Supplementary Information

Intrinsically Stretchable Fully π-Conjugated Polymers with Inter-aggregate Capillary Interaction for Deep-blue Flexible Inkjet-printed Light-emitting Diodes

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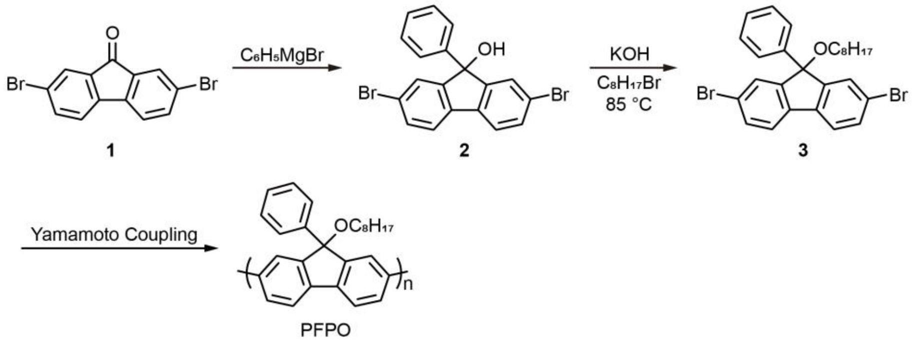
Synthesis:



Supplementary Fig. 1. Synthetic route of PFPO.

2,7-dibromo-9-phenyl-9H-fluoren-9-ol (2): In a nitrogen atmosphere, compound **1** (0.47 g, 1 mmol) was solved in THF (40 mL). After adding the THF solution of phenyl magnesium bromide (1 mol L^{-1}, 1.6 mL), the mixture was stirred for 48 hours at 85°C. Then the reaction was quenched by NH_4Cl aqueous solution and the mixture was extracted with dichloromethane. The extracted organic solution was dried with Na_2SO_4, and solvent was evaporated in vacuum. Compound **2** (yield: 0.35g, 85%) was obtained from chromatography using an eluent of petroleum ether/dichloromethane (2:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.1 Hz, 4H), 7.43 (t, *J* = 1.1 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 2.54 (s, 1H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 152.12, 141.67, 137.61, 132.57, 128.63, 128.41,

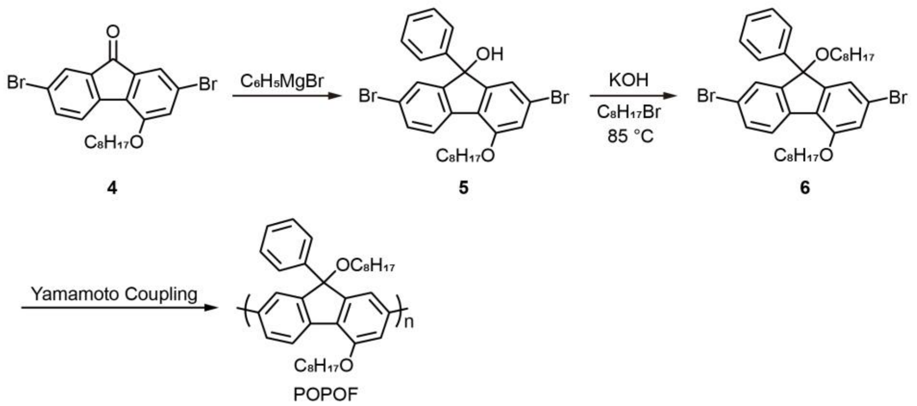
2,7-dibromo-9-(octyloxy)-9-phenyl-9H-fluorene (3): At room temperature, **2** (0.42 g, 1 mmol) and KOH (0.10 g, 1.78 mmol) were solved in THF (40 mL). After adding 1-bromooctane (0.30 g, 1.55 mmol), the mixture was stirred for 24 hours at 85°C. Then the mixture was separated by suction filtration using Buchner funnel. Compound **3** (yield: 0.50g, 94%) was obtained from chromatography using an eluent of petroleum ether/dichloromethane (6:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 4H), 7.38 – 7.36 (m, 2H), 7.28 (td, *J* = 5.8, 2.7 Hz, 3H), 7.24 (td, *J* = 4.3, 1.1 Hz, 2H), 2.97 (t, *J* = 6.3 Hz, 2H), 1.55 – 1.49 (m, 2H), 1.34 – 1.20 (m, 10H), 0.90 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 149.69, 142.41, 138.66, 132.34, 128.66, 128.43, 127.62, 125.56, 122.50, 121.45, 88.17, 63.59, 31.95, 30.02, 29.41, 29.37, 26.14, 22.78, 14.23.

Poly(9-(octyloxy)-9-phenyl-9H-fluorene) (PFPO): Compound **3** (0.53 g, 1.01 mmol) was added to an appropriate DMF (10 mL) and toluene (10 mL) solution containing $Ni(COD)_2$ (0.33 g, 1.20 mmol) 1,5-cyclooctadiene (0.15 mL, 1.20 mmol), and bpy (0.19 g, 1.23 mmol) in a Schlenk tube under argon. The reaction mixture was stirred for 36 h at 90°C to obtain a dark blue solution. The bromobenzene (0.5 mL) was added to solution for terminating reaction. The precipitate was separated by filtration. The solution should further purification to be subjected to alumina (Al_2O_3) column chromatography eluting with DCM to afford PFPO (yield: 0.28g, 75%) as an off-white powder.

GPC: M_n=7.52×10^4, M_w=13.01×10^4, PDI=1.73. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 4H), 7.50 (s, 2H), 7.39 (s, 3H), 7.24 (s, 2H), 3.08 (s, 2H), 1.35 (s, 2H), 1.22 (s, 10H), 0.85 (s, 3H).



Supplementary Fig. 2. Synthetic route of POPOF.

2,7-dibromo-4-(octyloxy)-9-phenyl-9H-fluoren-9-ol (5): The **4** was synthesized according to our previous report.[1] In a nitrogen atmosphere, compound **4** (0.47 g, 1 mmol) was solved in THF (40 mL). After adding the THF solution of phenyl magnesium bromide (1 mol L^{-1}, 1.6 mL), the mixture was stirred for 48 hours at 85°C. Then the reaction was quenched by NH_4Cl aqueous solution and the mixture was extracted with dichloromethane. Compound **5** (yield: 0.46g, 85%) was obtained from chromatography using an eluent of petroleum ether/dichloromethane (2:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 3H), 7.02 (dd, *J* = 10.3, 1.4 Hz, 2H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 1H), 1.98 – 1.91 (m, 2H), 1.60 (s, 1H), 1.53 (d, *J* = 7.4 Hz, 1H), 1.43 – 1.30 (m, 8H), 0.93 – 0.88 (m, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 155.44, 153.16, 151.55, 141.77, 137.12, 132.43,

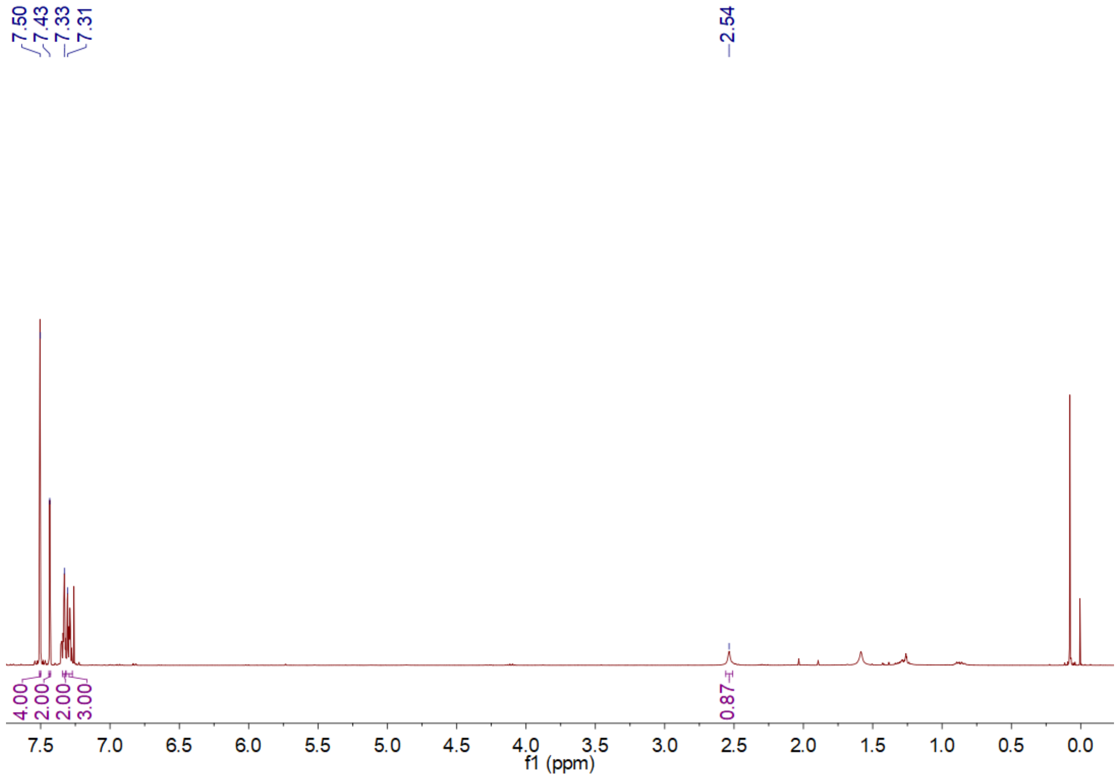
2,7-dibromo-4,9-bis(octyloxy)-9-phenyl-9H-fluorene (6): Compound **5** (0.55 g, 1.01 mmol) and KOH (0.10 g, 1.78 mmol) were solved in THF (40 mL) at room temperature. After adding 1-bromooctane (0.30 g, 1.55 mmol), the mixture was stirred for 24 hours at 85°C. Then the mixture was separated by suction filtration using Buchner funnel. Compound **6** (yield: 0.64g, 98%) was obtained from chromatography using an eluent of petroleum ether/dichloromethane (6:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.29 (qd, *J* = 5.0, 4.5, 1.7 Hz, 2H), 7.26 – 7.20 (m, 3H), 6.99 (dd, *J* = 12.4, 1.4 Hz, 2H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 6.3 Hz, 2H), 1.95 (p, *J* = 6.6 Hz, 2H), 1.55 – 1.50 (m, 2H), 1.46 – 1.29 (m, 12H), 1.23 (d, *J* = 15.8 Hz, 8H), 0.92 – 0.86 (m, 6H).

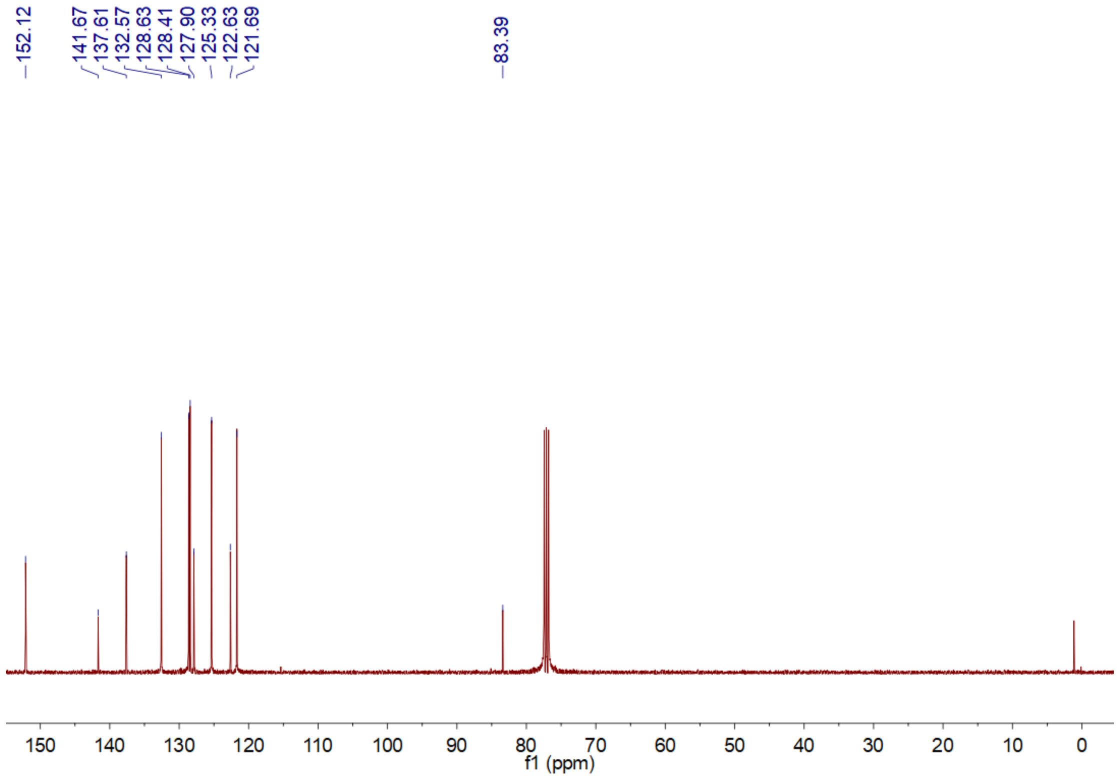
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 155.42, 150.82, 149.11, 142.56, 138.21, 132.20,

Poly(4,9-bis(octyloxy)-9-phenyl-9H-fluorene) (POPOF): Compound **6** (0.66 g, 1.00 mmol) was added to an appropriate DMF (10 mL) and toluene (10 mL) solution containing Ni(COD)$_2$ (0.33 g, 1.20 mmol) 1,5-cyclooctadiene (0.15 mL, 1.20 mmol), and bpy (0.19 g, 1.23 mmol) in a Schlenk tube under argon. The reaction mixture was stirred for 36 h at 90°C to obtain a dark blue solution. The bromobenzene (0.5 mL) was added to solution for terminating reaction. The precipitate was separated by filtration. The solution should further purification to be subjected to alumina (Al_2O_3) column chromatography eluting with DCM to afford POPOF (0.40g, 80%) as a yellow powder.

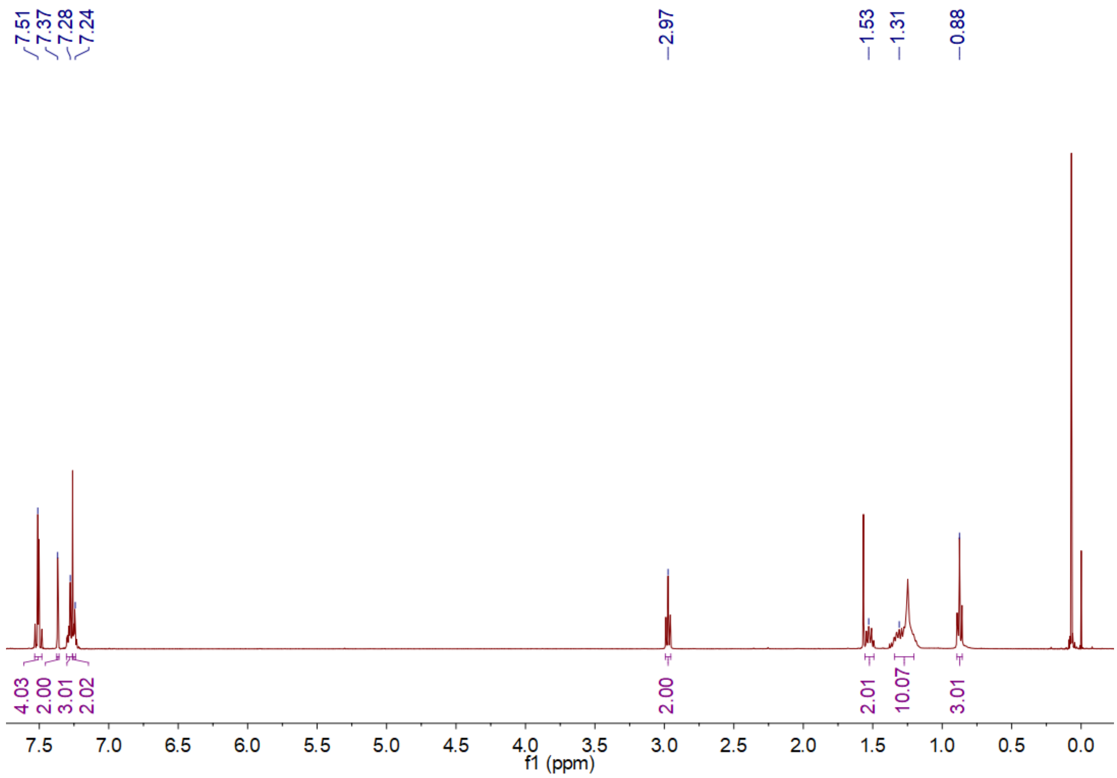
GPC: M_n=3.64×10^4, M_w=6.98×10^4, PDI=1.92. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.60 (s, 1H), 7.42 (s, 4H), 7.21 (s, 3H), 7.06 (s, 1H), 4.20 (s, 2H), 3.08 (s, 2H), 1.98 (s, 2H), 1.62 (s, 2H), 1.37 (s, 10H), 1.23 (s, 10H), 0.92 (s, 6H). In addition, PODPF was synthesized based on our previous report.[2]



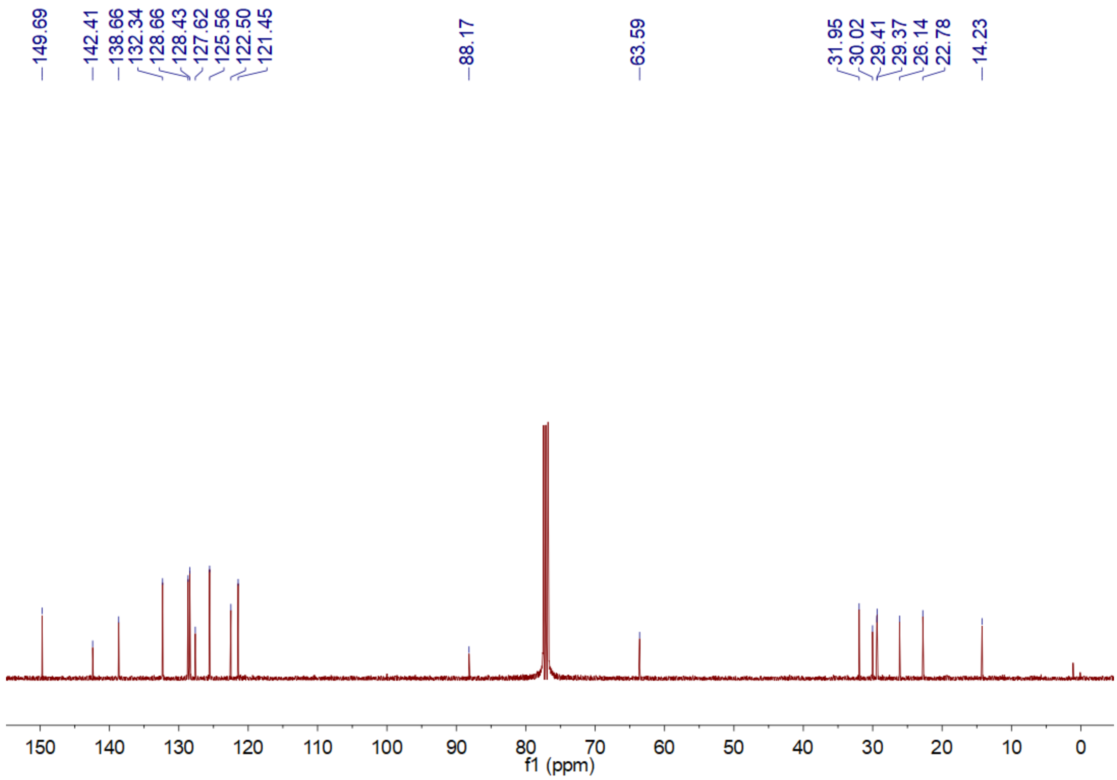
Supplementary Fig. 3. ^{1}H NMR spectrum of **2** in $CDCl_3$.



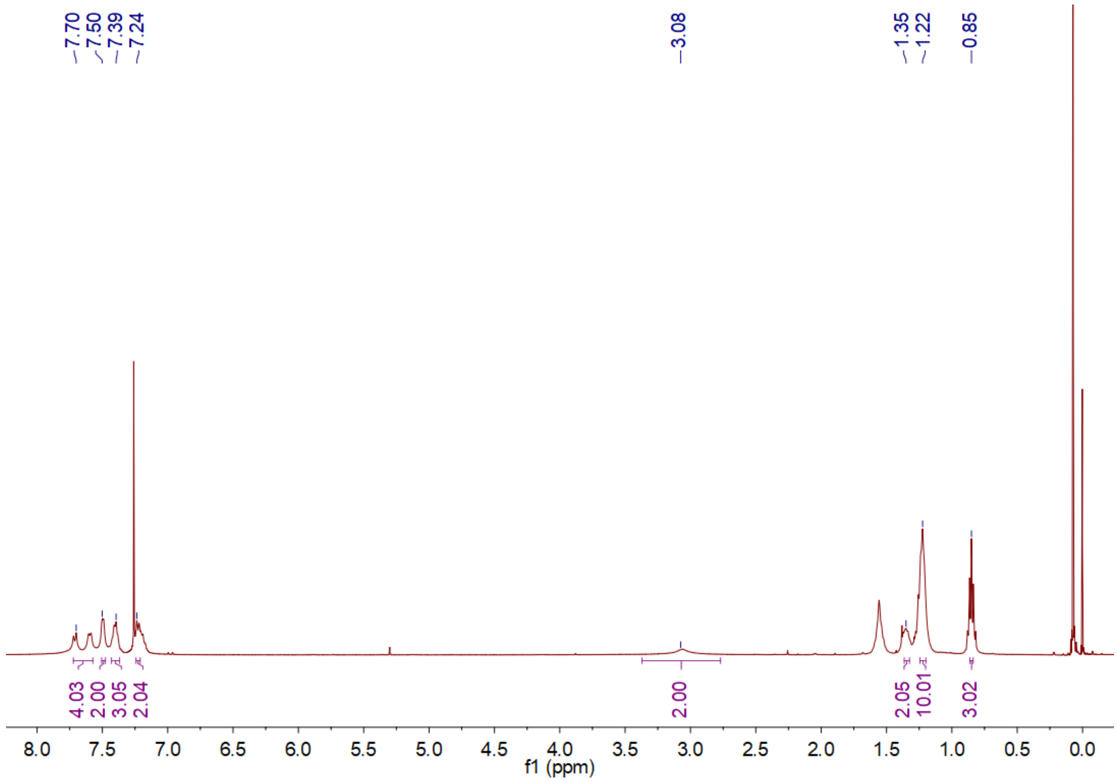
Supplementary Fig. 4. ^{13}C NMR spectrum of **2** in $CDCl_3$.



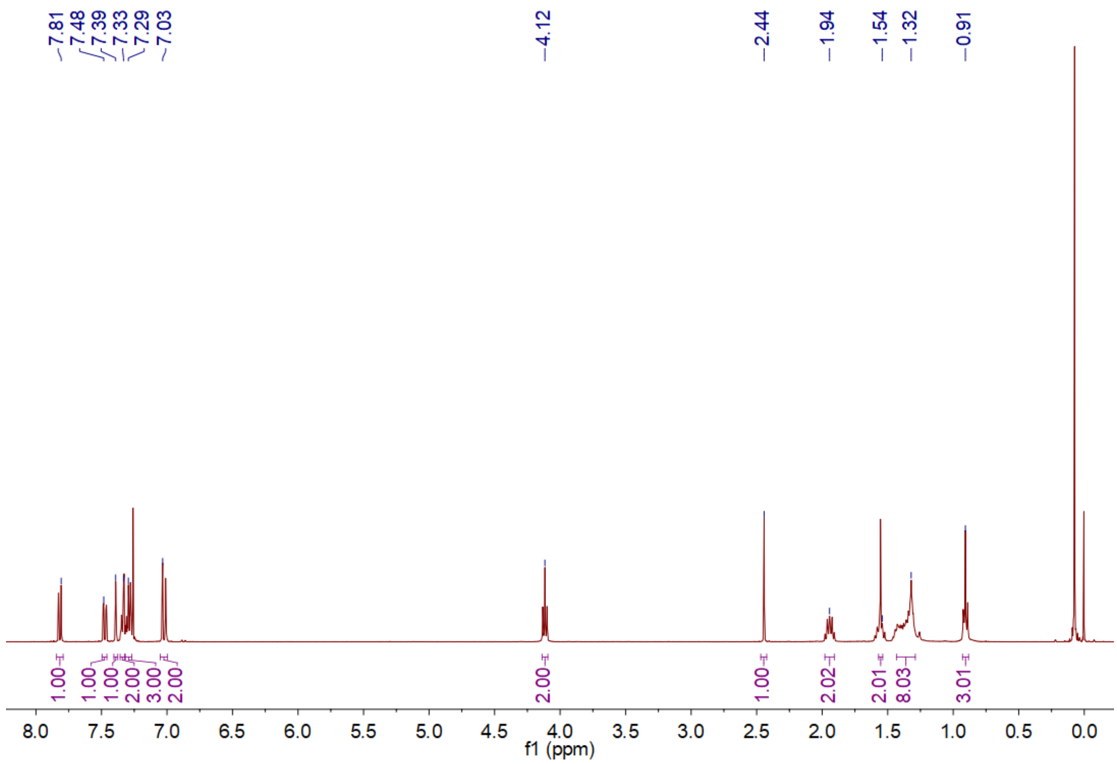
Supplementary Fig. 5. [1]H NMR spectrum of **3** in $CDCl_3$.



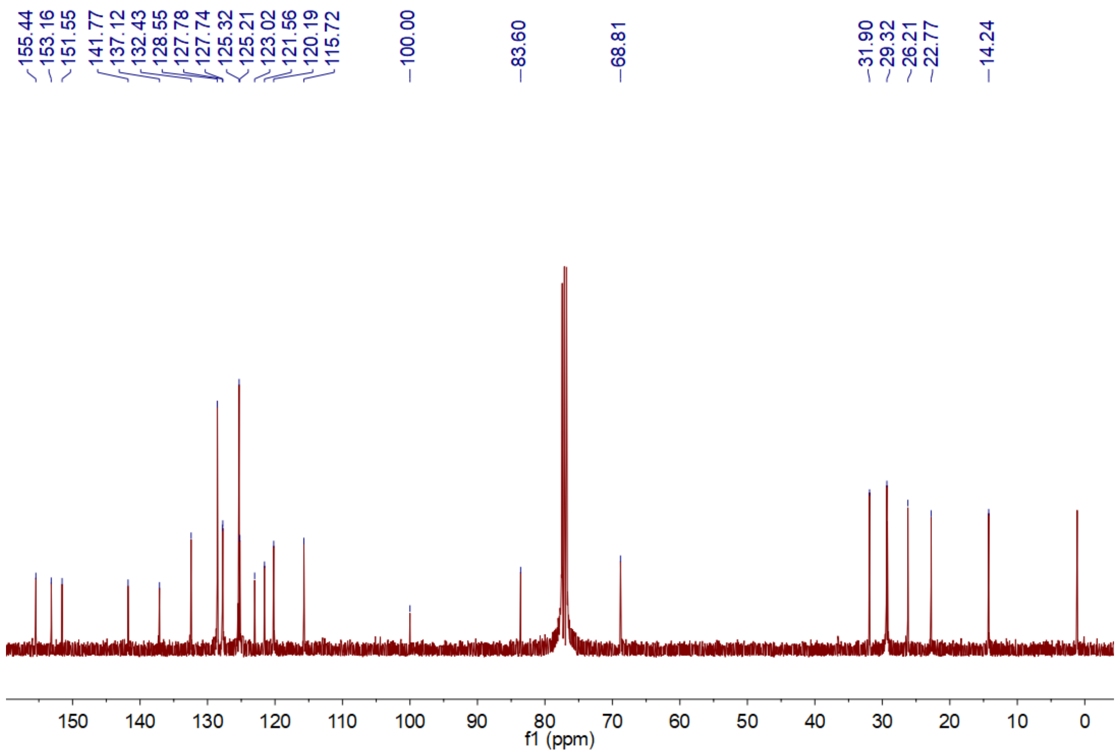
Supplementary Fig. 6. [13]C NMR spectrum of **3** in $CDCl_3$.



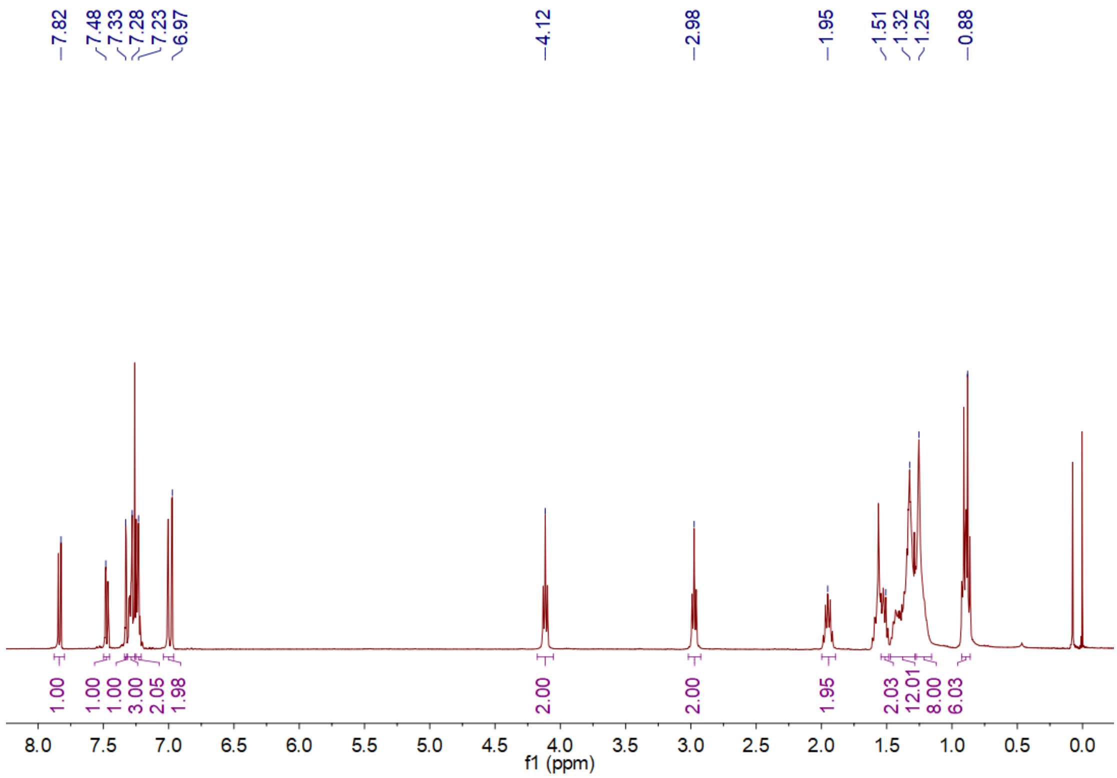
Supplementary Fig. 7. ^{1}H NMR spectrum of PFPO in $CDCl_3$.



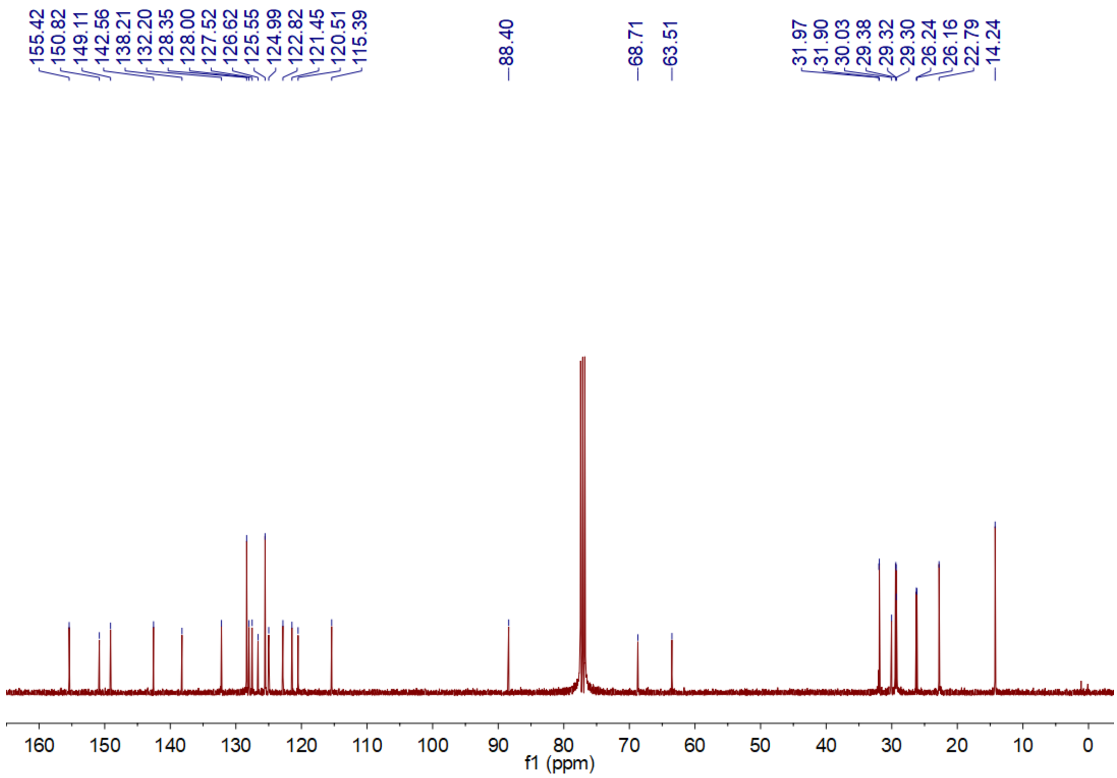
Supplementary Fig. 8. ^{1}H NMR spectrum of **5** in $CDCl_3$.



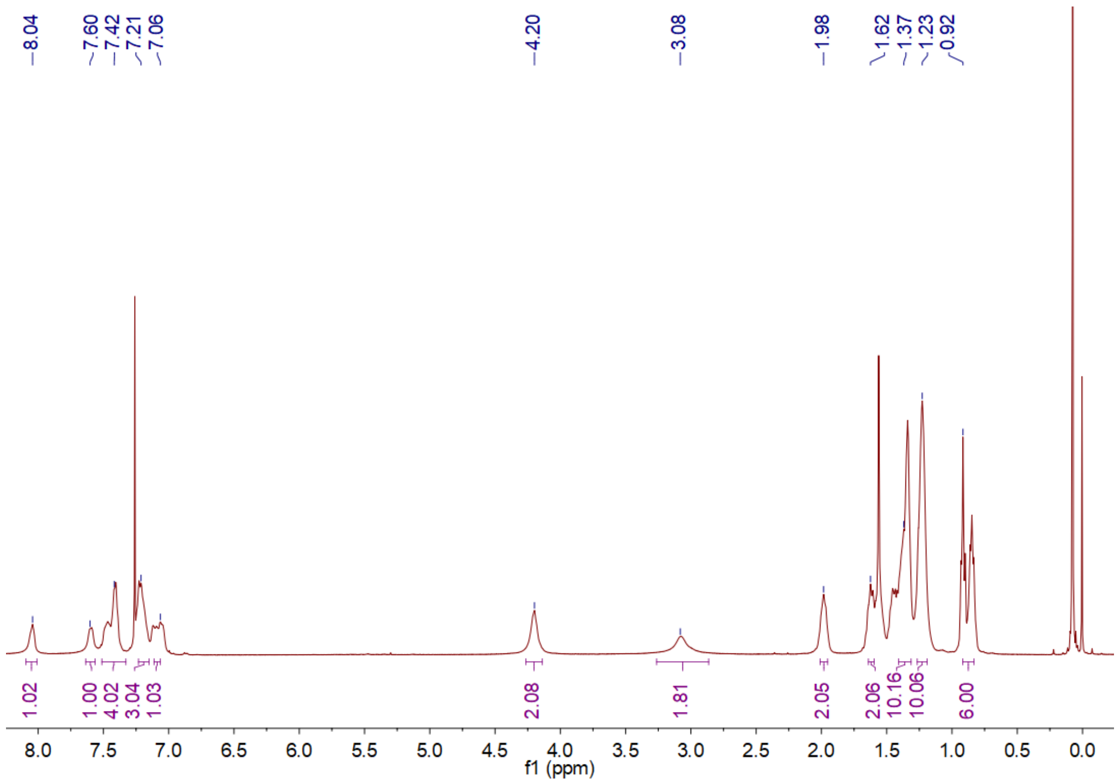
Supplementary Fig. 9. ^{13}C NMR spectrum of **5** in $CDCl_3$.



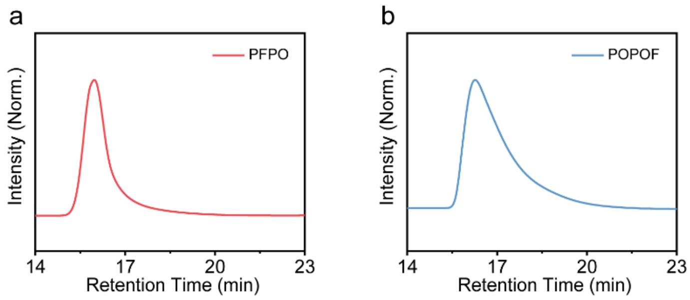
Supplementary Fig. 10. ^{1}H NMR spectrum of **6** in $CDCl_3$.



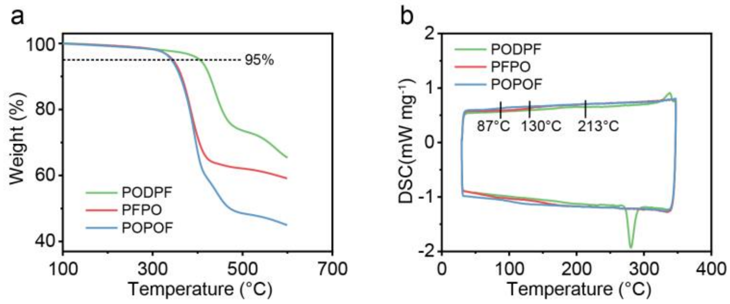
Supplementary Fig. 11. ^{13}C NMR spectrum of **6** in $CDCl_3$.



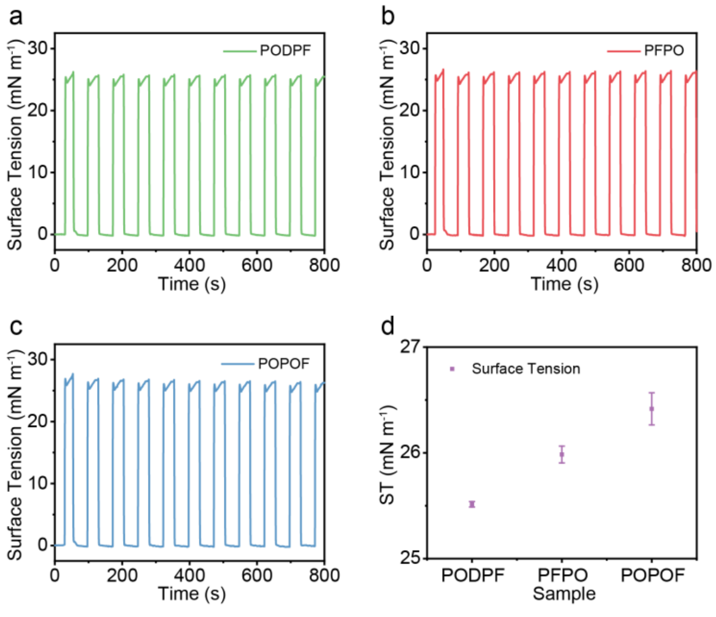
Supplementary Fig. 12. ^{1}H NMR spectrum of POPOF in $CDCl_3$.



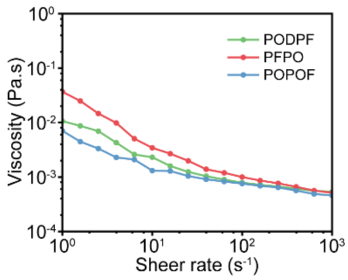
Supplementary Fig. 13. GPC curves of PFPO (a) and POPOF (b) using THF as the eluent.



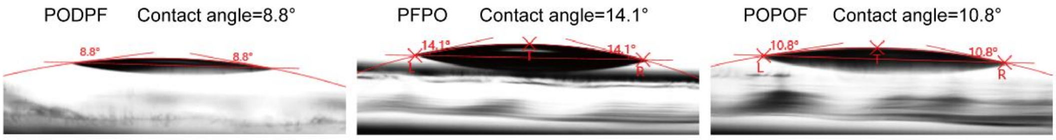
Supplementary Fig. 14. (a) TG and (b) DSC curves of three polymers.



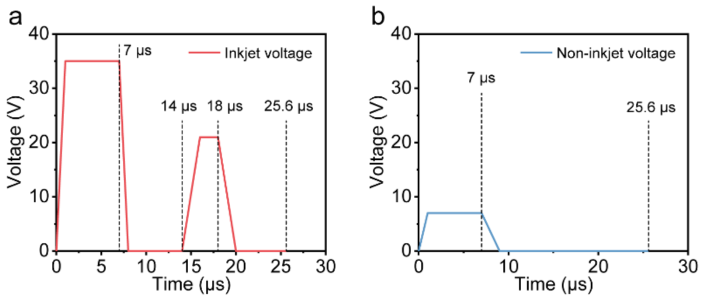
Supplementary Fig. 15. (a-c) Surface tension cyclic curves of three polymers measured by plate method in toluene solution at a concentration of 5 mg mL^{-1}. (d) Error analysis of surface tension.



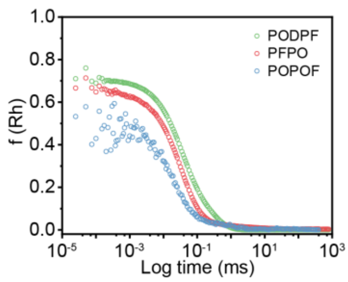
Supplementary Fig. 16. Viscosity curves of three polymers in toluene solution with a concentration of 5 mg/mL.



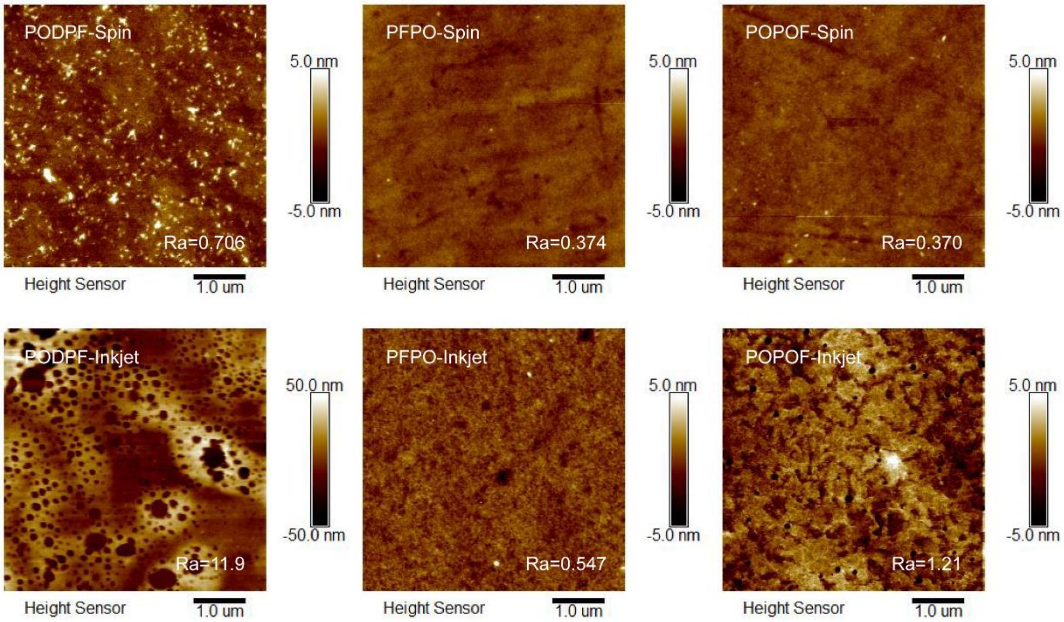
Supplementary Fig. 17. Contact angle measurement of three polymer ink (toluene solution with the polymer concentration of 5 mg mL^{-1}) on the surface of the PEDOT: PSS film.



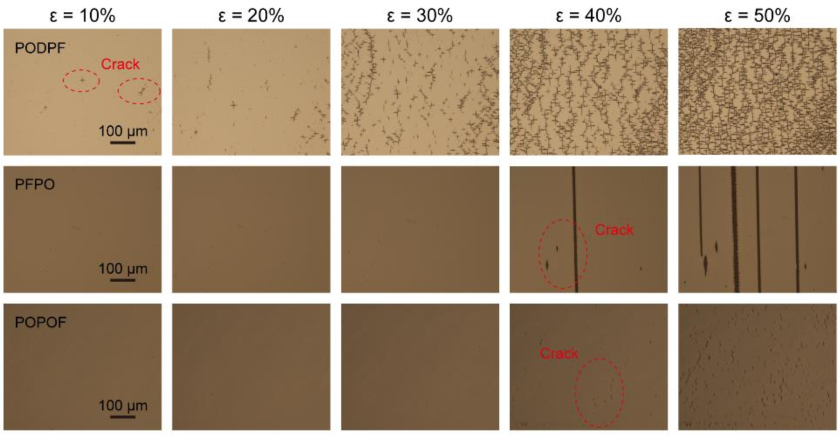
Supplementary Fig. 18. Pulse voltage waveform of inkjet printing. (a) Pulse voltage curve of ink droplet extrusion process. (b) Pulse voltage curve of ink droplet suspension stability process.



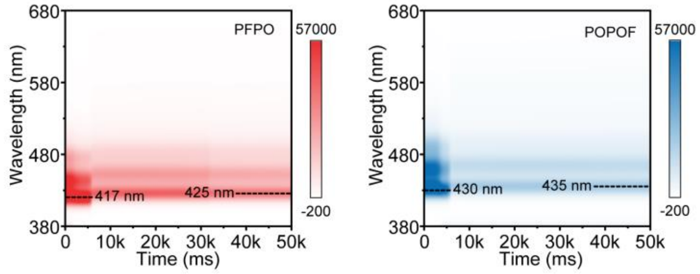
Supplementary Fig. 19. Normalized intensity correlation function ($g^2_{(t)}{}^{-1}$).



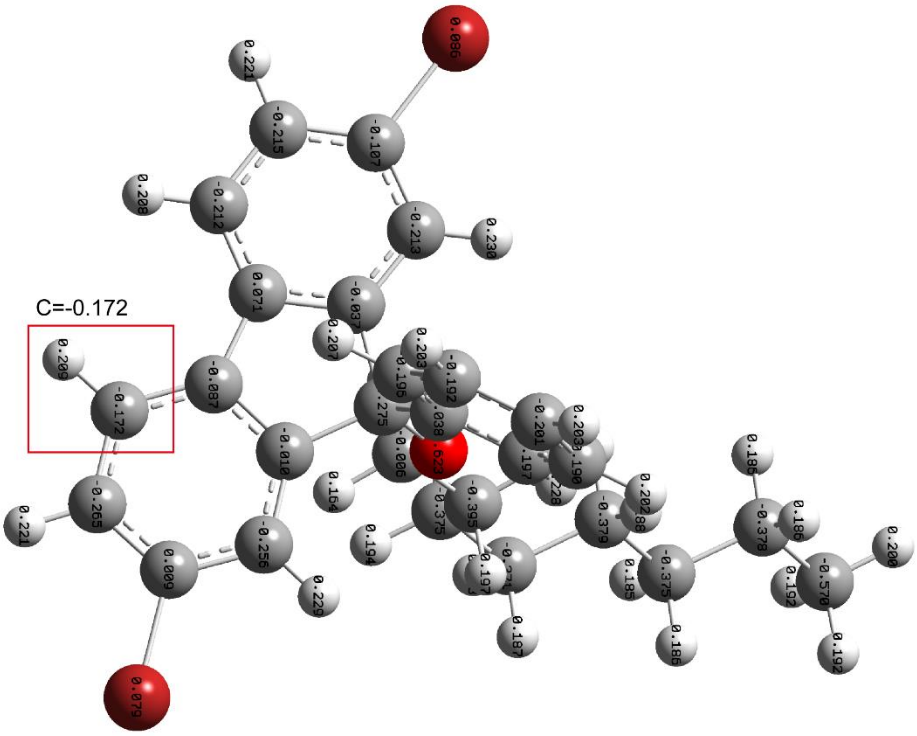
Supplementary Fig. 20. Atomic force microscopy images of spin-coated and inkjet films for three polymers.



Supplementary Fig. 21. Optical photographs of three films stretched on PDMS substrates.

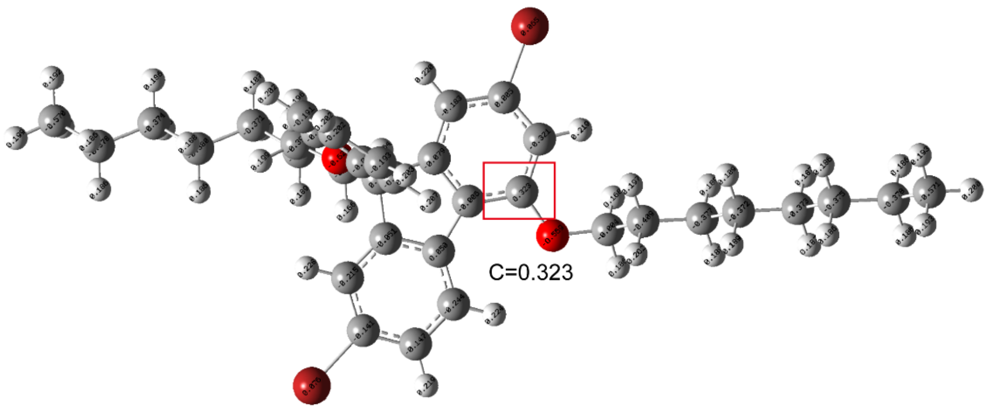


Supplementary Fig. 22. In situ coating-time dependent PL spectra of PFPO and POPOF in solution processing.



C	-1.05072	3.68509	-1.98873
C	-1.84334	2.55387	-2.19885
C	-1.72875	1.47211	-1.32511
C	-0.83402	1.53172	-0.24169
C	-0.04068	2.6479	-0.02161
C	-0.16175	3.7183	-0.91215
H	-1.12018	4.53726	-2.65585
H	-2.53314	2.52916	-3.03818
H	0.64929	2.69474	0.8142
C	-0.88291	0.23671	0.58578
C	-1.91757	-0.57485	-0.21147
C	-2.40235	0.16304	-1.30619
C	-2.36179	-1.86378	0.04345
C	-3.35953	-0.3922	-2.15601
C	-3.31364	-2.40756	-0.82358
H	-1.98891	-2.4332	0.88818
C	-3.81643	-1.68957	-1.91082
H	-3.75063	0.16421	-3.00359
H	-4.5581	-2.14342	-2.5589
C	-1.35603	0.49899	2.02288
C	-0.58721	0.10213	3.12096
C	-2.58002	1.14501	2.24838
C	-1.03622	0.3481	4.42169
H	0.35907	-0.39706	2.95386
C	-3.02544	1.38905	3.54513
H	-3.18884	1.45951	1.40493
C	-2.25344	0.99061	4.63967
H	-0.42689	0.03359	5.26515
H	-3.97663	1.89111	3.70104
H	-2.60024	1.18073	5.65187
C	1.0352	-0.76475	-0.5356
H	0.40158	-1.44279	-1.12467
H	1.2188	0.13343	-1.14218
C	2.35096	-1.44218	-0.17308
H	2.93239	-0.75448	0.45258
H	2.13429	-2.32464	0.44395
C	3.15328	-1.85681	-1.41484
H	3.39259	-0.96375	-2.01091
H	2.5193	-2.48811	-2.05352
C	4.45191	-2.62039	-1.10537
H	4.87372	-2.98757	-2.0516
H	4.21231	-3.51583	-0.51293
C	5.52396	-1.79959	-0.37463
H	5.73379	-0.88555	-0.95062
H	5.1415	-1.46432	0.59932
C	6.83169	-2.57208	-0.1571
H	6.62145	-3.48977	0.41256
H	7.22454	-2.9036	-1.13003
C	7.90981	-1.76093	0.5731
H	7.51798	-1.4316	1.54604
H	8.11955	-0.84366	0.00457
O	0.38092	-0.41163	0.68468
C	9.21243	-2.53924	0.78469
H	9.9609	-1.9333	1.30805
H	9.04114	-3.44447	1.38031
H	9.64742	-2.85198	-0.17267
Br	0.91797	5.27578	-0.6494
Br	-3.94968	-4.18503	-0.51266

Supplementary Fig. 23. Natural population analysis of atomic charge for PFPO.

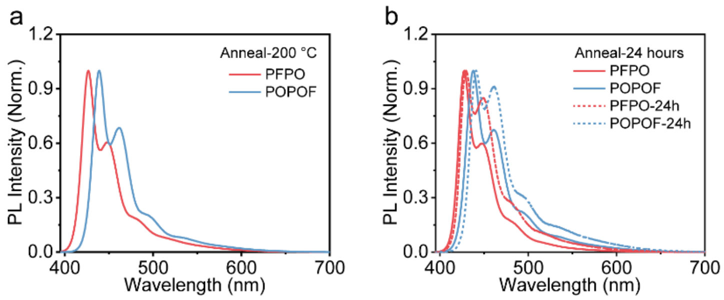


C	-0.62036	-3.69881	-1.29733
C	0.2555	-2.61101	-1.23462
C	-0.06969	-1.5252	-0.41833
C	-1.25837	-1.54379	0.33595
C	-2.13441	-2.61662	0.28149
C	-1.79772	-3.68982	-0.54846
H	-0.39007	-4.55154	-1.92681
H	1.17059	-2.61126	-1.81485
H	-3.04949	-2.62837	0.86406
C	-1.40592	-0.25863	1.16319
C	-0.14081	0.50814	0.74059
C	0.61872	-0.25014	-0.16183
C	0.24414	1.77715	1.15213
C	1.82294	0.26751	-0.66919
C	1.43724	2.27268	0.62994
H	-0.34915	2.35477	1.85148
C	2.2302	1.54661	-0.26141
H	3.15087	1.98601	-0.62065
C	-1.40669	-0.54848	2.67102
C	-2.4449	-0.1009	3.49325
C	-0.34982	-1.27054	3.24367
C	-2.42531	-0.37213	4.86444
H	-3.26444	0.45655	3.05712
C	-0.332	-1.53915	4.61004
H	0.46359	-1.62565	2.61665
C	-1.37224	-1.09004	5.42799
H	-3.24051	-0.01805	5.49039

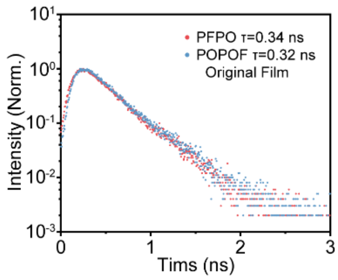
H	0.49499	-2.10076	5.03659
H	-1.35942	-1.2998	6.49426
C	-2.83355	0.84995	-0.46932
H	-2.02934	1.51796	-0.80889
H	-2.83823	-0.03035	-1.12747
C	-4.17934	1.56252	-0.5215
H	-4.9463	0.88012	-0.13605
H	-4.14933	2.42255	0.16112
C	-4.53387	2.03312	-1.93933
H	-4.58661	1.16358	-2.61108
H	-3.71671	2.66233	-2.31978
C	-5.84852	2.82547	-2.03518
H	-5.93677	3.23211	-3.05257
H	-5.7959	3.69599	-1.36459
C	-7.11365	2.01555	-1.71807
H	-7.1435	1.12517	-2.36424
H	-7.07122	1.64104	-0.68601
C	-8.4075	2.8191	-1.9037
H	-8.37574	3.71288	-1.26257
H	-8.45965	3.19085	-2.9381
C	-9.67796	2.01835	-1.59022
H	-9.62691	1.64891	-0.55606
H	-9.70951	1.12491	-2.23002
O	-2.60723	0.45347	0.88446
C	-10.965	2.82761	-1.77995
H	-11.8531	2.22845	-1.54844
H	-10.97875	3.70935	-1.12731

H	-11.06217	3.18129	-2.8139
Br	-2.98272	-5.18983	-0.65902
Br	2.03138	4.01669	1.15326
O	2.50258	-0.52099	-1.54744
C	3.74968	-0.08133	-2.10413
H	3.67569	0.97025	-2.40957
H	3.8618	-0.67897	-3.0138
C	4.93251	-0.31847	-1.1663
H	4.78761	0.24236	-0.2344
H	4.94596	-1.38126	-0.89215
C	6.26905	0.07716	-1.80923
H	6.24311	1.14149	-2.08622
H	6.40218	-0.47873	-2.74914
C	7.4756	-0.17755	-0.89596
H	7.34201	0.3776	0.04396
H	7.50157	-1.2417	-0.61939
C	8.81515	0.21507	-1.53217
H	8.78783	1.27965	-1.80838
H	8.94646	-0.33923	-2.47343
C	10.02265	-0.04085	-0.62127
H	9.89199	0.51331	0.3202
H	10.05037	-1.10541	-0.34455
C	11.36331	0.35091	-1.25592
H	11.33596	1.41481	-1.53144
H	11.49382	-0.20284	-2.19664
C	12.56389	0.09152	-0.34018
H	13.50477	0.38151	-0.82161
H	12.4794	0.65916	0.59473
H	12.63866	-0.9705	-0.07562

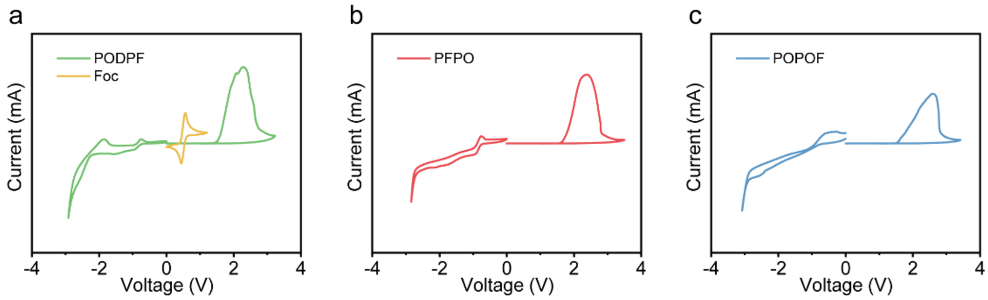
Supplementary Fig. 24. Natural population analysis of atomic charge for POPOF.



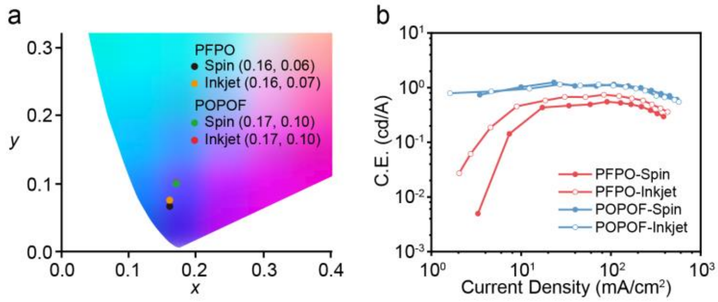
Supplementary Fig. 25. (a) PL spectra of annealed films for PFPO and POPOF. (b) PL spectra of two films kept in the air after 24 hours.



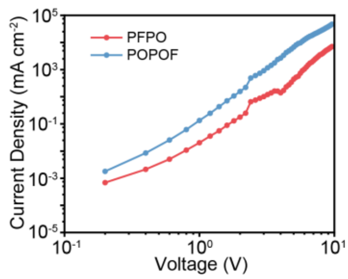
Supplementary Fig. 26. Decay time spectra of spin-coated films for PFPO and POPOF.



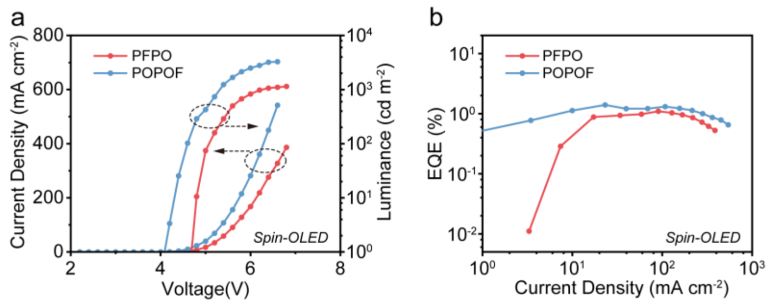
Supplementary Fig. 27. Cyclic voltammetry curves for three polymer films. Cyclic voltammetry curves of PODPF (a), PFPO (b) and POPOF (c) films.



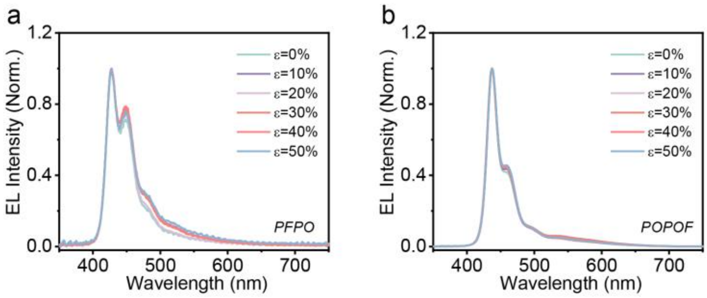
Supplementary Fig. 28. (a) CIE and (b) Current efficiency versus current density curves of spin-coated and inkjet PLEDs for PFPO and POPOF.



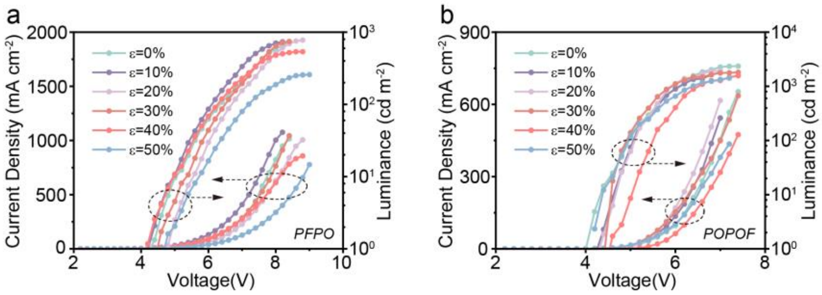
Supplementary Fig. 29. Double logarithmic plots of current density vs. applied voltage for the hole transport devices.



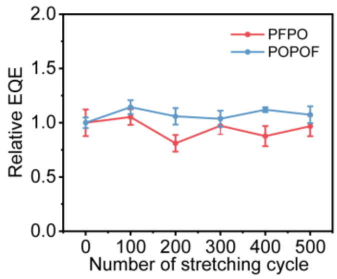
Supplementary Fig. 30. (a) *J-L-V* characteristics and (b) EQE of spin-coated PLEDs based on PFPO and POPOF.



Supplementary Fig. 31. EL spectra of (a) PFPO and (b) POPOF films under different stretching degrees.



Supplementary Fig. 32. Corresponding current *J*-*V*-*L* curves of (a) PFPO and (b) POPOF films under different stretching degrees.



Supplementary Fig. 33. Relative highest EQE statistics of PLEDs using PFPO and POPOF films with cyclic strain.

Supplementary Table 1. The fundamental chem-physical properties of three polymers.

	M_n	PDI	T_d [°C]	T_g [°C]	HOMO [a)]	LUMO [a)]	Eg [b)]
PODPF	60k	1.8	405	213	5.97	2.32	3.65
PFPO	75k	1.7	342	130	6.15	2.33	3.82
POPOF	36k	1.9	342	87	5.97	2.40	3.57

[a)] Determined by cyclic voltammetry in acetonitrile. [b)] Calculated from E_g = lowest unoccupied molecular orbital-highest occupied molecular orbital (LUMO-HOMO), LUMO, and HOMO levels were measured by cyclic voltammetry.

Supplementary Table 2. The fundamental photophysical properties of PFPO and POPOF.

	Sol. [a)]: UV/PL	Film: UV/PL	Φ_{film} [b)]	τ_{film} [ps] [c)]	k_r^{film}[ns^{-1}] [d)]	k_{nr}^{film}[ns^{-1}] [e)]
PFPO	395/417,442,474	390/425,452,483	35.19	0.34	1.04	1.90
POPOF	403/430,458,492	396/435,463,495	39.21	0.32	1.23	1.90

[a)] Measured in the toluene solution with a concentration of 10^{-5} mol L^{-1}; [b)] Absolute photoluminescence quantum yield. [c)] Lifetime calculated from fluorescence decay. [d)] calculated from $k_r=\Phi/\tau$, [e)] calculated from $k_{nr}=1/\tau-k_r$.

Supplementary References

1. An X., *et al.* Universal 4-qualifiable fluorene-based building blocks for potential optoelectronic applications. *Chin. Chem. Lett.* **33**, 5137-5141 (2022).
2. Lin J.-Y., *et al.* A Rational Molecular Design of β-Phase Polydiarylfluorenes: Synthesis, Morphology, and Organic Lasers. *Macromolecules.* **47**, 1001-1007 (2014).