Supporting information

Developing conjugated polymers with broad-band absorption covering visible and near-infrared regions for electrochromism

Guoqiang Kuang[1], Hongbin Yin[1], Chenming Li[2], Yijie Tao[1]*, Yafei Guo[2]*, Shiguo Zhang[1]*

[1] College of Materials Science and Engineering, Hunan University, Changsha, China

[2] Systems Engineering Institute, AMS，PLA, Beijing, China

Corresponding author:

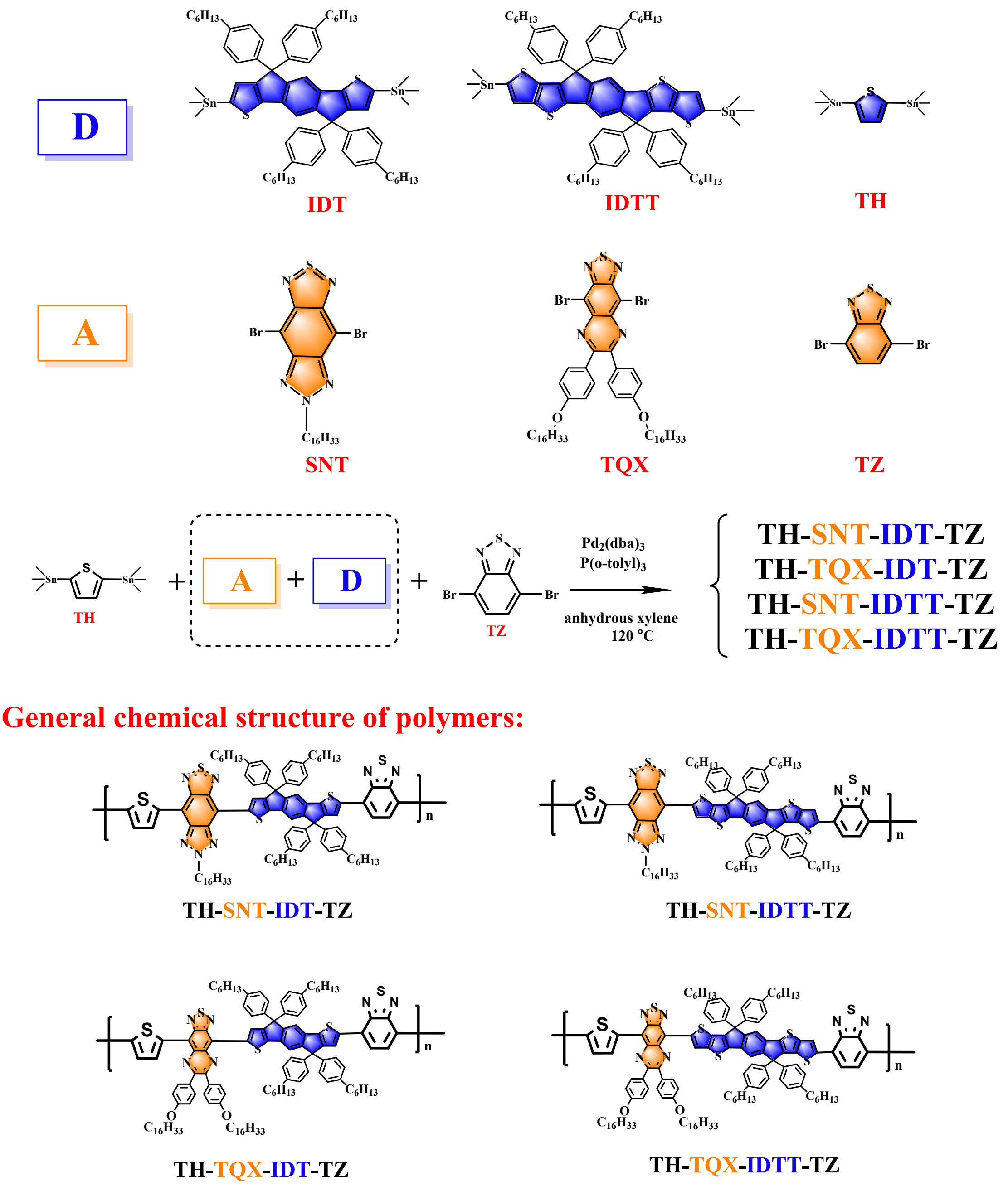
Yijie Tao: taoyijie@hnu.edu.cn

Yafei Guo: guoyafei1010@163.com

Shiguo Zhang: zhangsg@hnu.edu.cn

Synthesis details

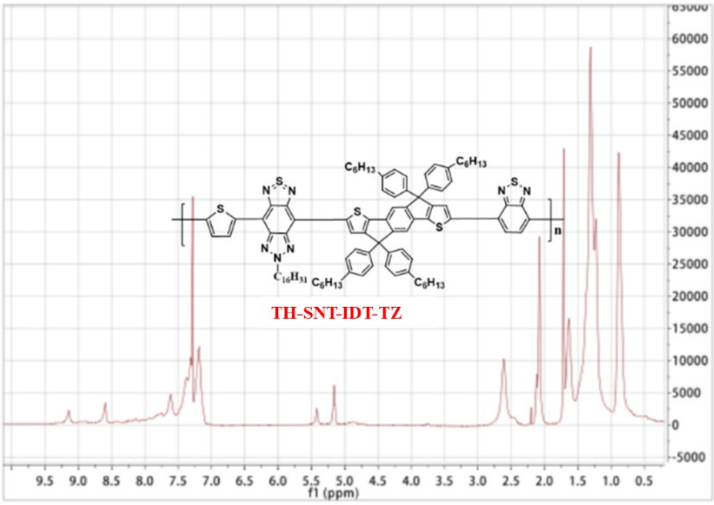
All chemicals were obtained from Sigma-Aldrich and Alfar-Aesar without purification. Anhydrous toluene was distilled over Na/naphthalene before use. The synthetic route to conjugated polymers is shown in Scheme S1. The syntheses of TQX-2Br, SNT-2Br, IDT-$SnMe_3$, and IDTT-$SnMe_3$ were performed based on the literature [1-3]. Chemical reagents, such as Tz, Th-$SnMe_3$, P (o-tolyl)$_3$, and $Pd_2(dba)_3$, were purchased from Shenzhen Ruixun Optoelectronics Company, and all drugs were of analytical grade. ITO glass was purchased from Zhuhai Kaiwei Electronic Components Co., Ltd., and the other reagents were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd.

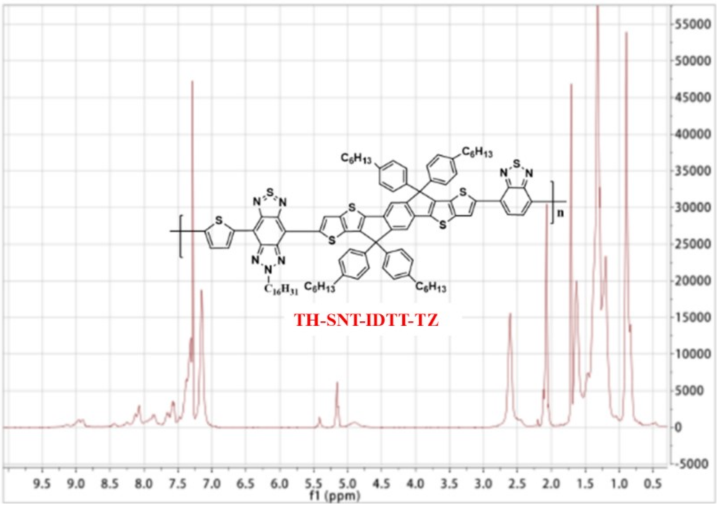


Scheme S1 Synthetic route and chemical structure of copolymers via Stille coupling.

General procedure for the synthesis of polymers via Stille coupling

The polymer was prepared by Stille coupling using the following steps. Monomers D1 (Th-$SnMe_3$), D2 (IDT-$SnMe_3$ or IDTT-$SnMe_3$), A1 (SNT-2Br or TQX-2Br), and A2 (TZ) were placed in a double-necked bottle at a ratio of 1:1:1:1, with the introduction of nitrogen gas for 5 min. Subsequently, 4 mol% $Pd_2(dba)_3$, 8 mol% $P(o\text{-tolyl})_3$, and 10 mL anhydrous xylene were added. A vacuum pump was used to replace the nitrogen gas three times, followed by the addition of 10mL toluene. The mixture was then heated to 140 °C for 48-hour reaction. After the reaction, the mixed solvent was added dropwise to the methanol for precipitation. The filtered material was tightly wrapped in clean filter paper and preserved in a Soxhlet extractor for further purification. The mixture was heated to 110 °C and rinsed sequentially with methanol, hexane, and chloroform. The obtained chloroform solution was concentrated in a rotary evaporator, and the concentrated mixture was dropped into methanol for precipitation. The filtered precipitate was then placed in a vacuum-drying oven for 24 h to obtain the target polymer. The ^{1}HNMR spectra of the synthetic polymers are shown in **Fig. S1.**


TH-SNT-IDT-TZ
S
N
C16H31
C6H13
n
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000


TH-SNT-IDTT-TZ
S
N
C16H31
C6H13
n
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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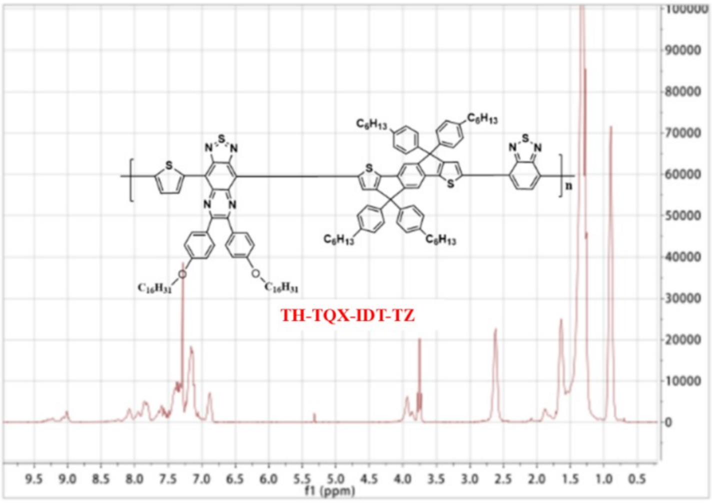
TH-TQX-IDT-TZ
S
N
O
C16H31
C6H13
n
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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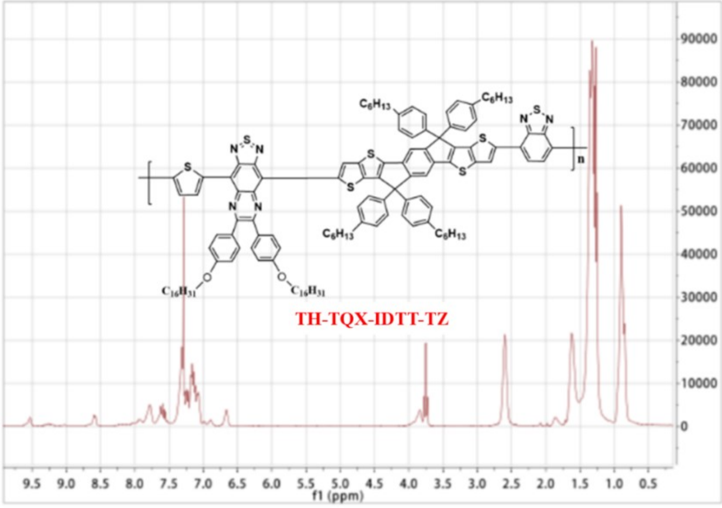

Fig. S1 ^{1}HNMR spectra of copolymers prepared via DArP.

TH-SNT-IDT-TZ: dark gray solid in yield of 61%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.41–7.23 (m, 20H), 5.21 (m, 1H), 2.59 (t, 8H), 2.09 (t, 8H), 1.69–1.24 (m, 56H), 0.88 (t, 18H).

TH-SNT-IDTT-TZ: dark solid in yield of 73%, HNMR (400 MHz, $CDCl_3$): δ 7.67 (s, 2H), 7.41–7.23 (m, 20H), 5.19 (m, 1H), 2.59 (t, 8H), 2.08 (t, 8H), 1.72–1.21 (m, 56H), 0.88 (t, 18H).

TH-TQX-IDT-TZ: dark solid in yield of 68%, HNMR (400 MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.40–7.21 (d, 24H), 6.89 (s, 2H), 3.76 (t, 4H), 2.59 (t, 8H), 1.67–1.28 (m, 88H), 0.88 (t, 18H).

TH-TQX-IDTT-TZ: dark solid in yield of 62%, HNMR (400 MHz, $CDCl_3$): δ 7.83 (s, 2H), 7.36–7.09 (d, 24H), 6.69 (s, 2H), 3.76 (t, 4H), 2.59 (t, 8H), 1.66–1.30 (m, 88H), 0.88 (t, 18H).

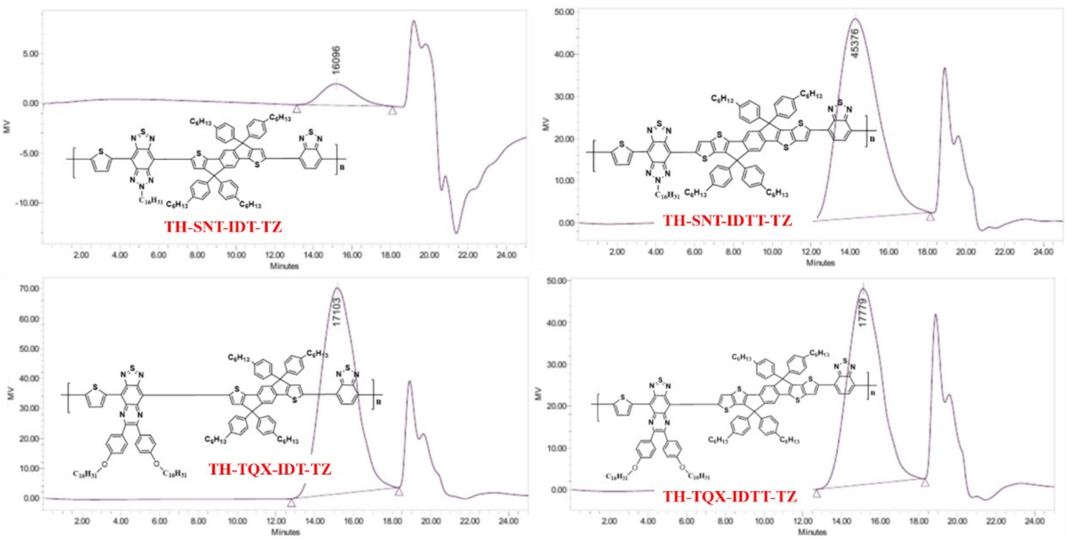

Fig. S2 GPC traces of polymers synthesized via DArP.

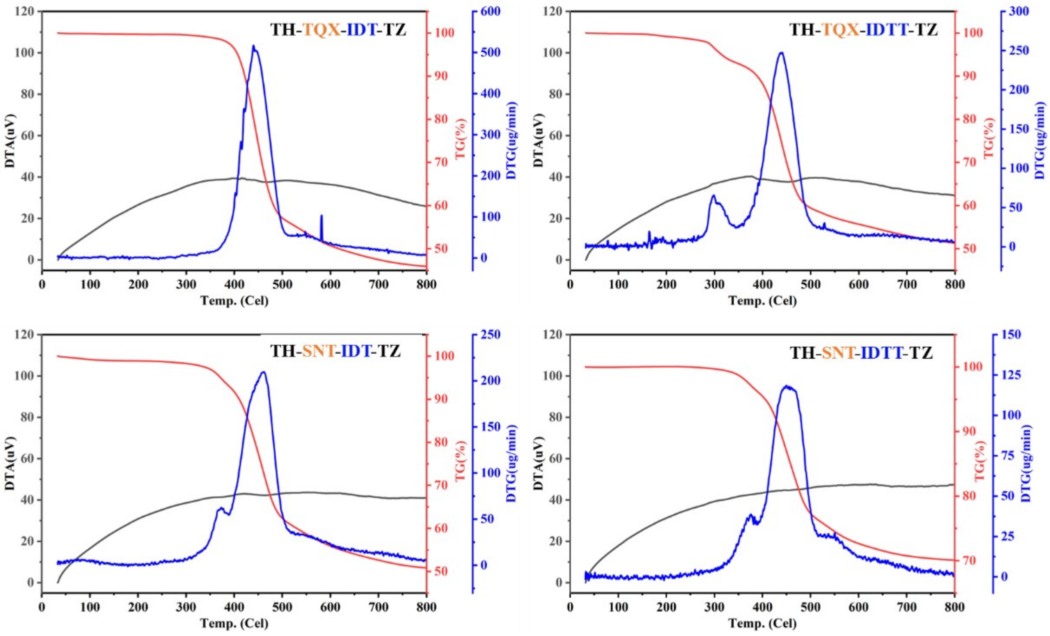

Fig. S3 TGA curves of polymers synthesized via DArP.

Table S1 Molecular weights, PDI, and thermal decomposition temperatures of the synthesized polymers.

Polymer	**Mn (Da)**	**Mw (Da)**	**PDI**	**T_d (°C)**[a]
TH-SNT-IDT-TZ	8636	19099	2.2	371.3
TH-SNT-IDTT-TZ	17476	57677	3.3	405.2
TH-TQX-IDT-TZ	9824	21940	2.2	406.7
TH-TQX-IDTT-TZ	10375	22641	2.2	314.1

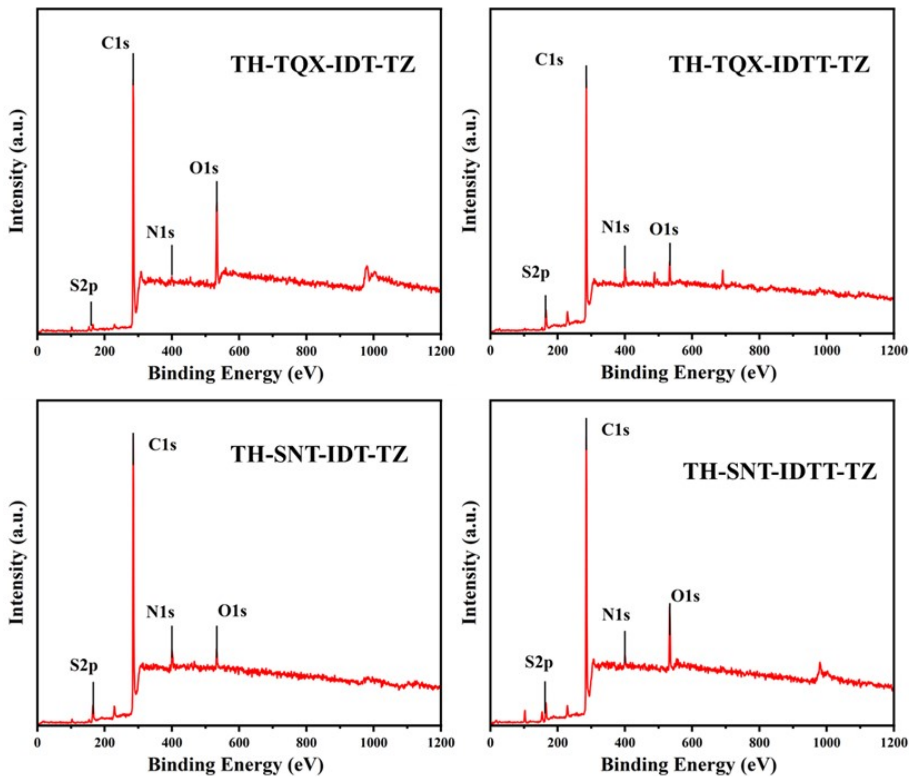

Fig.S4 X-ray photoelectron spectroscopy (XPS) spectra of Full spectrum for the synthesized copolymers.

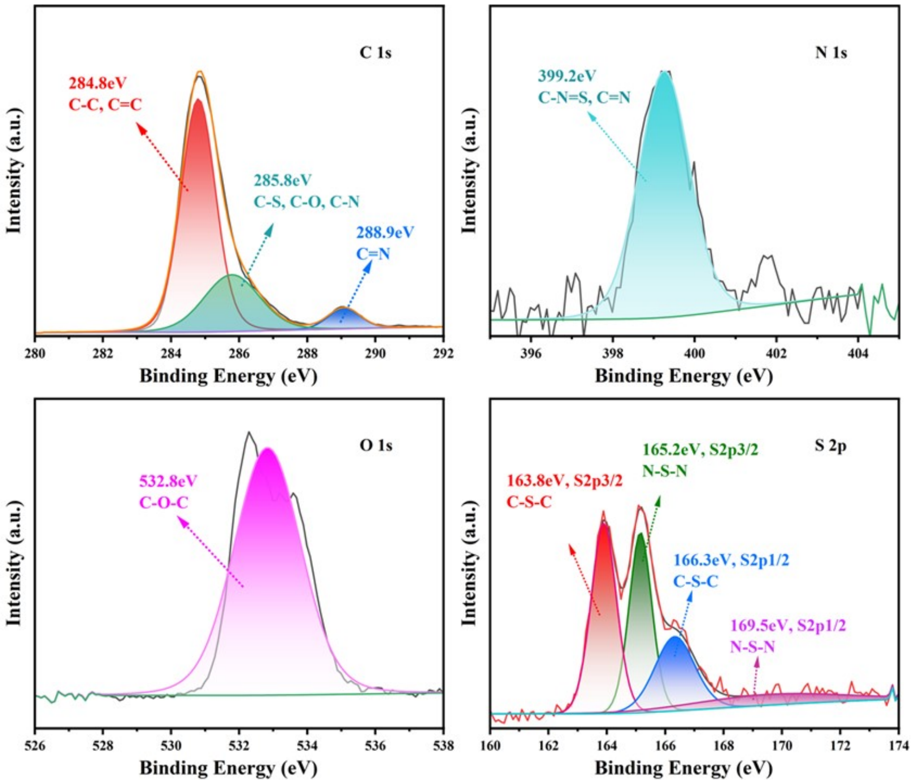

Fig.S5 C1s, N1s, O1s and S2p curves for the synthesized copolymer TH-TQX-IDT-TZ.

Table S2 Elemental content analysis of the synthesized copolymers.

Polymer	**C(at.%)**	**N(at.%)**	**O(at.%)**	**S(at.%)**
TH-TQX-IDT-TZ	**86.84**	**6.80**	**4.98**	**1.38**
TH-TQX-IDTT-TZ	**87.36**	**3.79**	**3.54**	**5.31**
TH-SNT-IDT-TZ	**89.59**	**3.94**	**2.31**	**4.16**
TH-SNT-IDTT-TZ	**87.33**	**2.03**	**6.99**	**3.65**

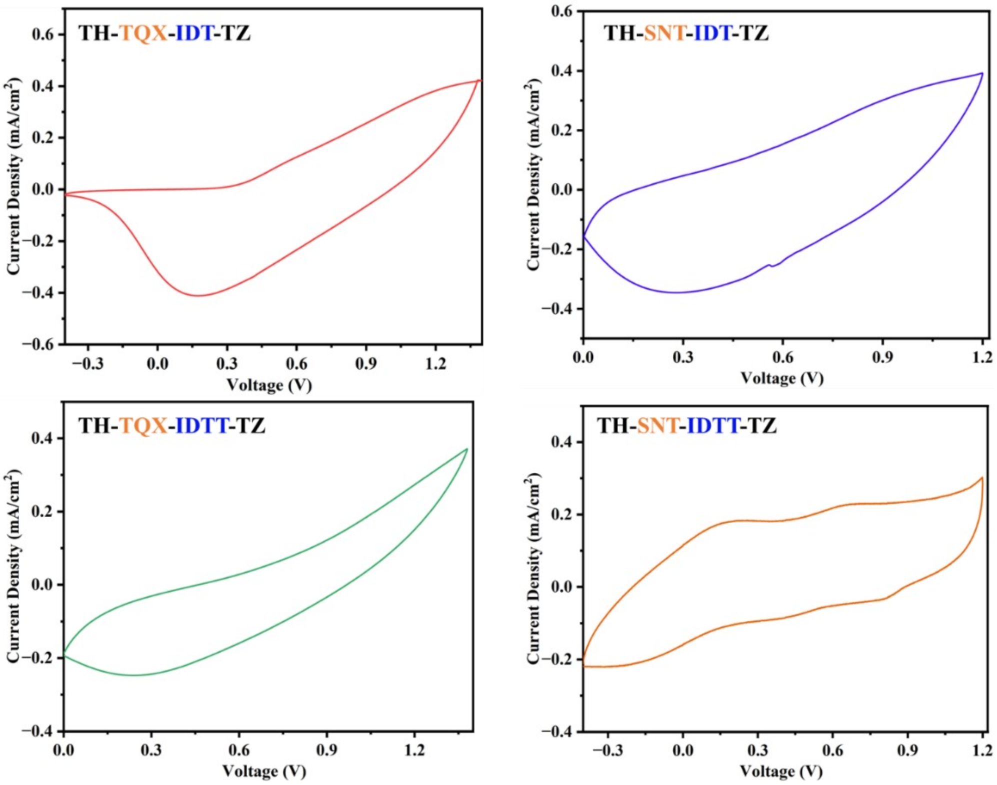

Fig. S6 Cyclic voltammograms of polymer films in an electrolyte solution of 0.2 M $LiClO_4$/PC at a scan rate of 50 mV/s.

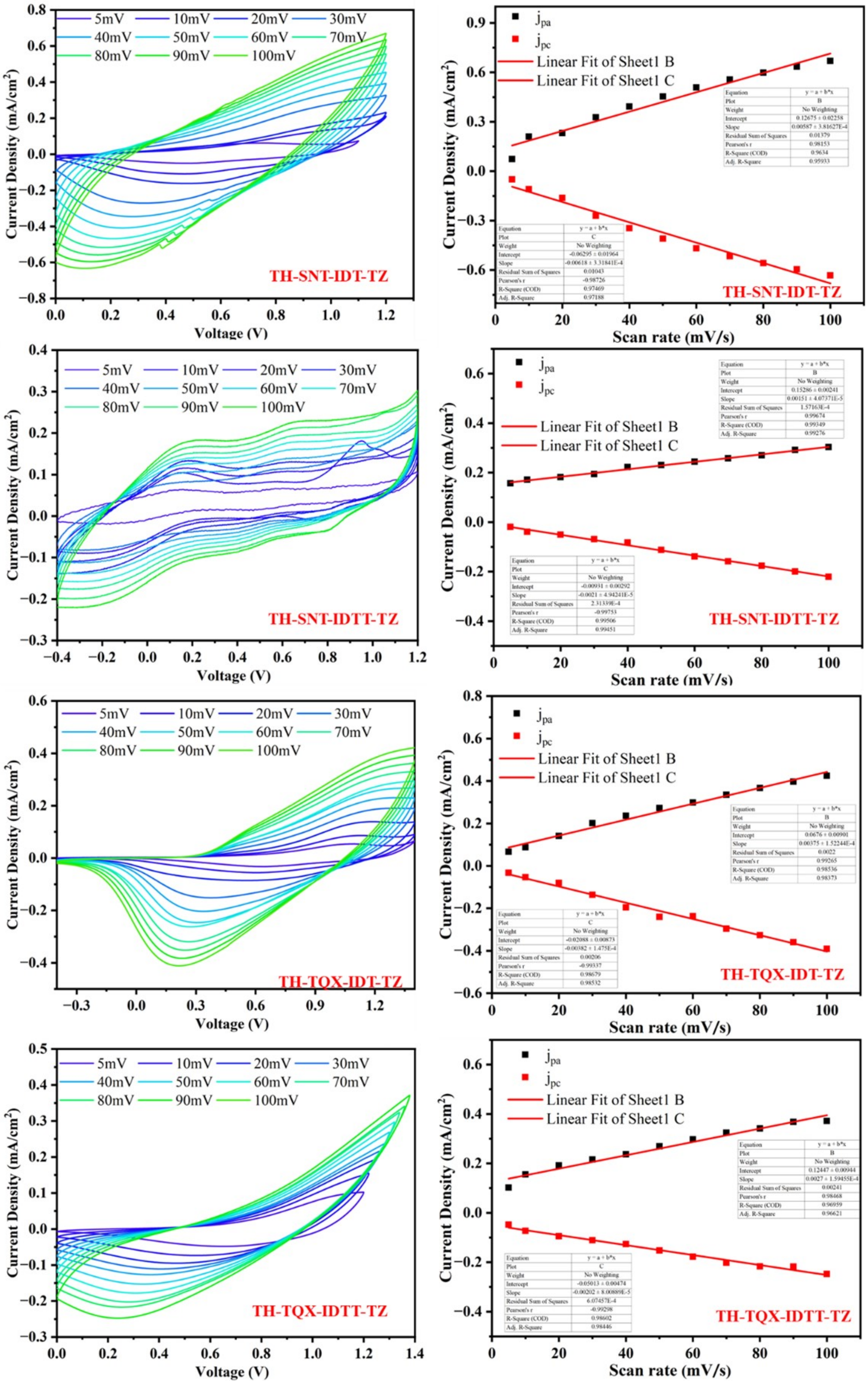

Fig. S7 Cyclic voltammetry curves of polymer films in 0.2 M $LiClO_4$/PC solution at different scanning rates and linear relationships between the peak current and scan rate.

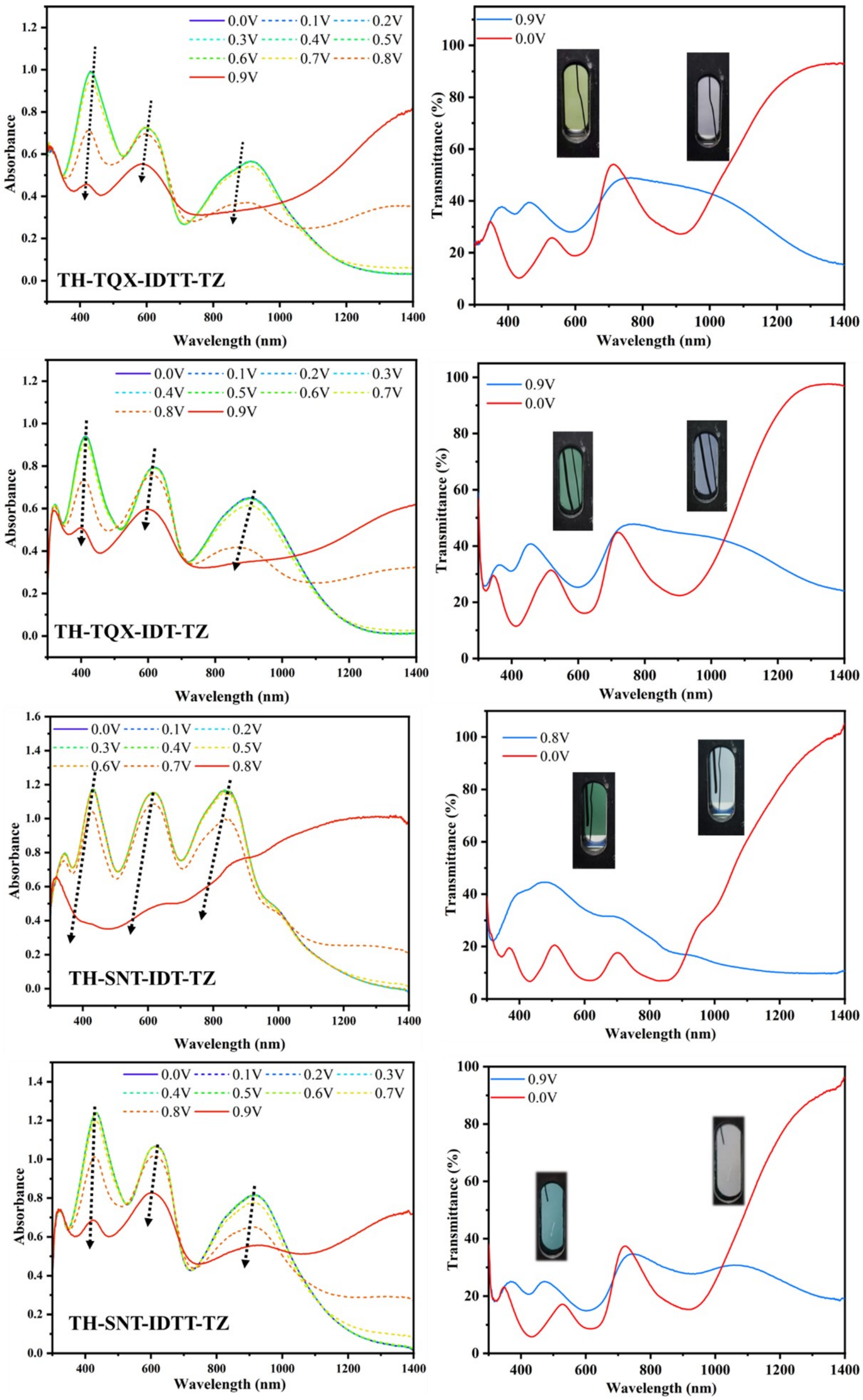

Fig. S8 Spectroelectrochemical, transmittance spectra and optical images of copolymers under various external potentials.

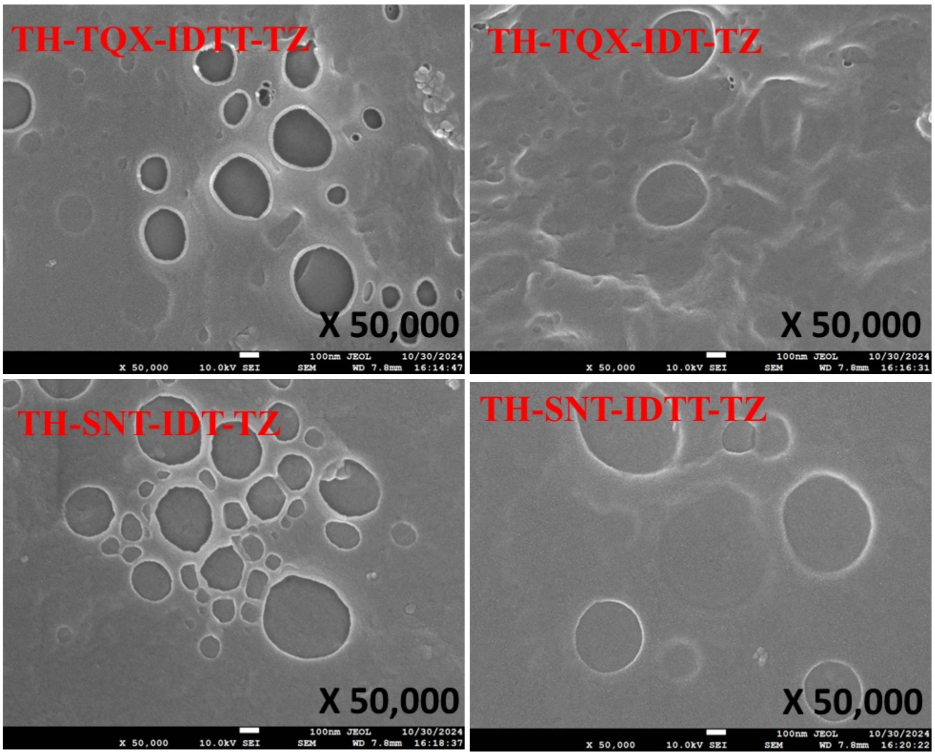

Fig. S9 SEM images of prepared copolymer films.

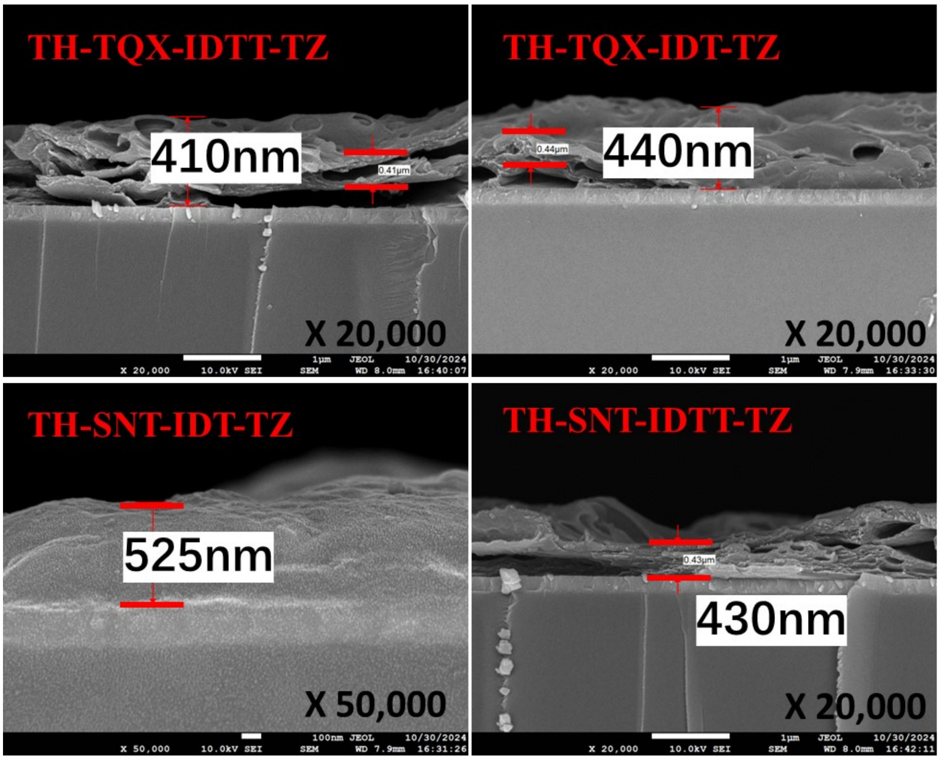

Fig. S10 Cross-sectional images of the prepared copolymer films.

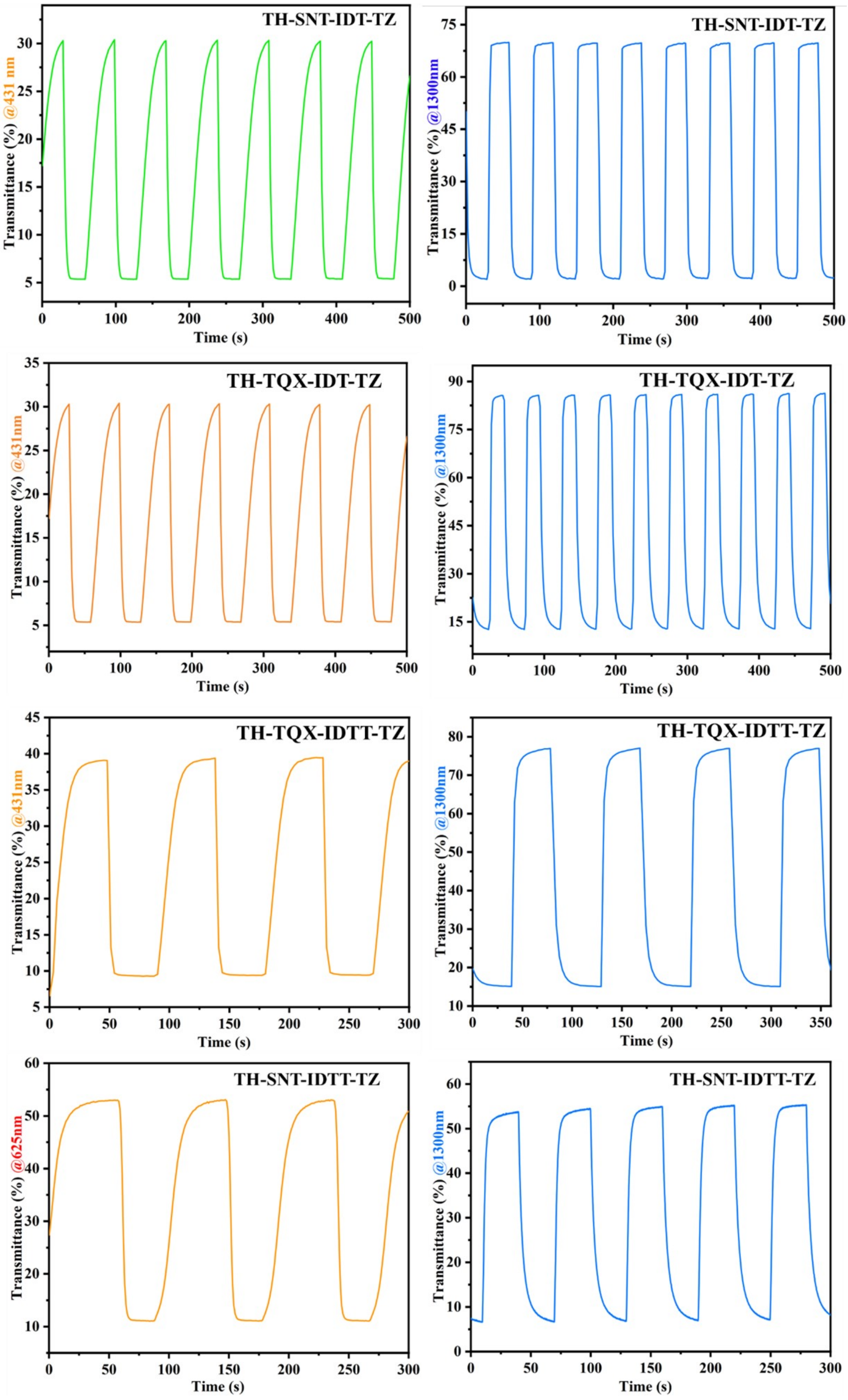

Fig. S11 Electrochromic switching of polymer films monitored at maximum absorption in 0.2 M $LiClO_4$/PC.

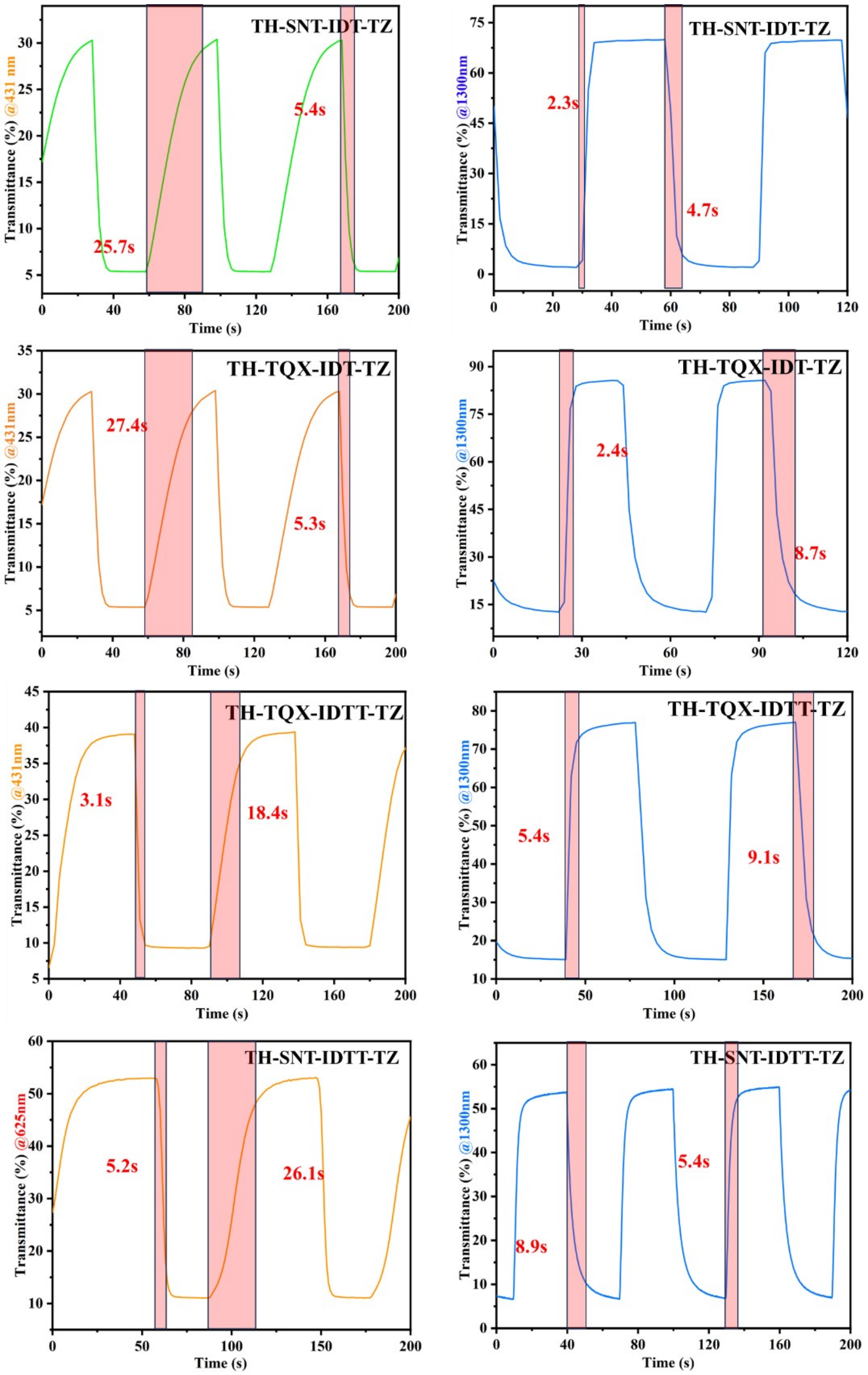

Fig. S12 Calculated switching time of polymer films monitored at maximum absorption in 0.2 M $LiClO_4$/PC.

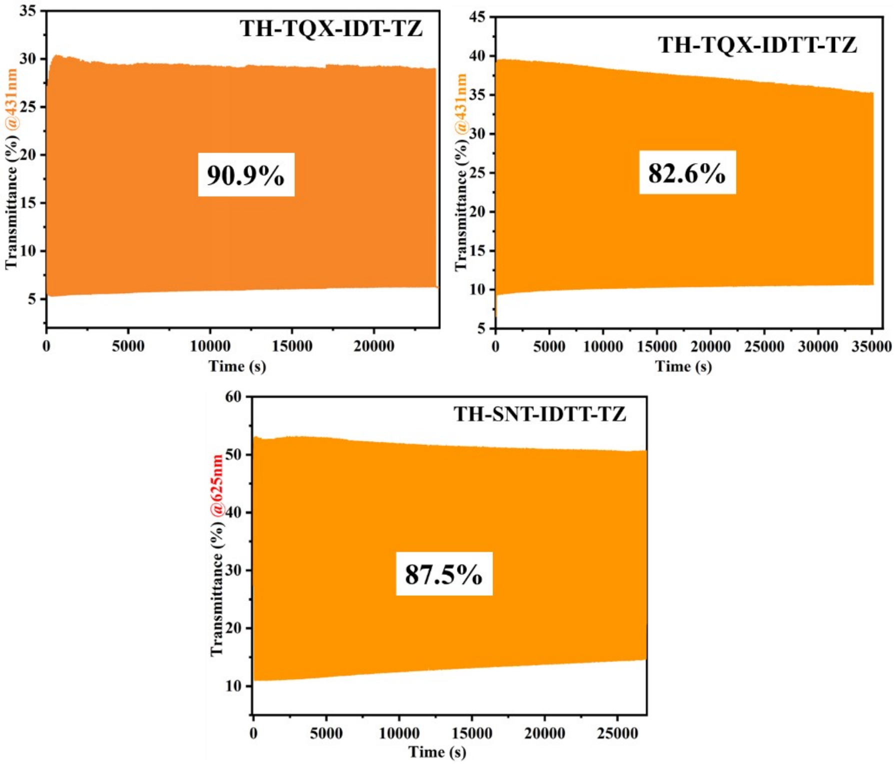

Fig. S13 Cyclic stability of polymer films monitored at maximum absorption in visible area in 0.2 M $LiClO_4$/PC.

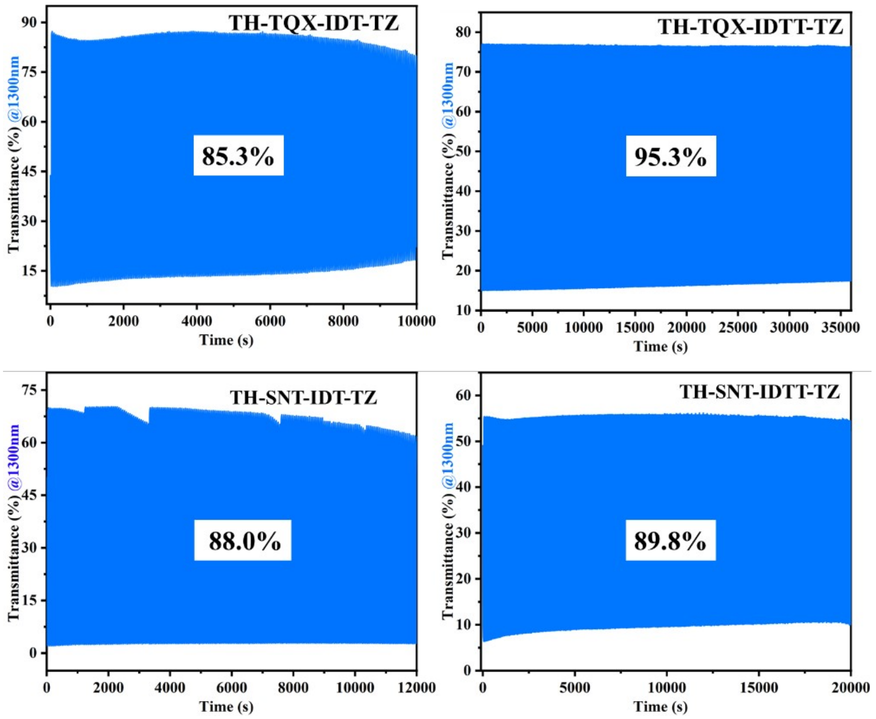

Fig. S14 Cyclic stability of polymer films monitored at maximum absorption in NIR area in 0.2 M LiClO4/PC.

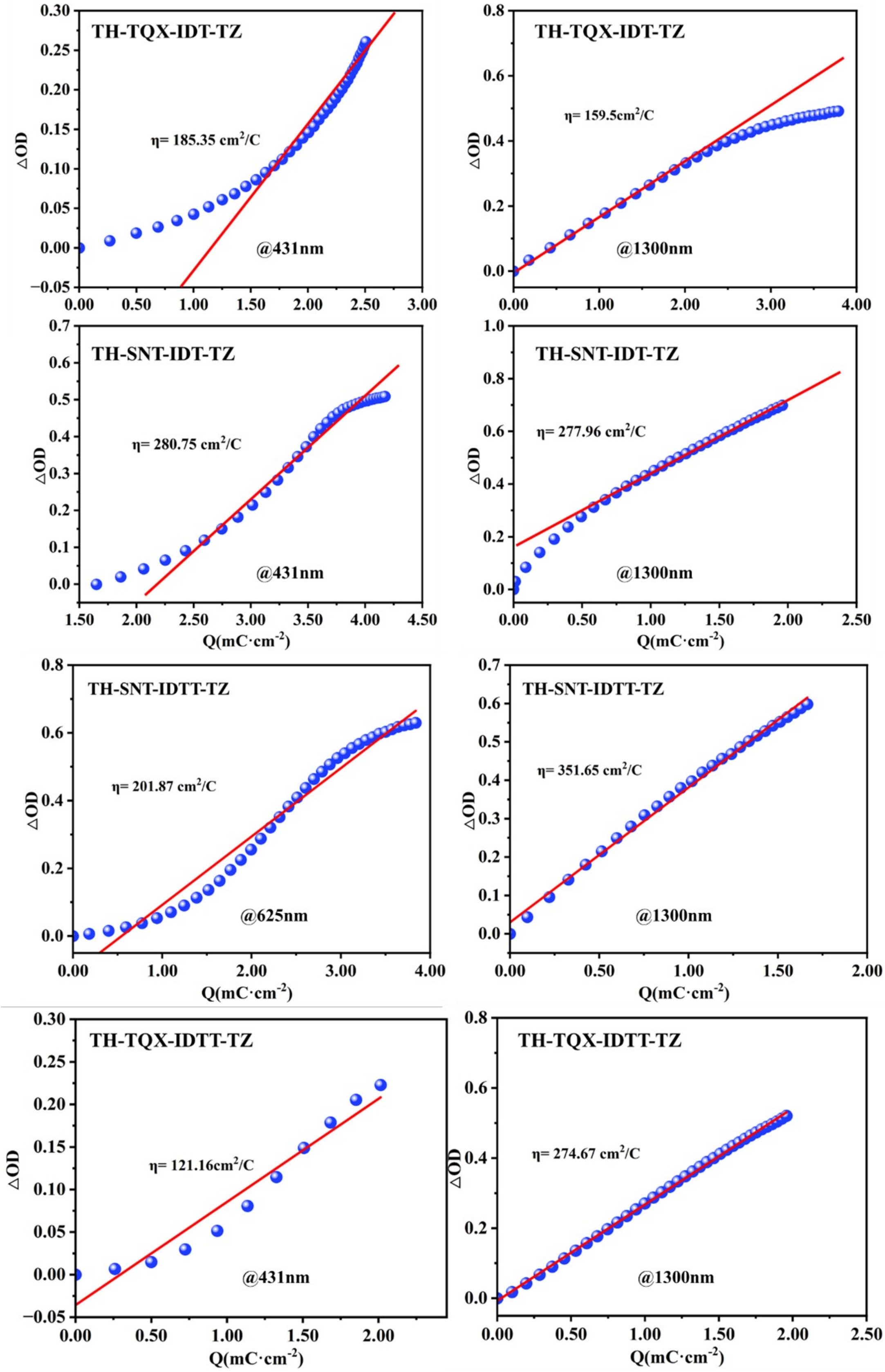

Fig. S15 Coloring efficiency of homopolymer films calculated at the maximum absorption.

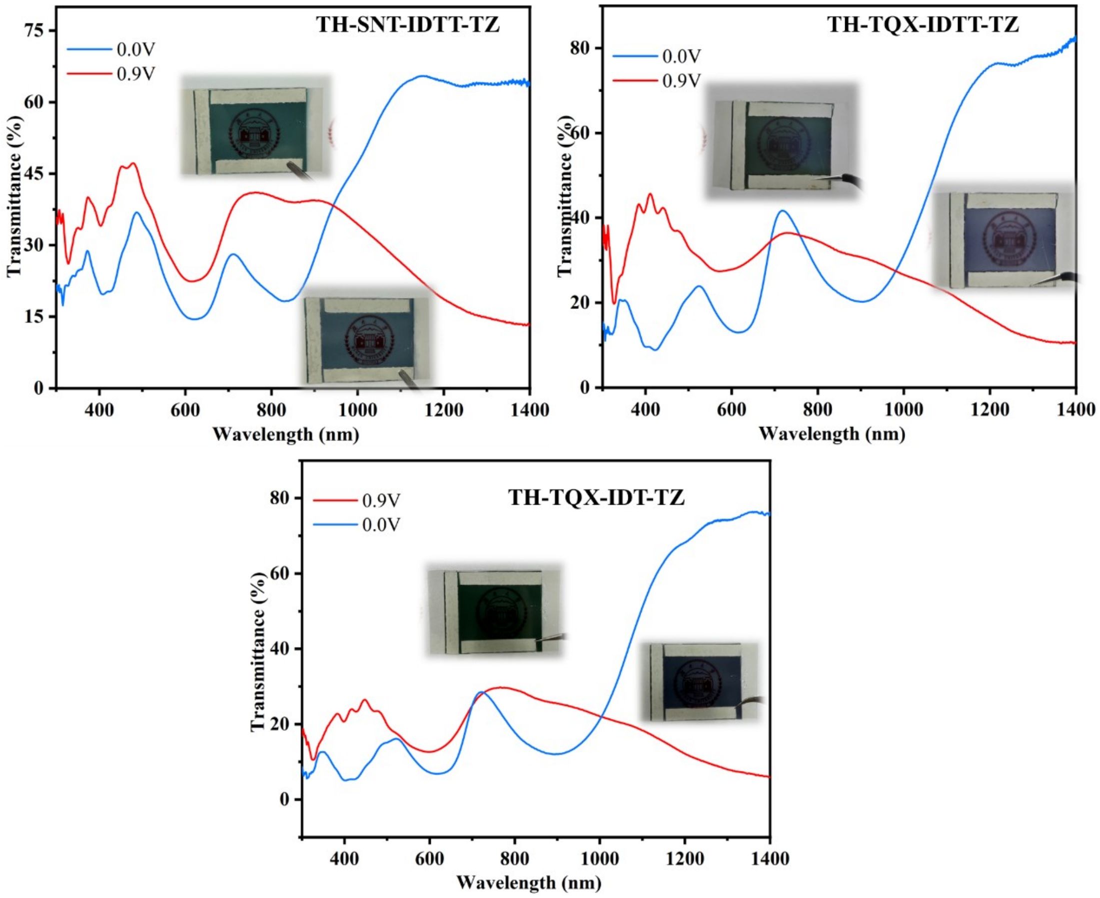

Fig. S16 Transmittance spectra and optical images of ECDs under various applied external potentials.

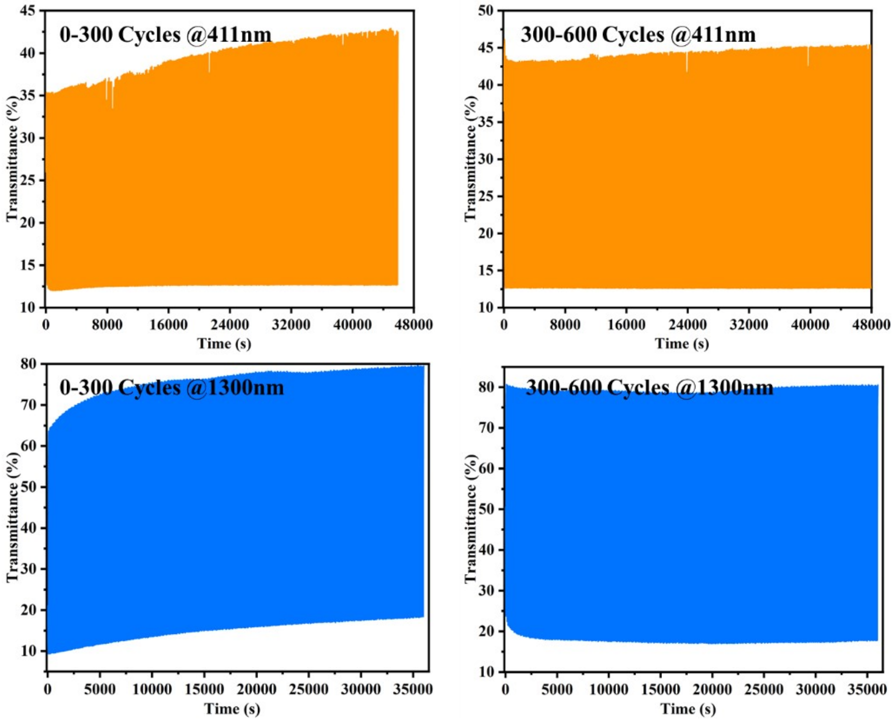

Fig. S17 Cyclic stability of the ECD based on TH-TQX-IDT-TZ monitored at the maximum absorption.

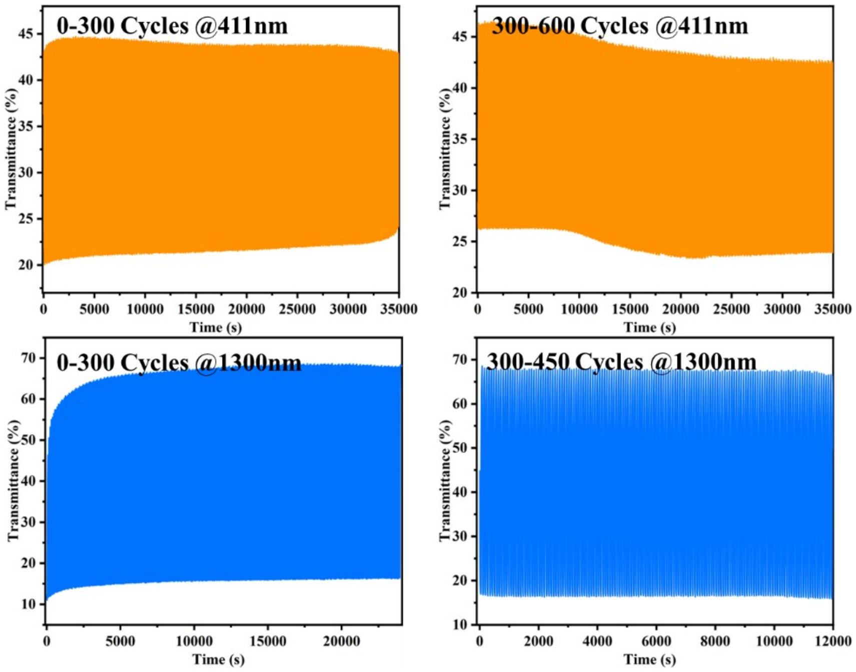

Fig. S18 Cyclic stability of the ECD based on TH-TQX-IDTT-TZ monitored at the maximum absorption.

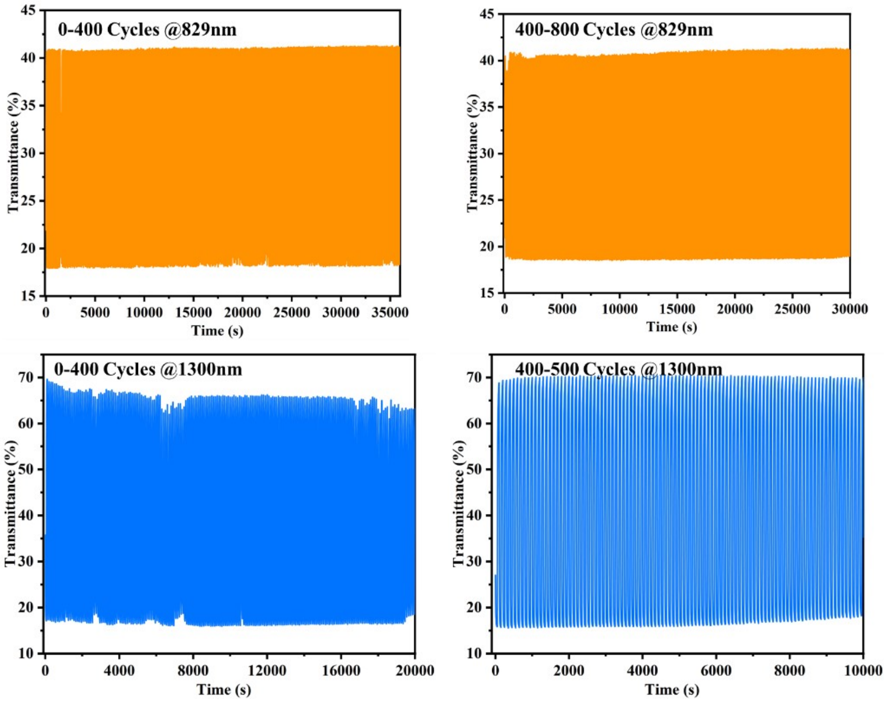

Fig. S19 Cyclic stability of the ECD based on TH-SNT-IDTT-TZ monitored at the maximum absorption.

References

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[3] F. Verstraeten, S. Gielen, P. Verstappen, J. Raymakers, H. Penxten, L. Lutsen, K. Vandewal, W. Maes, Efficient and readily tuneable near-infrared photodetection up to 1500 nm enabled by thiadiazoloquinoxaline-based push–pull type conjugated polymers, Journal of Materials Chemistry C, 8 (2020) 10098-10103.