

# Supporting Information

## Digital Memory Characteristics of Aromatic Polyimides Based on Pyridine and Its Derivatives

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### Synthesis of PVPy-*i* Polymers

Aliphatic polyvinyls bearing pyridine moiety and its derivatives (PVPy-*i*: PVPy-1, PVPy-2, PVPy-3, and PVPy-4) were prepared by the RAFT polymerization reactions of vinyl monomers containing pyridine unit and its derivatives (Scheme S1) as follows.

**Materials.** All chemicals were purchased from Sigma-Aldrich (St Louis, MO, USA). All reagents were used as received.

**Synthesis of Monomers.** Pyridine derivative monomers were synthesized by Suzuki-reaction and several organic reactions in the following.

*4-Vinylpyridine.* This monomer was purchased from Sigma-Aldrich.

*4-(Vinylphenyl)pyridine.* Bromopyridine (3.000 g, 0.0190 mol), 4-vinylphenyl boronic acid (2.940 g, 0.0199 mol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.219 g, 0.19 mmol) were dissolved in a toluene/EtOH mixture (50 mL/25 mL). A K<sub>2</sub>CO<sub>3</sub> solution (5.510 g in 25 mL H<sub>2</sub>O) was added to the reaction mixture and then stirred at 90 °C (reflux) for 20 h. Then, the reaction solution was diluted with CHCl<sub>3</sub> and washed with brine. The organic and aqueous phase layers were separated. The organic layer was dried over MgSO<sub>4</sub>. Removal of the used solvent gave residue. The residue was purified by silica column chromatography with hexane and ethyl acetate (1:1 volume) as the eluent, obtaining the target monomer product in white solid. Yield: 89%. The product was characterized in deuterated chloroform (CDCl<sub>3</sub>) by using a Bruker nuclear magnetic resonance (NMR) spectrometer (model AV300 FT-NMR, Rheinstetten, BW, Germany) with a proton (<sup>1</sup>H) probe. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ (ppm)): 8.66–8.64 (m, 2H, aromatic proton), 7.63–7.59 (d, 2H, aromatic proton), 7.55–7.49 (m, 4H, aromatic proton), 6.83 – 6.70 (q, 1H, vinyl proton), 5.88–5.78 (d, 1H, vinyl proton), 5.37–5.29 (d, 1H, vinyl proton) (Figure S16a).

*2-Phenyl-(4-vinylphenyl)pyridine.* This monomer was prepared in a two-step reaction as follows. In the first step, 2,4-Dibromopyridine (5.000 g, 0.0211 mol) and phenyl boronic acid pinacol ester (4.738 g, 0.0232 mol) were dissolved in acetonitrile (140 mL). Pd(OAc)<sub>2</sub> (5 mol%, 0.497 g), PPh<sub>3</sub> (20 mol%, 2.325 g) and KOH (2.400 g) were added into the reaction solution and stirred for 24 h at 70 °C under an argon atmosphere. The reaction mixture was allowed to reach to room temperature, solid was filtered off. The filtrate solution was concentrated in vacuo and the residue re-dissolved in methylene chloride (MC). The organic solution was washed two times with water and brine. The organic layer was dried over MgSO<sub>4</sub>. The residue crude product was purified by silica column chromatography with hexane and methylene chloride (1:1 volume) as the eluent, giving the target 4-bromo-2-

phenylpyridine product in colorless liquid. Yield: 71%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 8.51–8.49 (d, 1H, aromatic proton), 7.98–7.94 (m, 3H, aromatic proton), 7.51–7.38 (m, 4, aromatic proton).

In the second step, the obtained 4-bromo-2-phenylpyridine (3.700 g, 0.0157 mol), 4-vinylphenyl boronic acid (2.448 g, 0.0165 mol), and  $\text{Pd}(\text{PPh}_3)_4$  (0.182 g, 0.158 mmol) were dissolved in a toluene/EtOH mixture (41 mL/20 mL). A  $\text{K}_2\text{CO}_3$  solution (4.570 g in 20 mL  $\text{H}_2\text{O}$ ) was added to the reaction mixture and then stirred at 90 °C (reflux) for 20 h. Then, the reaction solution was diluted with  $\text{CHCl}_3$  and washed with brine. The organic and aqueous phase layers were separated and then the obtained organic layer was further dried over  $\text{MgSO}_4$ . Removal of the used solvent gave residue. The residue was purified by silica column chromatography with a hexane/ethyl acetate mixture (2:1 in volume) as the eluent, giving the target monomer product, 2-phenyl-(4-vinylphenyl)pyridine in solid. Yield: 87%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 8.75–8.71 (br, 1H, aromatic proton), 8.07–8.01 (br, 2H, aromatic proton), 7.94–7.91 (br, 1H, aromatic proton), 7.71–7.64 (d, 2H, aromatic proton), 7.57–7.40 (m, 6H, aromatic proton), 6.84–6.72 (q, 1H, vinyl proton), 5.89–5.80 (d, 1H, vinyl proton), 5.37– 5.31 (d, 1H, vinyl proton) (Figure S16b).

*2,6-Diphenyl-(4-vinylphenyl)pyridine*. This monomer was synthesized in a three-step reaction from 2,6-dichloro-4-aminopyridine. In the first step, 2,6-dichloro-4-aminopyridine (4.000 g, 0.0245 mol), phenyl boronic acid (6.280 g, 0.0515 mol),  $\text{Pd}(\text{PPh}_3)_4$  (0.567 g, 0.4910 mmol) were dissolved in a toluene/EtOH mixture (64 mL/32 mL). A  $\text{K}_2\text{CO}_3$  solution (14.240 g in 32 mL  $\text{H}_2\text{O}$ ) was added to the reaction mixture and then stirred at 90 °C (reflux) for 20 h. Then, the reaction solution was diluted with  $\text{CHCl}_3$  and then washed with brine. The organic and aqueous phase layers were separated; the organic layer was dried over  $\text{MgSO}_4$ . Removal of the used solvent gave residue. The residue was purified by silica column chromatography with a hexane/ethyl acetate mixture (1:1 in volume) as the eluent, producing the target

product, 2,6-diphenyl-4-aminopyridine in slightly yellow solid. Yield: 84%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 8.08–8.04 (m, 4H, aromatic proton), 7.48–7.36 (m, 6H, aromatic proton), 6.92 (s, 2H, aromatic proton), 4.19 (br, 2H, amine).

In the second step, the obtained 2,6-diphenyl-4-aminopyridine (3.750 g, 15.4 mmol) and  $\text{Cu(I)Br}$  (11.500 g, 80.3 mmol) were dissolved in 48% hydrobromic acid (150 mL) at 0 °C. Sodium nitrite (22.500 g, 326 mmol) was dissolved in water (100 mL) and then slowly added to the reaction flask for 1 h, then followed by stirring for 24 h at room temperature. The reaction solution was basified with sodium hydroxide aqueous solution (NaOH 150 g in 300 mL  $\text{H}_2\text{O}$ ). The mixture was extracted with ether three times. The obtained organic layer was dried over  $\text{MgSO}_4$  and filtered; the filtrate solution was concentrated in vacuo. The obtained bright orange oil was treated with MeOH, giving 2,6-diphenyl-4-bromopyridine in bright orange powder. Yield: 59%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 8.12–8.08 (m, 4H, aromatic proton), 7.83 (s, 2H, aromatic proton), 7.52–7.41 (m, 6, aromatic proton).

In the final step, the obtained 2,6-diphenyl-4-bromopyridine (0.448 g, 0.00144 mol), 4-vinylphenyl boronic acid (0.235 g, 0.00158 mol), and  $\text{Pd(PPh}_3)_4$  (0.017 g, 0.00144 mmol) were dissolved in a toluene/EtOH mixture (4 mL/2 mL). A  $\text{K}_2\text{CO}_3$  solution (0.440 g in 2 mL  $\text{H}_2\text{O}$ ) was added the reaction mixture and then stirred at 90 °C (reflux) for 20 h. Then, the reaction solution was diluted with  $\text{CHCl}_3$  and washed with brine. The organic and aqueous phase layers were separated; the organic layer was dried over  $\text{MgSO}_4$ . Removal of the used solvent gave residue. The residue was purified by silica column chromatography with a hexane/ethyl acetate mixture (3:1 in volume) as the eluent, producing the target monomer, 2,6-diphenyl-(4-vinylphenyl)pyridine in solid. Yield: 82%.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)): 8.23–8.17 (m, 4H, aromatic proton), 7.89 (s, 2H, aromatic proton), 7.76–7.70 (br, 2H, aromatic proton), 7.60–7.40 (m, 8H, aromatic proton), 6.85–6.73 (q, 1H, vinyl proton), 5.91–5.80 (d, 1H, vinyl proton), 5.38–5.31 (d, 1H, vinyl proton) (Figure S16c).

**Polymers.** PVPy-*i* Polymers were prepared from 4-vinylpyridine and its derivatives by radical atomic fragmentation transfer (RAFT) polymerizations. A typical procedure for the RAFT polymerizations is given as follows. 4-(Vinylphenyl)pyridine (a monomer: 2.000 g, 0.0110 mol), benzylsulfanylthiocarbonylsufanylpropionic acid (BSPA, a chain transfer agent: 0.030 g, 0.00011 mol), and azobisisobutyronitrile (AIBN, an initiator: 0.0089 g, 0.052 mmol) were dissolved in toluene (5.51 mL) and placed in schlenk flask; here, [Monomer]/[CTA]/[AIBN] = 200/2/1. The mixture was degassed by three times of freeze-pump-thaw cycles. The reaction mixture was stirred at 65 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The concentrated polymer solution was purified by precipitation into MeOH several times. The precipitate was dried *in vacuo* for 24 h, giving the target polymer product, poly(4-(vinylphenyl)pyridine) (PVPy-2). The other PVPy-*i* polymers were prepared in the same manner.

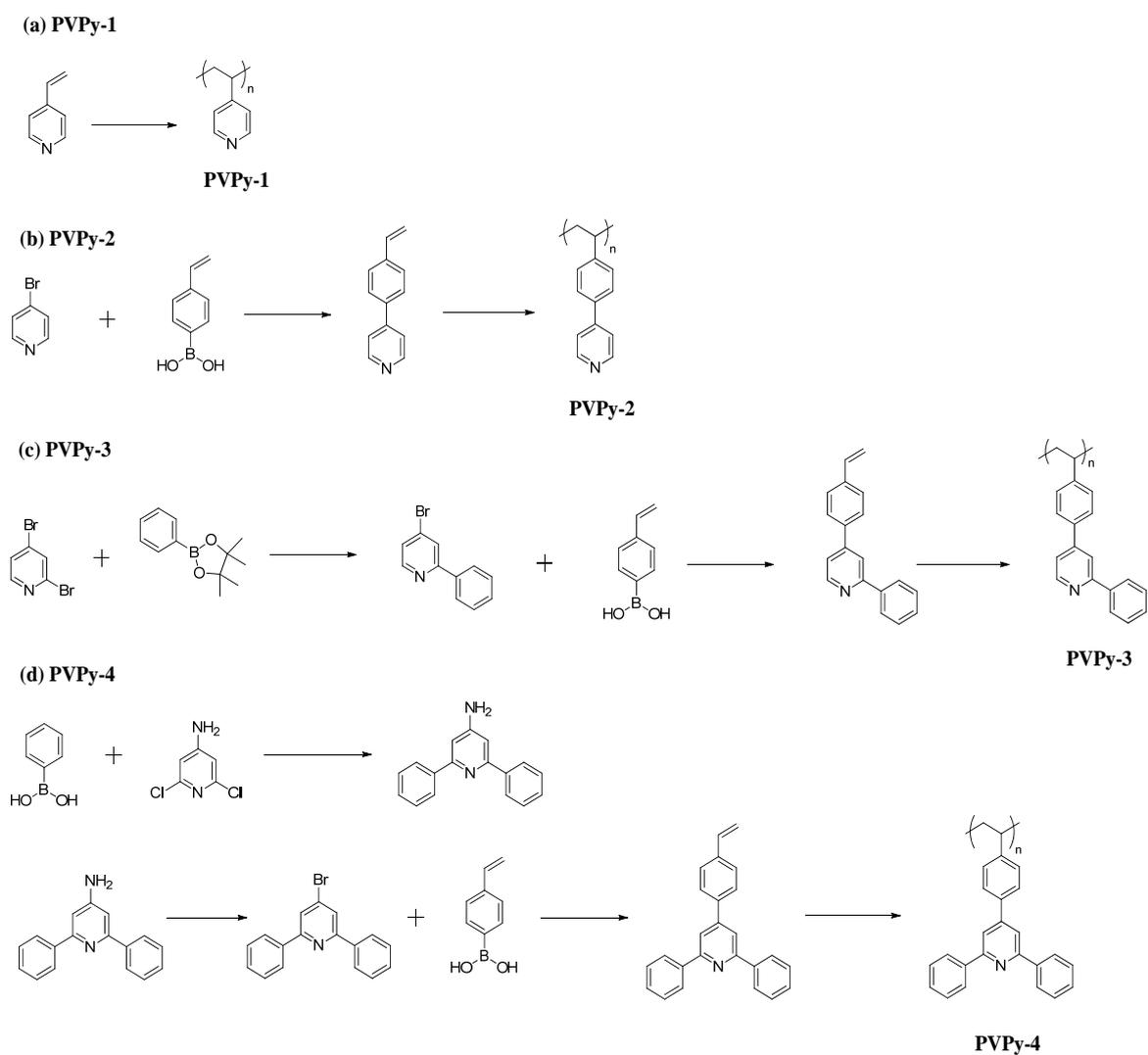
*Poly(4-vinylpyridine) (PVPy-1).* <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ (ppm)): 8.52–8.08 (br, 2H, aromatic proton), 6.64–6.12 (br, 2H, aromatic proton), 2.06–1.10 (br, 3H, hydrocarbon backbone) (Figure S17a).

*Poly(4-(vinylphenyl)pyridine) (PVPy-2).* <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ (ppm)): 8.73–8.32 (br, 2H, aromatic proton), 7.47–6.90 (br, 4H, aromatic proton), 6.74–6.37 (br, 2H, aromatic proton), 2.40–1.07 (br, 3H, hydrocarbon backbone) (Figure S17b).

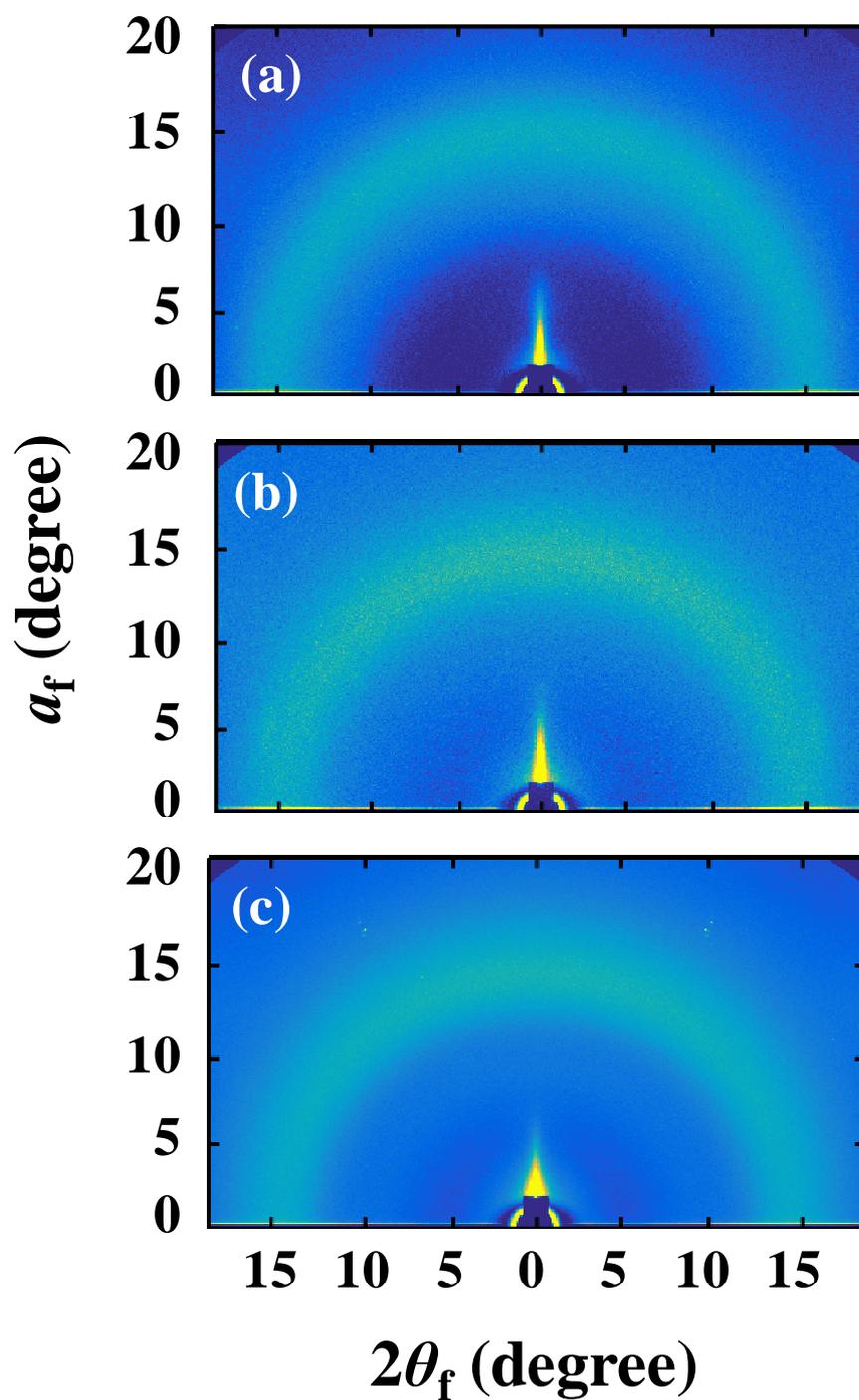
*Poly(2-phenyl-(4-vinylphenyl)pyridine) (PVPy-3).* <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ (ppm)): 8.66–8.21 (br, 1H, aromatic proton), 8.06–7.57 (br, 3H, aromatic proton), 7.50–6.84 (br, 6H, aromatic proton), 6.78–6.27 (br, 2H, aromatic proton), 2.45–0.99 (br, 3H, hydrocarbon backbone) (Figure S17c).

*Poly(2,6-diphenyl-(4-vinylphenyl)pyridine) (PVPy-4).* <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>, δ (ppm)):

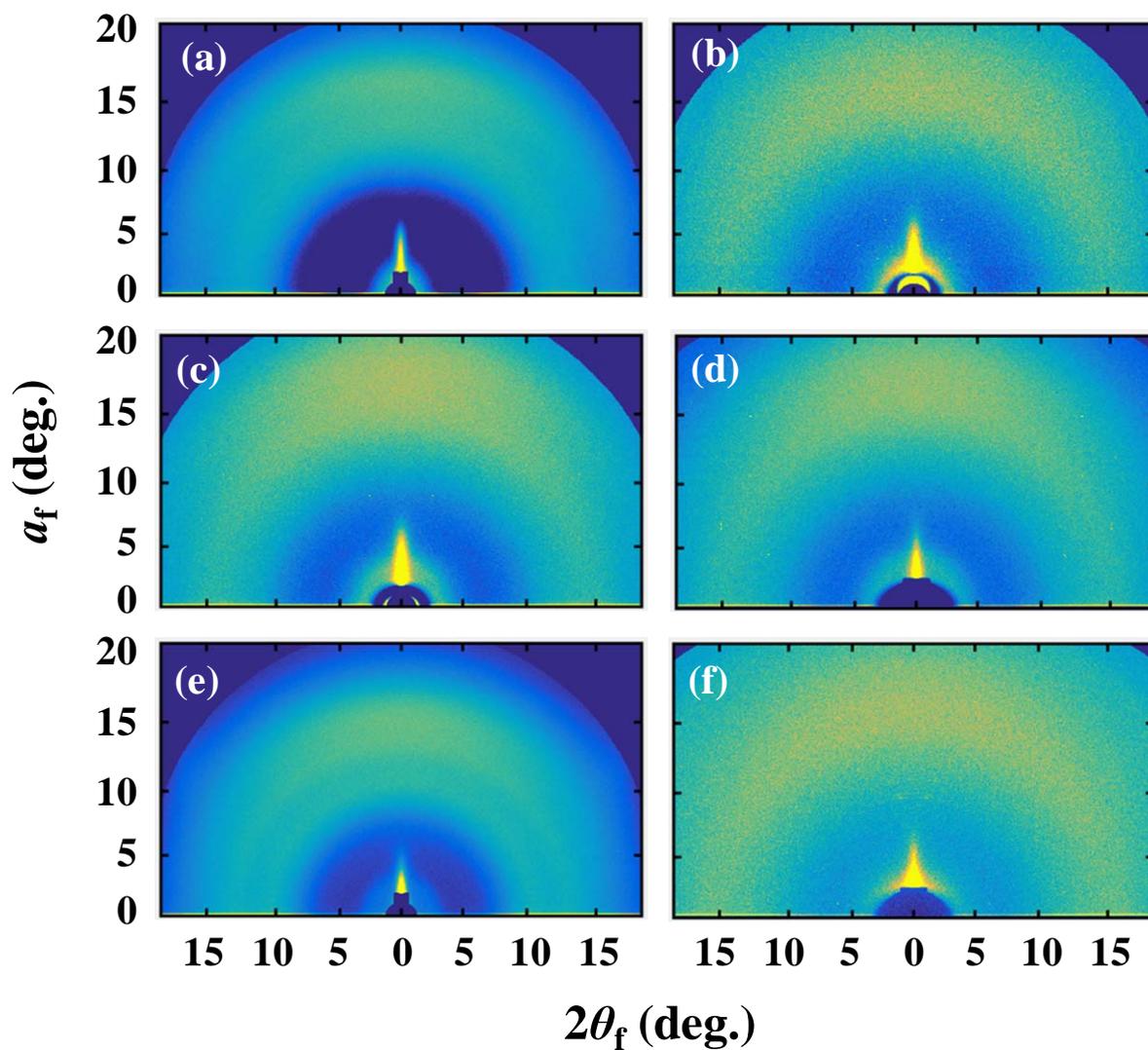
8.27–6.39 (br, 16H, aromatic proton), 1.66–1.17 (br, 3H, hydrocarbon backbone) (Figure S17d).



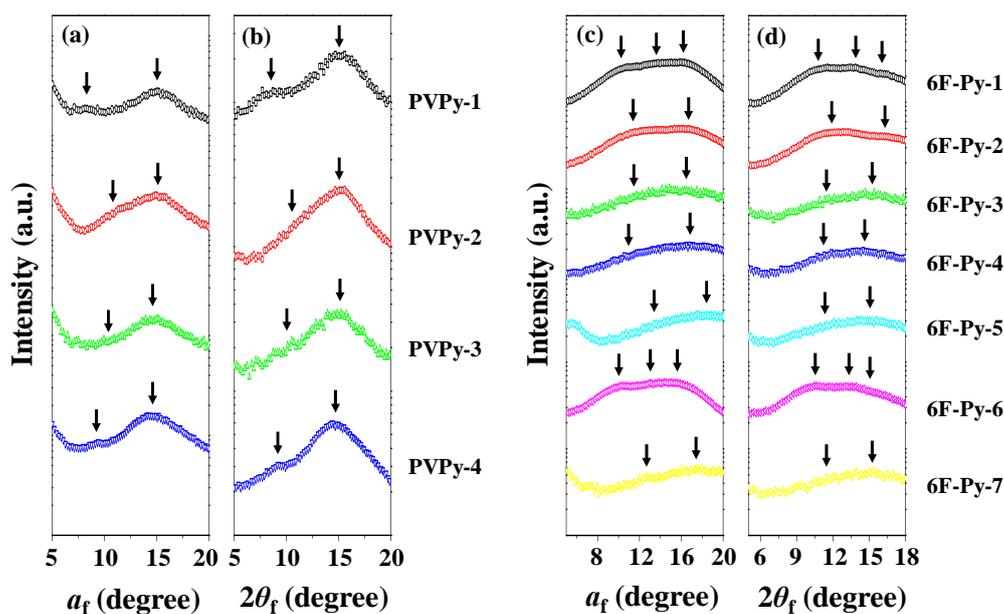
**Scheme S1.** Synthetic schemes of PVPy-*i* polymers.



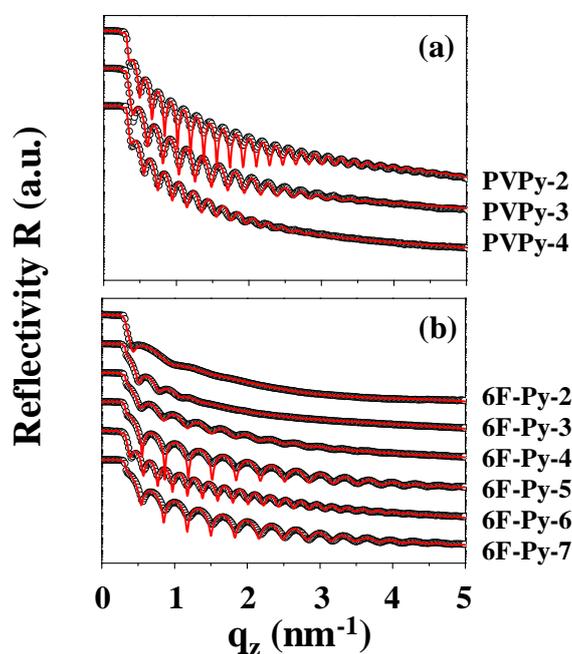
**Figure S1.** Synchrotron GIXS images measured for PVPy-*i* polymer films: (a) PVPy-2 (38.30 nm thick); (b) PVPy-3 (31.26 nm thick); (c) PVPy-4 (33.41 nm thick). An X-ray source of  $\lambda = 0.1230$  nm (wavelength) was used.



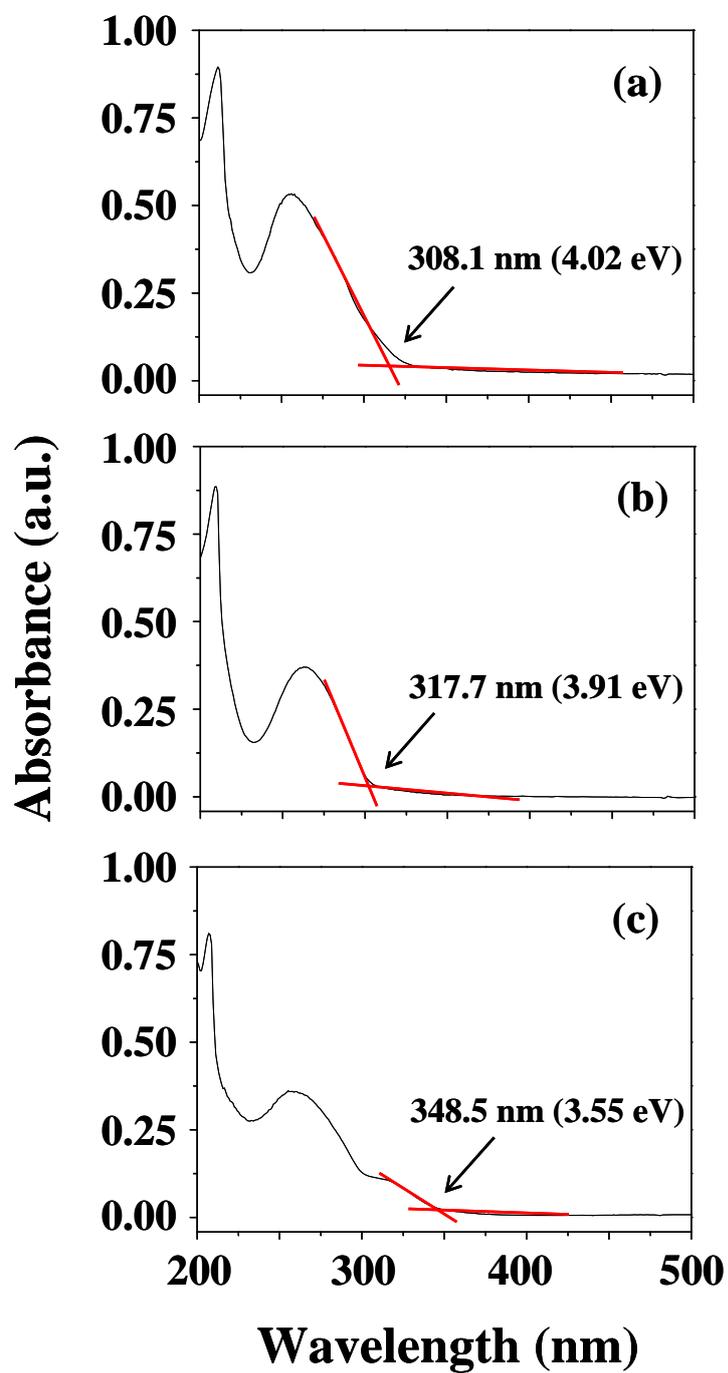
**Figure S2.** Synchrotron GIXS images measured for 6F-Py-*i* polymer films: (a) 6F-Py-2 (9.76 nm thick); (b) 6F-Py-3 (20.72 nm thick); (c) 6F-Py-4 (19.01 nm thick); (d) 6F-Py-5 (18.77 nm thick); (e) 6F-Py-6 (29.86 nm thick); (f) 6F-Py-7 (19.09 nm thick). An X-ray source of  $\lambda = 0.1230$  nm (wavelength) was used for 6F-Py-3, 6F-Py-4, 6F-Py-5 and 6F-Py-7; an X-ray source of  $\lambda = 0.1110$  nm was used for 6F-Py-2 and 6F-Py-6.



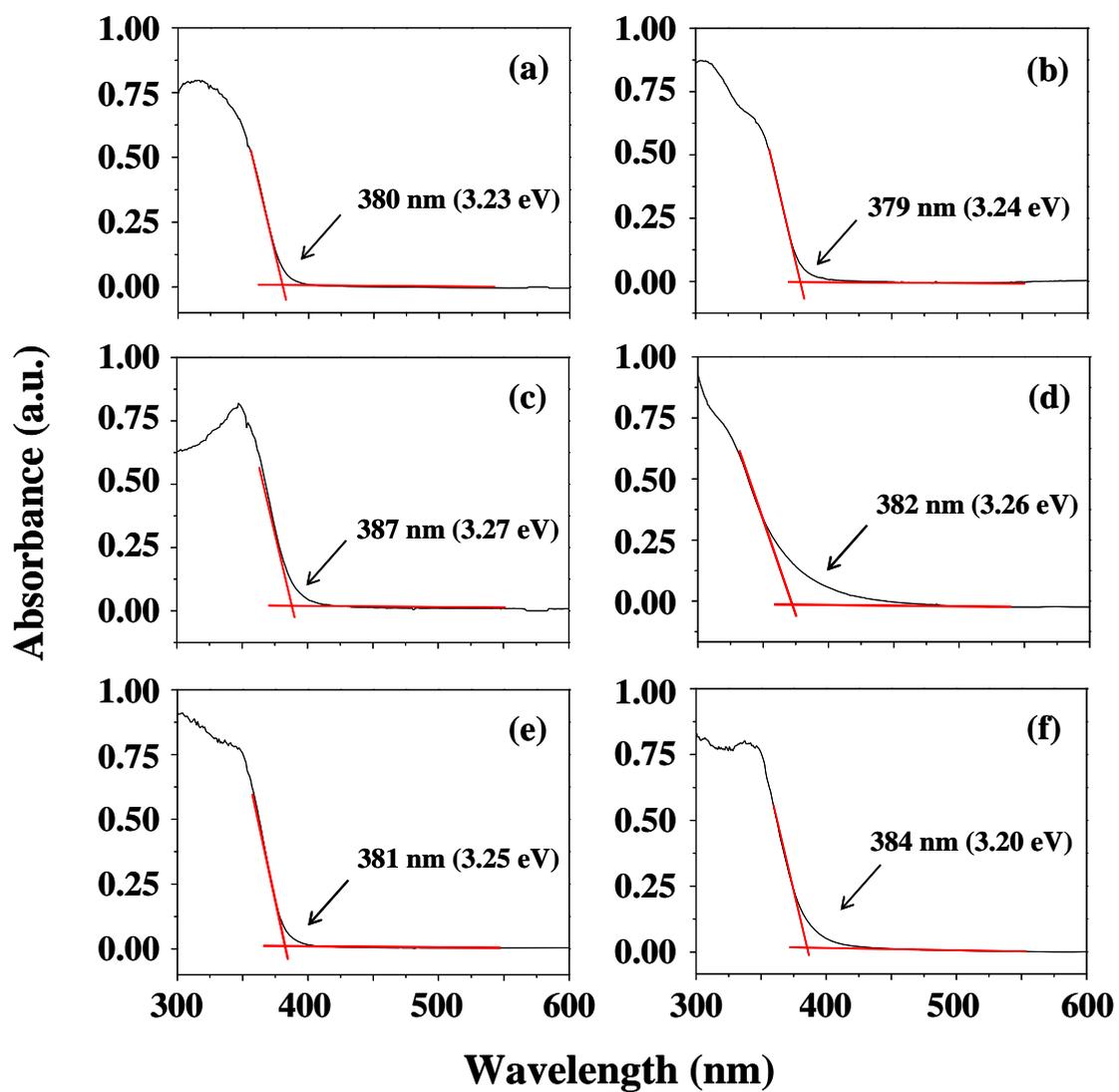
**Figure S3.** Out-of-plane and in-plane scattering profiles extracted from the 2D GIXS images in Figures 2a-b and S2: (a, c) out-of-plane scattering profiles; (b, d) in-plane scattering profiles. The out-of-plane scattering profiles were extracted along the meridian line at  $2\theta_f = 0^\circ$  from the 2D scattering images; the in-plane scattering profiles were extracted along the equatorial line at  $\alpha_f = 0.24^\circ$  to  $0.30^\circ$  from the 2D scattering images.



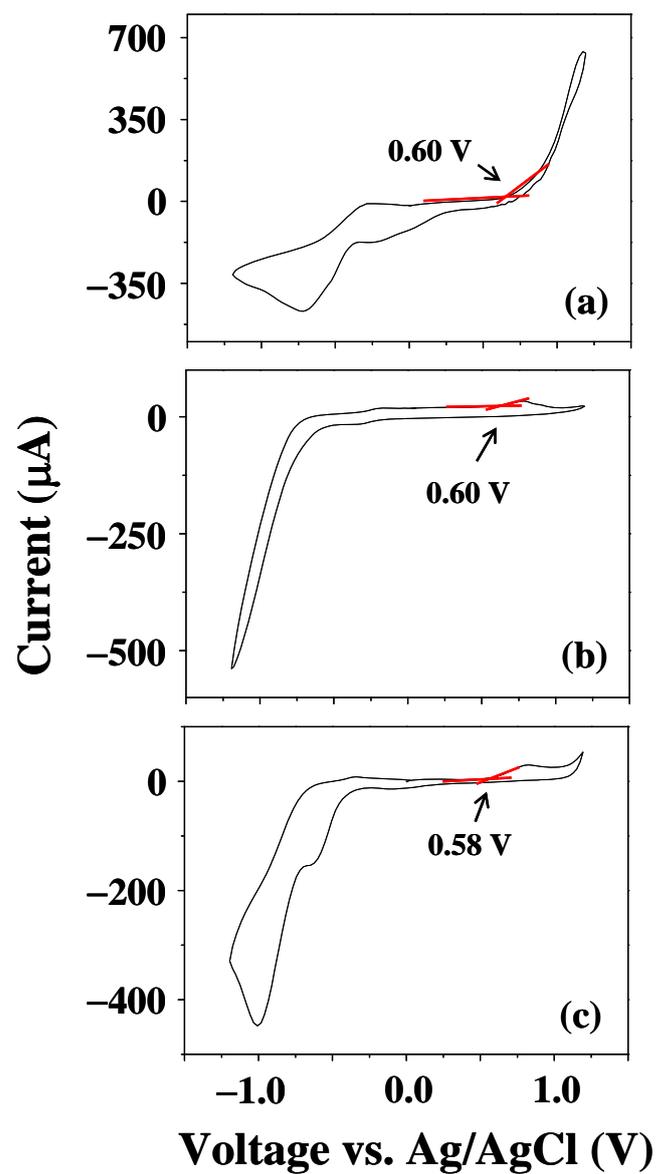
**Figure S4.** Synchrotron XR profiles measured for polymer films; (a) PVPy-*i*: PVPy-2 (38.30 nm thick), PVPy-3 (31.26 nm thick), and PVPy-4 (33.41 nm thick); (b) 6F-Py-*i*: 6F-Py-2 (9.76 nm thick), 6F-Py-3 (20.72 nm thick), 6F-Py-4 (19.01 nm thick), 6F-Py-5 (18.77 nm thick), 6F-Py-6 (29.86 nm thick), and 6F-Py-7 (19.09 nm thick). An X-ray source of  $\lambda = 0.1240$  nm (wavelength) was used for the XR measurements.



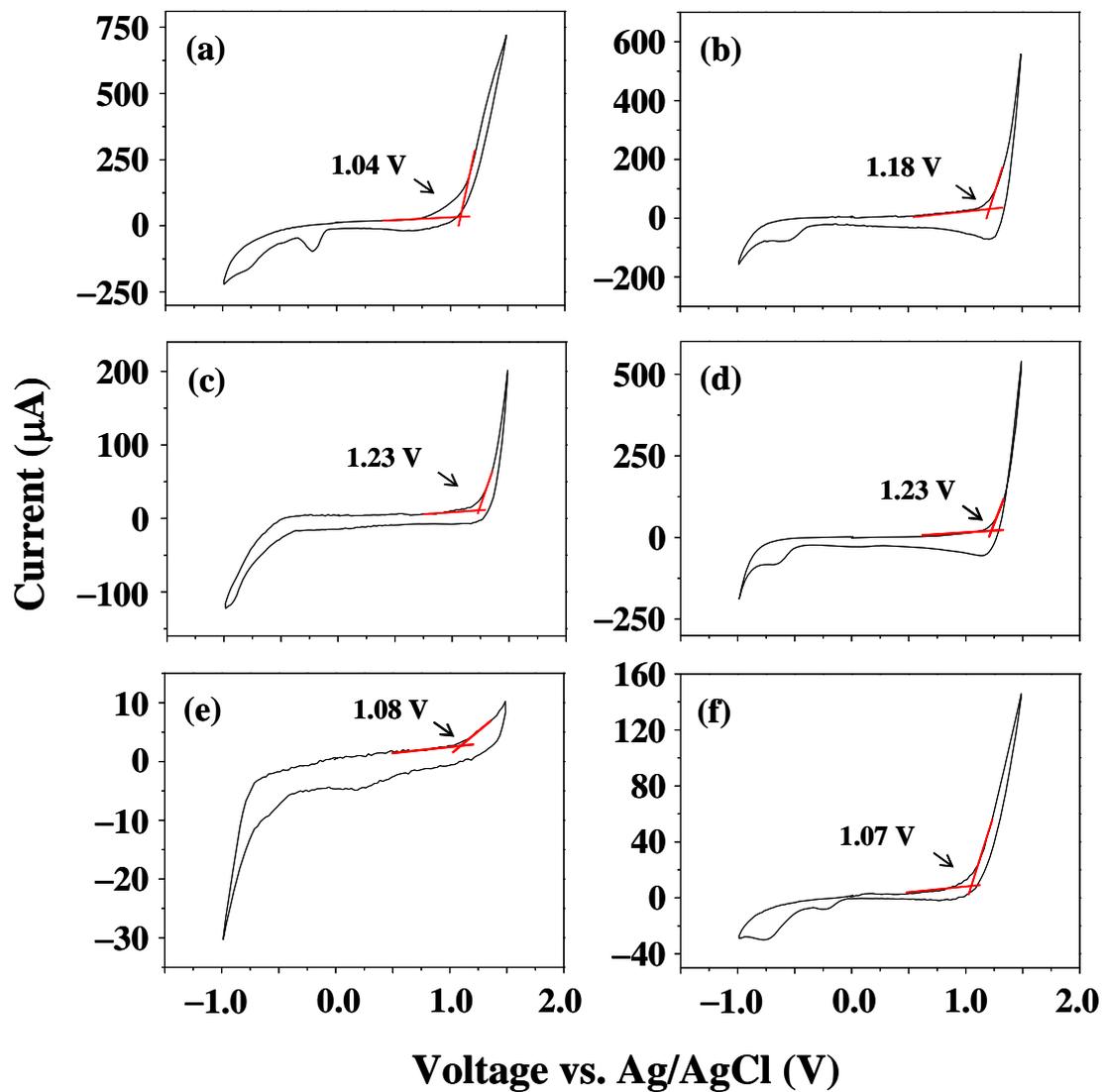
**Figure S5.** UV-vis spectra measured for PVPy-*i* polymers: (a) PVPy-2; (b) PVPy-3; (c) PVPy-4. UV-vis spectra were measured in thin films coated on quartz substrates.



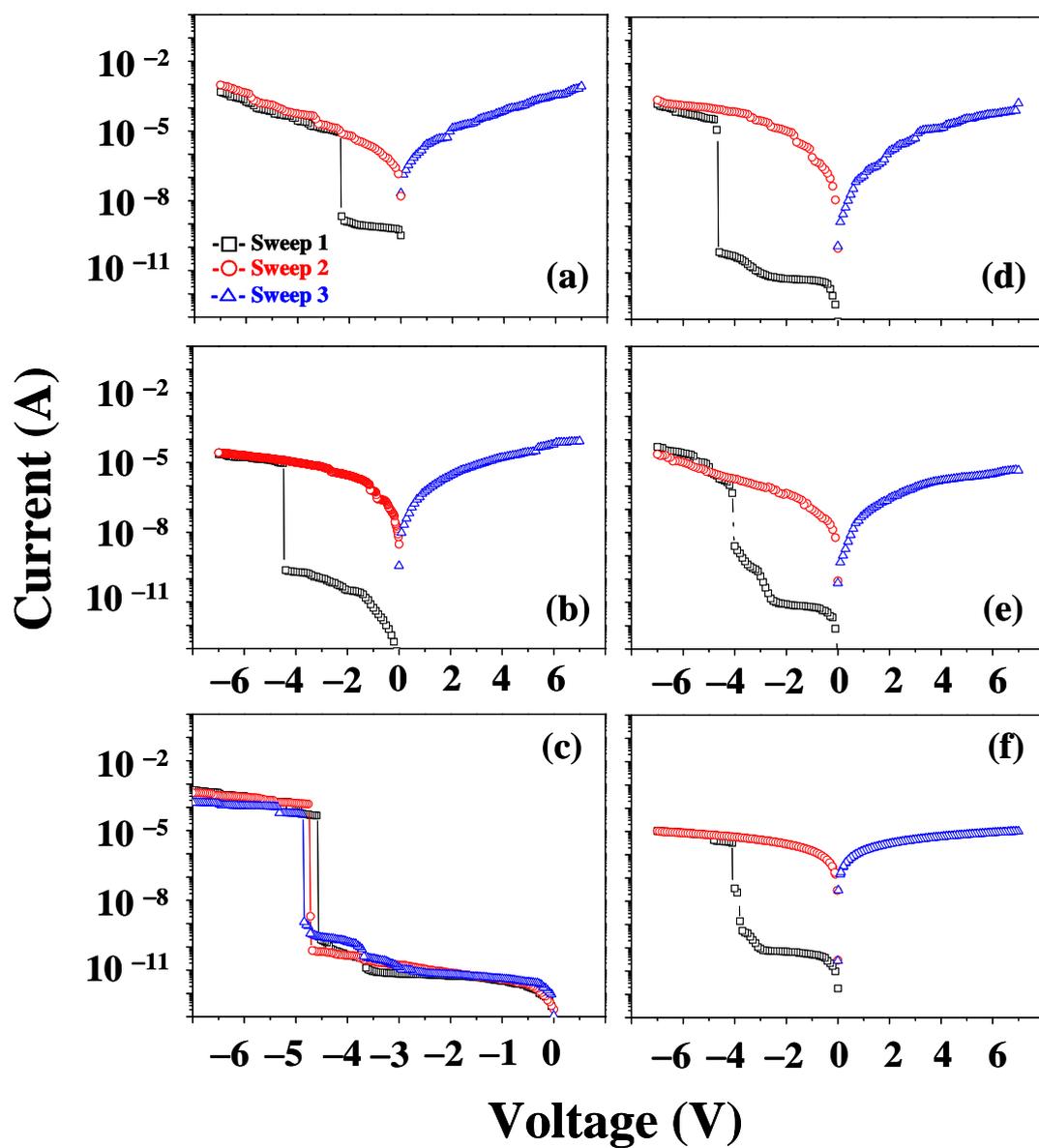
**Figure S6.** UV-vis spectra measured for 6F-Py-*i* polymers: (a) 6F-Py-2; (b) 6F-Py-3; (c) 6F-Py-4; (d) 6F-Py-5; (e) 6F-Py-6; (f) 6F-Py-7. UV-vis spectra were measured in thin films coated on quartz substrates.



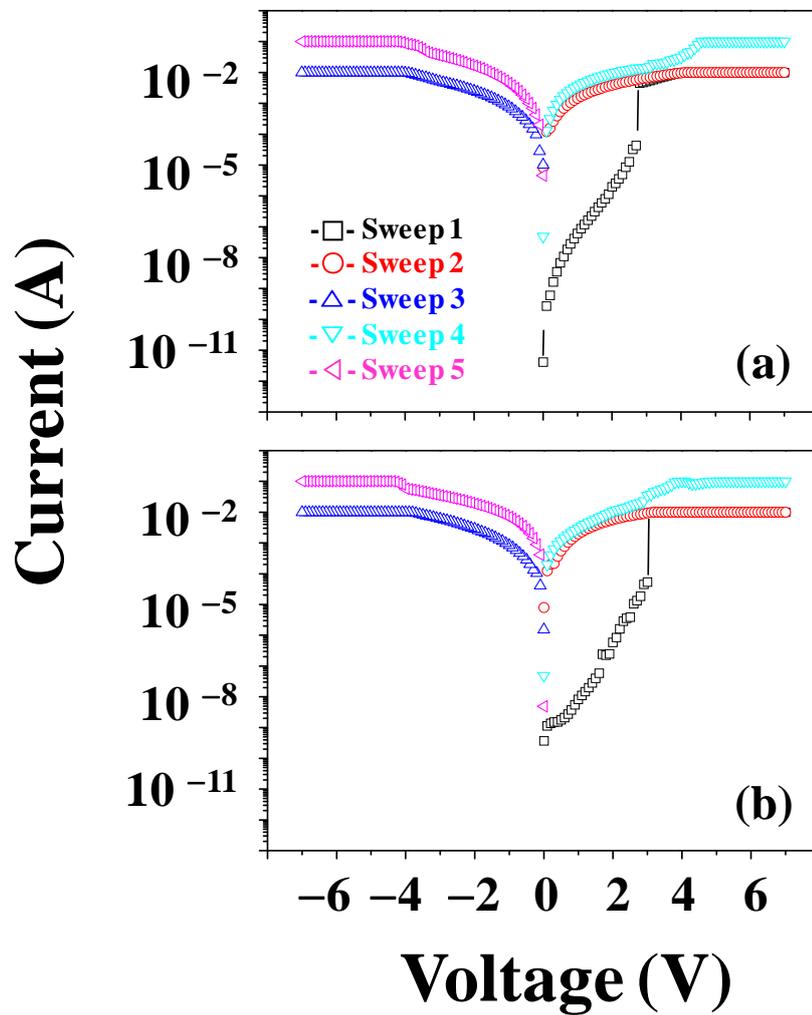
**Figure S7.** CV responses measured for PVPy-*i* polymers: (a) PVPy-2; (b) PVPy-3; (c) PVPy-4. CV measurements were carried out at 20 °C in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile using a platinum gauze counter electrode and an Ag/AgCl (saturated KCl) reference electrode; the polymers were coated on the gold (Au) electrode deposited on silicon wafer. A scan rate of 100 mV/s was used.



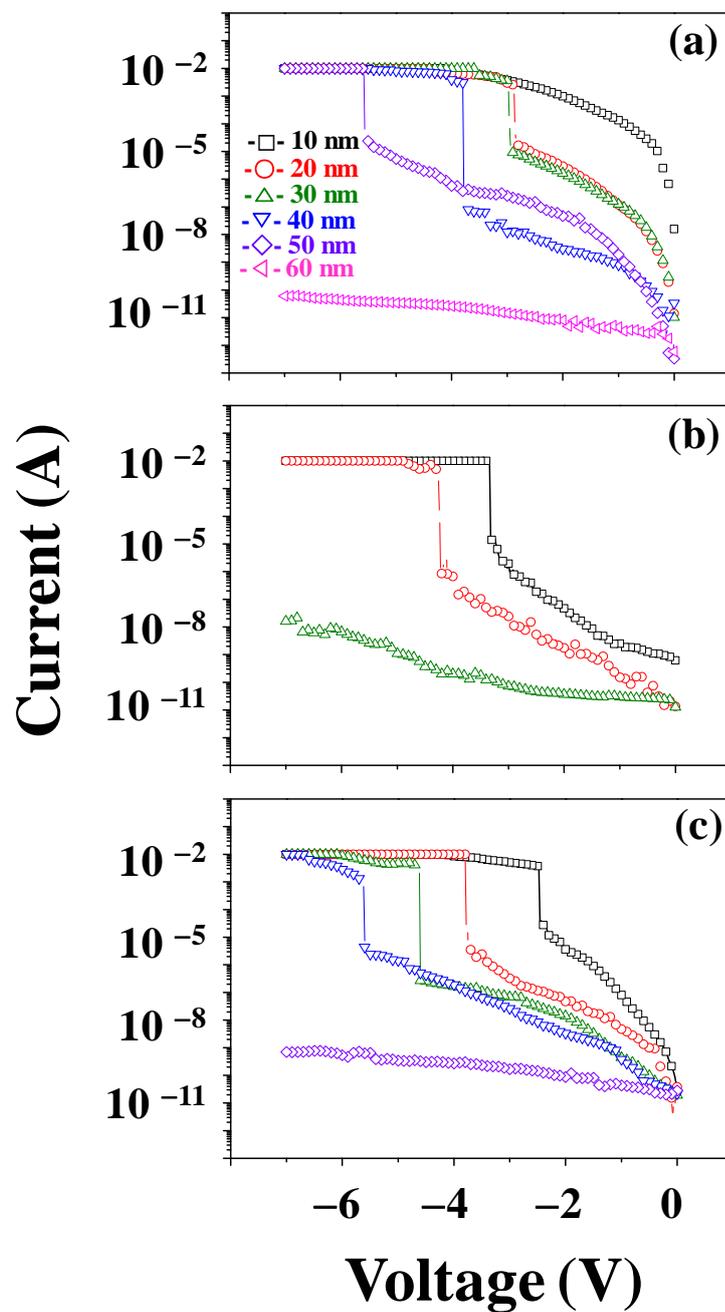
**Figure S8.** CV responses measured for 6F-Py-*i* polymers: (a) 6F-Py-2; (b) 6F-Py-3; (c) 6F-Py-4; (d) 6F-Py-5; (e) 6F-Py-6; (f) 6F-Py-7. CV measurements were carried out at 20 °C in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile using a platinum gauze counter electrode and an Ag/AgCl (saturated 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.



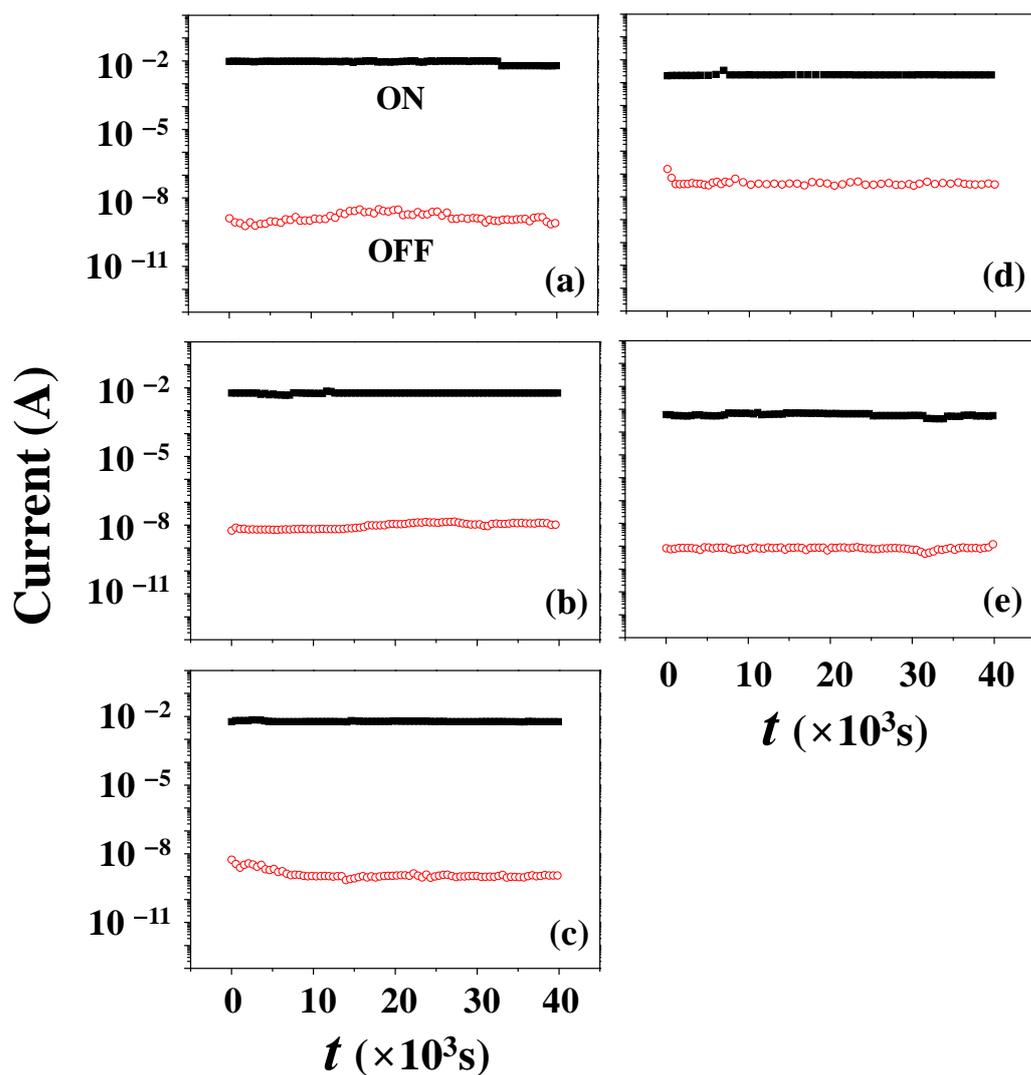
**Figure S9.**  $I$ - $V$  curves of Al/PVPy- $i$ /Al devices, which were measured with a compliance current set of 0.01 A in air ambient condition; PVPy-3: (a) 11.46 nm thick, (b) 18.52 nm thick, and (c) 28.61 nm thick; PVPy-4: (d) 10.69 nm thick, (e) 19.28 nm thick, and (f) 29.93 nm thick. The electrode contact area was  $100 \times 100 \mu\text{m}^2$ .



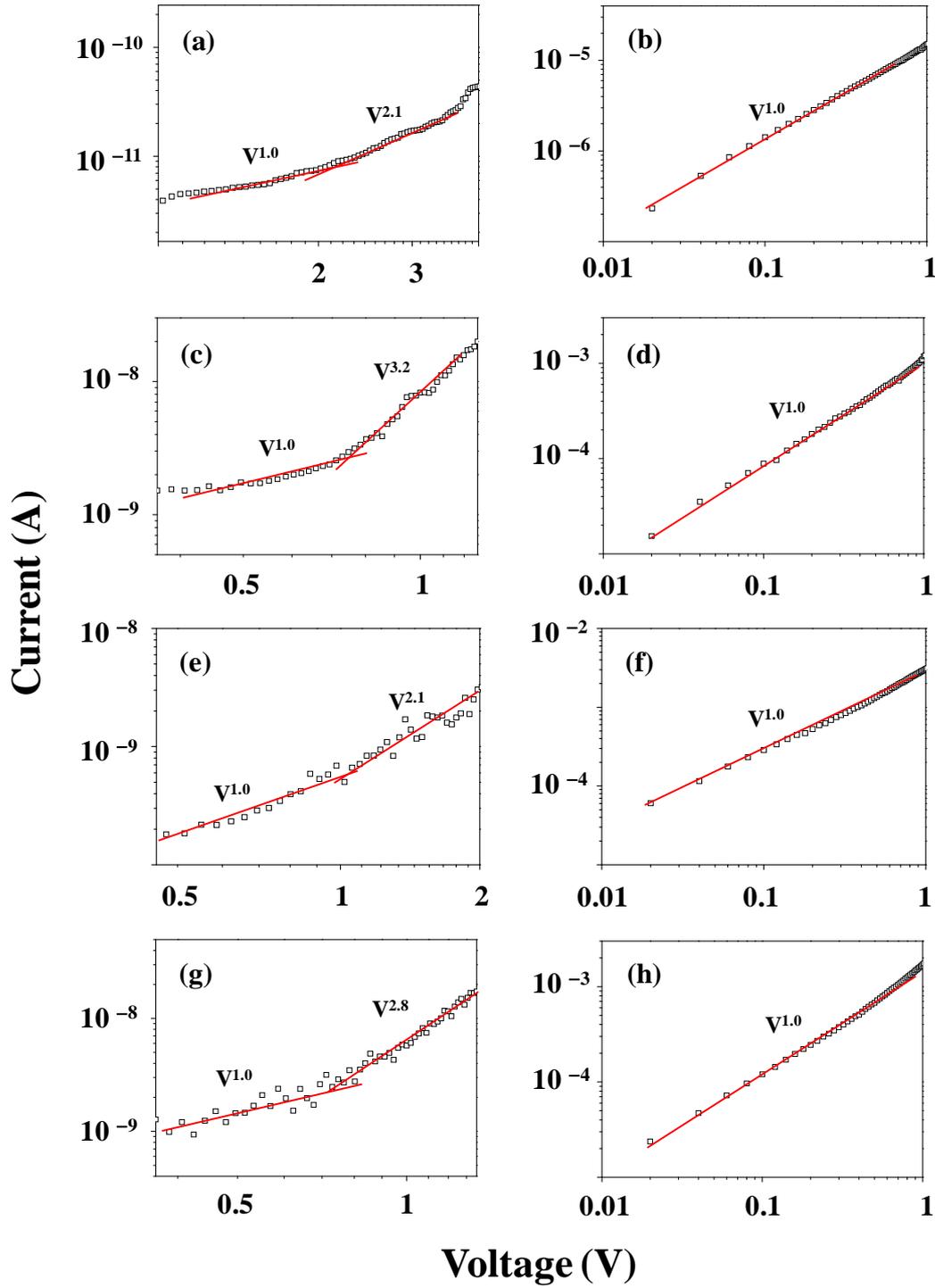
**Figure S10.**  $I$ - $V$  curves of boron-doped Si/6F-Py- $i$ /Al devices: (a) 6F-Py-1 (21.76 nm thick); (b) 6F-Py-2 (21.39 nm thick). The voltage sweeps 1 to 3 were conducted with a compliance current set of 0.01 A in air ambient condition; subsequently the voltage sweeps 4 and 5 were carried out with a compliance current set of 0.1 A in air ambient condition. The electrode contact area was  $300 \times 300 \mu\text{m}^2$ .



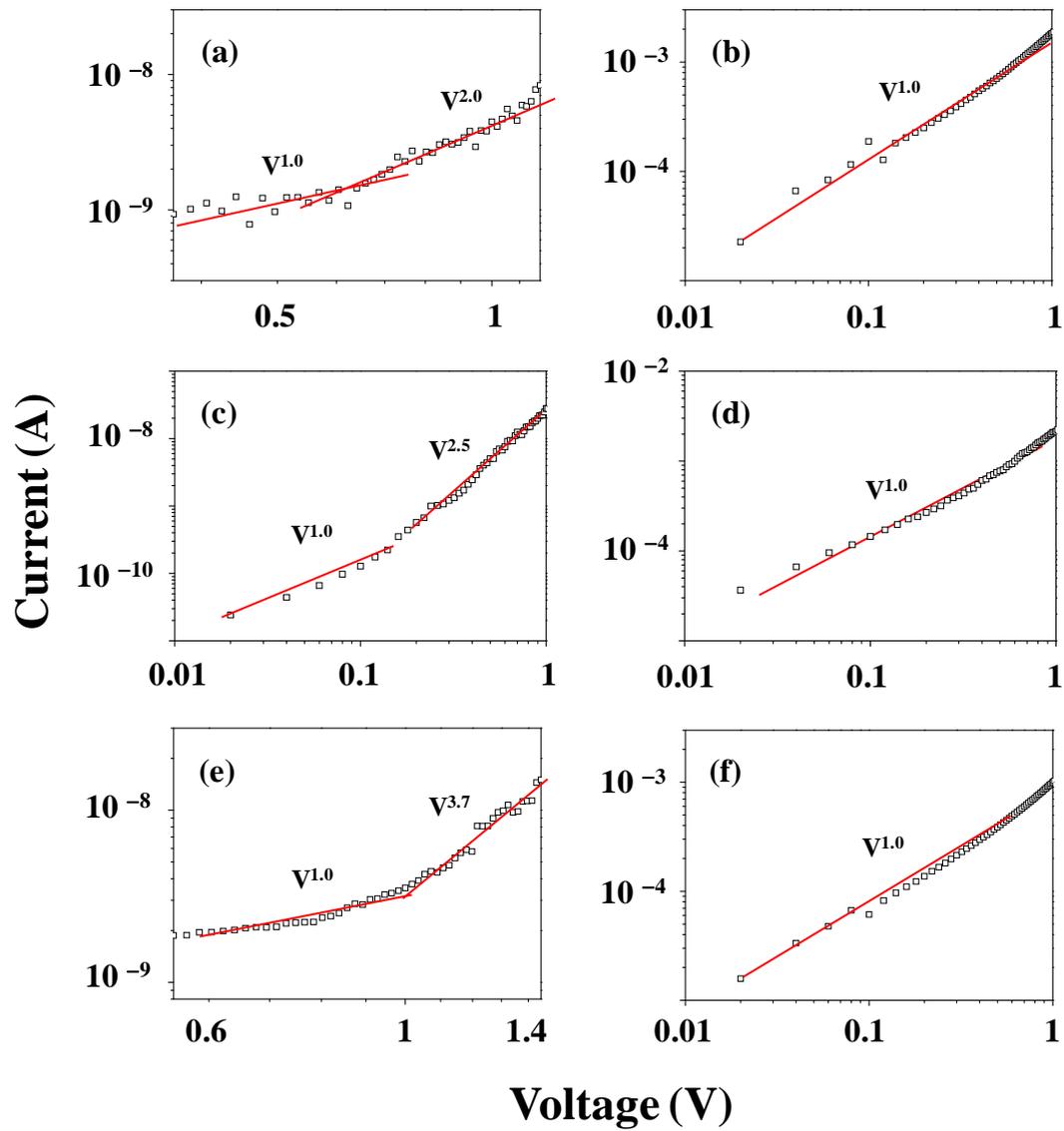
**Figure S11.**  $I$ - $V$  curves of boron-doped Si/6F-Py- $i$ /Al devices with various film thicknesses, which were measured with a compliance current set of 0.01 A in air ambient condition: (a) 6F-Py-1; (b) 6F-Py-3; (c) 6F-Py-6. The electrode contact area was  $300 \times 300 \mu\text{m}^2$ .



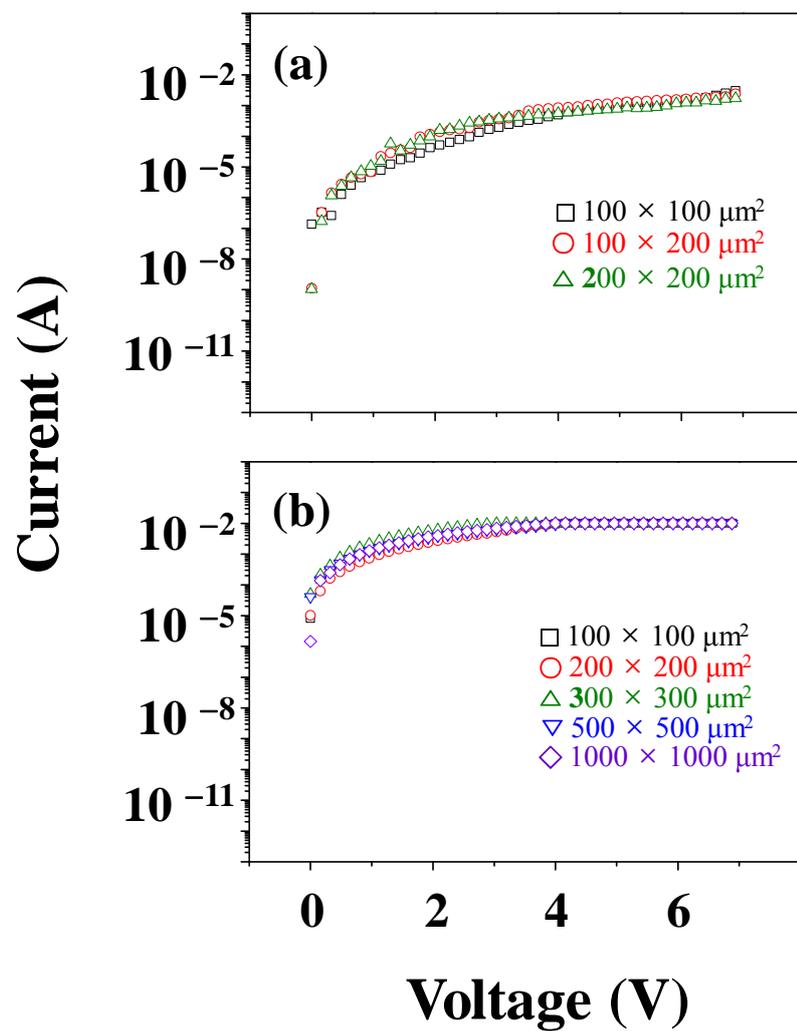
**Figure S12.** Retention times of the boron-doped Si/6F-Py-*i*/Al devices in the ON- and OFF-states, which were measured with a compliance current of 0.01 A in air ambient condition: (a) 6F-Py-2 (21.39 nm); (b) 6F-Py-4 (23.00 nm thick); (c) 6F-Py-5 (19.92 nm thick); (d) 6F-Py-6 (19.97 nm thick); (e) 6F-Py-7 (20.19 nm thick). The reading voltage was 1.0 V for the ON- and OFF-states. The electrode contact area was  $300 \times 300 \mu\text{m}^2$ .



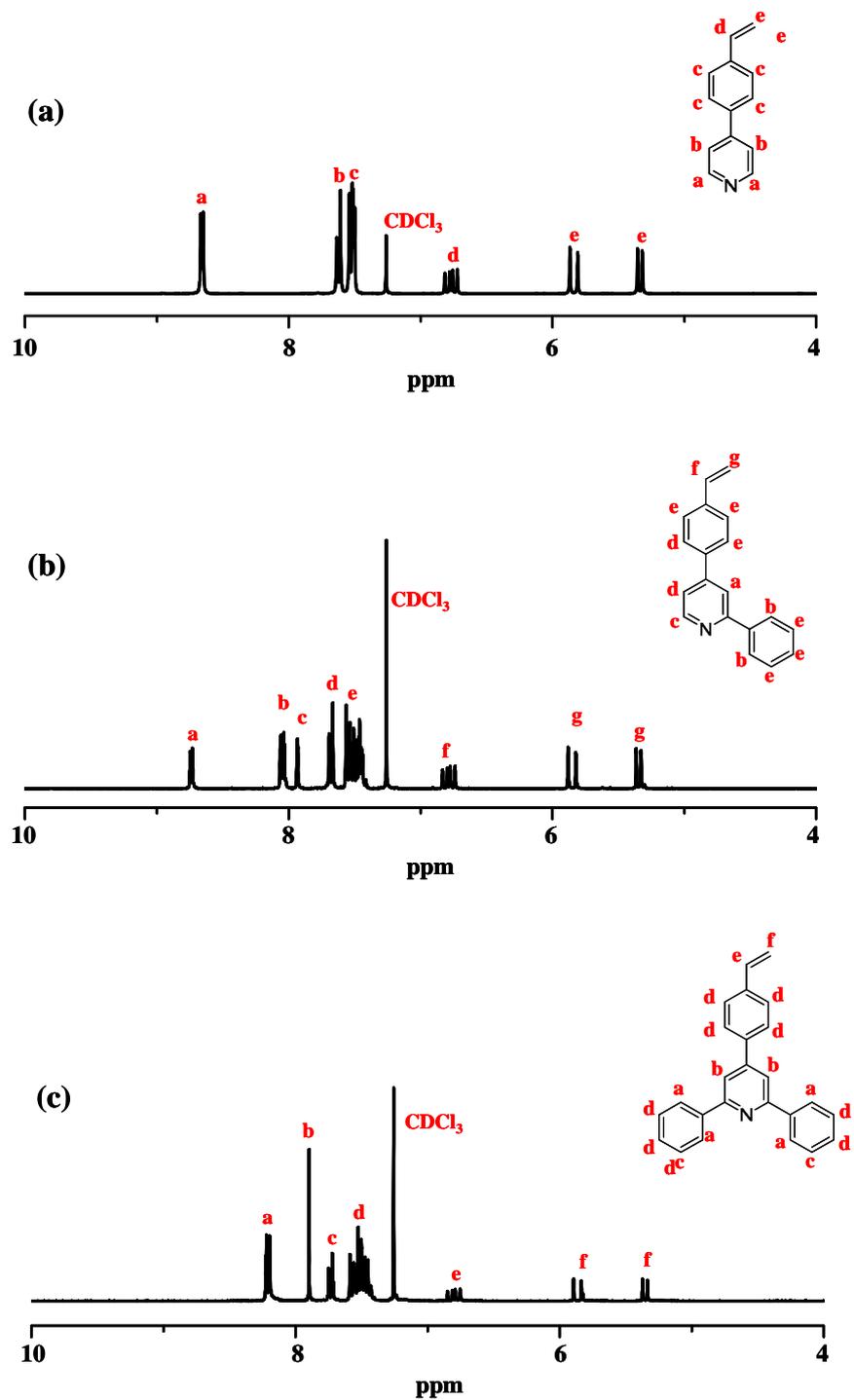
**Figure S13.**  $I$ - $V$  data analysis of the Al/PVPy- $i$ /Al and boron-doped Si/6F-Py- $i$ /Al devices in the OFF- and ON-states, which were measured with a compliance current of 0.01 A in air ambient condition: (a, b) PVPy-3 (28.61 nm); (c, d) 6F-Py-2 (21.39 nm); (e, f) 6F-Py-3 (19.98 nm thick); (g, h) 6F-Py-4 (23.00 nm thick). The symbols are the measured data; the solid red lines in the OFF-states (a, c, e, g) represent the fit lines using Ohmic conduction and trap-limited SCLC models whereas the red lines in the ON-states (b, d, f, h) represent the fit lines using Ohmic conduction model.



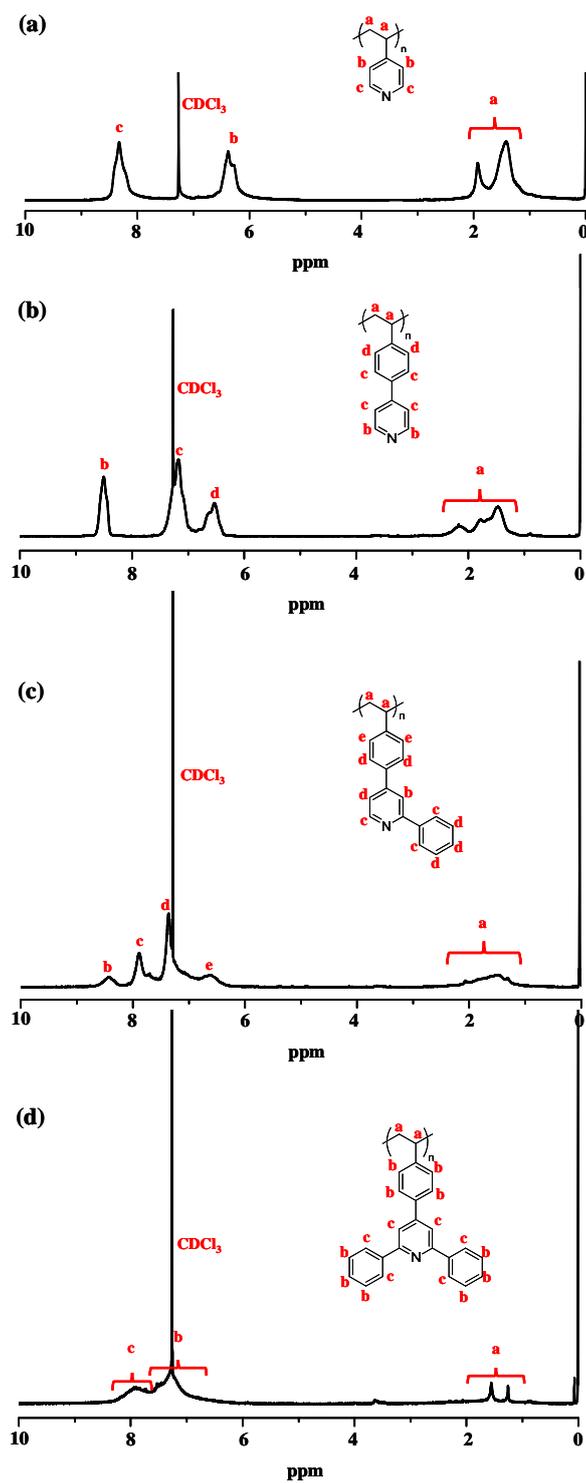
**Figure S14.**  $I$ - $V$  data analysis of the boron-doped Si/6F-Py- $i$ /Al devices in the OFF- and ON-states, which were measured with a compliance current of 0.01 A in air ambient condition: (a, b) 6F-Py-5 (19.92 nm thick); (c, d) 6F-Py-6 (19.97 nm thick); (e, f) 6F-Py-7 (20.19 nm thick). The symbols are the measured data; the solid red lines in the OFF-states (a, c, e) represent the fit lines using Ohmic conduction and trap-limited SCLC models whereas the red lines in the ON-states (b, d, f) represent the fit lines using Ohmic conduction model.



**Figure S15.**  $I$ - $V$  curves of the Al/PVPy- $i$ /Al and boron-doped Si/6F-Py- $i$ /Al devices with different electrode sizes, which were measured with a compliance current of 0.01 A in air ambient condition; ON-state: (a) PVPy-4 (10.69 nm thick); (b) 6F-Py-1 (21.76 nm thick).



**Figure S16.** <sup>1</sup>H NMR spectra of the vinyl monomers containing pyridine derivatives: (a) 4-(vinylphenyl)pyridine; (b) 2-phenyl-(4-vinylphenyl)pyridine; (c) 2,6-diphenyl-(4-vinylphenyl)pyridine. In the measurements, the solvent was CDCl<sub>3</sub>.



**Figure S17.**  $^1\text{H}$  NMR spectra of PVPy-*i* polymers: (a) PVPy-1; (b) PVPy-2; (c) PVPy-3; (d) PVPy-4. In the measurements, the solvent was  $\text{CDCl}_3$ .