

Supporting Information

Uncovering Ion Trapping in Amorphous Electrochromic Polymer Films

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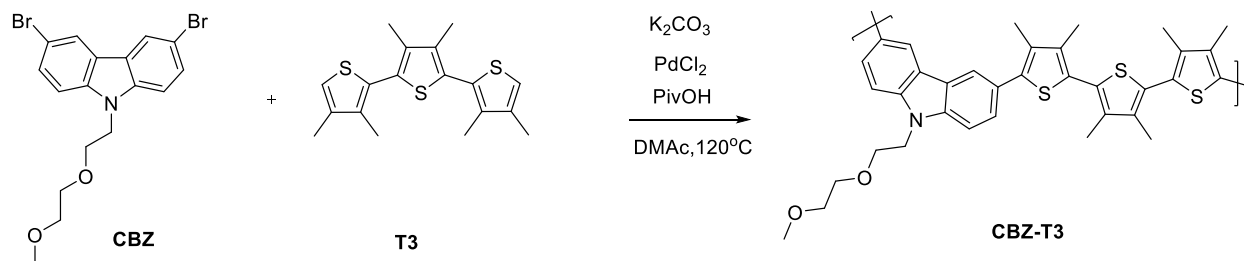
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1. General Procedures and Experimental Details

S1.1 Synthesis details of CBZ-T3 and CBZ-T2¹

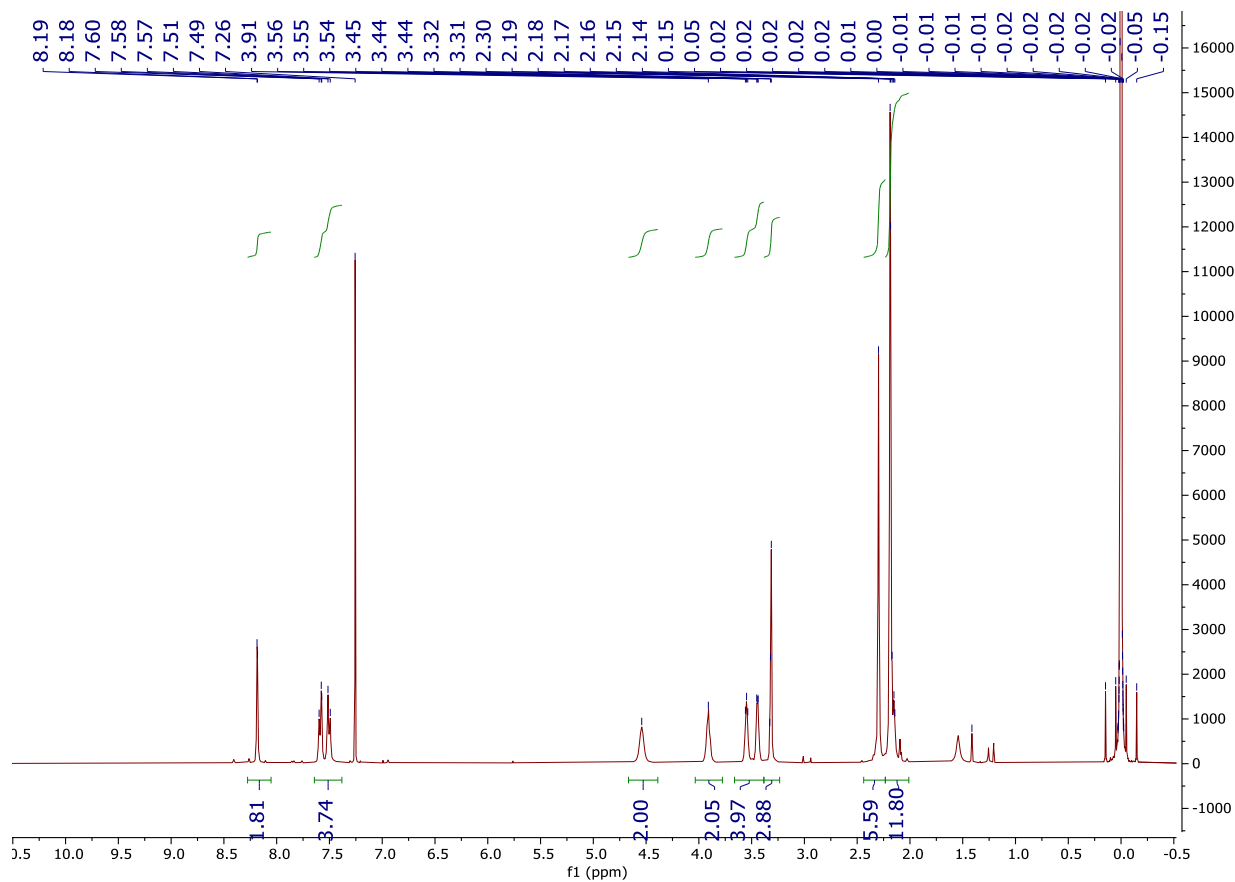
Poly(CBZ-T3)



CBZ (0.500 g, 1.17 mmol), **T3** (0.389 g, 1.17 mmol), potassium carbonate (0.421 g, 3.04 mmol), palladium chloride (0.004 g, 0.023 mmol), and pivalic acid (0.036 g, 0.351 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk tube was put under a vacuum, followed by backfilling three times with nitrogen. De-gassed *N,N*-dimethylacetamide (5 mL) was added to this tube under nitrogen. This reaction mixture was heated at 120 °C for 24 h. After stopping the reaction, it was precipitated with 100mL Methanol/1N HCl(1/1). Next, the precipitates were filtered, dried, and dissolved into 15mL chloroform, followed by the addition of palladium scavenger, and were stirred at 50 °C for 2 hours. These components were filtered and precipitated into methanol. Finally, the solid was filtered and dried under vacuum to obtain **CBZ-T3** as a yellow powder (0.65 g, 88%).

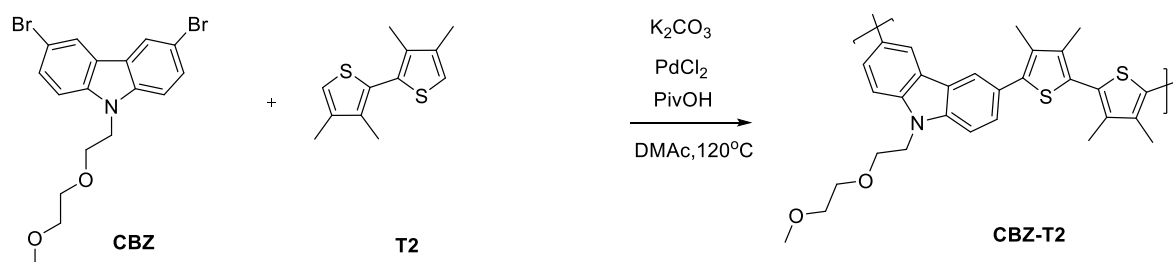
NMR confirmation of CBZ-T3¹

¹H NMR (400 MHz, CDCl₃): δ ppm 8.19 (s, 2H), 7.60-7.49 (m, 4H), 4.54 (s, 2H), 3.91 (m, 2H), 3.55-3.44 (m, 4H), 3.31 (s, 3H), 2.30 (s, 6H), 2.19-2.18 (m, 12H); GPC: *M_n* = 10.4kDa; *Đ* = 2.1.



^1H NMR of CBZ-T3

Poly(CBZ-T2)

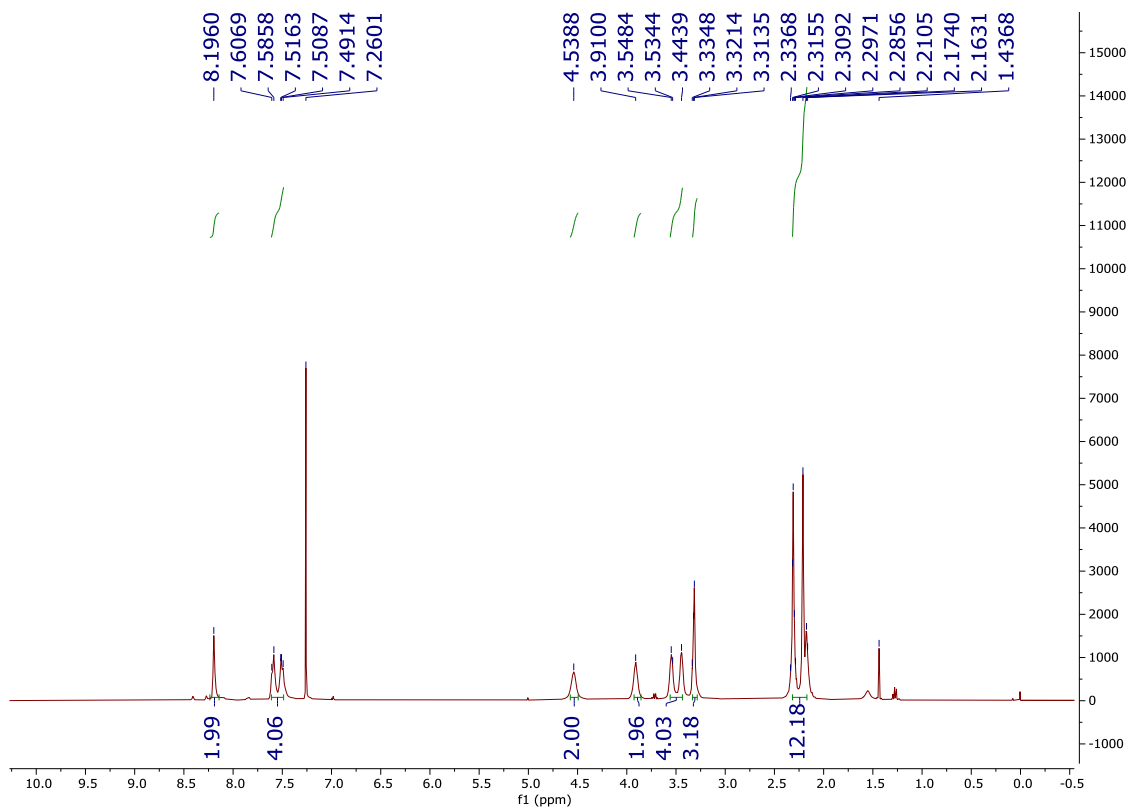


CBZ (0.44 g, 1.0 mmol), **T2** (0.23 g, 1.0 mmol), potassium carbonate (0.42 g, 3.1 mmol), palladium chloride (7 mg, 0.04 mmol), and pivalic acid (0.31 g, 0.31 mmol) were added in a dry Schlenk tube under nitrogen. The Schlenk was put under high vacuum, followed by the backfilling with nitrogen thrice. De-gassed *N,N*-dimethylacetamide (2 mL) was added to the tube. The reaction mixture was heated at 120 °C for 24 h. The reaction was stopped and precipitated with 100mL Methanol/1N HCl(1/1). After stopping the reaction, it was precipitated with 100mL

Methanol/1N HCl(1/1). Next, the precipitates were filtered, dried, and dissolved into 10mL chloroform, followed by the addition of palladium scavenger, and were stirred at 50 °C for 2 hours. These components were filtered and precipitated into methanol. Finally, the solid was filtered and dried under vacuum to obtain **CBZ-T2** as a yellow powder (0.45 g, 90%).

NMR confirmation of CBZ-T2¹

¹H NMR (400 MHz, CDCl₃): δ ppm 8.20 (s, 2H), 7.60-7.50 (m, 4H), 4.54 (s, 2H), 3.91 (m, 2H), 3.55-3.44 (m, 4H), 3.32 (s, 3H). 2.33-2.17 (m, 12H); GPC: M_n = 12.9 kDa; $\bar{D}$ = 4.6.



¹H NMR of CBZ-T2

S1.2: Fc/Fc⁺ Calibration of the Ag/AgCl Reference Electrode

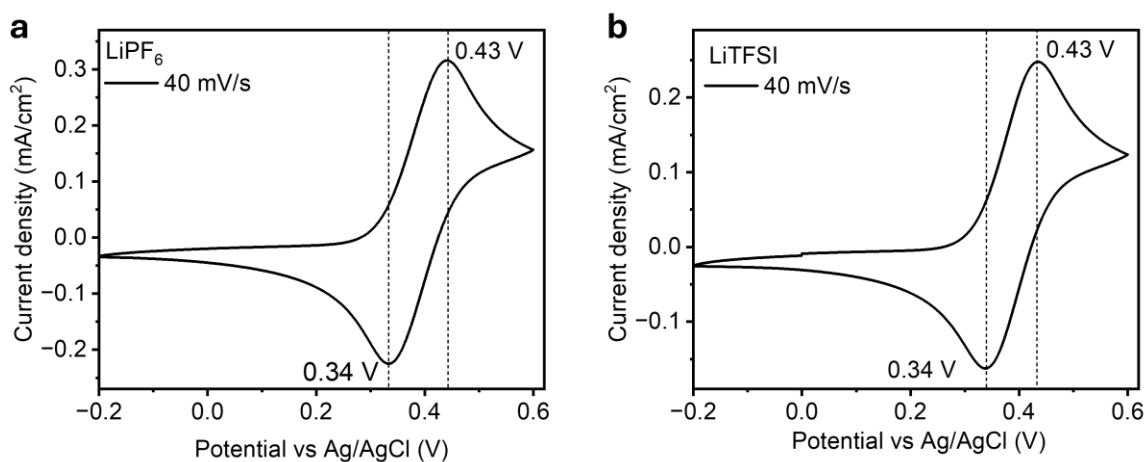


Figure S1: CV of 5mM ferrocene at 40 mV/s in (a) 0.2M LiPF₆ in PC and (b) 0.2M LiTFSI in PC. The dashed lines show the reduction and oxidation peak potentials used to determine $E_{1/2}$ vs. Ag/AgCl.

S1.3 Computational Details

S.1.3.1. Density Functional Theory (DFT)

All quantum-chemical calculations were performed using Gaussian16 software.² Geometry optimizations of CBZ-T3 oligomers (trimer and pentamer models) and their oxidized/polaronic states were carried out using the range-separated hybrid functional CAM-B3LYP³ with the 6-311+G(d,p) basis set⁴. This level of theory was selected for its ability to describe charge-transfer excitations and polaron localization in conjugated systems accurately. Time-dependent DFT (TD-DFT) calculations were performed at the same level to obtain vertical excitation energies enabling assignment of the experimentally observed 600–650 nm absorption features. Solvent effects from chloroform were incorporated using the Conductor-like Polarizable Continuum Model (CPCM).⁵

S.1.3.2. Molecular Dynamics (MD) Simulation

Classical MD simulations were performed in the FORCITE module of Materials Studio (V. 8, Accelrys Ltd., San Diego) using the COMPASS III force field, which is parameterized for polymer-ion interactions and provides reliable conformational energetics for π -conjugated systems. Initial CBZ-T3 oligomers and anions (PF₆⁻ and TFSI⁻) were energy-minimized and subjected to equilibration under NVT/NPT ensembles at 298 K. Production trajectories were then collected under the NVT ensemble for 20 ns, from which representative low-energy geometries

were extracted and subsequently re-optimized using Gaussian16 at the CAM-B3LYP/6-311+G(d,p) level. Binding energies were computed as

$$E_{bind} = E_{polymer-anion} - (E_{polymer} + E_{anion}) \quad \text{Equation S1}$$

providing a direct measure of polymer-anion stabilization.

2. Measurement Details

S2.1 Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS samples were prepared using the same method described under section 4.2, thin film preparation. For doped state measurements, the polymer films were electrochemically doped at the oxidizing potential held until the current reached a steady state, then the polymer films were carefully taken out from the cuvette, washed with propylene carbonate and ethanol, followed by drying using a nitrogen gun, and finally measured by GIWAXS. All GIWAXS measurements in this work were performed ex-situ. As shown in **Figure S2**, both the 2D patterns and the extracted in-plane and out-of-plane line cuts display broad diffuse scattering without distinct sharp Bragg reflections, indicating that the CBZ-T3 films remain predominantly amorphous in the dry, neutral, doped, and cycled states.

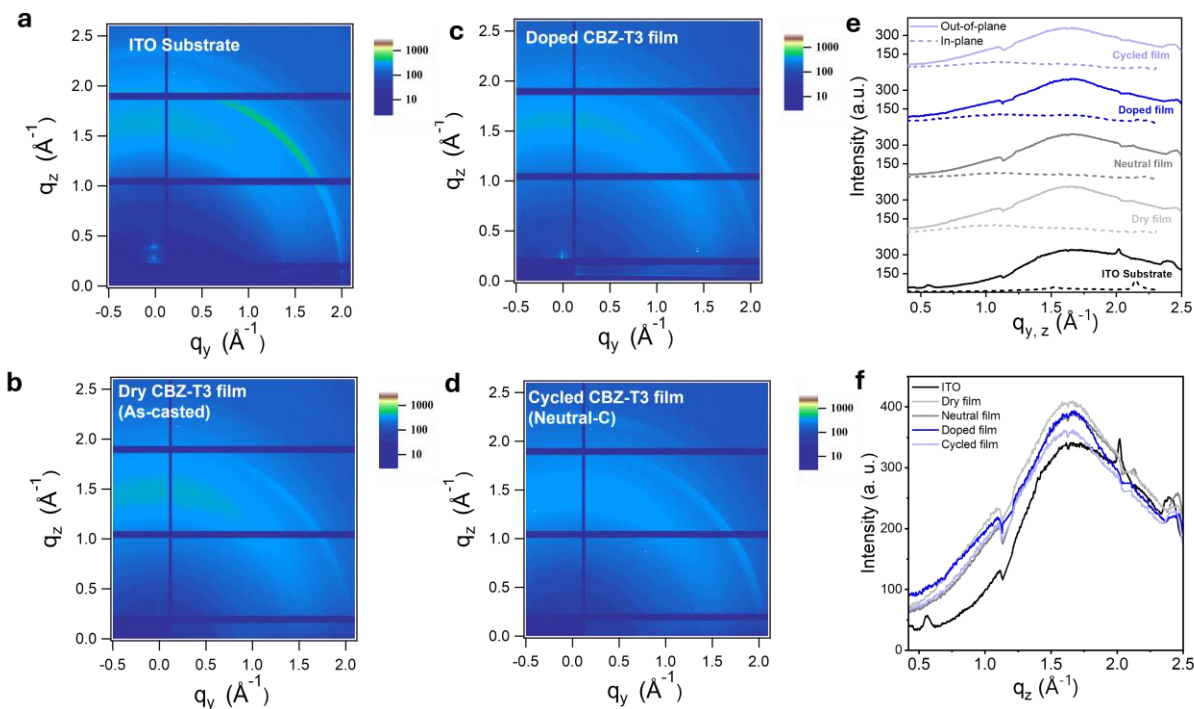


Figure S2: 2D GIWAXS data of (a) bare ITO substrate, CBZ-T3 polymer film in (b) pristine dry state, (c) doped state, (d) cycled neutral state, (e) stacked in-plane (dashed) and out-of-plane (solid) line-cut profiles of the corresponding samples, and (f) overlaid out-of-plane GIWAXS line-cut profiles for direct comparison.

S2.2. Electrochemical Techniques

S2.2.1 Step-Potential Fast Coulometry (SPFC) analysis and charge-accumulation calculation

The polymer films were cycled using step-potential fast coulometry (SPFC). In SPFC, the working electrode potential is stepped between an oxidation potential E_{ox} (+0.95 V vs Ag/AgCl, coloring, p-doping) and a reduction potential E_{red} (−0.40 V vs Ag/AgCl, bleaching, dedoping), and the resulting current-time (I-t) curve is recorded for each step with a fixed step duration of 60 sec. The charge for each step was obtained by integrating the I-t curve. Next, the net charge (Q_{net}) trapped in each step was obtained by subtracting the oxidative charge (Q_{ox}) and the reductive charge (Q_{red}) for each cycle.

$$Q_{net} = Q_{ox} - Q_{red} \quad \text{Equation S2}$$

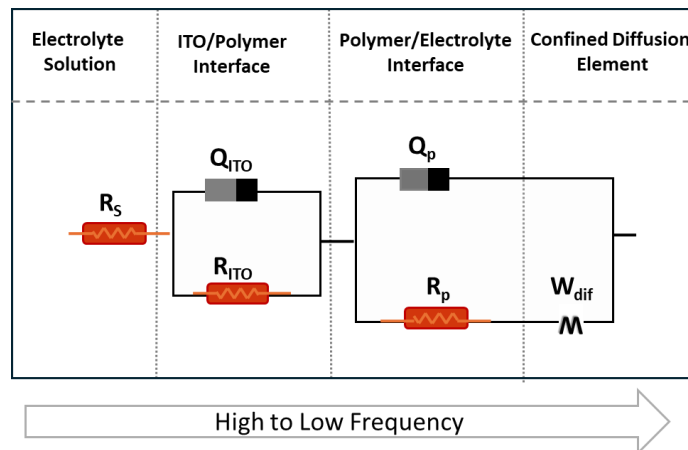
The accumulated charge (Q_{acc}) after 150 cycles was calculated by

$$Q_{acc} = \sum_{n=1}^{150} Q_{net,n} \quad \text{Equation S3}$$

S2.2.2 *Electrochemical Impedance Spectroscopy (EIS)* is a steady-state technique in which an electrochemical system is perturbed by a small-amplitude sinusoidal signal over a wide range of frequencies. The resulting current response is analyzed relative to the applied potential and modeled using an equivalent circuit. In this way, EIS enables a complex electrochemical system to be decomposed into contributions from processes with distinct time constants, such as double-layer charging/discharging, electrode charge-transfer kinetics, and mass transport.⁶⁻⁷

EIS data for CBZ-T3 films were collected at the oxidation onset potential. At this potential (low-doping regime), ions begin to migrate toward and into the polymer, but the electronic conductivity of the film is not yet high enough to mask interfacial resistances. We therefore selected this bias as a condition where both interfacial processes and ion transport within the film remain resolvable. EIS was measured at the onset potential before and after prolonged cycling, so that changes in the spectra directly reflect cycling-induced modifications of the polymer/electrolyte interface and ion-transport pathways at a fixed applied bias.

To analyze the spectra, we used an equivalent circuit consisting of two R-Q subcircuits to describe the ITO contact region and the polymer/electrolyte interface, together with a finite-length diffusion element to capture ion transport within the film. In this model, R_s represents the solution resistance; Q_{ITO} and R_{ITO} are the constant phase element and resistance associated with the ITO/polymer interface; Q_p and R_p describe the interfacial capacitance (modeled as a CPE) and resistance at the polymer/electrolyte interface. The diffusion element W_{dif} , (denoted as “M” in the circuit), represents finite-length diffusion within the polymer layer.



Scheme S1: Equivalent circuit diagram used for fitting EIS data

At high frequency, the Q_p is a constant phase element that describes a non-faradic interfacial charging at the polymer/electrolyte interface. The applied DC onset potential will inject a hole in the polymer, which will reorganize ions and polymer conformation to form an effective double layer or near-interface capacitance. The phase element is used here because of the roughness and heterogeneity of the polymer interface. Next, the circuit includes a charge-transfer resistance (R_{ct}), which captures the kinetics of electron transfer and counter-ion uptake associated with formation of the oxidized (p-doped) polymer state. At low frequency, the spectra are dominated by a finite-length diffusion process, composed of R_{dif} , τ_{dif} , and a_3 elements. R_{dif} is the resistance experienced by ions to diffuse inside the polymer matrix, and τ_{dif} is the time constant for this process. The a_3 exponent value close to 1 indicates behavior closer to an ideal capacitive/bounded-diffusion response. The ' χ^2 ' estimates the goodness of fitting; a value closer to zero means excellent fitting. The effective diffusion coefficient⁸⁻⁹ was calculated using the following equation, where L is the film thickness.

$$D_{eff} = \frac{L^2}{\tau_{dif}}$$

Equation S4

S2.3. Electrochemical Quartz Microbalance with Dissipation monitoring (EQCM-d)

S2.3.1 Brief Description: EQCM-d techniques rely on the change in oscillation frequency of the sensor and its correlation with mass of the sensor. As per Sauerbrey's equation, the electrode mass change is inversely proportional to the sensor's oscillation frequency for a stiff and perfect plastic electrode. However, the CBZ-T3 polymer swells when it meets the liquid electrolyte. This leads to the viscous response, and the Sauerbrey equation loses its validity. In such conditions of soft and viscous electrode mass, the Voigt model can be considered, wherein the crystal sensor's energy dissipation after electric field removal is monitored. This energy decay depends on the properties of the deposited layer and contact medium.

$$D = \frac{E_{\text{diss}}}{2\pi E_{\text{stored}}} \quad \text{Equation S5}$$

where E_{diss} is the energy loss after the removal of the electric field and E_{stored} is the energy stored in the oscillating crystal.

S2.3.2 Data Collection: Firstly, a baseline for a cleaned gold quartz sensor was collected in air followed by pumping solvent (propylene carbonate, PC), and electrolyte (0.2M LiPF₆/PC) at 100μL/min flow rate. After achieving a stable frequency response under flow, the sensor was allowed to stabilize for an additional 15 minutes, and simultaneously, changes in the frequency and dissipation were recorded.

Next, this sensor was cleaned by etching in an O₂-plasma etcher for an additional 10 minutes. A thorough cleaning was performed by sonicating it in water, acetone, and ethanol for 10 minutes each, respectively. A 20 mg/mL CBZ-T3 polymer solution was prepared in chloroform, and ~60μL aliquot of the polymer solution was spin-coated at 1500 rpm for 30 sec on this cleaned gold quartz sensor. The thickness of CBZ-T3 film was estimated by modelling the frequency response in the stitched baseline file of bare and coated sensors in air. Sauerbrey Model in QTools software (Biolin Scientific) was employed. A three-electrode electrochemical cell was used for baseline and electrochemical measurements in normal laboratory conditions at room temperature. The CBZ-T3 film-coated Au quartz sensor was used as the working electrode and leakless Ag/AgCl as the reference electrode. The baseline conditions were replicated during the electrochemical measurements until stable frequency and dissipation responses were measured.

The CBZ-T3 polymer-coated films were equilibrated for an additional 15 minutes. For cycling measurements, the SPFC and EQCM-d measurements were performed simultaneously.

S2.3.3 Modelling: First, we assess whether the Sauerbrey rigid-film or Voigt viscoelastic model approximation is applicable. We examined the overtone dependence of the QCM response during potential cycling. **Figures S2a and S2b** shows the normalized frequency shifts $\Delta f_n/n$ and dissipation shifts ΔD_n for $n = 3$ and 5 for CV at 25 mVs^{-1} . The $\Delta f_n/n$ curves do not collapse onto a single trace, and the dissipation changes reach $|\Delta D_n| \approx 0.2 \times 10^{-6}$ per cycle, indicating a viscoelastic, swelling film rather than a rigid Sauerbrey layer. Similar behavior is observed over extended cycling (**Figure S2e**), where both Δf and ΔD oscillate. These deviations from overtone-independent, low-dissipation behavior justify the use of a Voigt viscoelastic model for quantifying mass and thickness.

The electrode mass change during cycling was measured by using the viscoelastic Voigt Model in QTools software. This modelling software utilizes the fluid properties such as density (ρ) and viscosity (η) to quantify film properties such as elasticity (μ), mass (m), and thickness (δ) of the film. Based on the properties of propylene carbonate, a density of 1230 kgm^{-3} at 25°C was presumed for the 0.2M LiPF_6 in PC. The dry polymer film's density was approximated from the ratio of the mass of deposited film to the volume of the film¹⁰ ($\sim 3500 \text{ kgm}^{-3}$). The polymer-electrolyte layer density was calculated to be $\sim 2795 \text{ kgm}^{-3}$. For each sample, at least three overtones out of the 1st, 3rd, 5th, 7th, and 9th overtones were modeled using Qtools broadband procedure to obtain a minimum χ^2 fit error.

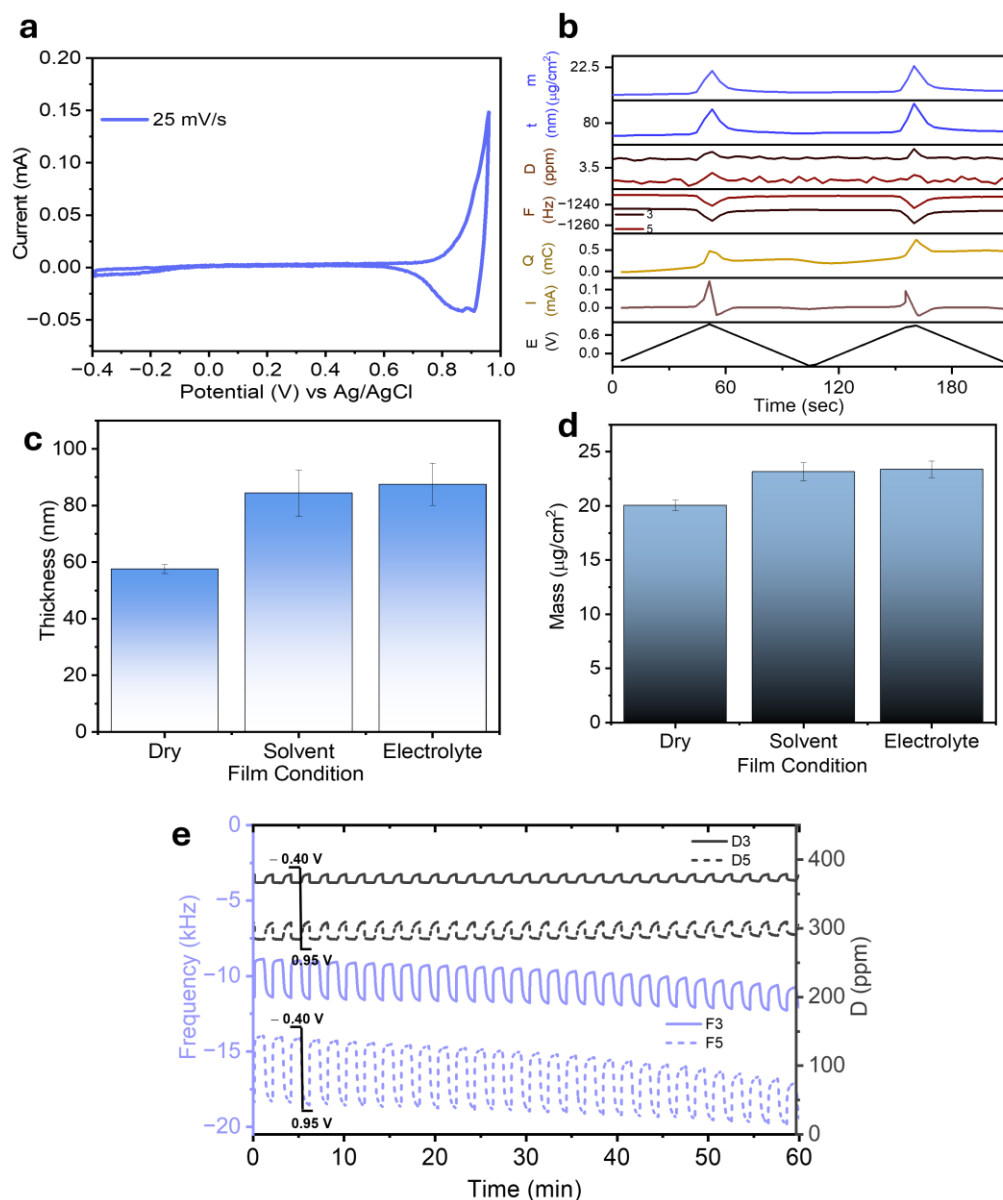


Figure S3: (a) CV At 25 mV/s, (b) change in potential (E) vs Ag/AgCl, current (I), charge (Q), frequency (f), dissipation (d), thickness (t) and mass (m) for 5 consecutive CV cycles at 25 mV /s, (c) change in thickness, (d) change in mass under different film conditions, and (e) overtone-dependent frequency shifts (Δf_n) and finite dissipation changes (ΔD_n , up to a few hundred ppm) for $n = 3$ and 5 during SPFC cycling, demonstrating viscoelastic behavior and deviation from the rigid-film Sauerbrey limit.

S2.4: Fourier Transform Infrared spectroscopy (FT-IR)

A peak corresponding to the P-F stretching vibration of PF_6^- is observed at 848 cm^{-1} in **Figure S4a**. Apart from solvent contributions, **Figure S4b** shows distinct peaks at 1625 cm^{-1} (C-N), 1600 cm^{-1} (C=C, carbazole moiety), 1480 cm^{-1} (C-C, carbazole), and 1444 cm^{-1} (C=C for thiophene), 848 cm^{-1} (P-F, electrolyte), and 730 cm^{-1} (C-S of thiophene).¹¹⁻¹⁴ With doping, the

bands at 1625, 1600, and 730 cm^{-1} shift to lower wavenumber along with an increase in the intensity of P-F (848) and C-S (730) bands. This reflects PF_6^- counterion incorporation during the doping process.

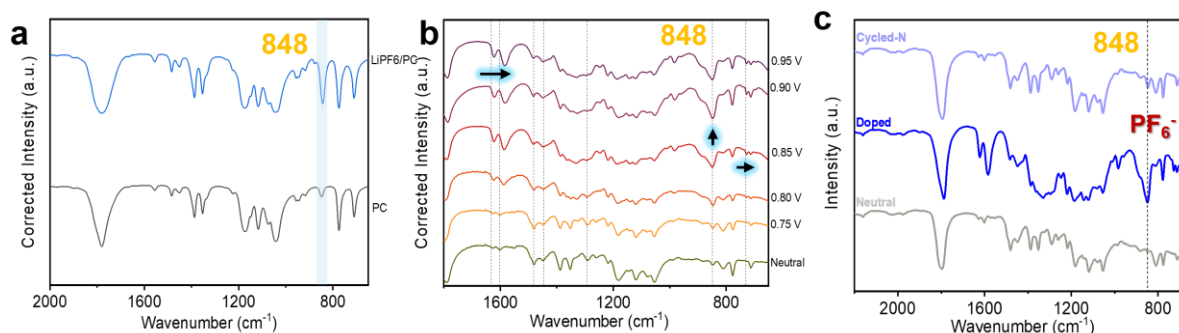


Figure S4: Overlay of FTIR spectra of (a) solvent and electrolyte, (b) polymer thin films at different doping states obtained at specified potentials, and (c) polymer thin film in neutral, doped, and cycled states.

S2.5: X-ray Photoelectron Spectroscopy (XPS)

XPS samples were prepared using the same method described under the section ‘thin film preparation and characterization’.

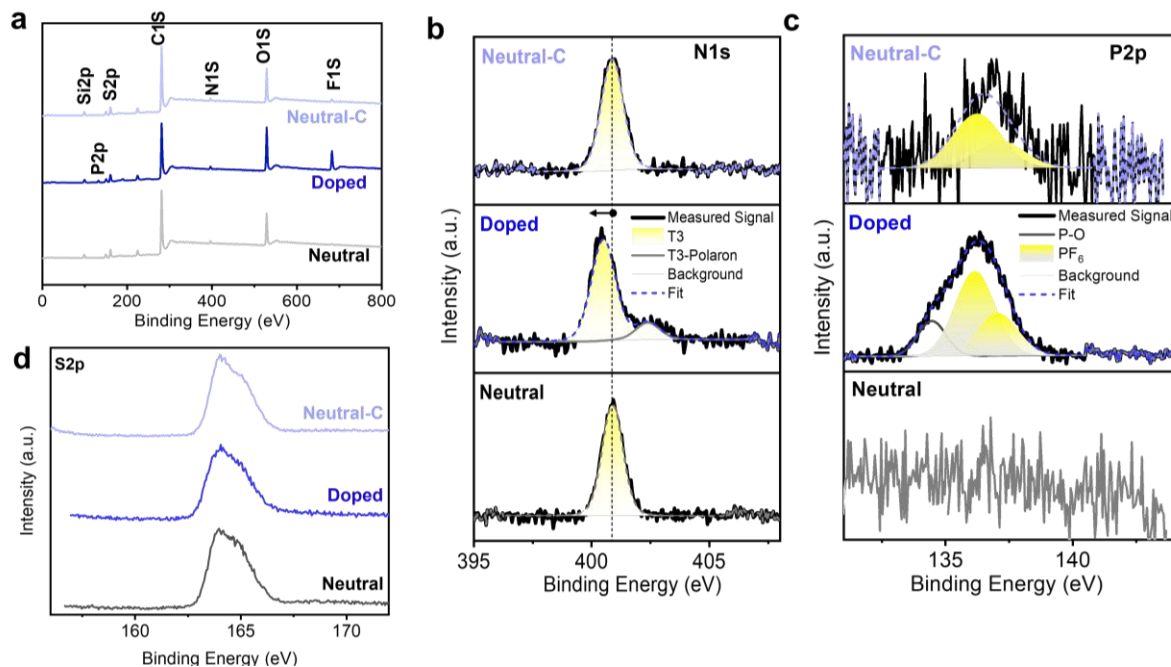


Figure S5: (a) Complete XPS survey scan, high resolution deconvoluted (b) N 1s, (c) P 2p, and (d) S 2p XPS spectra for CBZ-T3 polymer film in neutral state, doped state, and cycled state.

The elemental composition calculation and deconvolution of spectral peaks were obtained by using CASA XPS software. The doping percentage was calculated by using the following formula,

$$\% \text{ Doping} = \frac{\text{Area of Fluorine/ASF of F} \times \text{no. of F}}{\text{Area of Nitrogen/Atom/ASF of atom} \times \text{no. of atom}}$$

Equation S6

Here, the area of the element was obtained from CASA XPS for F and N. The relative atomic sensitivity factor (ASF) for fluorine (F) is 1, and for Nitrogen (N) is 0.447. The fitting of the S 2p regions in **Figure 4a** was fitted using standard constraints: a spin-orbit doublet with fixed 2p_{3/2}–2p_{1/2} splitting (~1.18 eV), a 2:1 area ratio, and a common FWHM for all components belonging to the same chemical environment, with a Shirley background.

S2.6: Electrochromic Behavior of CBZ-T3 Polymer Film in 0.2M LiPF₆ in PC

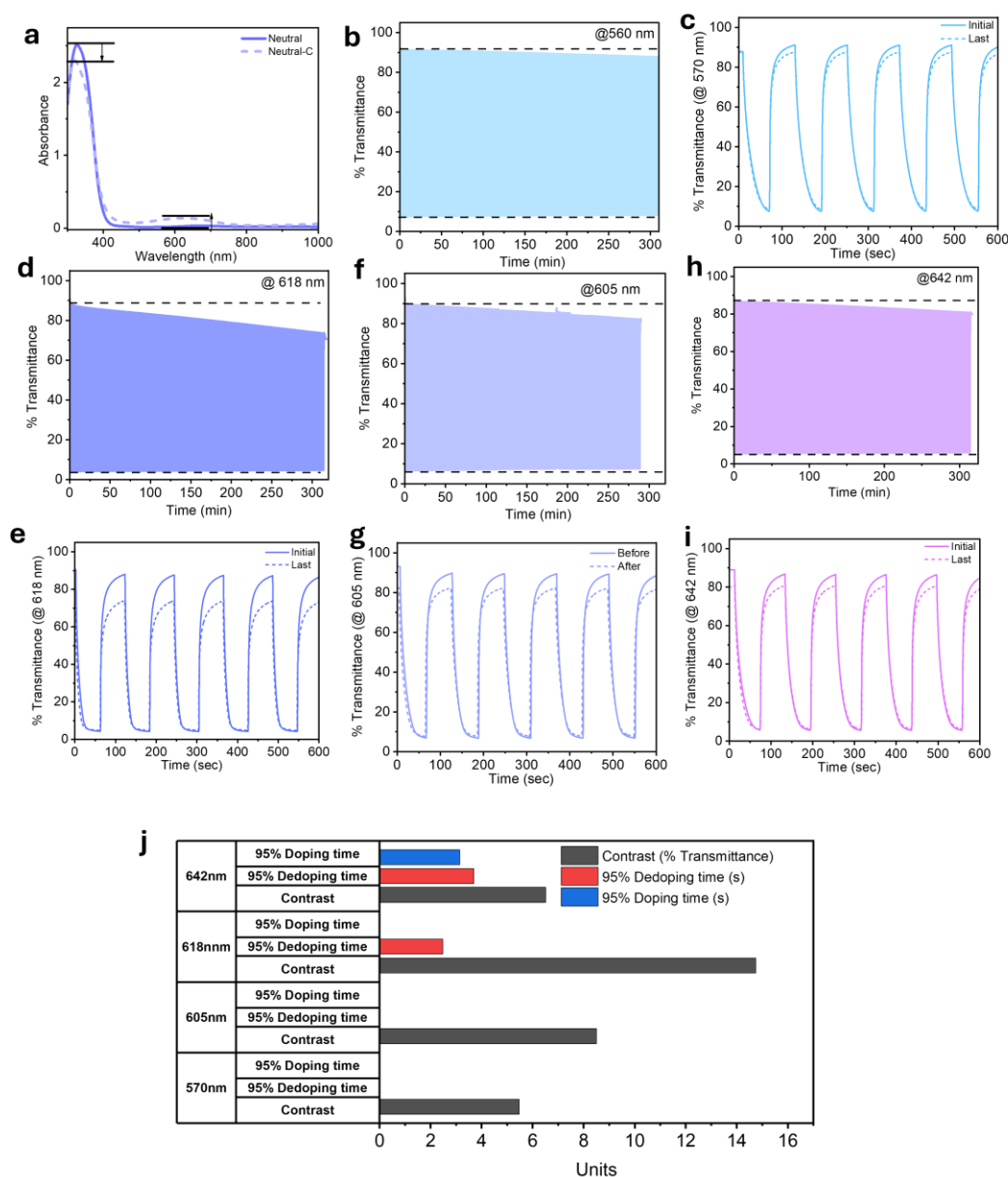


Figure S6: 0.2M LiPF₆ in PC; kinetics of CBZ-T3 polymer and comparison of their initial and last cycle at (a) UV-vis absorption spectra in before and after cycled neutral states (b, c) 560 nm, (d, e) 605nm, (f, g) 618nm, (h, i) 642nm, and (j) histogram representing comparison of kinetic parameters at different wavelengths.

S2.7: Kinetics Stretched Growth Exponential Function Fitting

The reduction of the polymer, leading to the dedoping of the polymer, is a complex process. It includes multiple processes: a) immediate ion migrations, b) volume change, and c) polymer conformation relaxation.¹⁵ Therefore, the stretched exponential function has been used to empirically describe a range of physical properties in complex polymer systems. It can also be used to fit a distribution of diffusion times in swelling/shrinking polymers. The distribution of times is thought to arise from local variations in the diffusion coefficients within the polymer due to local differences in oxidation level, swelling, crosslinking, chain stiffness, etc. These parameters would be expected to affect the scattering of ions, and thereby the diffusion coefficient. Hence, the ion trapping, which is also an implication of the change in the above-mentioned processes, can be understood using the stretched exponential function. The variation in exponential characteristics should provide a direct indication of how badly the energy distribution occurs on polymer matrix upon continuous cycling (ion trapping). The fitting function can be described as

$$T(t) = T_0 + (A - T_0)(1 - e^{-(t/\tau)^\beta}) \quad \text{Equation S7}$$

Here, T_0 is the initial transmittance of the polymer in its doped state (low transparency due to charge carriers absorbing light). A is the Final transmittance after dedoping (higher transparency as ions are expelled, reducing charge carriers). τ is the characteristic timescale for ion detrapping. Larger values will indicate slower release of ions from traps. β represents the stretching exponent, which could vary between 0 and 1 ($0 < \beta \leq 1$). This factor represents how the traps are distributed. $\beta \approx 1$: Single dominant trap type (narrow energy distribution). $\beta \ll 1$: Broad distribution of trap depths (e.g., shallow, deep, and irreversible traps)

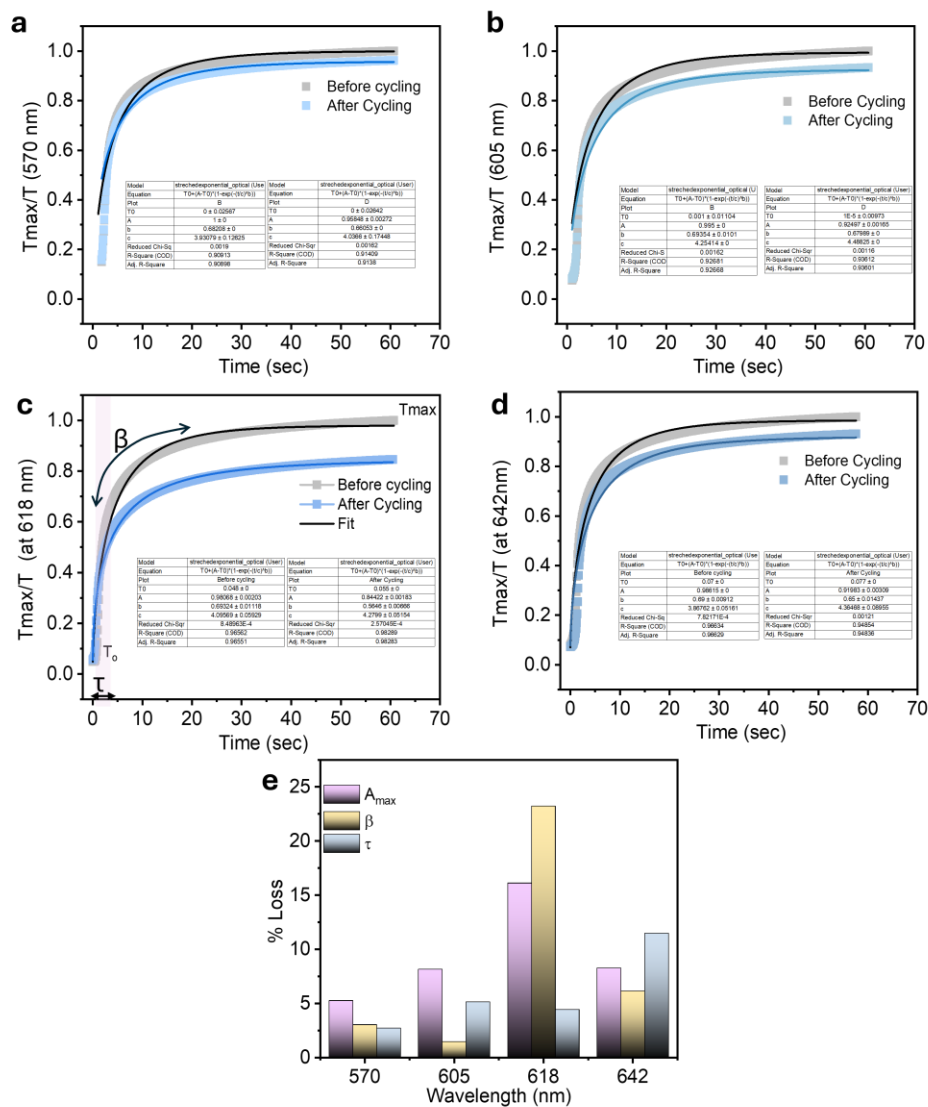


Figure S7: Comparison of kinetics ($T_{\max}/T$) in neutral state before and after cycling, fitted with the exponential growth equation for (a)570nm, (b)605nm, (c)618nm, (d)642 nm, and (e) %loss in parameters.

S2.8: Electrochromic behavior of CBZ-T2 polymer film in 0.2M LiPF₆ in PC

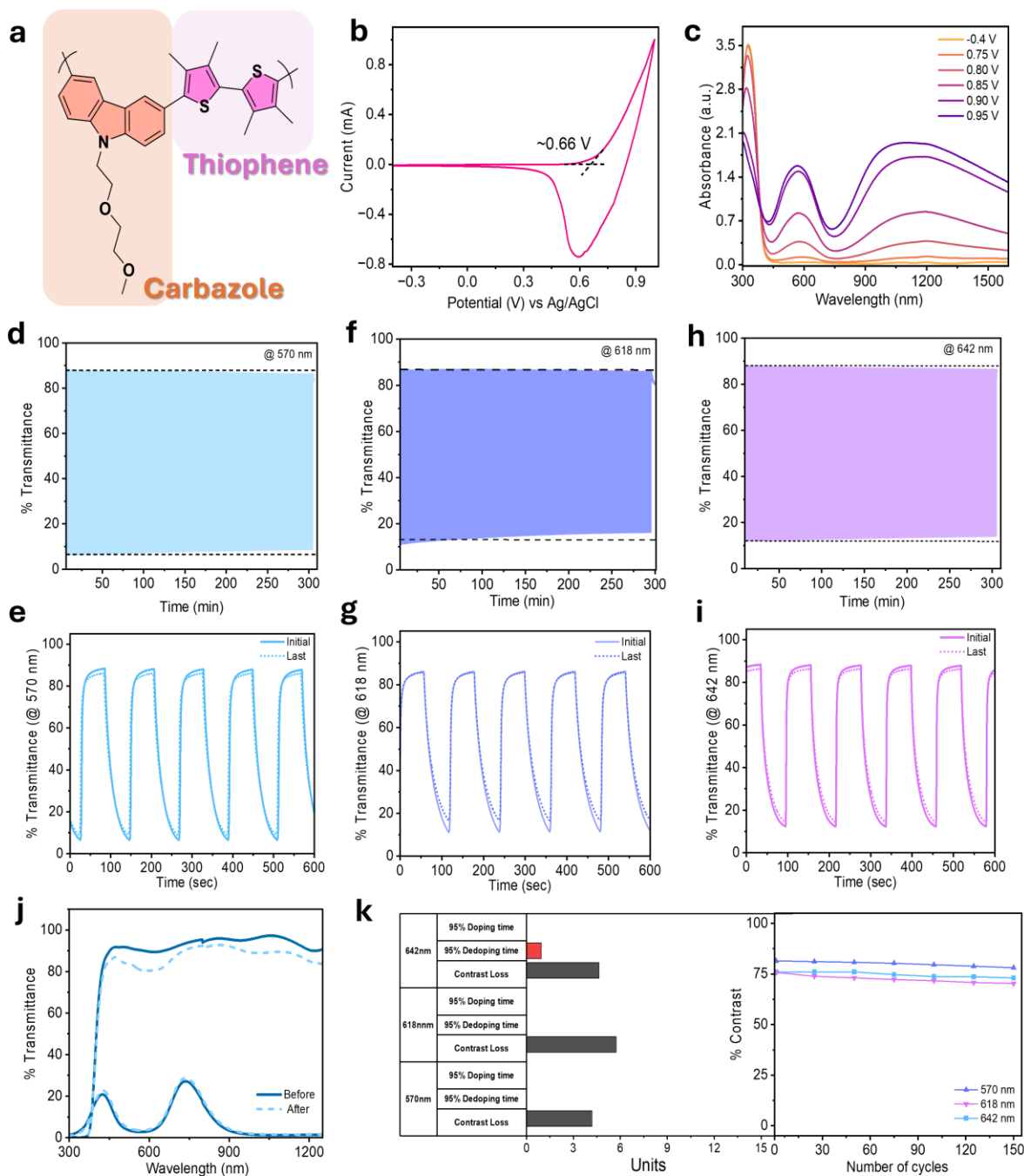


Figure S8: Kinetic investigation of CBZ-T2 polymer (a) structure, (b) CV, (c) spectro-electrochemical data, kinetics at (d,e) 570 nm, (f, g) 618 nm, (h i) 642nm, (j) histogram representing comparison of kinetic parameters at different wavelengths, inset overlay of absorption spectra in the neutral and doped state before and after 150 cycles, (k) change in contrast over 150 cycles.

S2.9: Raman Spectroscopy

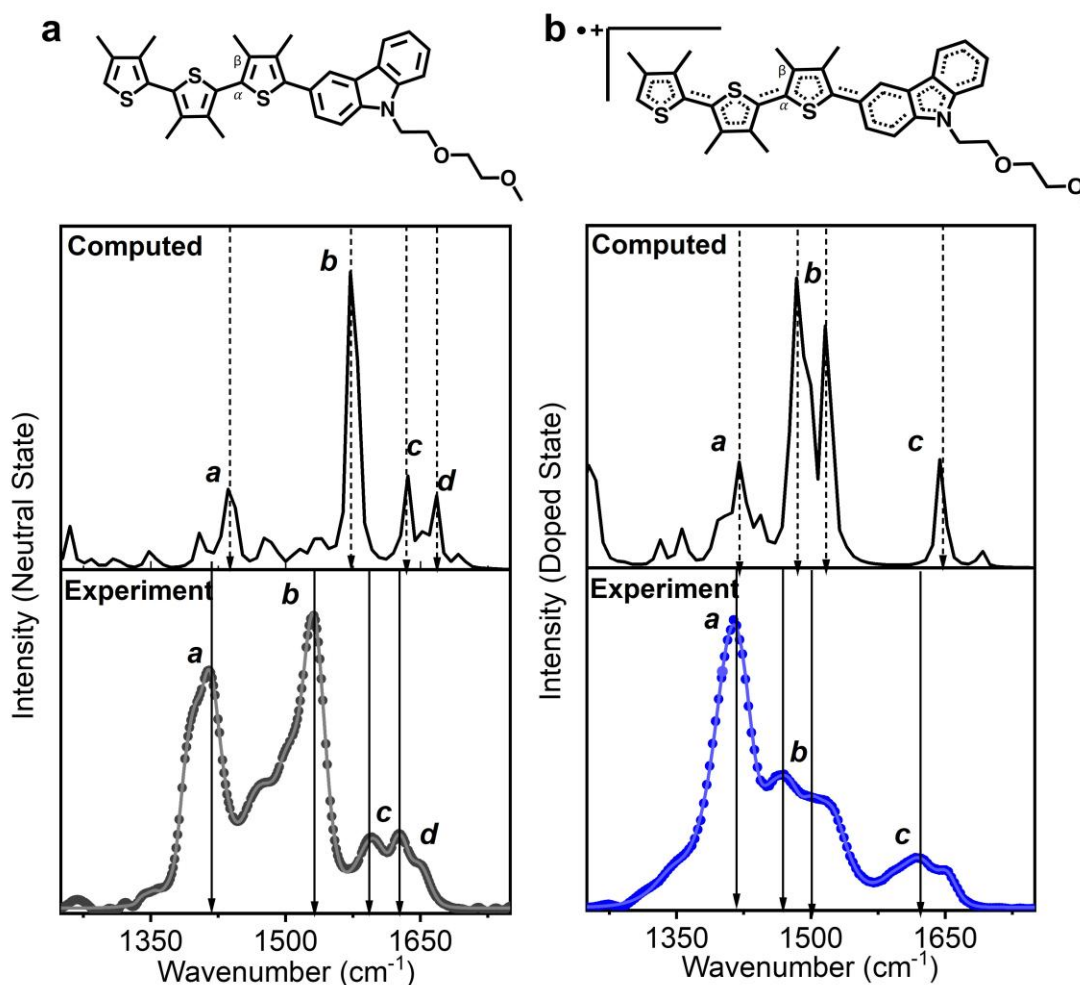


Figure S9: Comparison of computed and experimentally collected Raman spectra of CBZ-T3 polymer in (a) neutral state and (b) doped state.

Discussion: The C=C labeled for symmetric stretch from $1350\text{--}1420\text{ cm}^{-1}$ range shifts after doping; however, it shows a slight shift in the neutral state obtained after cycling. The C-C ($\text{C}\alpha\text{--C}\alpha$ and $\text{C}\beta\text{--C}\beta/\text{C--N}$) gets red-shifted, which signifies elongation of bond length between thiophenes during delocalization, whereas after cycling, this shift didn't recover. The asymmetric stretch of C=C significantly red-shifts and shows depleted intensity. This intensity decrease could be attributed to the injection of charge carriers (polarons/bipolarons) into the polymer backbone during the doping process.¹⁶ These carriers disrupt the regular π -conjugation and increase the quinoid character of the backbone, altering the force constants and symmetry of the C=C bonds. Whereas the Red Shift occurs due to increased backbone planarity and delocalization of charge.

Next, the ratio of the area under C–C stretching peaks (1470 and 1499 cm^{-1}) to the C=C stretching peak (1529 cm^{-1}) was calculated. This reflects enhanced backbone disorder and the formation of polarons/bipolarons, as the backbone shifts from aromatic to quinoid character.¹⁷ Carbazole ring modes ($\sim 1594\text{--}1650\text{ cm}^{-1}$) shift on doping but recover after cycling, consistent with the N 1s invariance and indicating that persistent changes are thiophene-centered.

S2.10: Evaluation of Electrochromic Behavior of Cycled CBZ-T3 Polymer Film in 0.2M LiTFSI in PC

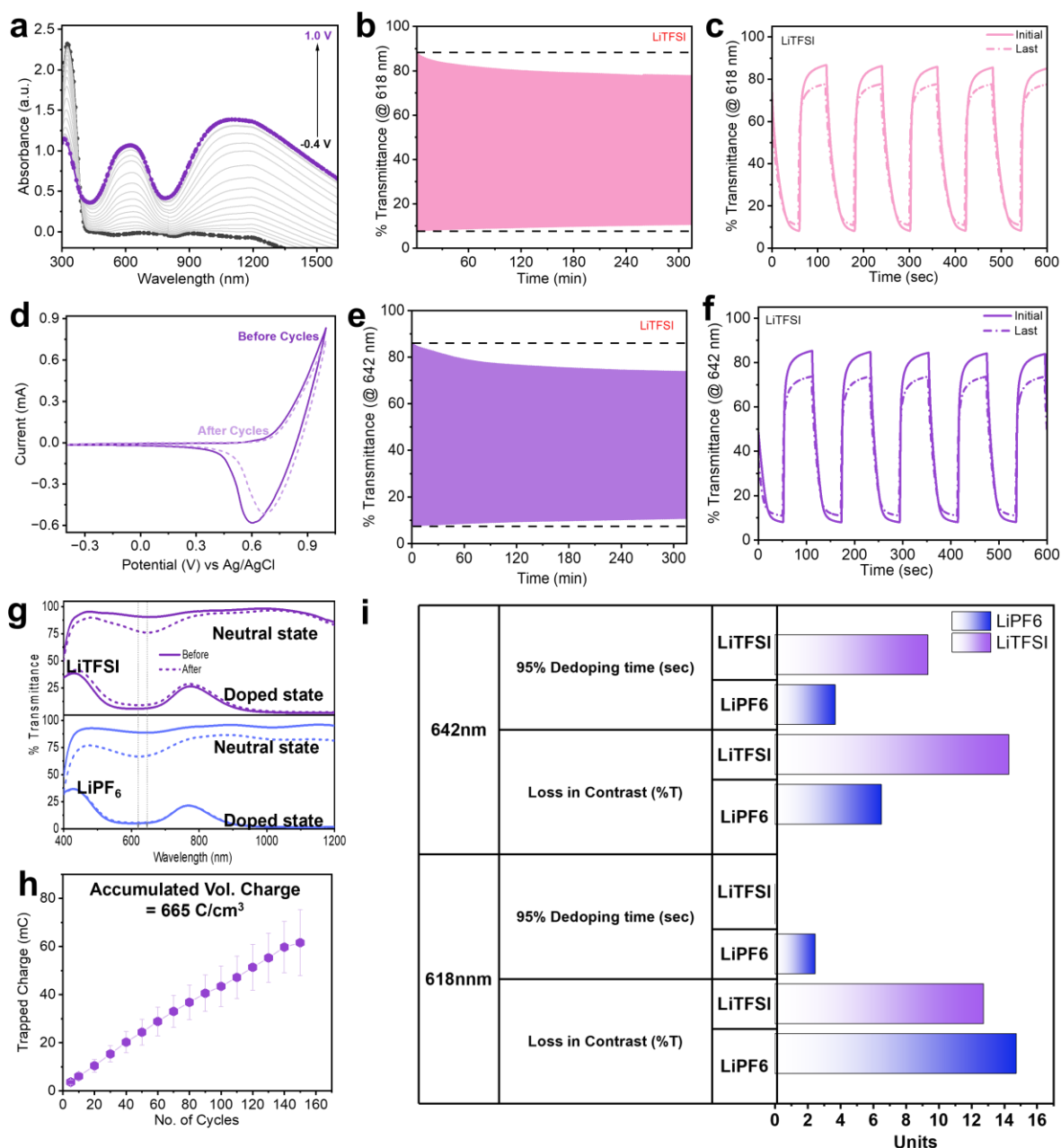


Figure S10: Long-time performance of CBZ-T3 polymer in 0.2 M LiTFSI in PC; (a) absorption spectra via potential application from -0.4 V to 1 V, kinetics at 618 nm using SPFC from -0.4 V to 0.95 V vs Ag/AgCl (b) for 150 consecutive cycles, (c) overlay of first and last cycles, (d) overlay of cyclic voltammograms before and after cycles, kinetics at 642 nm (e) for 150 consecutive cycles, (f) overlay of first and last cycles, (g) comparison for transmittance overlay at neutral and doped state for LiTFSI and LiPF₆, (h) accumulated charge over 150 SPFC cycles and (i) bar graph for switching kinetics metric for LiTFSI and LiPF₆ at 618 nm and 642 nm.

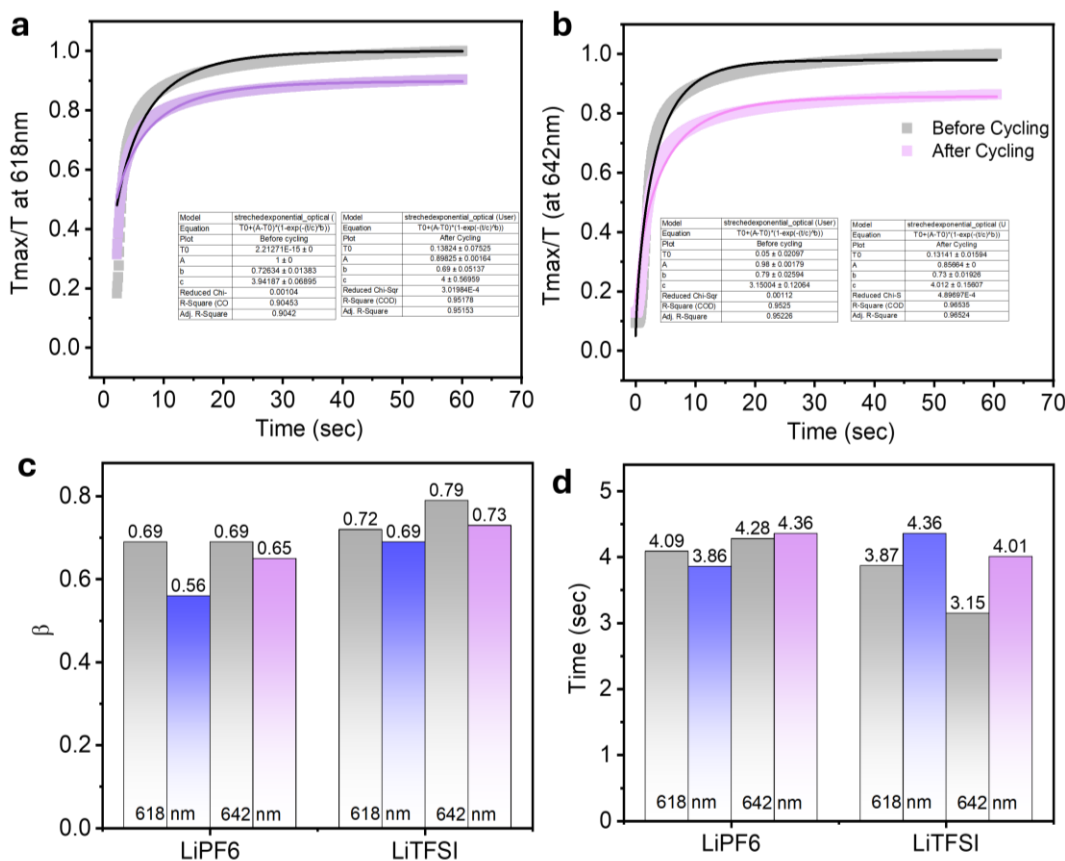


Figure S11: Comparison of kinetics ($T_{\max}/T$) in neutral state before and after cycling, fitted with the exponential growth equation for LiTFSI case (a) 618 nm, (b) 642 nm, Comparison of (c) β and (d) τ between LiPF₆ and LiTFSI.

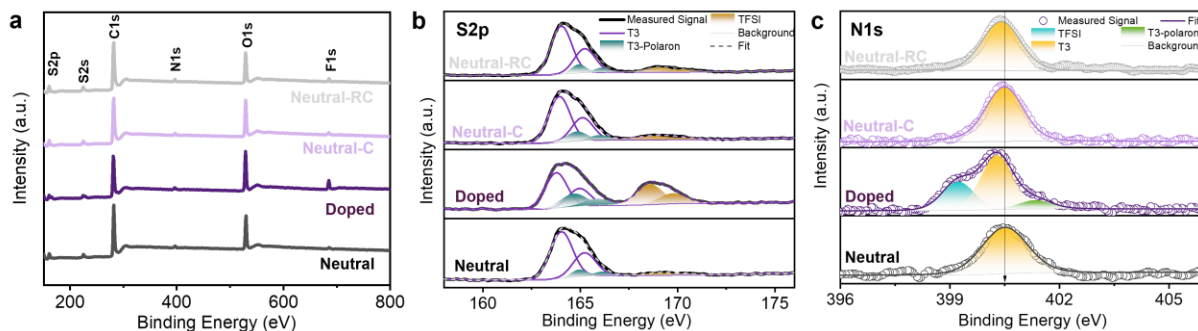


Figure S12: XPS spectra of CBZ-T3 film in LiTFSI electrolyte in neutral state, doped state, neutral state after cycling (neutral-C), and neutral state after recovery (neutral-RC): (a) overlay of XPS survey scan, (b) deconvoluted S2p spectra, and (c) deconvoluted N1s spectra.

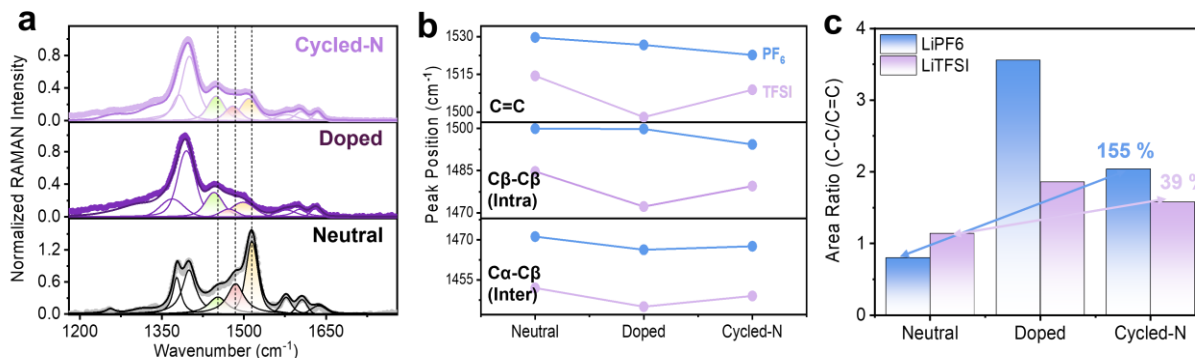


Figure S13: Characterization of CBZ-T3 film in LiTFSI electrolytic conditions; (a) comparison of fitted Raman spectra, comparison of fitted Raman spectral parameters between LiPF₆ and LiTFSI, (b) shift in peak position obtained from fitting Raman spectra, and (c) area ratio of C-C and C=C.

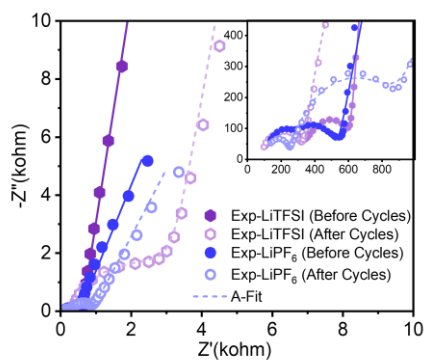


Figure S14: Comparison of electrochemical impedance spectra (EIS) at onset potential in frequency range 10⁶ to 10⁻² Hz for LiPF₆ and LiTFSI, inset provides high frequency region.

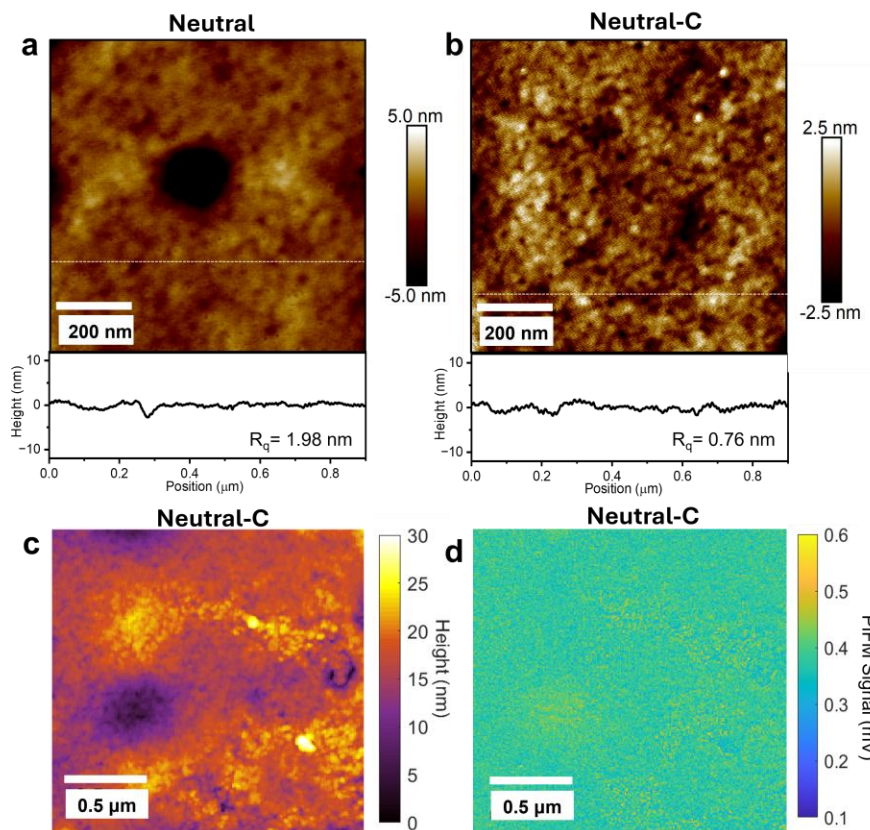


Figure S15: AFM of dried CBZ-T3 thin films in LiTFSI electrolyte with R_q value; (a) neutral state, (b) neutral state after cycling, (c) topography image, and (d) PiFM image for neutral state after cycling. (Note: In AFM, utilizing the threshold height function to analyze cases where the surface may or may not contain large voids/craters)

S2.11: Recovery Metrics

To quantify the evolution of the thiophene-localized absorption band while minimizing run-to-run scaling differences, we define a dimensionless area ratio for each spectrum ‘x’ (=point I to IV)’;

$$A_x = \frac{\text{Band Area (600–650)}}{\text{Band Area (478–490)}} \quad \text{Equation S8}$$

Here, the numerator integrates the area of the 600-650 nm absorption band associated with trapped polarons, while the denominator integrates a nearby reference window (478-490 nm), which was found to be largely unchanged across different absorption spectra. This internal normalization stabilizes the baseline and cancels overall intensity drift. We then compare each state ‘x’ to the initial neutral spectrum (Point I) to describe the following relative spectral contrast;

$$F_{x/I} = \frac{A_x}{A_I} \quad \text{Equation S9}$$

Values $F_{x/I} > 1$ indicate that the normalized 600–650 nm band in the state x is larger than in the pristine neutral film, whereas $F_{x/I} < 1$ indicates a decrease. Finally, we report the relative change in this band as a percentage, which provides us with information about the relative spectral absorption % with respect to point I;

$$\% \Delta \text{Abs} = (F_{x/I} - 1) * 100 \quad \text{Equation S10}$$

To quantify how closely each state recovers, we define a recovery fraction that tells how much of the relative spectral contrast (caused by trapped ions) has been recovered by the recovery protocol with respect to point II;

$$\% \text{ Recovery Fraction (\% RF)} = \left(1 - \frac{F_{x/I}}{F_{II/I}}\right) * 100 \quad \text{Equation S11}$$

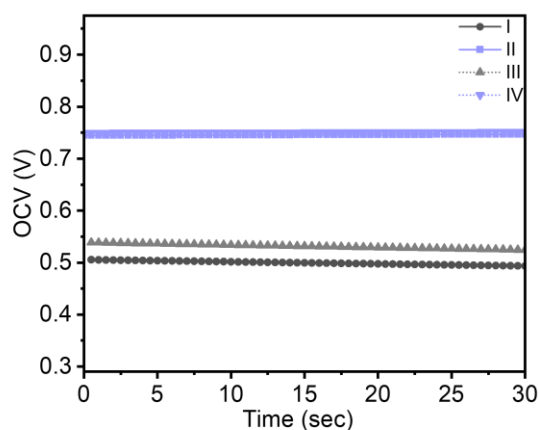


Figure S16: Open circuit potential captured at points I to IV.

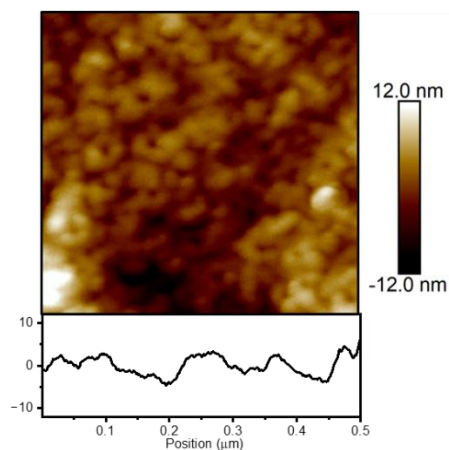


Figure S17: AFM image of recovered neutral film (neutral-R).

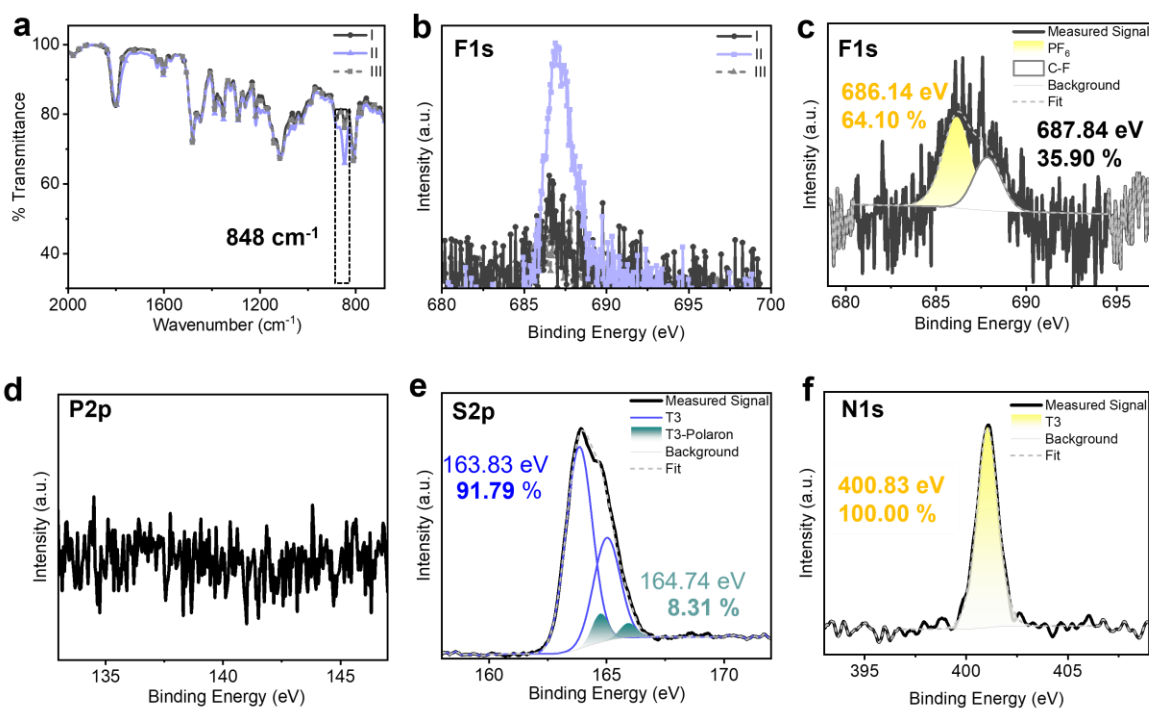


Figure S18: Characterization of CBZ-T3 polymer film after recovery, (a) FTIR spectra, (b) F 1s XPS spectra, deconvoluted XPS spectra for (c) F 1s, (d) P 2p, (e) S 2p, and (f) N 1s.

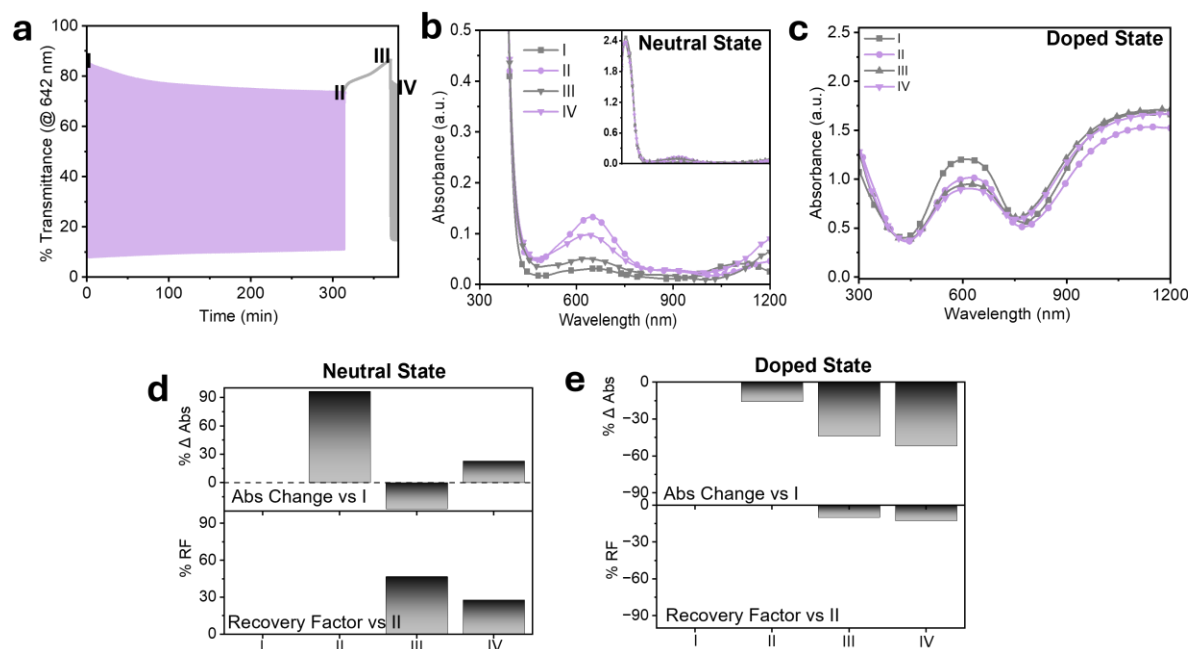


Figure S19: Recovery of CBZ-T3 polymer film in 0.2M LiTFSI; (a) consecutive cycling with recovery, (b) OCV, (c) absorbance overlay at four different points in (c) neutral state and (d) doped state, % change in absorbance for graph 'b and c' with respect to point I and % recovery fraction with respect to point II for (e) Neutral state and (f) Doped state.

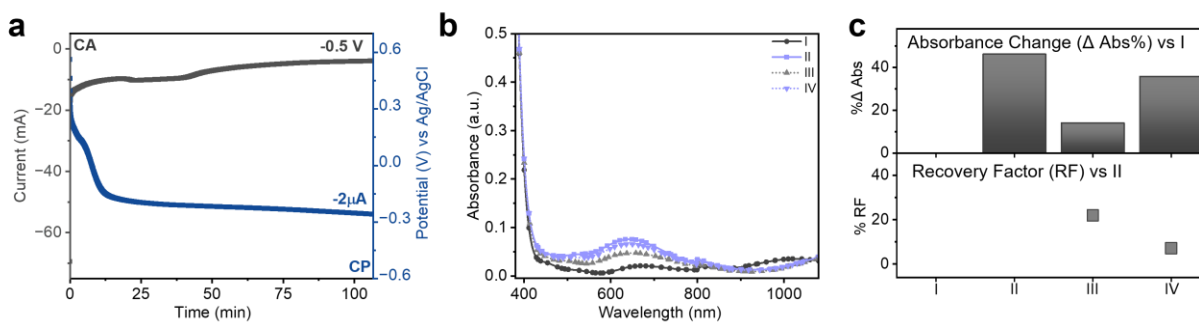


Figure S20: (a) Current and potential vs time using chronoamperometry (CA, V= -0.5 V vs Ag/AgCl) and Chronopotentiometry (CP, I= -2μA vs Ag/AgCl), For Chronoamperometric recovery data; (b) absorption spectra at four points, (c) % change in absorbance for graph 'b' with respect to point I and % recovery fraction with respect to point II.

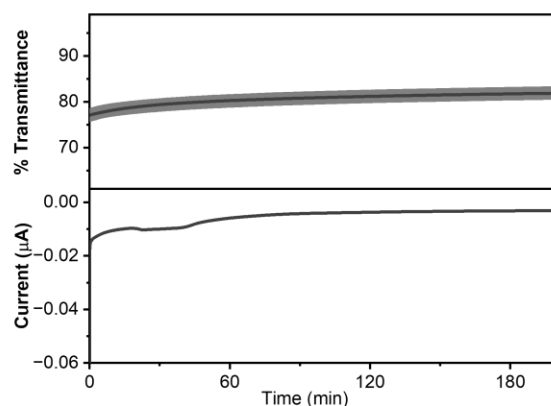


Figure S21: Current change and transmittance change vs time (fitted using equation 1) during chronoamperometry (CA) application for LiPF₆ electrolyte.

By using the equations provided in **section 2.11** based on fitting comparison, CA at -0.5 V yields a smaller fast-channel amplitude and longer τ_2 than CP (**Table S18**), mathematically reaffirming that CP more effectively mobilizes trapped ions.

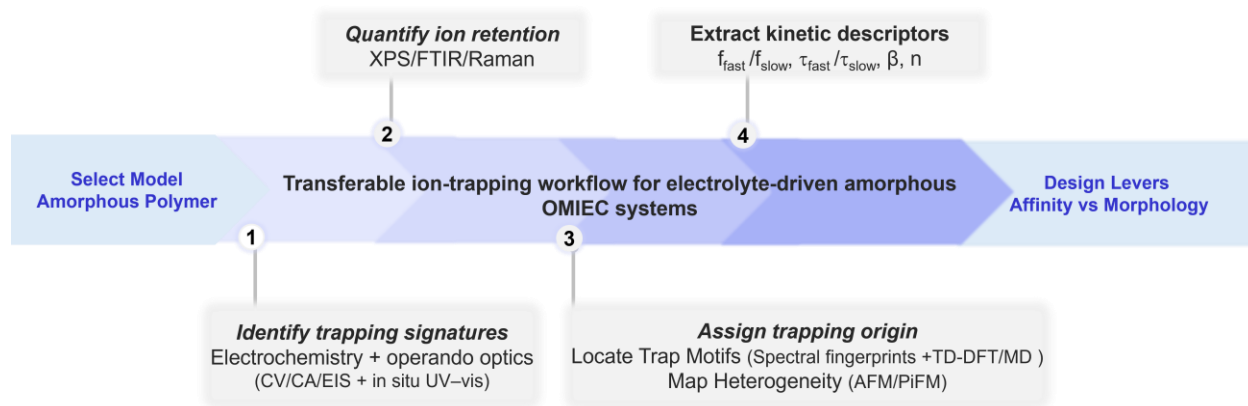


Figure S22: Schematic of a transferable ion-trapping workflow for amorphous electrochromic polymers, outlining how trapping signatures, trap origin, ion retention, and kinetic descriptors can be systematically extracted from the set of measurements used in this work.

S2.12: Tables

Table S1: EIS fitting parameters for CBZ-T3 polymer in 0.2M LiPF₆/PC electrolyte at onset potential

State	R_s (Ω)	$Q_{ITO} * 10^{-6}$ ($F.s^{(a1-1)}$)	$a1$	R_{ITO} (Ω)	$C_P * 10^{-3}$	R_P (Ω)	R_{dif} (Ω)	t_{dif} $* 10^{-3}$	$a3$	χ^2	$D * 10^{-8}$
Before Cycles	98.9	0.29	0.86	157.2	3.4	285.1	7.8	0.41	0.82	0.039	68.10
After Cycles	98.9	0.29	0.86	157.7	1.3	647.7	97.4	20.82	0.73	0.041	1.32

C_p = Double layer capacitance (F), R_p = Charge transfer resistance (Ω), R_{dif} =Diffusion resistance (Ω), t_{dif} = Time for diffusion (sec), D = Diffusion Coefficient ($\text{cm}^2 \text{s}^{-1}$)

Table S2: % Elemental composition of elements obtained from CASA XPS software

Element	Neutral	Doped	Neutral-C
C1s	80.51	68.60	80.22
O1s	14.53	19.70	18.56
N1s	0.80	1.26	1.03
S2p	5.09	2.80	7.02
F1s	0.28	6.04	0.74
P2p	Not detected	1.59	0.13

Table S3: % Composition of F 1s elemental species

F1S (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C
PF ₆	-	74.09% (686.73)	84.95% (686.93)
	-	19.95% (688.08)	-
	-	5.96% (689.63)	15.05% (689.92)

Table S4: % Composition of P 2p elemental species

P2p (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C
PF ₆ (2p _{3/2})	-	51.64 % (136.15)	66.67% (136.25)
PF ₆ (2p _{1/2})	-	25.82% (137.06)	33.33% (137.15)
Oxides of P		15.03% (134.46)	
		7.51% (135.36)	

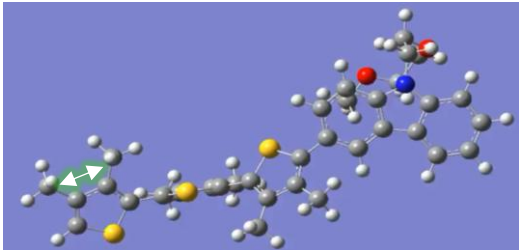
Table S5: % Composition of N 1s elemental species

N1S (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C
-C-N	100% (400.74)	86.41% (400.37)	100% (400.69)
-C=N ⁺		13.59% (402.21)	

Table S6: % Composition of S 2p elemental species obtained by deconvolution

Species (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C
CBZ-T3-Thiophene-2p _{3/2}	61.73% (163.98)	45.60% (163.84)	56.48% (164.00)
CBZ-T3-Thiophene-2p _{1/2}	30.87 % (165.16)	22.30 % (165.03)	28.24% (165.18)
(Thiophene) ⁿ⁺ 2p _{3/2} ^{''}	4.94% (164.98)	19.51% (164.60)	10.20% (164.85)
(Thiophene) ⁿ⁺ 2p _{1/2} ^{''}	2.47% (166.18)	9.76% (166.02)	5.10% (166.03)
Oxides of S		1.56% (167.62)	
Oxides of S		0.78% (168.80)	

Table S7: Peak assignment for computed RAMAN spectra of CBZ-T3 polymer in neutral state

Peak (cm ⁻¹)	Vibration	Assignment
a (1440)		C _β =C _β

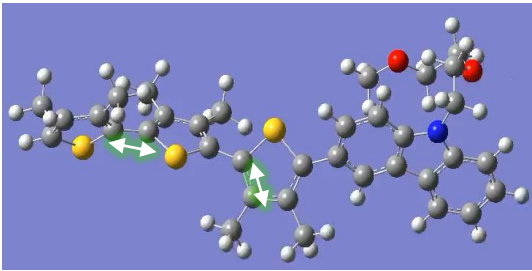
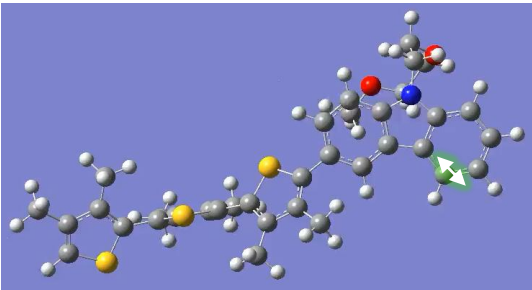
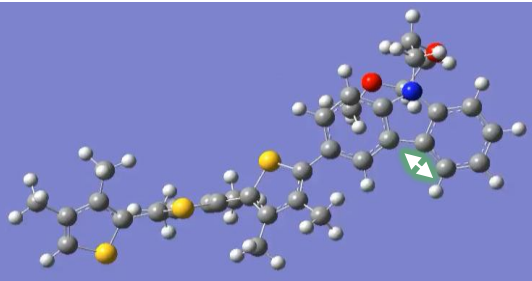
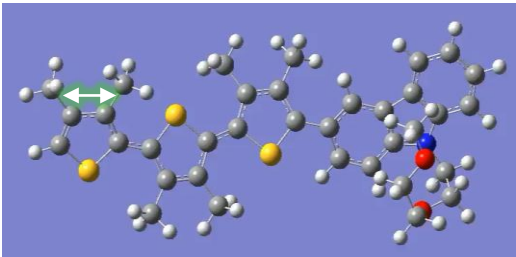
b (1575)		Quinoid structure $C_{\alpha}-C_{\beta}$
c (1634)		Benzene's Cs
d (1665)		Benzene's Cs

Table S8: Peak assignment for computed RAMAN spectra of CBZ-T3 polymer in the doped state

Peak (cm^{-1})	Vibration	Assignment
a (1445)		$C_{\beta}=C_{\beta}$

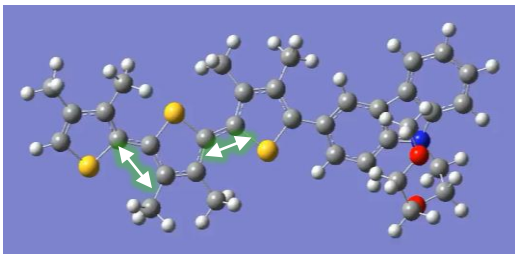
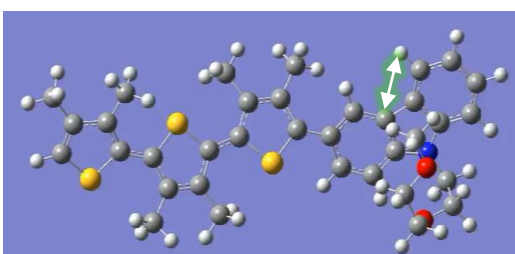
b (1519)		$C\alpha-C\alpha, C\alpha-C\beta$
c (1644)		Benzene's C_s

Table S9: Peak fitted parameters for experimental RAMAN Spectra obtained by Voigt fitting

Peak Number	Neutral			Doped			Neutral-C		
	Peak Centre	Area	FWHM	Peak Centre	Area	FWHM	Peak Centre	Area	FWHM
1	1324.8	16.18	84.59	1311.6	4.12	57.43	1355.3	10.38	56.54
2	1392.5	11.98	21.99	1364.9	14.98	72.69	1389.1	7.32	49.58
3	1414.8	49.29	37.84	1413.3	44.98	45.06	1415.5	38.44	41.23
4	1471.2	18.12	43.38	1466.3	28.64	47.72	1467.6	12.37	41.74
5	1499.9	16.75	32.42	1499.8	9.14	41.39	1494.2	5.75	43.58
6	1529.7	43.76	32.64	1526.7	10.60	39.01	1522.7	8.88	42.97
7	1594.6	10.96	35.05	1583.9	6.12	74.16	1594.4	1.56	32.72
8	1626.3	6.14	23.43	1622.8	7.00	51.25	1623.8	3.01	29.12
9	1649.5	3.67	25.76	1654.7	1.78	24.68	1654.8	4.29	31.18
Area Ratio		0.80			3.56			2.04	

Table S10: Peak assignment of experimental RAMAN peaks obtained using Voigt fitting

Label	C=C (Symmetric Stretch)	$C\alpha-C\alpha$ (Inter-ring Thiophene)	$C\beta-C\beta$ (Intra-ring Thiophene)	C=C (Asymmetric Stretch)
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Neutral	1392.4	1414.8	1471.2	1499.9	1529.7
Doped	1364.9	1413.3	1466.3	1499.8	1526.7
Neutral-C	1389.1	1415.5	1467.6	1494.3	1522.8
Doping Shift	Red	Constant	Red	Constant	Red
Cycled Shift	Recovered	Constant	Same	Red	Red

Table S11: % Composition of N 1s elemental species in CBZ-T3 film in LiTFSI

Species (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C	Neutral-RC
-C-N	100% (400.50)	58.34% (400.29)	95.16% (400.49)	100% (400.42)
-C=N ⁺		10.36% (401.37)		
TFSI		31.30% (399.22)	4.84% (399.04)	

Table S12: % Composition of S 2p elemental species obtained by deconvolution in CBZ-T3 film in LiTFSI

Species (%) (Binding Energy (eV))	Neutral	Doped	Neutral-C	Neutral-RC
CBZ-T3-Thiophene- 2p _{3/2}	57.84% (164.03)	31.50% (163.78)	50.58% (163.92)	53.59% (164.02)
CBZ-T3-Thiophene- 2p _{1/2}	28.92% (165.20)	15.75% (164.95)	25.29% (165.20)	26.80% (165.22)
(Thiophene) ⁿ⁺ 2p _{3/2} ''	5.72% (164.93)	13.57% (164.67)	9.68% (164.82)	6.75% (164.92)
(Thiophene) ⁿ⁺ 2p _{1/2} ''	2.89% (166.11)	6.79% (165.84)	4.84% (166.00)	3.38% (166.10)
TFSI	3.04% (169.12)	21.59% (168.57)	6.40% (168.76)	6.32% (169.02)
TFSI	1.52% (170.30)	10.80% (169.77)	3.20% (169.94)	3.16% (170.22)

Using **equation S3**, the TFSI⁻ dopant ion fraction was calculated, which increased from ~7.20 % before cycling (point I) to ~15.90% after cycling (point II) in the neutral state.

Table S13: Peak fitted parameters for experimental Raman Spectra of LiTFSI cycled CBZ-T3 films obtained by Voigt fitting

Peak Number	Neutral			Doped			Neutral-C		
	Peak Centre	Area	FWHM	Peak Centre	Area	FWHM	Peak Centre	Area	FWHM
1	1313.2	2.54	40.81	1312.2	14.64	79.77	1314.1	10.82	64.62
2	1377.2	18.83	17.98	1368.7	11.52	49.59	1381.5	13.02	29.89
3	1399.6	37.78	30.03	1394.8	36.74	37.78	1400.2	38.00	34.43
4	1452.3	19.54	41.26	1445.2	14.06	38.22	1449.0	13.24	35.54
5	1484.7	32.25	37.44	1498.0	9.50	50.18	1479.5	6.93	33.36
6	1514.4	45.08	25.90	1472.2	3.57	35.47	1508.9	12.73	36.71
7	1577.09	9.57	22.91	1577.1	4.11	41.84	1578.0	3.23	41.71
8	1605.9	6.23	21.84	1601.3	4.08	29.26	1604.1	3.81	26.11
9	1636.5	5.21	31.87	1631.8	2.53	22.14	1634.42	1.89	18.38
Area Ratio		1.14			1.86				1.58

Table S14: Comparison of EIS fitting parameters for CBZ-T3 polymer in 0.2M LiPF₆/PC and LiTFSI/PC electrolyte at onset potential

Electrolyte	R _s	Q _{ITO} *10 ⁻⁶	a ₁	R _{ITO}	Q _{dl} *10 ⁻⁶	a ₂	C _{dl} *10 ⁻³	R _{CT}	τ _{RC}	R _{dif}	t _{dif} *10 ⁻³	a ₃	χ ²	D *10 ⁻⁸
LiPF ₆	99	0.29	0.86	157.2	4.52	0.77	3.400	285.1	0.97	7.80	0.41	0.82	0.039	68.10
LiPF ₆ Cycled	99	0.29	0.86	157.7	20.92	0.82	1.300	647.7	0.84	97.45	20.82	0.73	0.041	1.32
LiTFSI	90	12.63	0.89	260.0	0.58	0.79	0.082	292.5	0.02	12.09	1.70	0.92	0.021	16.30
LiTFSI- Cycled	90	0.67	0.78	251.4	13.99	0.91	0.168	4257	0.72	1004	61.00	0.91	0.047	0.45

C_{dl}= Double layer capacitance (F), R_{CT}= Charge transfer resistance (Ω), τ_{RC}= RC time constant (sec), R_{dif}=Diffusion resistance (Ω), t_{dif}= Time for diffusion (sec), D= Diffusion Coefficient (cm²/s)

Table S15: % Elemental composition of elements obtained from CASA XPS software for the recovered neutral state (LiPF₆ cycled, point III)

Element	C1s	O1s	N1s	S2p	F1s	P2p
% Species	80.36	12.44	1.38	5.40	0.37	0.05

Table S16: % Composition of S 2p elemental species obtained by deconvolution for the recovered neutral state (LiPF₆ cycled, point III)

Species	CBZ-T3- Thiophene-2p _{3/2}	CBZ-T3- Thiophene-2p _{1/2}	(Thiophene) ⁿ⁺ 2p _{3/2} ''	(Thiophene) ⁿ⁺ 2p _{1/2} ''
Species (%) (Binding Energy (eV))	60.79% (163.83)	31.00% (165.01)	5.47% (164.73)	2.27% (165.92)

Table S17: % Composition of N 1s, F 1s and P 2p elemental species obtained by deconvolution for the recovered neutral state (LiPF₆ cycled, point III)

Elements	N1s	F1s		P2p
	-C-N	PF ₆	-C-F	
Species (%) (Binding Energy (eV))	100% (400.83)	64.10% (686.15)	35.90% (687.14)	-

Table S18: Fitting for relaxation model for recovery

Technique	T ₀	T ₁	T ₂	τ ₁ (sec)	τ ₂ (sec)	n	χ ²
LiPF ₆ -CP	77.02 ± 0.005	7.00 ± 0.01	2.33 ± 0.006	432.40 ± 1.02	3384.69 ± 31.77	1.25 ± 0.01	0.989
LiPF ₆ -CA	77.08 ± 0.001	1.87 ± 0.001	3.69 ± 0.001	1060.12 ± 0.49	7861.21 ± 4.89	1.01 ± 0.01	0.999
LiTFSI-CP	72.49 ± 0.002	4.82 ± 0.01	8.54 ± 0.070	342.21 ± 1.57	2787.01 ± 19.42	2.16 ± 0.01	0.973

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