Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

# $\pi$-Conjugated Polymers Derived from 2,5-Bis(2-decyltetradecyl)-3,6-di(selenophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione for High-Performance Thin Film Transistors

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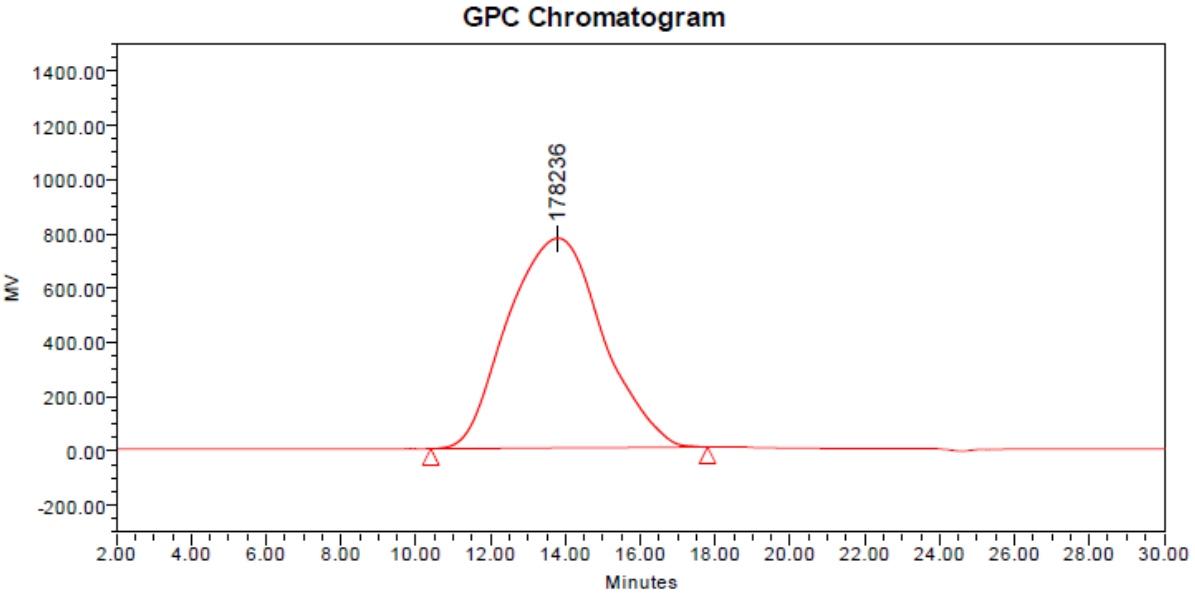
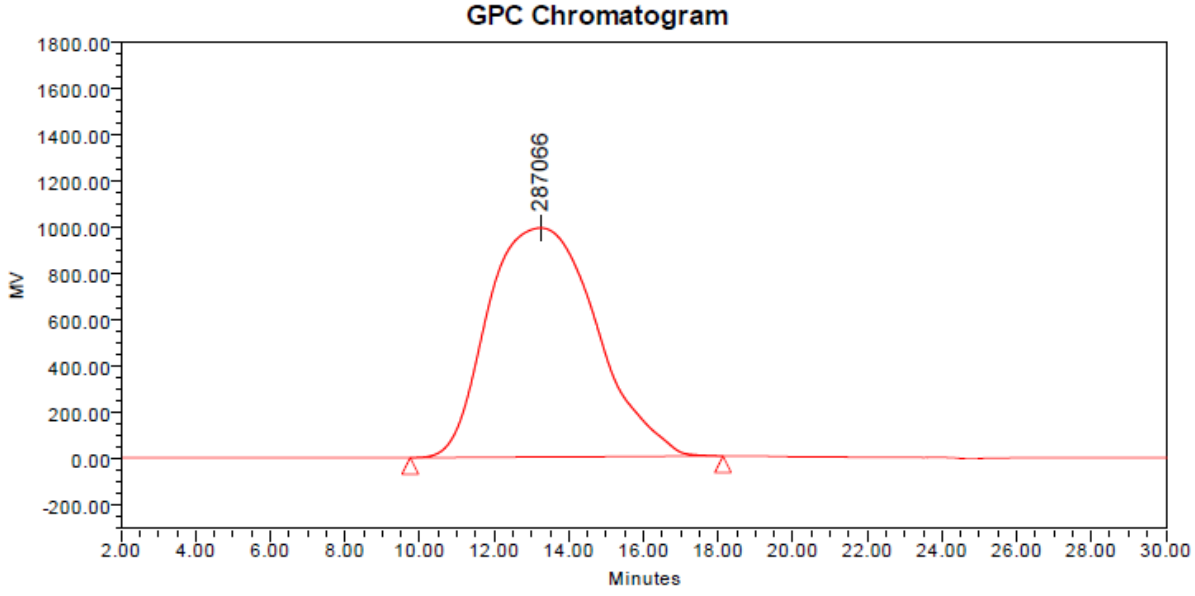



**Peak Results**

| | Peak name | Mn | Mw | MP | Polydispersity | Mz | Mz/Mw | % Area | Retention Time |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Peak1 | 114044 | 275339 | 178236 | 2.414320 | 532888 | 1.935389 | 100.00 | 13.802 |

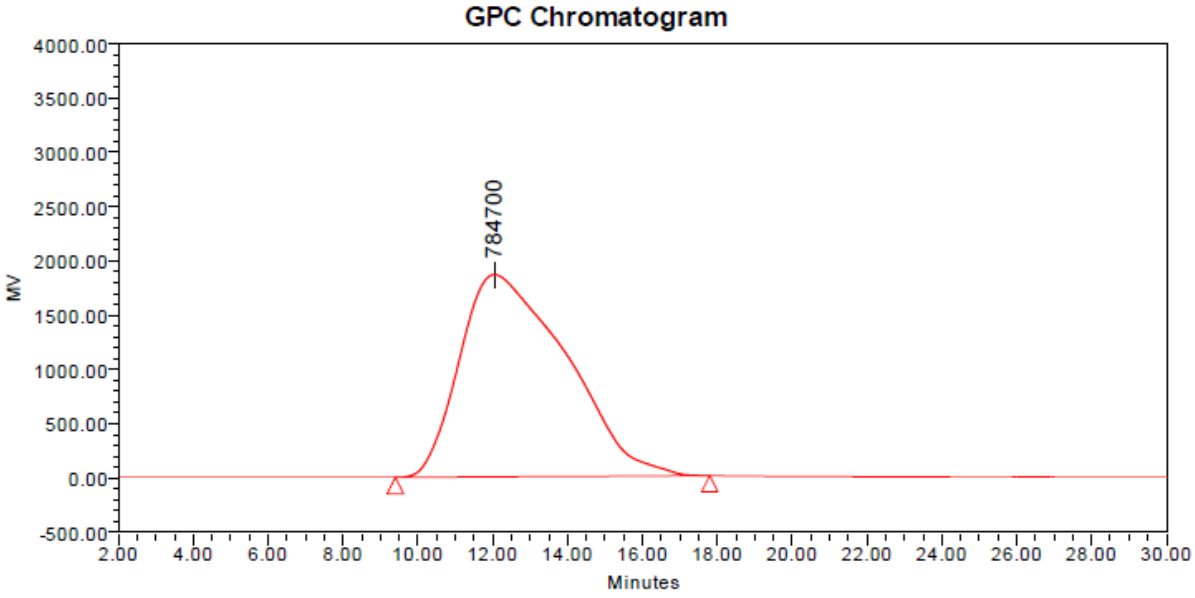
**Fig. S1** GPC chromatogram of DSDPP-BT.




**Peak Results**

| | Peak name | Mn | Mw | MP | Polydispersity | Mz | Mz/Mw | % Area | Retention Time |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Peak1 | 140732 | 405369 | 287066 | 2.880434 | 815905 | 2.012747 | 100.00 | 13.238 |

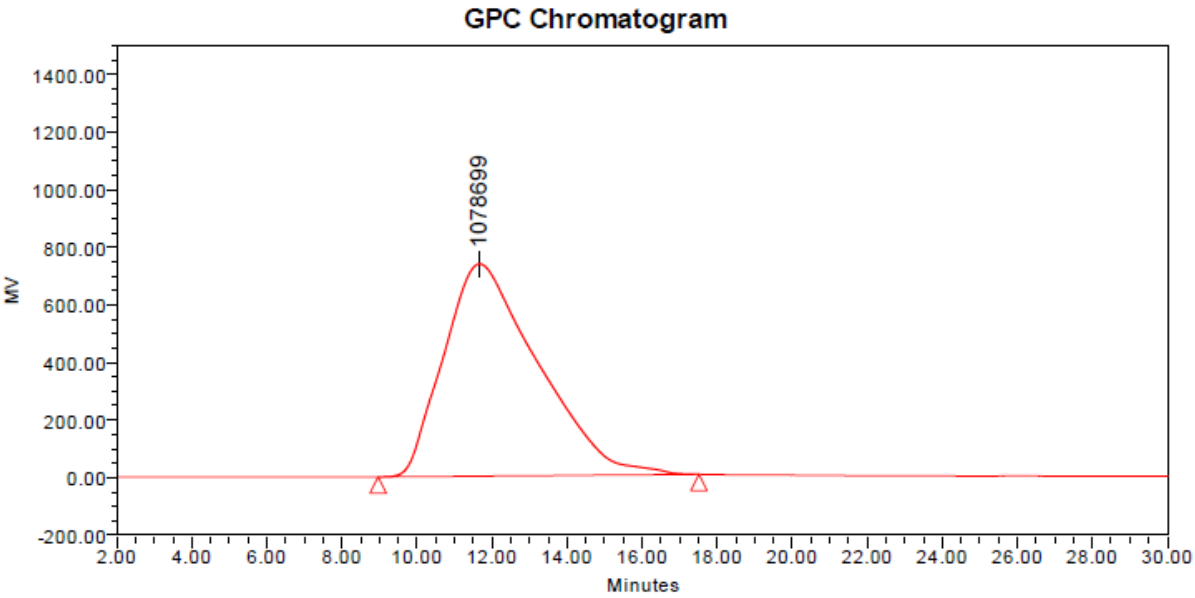
**Fig. S2** GPC chromatogram of DSDPP-TVT.




**Peak Results**

| | Peak name | Mn | Mw | MP | Polydispersity | Mz | Mz/Mw | % Area | Retention Time |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Peak1 | 217312 | 697204 | 784700 | 3.208302 | 1370194 | 1.965270 | 100.00 | 12.047 |

**Fig. S3** GPC chromatogram of DSDPP-BS.




**Peak Results**

| | Peak name | Mn | Mw | MP | Polydispersity | Mz | Mz/Mw | % Area | Retention Time |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Peak1 | 346983 | 1077195 | 1078699 | 3.104461 | 1969056 | 1.827947 | 100.00 | 11.670 |

**Fig. S4** GPC chromatogram of DSDPP-SVS.

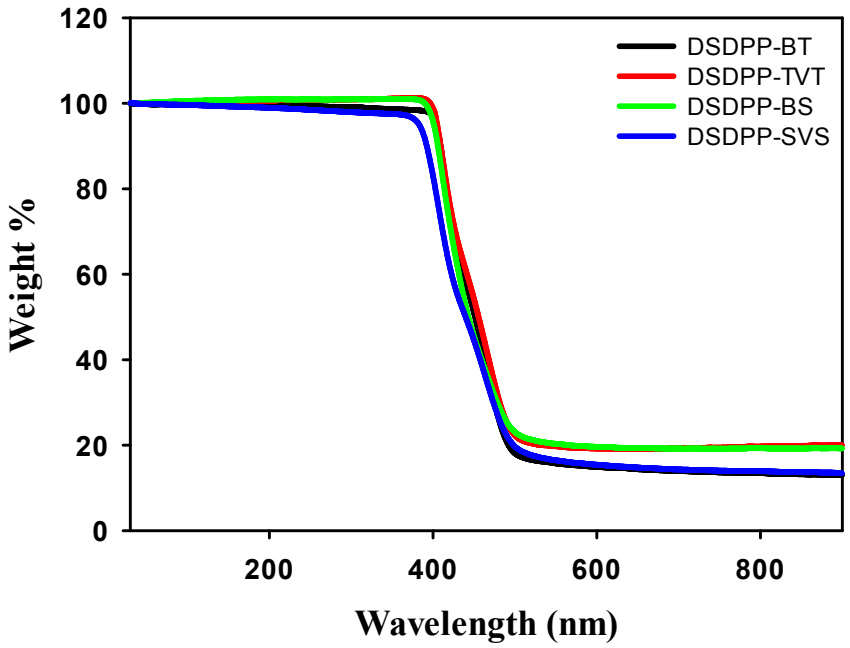



**Fig. S5** TGA thermograms of DSDPP-based polymers.

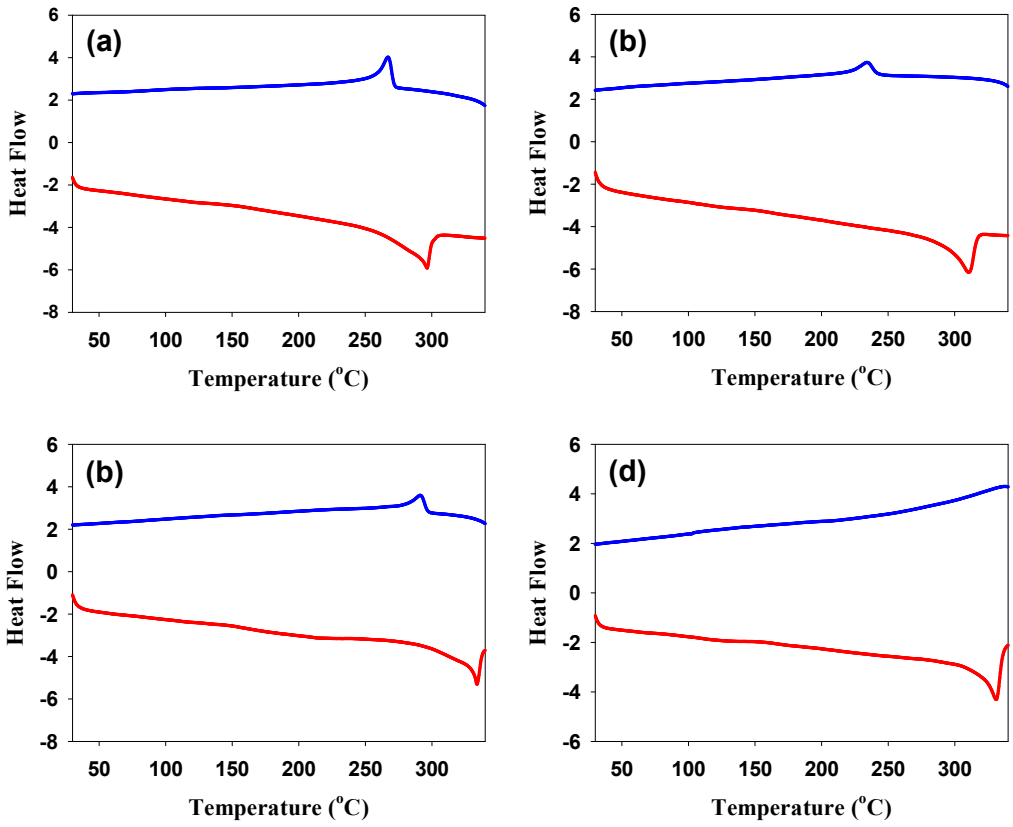



**Fig. S6** DSC thermograms of DSDPP-based polymers. (a): DSDPP-BT, (b): DSDPP-TVT, (c): DSDPP-BS, (d): DSDPP-SVS.

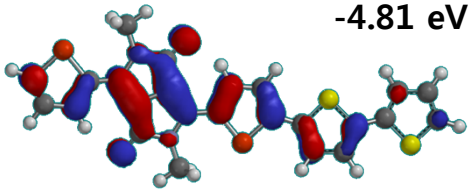
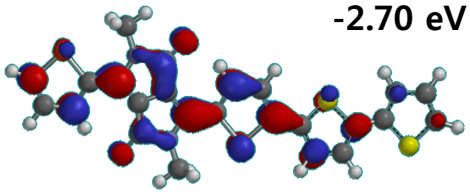
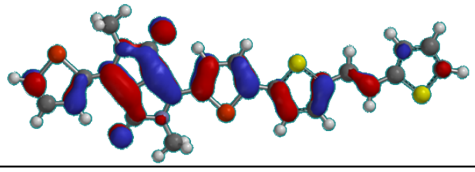
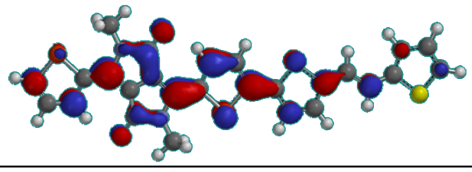
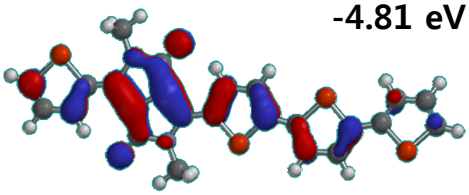
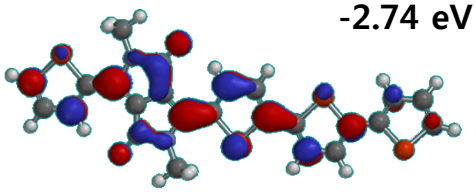
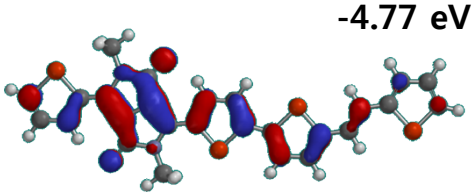
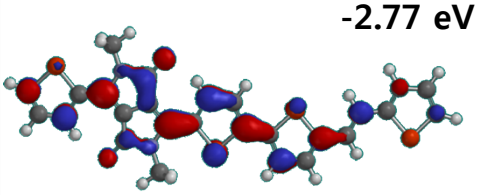
| | HOMO | LUMO |
|---|---|---|
| DSDPP-BT |  -4.81 eV |  -2.70 eV |
| DSDPP-TVT |  -4.75 eV |  -2.71 eV |
| DSDPP-BS |  -4.81 eV |  -2.74 eV |
| DSDPP-SVS |  -4.77 eV |  -2.77 eV |

**Fig. S7** Calculated molecular orbitals for the model of DSDPP-based polymers. (DFT method, B3LYP/6-31G*). The side chains were replaced with methyl groups to simplify the calculation.

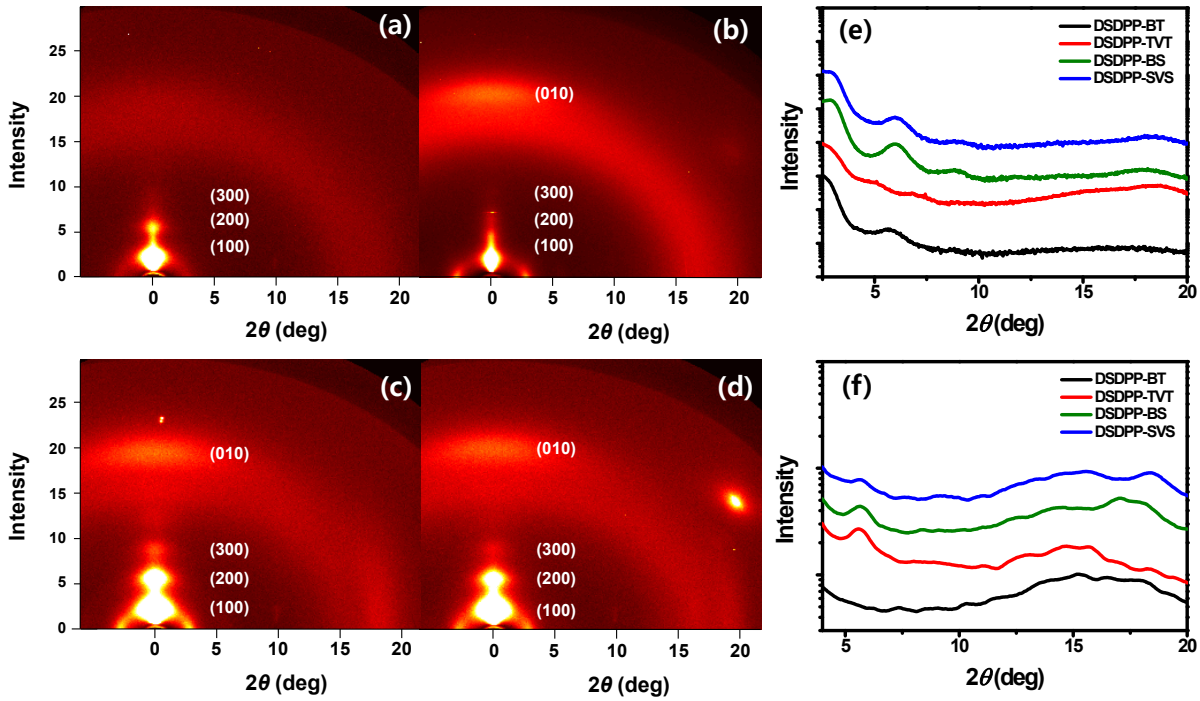



**Fig. S8** 2D GI-XRD patterns of as-spun films of DSDPP-based polymers : (a) DSDPP-BT, (b) DSDPP-TVT, (c) DSDPP-BS, and (d) DSDPP-SVS. (e) out-of-plane profiles, (f) in-plane profiles.

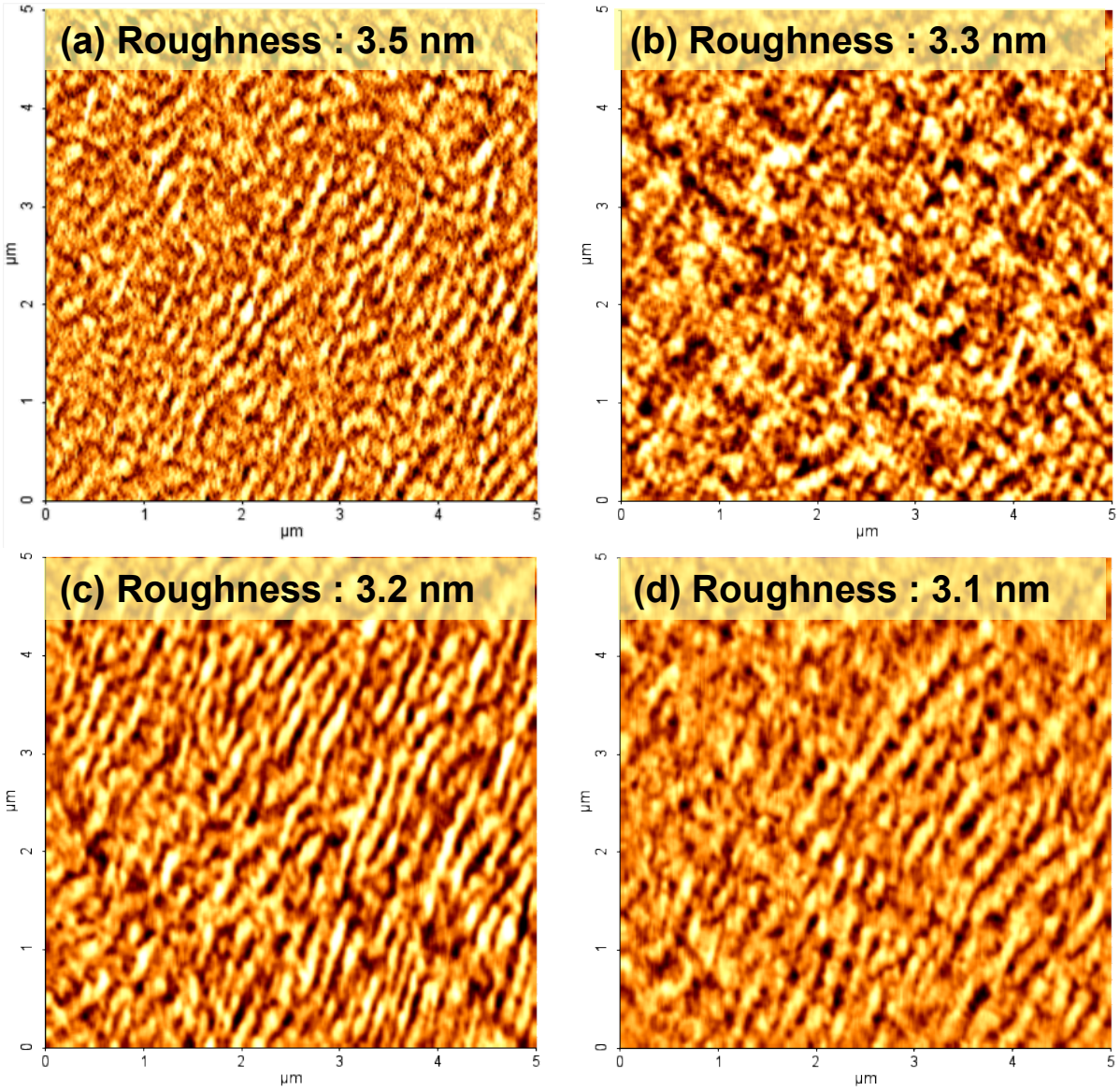



**Fig. S9** AFM images of the height of (a) DSDPP-BT, (b) DSDPP-TVT, (c) DSDPP-BS, and (d) DSDPP-SVS polymer as-cast thin films (5 × 5 $\mu$m).

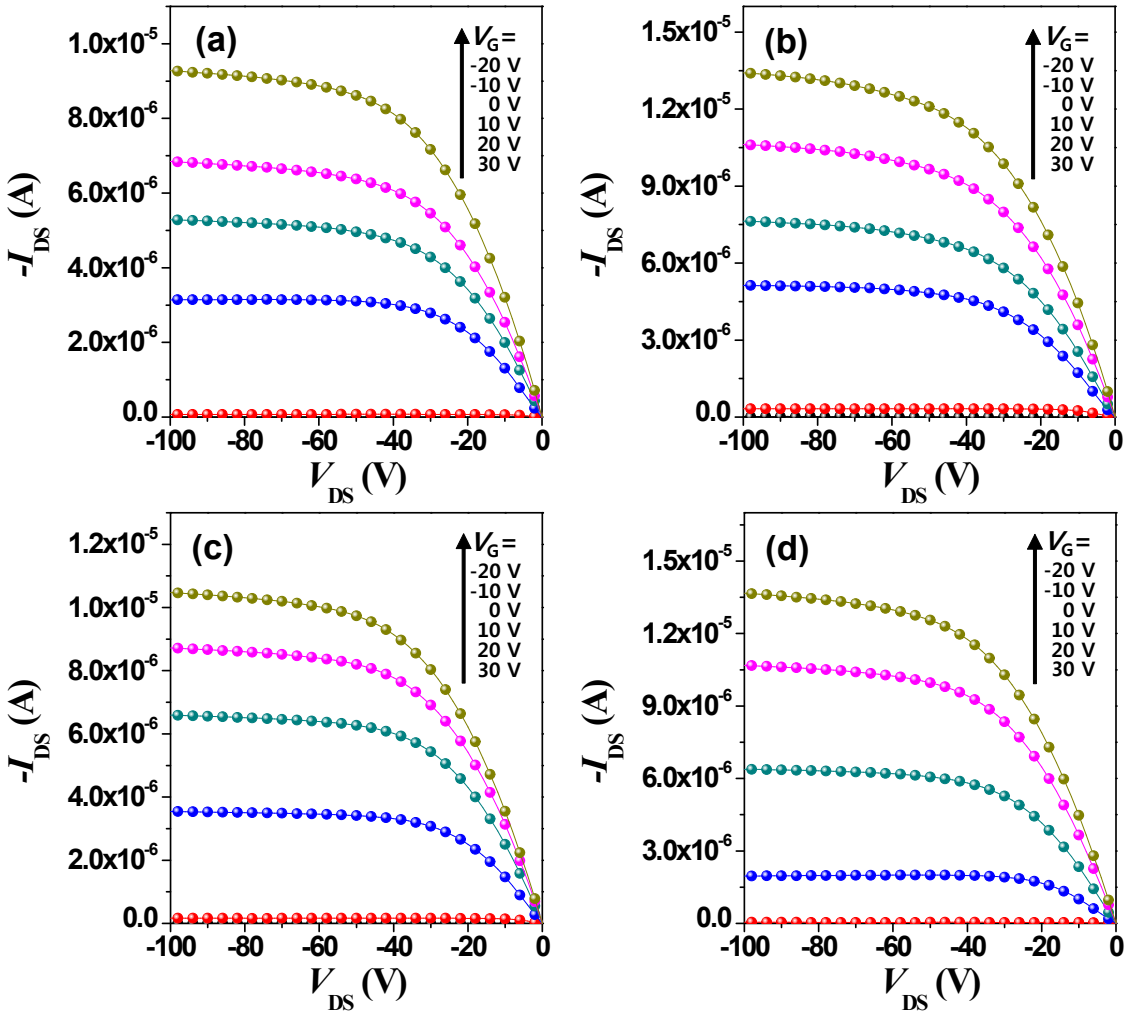



**Fig. S10** Output characteristics of DSDPP-based polymer TFT devices at $V_{DS}$= –100 V ($L$ = 100 $\mu$m, $W$ = 1500 $\mu$m). *sample: as-spun film. (a): DSDPP-BT, (b): DSDPP-TVT, (c): DSDPP-BS, (d): DSDPP-SVS.

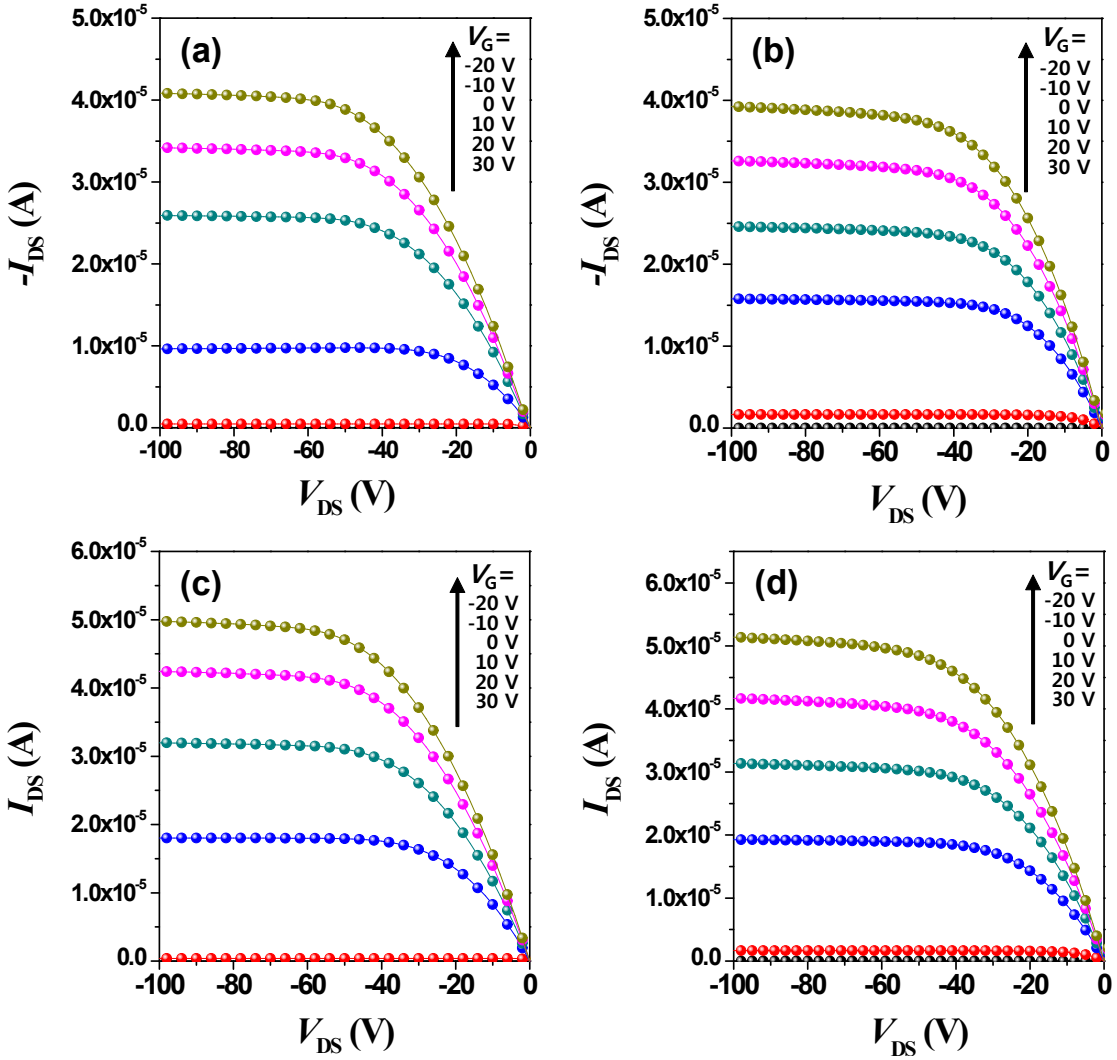



**Fig. S11** Output characteristics of DSDPP-based polymer TFT devices at $V_{DS}$= –100 V ($L$ = 100 $\mu$m, $W$ = 1500 $\mu$m) after thermal annealing at 200 °C. (a): DSDPP-BT, (b): DSDPP-TVT, (c): DSDPP-BS, (d): DSDPP-SVS.

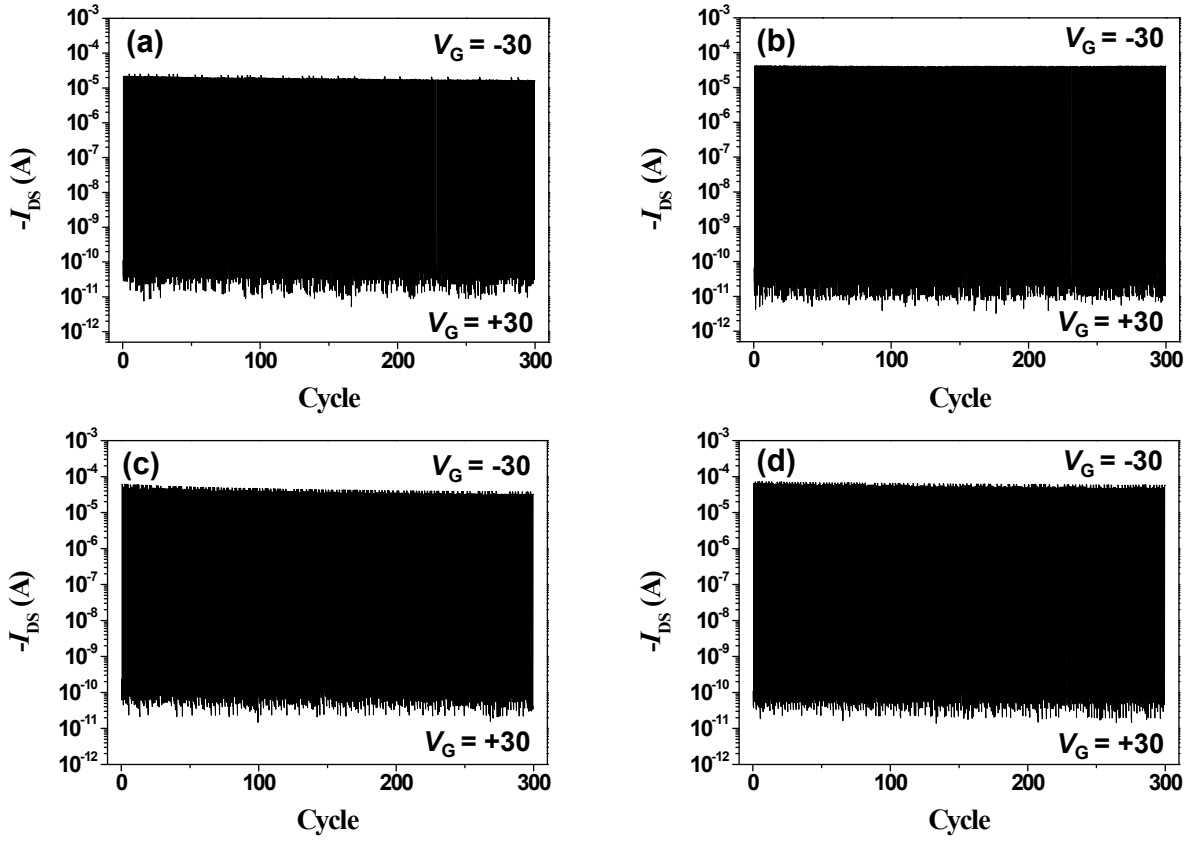



**Fig. S12** Operational stability of the DSDPP-based polymers device during current on/off cycle test in air (300 cycles, at $V_{DS}$ = -100 V, $V_G$ = 30 V (off) and $V_G$ = -30 V (on)). *TFTs made from thermally annealed films. ($T_{annealing}$ = 200 °C for 10 min). (a): DSDPP-BT, (b): DSDPP-TVT, (c): DSDPP-BS, (d): DSDPP-SVS.