

Color-to-white switching electrochromic devices constructed by combining fused thienothiophene polymers and high-reflectivity electrolyte

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Materials

All chemical reagents and solvents used in polymer synthesis, electrolyte preparation and device fabrication are sourced from Shanghai Aladdin Bio-Chem Technology Co., LTD and Sinopharm Chemical Reagent Co, LTD, China. Polymethyl methacrylate (PMMA, $M_w \sim 1,000,000$) and Poly(vinylidene fluoride) (PVDF, $M_w \sim 150,000$) are obtained from Arkema Co., LTD, France. Titanium dioxide (TiO_2) is a product of Shanghai Macklin Biochemical Co., Ltd, China. And ITO glass ($< 17 \Omega / sq^{-1}$) was obtained from Zhuhai Kaivo Optoelectronic Technology Co., Ltd, China. 5,7-Dibromo-2,3-dihydrothieno[3,4-

b][1,4]dioxine (EDOT-2Br), indacenodithieno[3,2-b]thiophene (IDTT), tri(thienothiophene) (TTT) are synthesized according to the reported references [1-3].

General procedure for the synthesis of polymers

All of the polymers in this manuscript were synthesized via direct arylation polymerization (DArP) with the same polymerization condition except the applied monomer and their feed ratio, and the corresponding monomer structure and feed ratio for these three polymers are given in Fig.S1 and Table.S1. Compound M-H (0.25mmol) and M-Br (0.25mmol) were charged in a 50mL two-neck flask. K_2CO_3 (0.75mmol), Pivalic acid (0.08mmol), and $Pd(OAc)_2$ (0.00125mmol) were added into the flask, and the mixture was degassed by three freeze/pump/thaw cycles to fill with argon. Then, 7mL Dimethylacetamide was injected into the flask, and the mixture was degassed and filled with argon again. The mixture was heated at 100°C and reacted for 48h. After cooling to room temperature, the mixture was dropwise added into cold methanol and cooled in a fridge for 30 min. The precipitate was collected and washed by 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 1H NMR spectra are shown as followed in

Fig.S2. For the TTT homopolymer preparation, the mixture was heated at 80°C for reaction to further reduce the β -coupling.

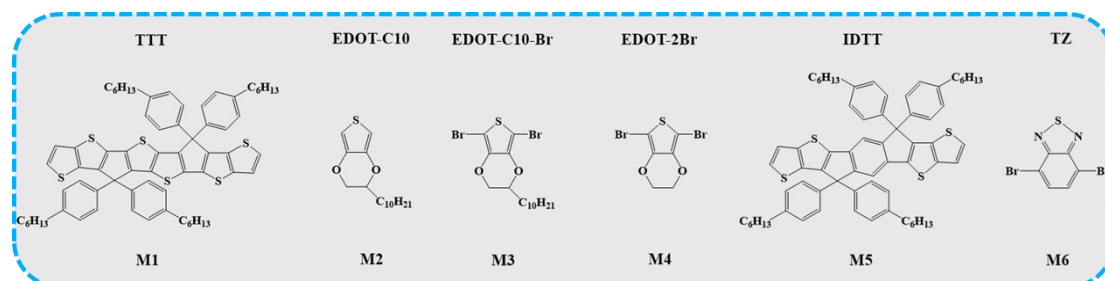
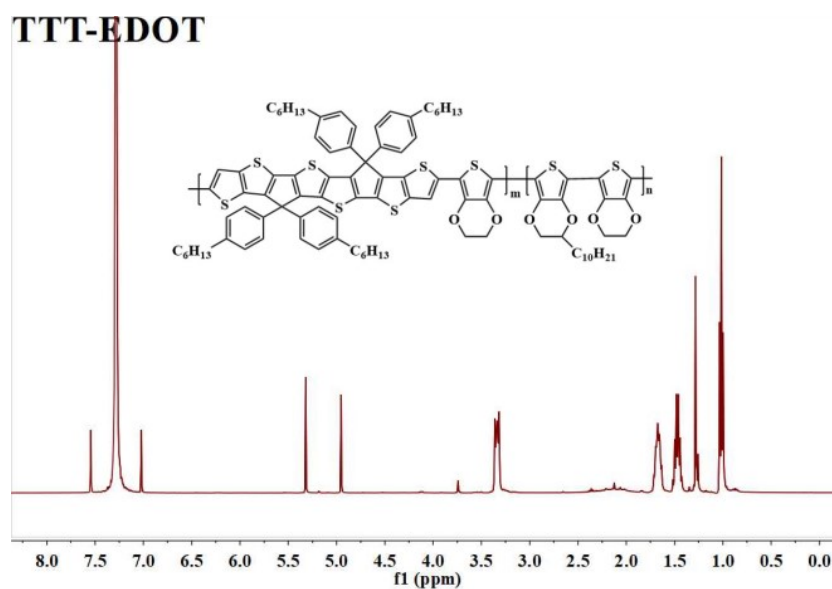


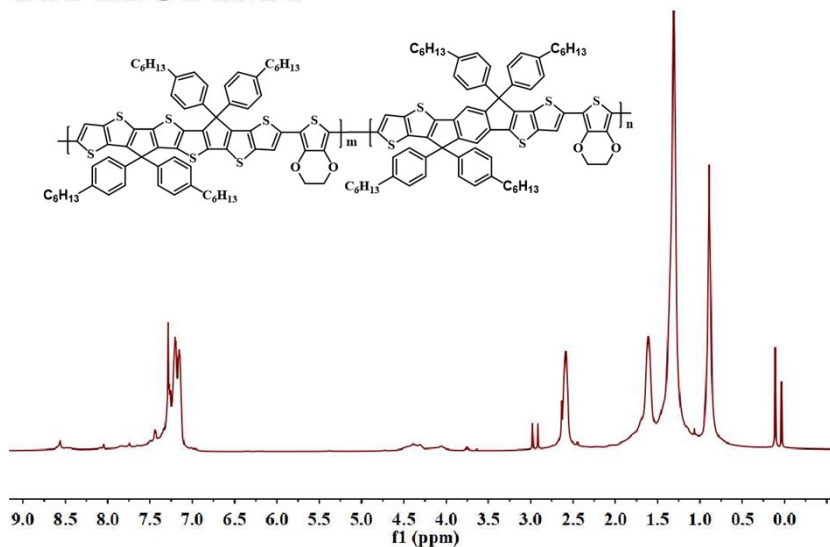
Fig. S1. The chemical structure of the applied monomers.

Table S1. Detailed monomer feed ratio for synthesizing the corresponding polymers.

| Polymer | Feeding ratio |
|---------------|---------------------|
| TTT-EDOT | M1:M2:M4=1:1:2 |
| TTT-EDOT-IDTT | M1:M4:M5=1:2:1 |
| TTT-EDOT-TZ | M1:M2:M3:M6=2:1:1:2 |



TTT-EDOT-IDTT



TTT-EDOT-TZ

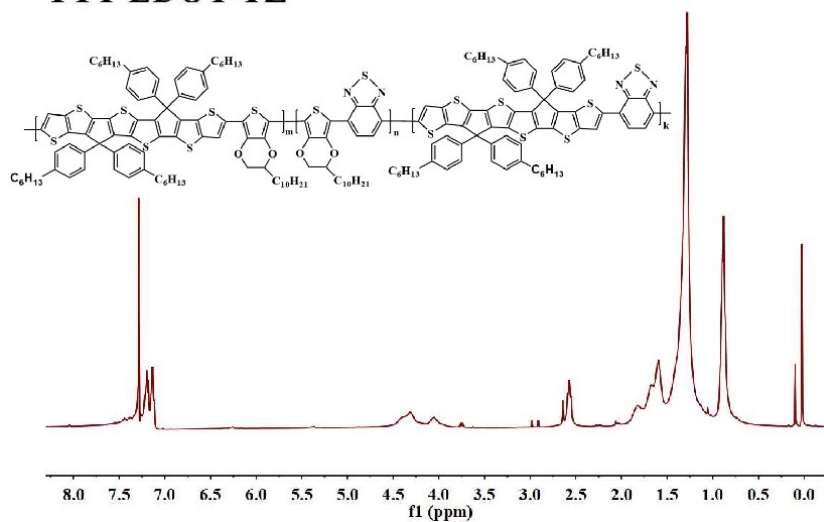


Fig. S2. ^1H NMR spectra of the synthesized polymers.

P(TTT-EDOT) blue solid in yield of 67%. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (s, 1H), 7.31-7.20 (m, 10H), 7.00 (d, 8H), 5.29 (s, 1H), 4.93 (t, 8H), 1.65 (t, 8H), 1.45 (t, 8H), 1.26 (m, 24H), 0.99 (t, 12H).

P(TTT-EDOT-IDTT) red solid in yield of 72%. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 2H), 7.32 (s, 1H), 7.30 – 7.22 (m, 20H), 7.15 (d, 16H), 6.94 (s, 1H), 4.58-4.22 (t, 8H), 2.59 (t, 16H), 1.59 (t, 16H), 1.28 (m, 48H), 0.87 (t, 24H).

P(TTT-EDOT-TZ) black solid in yield of 70%. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.34 (m, 6H), 7.17 (d, 24H), 7.11-7.09 (m, 30H), 4.16 (t, 12H), 2.56 (t, 24H), 1.61 (t, 24H), 1.26 (m, 72H), 0.86 (t, 36H).

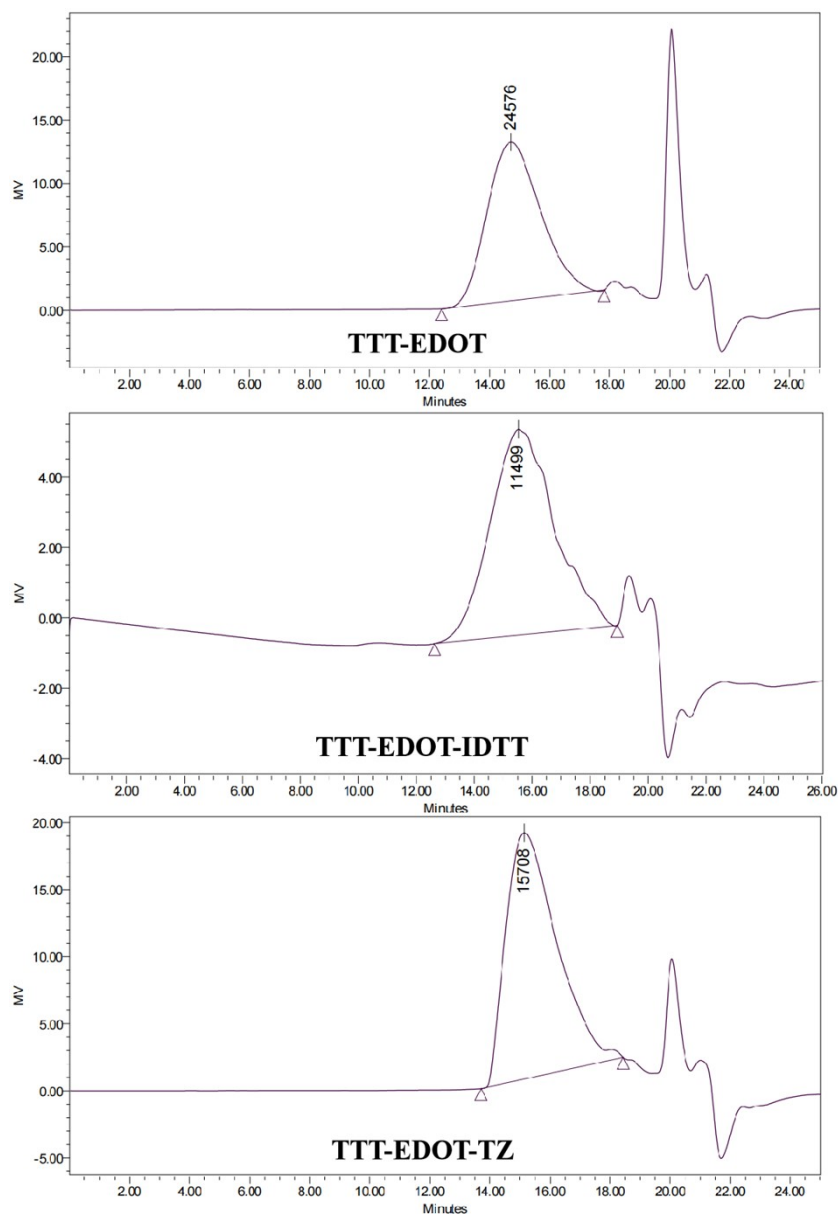


Fig. S3. GPC traces of the synthesized polymers.

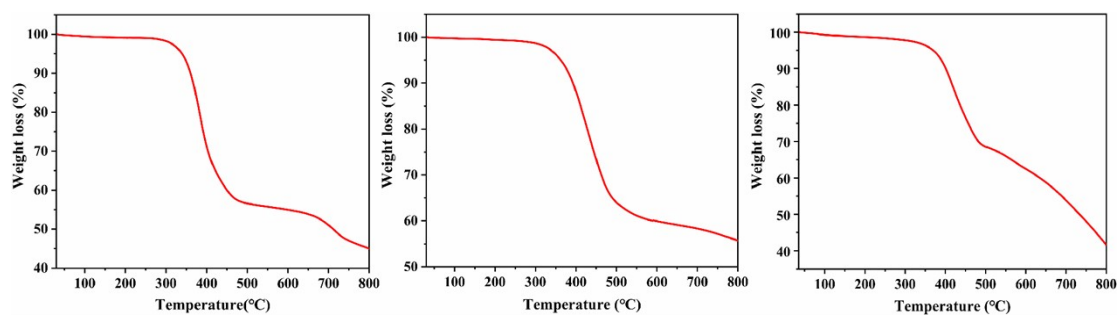


Fig. S4. TGA curves of the synthesized polymers (a) TTT-EDOT, (b) TTT-EDOT-IDTT, and (c) TTT-EDOT-TZ.

Table.S2. Yield, molecular weights, PDI, decomposition temperature (t_d) of the prepared polymers.

| Polymer | Yield (%) | Mn (Da) | Mw (Da) | PDI | t_d (°C) ^a |
|---------------|-----------|---------|---------|------|-------------------------|
| TTT-EDOT | 67% | 13882 | 28658 | 2.15 | 339 |
| TTT-EDOT-IDTT | 72% | 4609 | 16889 | 3.66 | 362 |
| TTT-EDOT-TZ | 70% | 6644 | 14022 | 3.13 | 369 |

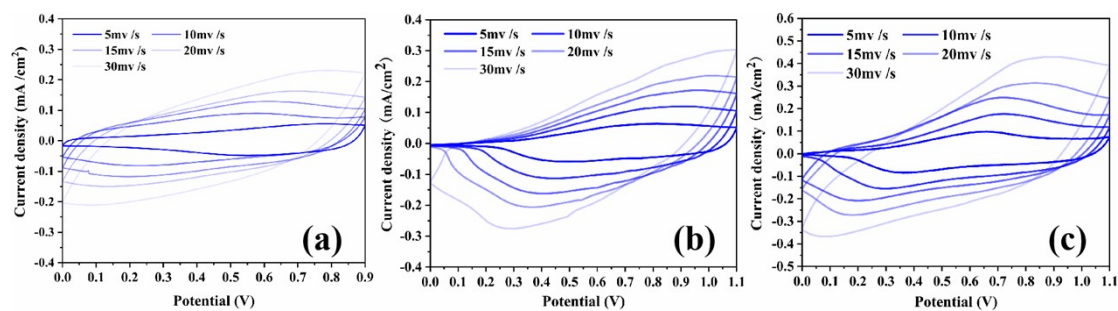
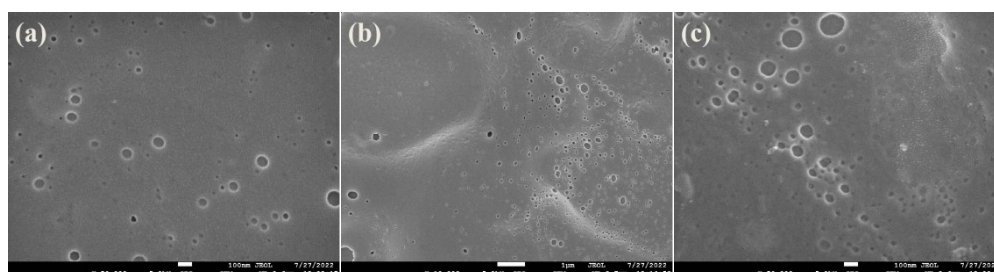


Fig. S5. Cyclic voltammograms of (a) TTT-EDOT, (b) TTT-EDOT-IDTT, and (c) TTT-EDOT-TZ films in 0.1M LiClO₄/PC under various scan rates.



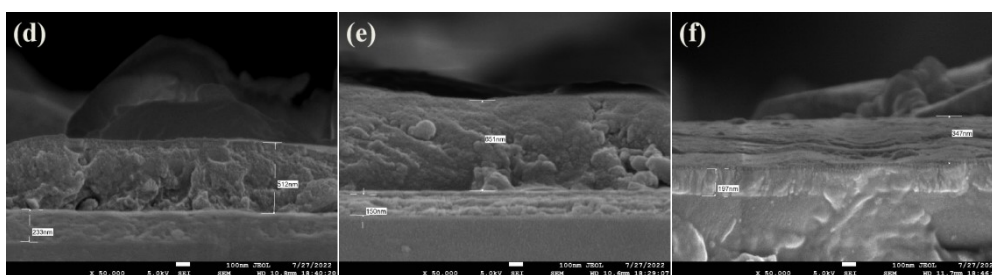


Fig. S6. Surface images and cross-sectional images of the spray-coated polymer films (a) and (d) TTT-EDOT, (b) and (e) TTT-EDOT-IDTT, (c) and (f) TTT-EDOT-TZ.

Table. S3. Optical and electrochemical properties of polymers in solution and in film state.

| Polymer | $\lambda_{\max, \text{sol}}$ (nm) ^a | $\lambda_{\max, \text{film}}$ (nm) | $\lambda_{\text{onset, film}}$ (nm) | E_{onset} (V) | E_{g} (eV) ^b | HOMO (eV) ^c | LUMO (eV) ^d |
|---------------|---|---------------------------------------|--|---------------------------|-------------------------------------|---------------------------|---------------------------|
| TTT-EDOT | 560 | 533 | 689 | 0.41 | 1.80 | -5.21 | -3.41 |
| TTT-EDOT-IDTT | 550 | 540 | 660 | 0.27 | 1.88 | -5.07 | -3.19 |
| TTT-EDOT-TZ | -- | --- | 770 | 0.31 | 1.61 | -5.11 | -3.5 |

^a UV-vis spectrum recorded in chloroform. ^b $E_{\text{g}} = 1240/\lambda_{\text{onset, film}}$. ^c $E_{\text{HOMO}} = -(E_{\text{onset, ox vs Ferrocene}}) - 4.8 \text{ eV}$. ^d $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$.

Table. S4. Summary of electrochromic properties of the prepared polymer films.

| Polymer | T_{\max} (nm) | Optical | Response time (s) | | CE | Switching |
|---------------|-----------------|--------------|-------------------|----------------|---|------------------------|
| | | Contrast (%) | T_{c} | T_{b} | (cm^2/C) ^a | Stability ^b |
| TTT-EDOT | 533 | 40 | 5 | 16 | 465.03 | 99% |
| TTT-EDOT-IDTT | 540 | 41 | 10 | 24 | 395.81 | 79% |
| TTT-EDOT-TZ | 474 | 43 | 7 | 28 | 444.24 | 95% |

^a Calculated at the maximum absorption. ^b the ratio of the retaining optical contrast after 500 switching cycles.

Table. S5. Summary of the TiO_2 , ion salt, DMF, acetone, PMMA and PVDF components for each electrolyte preparation

| Num | PMMA | acetone | DMF | BMIM- | PVDF | PMMA | TiO_2 |
|-----|------------------|---------|-----|-------|------|------|----------------|
| | content (wt%) | | | TFSI | | | |

| | | | | | | | |
|---|-----|------|------|-----|--------|-------|--------|
| 1 | 0% | 2 ml | 2 ml | 3 g | 1.75 g | -- | 0.25 g |
| 2 | 4% | 2 ml | 2 ml | 3 g | 1.55 g | 0.2 g | 0.25 g |
| 3 | 8% | 2 ml | 2 ml | 3 g | 1.35 g | 0.4 g | 0.25 g |
| 4 | 12% | 2 ml | 2 ml | 3 g | 1.15 g | 0.6 g | 0.25 g |
| 5 | 16% | 2 ml | 2 ml | 3 g | 0.95 g | 0.8 g | 0.25 g |

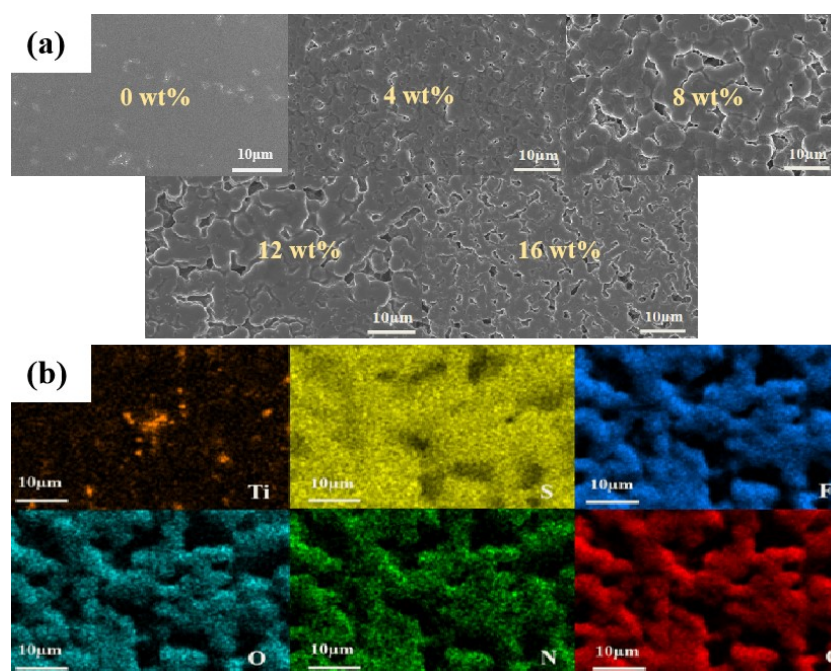


Fig. S7. (a) Surface morphology of different PMMA contents and (b) the corresponding EDS mapping of polymer electrolyte films of 12 wt % PMMA content.

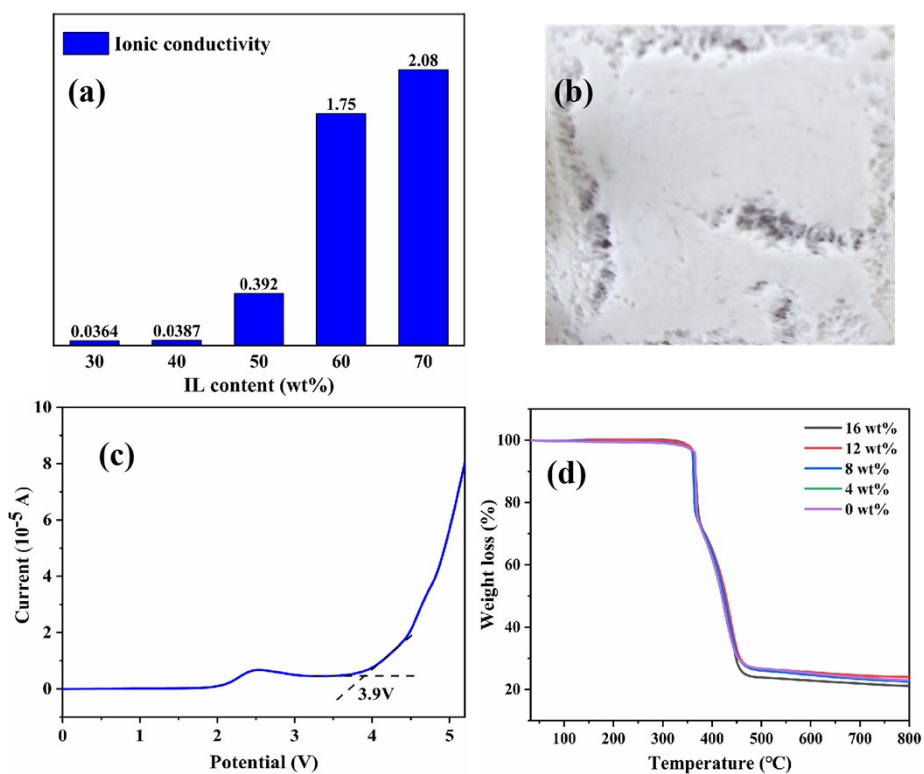


Fig. S8. (a) Ionic conductivity of electrolytes with different ionic liquid contents. (b) Optical image of an electrolyte with 70 wt% BMIMTFSI content. (c) LSV curves of the electrolyte containing 8 wt% PMMA. (d) TGA curves of the electrolytes with different PMMA contents.

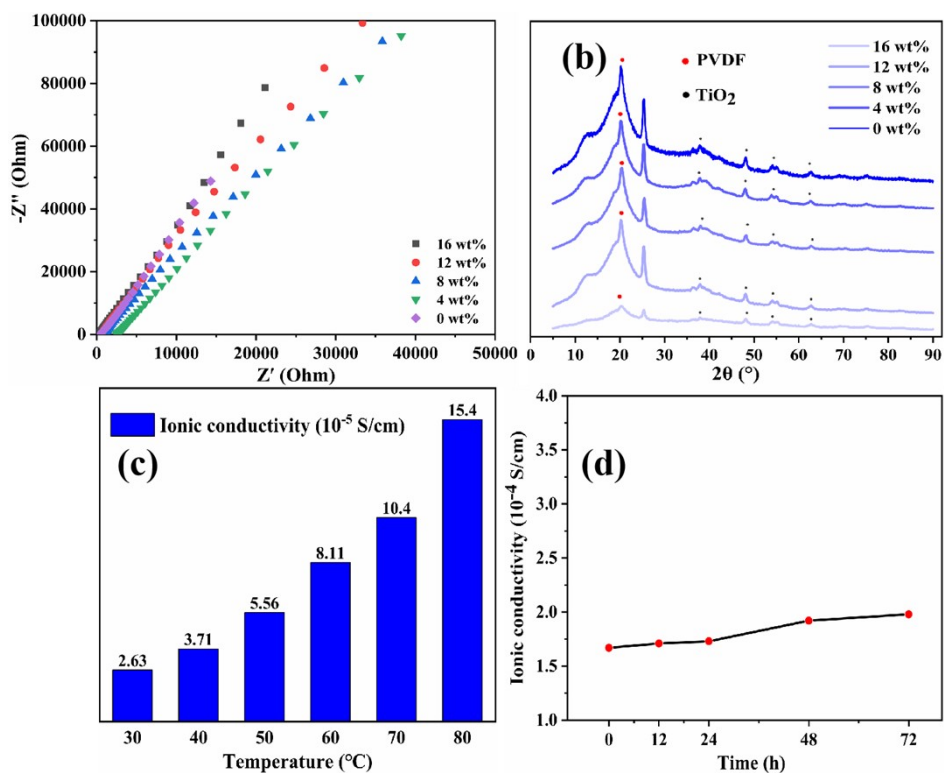


Fig. S9. (a) Electrical impedance Spectroscopy (EIS) and (b) X-ray diffraction patterns of the electrolytes prepared with different PMMA contents. (c) Ionic conductivity of the electrolyte prepared with PMMA content of 16 wt% in different temperatures. (d) Ionic conductivity of electrolyte of 16 wt% PMMA content at different placement times at 80°C.

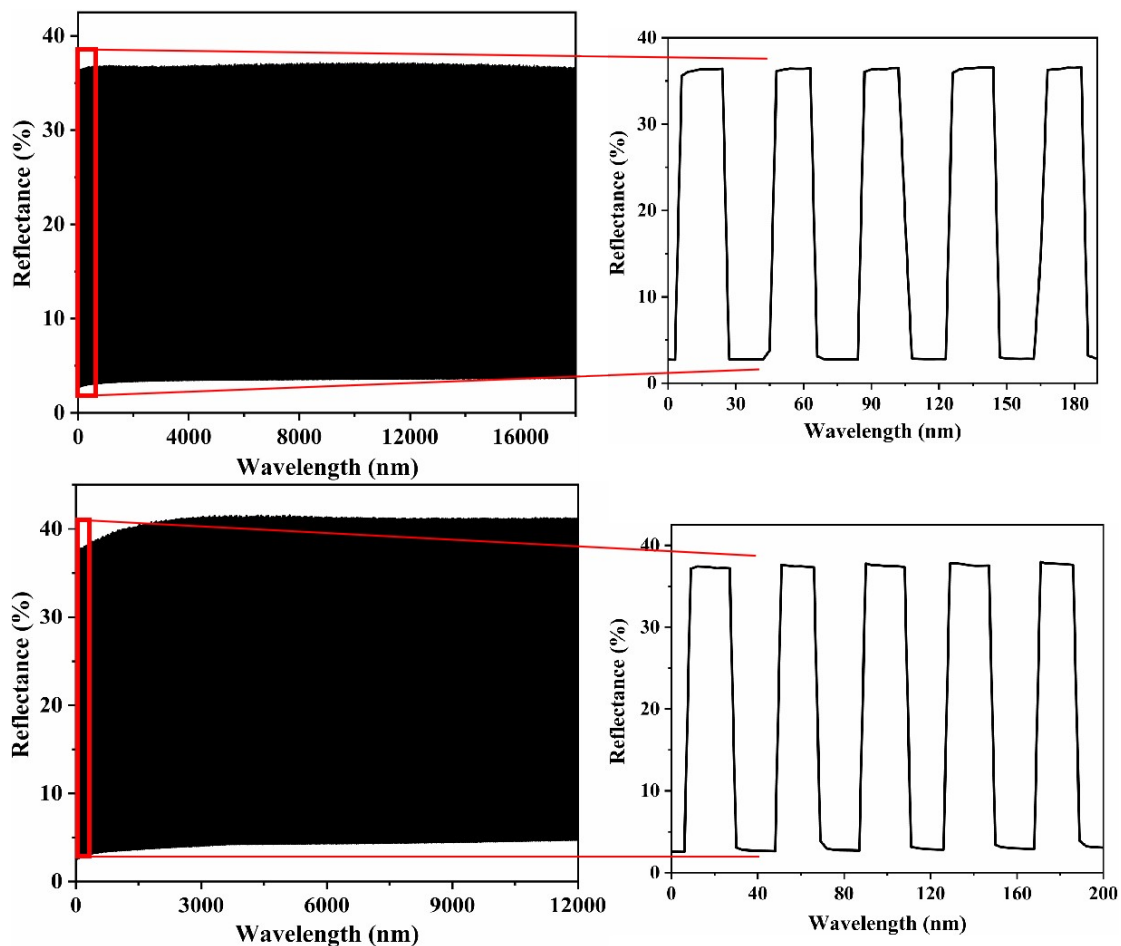


Fig. S10. Switching response of the ECDs assembled based on (a) TTT-EDOT-IDTT and (b) TTT-EDOT-TZ at 520 nm, 519 nm, and 520 nm between 2.0 V and -2 V .

Table. S6. Lab values and chromatic aberrations of the ECDs with various ECPs in colored and bleached states.

| | | | |
|--------------------------------------|--------------|--------------|--------------|
| TTT-EDOT | L* | a* | b* |
| Colored | 34.00 | 5.46 | -22.3 |
| Bleached | 58.31 | -6.66 | -9.86 |
| $\Delta E^*=29.63$ | | | |
| TTT-EDOT-IDTT | L* | a* | b* |
| Colored | 39.56 | 23.84 | -15.7 |
| Bleached | 67.99 | -5.30 | -0.20 |
| $\Delta E^*=43.56$ | | | |

| TTT-EDOT-TZ | L* | a* | b* |
|--------------------|-------|-------|--------|
| Colored | 40.14 | 0.82 | -15.61 |
| Bleached | 60.81 | -5.90 | -8.01 |
| $\Delta E^*=23.02$ | | | |

Reference

- [1] Y. Li, J.-D. Lin, X. Liu, Y. Qu, F.-P. Wu, F. Liu, Z.-Q. Jiang, S.R. Forrest, Near-Infrared ternary tandem solar cells, *Advanced Materials*, 30 (2018) 1804416.
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- [3] B.D. Reeves, C.R.G. Grenier, A.A. Argun, A. Cirpan, T.D. McCarley, J.R. Reynolds, Spray coatable electrochromic dioxathiophene polymers with high coloration efficiencies, *Macromolecules*, 37 (2004) 7559-7569.