Supporting Information

Bio-Based Encapsulation Materials Enabling Recyclable and Stable Perovskite Solar Cells

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Methods

Materials for devices fabrication

Formamidinium hydroiodide (FAI) was purchased from Dysol. Nickel oxide (NiO_x) nanoparticles, methylammonium iodide (MAI), cesium iodide (CsI), methylammonium chloride (MACl), and 2-(4-fluorophenyl)ethylammonium iodide (4-F-PEAI) were purchased from Advanced Election Technology Co., Ltd. 1,3-Propyldiammonium diiodide (PDADI), C_{60}, bathocuproine (BCP), and lead chloride ($PbCl_2$) were purchased from Xi'an Yuri Solar Co., Ltd. Anhydrous solvents—including isopropanol (IPA), chlorobenzene (CB), N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO)—were purchased from J&K Scientific Ltd. Me-4PACz and lead iodide (PbI_2) were purchased from TCI. Photovoltaic-grade EVA and POE encapsulation films were provided by Towngas Energy Academy (ShenZhen) Co., Ltd.

Device fabrication

Patterned ITO substrates were ultrasonically cleaned sequentially in distilled water, acetone, and IPA (15 min each). Me-4PACz was dissolved in IPA (0.5 mg mL^{-1}). NiO_x was dispersed in distilled water/IPA (v/v = 3:1) at 5 mg mL^{-1} following a reported protocol,[1] then filtered before use. The perovskite precursor was prepared by dissolving CsI, FAI, and PbI_2 in DMF/DMSO (v/v = 4:1) to yield $Cs_{0.05}FA_{0.95}PbI_3$ at 1.4 M; 5% excess PbI_2, 3% $PbCl_2$, 10% MACl, and 1.4 mg 4-F-PEAI were added as reported.[1] Cleaned ITO was UV-treated for 30 min to render the surface hydrophilic. NiO_x dispersion was spin-coated in air at 3000 rpm for 30 s without annealing, then substrates were transferred into an N_2-filled glovebox. Me-4PACz was deposited on NiO_x/ITO as the hole-transport layer at 4000 rpm, followed by annealing at 100 °C. The perovskite precursor was spin-coated using 2000 rpm (10 s) then 5000 rpm (50 s); 180 μL CB was dripped 5 s before the end of the second step. Films were annealed at 100 °C for 30 min and cooled to room temperature. PDADI (0.5 mg mL^{-1} in IPA) was spin-coated at 5000 rpm for 30 s as a surface passivator, followed by 100 °C annealing for 10 min. Finally, 25-nm C_{60}, 6-nm BCP, and 100-nm Ag were thermally evaporated in high vacuum ($< 2 \times 10^{-6}$ torr) through a metal shadow mask to complete the device.

PTFF synthesis

2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediol (OFHDO), tris(trifluoromethylsulfonyloxy) scandium ($Sc(OTF)_3$), 2,5-furandicarboxylicacid (FDCA) and 1,3-Propanediol were purchased from Aladdin. PTFF was synthesized via a one-pot process by charging all reagents into a three-necked flask. In the polycondensation reaction, FDCA and diol are in a ratio of 1:3, and the molar ratio of propylene glycol to OFHDO in the diol monomer is 9:1, while $Sc(OTF)_3$ was used as catalyst at 0.6 ‰ of total reactants. The mixture was heated under mechanical stirring; the initial esterification proceeded under N_2. After completion, the system was evacuated (≤70 Pa) to remove generated H_2O and unreacted alcohols. The resulting polymer was hot-pressed into thin films for solar-cell encapsulation. The polymerization conditions are summarized in Table S1.

Characterization

^{1}H NMR spectra were recorded on a Bruker spectrometer (^{1}H 600 MHz). Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC 3 to investigate the thermal transition behaviors of PTFF. For adhesion evaluation, PTFF, POE, and EVA films were cut to 1 cm × 1 cm and hot-pressed between a substrate and cover plate at a constant load of 10 kgf. Tensile tests were conducted on a universal testing machine (Instron-1121 tester, Instron Corp., USA). Modulus (G', G'') and viscoelastic properties were obtained using a dynamic thermomechanical analyzer (Discovery DMA850, Waters Corp., USA). Water vapor transmission rate was measured with a C390H system (LabThink). Modulus–temperature curves were recorded on a discovery hybrid rheometer (HR-2, Waters Corp., USA). Thermal decomposition was evaluated using a simultaneous thermal analysis–mass spectrometry (STA–MS) setup (STA449F5–Thermostar, NETZSCH, Germany). Current–voltage (*J*–*V*) characteristics for small area devices (contact area 0.068 cm^2) were measured in an N_2-filled glovebox using an optical mask of 0.04 cm^2 with a Keithley 2400 (scan rate 10mV/s, step 0.02V) under an AAA solar simulator (SS-F5, EnliTech; 100 mW cm^{-2}, AM 1.5G), a silicon solar cell with a KG-2 filter calibrated by National Renewable Energy Laboratory (NREL) was employed for illuminance correction; for the 10*10cm^2 minimodules (aperture area 53.0 cm^2) the *J*-*V* measurements were collected in ambient air with a scan delay of 50 ms and a step of 0.1V at room temperature. FTIR spectra were collected using a PerkinElmer FTIR spectrometer. Weight-average molecular weight (M_w), number-average molecular weight (M_n), and the polymer dispersity index (PDI) of PTFF were obtained by gel permeation chromatography (GPC) using a Shodex GPC HFlP-805 column and a Waters 1515 HPLC with OPTIL AB DSP interferometric refractometer (Wyatt Technology) as detector. The eluent was hexafluoroisopropanol (containing 0.005 mol/L CF_3COONa) at a flowrate of 1.0 mL /min at 30 °C. Monodispersed polymethyl methacrylate was used as the standard sample.

Stability test

All devices used to evaluate the effectiveness of PTFF encapsulation are initially encapsulated via thermal lamination within a nitrogen-filled glove box. For the thermal cycling tests, we utilize a refrigerator set to -40 °C as the cold source, and an 85 °C hot plate serves as the heat source. Each device remains at these temperature extremes for 5 minutes, constituting one complete cycle, followed by a 5-minute stabilization period at room temperature before conducting current-voltage (J-V) measurements.

To assess operational stability, the encapsulated devices are tested under MPPT conditions. This involves exposure to continuous one sun illumination, calibrated using a standard solar cell, provided by an LED light source with a spectral range of 400 to 1,000 nm. These tests are conducted in ambient air conditions (ISOS-L-1) without additional heat dissipation measures, ensuring a rigorous evaluation of the PTFF's barrier and adhesive properties under realistic operational conditions. Additionally, for the damp-heat stability tests, a UV-curable adhesive is applied along the edges of the cover glass. This secondary encapsulation step enhances the moisture barrier capabilities, providing further insights into the robustness of the PTFF encapsulating layer under humid conditions.

Recycling method of PTFF

Initially, the encapsulated device is frozen in liquid nitrogen for approximately 15 seconds, rendering the PTFF brittle at extremely low temperatures and thereby facilitating its separation from the substrate. A single-sided blade is then inserted into the gap between the cover glass and the substrate to gently separate them. Typically, the PTFF adhering to the device side will detach first. Should any PTFF remain adhered beneath the cover glass, the blade peeling process can be repeated following additional liquid nitrogen application. This peeling technique can also be accomplished through high-temperature exposure. By heating the encapsulated device to 120 degrees Celsius, a peeling effect similar to that achieved with liquid nitrogen can be accomplished using the blade.

Following separation, 800-grit sandpaper is used to meticulously polish the surface of the recycled PTFF. This step is crucial to remove any residual silver electrodes and perovskite, ensuring that the material recycled is free of impurities. To address potential environmental concerns associated with fluorinated polymers, the polishing residues are collected. Trace amounts of residual polymers are then extracted by leaching with hexafluoroisopropanol—a solvent that does not dissolve perovskite and silver but effectively processes PTFF. The resultant solution is poured into a PTFE mold and dried to recover the PTFE content.

Afterward, deionized water is employed to cleanse any dust from the polymer's surface, which is then air-dried. The processed PTFF is layered between two polyimide films and subjected to hot pressing at 120 °C under 5 MPa pressure for 30 seconds, resulting in a regenerated PTFF film. This comprehensive process ensures the integrity and functionality of the recycled PTFF, aligning with sustainability and environmental safety standards.

Assessment of the possibility of fluoride leakage

Recycled PTFF was subjected to exhaustive extraction in deionized water at 50 °C, maintaining a polymer-to-solvent ratio of 1 mg/mL. The leachate obtained under these accelerated aging conditions was subsequently analyzed for fluorine content using Inductively Coupled Plasma (ICP) spectroscopy. The measured fluorine concentration of 0.143 ppm indicates a minimal risk of fluorine leak from the material, underscoring the material's environmental safety under these testing conditions.

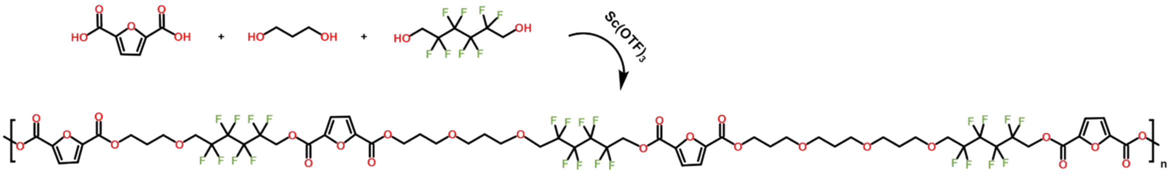

Fig. S1. The synthesis route and structural formula of the target product PTFF.

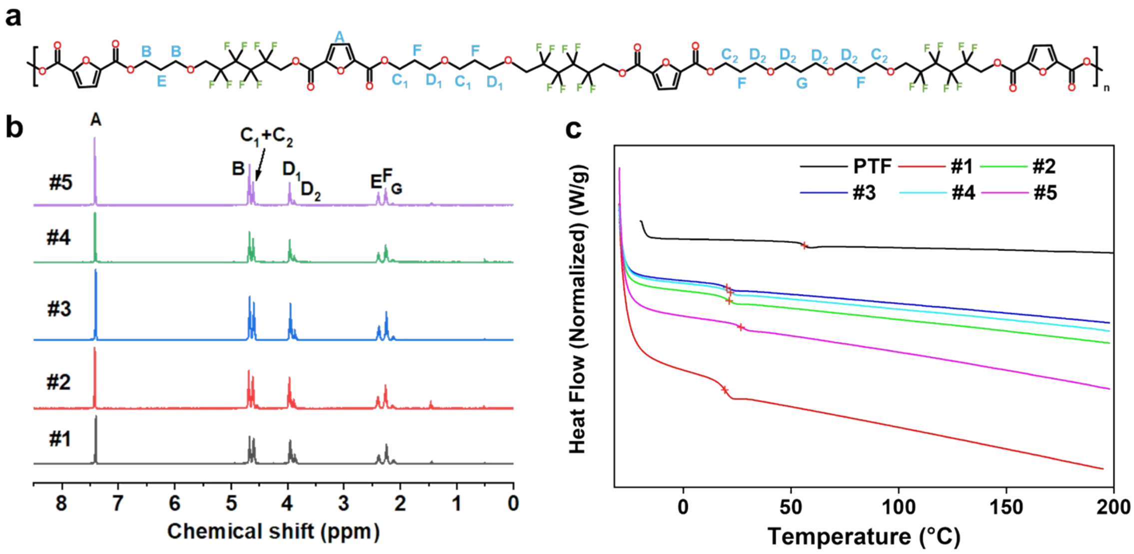

Fig. S2. (a) molecular structure of PTFF. (b) ^{1}H NMR spectra of selected PTFF series polymers. (c) DSC measurement and T_g analysis of PTFF series polymers and Poly (2,5-furandicarboxylic acid) propylene glycol ester (PTF) without block structure.

The proportion of each segment in the PTFF structure is calculated according to the following formulas:

$B+C_1+C_2 = 2A$

$2G = D_2$

$2E = B$

$C_1+C_2 = D_1 = F$

Total amounts of ether bonds = （C_1+C_2） / (C_1+C_2+B)

Triethylene glycol = $2G * \text{Ether} / (C_1+C_2)$

The chemical environment of hydrogen atoms represented by each letter is marked in Fig. S2a.

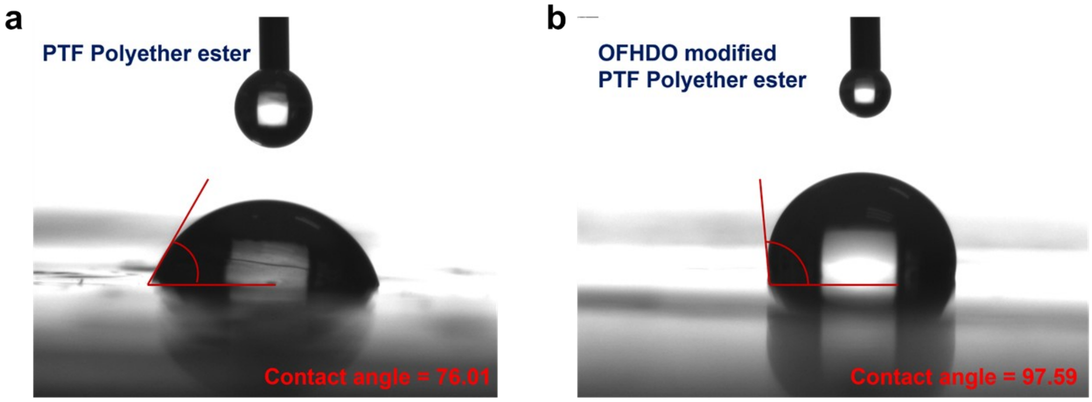

Fig. S3. Contact angle of polyether ester (a) without OFHDO doping and (b) with OFHDO reinforcement.

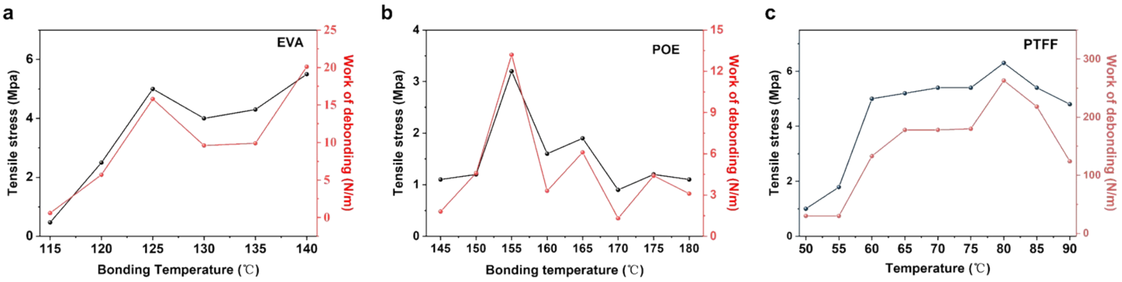

Fig. S4. Tensile stress and corresponding work of debonding calculation of (a) EVA, (b) POE and (c) PTFF.

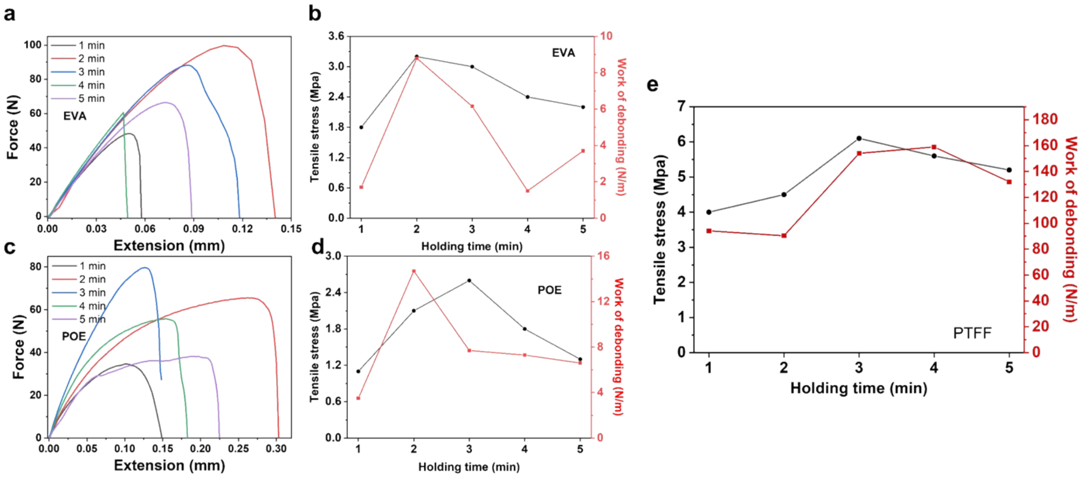

Fig. S5. Exploration of the optimal hot-pressing time with fixed optimal hot-pressing temperature. (a) Stress-strain curve of EVA from shear tensile test. (b) Calculated work of debonding of (a). (c) Stress-strain curve of POE from shear tensile test; (d) calculated work of debonding of (c). (e) calculated work of debonding of PTFF in **Fig. 2e**.

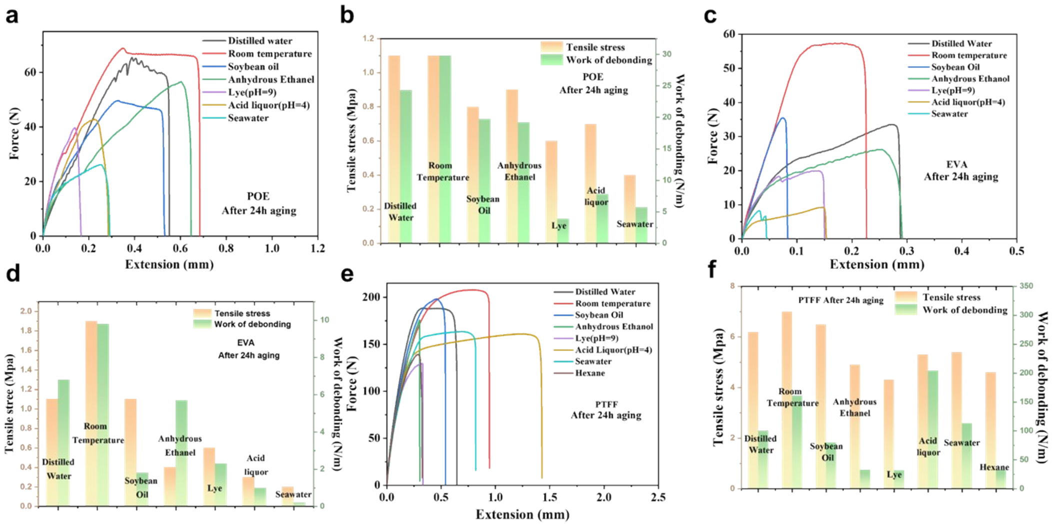

Fig. S6. 24h solvent aging experiment of encapsulation films, all encapsulation films are immersed into the solvents mentioned in the Fig.S6 for 24h. After that, films were dried and used to bond the substrate and cover glass for sheer-tensile tests. (a) Stress-strain curve from shear tensile test of POE. (b) The calculated tensile stress and work of debonding of POE from (a). (c) Stress-strain curve from shear tensile test of EVA; (d) The calculated tensile stress and work of debonding of EVA from (c). (e) Stress-strain curve from shear tensile test of PTFF; (f) The calculated tensile stress and work of debonding of PTFF from (e).

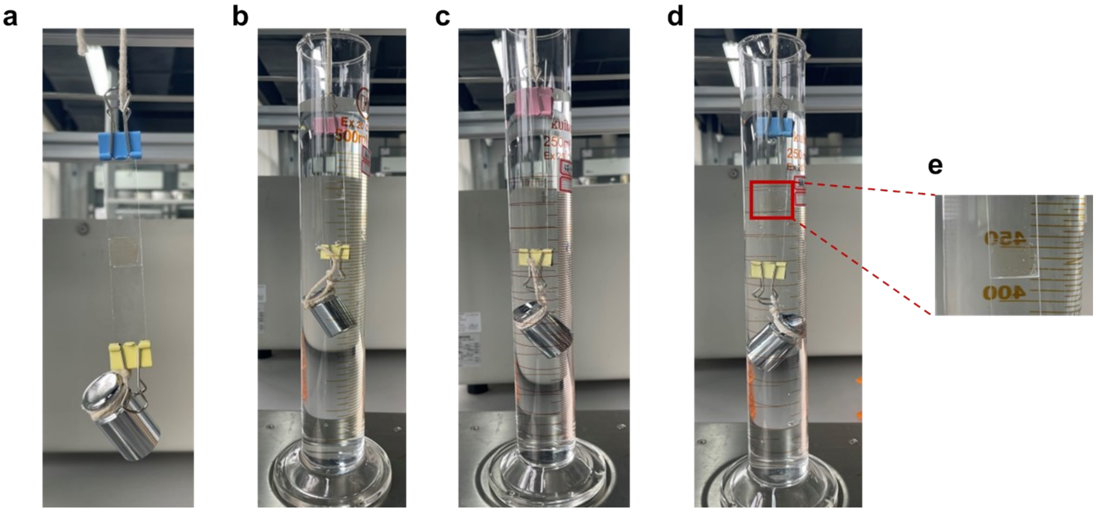

Fig. S7. Underwater adhesive force reliability evaluation of PTFF. The substrates and cover glasses are bonded with PTFF (the bonding area is 1*1 cm^2), and then a 100g weight is loaded onto them. Afterwards, the experimental system is placed separately in (a) ambient air, (b) seawater, (c) lye (pH=9), and (d) acid liquor (pH=4) for 24h, and the bonding area is magnified in (e). During the testing period, the samples under all conditions maintained good adhesion without detachment or displacement

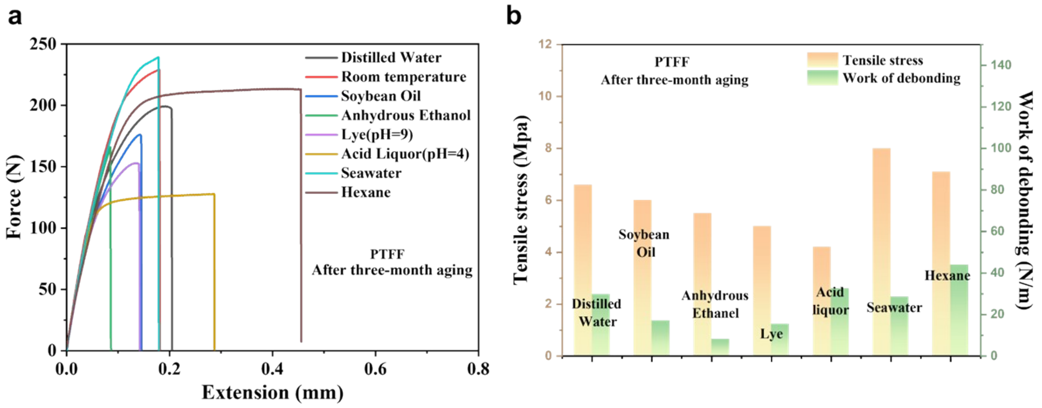

Fig. S8. Three-month solvent aging test of PTFF. (a) Stress-strain curve from the shear tensile test of the aged PTFF. (b) The calculated tensile stress and work of debonding of PTFF from (a).

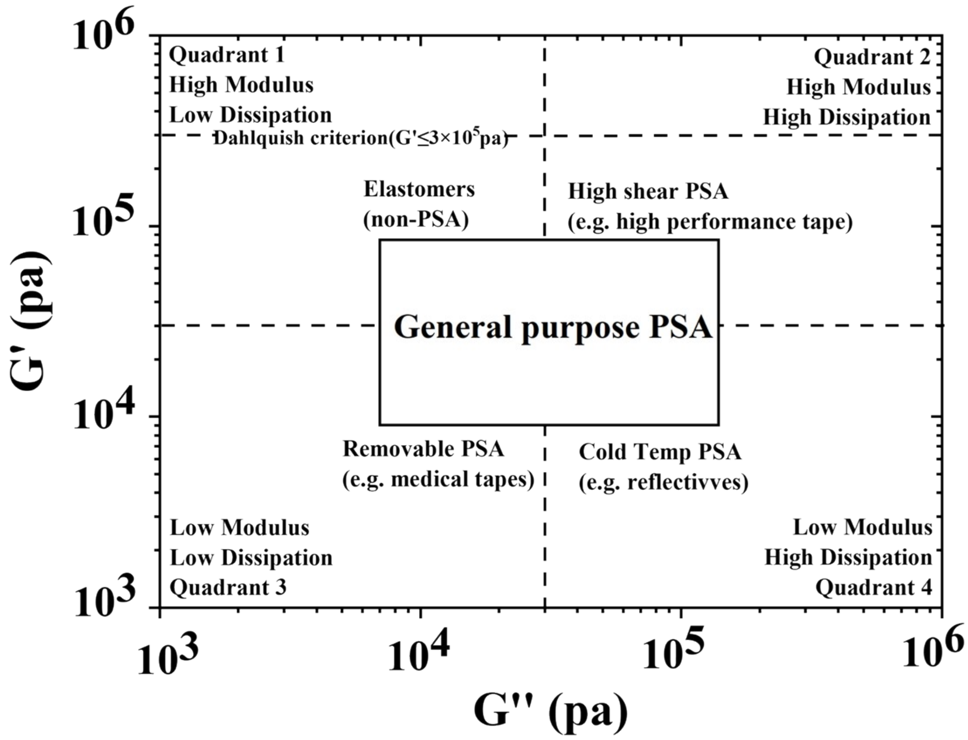

Fig. S9. Analysis of pressure-sensitive adhesive types based on viscoelastic window.

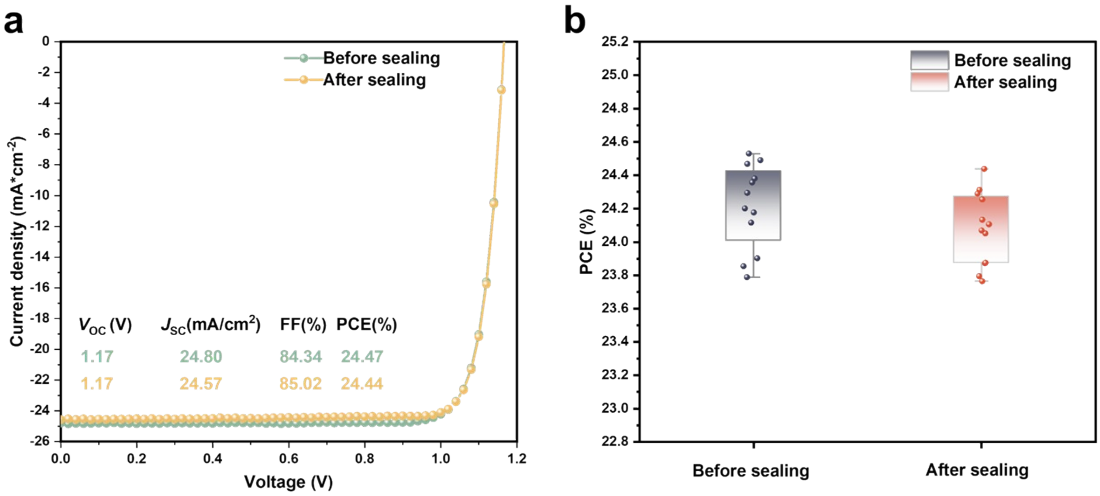

Fig. S10. *J*-*V* curve comparison and statistical chart of the performance for small area devices before and after PTFF encapsulating. The active area of the devices is 0.067 cm^2 and the optical mask used during the *J*-*V* test is 0.04cm^2.

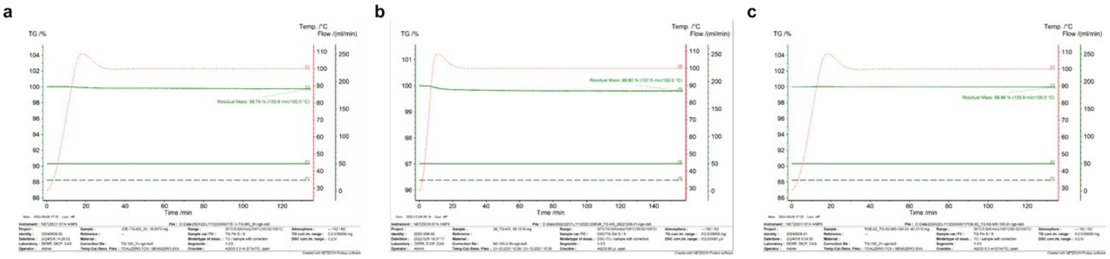

Fig. S11. TGA-MS test reports of (a) PTFF; (b) EVA and (c) POE. About 0.2% thermal weight loss is detected in EVA sample and water is detected by the MS.

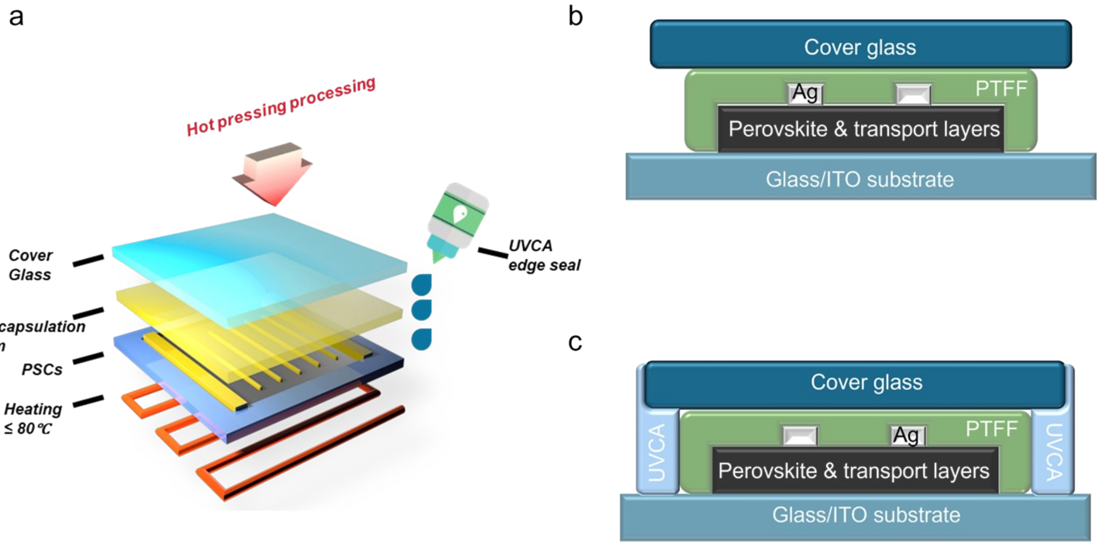

Fig. S12 **(a)** Schematic diagram of PTFF laminated encapsulation. (b) Cross-sectional diagram of the encapsulation structure for devices for MPP tracking and thermal cycle stability tests. (c) Sectional diagram of encapsulating structure for damp heat stability test (including edge seal).

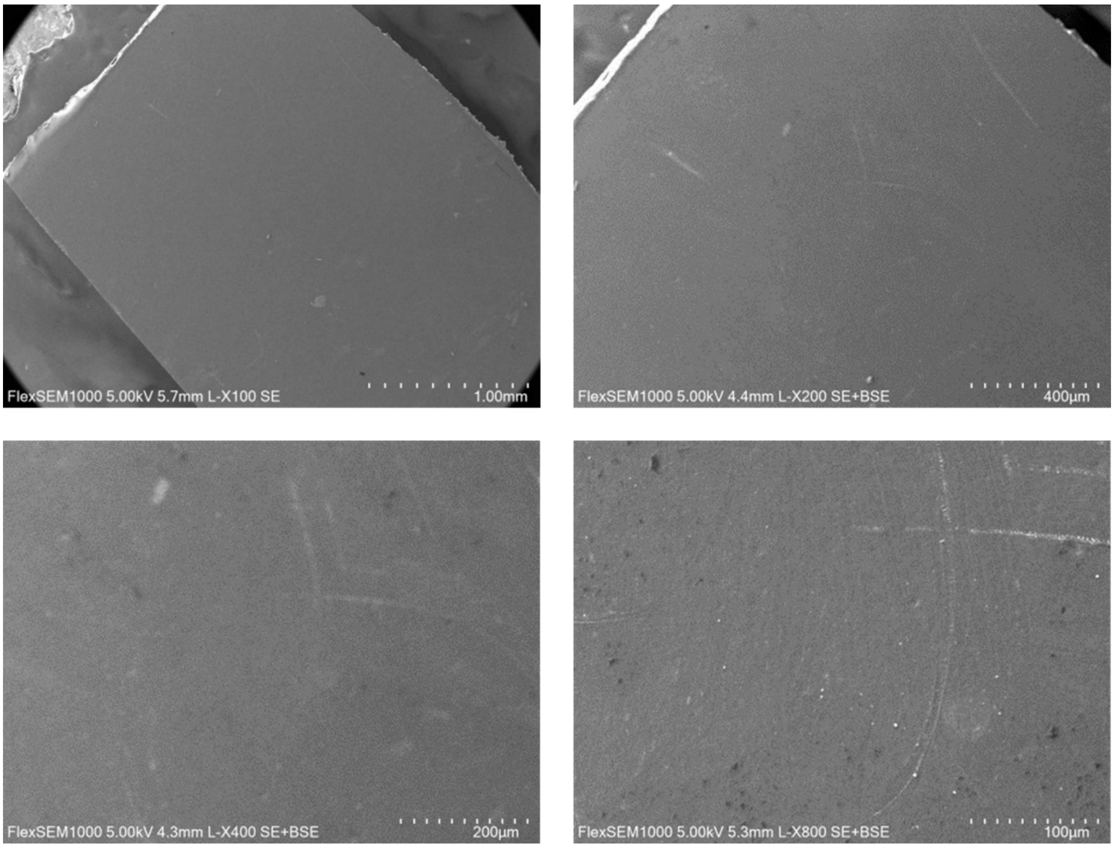

Fig. S13 SEM images of the surface of a newly fabricated PTFF

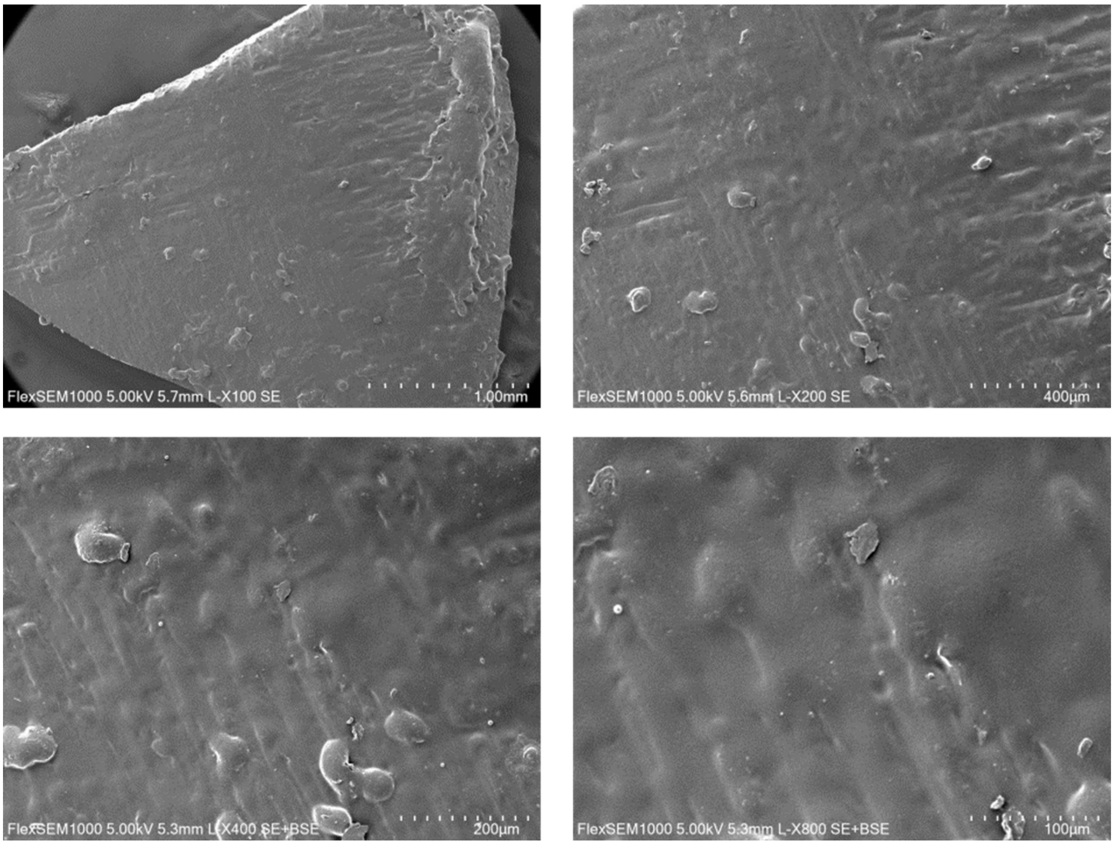

Fig. S14 SEM images of the surface of a recycled PTFF

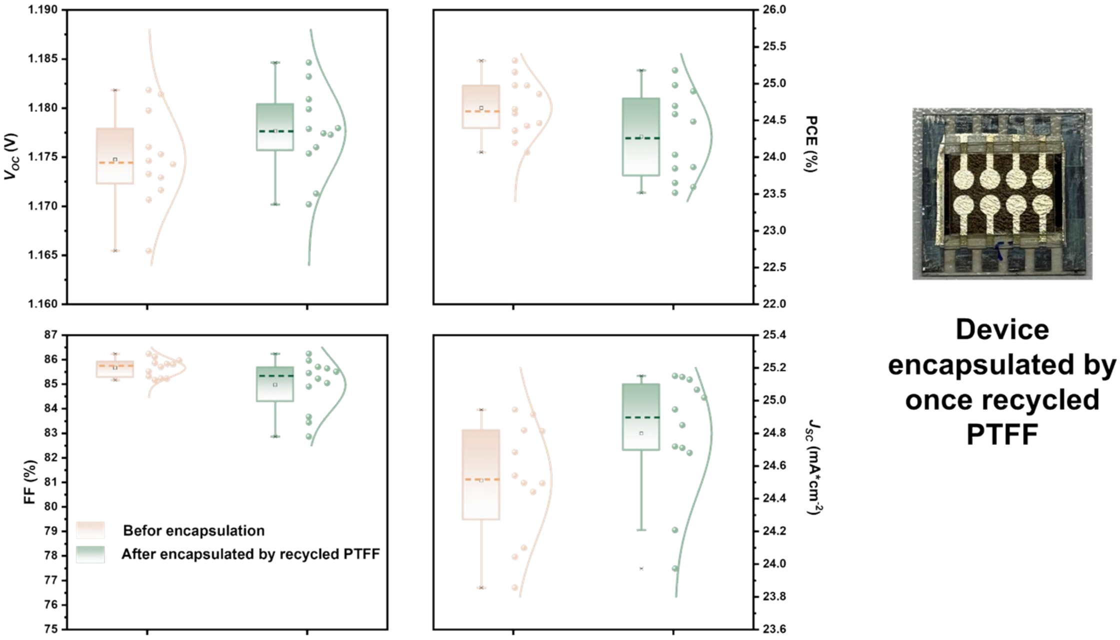

Fig. S15 Statistics on the performance changes of devices after one recycling cycle of PTFF encapsulation, with photographs of the actual devices.

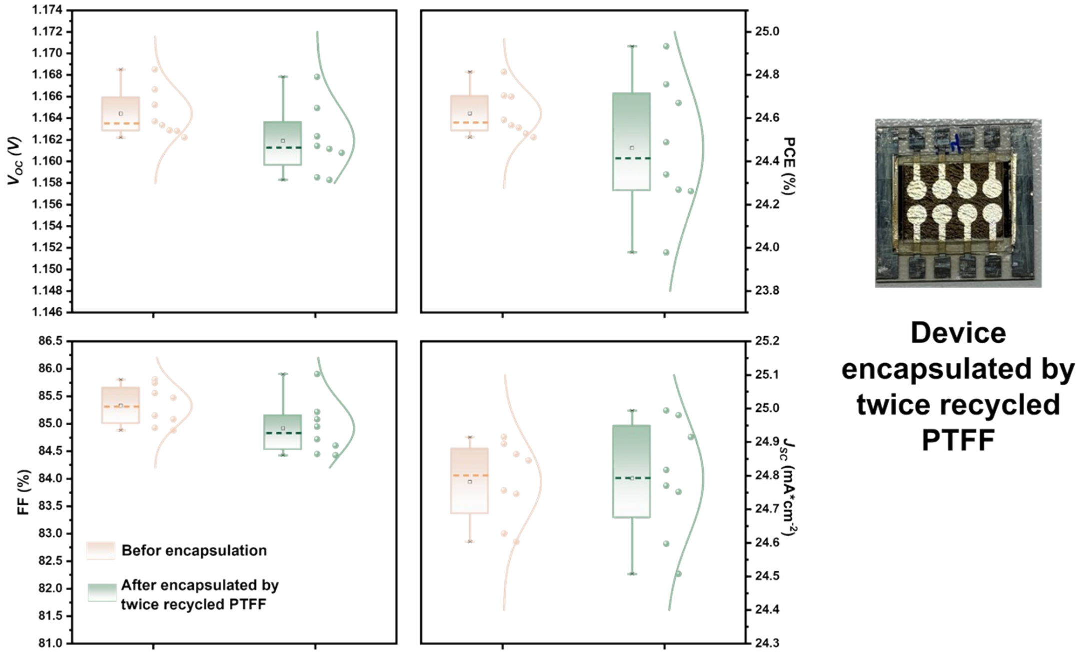

Fig. S16 Statistics on the performance changes of devices after two recycling cycles of PTFF encapsulation, with photographs of the actual devices.

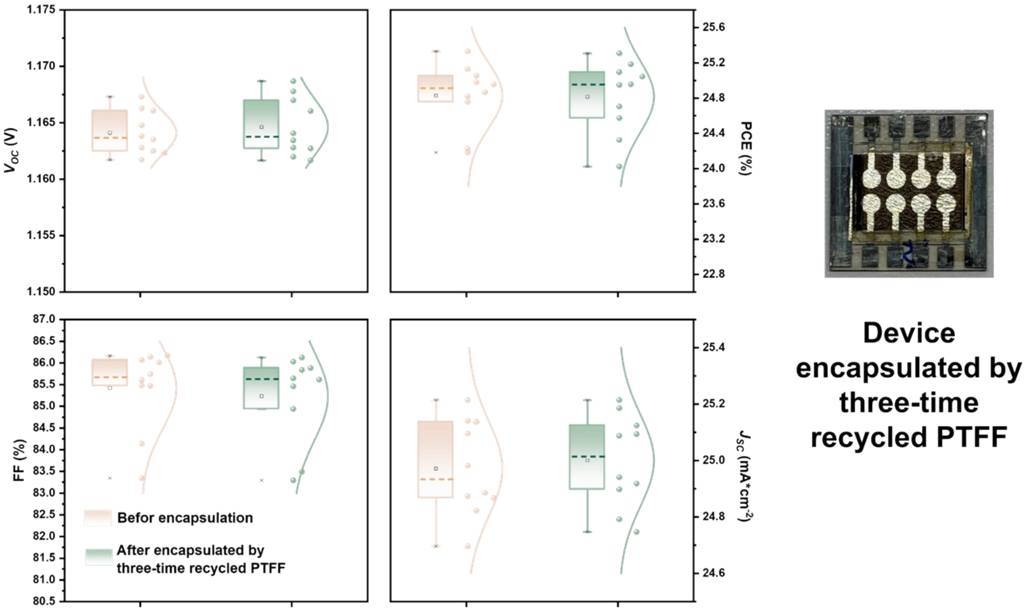

Fig. S17 Statistics on the performance changes of devices after three recycling cycles of PTFF encapsulation, with photographs of the actual devices.

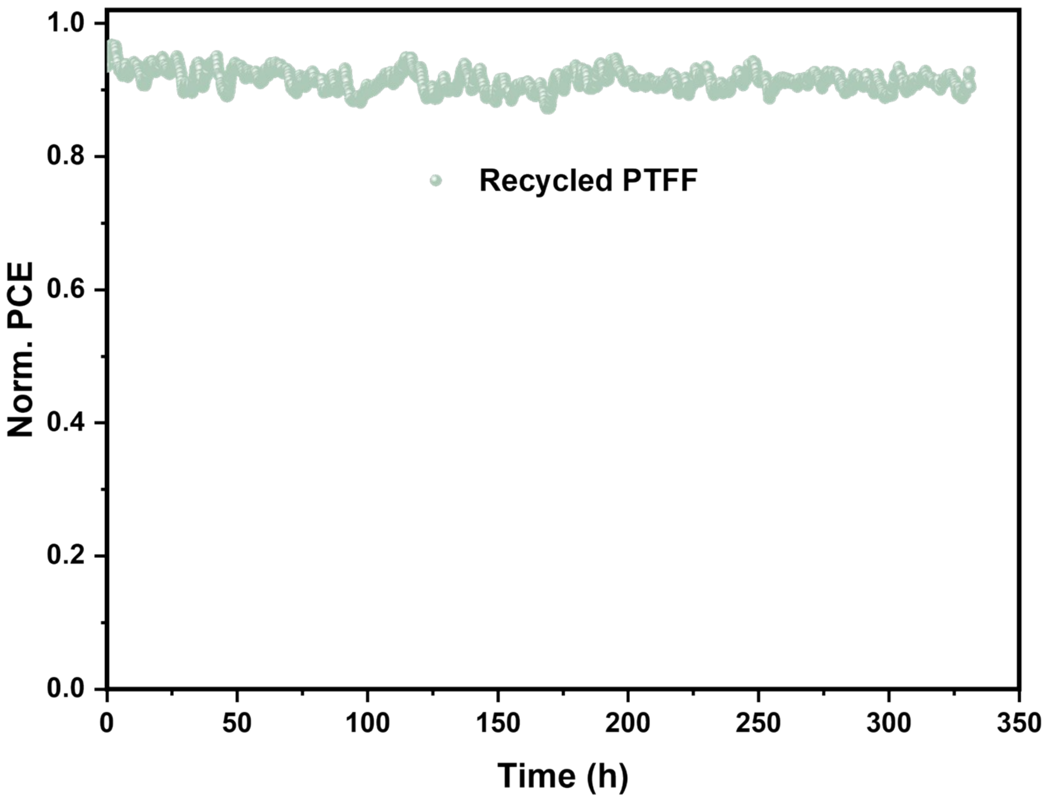

Fig. S18 Stability test of PSC encapsulated with twice-recycled PTFF under MPPT conditions. The test was conducted in humid air without any heat dissipation measures. Despite these challenging conditions, the recycled PTFF effectively isolates water and oxygen, thereby providing robust protection for the device.

Table S1

List of reaction conditions for the synthesis of PTFF series products

Sample	Conditions	DEG (%)	TEG (%)	EB (%)	T_g (℃)
#1	TER: 180 ℃,2h; TCR 210 ℃, 2h	47.2	17.2	64.4	18.97
#2	TER: 180 ℃,2h; TCR 200 ℃, 2h	14.8	16.2	31.0	20.63
#3	TER: 180 ℃,1.5h; TCR 200 ℃, 2h	23.7	15.9	39.6	22.13
#4	TER: 180 ℃,1.5h; TCR: 210 ℃, 2h	41.6	18.7	60.3	22.18
#5	TER: 180 ℃,1h; TCR: 210 ℃, 2h	34.1	4.8	38.9	27.46

Notes: DiEthylene Glycol (DEG), Triethylene glycol (TEG), Total amounts of ether bonds (EB), Time of esterification reaction (TER), Time of condensation reaction (TCR), glass transition temperature (T_g).

Table S2.

Water vapor transmission rate (WVTR) measurement.

WVTR (g/cm^2*24h)	25℃	35℃	55℃
EVA	12.468	31.479	149.470
POE	2.095	6.665	26.684
PTFF	8.957	15.512	30.829

Table S3.

Solvent aging test.

Condition	PTFF			EVA			POE		
	TS (Mpa)	EB (%)	WB (N/m)	TS (Mpa)	EB (%)	WB (N/m)	TS (Mpa)	EB (%)	WB (N/m)
Room temperature	7.0	9.4	161	1.9	2.3	9.8	1.1	6.9	29.8
Distilled water	6.2	6.5	100	1.1	2.9	6.8	1.1	5.5	24.3
Soybean oil	6.5	5.4	79.4	1.1	0.84	1.8	0.8	5.3	19.7
Anhydrous ethanol	4.9	3.0	32.2	0.4	2.9	5.7	0.9	6.5	19.2
Lye (pH=9)	4.3	3.3	31.4	0.6	1.5	2.3	0.6	1.7	3.89
Acid liquor (pH=4)	5.3	14.2	204	0.3	1.5	1.0	0.7	2.9	7.76
Seawater	5.4	8.2	113	0.2	0.45	0.2	0.4	2.9	5.7
Hexane	4.6	3.3	31.8	\	\	\	\	\	\

Notes: Tensile strength (TS), elongation at break (EB), work of debonding (WB).
The ageing time of each material under corresponding conditions is 24 hours. Both EVA and POE bonded samples are detached after 24h aging of hexane.

Table S4

Three-month solvent aging test.

Condition	PTFF		
	TS (Mpa)	EB (%)	WB (N/m)
Distilled water	6.6	2.1	29.65
Soybean oil	6.0	1.5	16.96
Anhydrous ethanol	5.5	0.87	8.01
Lye (pH=9)	5.0	1.4	15.29
Acid liquor (pH=4)	4.2	2.9	32.37
Seawater	8.0	1.8	28.52

Hexane	7.1	4.6	43.85

Table S5

Recyclability assessment of Fig. 7e

Sample	**TS (Mpa)**	**EB (%)**	**WB (N/m)**
Newly made PTFF	6.3	10.4	263
Recycled PTFF	7.8	11.1	222

The hot-pressing condition of both samples are the same. (80°C, 3min)

Table S6

Average value of multiple samples

Sample	**TS (Mpa)**	**EB (%)**	**WB (N/m)**
Newly made PTFF	6.9	3.4	205
Recycled PTFF	7.0	12.1	187

Multiple samples were used for tensile comparison before and after recycling, and the average values of tensile strength, elongation at break, and detachment work were calculated for statistical analysis.

Table S7

ICP-OES testing results

Sample	Ag (mg/L)	Pb (mg/L)
Newly made PTFF	0.001	0.009
Recycled PTFF	0.002	0.009

Table S8

Summary of PTFF molecular weight

Sample	**Mn** (g/mol)	**Mw**(g/mol)	**PDI**
#1	24627	57522	2.33
#2	23619	59798	2.53
#3	20700	49190	2.37
#4	18373	43993	2.39
#5	19330	44280	2.29

Molecular weight information obtained through GPC testing.

Reference

1. X. Huang, L. Bi, Z. Yao, Q. Fu, B. Fan, S. Wu, Z. Su, Q. Feng, J. Wang, Y. Hong, M. Liu, Y. An, M. Chen and A. K. Jen, *Adv. Mater.*, 2024, **36**, e2410564.