Electronic Supporting Information

Photo-Crosslinkable Diazirine Additives for Direct Photolithography of PEDOT:PSS

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Experimental Section

Materials. Poly(vinyl alcohol) (PVA, Mw ~8,100, 99.0%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 4-[3-(Trifluoromethyl)-3H-diazirin-3-yl]benzoic acid (>98%) was obtained from Yamu Chemistry (Tianjin) Co., Ltd. N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 97.0%), 4-dimethylaminopyridine (DMAP, 99.0%), and Triton X-100 (97.0%) were purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 99.0%) was purchased from Sigma-Aldrich. Isopropanol (analytical grade) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Toluene (99%) and nitric acid were obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. Polystyrene-*block*-poly(ethylene-ran-butylene)-*block*-polystyrene (SEBS, 88%) was provided by Asahi Kasei. Poly(methyl methacrylate)–*block*-poly(*n*-butyl acrylate)–*block*–poly(methyl methacrylate) (PMMA-PnBA-PMMA, LA2330) was provided by KURARAY company Anhydrous dimethyl sulfoxide (DMSO, 99%) was purchased from J&K Scientific. Deionized (DI) water was used throughout the experiments.

Preparation of MPVAL-PEDOT:PSS Films. Glass substrates with the dimension of 1.5 cm × 1.5 cm were sonicated in deionized water, acetone, and isopropanol sequentially for 10 min. SEBS and PMMA substrates were prepared by drop-casting its toluene solution (100 mg/mL) on glass wafer. Substrates were cleaned by UV ozone before use. The precursor solution was prepared with a mass ratio of MPVAL:PEDOT:PSS = 1:10. The mixture was then placed on a magnetic stirrer and stirred for 30 min to ensure the complete dissolution. Next, the spin-coating process was then performed at a rotation speed of 1500 rpm for 60 s. Upon completion, the coated film electrode was transferred to a hot plate and annealed at 45 °C for 2 hours to remove residual solvents, followed by natural cooling to room temperature (25°C) over 30 min.

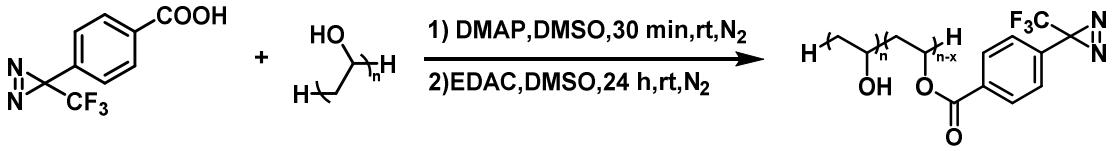
Photopatterning of MPVAL-PEDOT:PSS Films. Following the preparation and drying of the MPVAL-PEDOT:PSS composite film, a photolithography process was employed for patterning. First, a 5-inch soda-lime glass photomask (127 mm × 127 mm

× 2.3 mm) featuring predefined patterns and a line edge roughness of approximately 30 nm was placed in close contact with the film surface. Subsequently, the film was continuously exposed to UV light (wavelength: 365 nm, intensity: 25 mW cm^{-2}) for 15 min to ensure a complete crosslinking reaction. After exposure, the photomask was removed, and the film was developed by immersing it in deionized (DI) water for 30 s, followed by gentle rinsing with DI water. During this development process, the unexposed regions (masked areas) remained uncrosslinked and were readily dissolved and washed away, whereas the UV-exposed regions were firmly retained due to crosslinking-induced curing. Finally, the substrate was blown dry with a stream of high-purity nitrogen gas, yielding the MPVAL-PEDOT:PSS composite film with well-defined micro/nanoscale patterns.

Characterizations and measurement. Liquid-state ^{1}H, ^{19}F NMR and 2D ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature. The 2D HSQC spectra were recorded using standard Bruker pulse sequences. Liquid-state ^{13}C NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer at room temperature. The samples were dissolved in DMSO-d_6 at a concentration of approximately 10 mg/mL. For the photochemical evolution analysis, the MPVAL solutions were subjected to 365 nm UV irradiation (25 mW cm^{-2}) for 2 min prior to the NMR measurements. Structural changes in the films were analyzed using a Vertex70 Fourier-transform infrared spectrometer (FTIR) and an in-Via reflex Raman spectrometer. The UV–vis absorption spectra were measured with a SHZMADZU UV-3600 Plus spectrophotometer. X–ray photoelectron spectroscopy (XPS) was carried out by Thermo Fisher Scientific ESCALAB 250Xi. The surface morphology of the films were observed using a LEICA DM2700M optical microscope. The electrical conductivity was measured with a 4200A-SCS source/meter semiconductor parameter analyzer. Film thicknesses were measured by an ET 200A profilometer. The surface morphology of the films was observed using a LEICA DM2700M optical microscope and an atomic force microscope (AFM, Dimension ICON-PT, Bruker) in tapping mode. Grazing-incidence wide-angle X-ray scattering (GIWAXS) characterizations were conducted at

the BSRF-1W1A diffuse X-ray scattering beamline station with a grazing incidence angle of 0.15°.

Synthesis of the MPVAL



Scheme S1. Synthetic route of the diazirine-functionalized poly(vinyl alcohol) crosslinker (MPVAL).

4-[3-(Trifluoromethyl)-3H-diazirin-3-yl]benzoic acid (270 mg, 1.20 mmol), 4-dimethylaminopyridine (DMAP, 15 mg, 0.125 mmol), and poly(vinyl alcohol) (PVA, 440 mg, average Mw ~8100) were placed in a flame-dried, aluminum foil-covered 50 mL round-bottom flask under a nitrogen atmosphere. Anhydrous dimethyl sulfoxide (DMSO, 15 mL) was added via syringe, and the mixture was stirred for 30 min to obtain a homogeneous solution. Subsequently, a solution of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl, 240 mg, 1.25 mmol) in anhydrous DMSO (10 mL) was added dropwise to the flask at room temperature. The reaction mixture was stirred for 24 h at room temperature under a nitrogen atmosphere while being strictly protected from light. Upon completion, the reaction mixture was added dropwise into 100 mL of vigorously stirred deionized water. The resulting suspension was transferred to a regenerated cellulose dialysis tubing (MWCO: 1,000 Da) and dialyzed against frequent changes of deionized water for 3 days. Finally, the dialyzed solution was filtered through a nylon membrane (pore size: 1.0 μm) and freeze-dried to afford the MPVAL product as a white solid (yield: 93%).

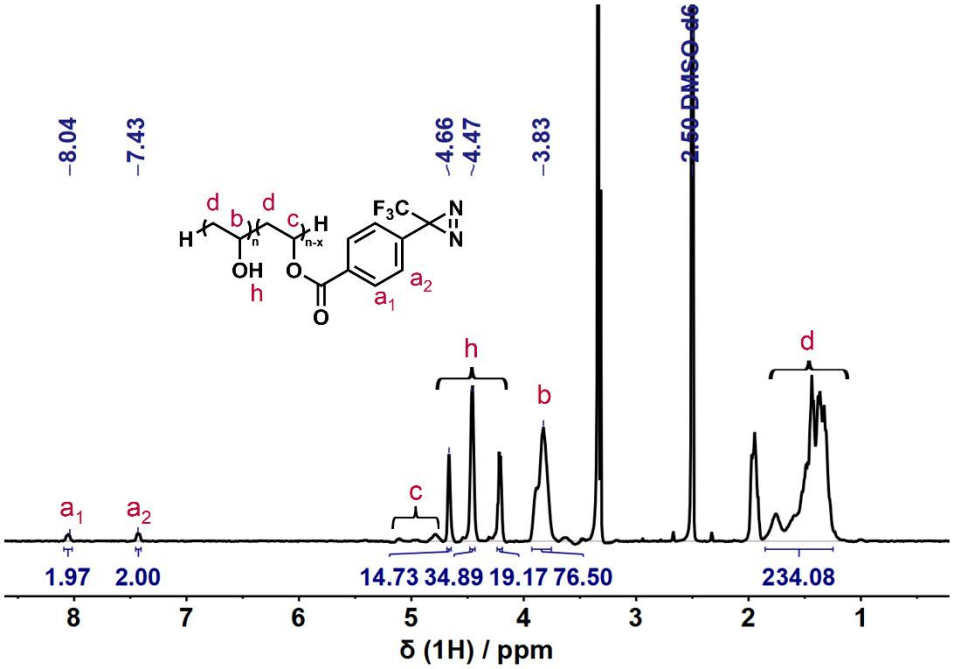


Fig. S1 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of the synthesized MPVAL crosslinker. The grafting ratio of the diazirine groups is determined to be approximately 0.8 mol%, based on the integral area ratio between the aromatic protons of the grafted moieties (a_2) and the methylene protons of the PVA backbone (d).

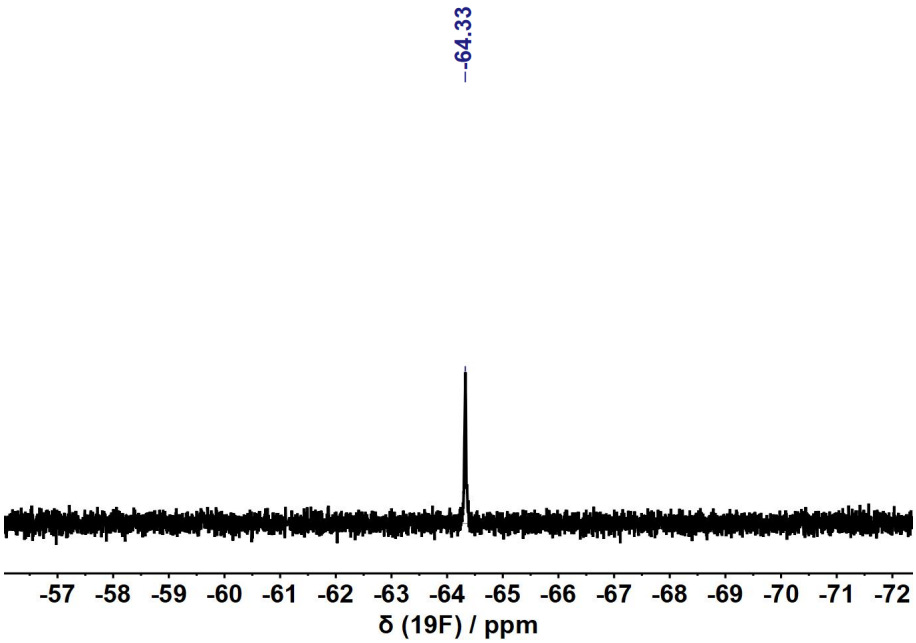


Fig. S2 ^{19}F NMR spectrum (376 MHz, DMSO-d_6, room temperature) of the pristine MPVAL crosslinker. The prominent peak at −64.3 ppm is assigned to the characteristic resonance of the intact diazirine group.

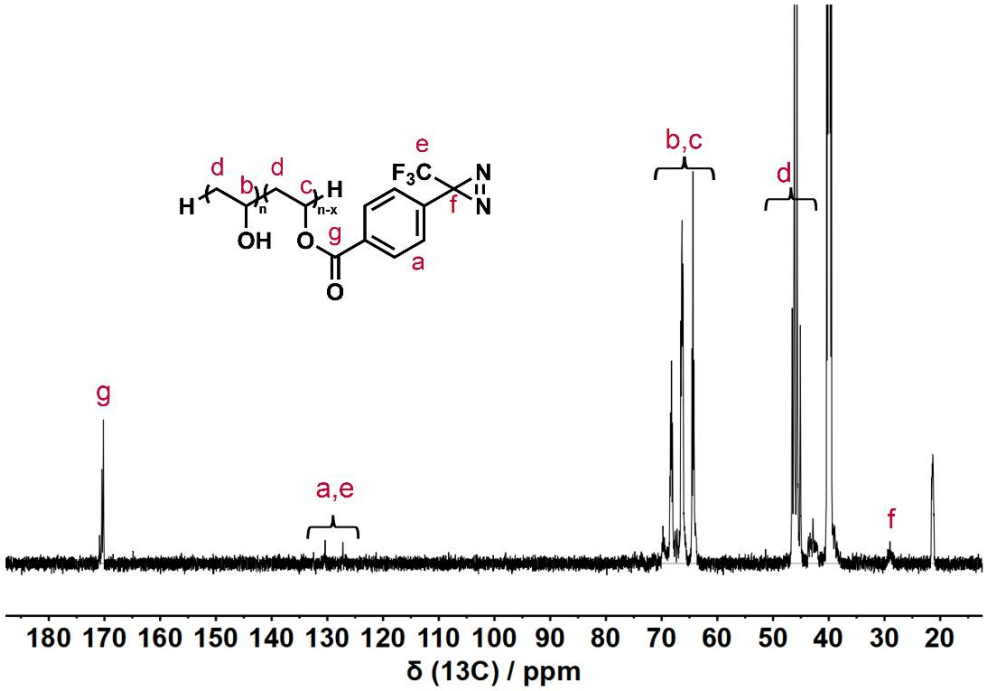


Fig. S3 ^{13}C NMR spectrum (150 MHz, DMSO-d_6, room temperature) of the synthesized MPVAL crosslinker. The signal at δ_C ~170 ppm is assigned to the carbonyl carbons of the ester groups, originating from both the grafted diazirine-functionalized moieties and the residual acetate groups inherent in the raw PVA. The signal at δ_C ~21 ppm is assigned to the acetate methyl groups of the poly(vinyl alcohol) (PVA) backbone.

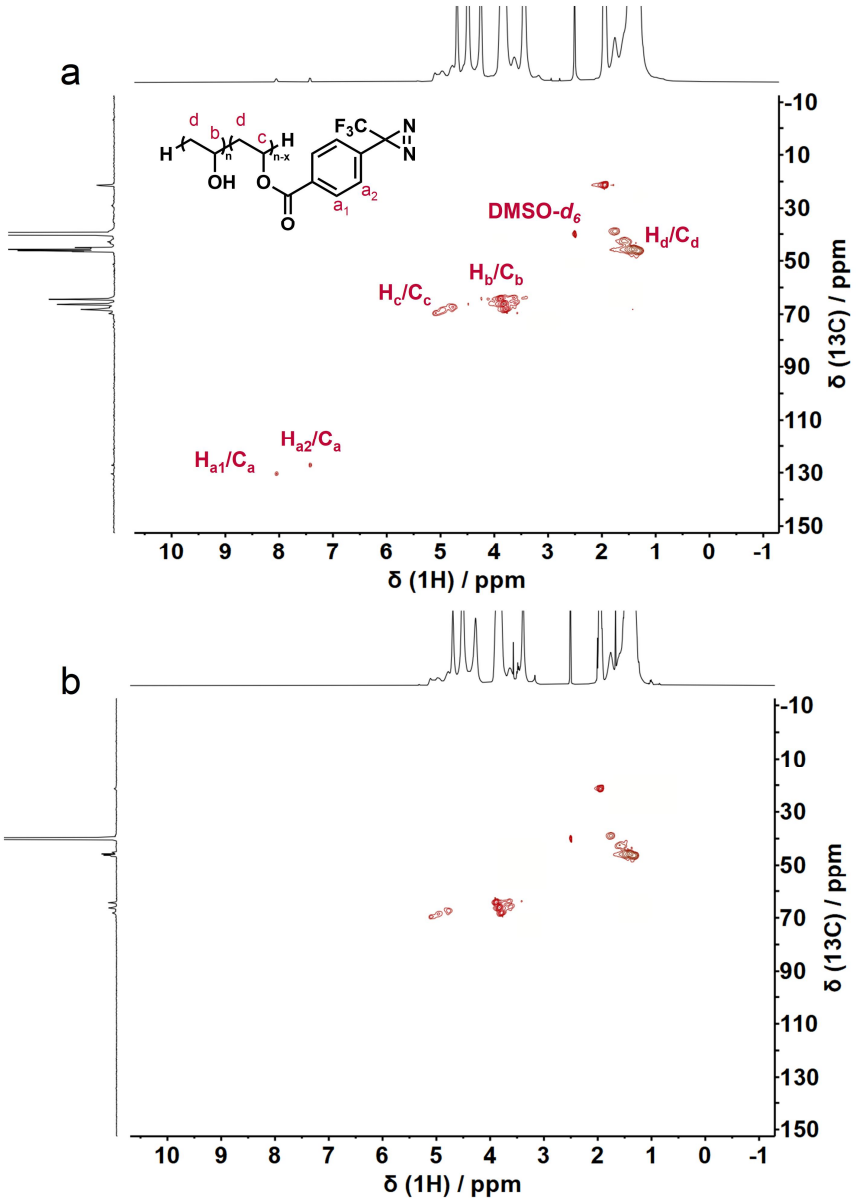


Fig. S4 2D ^{1}H–^{13}C HSQC NMR spectra of (a) the synthesized MPVAL crosslinker and (b) the raw material (PVA), recorded in DMSO-d_6. In spectrum (a), the correlations between δ_H 7.5–8.0 and δ_C 127–131 are assigned to the benzene ring, confirming the successful grafting of the diazirine groups. Meanwhile, the correlations between δ_H 4.8–5.1 and δ_C 69–71 (H_c/C_c) are assigned to the esterified methine groups of both the grafted diazirine groups and the residual acetate groups in the raw PVA. Similarly, the correlations at δ_H 3.7–3.9 and δ_C 69–71 (H_b/C_b), δ_H 1.2–1.9 and δ_C 42–47 (H_d/C_d), as well as δ_H 1.9–2.2 and δ_C ~21, are observed in both spectra (a) and (b). These shared signals are assigned to the PVA backbone structure and residual acetate methyl groups, respectively, demonstrating that the synthesized MPVAL effectively retains the structural integrity of the original PVA backbone.

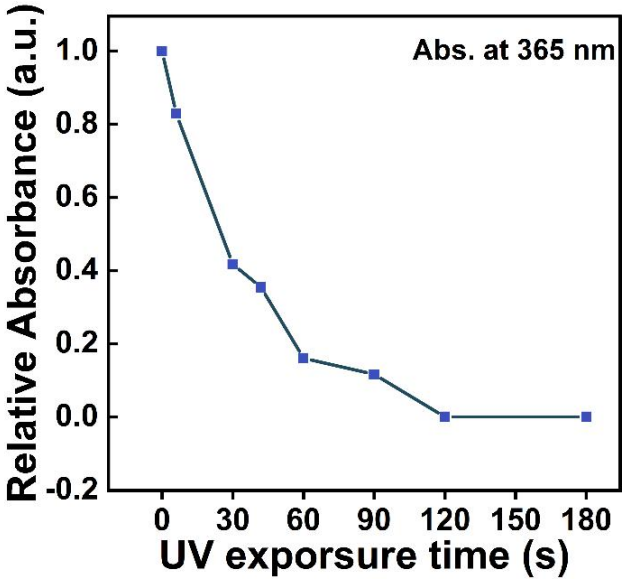


Fig. S5 Normalized UV-vis absorption spectra of the MPVAL solution showing the time-dependent photochemical evolution.

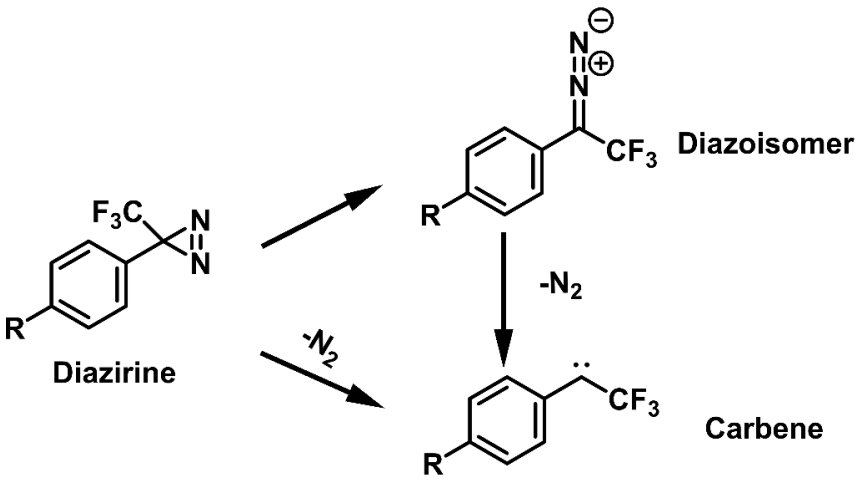


Fig. S6 Proposed photochemical activation pathways of the diazirine-functionalized crosslinker under UV irradiation. The schematic illustrates the photogeneration of the highly reactive singlet carbene radicals and the metastable diazoalkane intermediate species.

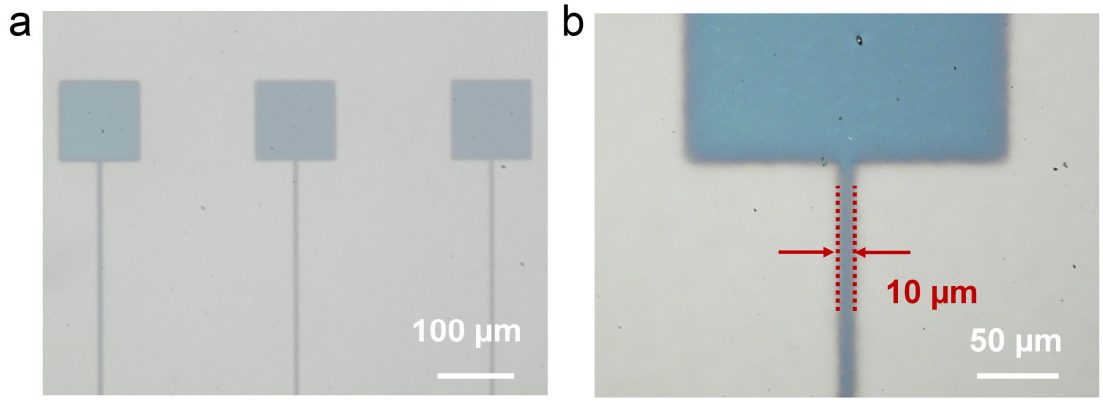


Fig. S7 Optical microscopy images demonstrating the high-resolution patterning capability of the direct photolithography method. (a) Low-magnification image of the patterned PEDOT:PSS arrays. (b) Magnified view highlighting a line pattern with a width of 10 μm.

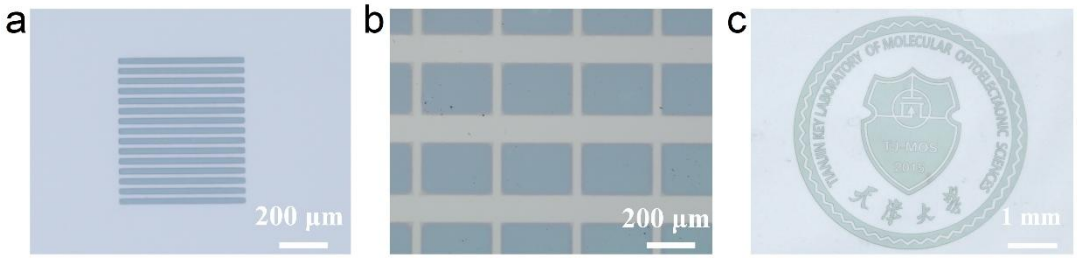


Fig. S8 Photographs of various PEDOT:PSS patterns fabricated on different substrates: (a) A high-resolution pattern on a SEBS substrate. (b) A square pattern on a PMMA-PnBA-PMMA substrate. (c) Large-area pattern fabrication on a rigid glass substrate.

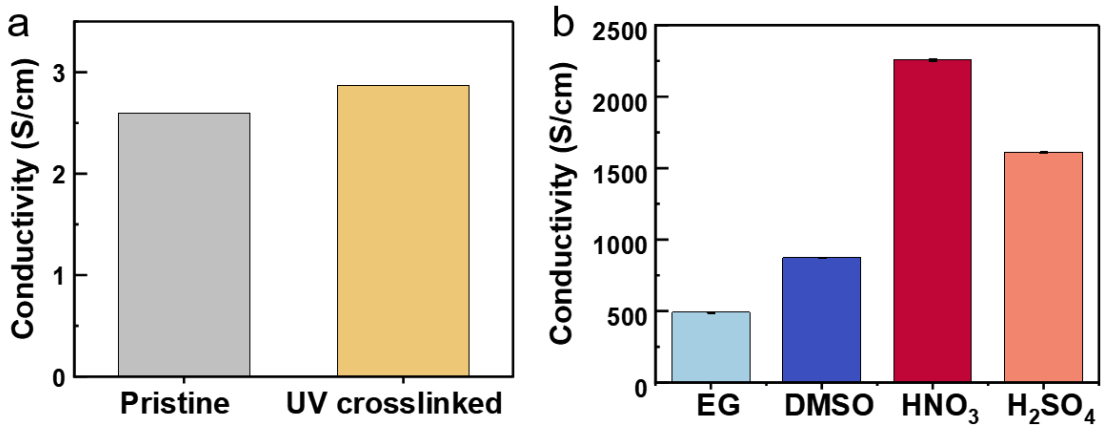


Fig. S9 Electrical conductivities of the MPVAL-PEDOT:PSS films. (a) Comparison of the initial conductivities between the pristine PEDOT:PSS and the UV crosslinked films, demonstrating that the intrinsic charge transport pathways are preserved. (b) Conductivities of the UV crosslinked films subjected to various post-treatment strategies, showing the highest conductivity after HNO_3 treatment.

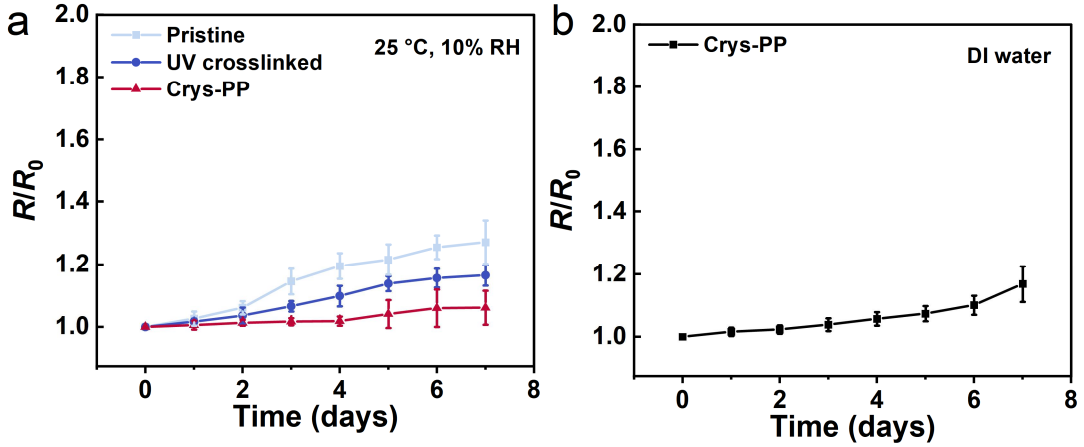


Fig. S10 Electrical stability of the films over a 7-day period. Relative resistance changes (R/R_0) of (a) the pristine, UV crosslinked, and Crys-PP films under ambient conditions (25 °C, 10% RH), and (b) the Crys-PP film continuously immersed in deionized (DI) water.

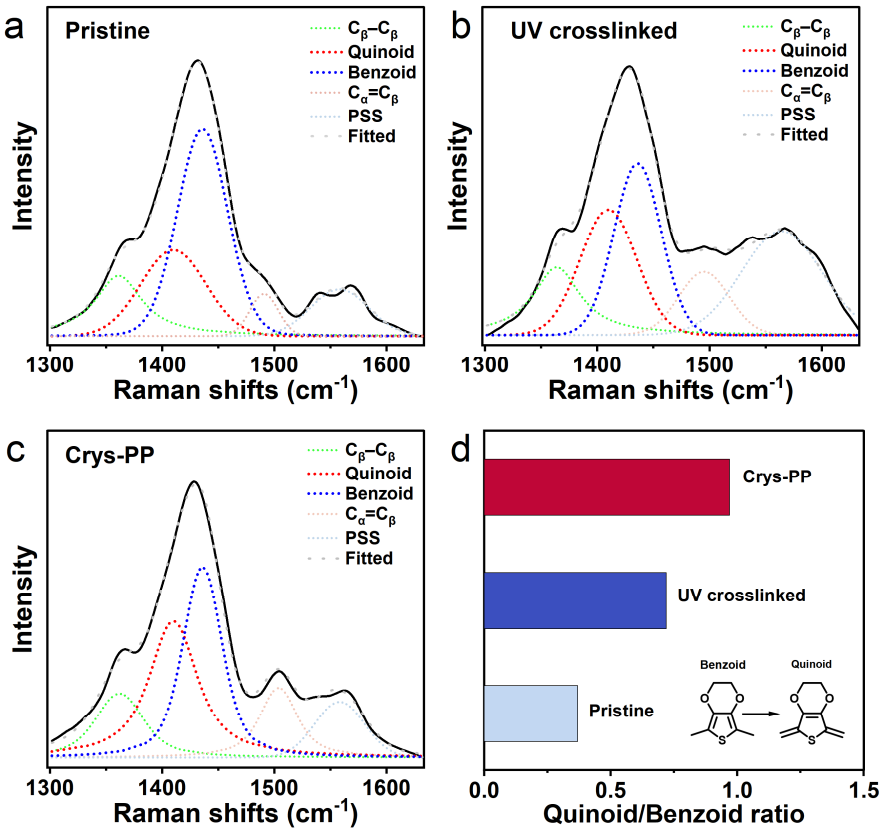


Fig. S11 Raman spectra and peak deconvolution profiles of the (a) pristine, (b) UV crosslinked, and (c) Crys-PP films. (d) Evaluated quinoid/benzoid integrated area ratios of the pristine, UV crosslinked, and Crys-PP films. The inset illustrates the structural transition from the coiled benzoid to the extended quinoid conformation.

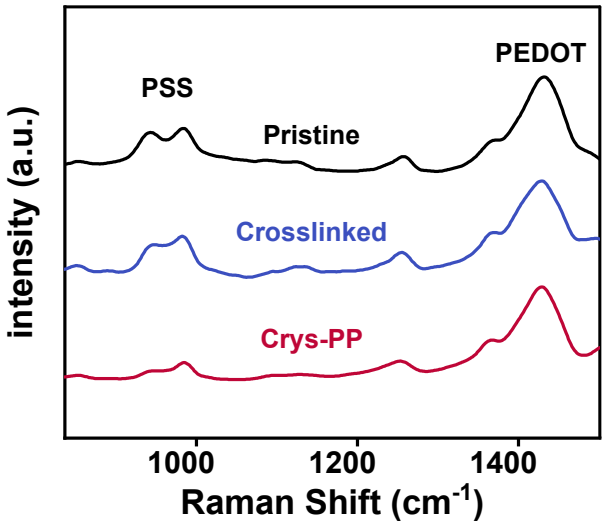


Fig. S12 Raman spectra of the pristine, UV crosslinked, and Crys-PP films. The weakened PSS peaks (800–1000 cm^{-1}) in the Crys-PP film indicate the removal of the insulating PSS phase.

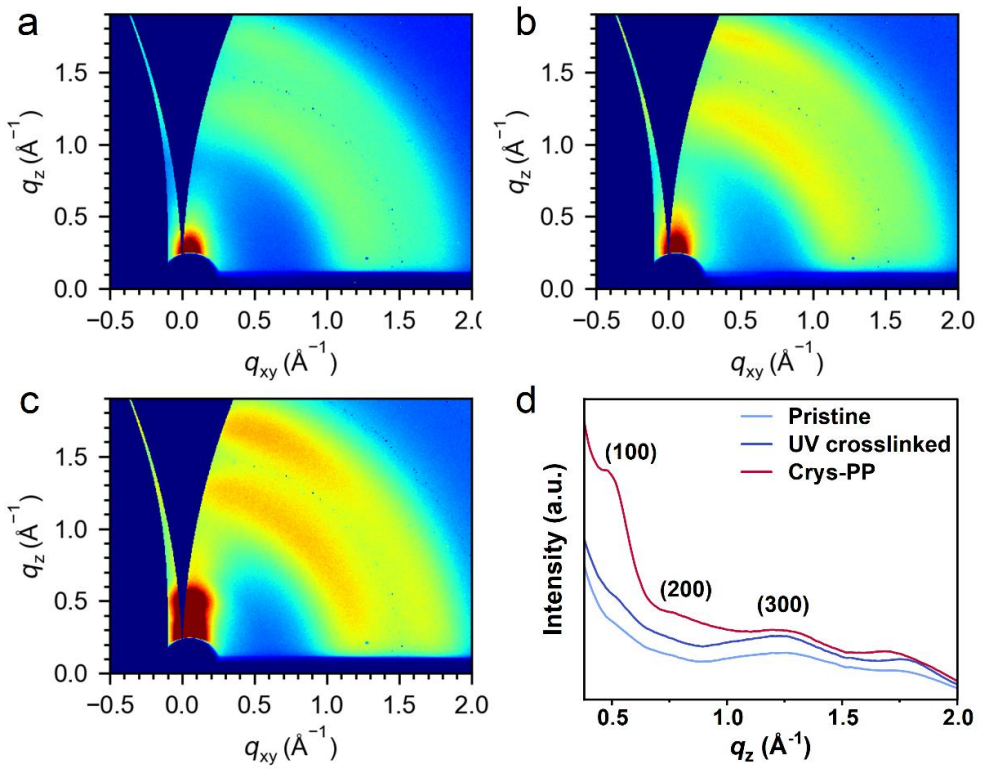


Fig. S13 2D Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) patterns of (a) pristine, (b) UV crosslinked, and (c) Crys-PP films. (d) The corresponding 1D GIWAXS intensity profiles extracted along the out-of-plane (q_z) direction.

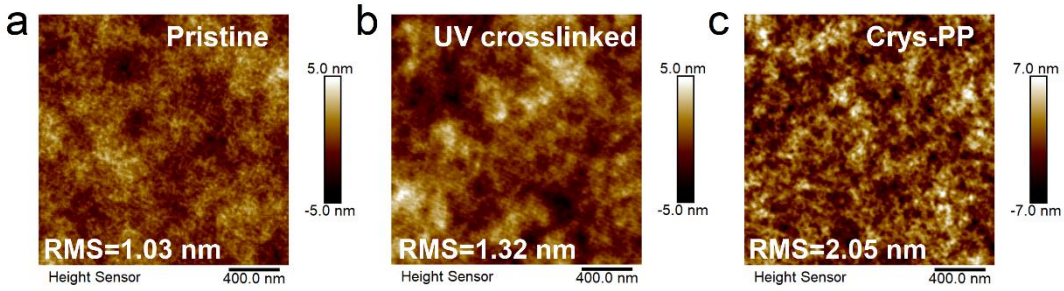


Fig. S14 AFM height images illustrating the morphological evolution of the (a) pristine, (b) UV crosslinked, and (c) Crys-PP films. The corresponding root-mean-square (RMS) roughness values are 1.03 nm, 1.32 nm, and 2.05 nm, respectively.