Electronic Supplementary Information (ESI)

Solutionally processed intrinsically conductive polymer films with high thermoelectric properties and good air stability

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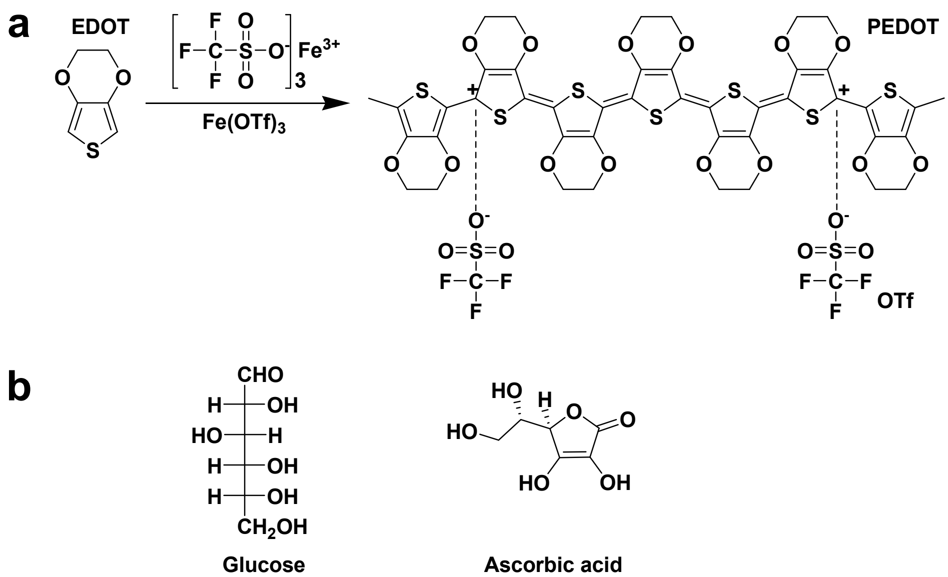

Scheme S1. a) Synthesis of PEDOT:OTf through the oxidative polymerization of EDOT by iron (III) trifluoromethanesulfonate ($Fe(OTf)_3$), b) the chemical structure of glucose, ascrobic acid and EDA.

$$\text{gluconic acid} + 2H^+ + 2e^- \rightleftharpoons \text{glucose} + H_2O \qquad E^{\Theta} = 0.05\ \text{V}$$

$$DHA + 2H^+ + 2e- \rightleftharpoons ASC + H_2O \qquad E^{\Theta} = 0.06\ \text{V}$$

$$SDA + H^+ + e- \rightleftharpoons ASC \qquad E^{\Theta} = 0.32\ \text{V}$$

$$DHA + H^+ + e- \rightleftharpoons SDA + H_2O \qquad E^{\Theta} = -0.20\ \text{V}$$

Where ASC is ascorbic acid, DHA is dehydroascorbic acid and SDA is semidehydroadcorbic acid radical.

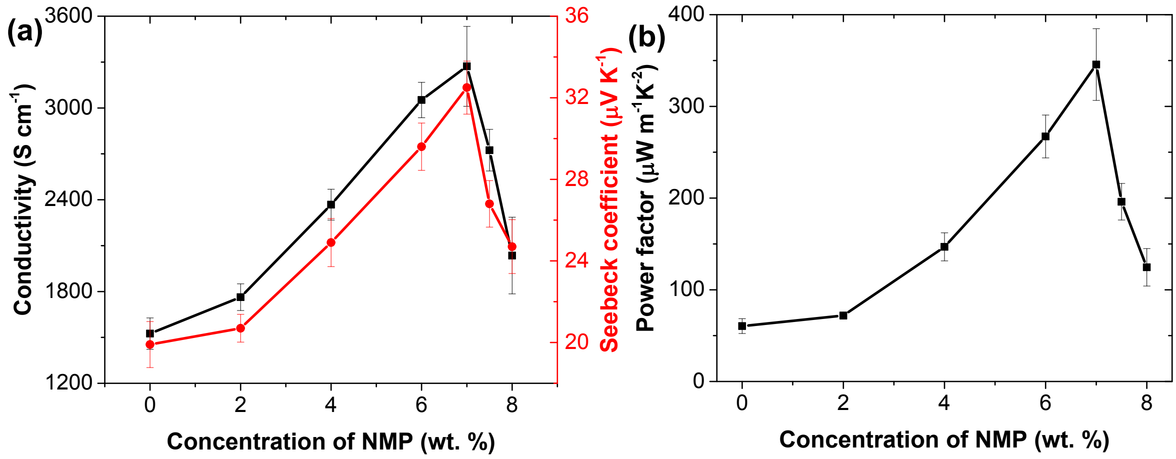

Fig. S1 Thermoelectric properties of the as-synthesized PEDOT:OTf films. Dependences of (a) the electrical conductivity, (b) Seebeck coefficient and (c) power factor of the as-synthesized PEDOT:OTf films on the concentration of NMP.

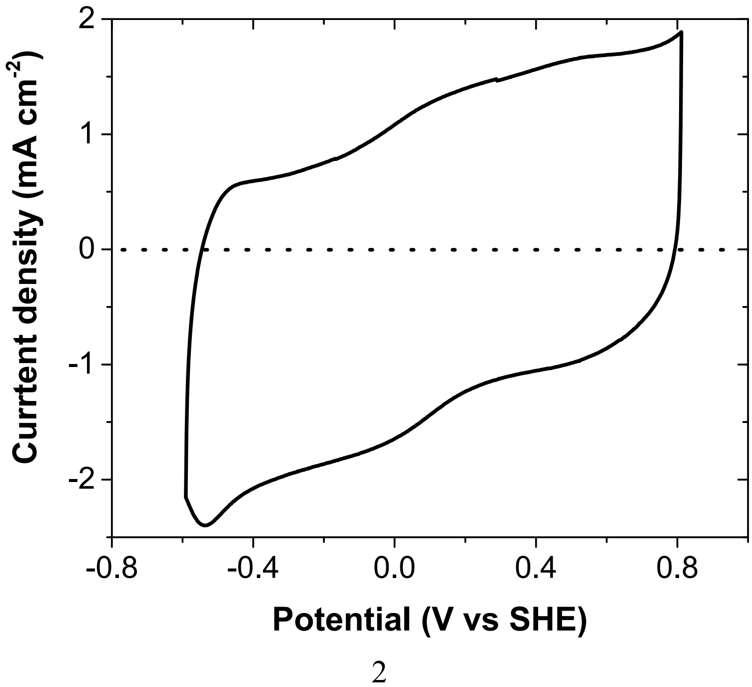

Fig. S2 CV curve of an as-synthesized PEDOT:OTf film in a 1.0 M KCl solution.

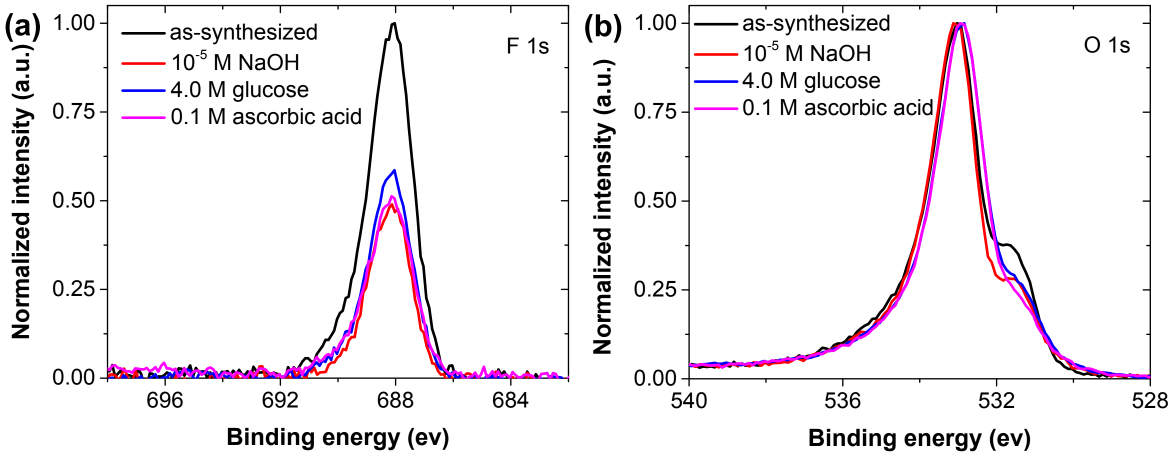

Fig. S3 (a) F_{1s} and (b) O_{1s} XPS spectra of as-synthesized, glucose-, ascorbic acid- and NaOH-treated PEDOT:OTf films.

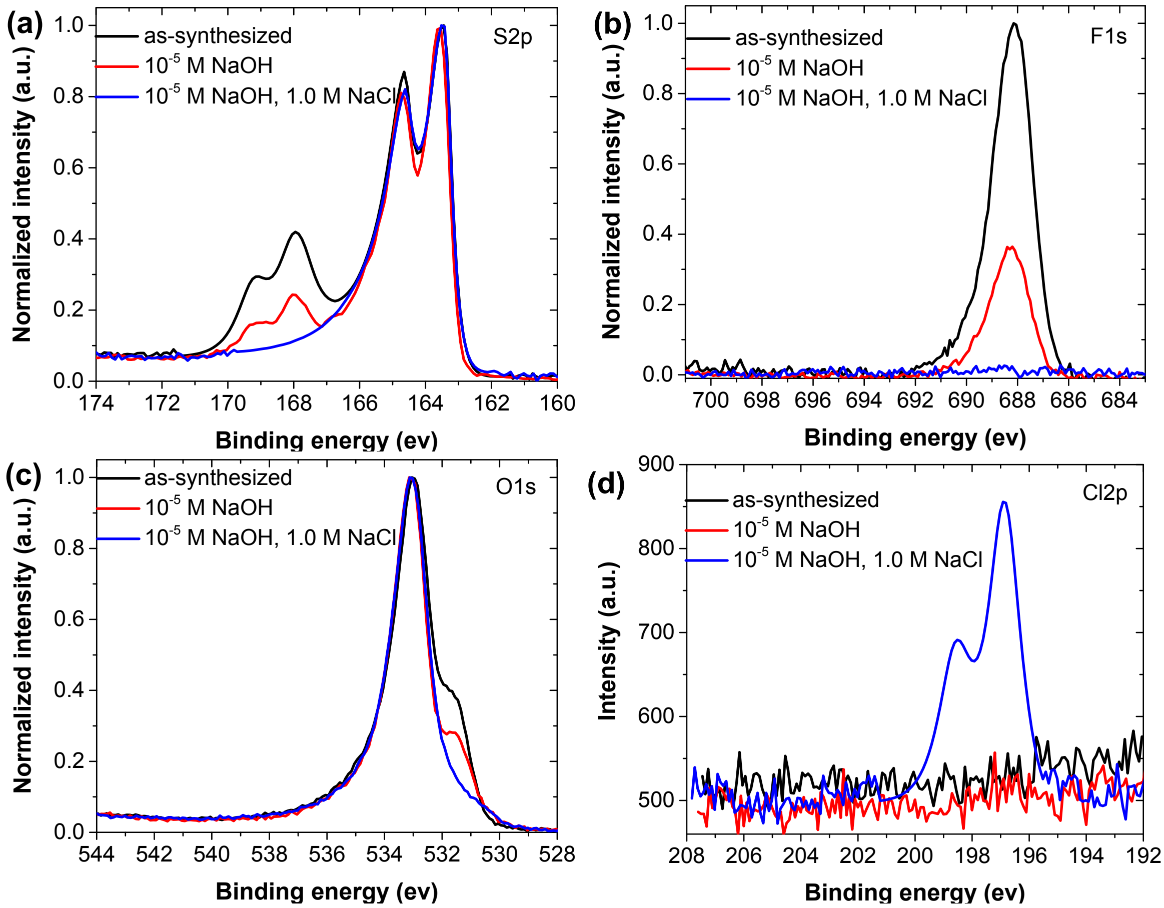

Fig. S4 (a) S 2p, (b) F 1s, (c) O 1s and (d) Cl 2p XPS spectra of as-synthesized and 10^{-5} M NaOH-treated, and 10^{-5} M NaOH-treated-then-1.0 M NaCl-treated PEDOT:OTf films.

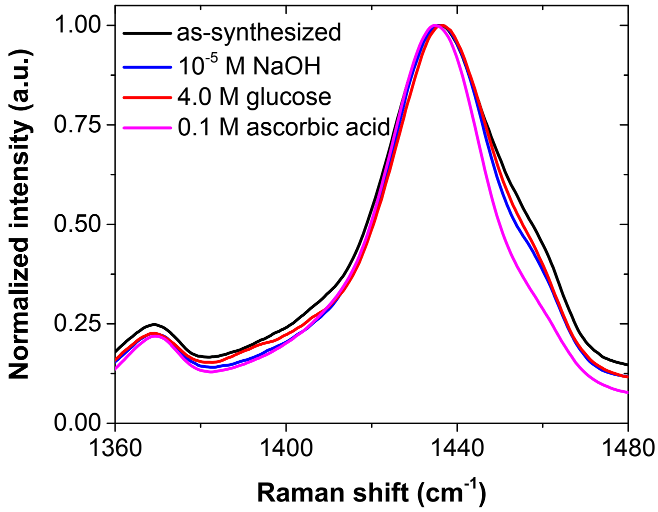

Fig. S5 Raman spectra of the as-synthesized and NaOH, glucose and ascorbic acid treated PEDOT:OTf films.

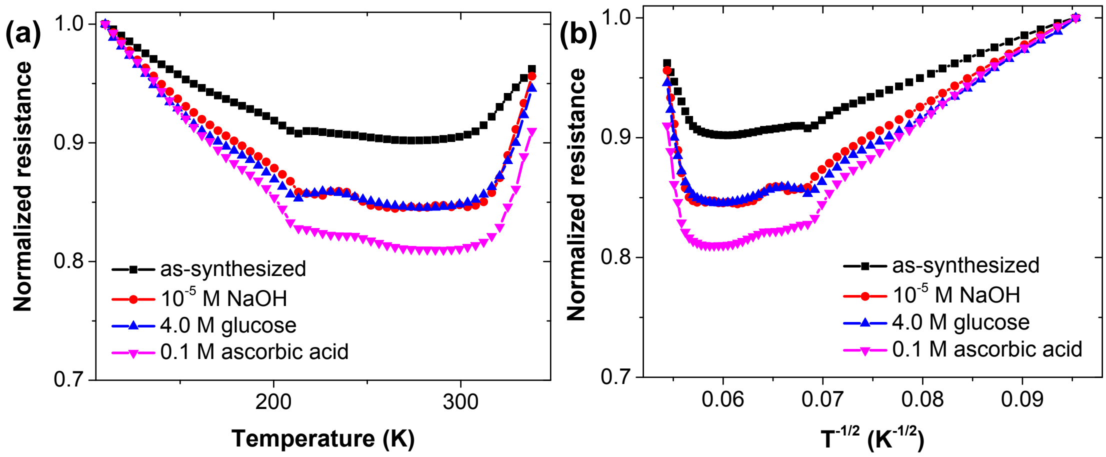

Fig. S6 (a) Temperature dependences of the resistances of PEDOT:OTf films treated with NaOH, glucose and ascorbic acid. (b) Analysis of resistance-temperature relationships with the 1D VRH model.

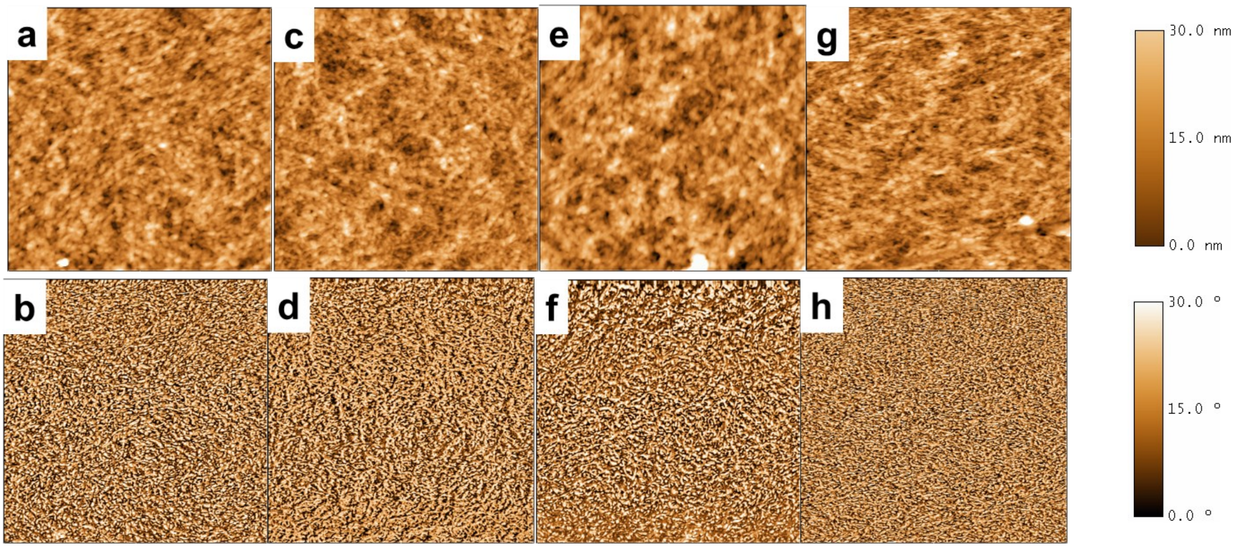

Fig. S7 AFM images of PEDOT:OTf films treated with glucose solutions of different concentration, (a) and (b) 0.5 M, (c) and (d) 1.0 M, (e) and (f) 2.0 M, and (g) and (h) 4.0 M. The dimension is 2×2 μm^2 for each AFM image.

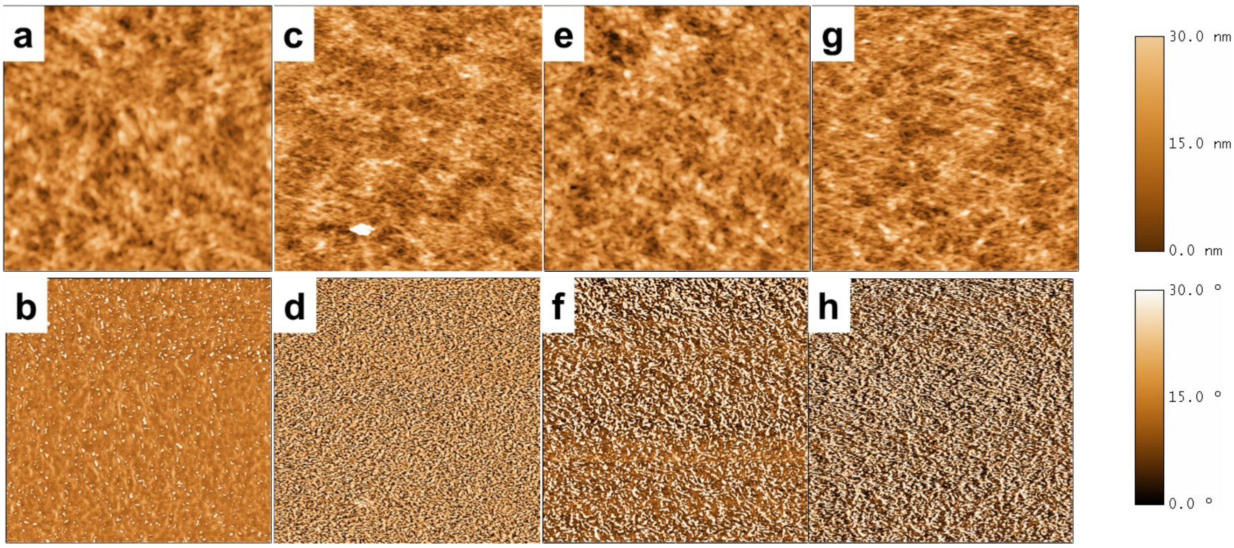

Fig. S8 AFM images of PEDOT:OTf films treated with ascrobic acid solutions of different concentration, (a) and (b) 0.1 M, (c) and (d) 0.25 M, (e) and (f) 0.5 M, and (g) and (h) 1.0 M. The dimension is 2×2 μm^2 for each AFM image.

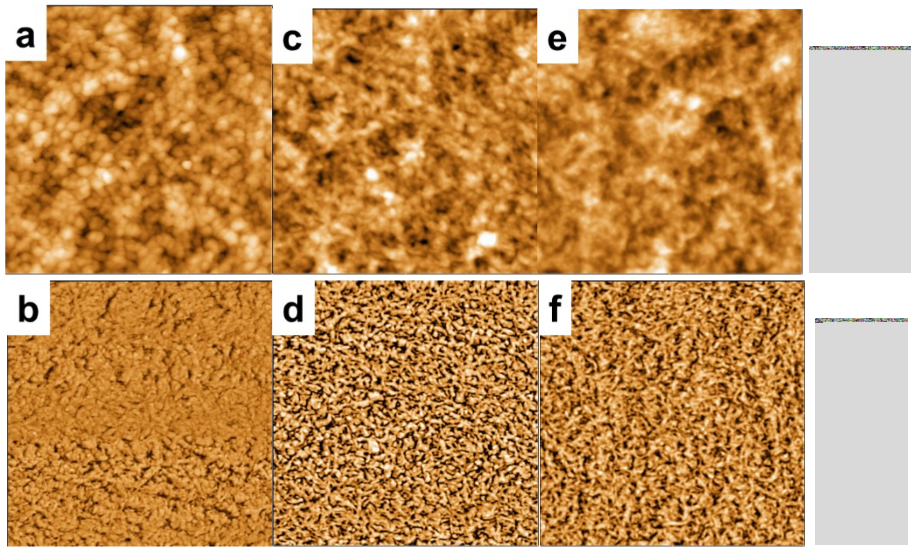

Fig. S9 AFM images of PEDOT:OTf films treated with NaOH solutions of different concentration, (a) and (b) 10^{-5} M, (c) and (d) 10^{-3} M, and (e) and (f) 10^{-1} M. The dimension is 2×2 μm^2 for each AFM image

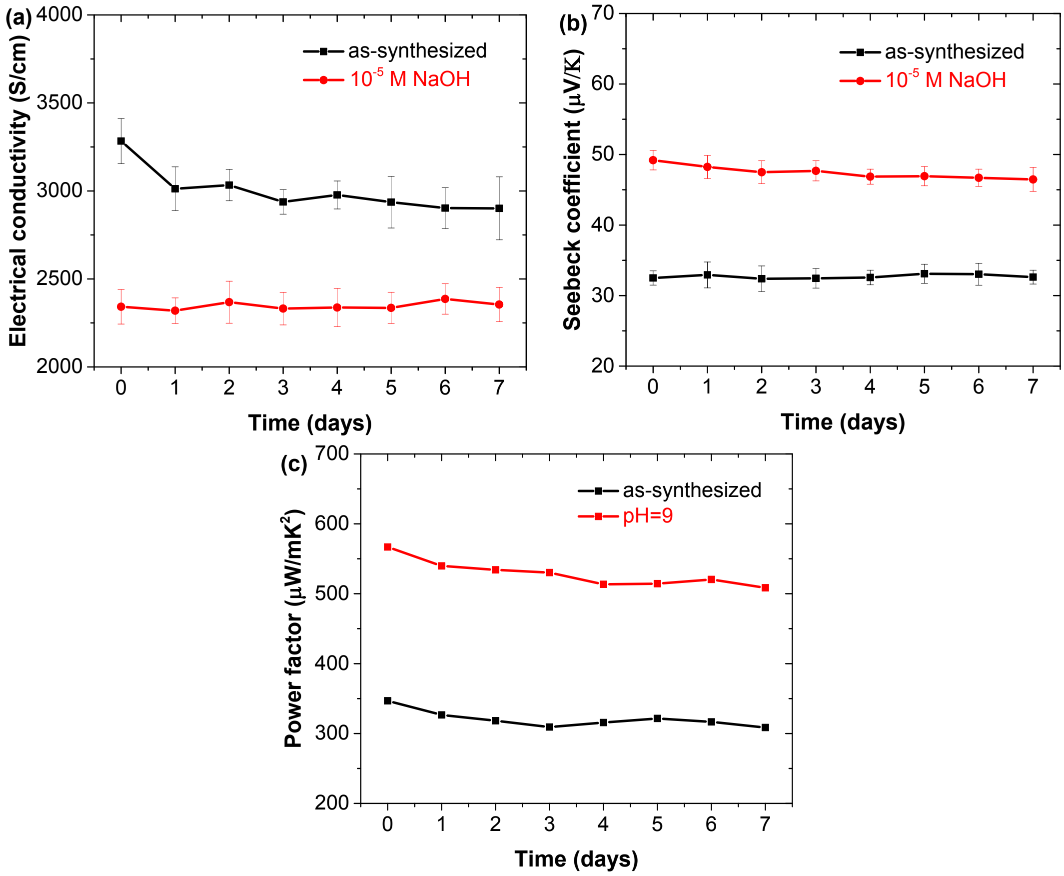

Fig. S10 Stability of as-synthesized and NaOH-treated PEDOT:OTf films. Variations of (a) the electrical conductivity, (b) Seebeck coefficient and (c) power factor over the time.

Table S1. Electrical conductivity, Seebeck coefficient, and power factor of PEDOT:OTf films treated with glucose, ascorbic acid and NaOH solutions.

Chemical	Redox potential (V)	Doping level (%)	Seebeck coefficient ($\mu V\ K^{-1}$)	Electrical conductivity ($S\ cm^{-1}$)	Maximum power factor ($\mu W\ m^{-1}\ K^{-2}$)
1.0 M Glucose	0.05[1]	16.1	39.7±0.4	2679±48	422±11
4.0 M Glucose		13.0	40.3±0.2	2363±198	384±32
0.10 M Ascorbic acid	0.06[2]	12.1	40.9±2.8	2304±19	387±53
0.25 M Ascorbic acid		11.8	41.3±1.0	2287±80	390±24
10^{-5} M NaOH	-	12.8	49.2±1.4	2342±98	568±64

Table S2. Summary of the highest power factors for the PEDOT family in literature. The polymers are prepared by different methods.

Polymer	Method	Seebeck coefficient ($\mu V\ K^{-1}$)	Electrical conductivity ($S\ cm^{-1}$)	Maximum power factor ($\mu W\ m^{-1}\ K^{-2}$)	Reference number
PEDOT:PSS	Secondary dopants (5 vol% DMSO, 0.3 vol% PEO)	38.4±7.1	1061±16	157.35	3
	Chemical dedoping (DMSO, (0.0175 wt%) Hydrazine)	67	578	112	4
	Acid and NaOH treatment (1M H_2SO_4 and 0.5 M NaOH aq)	39.2	2170	334	5
PEDOT:Tos	NaOH treatment (NaOH aq)	~20	~650	26	6
	Chemical dedoping (TDAE)	~220	~67	324	7
	Electrochemical dedoping	~117	~923	1270	8
PEDOT:OTf	NaOH treatment (NaOH aq)	49.2±1.4	2342±98	568±64	This work

References

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