

### Electronic Supplementary Information

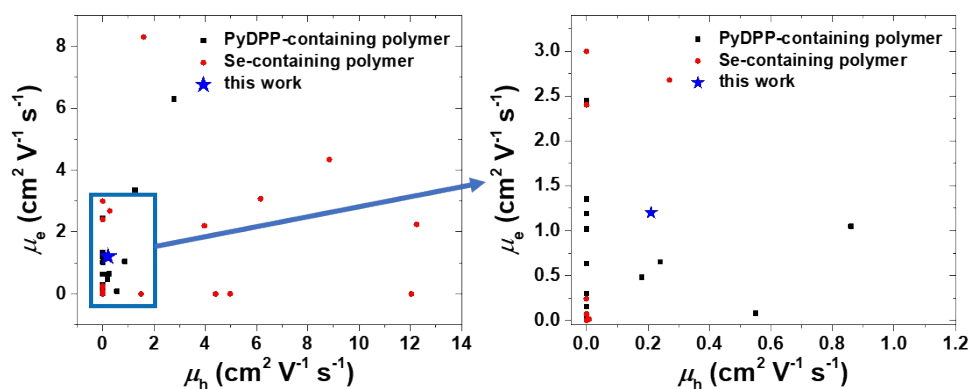
## **Understanding of Simultaneous Pyridine and Selenophene-containing Copolymers and their Polarity Conversion in Transistors**

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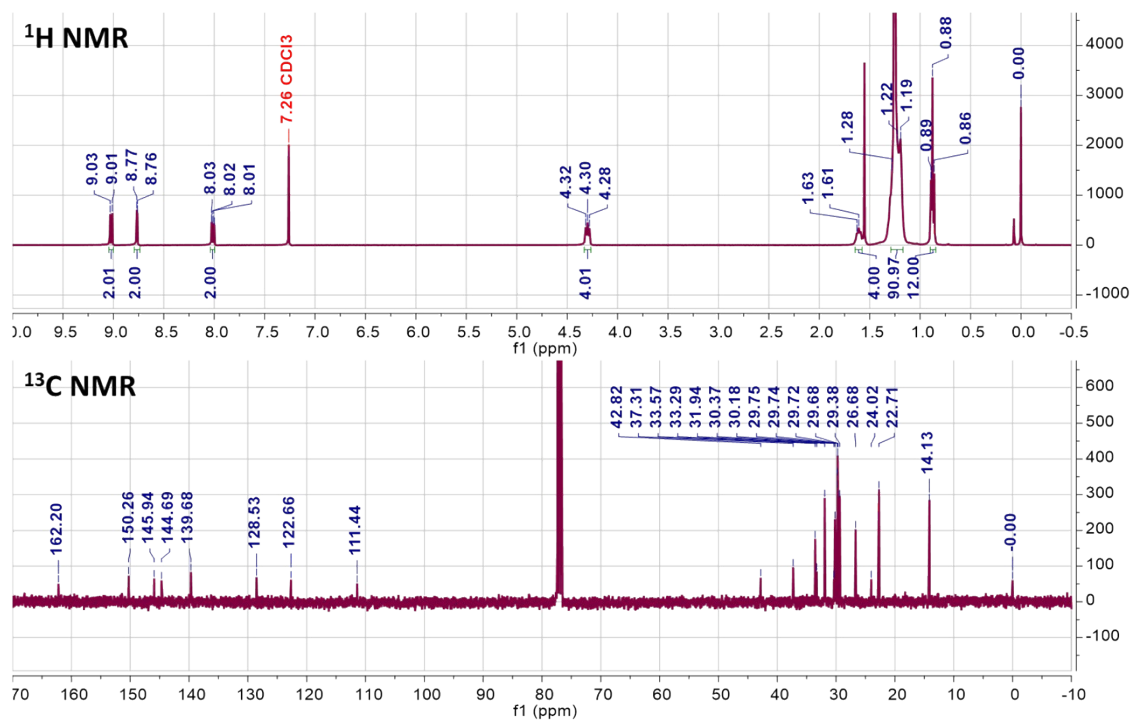


**Chart S1.** The charge carrier transports of PyDPP-containing and Se-containing polymers in OFET devices.

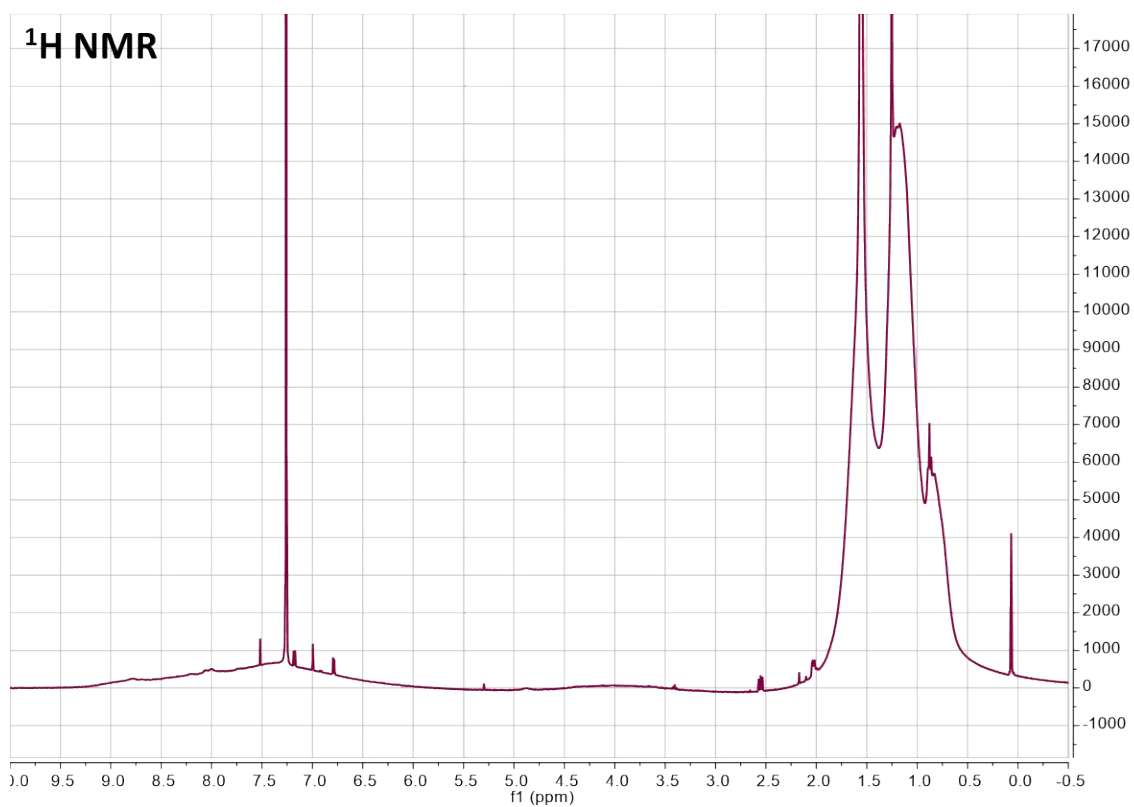
**Table S1.** The charge carrier transports of PyDPP-containing and Se-containing polymers in OFET devices.

| Name                       | unit  | $\mu_e$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) | $\mu_h$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) | ref            |
|----------------------------|-------|-------------------------------------------------------|-------------------------------------------------------|----------------|
| PDBPyTT                    | PyDPP | 3.36                                                  | 1.26                                                  | 1 <sup>1</sup> |
| DPPPy-BT2CN                | PyDPP | 0.3                                                   | -                                                     | 2 <sup>2</sup> |
| PDBPyDT2FBT                | PyDPP | 0.65                                                  | 0.24                                                  | 3 <sup>3</sup> |
| PDBPyBT                    | PyDPP | 6.3                                                   | 2.78                                                  | 4 <sup>4</sup> |
| PPyDPP1-BT                 | PyDPP | 1.05                                                  | 0.86                                                  | 5 <sup>5</sup> |
| PPyDPP1-4FBT               | PyDPP | 1.02                                                  | -                                                     | 5 <sup>5</sup> |
| PPyDPP2-4FBT               | PyDPP | 2.45                                                  | -                                                     | 5 <sup>5</sup> |
| PPyDPP1-4FTVT              | PyDPP | 1.19                                                  | -                                                     | 5 <sup>5</sup> |
| PPyDPP2-4FTVT              | PyDPP | 1.35                                                  | -                                                     | 5 <sup>5</sup> |
| PDPP[Py] <sub>2</sub> -T   | PyDPP | 0.63                                                  | -                                                     | 6 <sup>6</sup> |
| PDPP[Py] <sub>2</sub> -TF2 | PyDPP | 0.15                                                  | -                                                     | 6 <sup>6</sup> |
| PPyDPP-T                   | PyDPP | 0.004                                                 | 0.0008                                                | 7 <sup>7</sup> |
| PPyDPP-2FT                 | PyDPP | 0.021                                                 | 0.0003                                                | 7 <sup>7</sup> |
| PPyTDPP-TT                 | PyDPP | 0.48                                                  | 0.18                                                  | 8 <sup>8</sup> |
| PPyTDPP-BT                 | PyDPP | 0.08                                                  | 0.55                                                  | 8 <sup>8</sup> |
| PNDIBS                     | Se    | 0.07                                                  | -                                                     | 9 <sup>9</sup> |

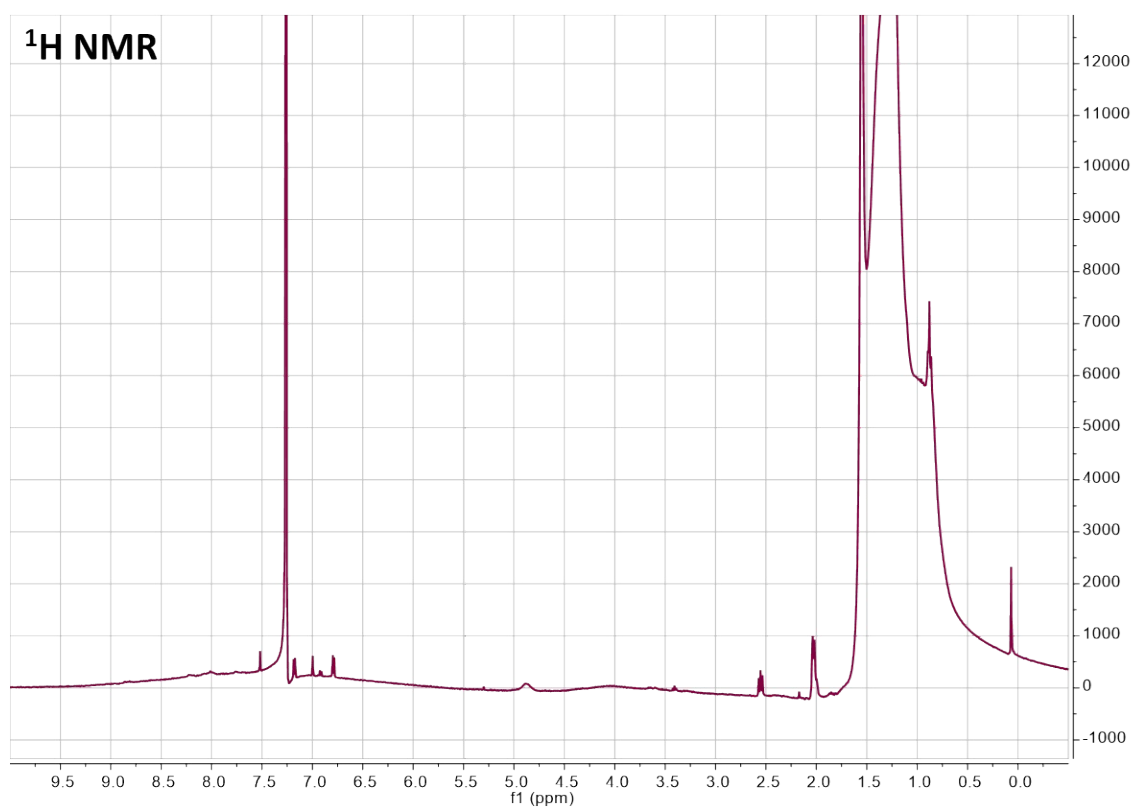
|                             |    |       |        |                  |
|-----------------------------|----|-------|--------|------------------|
| PNDI-SVS                    | Se | 2.4   | -      | 10 <sup>10</sup> |
| PTDPPSe-SiC4                | Se | 3.07  | 6.16   | 11 <sup>11</sup> |
| PTDPPSe-SiC5                | Se | 4.34  | 8.84   | 11 <sup>11</sup> |
| PTDPPSe-SiC6                | Se | 2.2   | 3.97   | 11 <sup>11</sup> |
| P-24-DPPDBSE                | Se | -     | 4.4    | 12 <sup>12</sup> |
| P-29-DPPDBSE                | Se | -     | 12.04  | 12 <sup>12</sup> |
| PNBS                        | Se | 8.3   | 1.6    | 13 <sup>13</sup> |
| PNBSF                       | Se | 3     | -      | 13 <sup>13</sup> |
| PDPPDTSE                    | Se | -     | 4.97   | 14 <sup>14</sup> |
| PCDSeBT                     | Se | -     | 0.001  | 15 <sup>15</sup> |
| PDPP(SE)- $\epsilon$ -C8C15 | Se | 2.25  | 12.25  | 16 <sup>16</sup> |
| eNDIBS                      | Se | 0.24  | -      | 17 <sup>17</sup> |
| PNBDO-STs                   | Se | 2.68  | 0.27   | 18 <sup>18</sup> |
| PNBDO-SSS                   | Se | 0.012 | 0.0084 | 18 <sup>18</sup> |
| P(DPP-alt-DTBSe)            | Se | -     | 1.5    | 19 <sup>19</sup> |



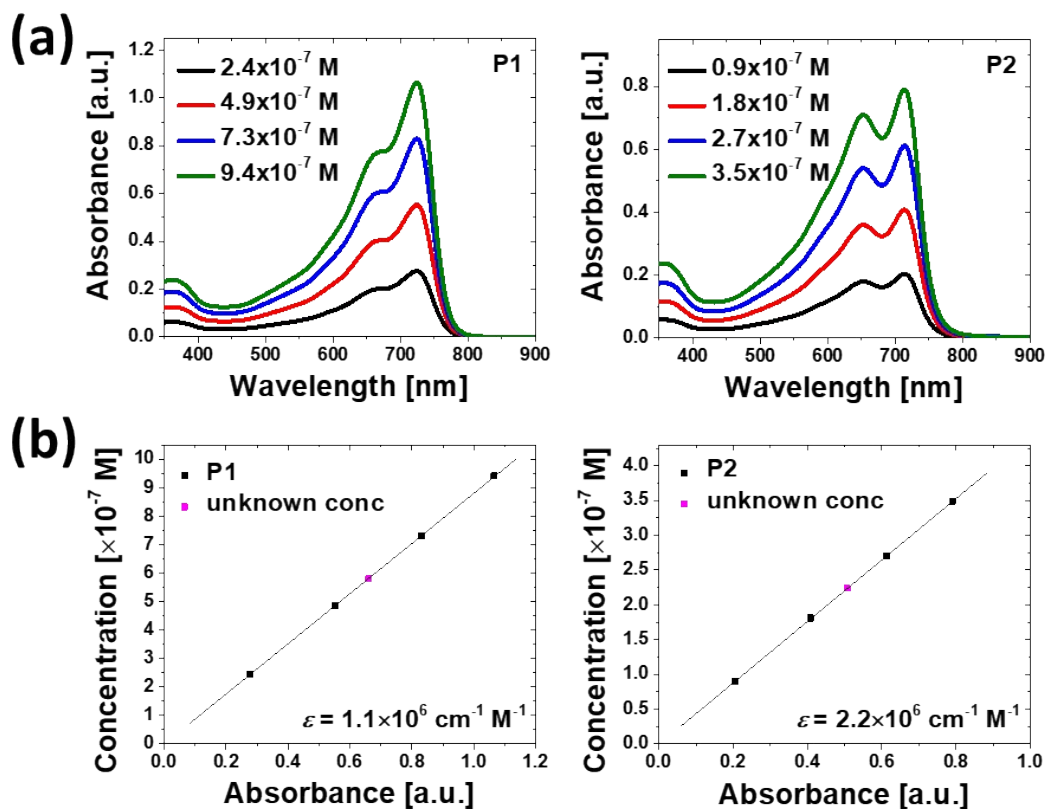
**Fig. S1** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy of 5PyDPP.



**Fig. S2** The <sup>1</sup>H NMR spectroscopy of P1.



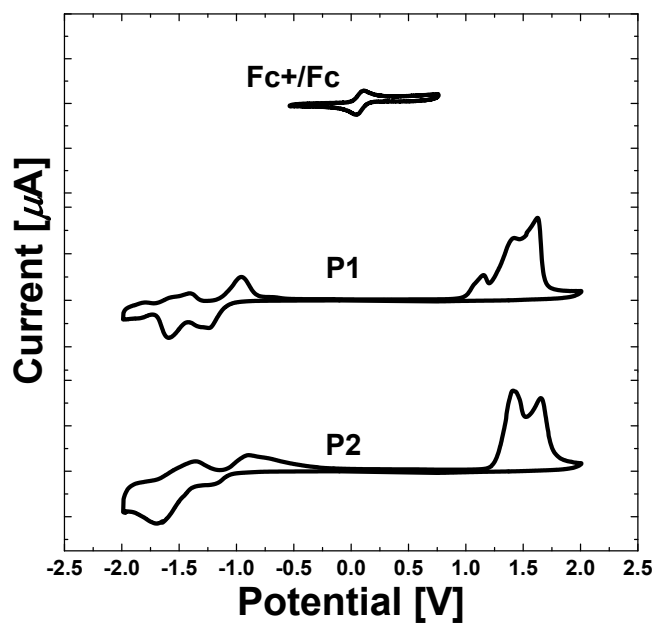
**Fig. S3** The <sup>1</sup>H NMR spectroscopy of P2.



**Fig. S4** (a) UV-vis absorption spectra at different concentrations of the polymers in chlorobenzene and (b) calibration plots of the concentration of chlorobenzene-polymer solutions according to the measured absorbances at each  $\lambda_{\text{max}}$ .

**Table S2.** Solubility of the Polymers in Chlorobenzene (mg/mL).

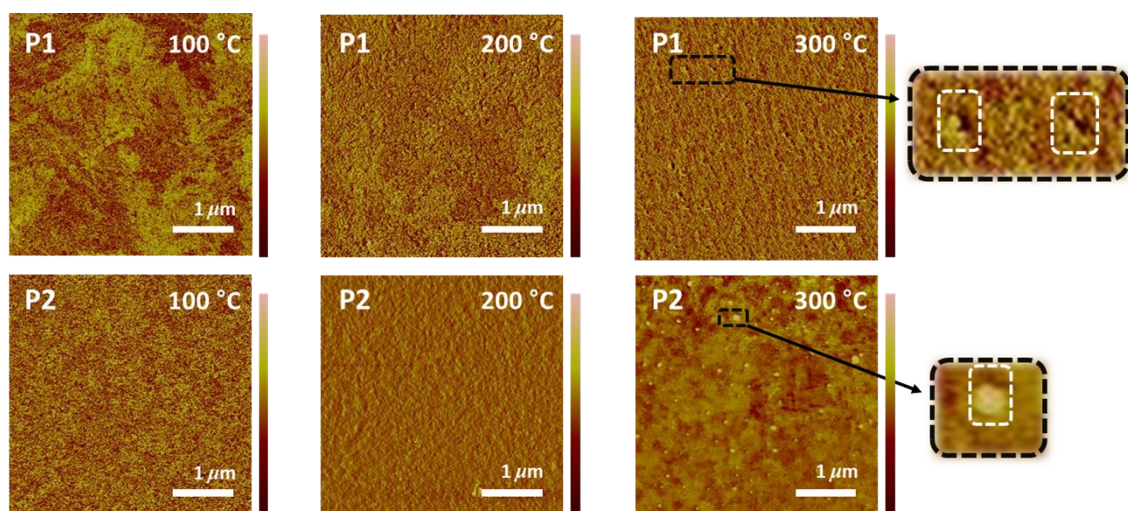
|                        | P1   | P2   |
|------------------------|------|------|
| Solubility<br>[mg/ mL] | 5.80 | 2.24 |



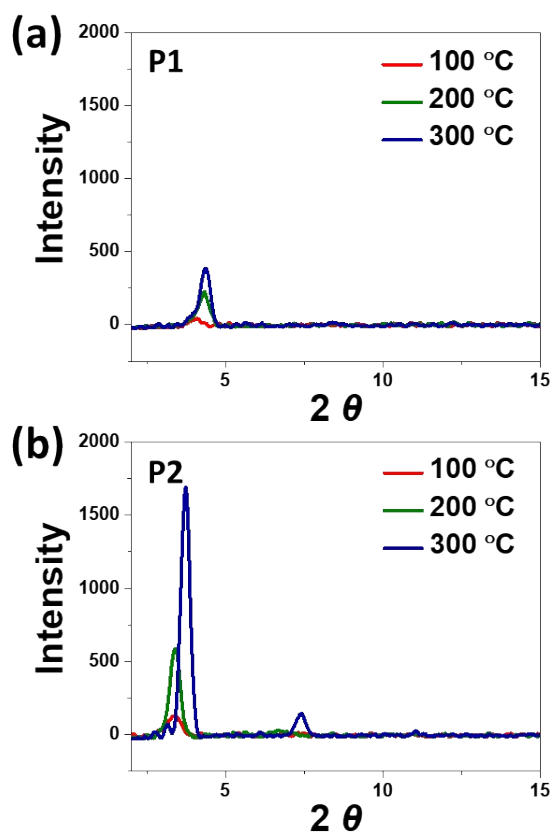
**Fig. S5** Cyclic voltammograms of the polymer films in  $n\text{-Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution (scan rate,  $100\text{ mVs}^{-1}$ ).

**Table S3.** Calculated dipole moments and energy levels of the BT units by DFT.

|           | Vector |        |        | Dipole Moment<br>[D] | $E_{\text{HOMO}}^{\text{DFT}}$<br>[eV] | $E_{\text{LUMO}}^{\text{DFT}}$<br>[eV] |
|-----------|--------|--------|--------|----------------------|----------------------------------------|----------------------------------------|
|           | x      | y      | z      |                      |                                        |                                        |
| <b>T1</b> | 1.4123 | 3.4552 | 2.3629 | 4.4178               | -5.11                                  | -3.51                                  |
| <b>T2</b> | 1.4103 | 4.1109 | 1.1614 | 4.4986               | -5.08                                  | -3.49                                  |



**Fig. S6** AFM phase images of annealed polymer films. The polymer films were formed by spin casting on SiO<sub>2</sub>/Si substrates.



**Fig. S7** 1D out-of-plane XRD patterns of spin-casted (a) P1 and (b) P2 films on SiO<sub>2</sub> substrates at different annealing condition.

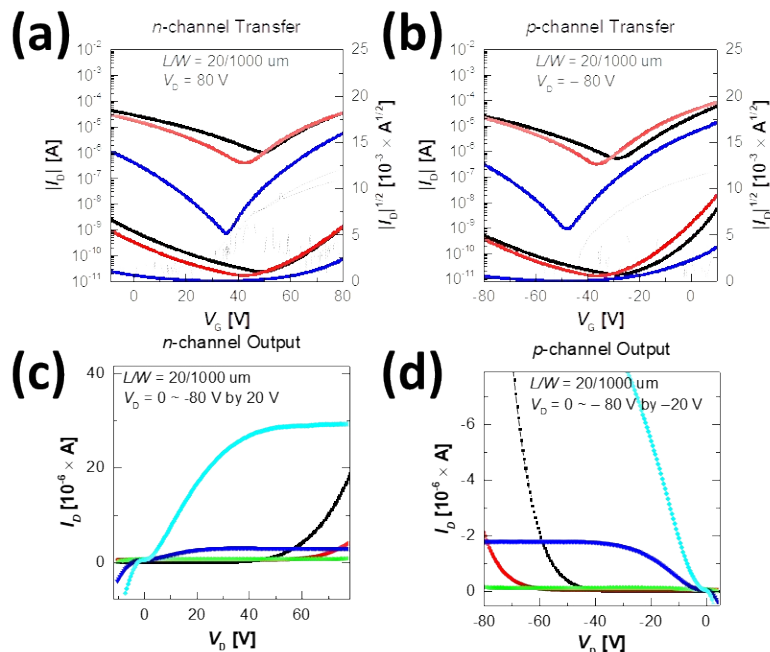
**Table S4.** Crystallographic parameters of spin-cast polymer films obtained from XRD at different annealing condition.

| polymer film | Temperature [°C] | $2\theta$ [°] | d-spacing [Å] |
|--------------|------------------|---------------|---------------|
| P1           | 100              | 4.115         | 21.46         |
|              | 200              | 4.3429        | 20.33         |
|              | 300              | 4.3718        | 20.20         |
| P2           | 100              | 3.3305        | 26.51         |
|              | 200              | 3.4173        | 25.83         |
|              | 300              | 3.7355        | 23.63         |

**Table S5.** 2D-GIXD crystallographic parameters of spin-cast polymer films at different annealing conditions.<sup>a</sup>

| Polymer film | $T_a$ [°C] | Lamellar spacing <sup>b</sup> |           |           | $\pi$ - $\pi$ spacing <sup>c</sup> |              |           |
|--------------|------------|-------------------------------|-----------|-----------|------------------------------------|--------------|-----------|
|              |            | $q_z$ [Å <sup>-1</sup> ]      | $d_z$ [Å] | $L_c$ [Å] | $q_{xy}$ [Å <sup>-1</sup> ]        | $d_{xy}$ [Å] | $L_c$ [Å] |
| P1           | As-cast    | 0.274                         | 22.90     | 122.2     | 1.741                              | 3.61         | 90.7      |
|              | 100        | 0.284                         | 22.15     | 162.6     | 1.747                              | 3.60         | 108.3     |
|              | 200        | 0.303                         | 20.77     | 309.0     | 1.743                              | 3.61         | 121.9     |
|              | 300        | 0.311                         | 20.22     | 387.1     | 1.738                              | 3.62         | 136.0     |
| P2           | As-cast    | 0.230                         | 27.36     | 167.1     | 1.758                              | 3.57         | 150.3     |
|              | 100        | 0.231                         | 27.18     | 217.5     | 1.758                              | 3.57         | 170.0     |
|              | 200        | 0.232                         | 27.06     | 242.5     | 1.754                              | 3.58         | 182.5     |
|              | 300        | 0.261                         | 24.09     | 425.8     | 1.754                              | 3.58         | 201.8     |

<sup>a</sup>The parameters were calculated from GIXD profiles; The parameters for <sup>b</sup>the lamellar spacing and <sup>c</sup>the  $\pi$ - $\pi$  spacing were derived from the peaks along  $q_z$  and  $q_{xy}$  axis, respectively.

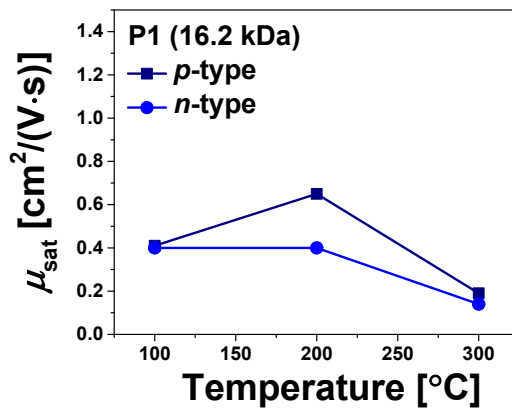


**Fig. S8** (a,b) Transfer and (c,d) output characteristics of the *n*-type and *p*-type devices of a low molecular weight P1 at different annealing conditions: 100 °C (black), 200 °C (red) and 300 °C (blue).

**Table S6.** Electrical characteristics of a low molecular weight P1 OFET Devices at different annealing conditions.

|                         | $T_a$<br>[°C] | <i>n</i> -channel                                             |                 |                  | <i>p</i> -channel                                             |                 |                  |
|-------------------------|---------------|---------------------------------------------------------------|-----------------|------------------|---------------------------------------------------------------|-----------------|------------------|
|                         |               | $\mu_e$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $V_{th}$<br>[V] | $I_{on}/I_{off}$ | $\mu_e$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $V_{th}$<br>[V] | $I_{on}/I_{off}$ |
| <b>P1</b><br>(16.2 kDa) | 100           | 0.4<br>(± 0.1)                                                | 47<br>(± 8)     | 10               | 0.41<br>(± 0.2)                                               | -26<br>(± 4)    | 10 <sup>2</sup>  |
|                         | 200           | 0.4<br>(± 0.02)                                               | 45<br>(± 2)     | 10 <sup>2</sup>  | 0.65<br>(± 0.03)                                              | -35<br>(± 0.1)  | 10 <sup>2</sup>  |
|                         | 300           | 0.14<br>(± 0.03)                                              | 36<br>(± 1)     | 10 <sup>4</sup>  | 0.19<br>(± 0.01)                                              | -35<br>(± 0.2)  | 10 <sup>4</sup>  |

4 devices for each condition were fabricated and used for mobility calculation.



**Fig. S9** Hole and electron mobilities of a low molecular weight P1 at different annealing conditions.

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