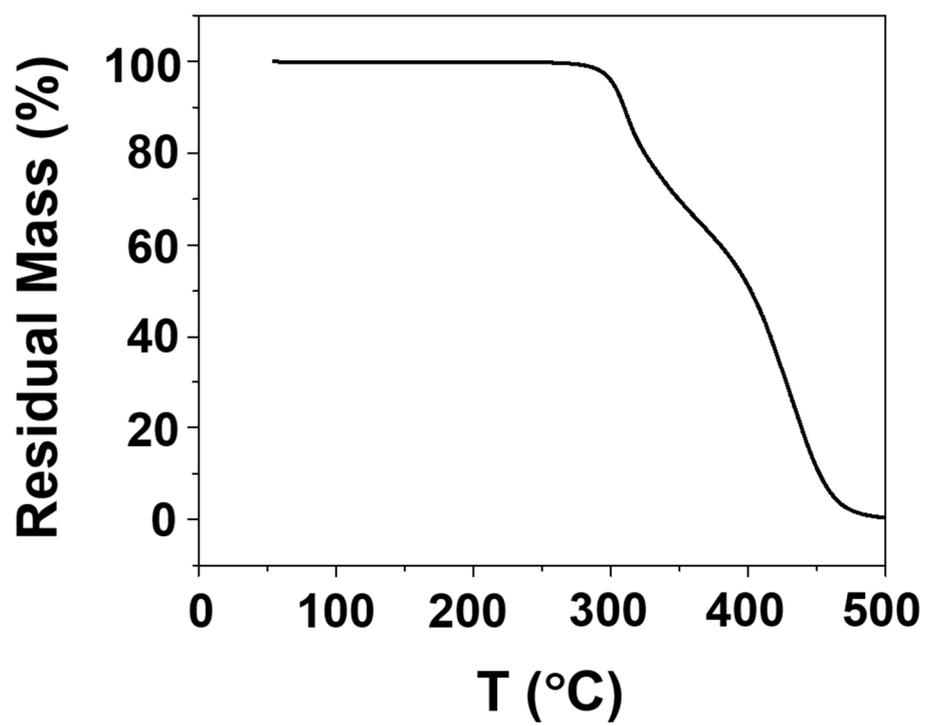


Figure S10. TGA thermogram of PEM measured with a rate of 10.0 °C/min in a nitrogen atmosphere.

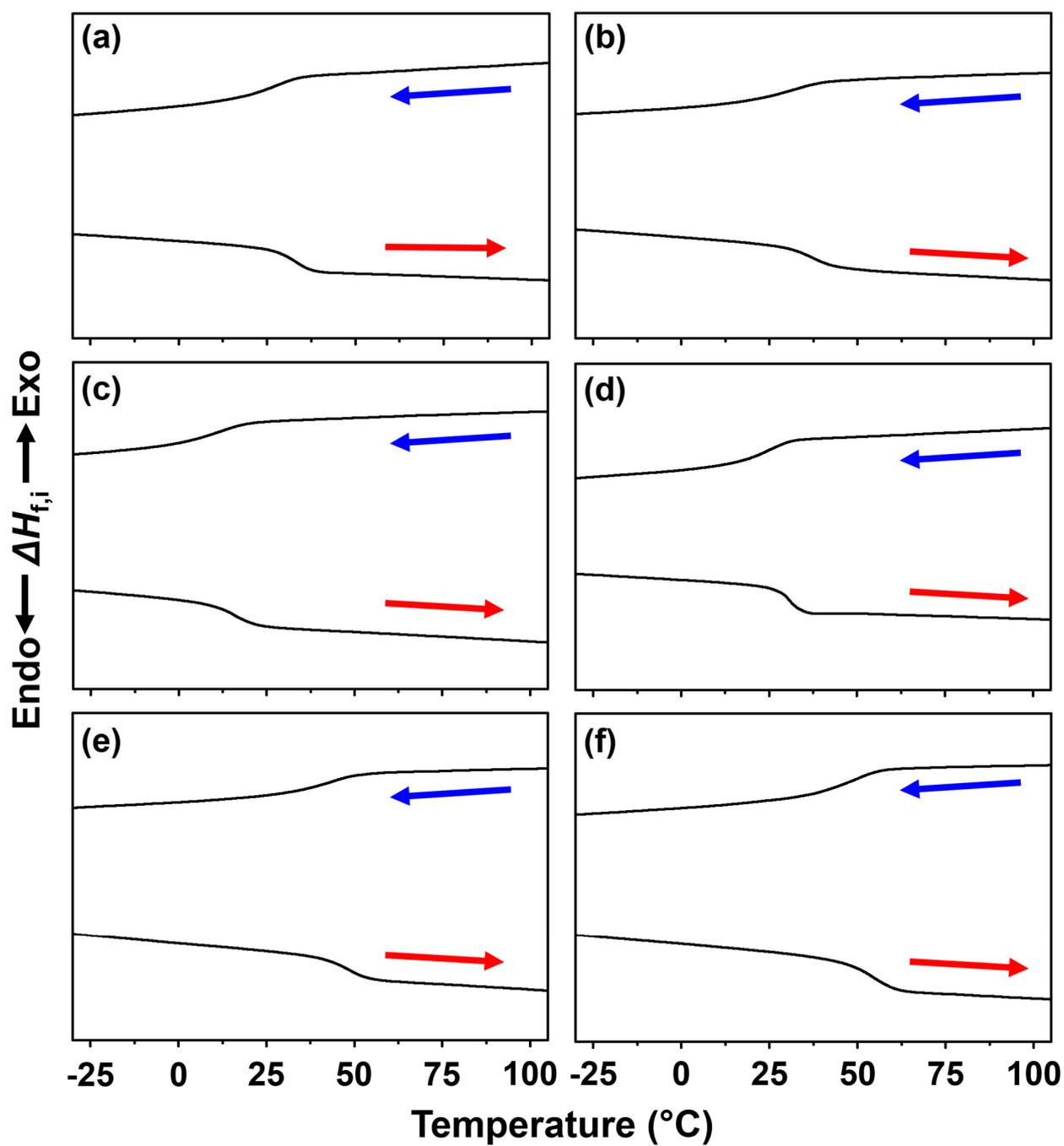


Figure S11. DSC thermograms measured with a rate of 10.0 °C/min in a nitrogen atmosphere: (a) PEM-Bz; (b) PEM-BzMe; (c) PEM-BzOMe; (d) PEM-BzOMe₂; (e) PEM-BzO₂C; (f) PEM-BzOMe₃.

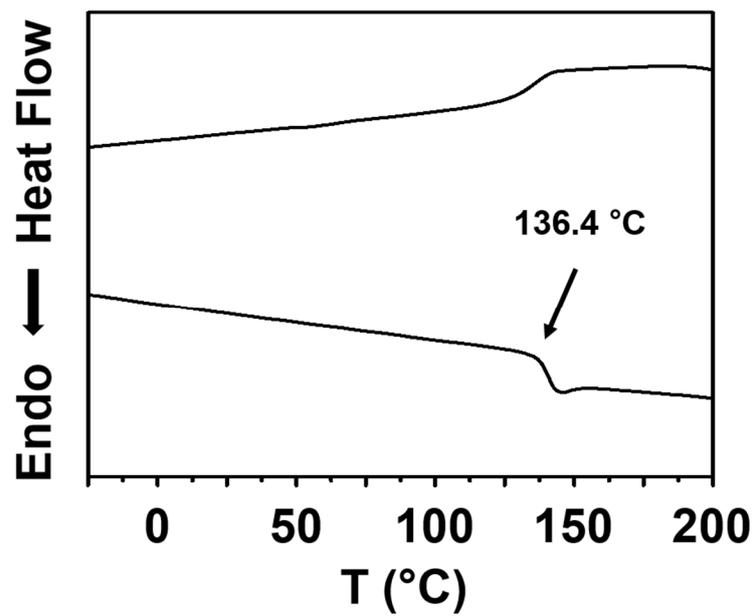


Figure S12. DSC thermogram of PEM measured with a rate of 10.0 °C/min in a nitrogen atmosphere.

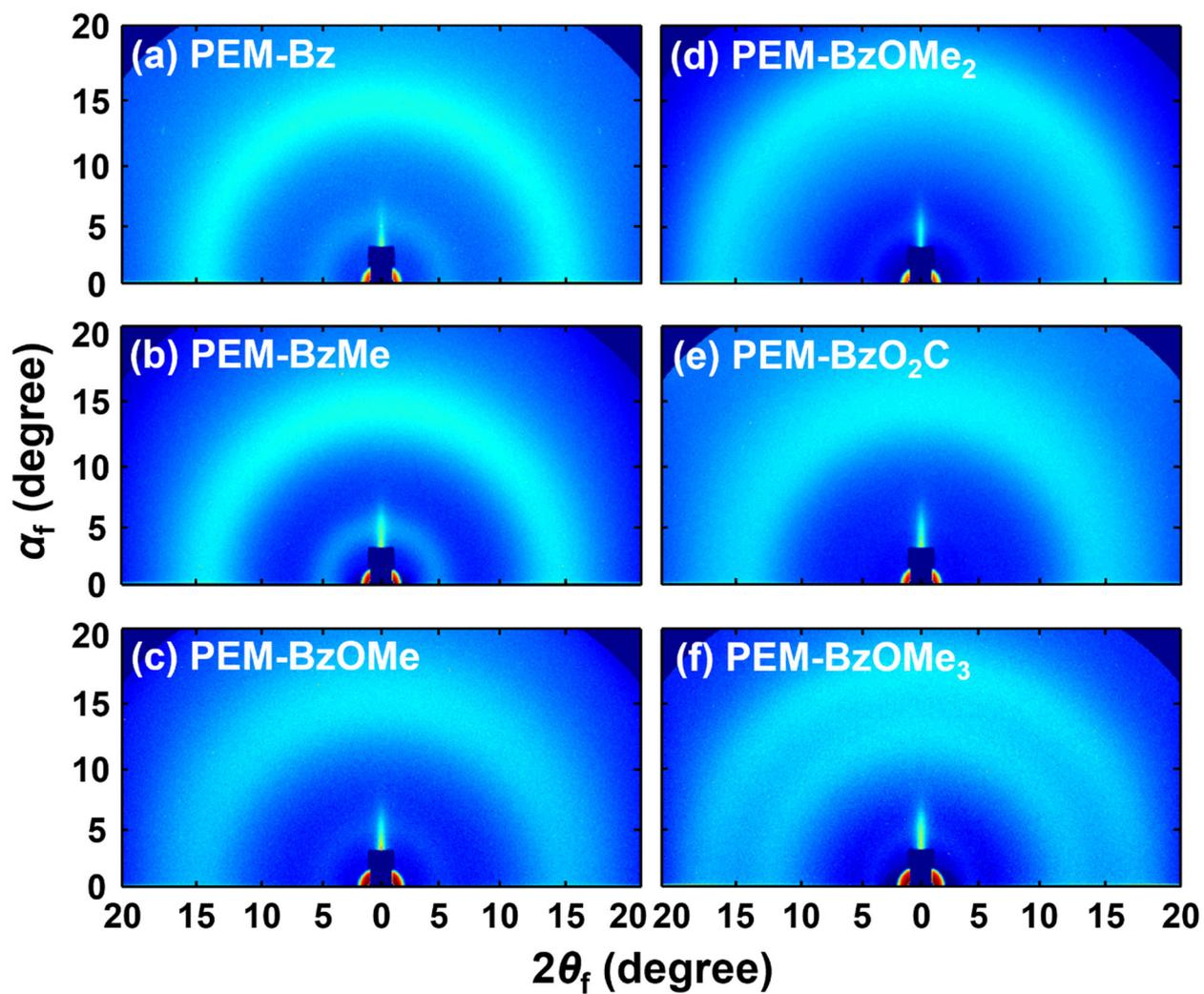


Figure S13. Representative synchrotron 2D GIXS patterns of nanoscale films (35–61 nm thick) of the polymers measured with an X-ray source of $\lambda = 0.1230$ nm at a sample-to-detector distance (SDD) of 210 mm: (a) PEM-Bz ($\alpha_i = 0.173^\circ$); (b) PEM-BzMe ($\alpha_i = 0.183^\circ$); (c) PEM-BzOMe ($\alpha_i = 0.183^\circ$); (d) PEM-BzOMe₂ ($\alpha_i = 0.183^\circ$); (e) PEM-BzO₂C ($\alpha_i = 0.183^\circ$); (f) PEM-BzOMe₃ ($\alpha_i = 0.183^\circ$).

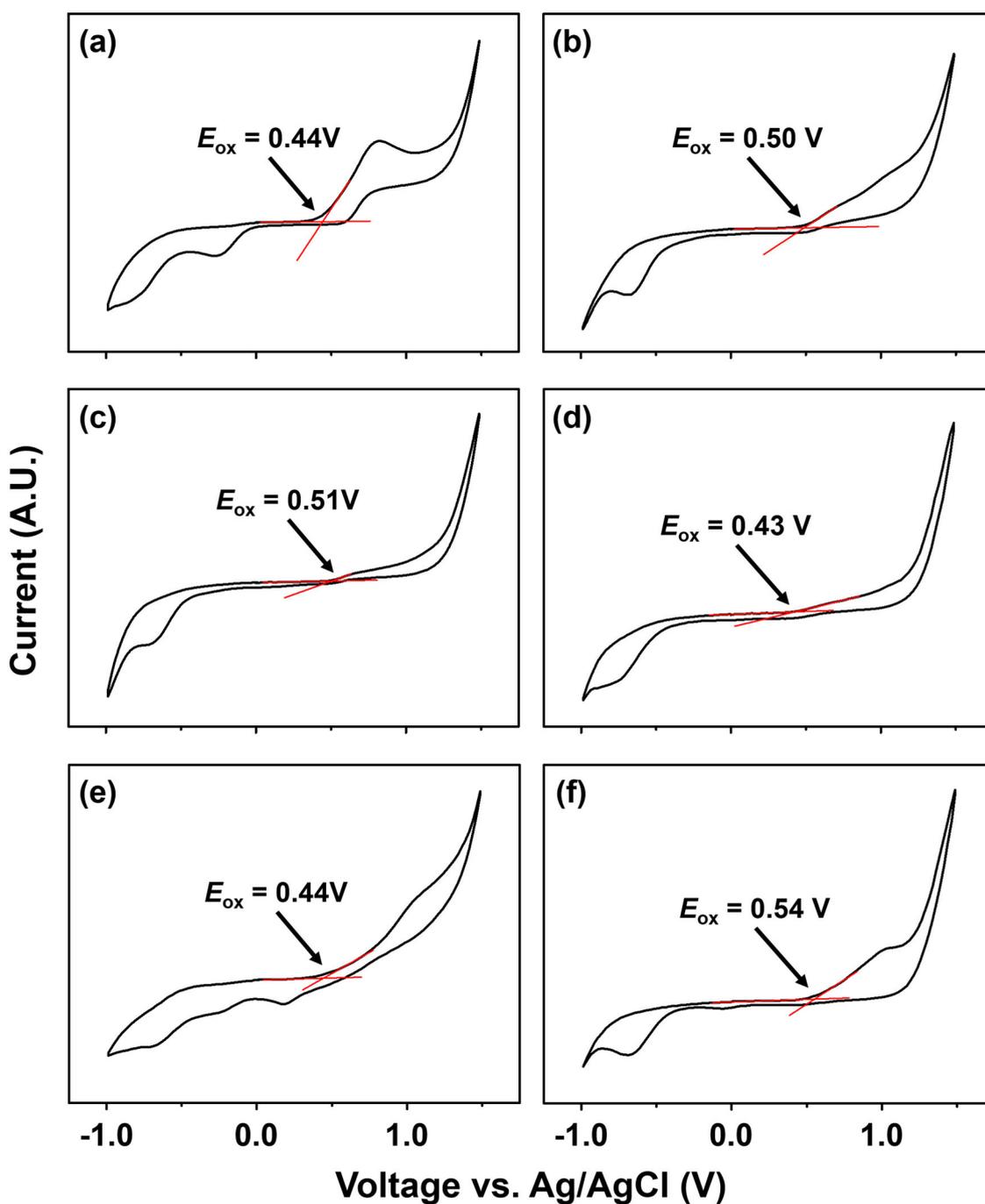


Figure S14. CV responses of polymers: (a) PEM-Bz; (b) PEM-BzMe; (c) PEM-BzOMe; (d) PEM-BzOMe₂; (e) PEM-BzO₂C; (f) PEM-BzOMe₃. CV measurements were carried out at 20 °C in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile using a platinum gauze counter electrode and an Ag/AgCl (saturated KCl) reference electrode; the polymers were coated on the gold (Au) electrode deposited on silicon wafer. A scan rate of 100 mV/s was used.

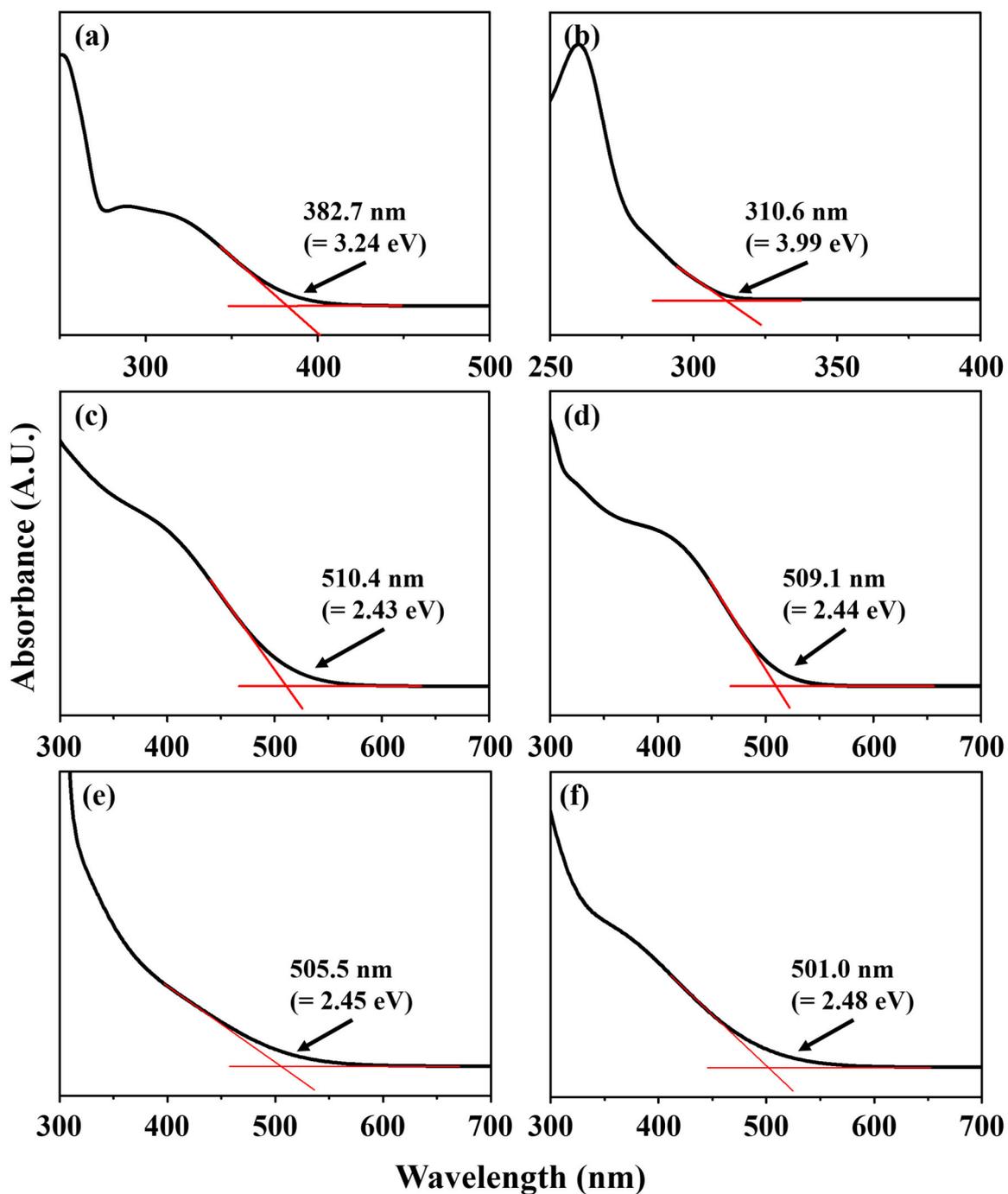


Figure S15. UV-vis spectra of polymers in films: (a) PEM-Bz; (b) PEM-BzMe; (c) PEM-BzOMe; (d) PEM-BzOMe₂; (e) PEM-BzO₂C; (f) PEM-BzOMe₃. UV-vis spectra were measured in thin films coated on quartz substrates.

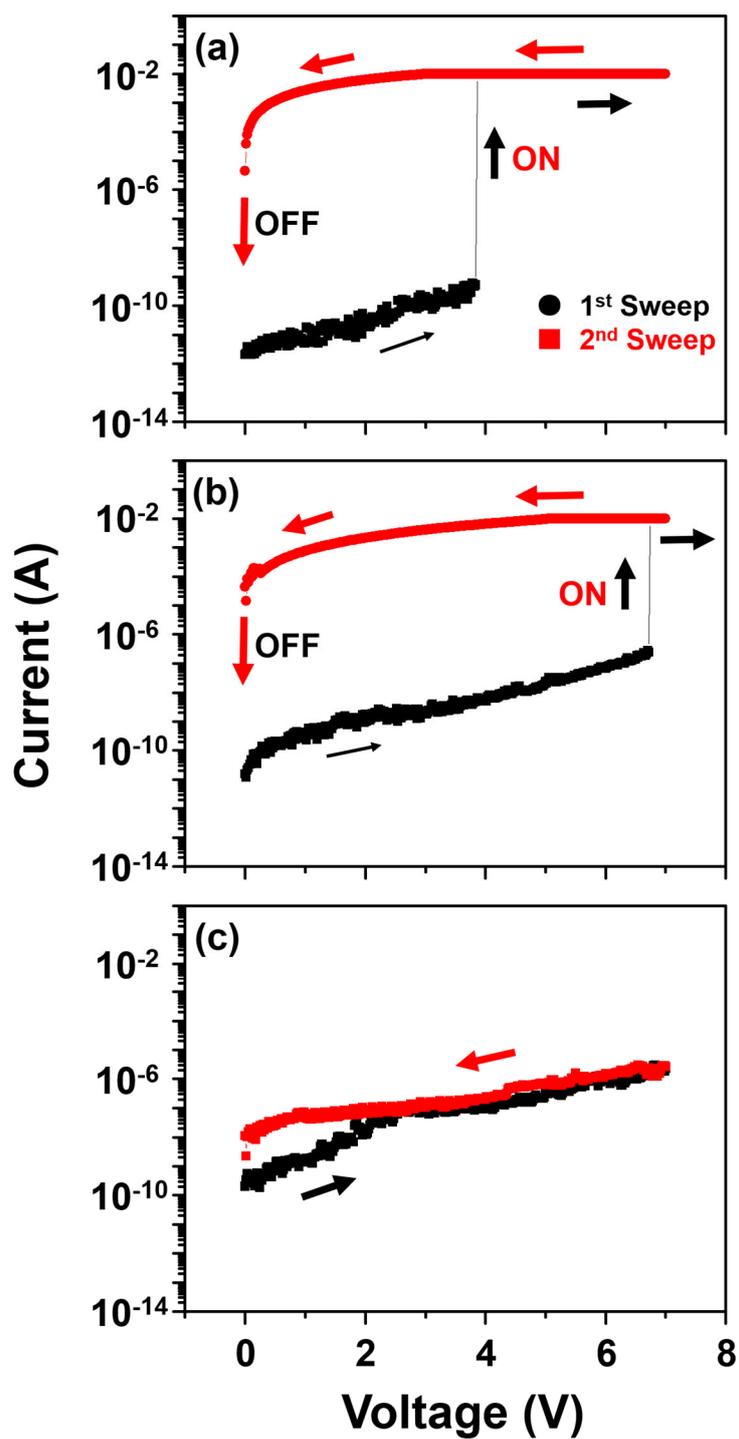


Figure S16. I - V curves of d-Si/PEM-BzOMe/Al devices, which were measured with a compliance current set of 0.01 A in air ambient condition; PEM-BzOMe layer: (a) 18.7 nm thick; (b) 31.1 nm thick; (c) 50.2 nm thick. The electrode contact area was $500 \times 500 \mu\text{m}^2$.

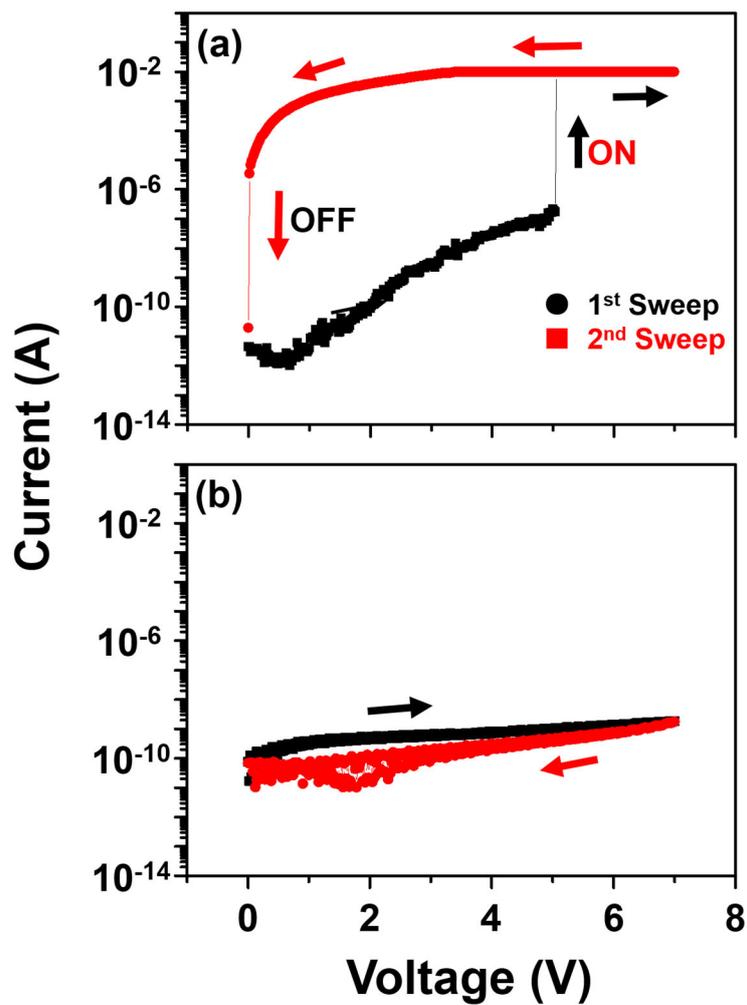


Figure S17. I - V curves of d-Si/PEM-BzOMe₂/Al devices, which were measured with a compliance current set of 0.01 A in air ambient condition; PEM-BzOMe₂ layer: (a) 23.3 nm thick; (b) 31.2 nm thick. The electrode contact area was $500 \times 500 \mu\text{m}^2$.

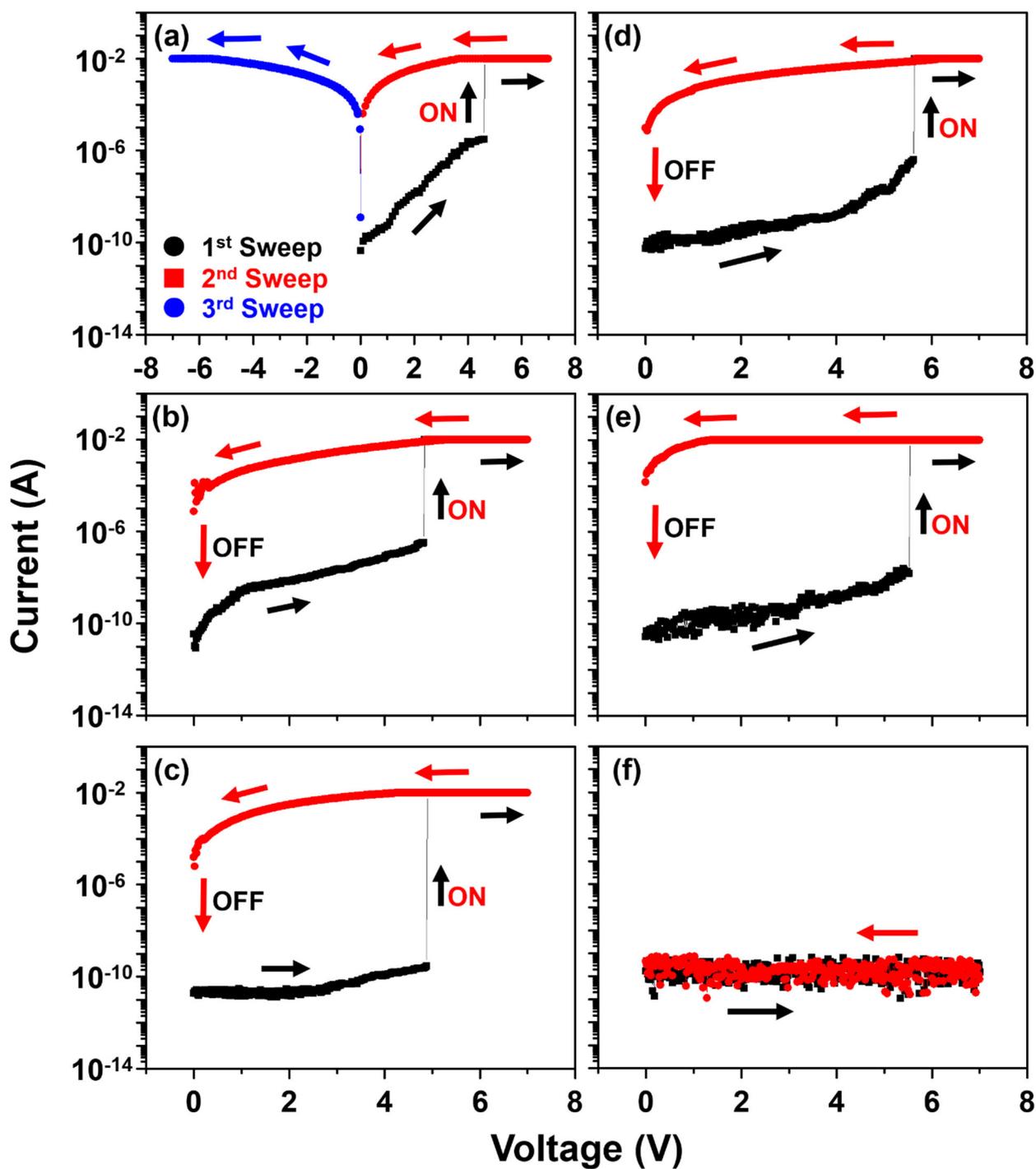


Figure S18. I - V curves of d-Si/PEM-BzO₂C/Al devices, which were measured with a compliance current set of 0.01 A in air ambient condition; PEM-BzO₂C layer: (a) 17.7 nm thick; (b) 38.0 nm thick; (c) 45.5 nm thick; (d) 84.6 nm thick; (e) 111.8 nm thick; (f) 136.2 nm thick. The electrode contact area was $500 \times 500 \mu\text{m}^2$.

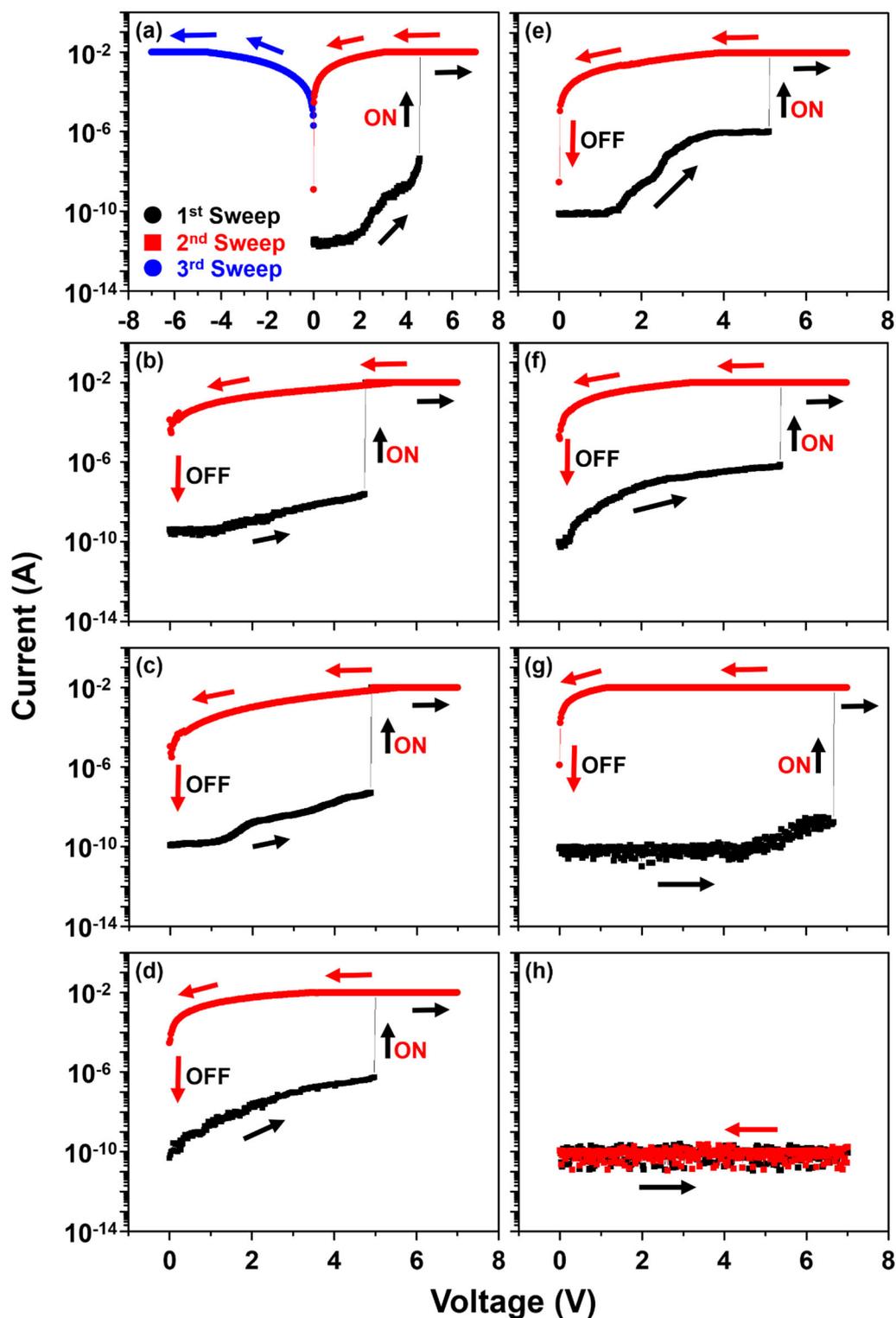


Figure S19. Representative I - V curves of d-Si/PEM-BzOME₃/Al devices, which were measured with a compliance current set of 0.01 A in air ambient condition; PEM-BzOME₃ layer: (a) 20.1 nm thick; (b) 32.2 nm thick; (c) 53.8 nm thick; (d) 82.4 nm thick; (e) 115.6 nm thick; (f) 142.7 nm thick; (h) 209.5 nm thick. The electrode contact area was $500 \times 500 \mu\text{m}^2$.

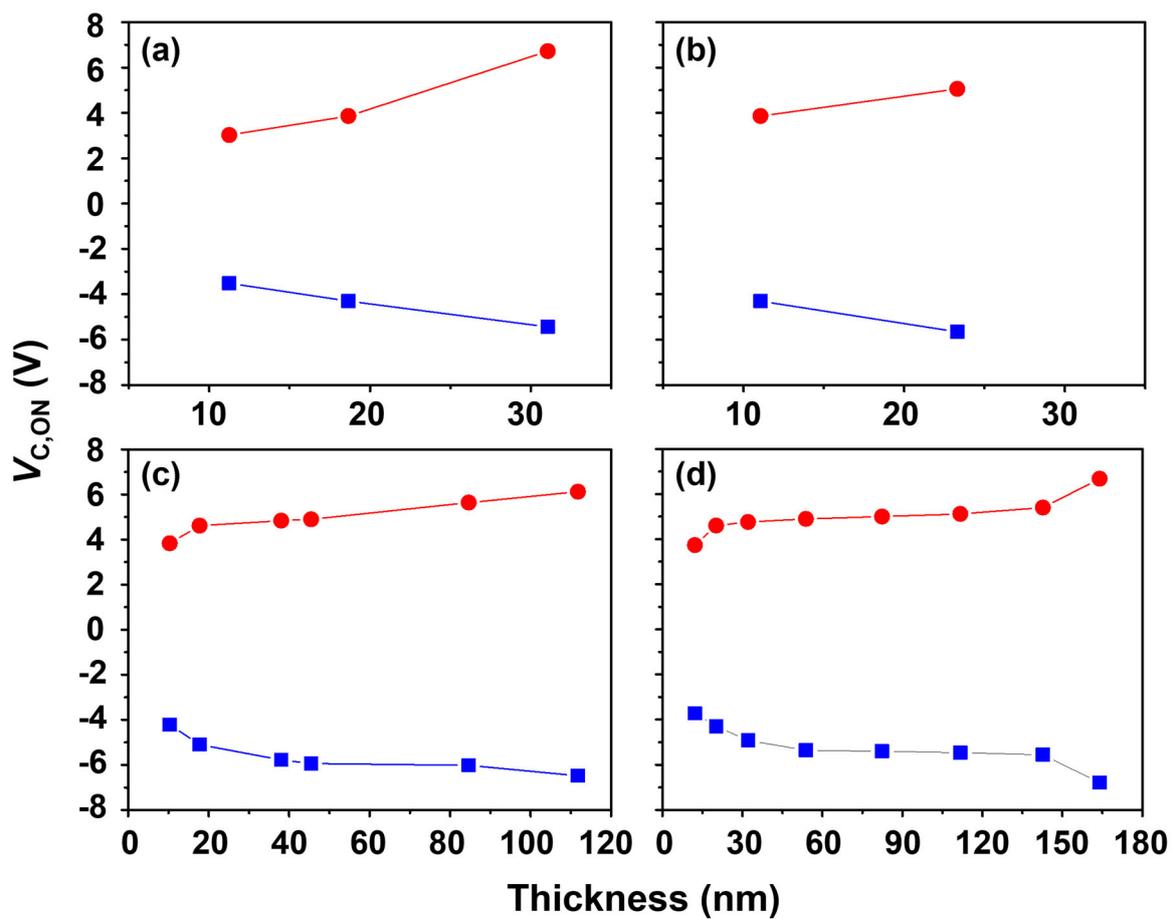


Figure S20. $V_{c,ON}$ variations in the memory devices fabricated with polymer films in various thicknesses: (a) PEM-BzOMe; (b) PEM-BzOMe₂; (c) PEM-BzO₂C; (d) PEM-BzOMe₃. The red dots represent the $V_{c,ON}$ values from positive sweeps and the blue squares represent the $V_{c,ON}$ values from negative sweeps during I - V curve analysis.

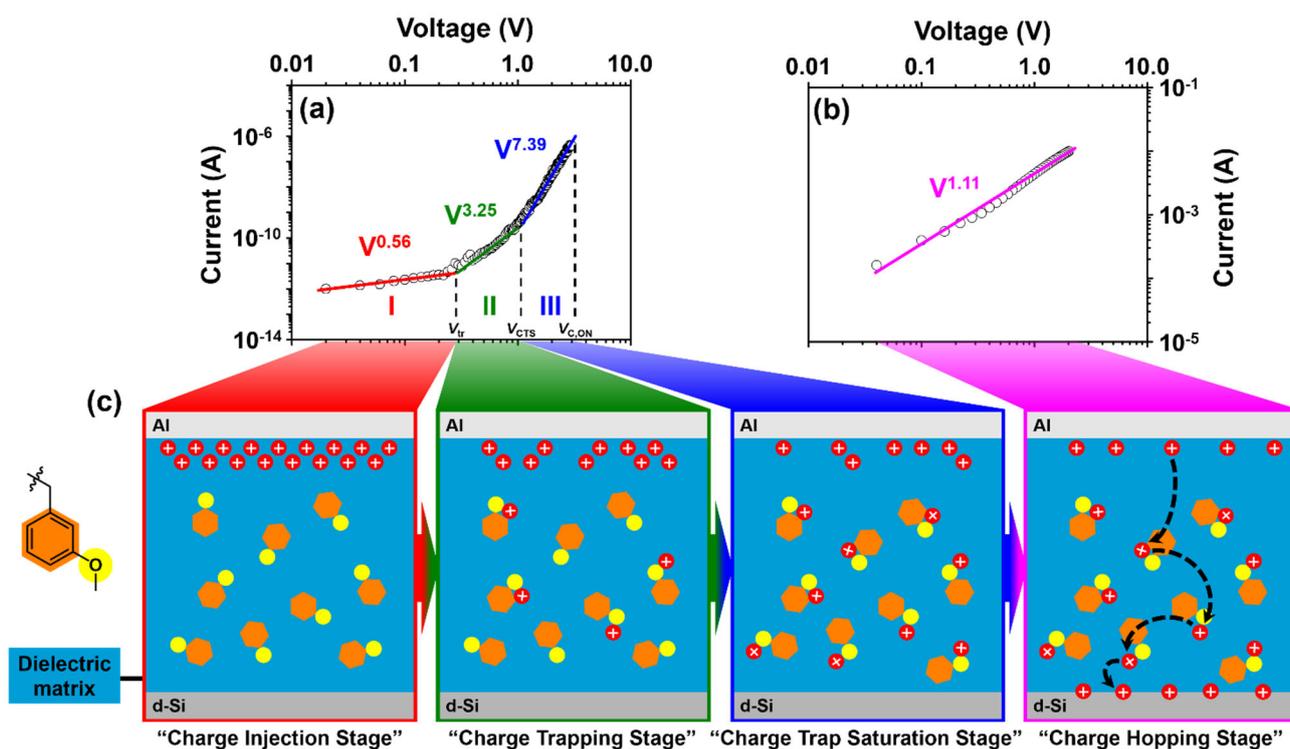


Figure S21. I - V data analysis of the d-Si/PEM-BzOMe(11.3 nm thick)/Al devices which were measured with a compliance current of 0.01 A in air ambient condition: (a) OFF-state where the symbols are the measured data and the solid lines represent the fit results using Schottky emission conduction and trap-limited SCLC models; (b) ON-state where the symbols are the measured data and the solid line represents the fit results using hopping conduction model; (c) schematic diagrams of charge injection, trap, trap-saturation, and hopping process (i.e., transportation) between two electrodes via using oxygen-based moieties (4-methoxybenzyl: BzOMe) as electroactive sites. V_{tr} is the voltage starting to transfer charges from the charge injection stage to the charge trapping stage; V_{CTS} denotes the on-set voltage reaching to the charge trap saturation stage from the charge trapping stage; $V_{c,ON}$ denotes the switching-ON voltage.

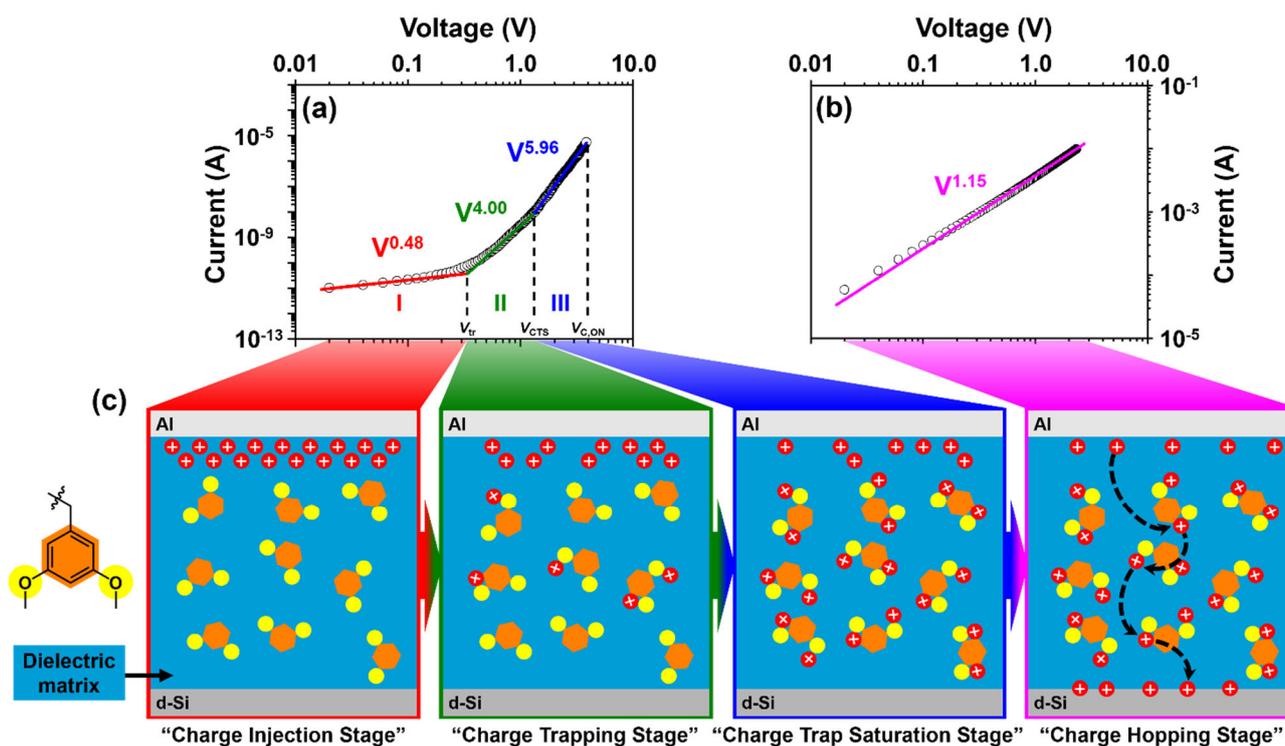


Figure S22. I - V data analysis of the d-Si/PEM-BzOMe₂(11.1 nm thick)/Al devices which were measured with a compliance current of 0.01 A in air ambient condition: (a) OFF-state where the symbols are the measured data and the solid lines represent the fit results using Schottky emission conduction and trap-limited SCLC models; (b) ON-state where the symbols are the measured data and the solid line represents the fit results using hopping conduction model; (c) schematic diagrams of charge injection, trap, trap-saturation, and hopping process (i.e., transportation) between two electrodes via using oxygen-based moieties (3,5-dimethoxybenzyl: BzOMe₂) as electroactive sites. V_{tr} is the voltage starting to transfer charges from the charge injection stage to the charge trapping stage; V_{CTS} denotes the on-set voltage reaching to the charge trap saturation stage from the charge trapping stage; $V_{c,ON}$ denotes the switching-ON voltage.

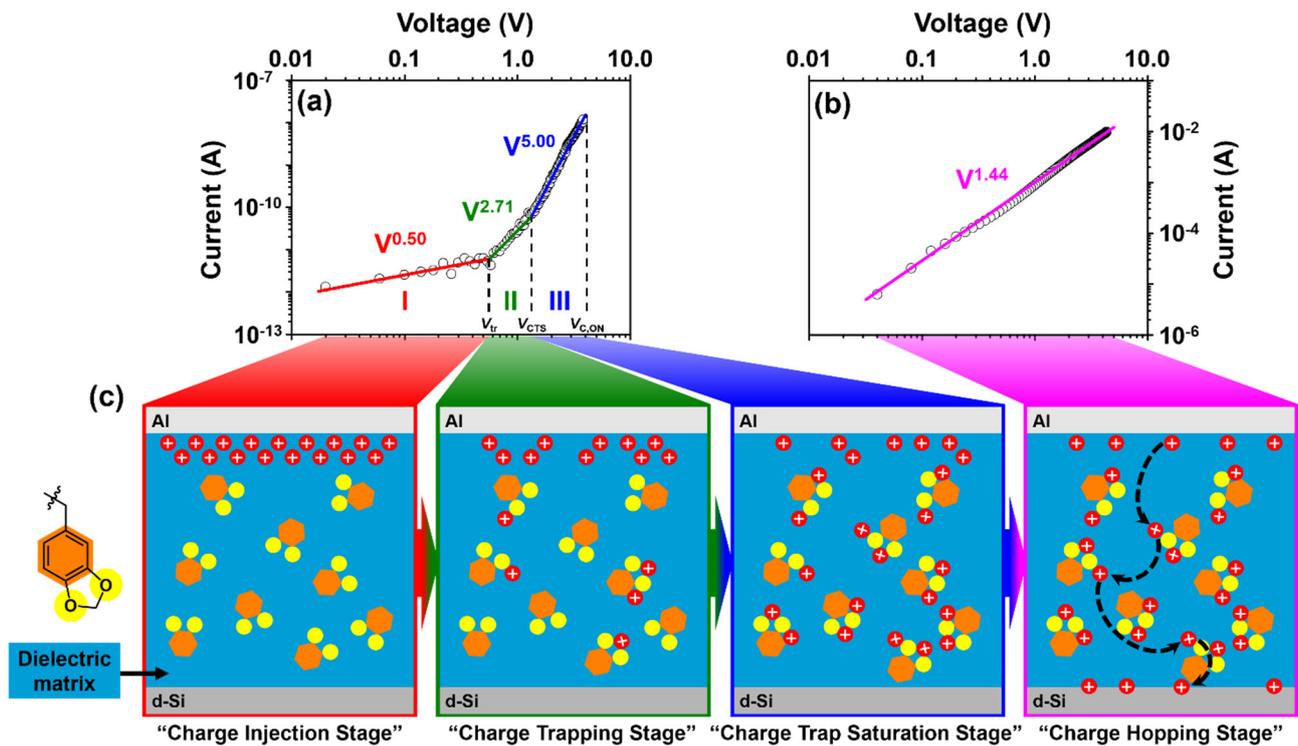


Figure S23. I - V data analysis of the d-Si/PEM-BzO₂C(10.3 nm thick)/Al devices which were measured with a compliance current of 0.01 A in air ambient condition: (a) OFF-state where the symbols are the measured data and the solid lines represent the fit results using Schottky emission conduction and trap-limited SCLC models; (b) ON-state where the symbols are the measured data and the solid line represents the fit results using hopping conduction model; (c) schematic diagrams of charge injection, trap, trap-saturation, and hopping process (i.e., transportation) between two electrodes via using oxygen-based moieties (piperonyl: BzO₂C) as electroactive sites. V_{tr} is the voltage starting to transfer charges from the charge injection stage to the charge trapping stage; V_{CTS} denotes the on-set voltage reaching to the charge trap saturation stage from the charge trapping stage; $V_{c,ON}$ denotes the switching-ON voltage.

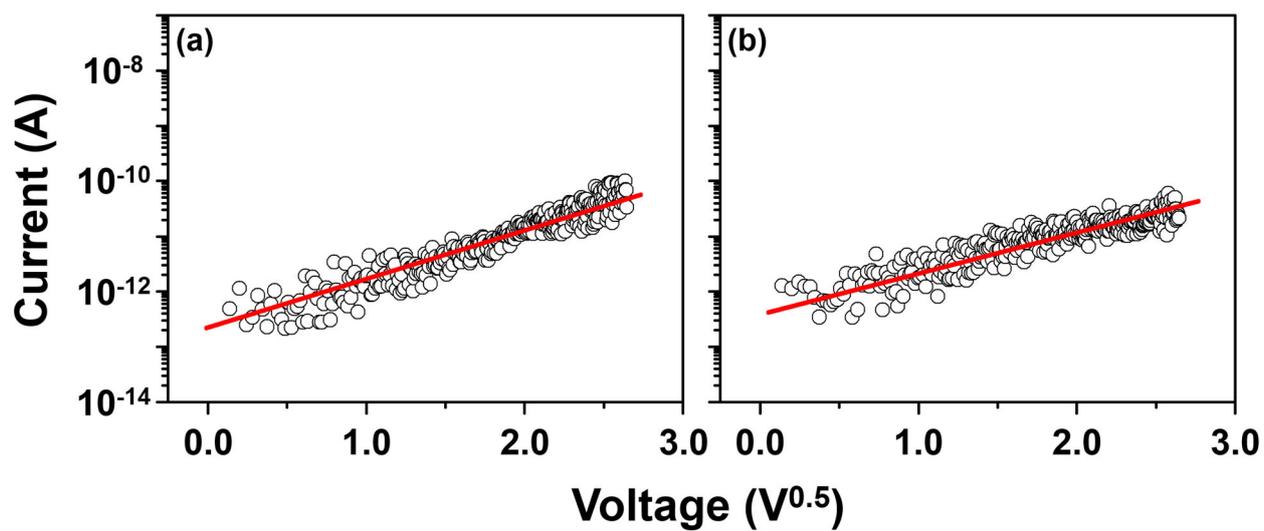


Figure S24. I - V data analysis of the d-Si/polymer/Al devices which were measured with a compliance current of 0.01 A in air ambient condition: (a) PEM-Bz (9.7 nm thick); (b) PEM-BzMe (12.0 nm thick). The symbols are the measured data and the solid lines represent the fit results using Schottky emission conduction model.

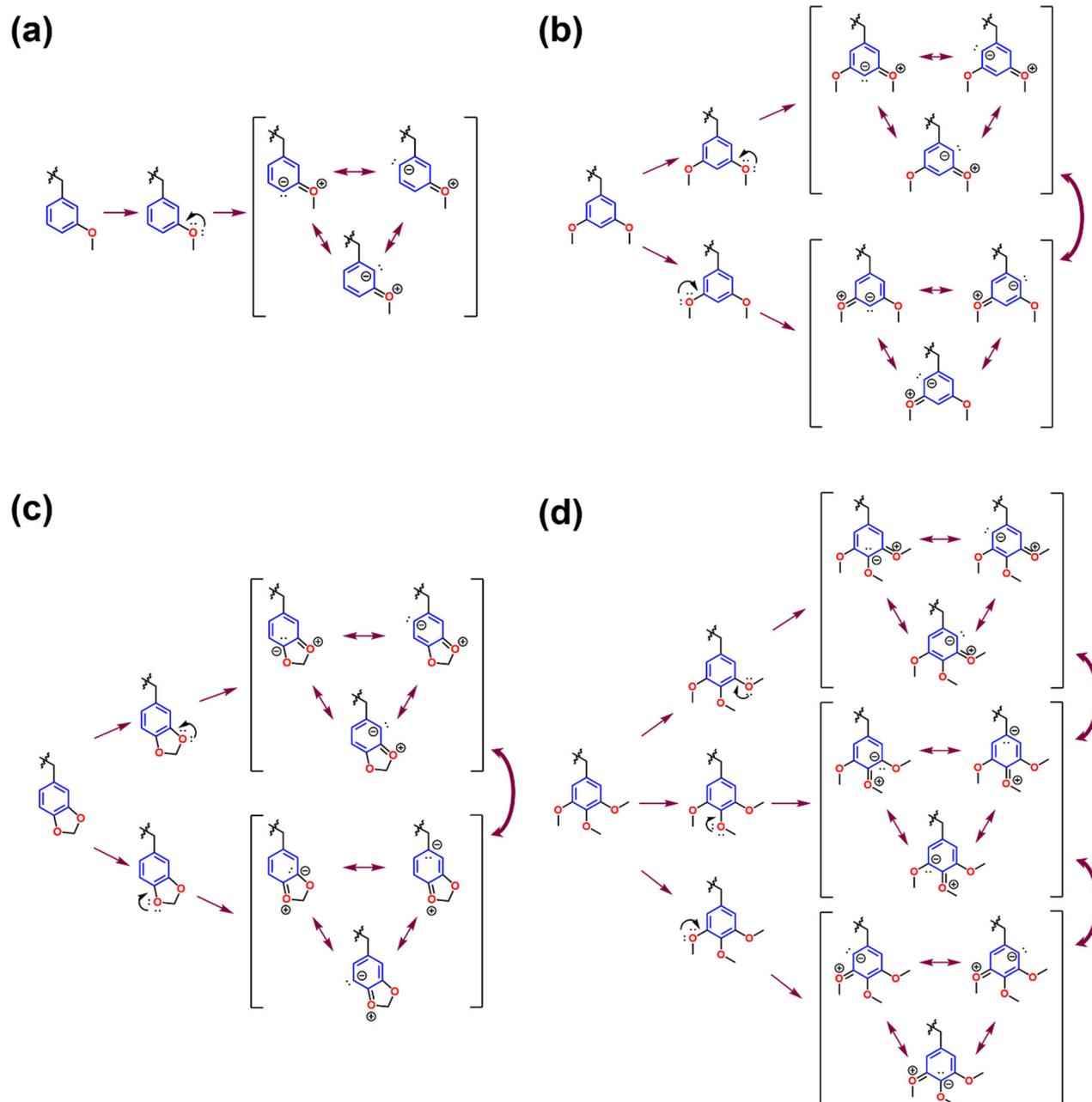


Figure S25. Possible resonances presented in the polymers revealing digital memory behaviors: (a) PEM-BzOMe; (b) PEM-BzOMe₂; (c) PEM-BzO₂C; (d) PEM-BzOMe₃.