Mixed-Valence Engineered Bipolar Polyimide Covalent Organic Framework Film for Multicolor Displays and Dual-Band Electrochromism

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Materials and Methods

Materials: Tris(4-aminophenyl)amine (TAPA), 1,4,5,8-Naphthalenete-tricarboxylic dianhydride (NTDA), N,N,N',N'-Tetrakis(4-aminophenyl)-1,4-phenylenediamine (TPPDA) and 3-Aminopropyltriethoxysilane (APTES) were purchased from Macklin (Shanghai, China). Propylene carbonate and lithium perchlorate ($LiClO_4$) were purchased from Aladdin (Shanghai, China). All chemicals and solvents were used as received.

ITO glass modified with APTES: Typically, ITO-coated glass (8 Ω) substrates were cleaned with water, ethanol and acetone sequentially before activated with dielectric barrier discharge (DBD) O_2-plasma for 2 minutes. Then, the substrates were submerged in APTES/ethanol/water mixture solution (v:v:v=5:18:2, 10 mL) and kept at room temperature under an argon atmosphere for 48 h. Finally, the glass substrates were removed from the reaction solution and thoroughly washed with water and ethanol, and dried for further use.[1]

Preparation of TAPA-PI COF film: In a typical procedure, TAPA (2.9 mg, 0.01 mmol) and NTDA (4 mg, 0.015 mmol) and a mixture of 1-Methyl-2-pyrrolidinone /Mesitylene/Isoquinoline (v:v:v=5:5:2, 3.6 mL) were charged in a vacuum pressure resistant tube, and ITO substrates was placed in the reaction bottle vertically. After ultrasonication for 10 minutes to ensure uniform dispersion, the mixture was quenched in a liquid nitrogen bath at 77 K. The mixture was degassed via three freeze-thaw cycles and reacted at 180 °C for 4 days. The precipitates were washed with acetone and

tetrahydrofuran and further activated by Soxhlet extraction using tetrahydrofuran for 2 days, respectively. The TAPA-PI COF film was obtained after dried at 70 ℃ for 24 hours.[2]

Preparation of TPPDA-PI COF film: TPPDA-PI COF film was prepared by using TPPDA as the reacting agent. TPPDA (4.72 mg, 0.01 mmol) and NTDA (5.36 mg, 0.015 mmol) and a mixture of 1-Methyl-2-pyrrolidinone/Mesitylene/Isoquinoline (v:v:v=5:5:2, 3.6 mL) were used and the procedure follows the steps described above with slight alteration. The mixture was degassed via three freeze-thaw cycles, and reacted at 200 °C for 5 days.

Preparation of DESW device: TPPDA-PI COF film deposited on ITO-glass substrate (2×2 cm) as the working electrode, 1 M $LiClO_4$ in acetonitrile as the electrolyte, and blank ITO-glass substrate as the counter electrode. The 3M foam double-sided tape is used for packaging. Finally, DESW is prepared by injecting the electrolyte into the interlayer space with a syringe. The measurements were performed in a two-electrode configuration (COF-coated ITO as working electrode, bare ITO as counter electrode), and the reported potentials are cell voltages without iR compensation.

Characterization: Powder X-ray diffraction (PXRD) patterns were collected on an AXS D8 Advance diffractometer using Cu-Kα radiation (λ=0.15418 nm) on a range of 2-30° at room temperature. Fourier transform infrared (FT-IR) spectra were recorded in the range of 400-4000 cm^{-1} on an IS50 Thermo-Fisher spectrometer with KBr pellets. Scanning electron microscopy (SEM) was performed on a SU8230 electron

microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were taken with a Talos F200X operated at 200 kV. All gases adsorption-desorption measurements at different temperatures were carried out on a Micromeritics ASAP 2460 instrument. The pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT). Atomic force microscope (AFM) image was carried out with Dimension Icon. The possible structure simulation of TAPA-PI COF and TPPDA-PI COF was carried out in Accelrys Materials Studio 8.0 software package. The resulting structure was geometrically optimized using the Forcite module, with a universal forcefield and charge using Qeq, respectively.[3] The simulated XRD patterns were determined by the Reflex module. Pawley refinement was conducted to optimize the lattice parameters iteratively until the R_{wp} value converges.

Electrochemical characterization: In-situ absorption spectra were monitored by PerkinElmer Lambda 1050+ UV-vis-NIR spectrophotometer at 298 K. TAPA-PI COF or TPPDA-PI COF film was put into an electrochemical cell with 0.1 M $LiClO_4$/Pc electrolyte as the working electrode. A platinum wire and fresh prepared Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The active area of the electrochromic film is 1.0 cm^2. The spectral changes and transmittance changes were in situ recorded under different applied voltage controlled by a CHI 760E potentiostat. For the determination of response time, the switching time are 60 s, to achieve a saturated color state. All UV-vis spectra were acquired on a

double-beam spectrophotometer. The precise procedure was as follows: First, to establish an accurate 100% transmittance baseline, a background scan was collected using identical blank ITO glass substrates in both the sample and reference beams. Subsequently, for the actual film measurements, the COF-coated ITO was placed in the sample beam while a blank ITO substrate was retained in the reference beam. This configuration directly isolates the optical response of the COF film by automatically subtracting the absorption, reflection, and scattering contributions inherently associated with the underlying glass and conductive ITO layer.

Computational methods: The computational investigation was carried out using a model compound possessing a closer chemical structure to that of the repeating unit of TAPA-PI and TPPDA-PI COF. The geometry optimization of the model compound was carried out through DFT calculations using the B3LYP correlation function with a basis set of 6-31G(+) (d, p), implemented in the Gaussian 09 package. Time-dependent density functional theory (TDDFT) calculations revealed the electronic transitions of neutral and ionic species.[3]

Calculation of coloration efficiency: The color contrast or transmittance change (Δ%T) of an EC material refers to the maximum optical contrast determined by the difference between the highest and the lowest transmittance at the target color, this is:

$$\Delta T\% = T_b - T_c \qquad \text{(S1)}$$

where T_b and T_c are the transmittance (%) at bleached and colored state, respectively.

The value of coloration efficiency (CE) was calculated according to the equation [4,5]:

$$\Delta OD = \log\left[\frac{T_b}{T_c}\right] \qquad \text{(S2)}$$

$$CE(\lambda) = \frac{\Delta OD}{Q_d} \qquad \text{(S3)}$$

where *OD* is optical density, Q_d is the injected/ejected charge density (C/cm^2), $Q_d=Q/A$.

Calculation of response time: The response times were determined as the time required for the transmittance change to reach 90% of the full optical modulation (i.e., t0.9) upon a potential step. For the TAPA-PI COF film, the coloring process was induced by a potential step from 0 V to +1.6 V, and the bleaching process was induced by a step from +1.6 V back to –0.1 V. For the TPPDA-PI COF film, the coloring step was from 0 V to +1.0 V, and the bleaching step was from +1.0 V to –0.2 V. All potentials reported herein are referenced to the Ag/Ag^+ couple.

Average transmittance:

$$\overline{T} = \frac{\int_{\lambda_1}^{\lambda_2} T(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} d\lambda} \qquad \text{(S4)}$$

Where $\overline{T}$ was average transmittance and T(λ) is the transmittance at wavelength λ.

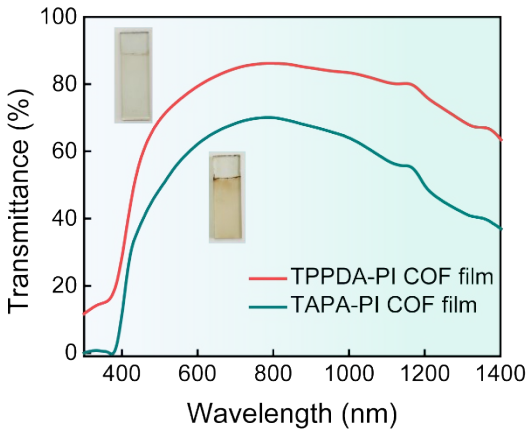

Fig. S1 Photographs and transmittance of PI COF films.

Table S1 Average transmittance of PI COF films.

Average transmittance	VIS	NIR
TAPA-PI COF film	56.2%	56.4%
TPPDA-PI COF film	73.8%	78.7%

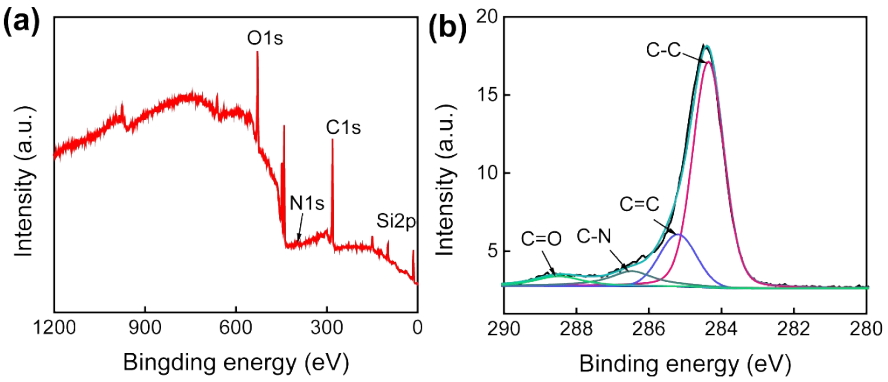

Fig. S2 XPS of NTDA-APTEs modification ITO substrate. (a) XPS spectrum and (b) high-resolution spectrum of C1s.

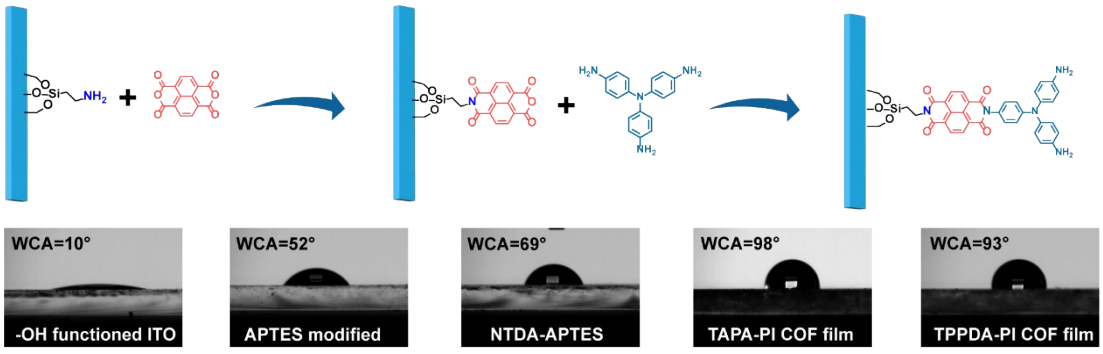

Fig. S3 Changes in water contact angle throughout the fabrication process: measurement sequence includes the initial substrate, after pretreatment, and after subsequent PI COF films growth.

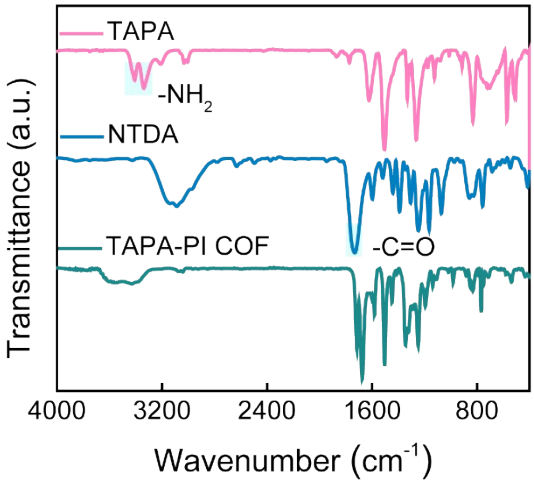

Fig. S4 FTIR spectrum of TAPA, NTDA and TAPA-PI COF.

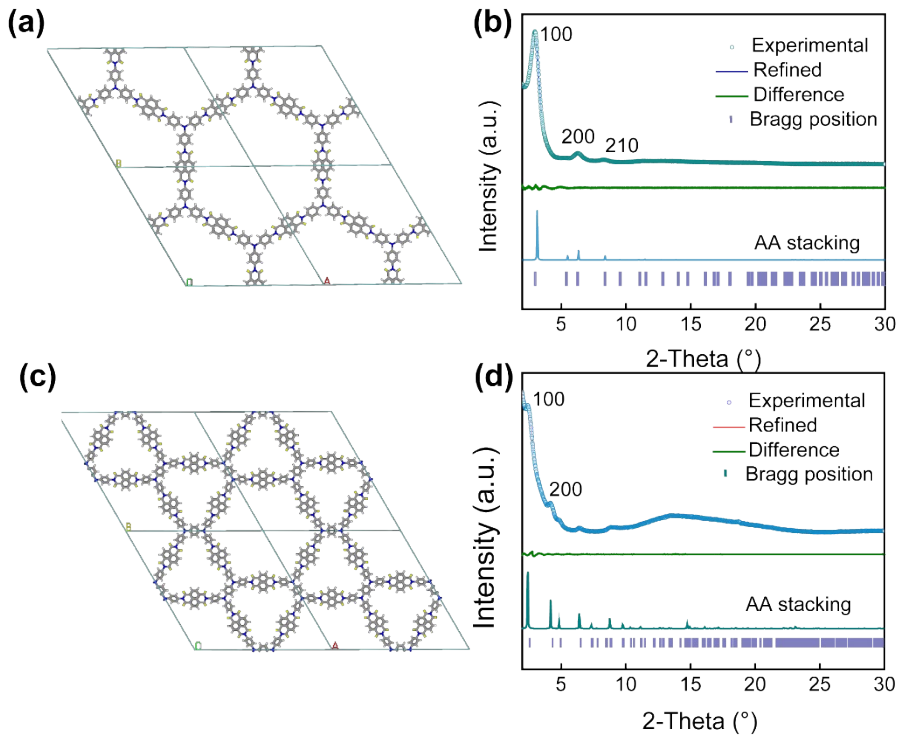

Fig. S5 Experimental PXRD pattern and Pawley refinement results. Pawley refined structural model of (a) TAPA-PI COF and (c) TPPDA-PI COF. Experimental XRD and optimized XRD of (b) TAPA-PI COF and (d) TPPDA-PI COF. The crystal cell parameters and refinement factors of TAPA-PI and TPPDA-PI COF as follows:

TAPA-PI COF: a=b=31.3635, c=3.7753, α=β=90°, γ=120°, R_{wp}=2.90%, R_p=2.23%;

TPPDA-PI COF: a=b=42.0555, c=3.2124, α=β=90°, γ=120°, R_{wp}=6.79%, R_p=5.48%.

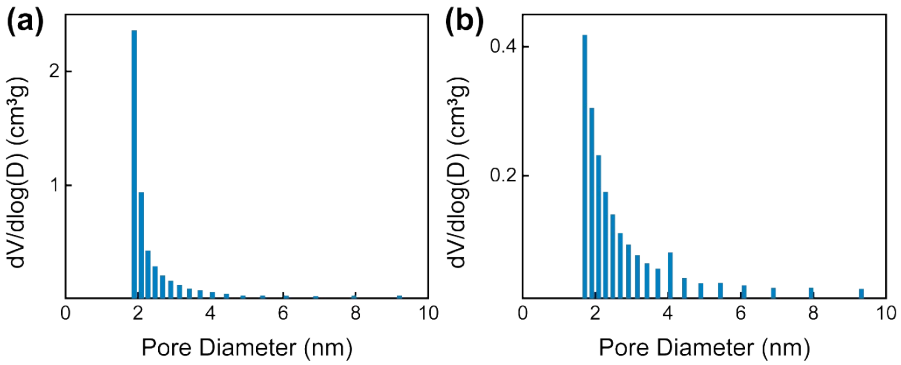

Fig. S6 Pore size distribution of PI COFs. (a) TAPA-PI PI COF; (b) TPPDA-PI COF.

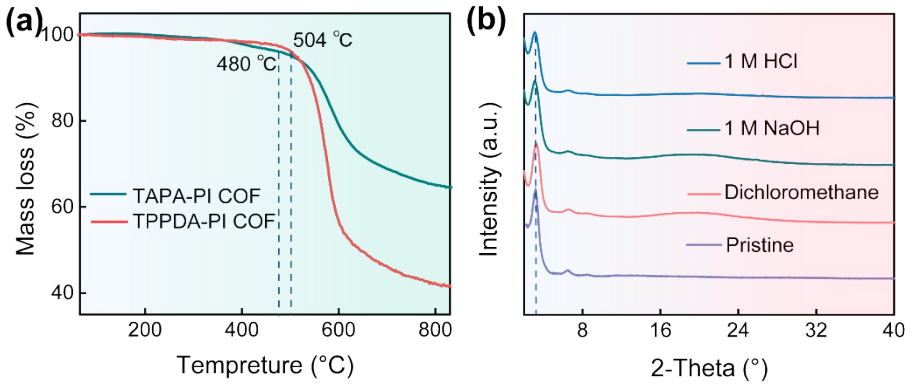

Fig. S7 Thermal/chemical stability of PI COFs. (a) TGA of TAPA-PI and TPPDA-PI COF; (b) PXRD spectra of TAPA-PI COF after 3 days of immersion in different solutions. TAPA-PI COF retains its crystallinity after three-day soaking in acidic (1M HCl), alkaline (1M NaOH), and organic solvents (Dichloromethane).

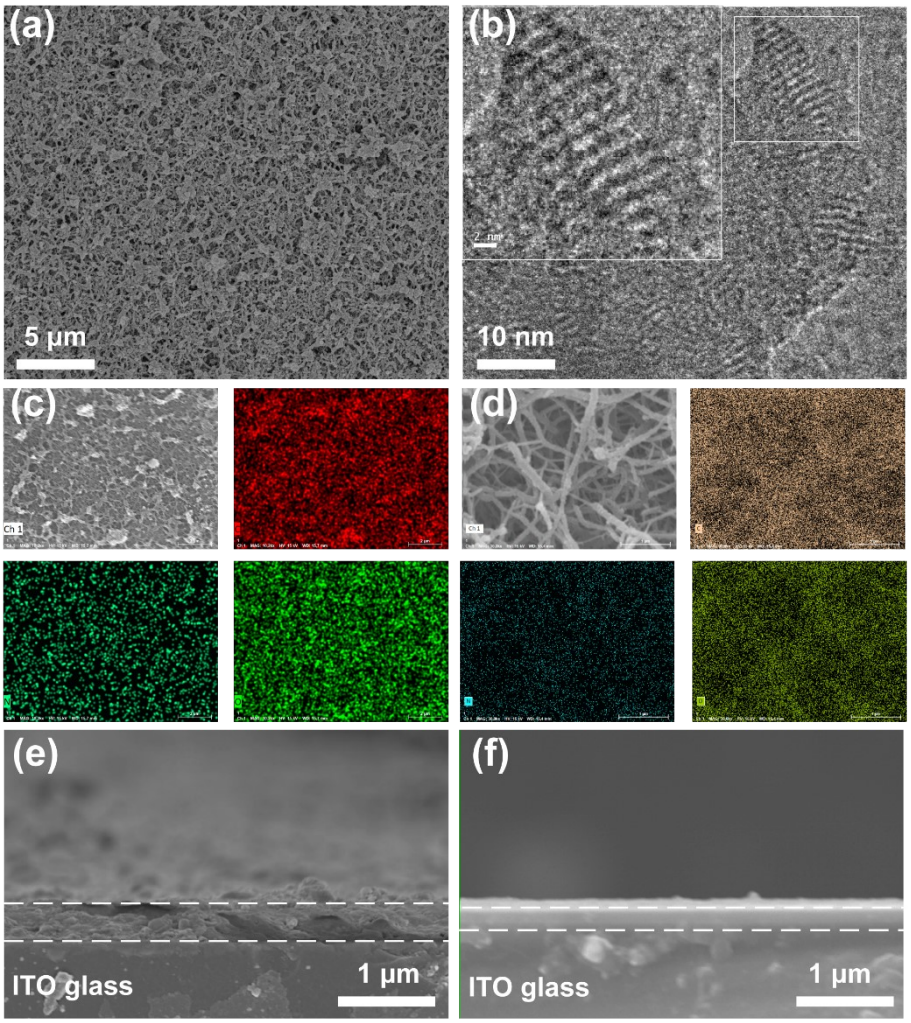

Fig. S8 Microstructure and element distribution of PI COF films. (a) SEM image and (b) TEM image of TAPA-PI COF film. Eds mapping of (c) TAPA-PI COF film and (d) TPPDA-PI COF film. SEM cross-section images of (e) TPPDA-PI COF film and (f) TAPA-PI COF film.

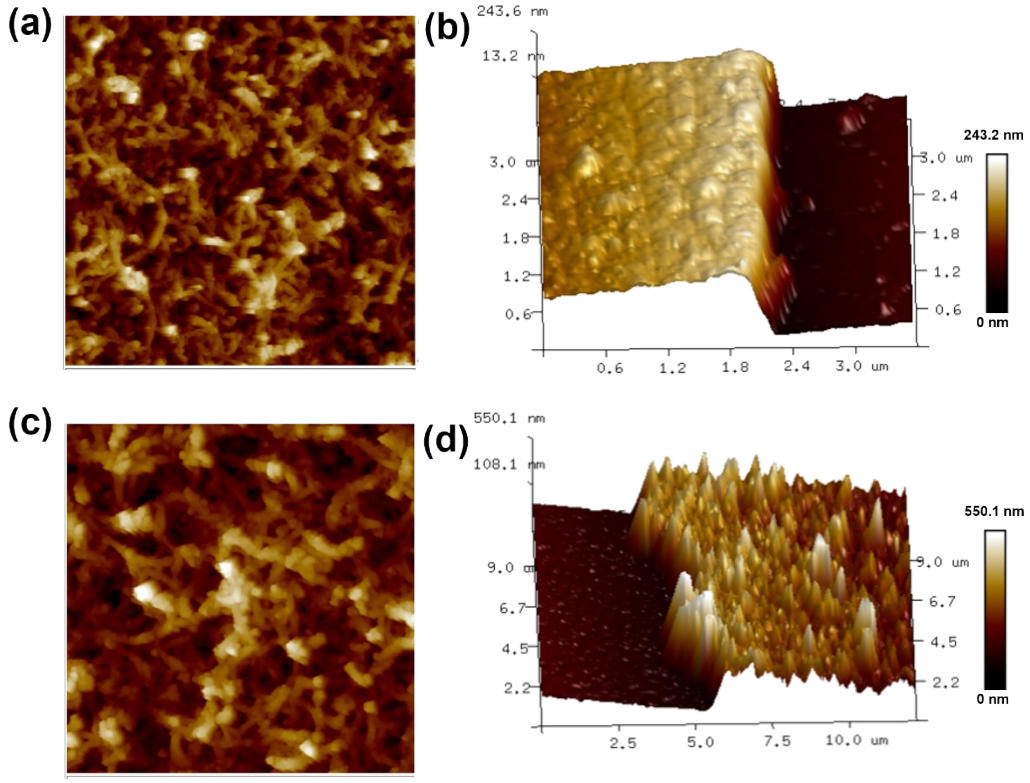

Fig. S9 Three-dimensional morphology of PI COF films. AFM images of TAPA-PI COF film (a-b) and TPPDA-PI COF film (c-d). TAPA-PI COF film: Rq=78.8 nm Ra=63.0 nm; TPPDA-PI COF film: Rq=145.1 nm Ra=114.0 nm.

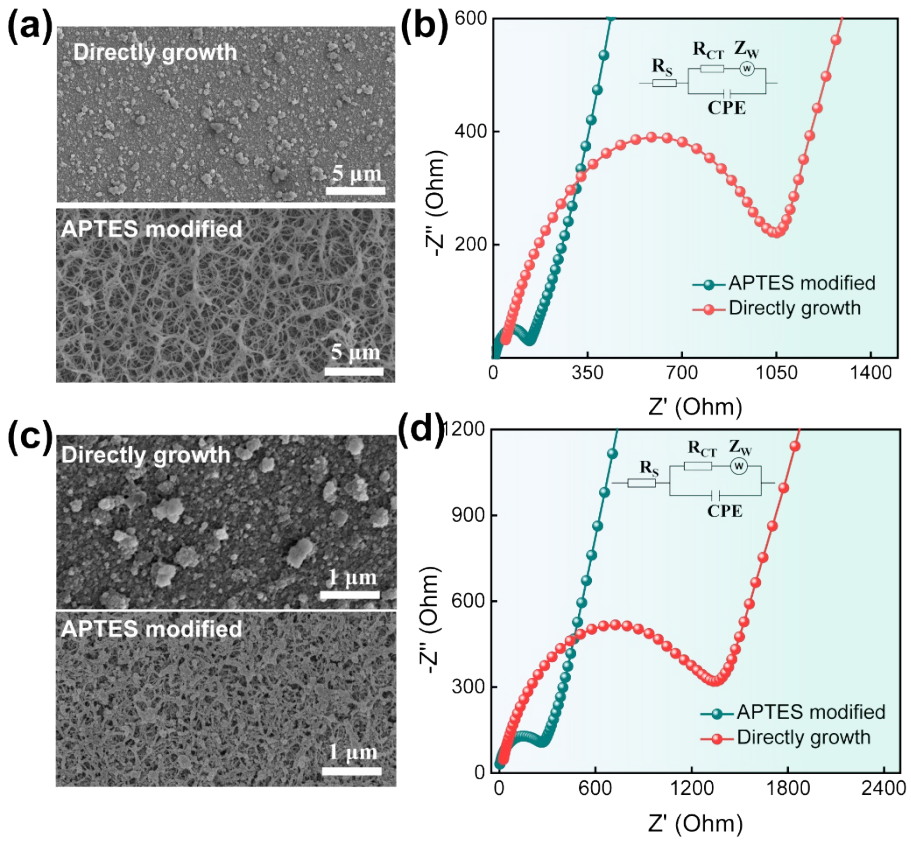

Fig. S10 Structure topography and EIS spectra of TPPDA-PI COF film(a-b) and TPPDA-PI COF film(c-d) preparation with APTEs modified and directly growth.

To investigate the impact of film morphology on charge transfer and ion diffusion, electrochemical impedance spectroscopy (EIS) was performed on PI COF films grown with and without APTES-assisted anchoring (Ag/AgCl reference, 10 mV amplitude, 10^{5}-10^{-1} Hz frequency range. Nyquist plots showed a single semicircle for all samples. The charge transfer resistance (Rct) was significantly lower for APTES-modified films (163 Ω for TAPA-PI COF and 296 Ω for TPPDA-PI COF), indicating facilitated electron transfer with low diffusion resistance.

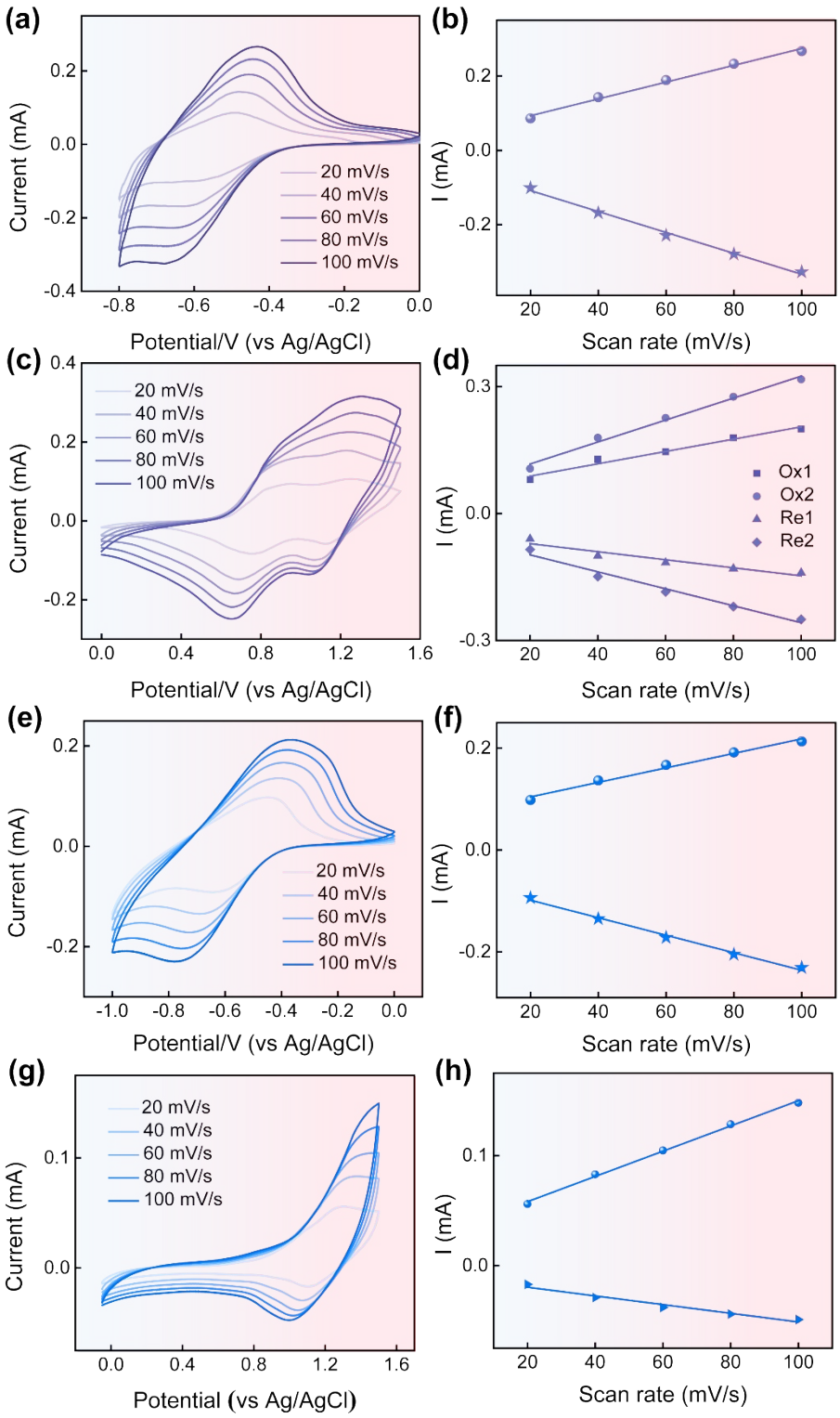

Fig. S11 CV curves and the relationship between peak current and scan rates of TAPA-PI COF (a-d) and TPPDA-PI COF (e-h) films at scan rates of 20, 40, 60, 80, 100 mV/s.

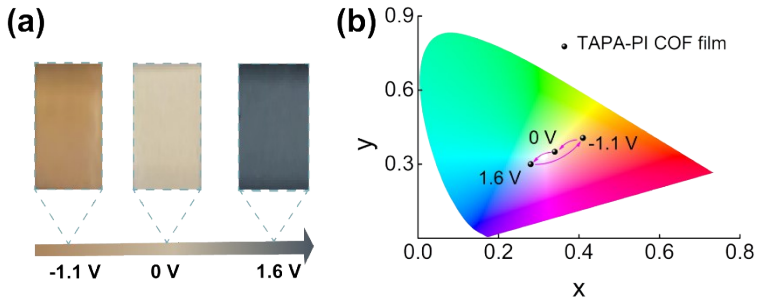

Fig. S12 Variation of color La*b* coordinates (a) and CIELAB diagram under different voltages of TAPA-PI COF film (b).

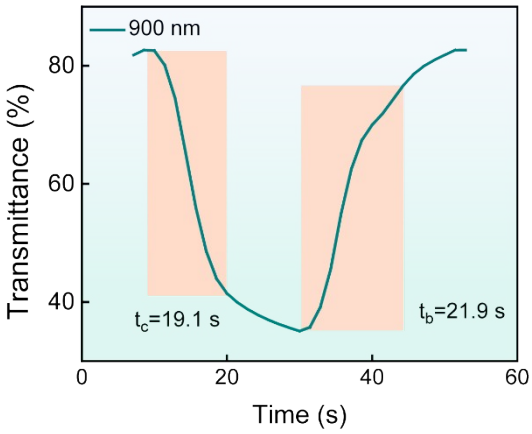

Fig. S13 Transmission rate variation speed of TPPDA-PI COF film at 900 nm (between -0.2 V and 1 V).

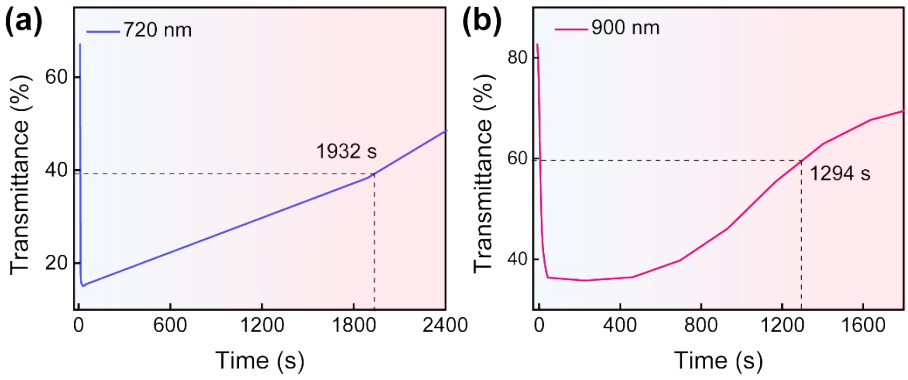

Fig. S14 The retention time of TAPA-PI COF film (a) and TPPDA-PI COF film (b), after removing applied voltages. Released at +1.6 V for TAPA-PI COF film and +1.0 V for TPPDA-PI COF film, respectively.

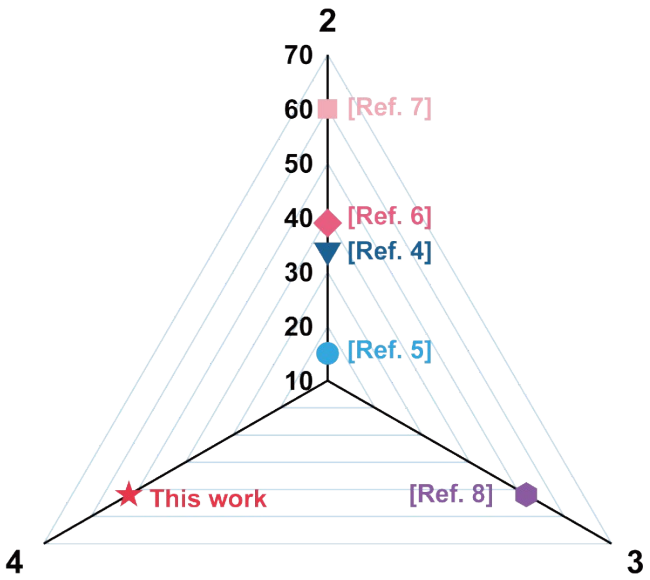

Fig. S15 Comparison of performance between different electrochromic COFs.

Currently, most reported EC COF systems exhibit only two or three color states, whereas our work achieves switching between at least four color states and demonstrates a high electrochromic contrast of 53% in the near-infrared region.

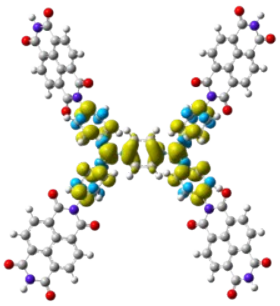

Fig. S16 Spin density of TPPDA-NTDA unit (radical cation) computed from DFT calculation using B3LYP function and 6-31G+(d,p) basis set (isosurface value = 0.004).

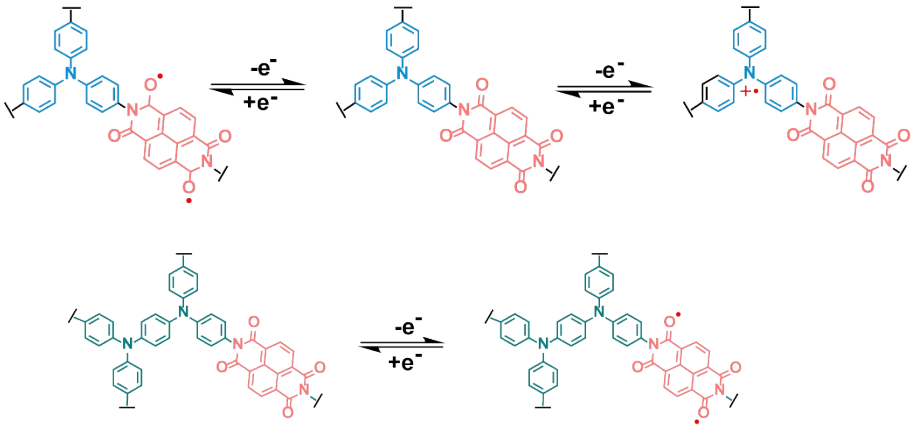

Fig. S17 Electron transfer pathways in the redox process of TAPA-NTDA (-1.0 V ~ +1.6 V) and TPPDA-NTDA units (-0.9 V ~ 0 V).

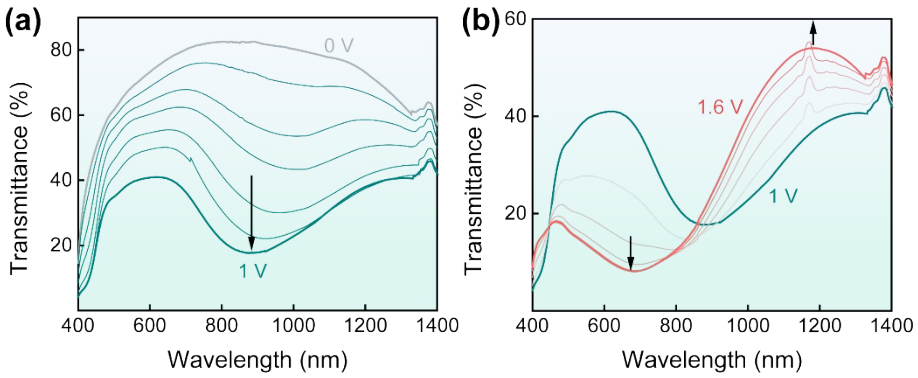

Fig. S18 Transmittance of DESW device at different voltage. (a) 0 V ~ 1 V. (b) 1 V ~ 1.6 V.

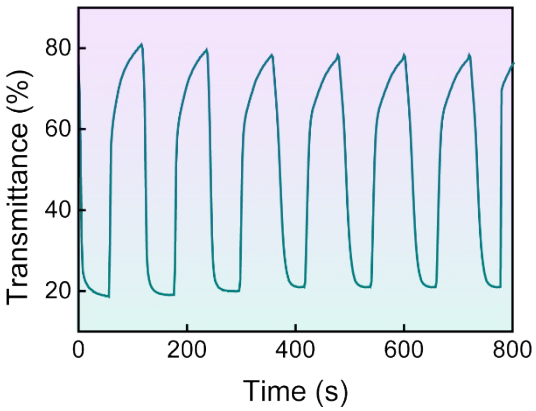

Fig. S19 The cyclic stability of the DESW was measured between -0.2 V and 1 V, with the voltage switched every 60 seconds.

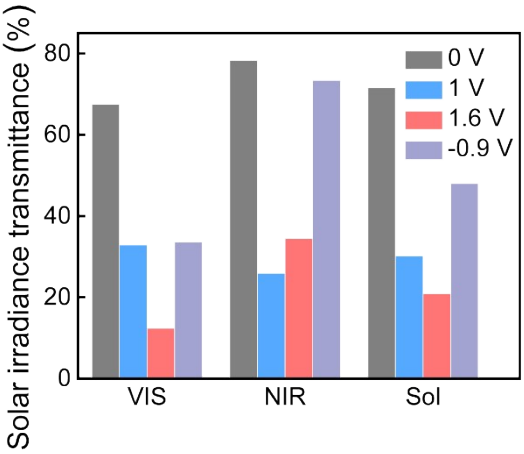

Fig. S20 Solar irradiance transmittance (T') of a DESW in different modes.

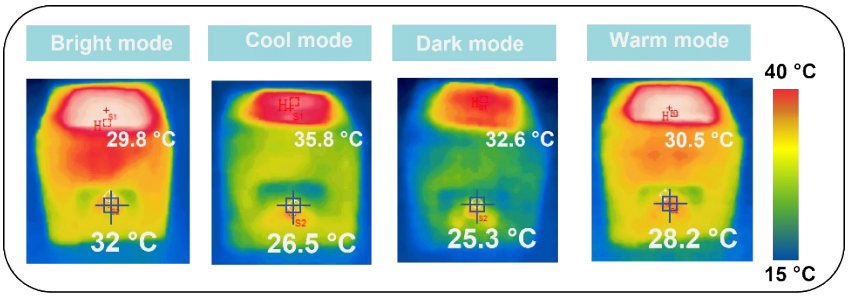

Fig. S21 Infrared thermal imaging images of the device in four modes after being illuminated by a simulated solar light source.

References

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