Supplementary Information (SI) for Journal of Materials Chemistry C.

Achieving black-to-transmissive conjugated copolymers enabling ultrabroad spectrum modulation based on benzobisthiadiazole derivatives

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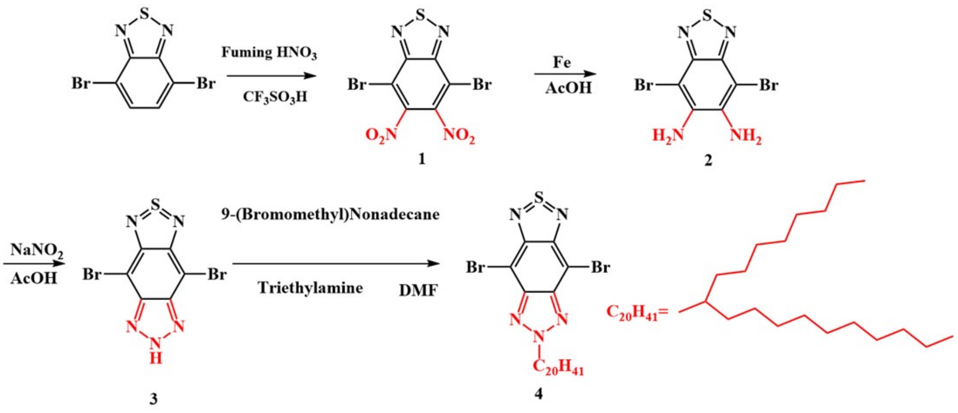
Materials and reagents

4,7-Dibromobenzo[c][1,2,5]thiadiazole (BTD-2Br), 3,4-dioxythiophene, thieno[3,2-b]thiophene, Butyllithium (n-BuLi), trimethylchlorostannane, tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), tri(o-tolyl)phosphine ($P(o\text{-}tol)_3$) were products of Sigma Aldrich and Alfar-Aesar. Other chemicals and solvents were obtained from Energy Chemicals (China), Sinopharm (China), Aladdin Chemicals (China). UV curing resin and curing agent were products of Hunan Jinhai Company, ITO glass, and PEDOT:PSS (15~17Ω/□) were purchased from

Zhuhai Kaivo company. ITO glass was ultrasonically washed with acetone and ethanol before use. Dimethyltin-indacenodithieno[3,2-b]thiophene (IDTT-$SnMe_3$), benzobisthiadiazole derivatives (SN-2Br), 2,5-dibromo-3,4-proplenedioxythiophene (ProDOT-2Br) were synthesized according to the reported literature [1-3].

Synthesis of benzobisthiadiazole derivatives (SN-2Br)



Scheme S1 synthesis route of the monomer benzobisthiadiazole derivatives (SN-2Br).

SN-2Br: ^1H NMR (400 MHz, $CDCl_3$) δ: 5.30(s, 1H), 4.83 (d, J = 7.2 Hz, 1H), 2.17(s, 2H), 1.56(s, 6H), 1.40-1.13(m, 28H), 0.86(dd, J = 12.2, 5.9 Hz, 6H).

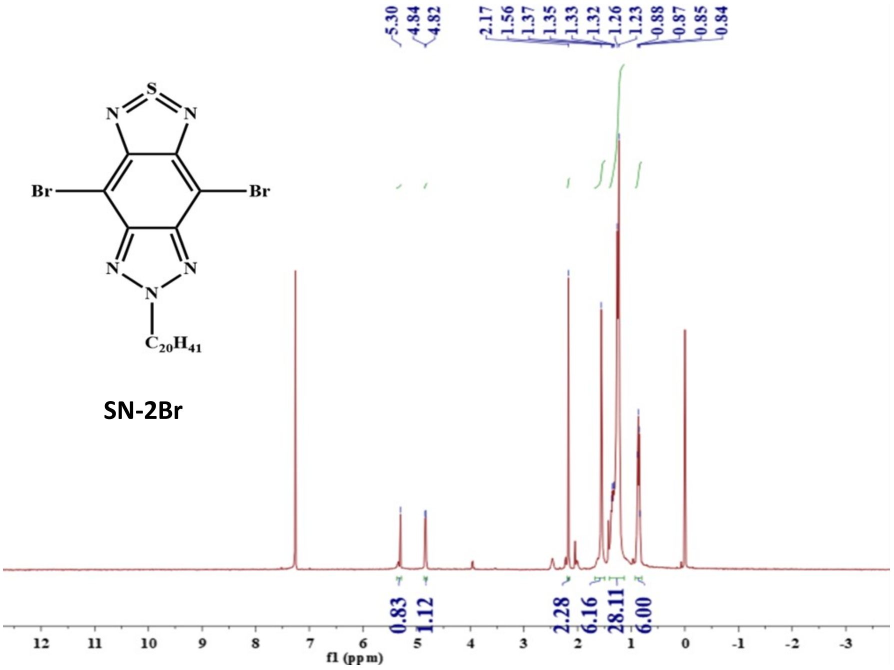
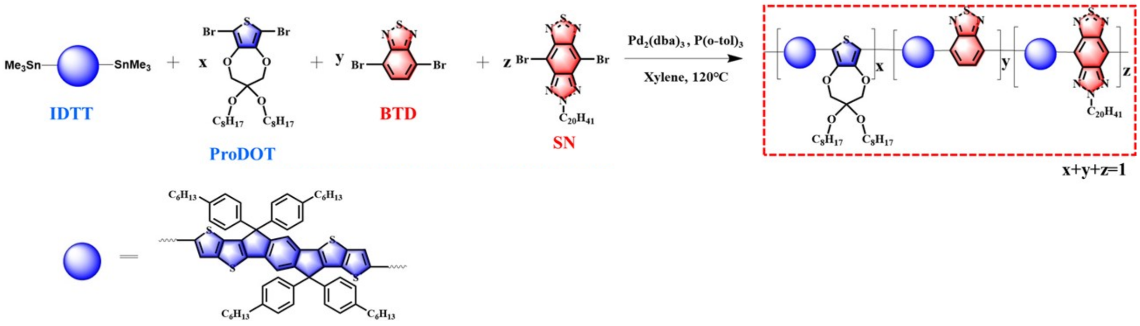


Fig.S1 ^{1}H NMR spectra of the monomer benzobisthiadiazole derivatives (SN-2Br).

General procedure for the synthesized copolymers

All of the copolymers were synthesized via Stille coupling, synthetic route of the random copolymers is given in Scheme S2. A two-neck flask was charged 1mmol IDTT-$SnMe_3$ and total 1mmol brominated monomers, then 0.02mmol $Pd_2(dba)_3$ and 0.04mmol $P(o\text{-}tol)_3$ was also added into the flask. The mixture was degassed by three freeze/pump/thaw cycles to fill with argon. 10ml anhydrous xylene was injected into the mixture via a springe, the mixture was degassed and filled with argon again. Subsequently, the flask was immersed into an oil bath pot and heated at 120°C to react for 48h. Then the mixture was cooled down to room temperature and dropwise added into 50ml cold methanol. The precipitate was collected and washed with Soxhlet extraction sequentially with methanol, hexane and finally chloroform. The chloroform fraction was concentrated via rotary evaporator and reprecipitated in methanol again.

Finally, the target polymer was collected and dried in vacuum. The ^{1}HNMR spectra of the synthetic polymers are shown as followed in **Fig.S2**.



Scheme S2 Synthetic route of the random copolymers.

IDTT-SN: ^{1}H NMR(400 MHz, CDCl$_3$) δ: 8.57(s, 1H), 7.75(s, 1H), 7.31(s, 16H), 7.19(s, 2H), 7.16 - 7.06(m, 6H), 5.32(d, J = 18.6 Hz, 2H), 2.59(d, J = 21.2 Hz, 30H), 1.57(s, 28H), 1.43 (s, 4H), 1.22(d, J = 26.3 Hz, 45H), 0.85(dd, J = 17.3, 12.8 Hz, 18H).

IDTT-ProDOT-SN: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.57(s, 1H), 7.98(s, 2H), 7.16-7.04(m, 18H), 4.0(d, 4H), 3.29(d, 4H),2.59(d, 10H), 1.57-1.22(m, 78H), 0.88(m, 21H).

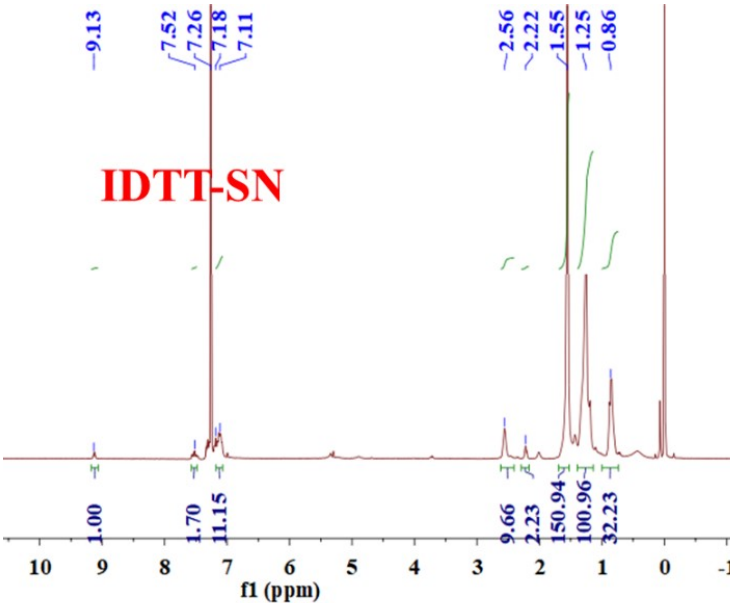
IDTT-BTD-SN : ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.57(s, 1H), 7.75(s, 1H), 7.58 - 7.50(m, 2H), 7.31(s, 16H), 7.19(s, 2H), 7.16 -7.06(m, 6H), 5.32(d, J = 18.6 Hz, 2H), 2.59(d, J = 21.2 Hz, 30H), 1.57(s, 28H), 1.43 (s, 4H), 1.22(d, J = 26.3 Hz, 45H), 0.85(dd, J = 17.3, 12.8 Hz, 18H).

IDTT-ProDOT-BTD-SN (3/1/1/1) (P1): ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.57(s, 1H), 7.54(s, 2H), 7.25(d, J = 44.9 Hz, 16H), 7.12(s, 5H), 5.30(s, 2H), 2.59(d, J = 18.4 Hz, 10H), 1.55(s, 28H), 1.24(t, J = 17.3 Hz, 41H), 0.85(dd, J = 17.3, 12.8 Hz, 18H).

IDTT-ProDOT-BTD-SN(2.75/0.5/1.25/1) (P2): ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.57(s, 1H), 7.52(s, 1H), 7.25(d, J = 45.0 Hz, 16H), 7.12(s, 3H), 5.32(d, J = 18.4 Hz, 2H), 2.59(d, J = 18.7 Hz, 22H), 2.26 – 2.18(m, 2H), 2.01(d, J = 5.6 Hz, 3H), 1.56(s, 33H), 1.43(s, 2H), 1.22(d, J = 25.5 Hz, 31H), 0.87(dd, J = 13.6, 6.3 Hz, 12H).

IDTT-ProDOT-BTD-SN(2.75/0.25/1.1/1.4) (P3): ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.57(s, 1H), 7.75(s, 1H), 7.58 – 7.50(m, 2H), 7.31(s, 16H), 7.19(s, 2H), 7.16 – 7.06(m, 6H), 5.32(d, J = 18.6 Hz, 2H), 2.59(d, J = 21.2 Hz, 30H), 1.57(s, 28H), 1.43(s, 4H), 1.22(d, J = 26.3 Hz, 45H), 0.85(dd, J = 17.3, 12.8 Hz, 18H).

IDTT-ProDOT-BTD-SN (2.75/0.25/1/1.5) (P4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57(s, 1H), 7.55(s, 2H), 7.25(d, J = 51.0 Hz, 16H), 7.13(s, 9H), 2.57(s, 10H), 1.57(s, 20H), 1.43(s, 3H), 1.39 – 1.13(m, 50H), 1.03(s, 2H), 0.93 – 0.75(m, 22H).



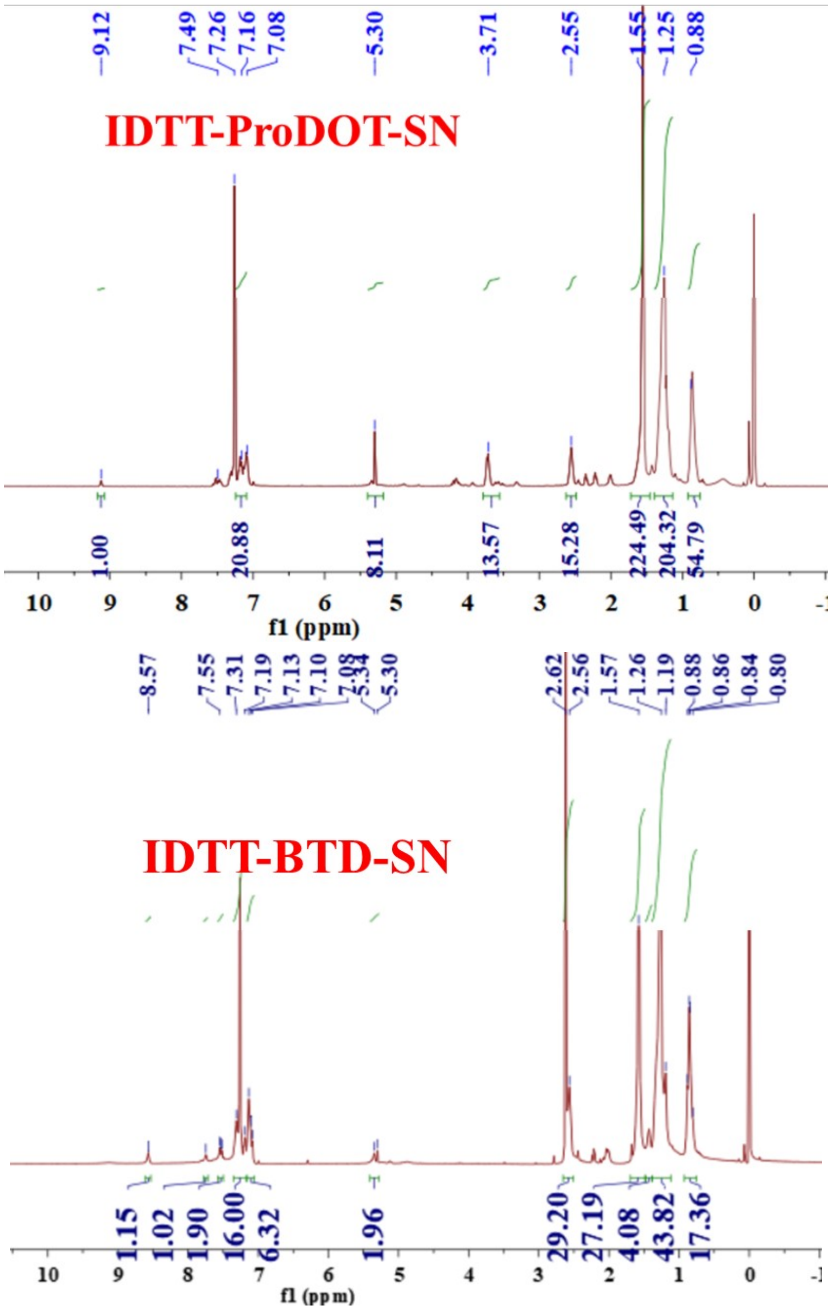
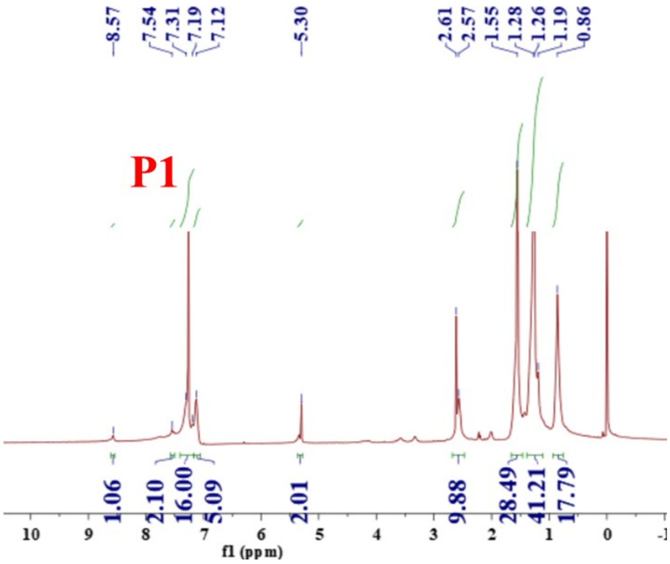
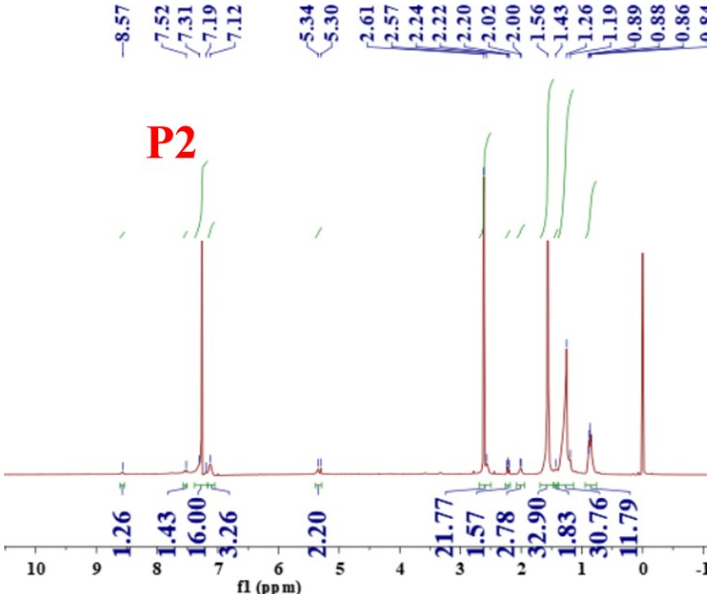
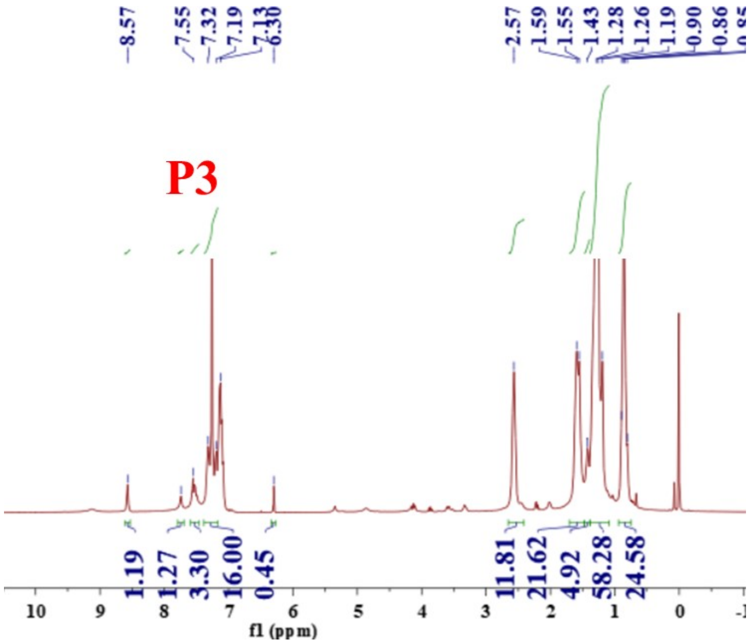


Fig.S2 ^{1}H NMR spectra of the synthesized random copolymers IDTT-SN, IDTT-ProDOT-SN, and IDTT-ProDOT-BTD.


P1
8.57
7.54
7.31
7.19
7.12
5.30
2.61
2.57
1.55
1.28
1.26
1.19
0.86
1.06
2.10
16.00
5.09
2.01
9.88
28.49
41.21
17.79
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


P2
8.57
7.52
7.31
7.19
7.12
5.34
5.30
2.61
2.57
2.24
2.22
2.20
2.02
2.00
1.56
1.43
1.26
1.19
0.89
0.88
0.86
1.26
1.43
16.00
3.26
2.20
21.77
1.57
2.78
32.90
1.83
30.76
11.79
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


P3
8.57
7.55
7.32
7.19
7.13
6.30
2.57
1.59
1.55
1.43
1.28
1.26
1.19
0.90
0.86
1.19
1.27
3.30
16.00
0.45
11.81
21.62
4.92
58.28
24.58
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

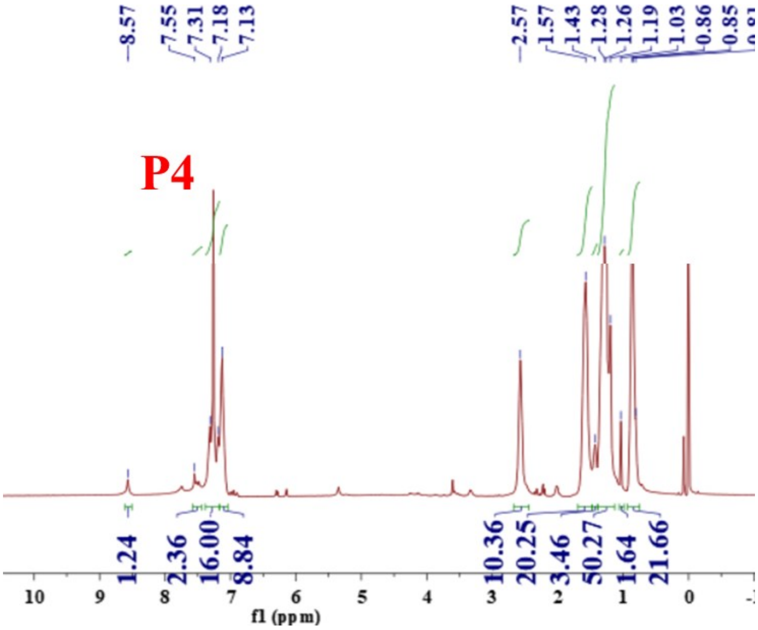
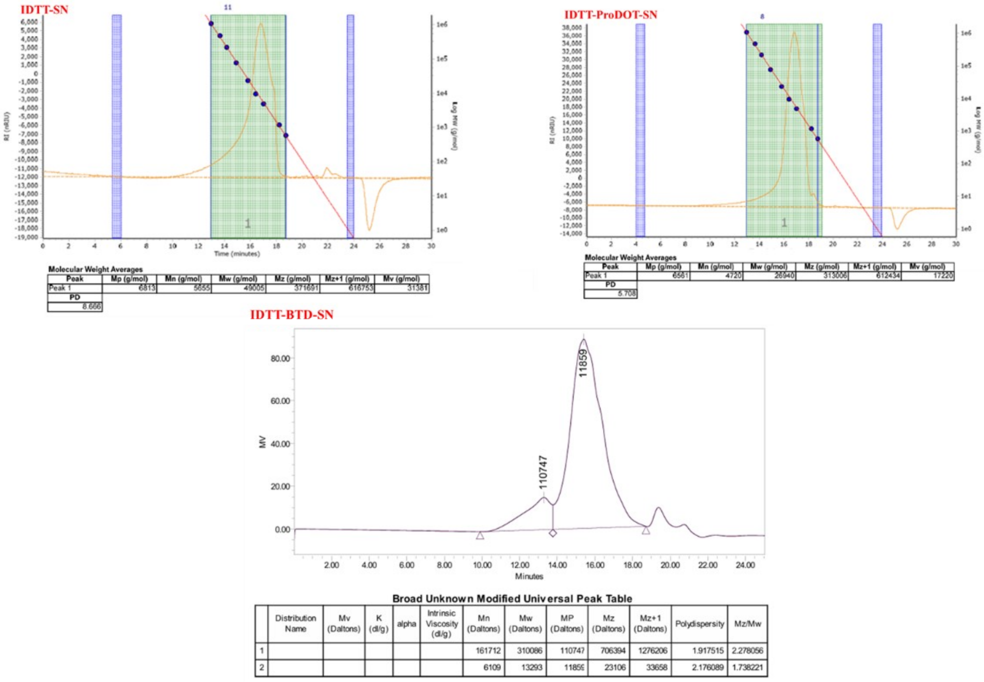


Fig.S3 ^{1}H NMR spectra of the synthesized random copolymers P1-P4.



IDTT-SN

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	6813	5655	49005	371691	616753	31381

PD
8.666

IDTT-ProDOT-SN

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	6561	4720	26940	313006	612434	17220

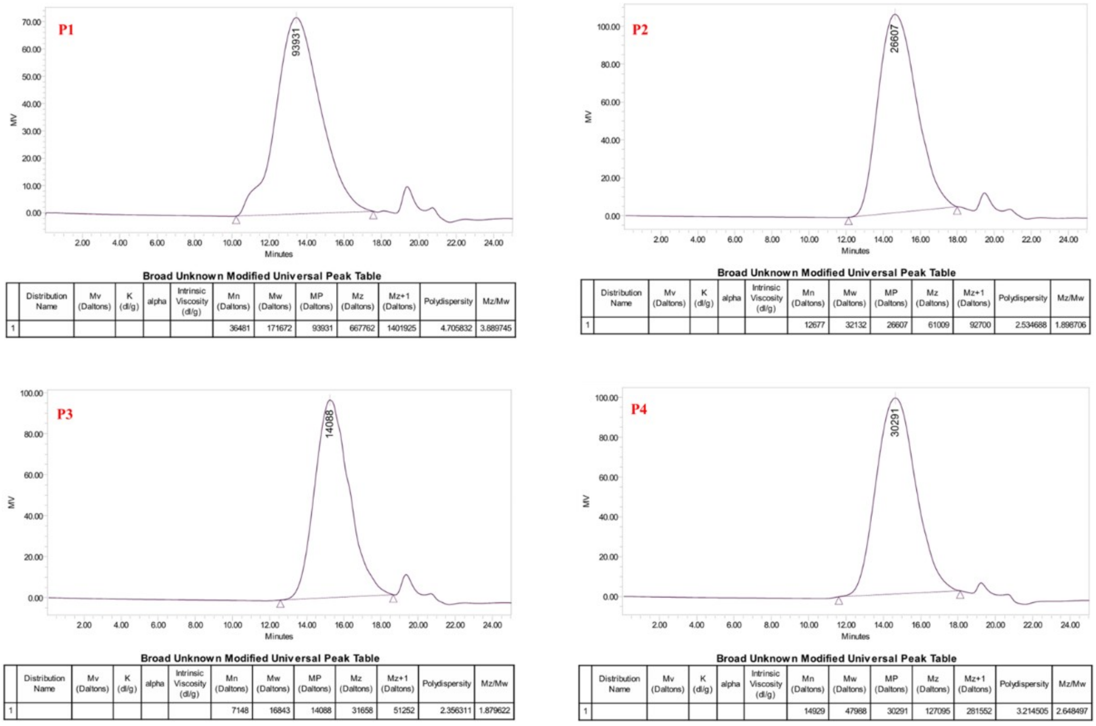
PD
5.708

IDTT-BTD-SN

Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						161712	310086	110747	706394	1276206	1.917515	2.278056
2						6109	13293	11859	23106	33658	2.176089	1.738221

Fig.S4 GPC graces of the synthesized copolymers IDTT-SN, IDTT-ProDOT-SN, and IDTT-ProDOT-BTD.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						36481	171672	93931	667762	1401925	4.705832	3.889745

Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						12677	32132	26607	61009	92700	2.534688	1.898706

Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						7148	16843	14088	31658	51252	2.356311	1.879622

Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						14929	47988	30291	127095	281552	3.214505	2.648497

Fig.S5 GPC graces of the synthesized copolymers P1-P4.

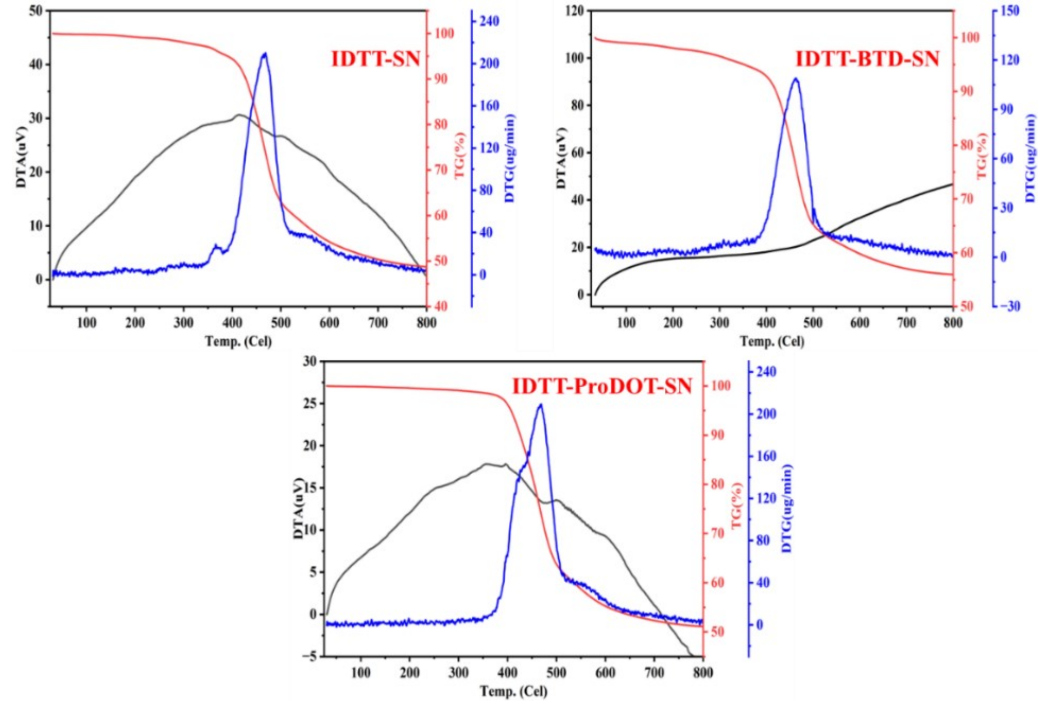


Fig.S6 TGA curves of the synthesized polymers IDTT-SN, IDTT-ProDOT-SN, and IDTT-ProDOT-BTD.

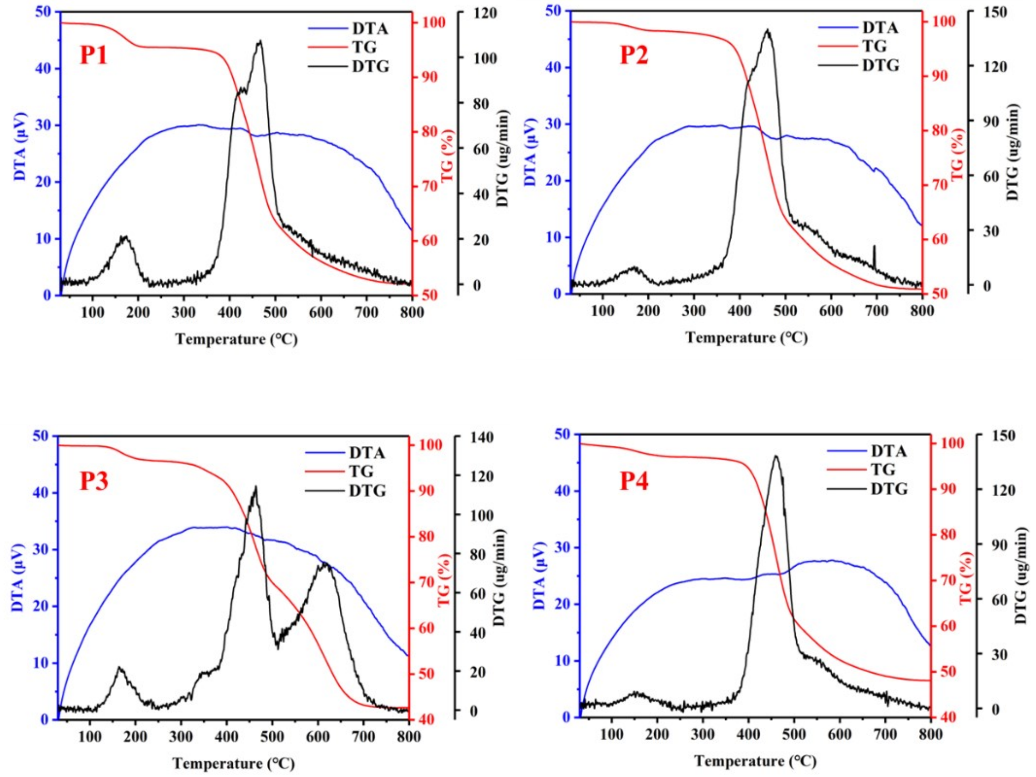


Fig.S7 TGA curves of the synthesized polymers P1-P4.

Table S1. Yield, molecular weights, PDI, and decomposition temperature (td) of the prepared polymers.

Polymer	**Yield（%）**	**Mn（Da）**	**Mw（Da）**	**PDI**	**$t_d{}^a$（°C）**
IDTT-SN	**70**	**8829**	**64382**	**7.29**	**390**
IDTT-ProDOT-SN	**62**	**4720**	**26940**	**5.71**	**407**
IDTT-TBD-SN	**78**	**6109**	**13293**	**2.2**	**352**
P1	**64**	**36481**	**171672**	**4.7**	**348**
P2	**55**	**12677**	**32132**	**2.5**	**390**
P3	**51**	**7148**	**16843**	**2.4**	**344**
P4	**60**	**14929**	**47988**	**3.2**	**396**

a t_d--- decomposition temperature of the polymers.

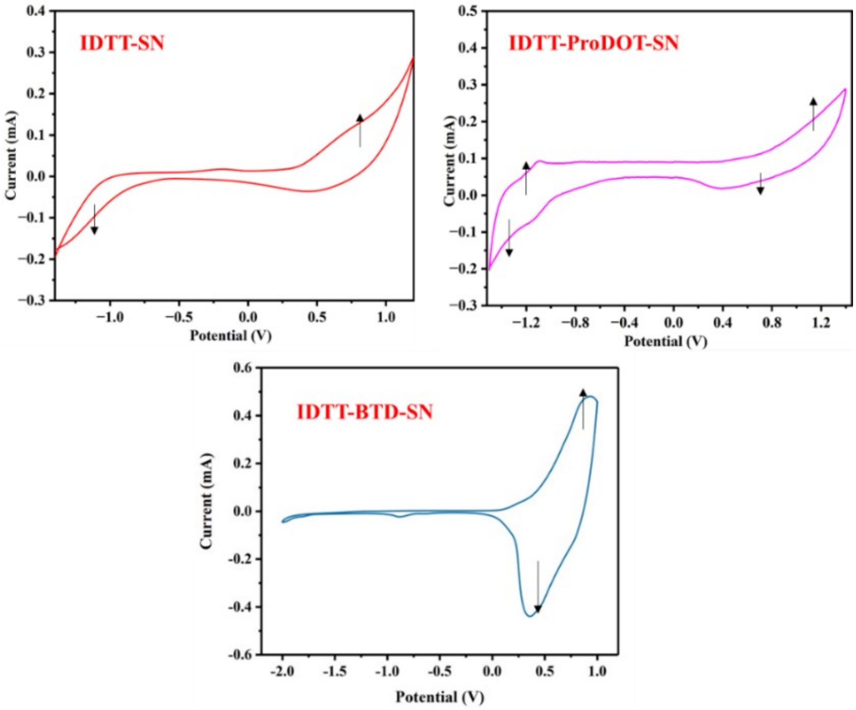


Fig.S8 Complete CV curves of the polymer films IDTT-SN, IDTT-ProDOT-SN, and IDTT-ProDOT-BTD at a scan rate of 5mV/s.

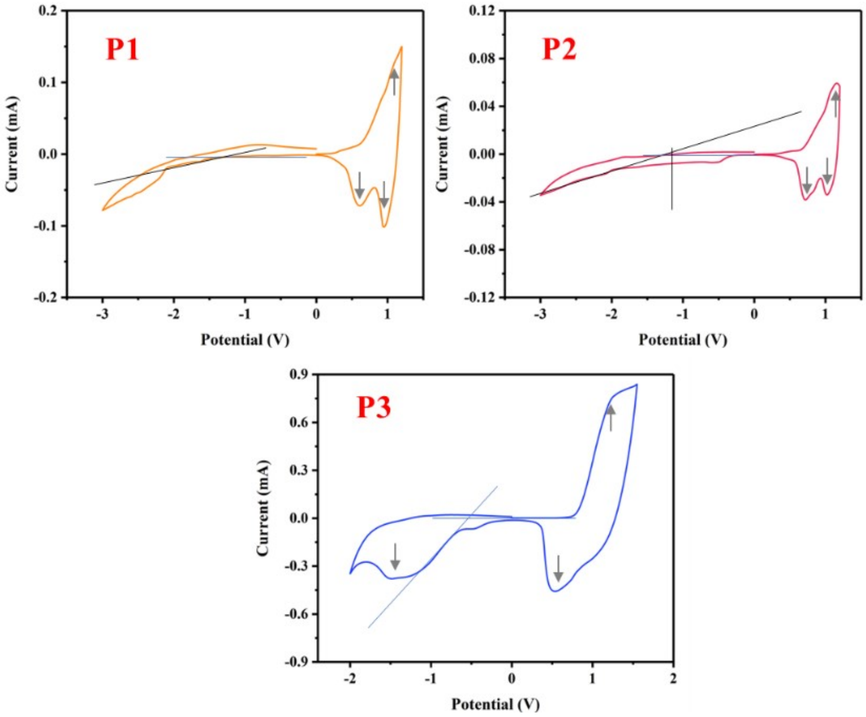


Fig.S9 Complete CV curves of the thin polymer films P1-P3 at a scan rate of 5mV/s.

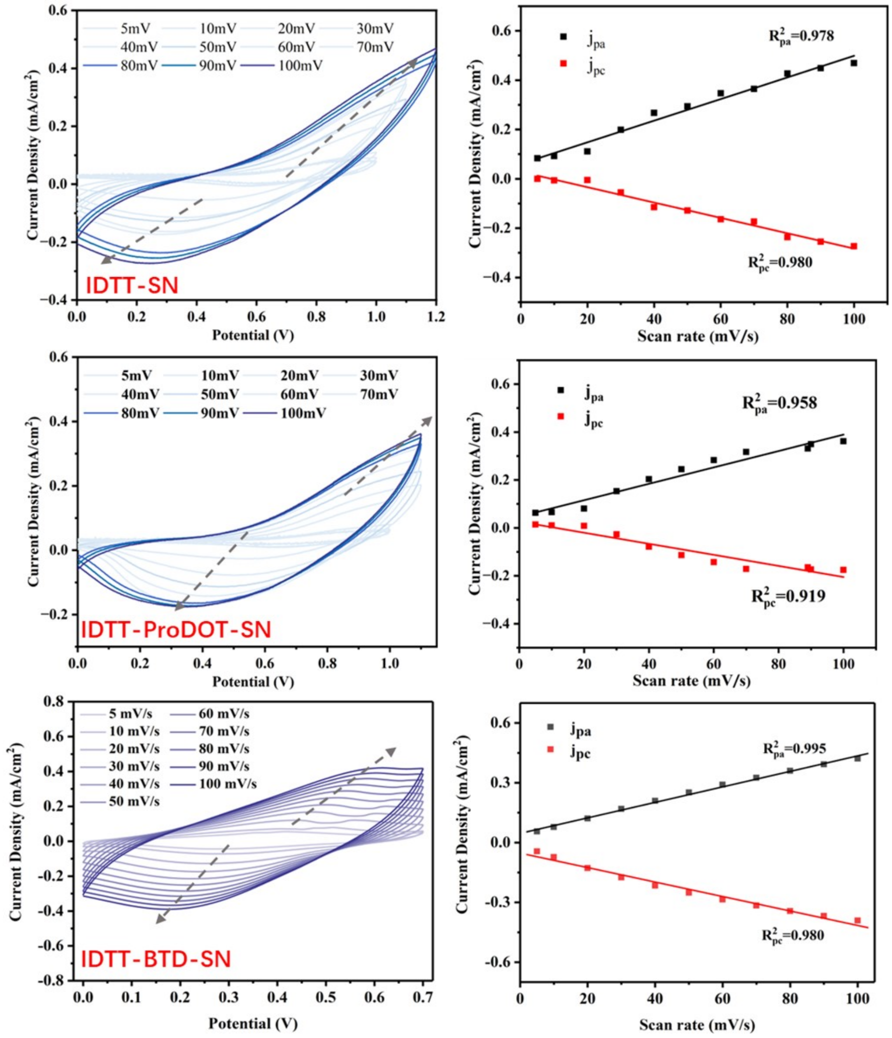


Fig. S10 Cyclic voltammograms of IDTT-SN, IDTT-ProDOT-SN, and IDTT-ProDOT-BTD films at scan rates of 5-100 mV/s (left). Linear relationship between peak current density and scan rate (right).

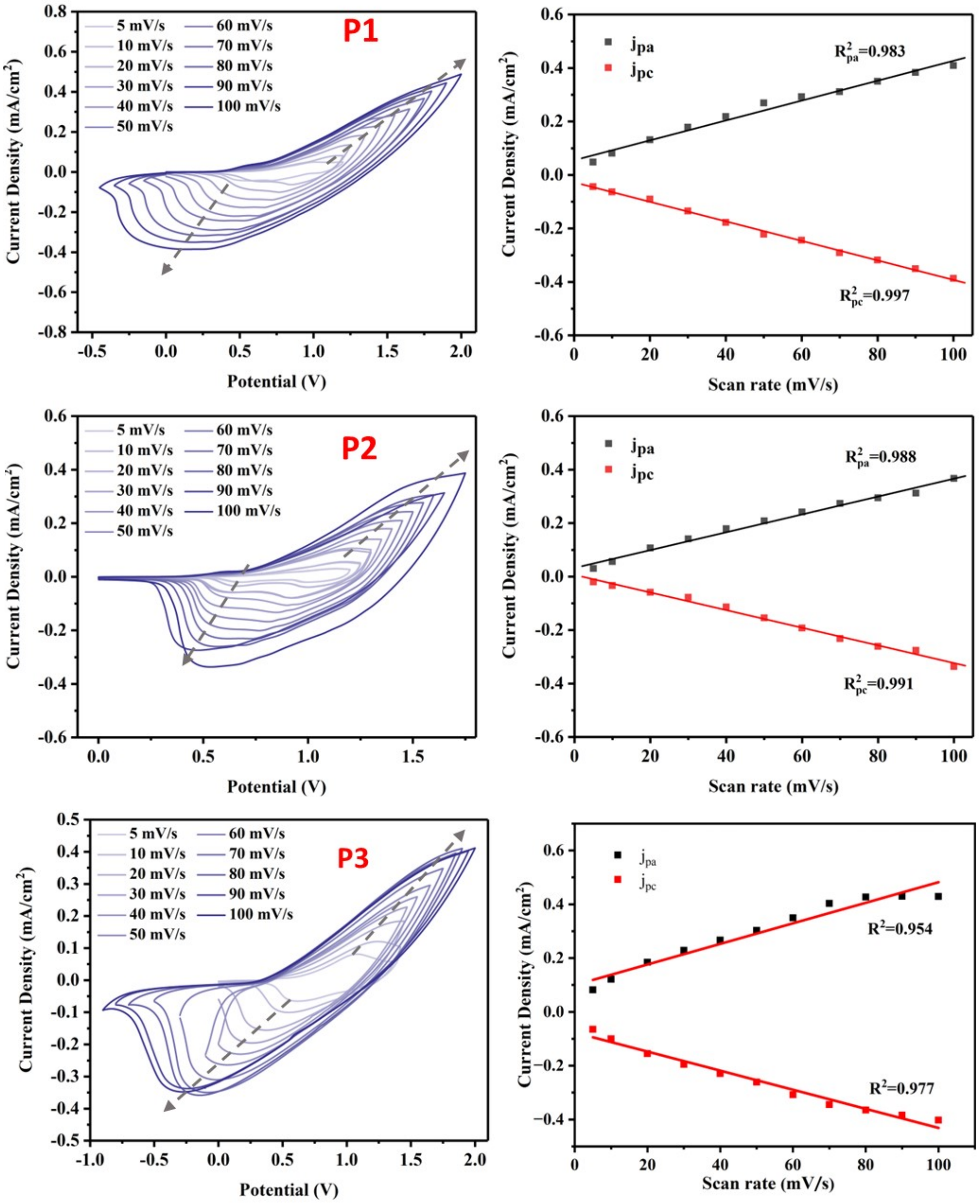


Fig. S11 Cyclic voltammograms of the polymer films P1-P4 at scan rates of 5-100 mV/s (left). Linear relationship between peak current density and scan rate (right).

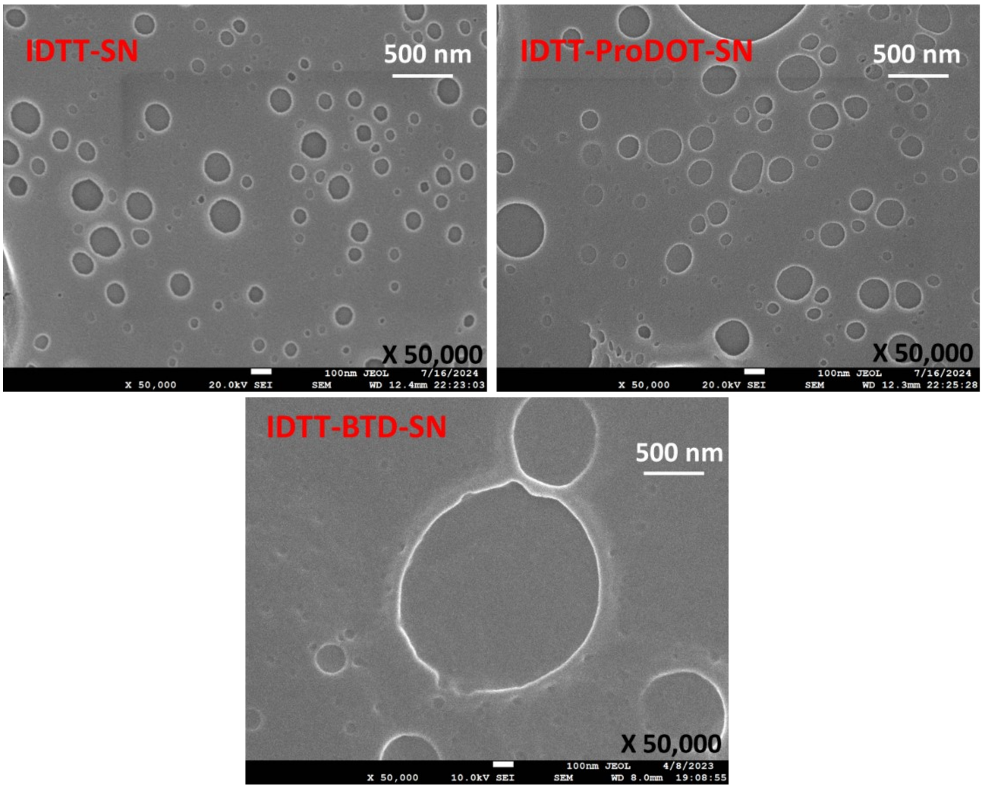


Fig.S12 SEM images of the surface of the polymer films IDTT-SN, IDTT-ProDOT-SN, and IDTT-BTD-SN.

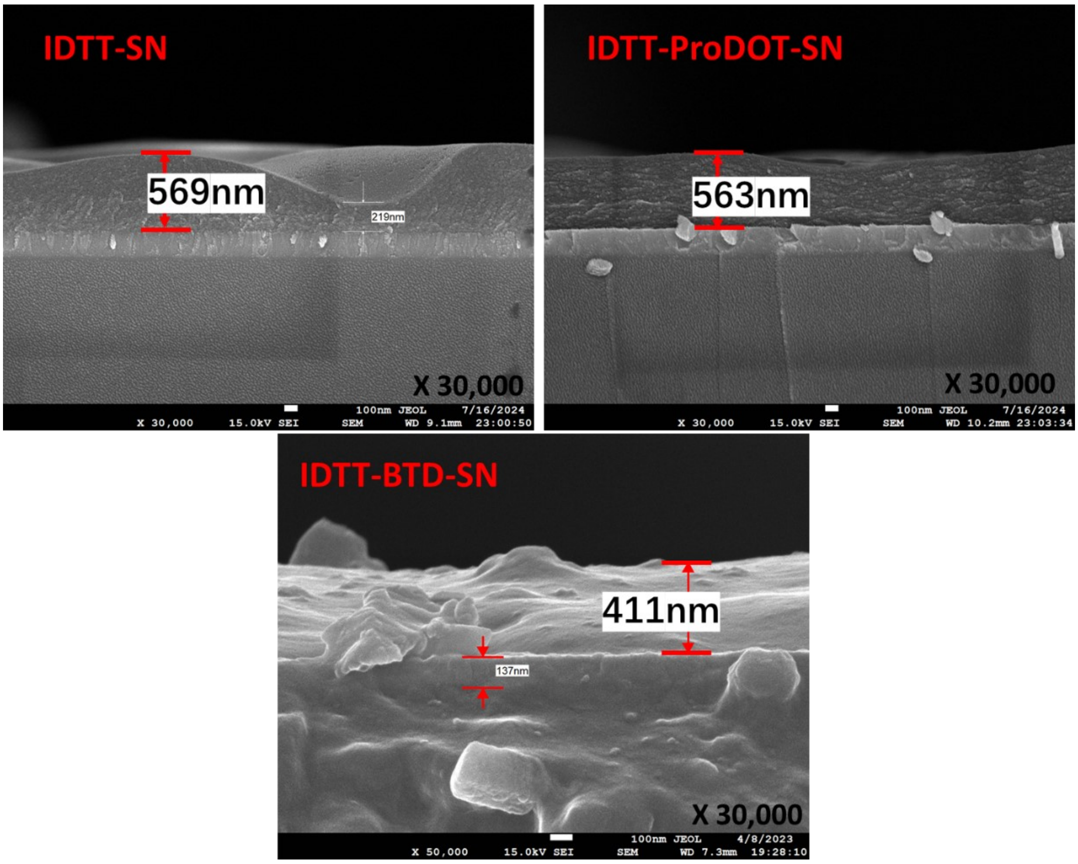


Fig.S13 SEM images of the cross-section of the polymer films IDTT-SN, IDTT-

ProDOT-SN, and IDTT-BTD-SN.

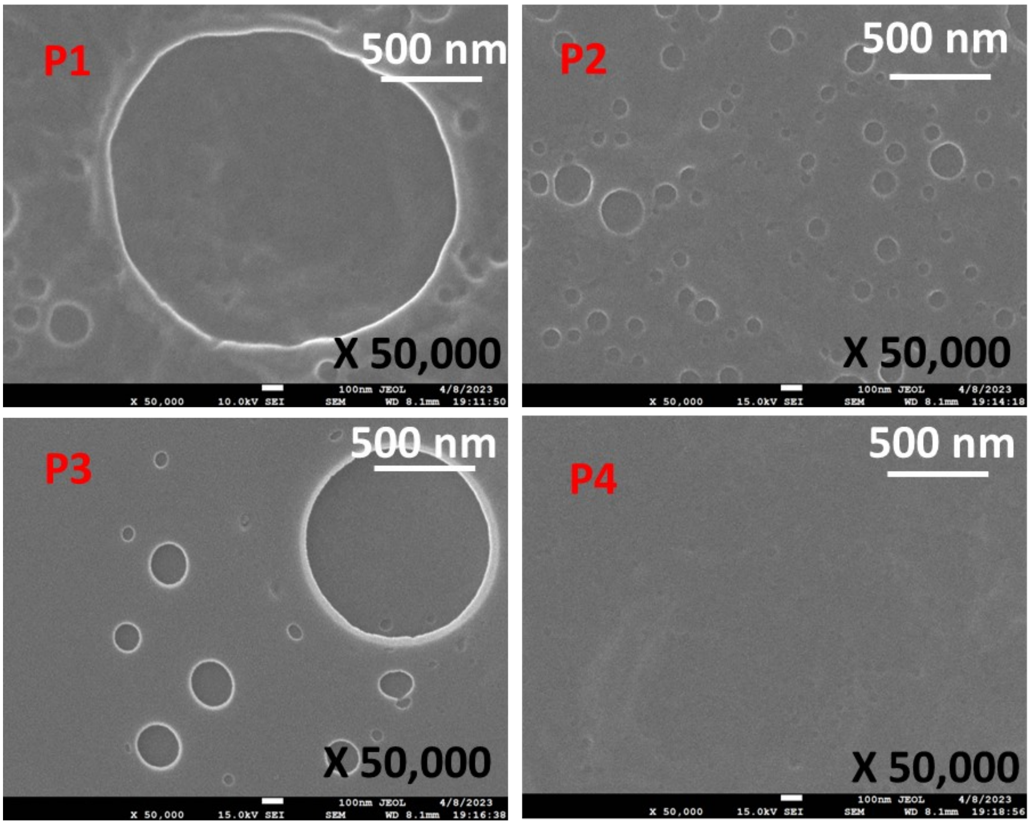


Fig.S14 Surface morphology images of the spray-coated films P1-P4.

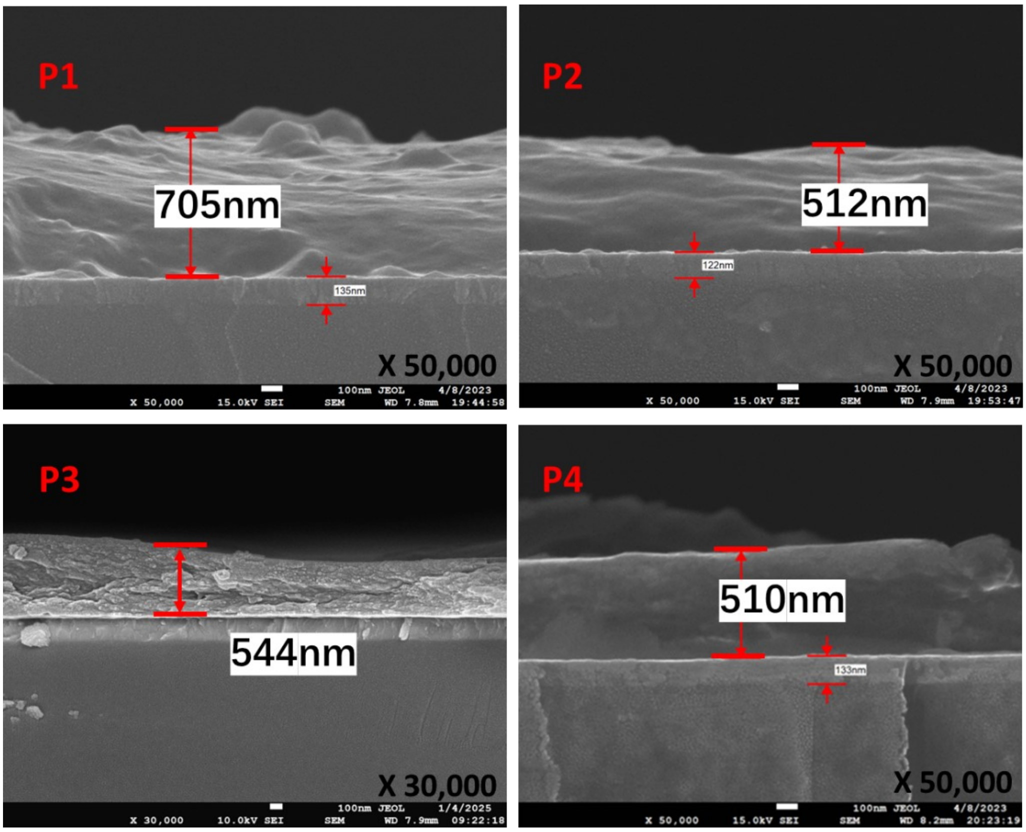


Fig.S15 Cross-sectional images of the spray-coated copolymer films P1-P4.

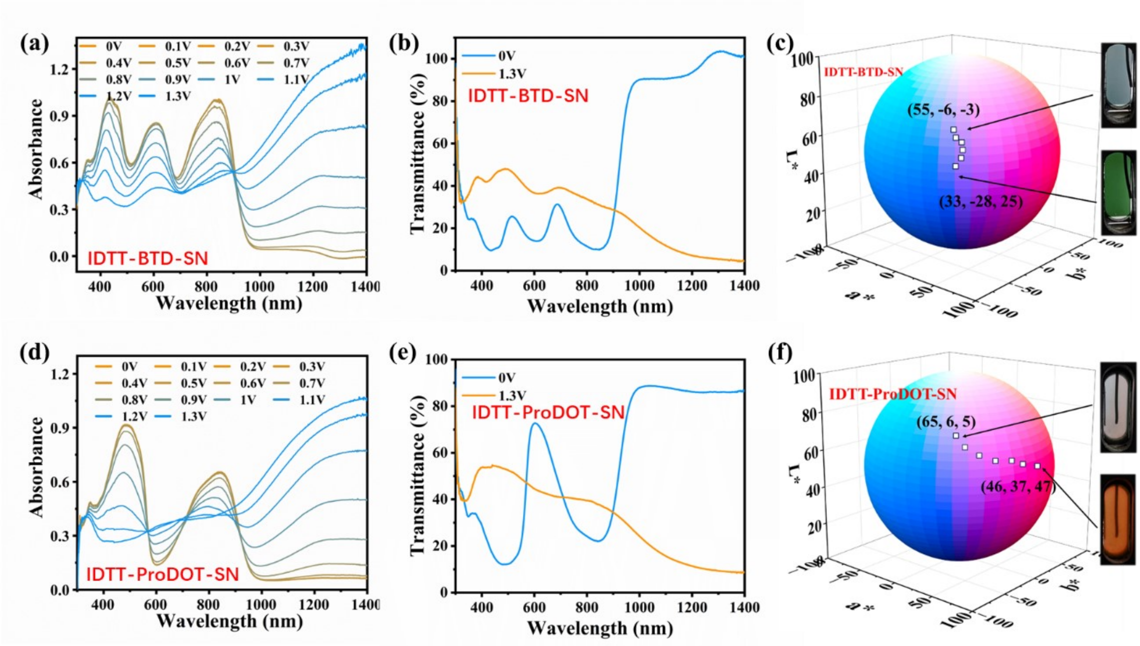


Fig.S16 Spectroelectrochemistry, transmittance, and CIE L*a*b* color coordinates for the polymers IDTT-BTD-SN and IDTT-ProDOT-SN and their corresponding photographs.

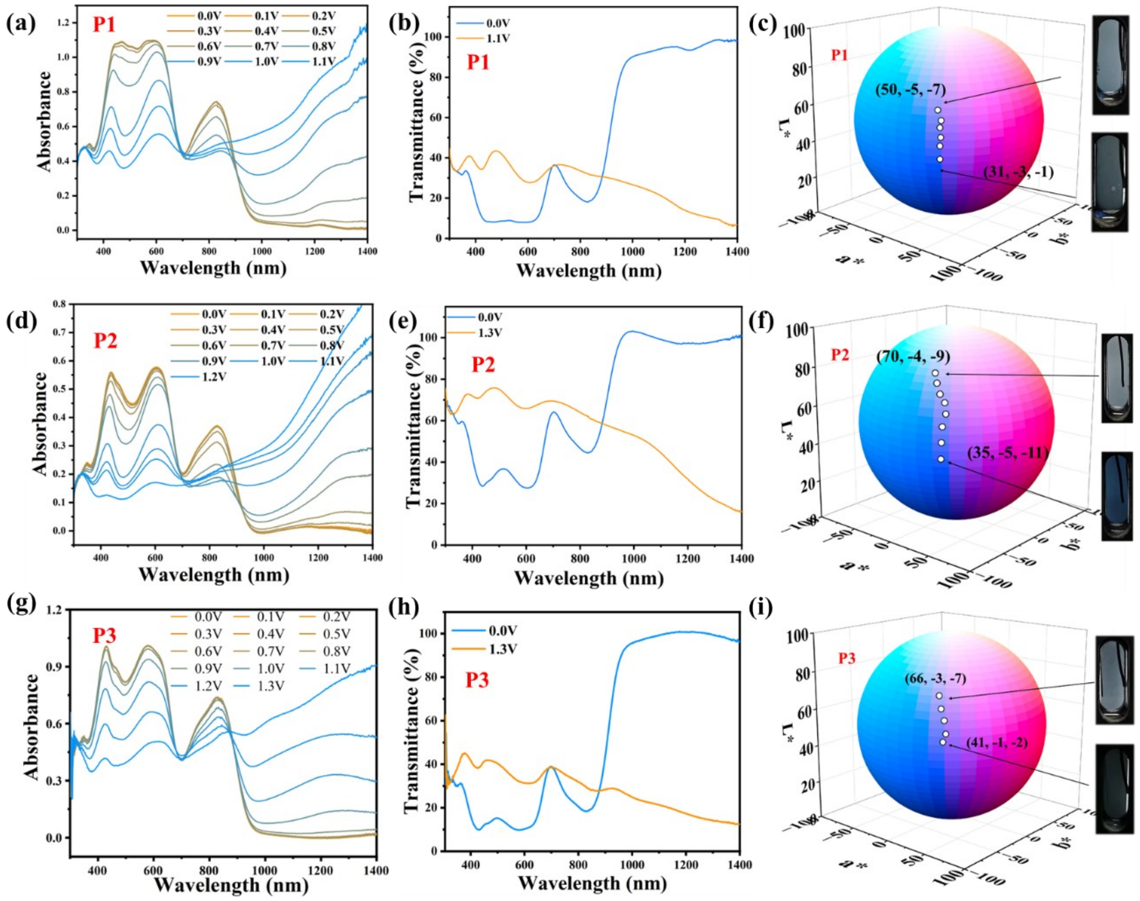


Fig.S17 Spectroelectrochemistry, transmittance, and CIE L*a*b* color coordinates for the polymers P1-P3 and their corresponding photographs.

Table S2 Summary of CIE L*a*b* color coordinates and chromatic aberrations for all polymer films.

Polymer		L*	a*	b*	ΔE*
IDTT-SN	neutral state	**58**	**33**	**46**	**61.69**
	oxidized state	**83**	**-1**	**1**	
IDTT-ProDOT-SN	neutral state	**46**	**37**	**47**	**55.55**
	oxidized state	**65**	**6**	**5**	
IDTT-BTD-SN	neutral state	**33**	**-28**	**25**	**41.86**
	oxidized state	**55**	**-6**	**-3**	
P1	neutral state	**31**	**-3**	**-1**	**20.02**
	oxidized state	**50**	**-5**	**-7**	
P2	neutral state	**35**	**-5**	**-11**	**35.07**
	oxidized state	**70**	**-4**	**-9**	
P3	neutral state	**41**	**-1**	**-2**	**25.57**
	oxidized state	**66**	**-3**	**-7**	
P4	neutral state	**44**	**1**	**4**	**27.48**
	oxidized state	**69**	**-2**	**-7**	

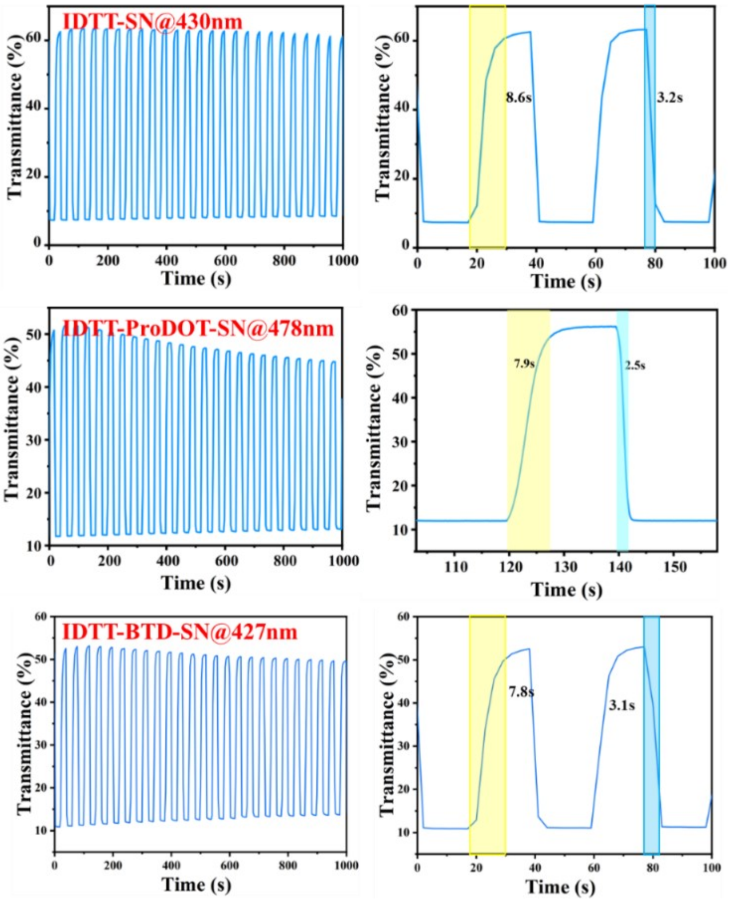


Fig.S18 Square-wave cyclic stability and switching response of polymers IDTT-SN, IDTT-ProDOT-SN, and IDTT-BTD-SN.

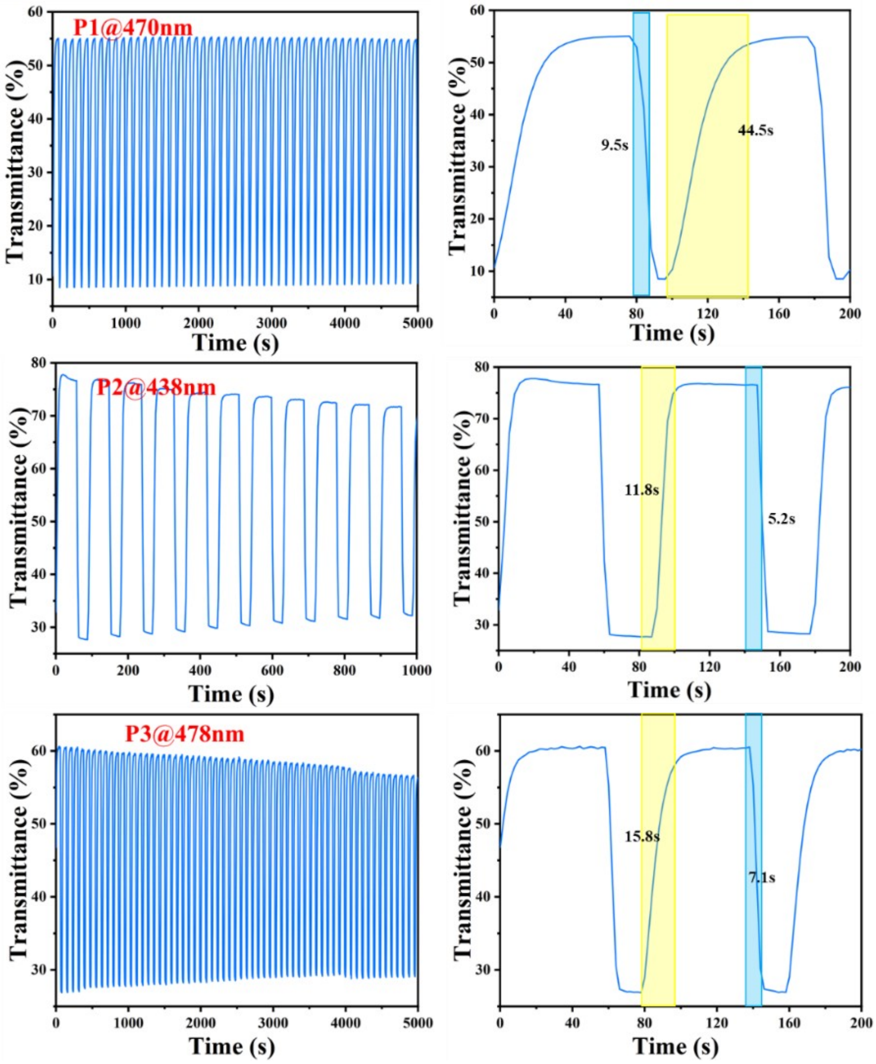


Fig.S19 Square-wave cyclic stability and switching response of polymers P1-P3.

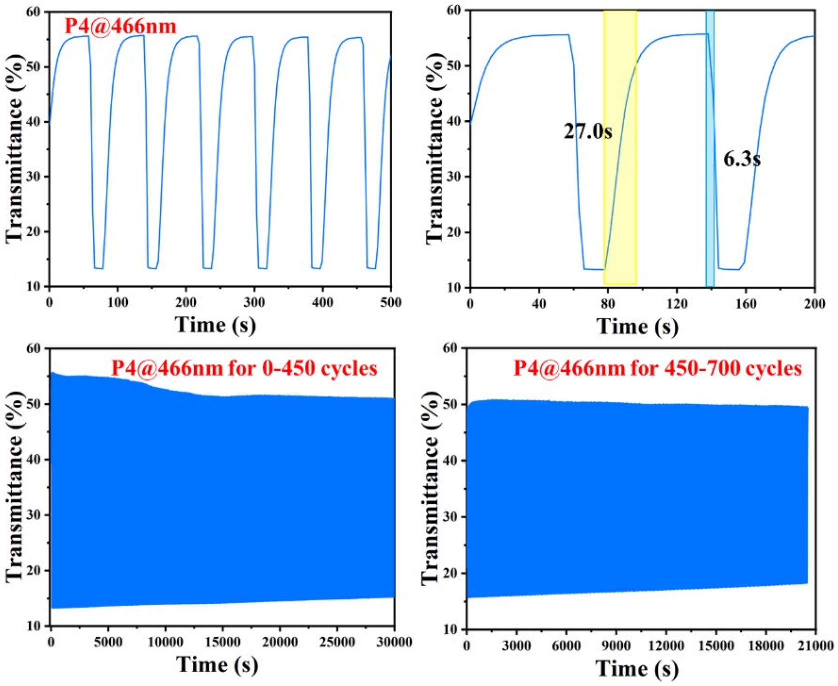


Fig.S20 Square-wave cyclic stability and switching response of polymer P4.

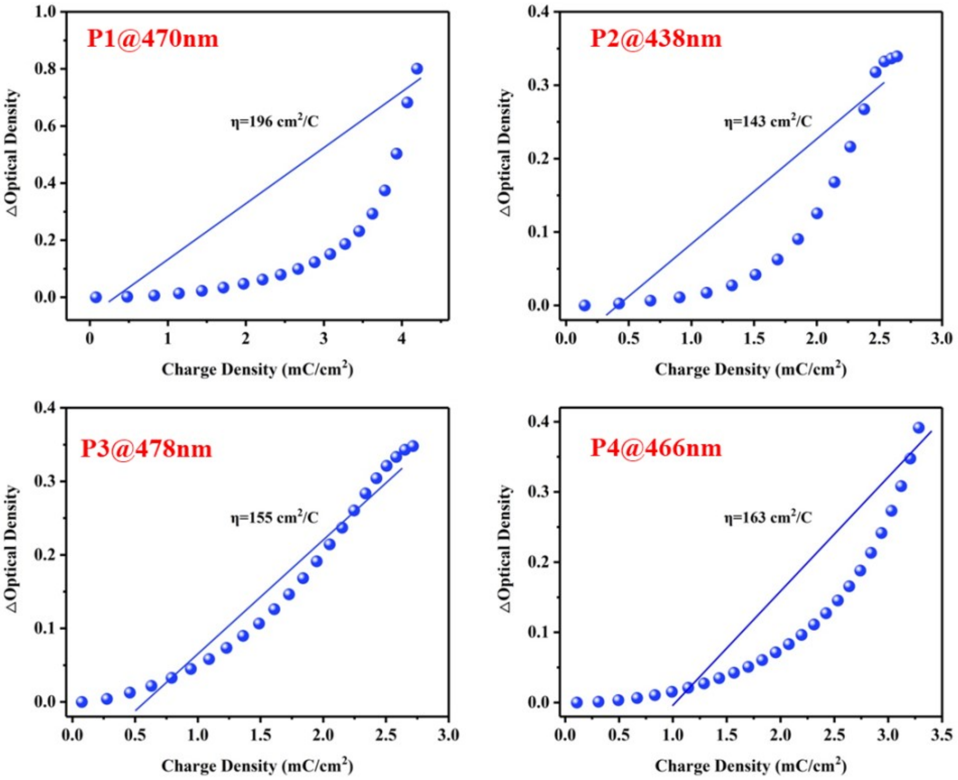


Fig.S21 Coloration efficiency of polymer P1-P4.

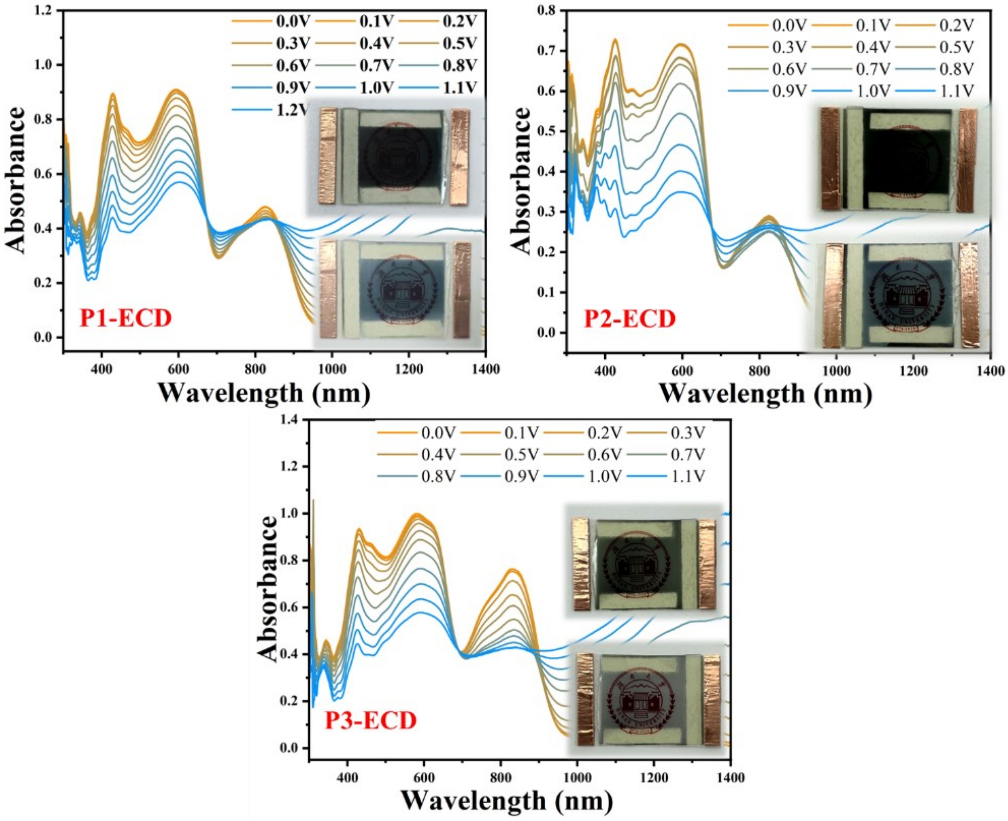


Fig.S22 Spectroelectrochemistry of the ECDs based on P1-P3 and their corresponding photographs.

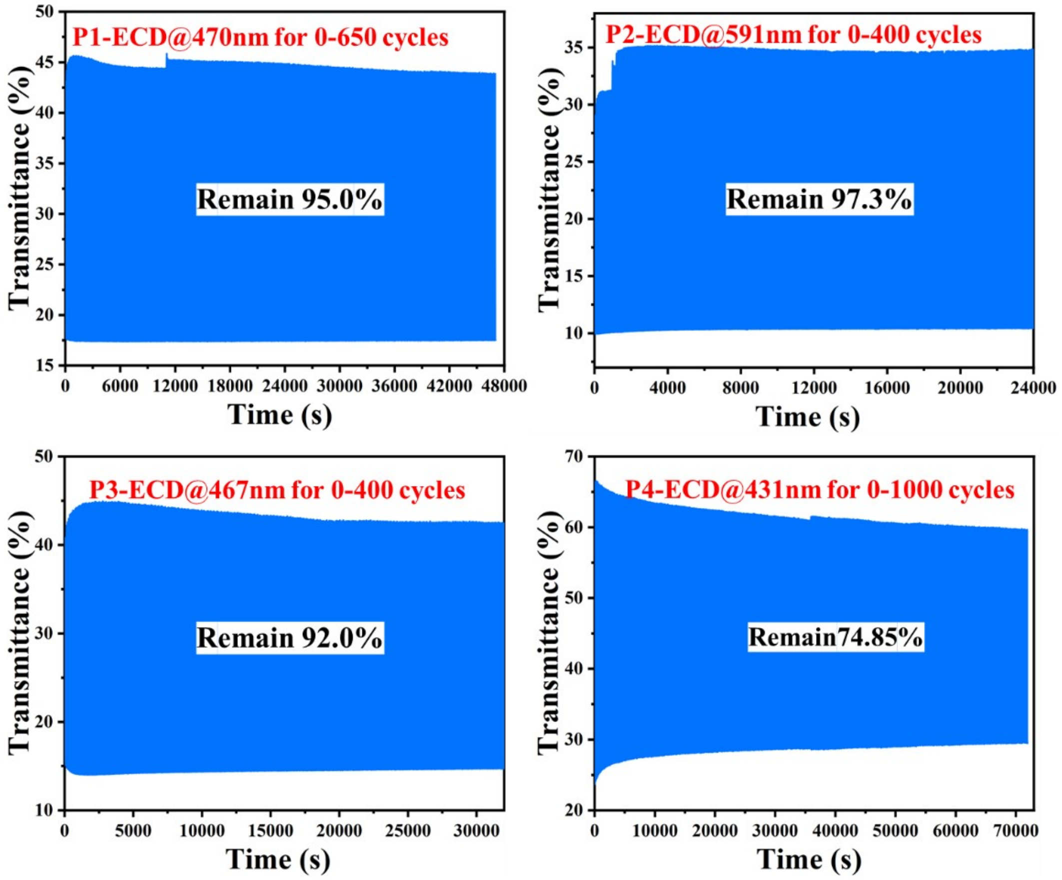


Fig.S23 Square-wave cyclic stability of the ECDs based on P1-P4.

Calculation of the CIE L*a*b* color coordinates:

Color coordinates and color differences can be determined according to ASTM D2244:2011 (Standard practice for calculation of color tolerances and color differences from instrumentally measured color coordinates), which is based on CIE-L*a*b* (CIELAB) standard from CIE, International Commission on Illumination. This system defines three parameters: L*, a* and b*, which represent black/white (lightness), red/green and yellow/blue color pairs, respectively. The color difference formula is used to calculate the difference between two colors in the Lab color space. A commonly used color difference formula is ΔE*ab (Delta E), which is calculated as follows:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$$L^* = 116\left({}^{Y}\!/_{Y_0}\right)^{1/3} - 16$$

$$a^* = 500\left[\left({}^{X}\!/_{X_0}\right)^{1/3} - \left({}^{Y}\!/_{Y_0}\right)^{1/3}\right]$$

$$b^* = 200\left[(Y / Y_0)^{1/3} - (Z / Z_0)^{1/3}\right]$$

X, Y, Z are the tristimulus values of the color sample, which is calculated by transmission $T\ (\lambda)$ spectra from 380nm to 780nm. X_0, Y_0, Z_0 are the tristimulus values of the CIE standard illuminant, which are constant values.

Calculation of the Solar Heat Gain Coefficient (SHGC):

Solar direct transmittance and reflectance factors τ_e and ρ_e can be calculated by transmission $T\ (\lambda)$ and reflection $R\ (\lambda)$ spectra from 300nm to 2500nm (from 300nm to 1400nm for our work), respectively,

$$\tau_e = \frac{\int T(\lambda) \cdot S(\lambda) d(\lambda)}{\int S(\lambda) d(\lambda)},\ \rho_e = \frac{\int R(\lambda) \cdot S(\lambda) d(\lambda)}{\int S(\lambda) d(\lambda)},$$

where $S\ (\lambda)$ is the standard AM 1.5G spectral irradiance.

SHGC represents the total solar energy transmitted indoors through the glazing and can be calculated by the following equation:

$$SHGC = \tau_e + \frac{\alpha_e h_i}{h_i + h_e},$$

with solar direct absorptance factor $\alpha_e = 1 - \tau_e - \rho_e$ (ρ_e is 0 in our work). h_i and h_e are the internal and external heat transfer coefficients, respectively. According to a European standard (EN 673), h_i = 7.7 W m^{-2} K^{-1} and h_e = 25.0 W m^{-2} K^{-1}.

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