Green Synthesis of Lactone-Based Conjugated Polymers for n-Type Organic Electrochemical Transistors

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Supporting Information

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1. Cyclic Voltammetry

Figure S1. Cyclic voltammetry curves of $p$(C-T), $p$(N-T), $p$(C-2T), and $p$(C-g2T) employing with (a) 0.1 M tetrabutylammonium phosphate in acetonitrile and (b) 0.1 M aq. NaCl electrolyte.
**Figure S2.** CV measurements of the polymers on ITO (5 cycles) in 0.1 M NaCl aqueous solutions.

**Table S1.** Optoelectronic properties summary of four conjugated polymers.

| Active material | $\lambda_{\text{max film}}^a$ [nm] | $E_{\text{red,org}}^b$ [V] | $E_{\text{red,aq}}^c$ [V] | $\Delta E_{\text{red}}^d$ [V] | $E_{\text{LUMO}}^e$ [eV] | $E_{\text{HOMO}}^f$ [eV] | $E_{g,\text{opt}}^g$ [eV] |
|----------------|-----------------------------------|----------------------------|----------------------------|-----------------------------|-------------------------|-------------------------|-------------------------|
| p(C-T)         | 771                               | -0.11                      | -0.09                      | 0.02                        | -4.25                   | -5.53                   | 1.29                    |
| p(N-T)         | 774                               | +0.12                      | +0.16                      | 0.04                        | -4.48                   | -5.76                   | 1.27                    |
| p(C-2T)        | 765                               | -0.17                      | -0.20                      | -0.03                       | -4.19                   | -5.43                   | 1.24                    |
| p(C-g2T)       | 922                               | -0.30                      | -0.24                      | 0.06                        | -4.06                   | -4.98                   | 0.92                    |

a) Absorption spectra of polymers thin films determined employing b) 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile or c) 0.1 M aq. sodium chloride as the supporting electrolyte. d) The difference in reduction peak between in 0.1 M tetrabutylammonium hexafluorophosphate and 0.1 M aq. sodium chloride; e) $E_{\text{LUMO}}$ was determined by the equation $E_{\text{LUMO}} = -(4.8 + E_{\text{red,org}} \text{ vs } \text{Fc/Fc}^+)$, the onset of Fc/Fc$^+$ reduction peak is 0.44 V; f) $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{g,\text{opt}}$; g) Optical bandgap ($E_{g,\text{opt}}$) derived from the onset of the absorption spectra of polymer films using the equation: $E_{g,\text{opt}} = 1240 / \lambda_{\text{onset}}$.

2. **Spectroelectrochemical Measurements**

![graph](image_url)

**Figure S3.** Spectroelectrochemical measurements conducted for p(C-g2T) in 0.1 M aq. sodium chloride.
3. OECT Device Performance

Figure S4. $I_D^{0.5}$ vs $V_G$ curves for (a) $p$(C-T), (b) $p$(N-T) and (c) $p$(C-2T).

Table S2. OECT device performance.

| Polymer     | $\mu_{sat, OECT}$<sup>a</sup> [cm$^2$ V$^{-1}$ s$^{-1}$] | $C_{sat}$<sup>b</sup> [F cm$^{-3}$] | $\mu_{sat} \times C_{sat}$<sup>c</sup> [F cm$^{-1}$ V$^{-1}$ s$^{-1}$] | $\mu C_{sat}$<sup>d</sup> [F cm$^{-1}$ V$^{-1}$ s$^{-1}$] | $g_m, norm$<sup>e</sup> [S cm$^{-1}$] |
|-------------|-------------------------------------------------|-----------------|---------------------------------|---------------------------------|-----------------|
| P90<sup>a</sup> | 2.4 × 10$^{-4}$                               | 200             | 0.048                           | ~0.06                           | 0.021           |
| BBL<sup>b</sup> | 7 × 10$^{-4}$                                 | 930             | 0.65                            | ~0.6                            | 0.3             |
| PgNaN<sub>3</sub><sup>c</sup> | (6.50 ± 1.01) × 10$^{-3}$ | 100 ± 6        | 0.652 ± 0.107                   | 0.662 ± 0.113                   | 0.212           |
| f-BT2TEG-T<sub>d</sub> | 0.0449                                         | 52              | 2.33                            | 2.30                            | 0.27            |
| f-BT12TEG-FT<sub>d</sub> | 0.0299                                         | 443             | 13.24                           | 15.20                           | 4.60            |
| BBL<sub>152</sub><sup>e</sup> | NA                                             | 589             | NA                              | 25.9                            | 11.1            |
| $p$(C-T)    | 0.018                                          | 97±9            | 1.75                            | 6.7±0.9                         | 0.80±0.16       |
| $p$(N-T)    | 0.018                                          | 73±9            | 1.31                            | 4.3±0.6                         | 0.72±0.23       |
| $p$(C-2T)   | 0.011                                          | 53±9            | 0.58                            | 1.0±0.3                         | 0.14±0.04       |

a) Obtained from reference [S3]; b) Obtained from reference [S3]; c) Obtained from reference [S3];
d) Obtained from reference [S4]; e) Obtained from reference [S5]; f) Saturation mobility extracted from the slope of $I_D^{1/2}$ vs $V_G$; g) Volumetric capacitance measured with electrochemical impedance spectroscopy; h) The product of the saturation mobility and the
volumetric capacitance. i) Extracted from the slope of OECT transfer curves and normalized by channel thickness and aspect ratio. j) maximum transconductance normalized device size.

4. Electrochemical Impedance Spectroscopy

Figure S5. Electrochemical impedance spectroscopy. a, c, e) Bode plots (log|Z| vs frequency, and phase vs. frequency) and effective capacitance for p(C-T), p(N-T), p(C-2T). All the data were recorded at an offset bias ($V_{\text{offset}}$) ($V_{\text{offset}}$ = -0.4 V vs. Ag/AgCl). The results fit $R_s(R_p||C)$ equivalent circuit where $R_s$ is the series resistance, $R_p$ and $C$ describe the parallel resistance and polymer film capacitance, respectively.; b, d, f) Capacitance fits of polymer films with different volumes.
5. Stability

Figure S6. Operational stability for a-c) over 30 minutes and d-f) first few switching cycles for a,d) p(C-T), b,e) p(N-T) and c,f) p(C-2T). OECTs retained around 12.5 %, 63.0 % and 72 % for p(C-T), p(N-T), and p(C-2T), respectively. The percentages were calculated by measuring the I_{D,0}/I_D after over 30 min of continuous ON/OFF switching.

Figure S7. Operational stability for over 1 hour for a) p(C-T), b) p(N-T) and c) p(C-2T). OECTs retained around 15.9 %, 71.3 % and 67.5 % for p(C-T), p(N-T), and p(C-2T), respectively. Percentage was calculated by measuring the I_{D,0}/I_D after over 1 hour of continuous ON/OFF switching. OECT were made using interdigitated electrodes having a
channel length of $L = 20 \, \mu m$ and width of $W = 39000 \, \mu m$ (39 parallel channels having $W = 1000 \, \mu m$).
6. Atomic Force Microscopy

Figure S8. AFM images of thin film for p(C-g2T) in (a) pristine, (b) hydrated, and (c) doped state.

7. GIWAXS Data

Figure S9. Two-dimensional grazing incidence X-ray scattering map of p(C-g2T)
Figure S10. One-dimensional grazing incidence X-ray scattering linecuts profiles along in-plane and out-of-plane directions.

Table S3. Summary of GWIAXS data, peak fit center, d-spacing and coherence length, dominant textures

| Polymers   | \( q_{(100)} \) (Å\(^{-1}\)) | \( d_{(100)} \) (Å) | \( L_{C(100)} \) (Å) | \( q_{(010)} \) (Å\(^{-1}\)) | \( d_{(010)} \) (Å) | \( L_{C(010)} \) (Å) | dominant texture               |
|------------|-------------------------------|----------------------|-------------------|-------------------------------|----------------------|-------------------|-------------------------------|
| p(C-T)     |                               |                      |                   |                               |                      |                   |                               |
| in-plane   | 0.29                          | 21.66                | 56.31             | 1.81                          | 3.47                 | 28.98             | Mixed edge-on/face-on         |
| out-of-plane | 0.33                         | 19.03                | 59.49             | 1.81                          | 3.47                 | 25.63             |                               |
| p(N-T)     |                               |                      |                   |                               |                      |                   |                               |
| in-plane   | 0.28                          | 22.43                | 51.38             | 1.83                          | 3.43                 | 33.56             | Mixed edge-on/face-on         |
| out-of-plane | 0.32                         | 19.63                | 76.09             | 1.83                          | 3.43                 | 28.87             |                               |
| p(C-2T)    |                               |                      |                   |                               |                      |                   |                               |
| in-plane   | -                             | -                    | -                 | 1.79                          | 3.51                 | 49.29             | edge-on                      |
| out-of-plane | 0.33                         | 19.03                | 87.10             | -                             | -                    |                   |                               |
| p(C-g2T)   |                               |                      |                   |                               |                      |                   |                               |
| in-plane   | -                             | -                    | -                 | 1.80                          | 3.49                 | 40.82             | edge-on                      |
| out-of-plane | 0.32                         | 19.33                | 87.10             | -                             | -                    |                   |                               |
8. Monomers and Polymers Synthesis.

8a. Monomer Synthesis

Scheme S1. Synthetic route to M1.

Reaction conditions: i) K$_2$CO$_3$, tetrabutylammonium bromide, DMF, RT; ii) Pd$_2$(dba)$_3$, P(o-tol)$_3$, toluene, reflux.

Compound 1 was purchased from Bide Pharmatech Co., Ltd., 2 was synthesized according to the literature.\[^{[S6]}\]

Compound 3: 6-bromoindoline-2,3-dione (1, 1.00 g, 9.99 mmol, 1.0 equiv.), 2 (2.50 g, 5.75 mmol, 1.3 equiv.), and potassium carbonate (1.83 g, 13.26 mmol, 3.0 equiv.) were mixed under N$_2$ atmosphere. DMF (50 ml) and tetrabutylammonium bromide (0.14 g, 0.442 mmol, 0.1 equiv.) were added and reacted under stirring at room temperature for 5 h. DMF was removed under vacuum. The residue was purified by silica gel column chromatography with eluent (EtOAc: CH$_2$Cl$_2$ = 1: 3) to give 1.10 g (50 %) compound 3 as a yellow liquid. $^1$H NMR (400 MHz, Chloroform-\(d\), 300K) $\delta$ (ppm): 7.43 (d, $J$ = 7.9 Hz, 1H), 7.34 (d, $J$ = 1.4 Hz, 1H), 7.24 (dd, $J$ = 7.9, $J$ = 1.4 Hz, 1H), 3.90 (t, $J$ = 5.1 Hz, 2H), 3.74 (t, $J$ = 5.1 Hz, 3H), 3.67 – 3.57 (m, 18H), 3.54 (dd, $J$ = 5.7, 3.6 Hz, 2H), 3.37 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, 300K) $\delta$ (ppm): 182.17, 158.27, 152.49, 133.37, 126.80, 125.95, 116.22, 115.42, 71.96, 70.85, 70.72, 70.66, 70.63, 70.59, 70.58, 70.53, 69.07, 59.04, 40.94. HRMS (ESI): m/z: calculated for C$_{21}$H$_{30}$BrNO$_8$Na: 526.1155, ([M+Na]$^+$) found: 526.1040.
Figure S10. $^1$H NMR of 3 in CDCl$_3$ at 300 K.

Figure S11. $^{13}$C NMR of 3 in CDCl$_3$ at 300 K.
Synthesis of M1: 3 (115.00 mg, 0.229 mmol, 2.0 equiv.), 2,5-bis(trimethylstannyldithiophene (46.83 mg, 0.114 mmol, 1.0 equiv.), Pd2(dba)3 (5.22 mg, 5.7×10^-3 mmol, 0.05 equiv.), and P(o-tol)3 (10.00 mg) were added to a microwave vial. The tube was sealed and flushed with argon. Degassed toluene (5.0 mL) was added, and the mixture was further degassed for 5 mins. The reaction was then heated to 110 °C for 12 h. Toluene was removed under vacuum. The residue was purified by silica gel column chromatography to give 63.64 mg (60 %) M1 as a red-brown liquid.

^1H NMR (500 MHz, Chloroform-d, 300K): 7.61 (d, J = 7.9 Hz, 2H), 7.59 (s, 2H), 7.39 – 7.35 (m, 4H), 4.00 (t, J = 4.8 Hz, 4H), δ (ppm) 3.80 (t, J = 4.9 Hz, 4H), 3.69 – 3.47 (m, 40H), 3.34 (s, 6H). ^13C NMR (126 MHz, CDCl3, 300K) δ (ppm) 182.06, 158.89, 152.36, 144.61, 142.84, 127.59, 125.93, 120.61, 116.76, 108.08, 71.90, 70.71, 70.61, 70.56, 70.55, 70.51, 70.48, 69.07, 59.02, 40.67. HRMS (ESI): m/z: calculated for C46H62N2O16SNa: 953.3820, ([M+Na]^+) found: 953.3714.

Figure S12. ^1H NMR of M1 in CDCl3 at 300 K.
Figure 13. $^1$H NMR of M1 in CDCl$_3$ at 300 K.

Scheme 2. Synthetic routes of M2

Reaction conditions: iii) NaH, DMF, 0 °C; iv) CrO$_3$, H$_2$O/CH$_3$COOH, DMF, 100 °C; v) Pd$_2$(dba)$_3$, P(o-tol)$_3$, toluene, reflux.

Compound 4 was purchased from Bide Pharmatech Co., Ltd.

Compound 5: 6-bromo-1H-pyrrolo[2,3-b]pyridine 4 (0.40 g, 2.03 mmol, 1.0 equiv.), 2 (1.15 g, 2.64 mmol, 1.3 equiv.), potassium carbonate (1.83 g, 13.26 mmol, 3.0 equiv.) were mixed under N$_2$ atmosphere. THF (30.0 ml) was added and reacted at room temperature for 5 h. DMF was removed under vacuum. The residue was purified by silica gel column chromatography with eluent (EtOAc: CH$_2$Cl$_2$ = 1: 3) to give 0.58 g (60 %) compound 5 as a colorless liquid. $^1$H NMR (400 MHz, chloroform-$d$, 300K) $\delta$ (ppm) 7.73 (d, $J = 8.1$ Hz, 1H), 7.35 (d, $J = 3.5$ Hz, 1H), 7.18 (d, $J = 8.1$ Hz, 1H), 6.41 (d, $J = 3.5$ Hz, 1H), 4.44 (t, $J = 5.2$ Hz,
2H), 3.82 (t, \( J = 5.2 \) Hz, 2H), 3.70 – 3.57 (m, 18H), 3.54 (dd, \( J = 5.7, 3.6 \) Hz, 2H), 3.37 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 300K) \( \delta \) (ppm) 134.33, 130.77, 129.57, 119.31, 119.21, 99.64, 71.94, 70.60, 70.58, 70.53, 70.51, 70.26, 59.06, 44.33. HRMS (ESI): m/z: calculated for C\(_{20}\)H\(_{31}\)BrN\(_2\)O\(_6\): 474.1365 ([M+H])\(^+\) found: 475.1437.

**Figure S14.** \(^1\)H NMR of 5 in CDCl\(_3\) at 300 K.
Figure S15. $^{13}$C NMR of 5 in CDCl$_3$ at 300 K.

Synthesis of M2: 3 (120.00 mg, 0.238 mmol, 2.0 equiv.), 2,5-bis(trimethylstannyl)thiophene (46.83 mg, 0.114 mmol, 1.0 equiv.) Pd$_2$(dba)$_3$ (5.00 mg, 6∙$10^{-3}$ mmol, 0.05 equiv.), and P(o-tol)$_3$ (10.00 mg) were added to a microwave vial. The tube was sealed and flushed with nitrogen. Degassed toluene (5.0 mL) was added, and the mixture was further degassed for 15 min. The reaction was then heated to 110 °C for 12 h. Toluene was removed under vacuum. The residue was purified by silica gel column chromatography with eluent (CH$_2$Cl$_2$: MeOH = 20:1) to give 55.48 mg (50 %) M2 as a red brown liquid. $^1$H NMR (400 MHz, chloroform-d, 300K), δ (ppm) 7.87 (d, $J = 7.8$ Hz, 2H), 7.83 (s, 2H), 7.47 (d, $J = 7.8$ Hz, 2H), 4.16 (t, $J = 5.7$ Hz, 4H), 3.93 (t, $J = 5.7$ Hz, 4H), 3.76 – 3.67 (m, 4H), 3.66 – 3.46 (m, 36H), 3.36 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 300K) δ (ppm) 180.49, 164.09, 159.08, 157.23, 147.62, 133.64, 129.32, 114.43, 110.75, 71.94, 70.61, 70.55, 70.53, 70.05, 66.87, 59.05, 38.43. HRMS (ESI): m/z: calculated for C$_{44}$H$_{66}$N$_4$O$_9$SNa, 955.3725, ([M+Na]$^+$) found: 955.3617.
Figure S16. $^1$H NMR of M2 in CDCl$_3$ at 300 K.

Figure S17. $^{13}$C NMR of M2 in CDCl$_3$ at 300 K.
Scheme S2. Synthetic route of S3.

Reaction condition: vi) Pd$_2$(dba)$_3$, P(o-tol)$_3$, toluene, reflux.

Synthesis of M3: 3 (122.5 mg, 0.243 mmol, 2.0 equiv.), 5,5'-bis(trimethylstanny)-2,2'-bithiophene 4 (60.13 mg, 0.122 mmol, 1.0 equiv.) 4 (51.02 mg, 0.122 mmol, 1.0 equiv.), Pd$_2$(dba)$_3$ (5.59 mg, 6.1×10$^{-3}$ mmol, 5 % equiv.) and P(o-tol)$_3$ (11.17 mg) were added to a microwave vial. The tube was sealed and flushed with argon. Degassed toluene (5 mL) was added, and the mixture further degassed. The reaction was then heated to 110 °C for 12 h. Toluene was removed under vacuum. The residue was purified by silica gel column chromatography with eluent (CH$_2$Cl$_2$: MeOH = 20:1) to give 86.63 g (70 %) compound M3 as red brown liquid. $^1$H NMR (500 MHz, chloroform-d, 300K) δ (ppm) 7.61 (d, $J = 7.7$ Hz, 2H), 7.51 (d, $J = 3.8$ Hz, 2H), 7.37 – 7.28 (m, 6H), 4.00 (t, $J = 5.0$ Hz, 4H), 3.80 (t, $J = 5.1$ Hz, 4H), 3.69 – 3.49 (m, 40H), 3.35 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 300 K) δ (ppm) 181.98, 159.02, 152.38, 143.08, 142.19, 138.98, 127.27, 125.89, 120.32, 116.43, 107.84, 95.55, 71.93, 70.77, 70.66, 70.61, 70.60, 70.54, 70.53, 69.19, 59.05, 40.69. HRMS (ESI): m/z: calculated for C$_{50}$H$_{64}$O$_6$S$_2$Na: 1035.3697, ([M+Na]$^+$) found: 1035.3594.
Figure S18. $^1$H NMR of M3 in CDCl$_3$ at 300 K.

Figure S19. $^{13}$C NMR of M3 in CDCl$_3$ at 300 K.

Scheme S3. Synthetic route of S4.
Reaction condition: vii) Pd$_2$(dba)$_3$, P(o-tol)$_3$, toluene, reflux.

7 was synthesized according to the literature. [S5]

Synthesis of M4: 3 (50.70 mg, 0.122 mmol, 2.0 equiv.), 5 (44.59 mg, 0.061 mmol, 1.0 equiv.), Pd$_2$(dba)$_3$ (2.79 mg, 3.1×10$^{-3}$ mmol, 5 % equiv.), Pd$_2$(dba)$_3$ (2.79 mg, 3.1×10$^{-3}$ mmol, 5 % equiv.) and P(o-tol)$_3$ (5.59 mg) were added to a microwave vial. The tube was sealed and flushed with argon. Degassed toluene (5.0 mL) was added, and the mixture further degassed. The reaction was then heated to 110 °C for 12 h. Toluene was removed under vacuum. The residue was purified by silica gel column chromatography with eluent (CH$_2$Cl$_2$: MeOH = 15:1) to give 45.77 mg (60 %) compound M4 as brow liquid.

$^1$H NMR (400 MHz, chloroform-$d$, 300K) δ (ppm) 7.58 (d, $J = 7.9$ Hz, 2H), 7.39 (s, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.28 (s, 2H), 4.44 (t, 4H), 4.00 (t, 8H), 3.86 – 3.75 (m, 8H), 3.68 – 3.50 (m, 42H), 3.36 (d, $J = 4.3$ Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$, 300K) δ (ppm) 181.80, 159.28, 153.72, 152.15, 143.83, 138.34, 125.89, 119.54, 117.99, 116.13, 115.17, 106.70, 72.01, 71.92, 71.68, 70.92, 70.65, 70.58, 70.57, 70.55, 70.51, 70.50, 70.07, 68.71, 59.11, 59.04, 40.39. HRMS (ESI): m/z: calculated for C$_{60}$H$_{64}$N$_2$O$_{22}$S$_2$Na: 1271.4957, ([M+Na]$^+$) found: 1271.4494.
Figure S20. $^1$H NMR of M4 in CDCl$_3$ at 300 K.

Figure S21. $^{13}$C NMR of M4 in CDCl$_3$ at 300 K.
8b. Polymer Synthesis

Scheme S4. Synthetic route of polymer p(C-T).

Reaction condition: p-toluenesulfonic acid (PTSA), toluene, reflux.

3,7-dihydrobenzo[1,2-b:4,5-b’]difuran-2,6-dione (dilactone) was synthesized according to the literature. [S7]

Synthesis of p(C-T): M1 (80.5 mg, 0.087 mmol, 1.0 equiv.), dilactone (16.45 mg, 0.087 mmol, 1.0 equiv), and P-toluenesulfonic acid monohydrate (4.95 mg, 0.028 mmol, 0.3 equiv.) were added to a microwave vial. The tube was sealed, flushed with argon, and then degassed toluene (1.0 mL) was added. The tube was stirred at 110 °C for 12 h. After cooling to room temperature, the polymer was precipitated into around 100 mL methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform fraction was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford p(C-T) as a black solid (60.6 mg, 65 %), 1H NMR (1,1,2,2-tetrachloroethane-d2, 393K, 500 MHz), δ (ppm) : 9.21-9.71 (broad), 7.48-6.26 (broad), 4.45-3.10 (m). MALDI-TOF shows Mw range between 4 kDa and 20 kDa.
Figure S22. $^1$H NMR of p(C-T) in tetrachloroethane-d$_2$ at 393 K.

Figure S23. MALDI-TOF of polymer p(C-T).
Scheme S5. Synthetic route of polymer p(N-T).

Reaction condition: p-toluenesulfonic acid monohydrate (PTSA), toluene, reflux.

Synthesis of p(N-T): M2 (47.6 mg, 0.051 mmol, 1.0 equiv.), dilactone (9.71 mg, 0.051 mmol, 1.0 equiv), and p-toluenesulfonic acid monohydrate (2.9 mg, 0.015 mmol, 0.3 equiv.) were added to a microwave vial. The tube was sealed and flushed with argon, and then degassed toluene (0.5 mL) was added. The mixture was thoroughly degassed under Argon, and then the argon inlet was removed. The tube was stirred at 110 °C for 12 h. After cooling to room temperature, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into 100 mL methanol. The precipitates were filtered and dried under vacuum to afford p(N-T) as a green solid (33.3 mg, 60 %). $^1$H NMR (1,1,2,2-tetrachloroethane-d$_2$, 393K, 500 MHz), $\delta$ (ppm) : 9.41-7.82 (broad), 7.67-6.58 (broad), 4.55-3.10 (m). MALDI-TOF shows Mw range between 4 kDa and 20 kDa.
Figure S24. $^1$H NMR of polymer p(N-T) in tetrachloroethane-d$_2$ at 393 K.

Figure S25. MALDI-TOF of polymer p(N-T).
Scheme S6. Synthetic route of polymer p(C-2T).

Reaction conditions: p-toluenesulfonic acid monohydrate (PTSA), toluene, reflux.

Synthesis of p(C-2T): M3 (52.39 mg, 0.052 mmol, 1.0 equiv.), dilactone (9.84 mg, 0.052 mmol, 1.0 equiv), P-toluenesulfonic acid monohydrate (3 mg, 0.016 mmol, 0.3 equiv.) were added to a microwave vial. The tube was sealed and flushed with argon, and then degassed toluene (0.5 mL) was added. The mixture was thoroughly degassed under Argon, and then the argon inlet was removed. The tube was stirred at 110 °C for 3 h. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into 10 mL methanol. The precipitates were filtered and dried under vacuum to afford p(C-2T) as a black solid (30.4 mg, 50 %), $^1$H NMR (1,1,2,2-tetrachloroethane-d$_2$, 393K, 500 MHz), $\delta$ (ppm): 9.30-8.96 (m), 8.76-8.21 (broad), 7.58 (d, $J = 7.2$ Hz, 1H), 7.52-7.44 (m), 7.39-7.23 (m), 7.20 (s), 4.24-3.11 (m). MALDI-TOF with universal matrix shows Mw range between 4 kDa and 20 kDa.
Figure S26. $^1$H NMR of polymer p(C-2T) in tetrachloroethane-d$_2$ at 393 K.

Figure S27. MALDI-TOF of polymer p(C-2T).
Scheme S7. Synthetic route of polymer p(C-g2T).

Reaction conditions: p-toluenesulfonic acid monohydrate (PTSA), toluene, reflux.

Synthesis of p(C-g2T): M4 (35.46 mg, 0.028 mmol, 1.0 equiv.), dilactone (5.4 mg, 0.028 mmol, 1.0 equiv), p-toluenesulfonic acid monohydrate (1.62 mg, 0.008 mmol, 0.3 equiv.) were added to a microwave vial. The tube was sealed and flushed with argon, and then degassed toluene (0.5 mL) was added. The mixture was thoroughly degassed under Argon, and then the argon inlet was removed. The tube was stirred at 110 °C for 12 h. After cooling to RT, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into methanol. The precipitates were filtered and dried under vacuum to afford p(C-g2T) as a black solid (35.4 mg, 90 %), ¹H NMR (1,1,2,2-tetrachloroethane-d₂, 393K, 500 MHz), δ (ppm): 9.21-9.01 (m), 9.00-7.73 (broad), 7.50-7.13 (m), 7.12-6.28 (broad) (d, J = 7.2 Hz, 1H), 7.52-7.44 (m), 7..39-7.23 (m), 7.20 (s), 4.77-2.09 (m). MALDI-TOF with universal matrix shows Mw range between 4 kDa and 20 kDa.
Figure S28. $^1$H NMR of polymer p(C-g2T) in tetrachloroethane-d$_2$ at 393 K.

Figure S29. MALDI-TOF of polymer p(C-g2T).
9. References

[S1] I. P. Maria, B. D. Paulsen, A. Savva, D. Ohayon, R. Wu, R. Hallani, A. Basu, W. Du, T. D. Anthopoulos, S. Inal, J. Rivnay, I. McCulloch, A. Giovannitti, Adv. Funct. Mater. 2021, 38, 2008718

[S2] F. E. Nik, I. Matthiesen, A. Herland, T. Winkler, Micromachines 2020, 11 (7), 676.

[S3] X. Chen, A. Marks, B. D. Paulsen, R. Wu, R. B. Rashid, H. Chen, M. Alsufyani, J. Rivnay, I. McCulloch, Angew. Chem. Int. Ed. 2021, 60, 9368.

[S4] K. Feng, W. Shan, S. Ma, Z. Wu, J. Chen, H. Guo, B. Liu, J. Wang, B., Li, H. Y. Woo, S. Fabiano, W. Huang, X. Guo, Angew. Chem. Int. Ed. 2021, 133, 24400.

[S5] H. Wu, C. Yang, Q. Li, N. B. Kolhe, X. Strakosas, M. Stoeckel, Z. Wu, W. Jin, M. Savvakis, R. Kroon, D. Tu, H. Y. Woo, M. Berggren, S. A. Jenekhe, Simone Fabiano, Adv. Mater. DOI: 10.1002/adma.202106235.

[S6] M. Moser, T. C. Hidalgo, J. Surgailis, J. Gladisch, S. Ghosh, R. Sheelamanthula, Q. Thiburce, A. Giovannitti, A. Salleo, N. Gasparini, A. Wadsworth, I. Zozoulenko, M. Berggren, E. Stavrinidou, S. Inal, I, McCulloch, Adv. Mater. 2020, 32, 2002748.

[S7] T. Lei, J. Dou, X. Cao, J. Wang, J. Pei, J. Am. Chem. Soc. 2013, 135, 12168.