Supporting Information

Designing *n*-type all-ionic thermoelectric polymers with improved air stability via a solution-processing anion exchange technique

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1. **General procedures and experimental details, materials and method**

   a. **Chloride-based PDADMAC and MADQUAT polymer thermoelectric film preparation**

Polydiallyldimethylammonium chloride (PDADMAC) (20wt.% in water), poly(2-dimethylamino)ethyl methacrylate) methyl chloride quaternary salt (MADQUAT), silver tetrafluoroborate (AgBF$_4$, 98%), tetrakis (acetonitrile) copper(I) hexafluorophosphate ([(CH$_3$CN)$_4$Cu]PF$_6$, 97%), tetrahydrofuran (THF, anhydrous, >99.9%), and methanol (CH$_3$OH, anhydrous, 99.8%) were purchased from Sigma-Aldrich. Solid MADQUAT was used as purchased whereas PDADMAC was precipitated out using THF followed by drying the solids in a vacuum oven for 72 hours. The two chloride-based polymers were fully dissolved in methanol by heating each polymer solution (30 mg/mL) on a hot plate at 50 °C for one hour. The 1" by 1" indium-tin-oxide (ITO) glass substrates were cleaned by sonication in deionized water, acetone and isopropanol, each for 15 minutes and then were subject to ozone cleaning for another 15 minutes. The polymer ink was spin-coated onto ITO-patterned glass substrates followed by annealing the samples at 100 °C for an hour inside the N$_2$-filled glovebox. The thickness of PDADMAC and MADQUAT films were measured to be 500 nm and 550 nm, respectively. Samples were stored in the glovebox before being taken out for thermoelectric measurements and other characterizations.

   b. **BF$_4^-$/PF$_6^-$ - based ionic polymer thermoelectric film preparation via anion exchange reaction**

To ensure a complete anion exchange, the weights of AgBF$_4$ and [(CH$_3$CN)$_4$Cu]PF$_6$ as exchange precursors are calculated based on the 1:1 molar ratio between BF$_4^-$ /PF$_6^-$ and Cl$^-$. The entire sample preparation process was also done in a N$_2$-filled environment. AgBF$_4$ was

dissolved in methanol in a separate vial – instant dissolution was observed. $[(CH_3CN)_4Cu]PF_6$ was dissolved in methanol in another vial and the solution was heated for 1 hour to allow for complete dissolution. As illustrated in **Figure 2** in the main text, each polymer solution was mixed with $AgBF_4$ and $[(CH_3CN)_4Cu]PF_6$ solutions, respectively, and cloudy white precipitates formed in each post-mixing solution. The white precipitates were filtered out using a PVDF filter and a clear colorless solution was obtained. A 2D well was created on each ITO patterned substrate by painting a thin layer of Novec polymer coating along the four edges of the substrate. Each filtered solution was drop-casted onto several ITO patterned glass substrates within the 2D wells to obtain uniform, continuous films with sufficient thickness. All the films were allowed to dry and were annealed at 100 °C for one hour to eliminate any possible polar solvent or moisture. The thicknesses of MADQUAT*BF_4^- , MADQUAT*PF_6^-, PDADMAC*BF_4^- and PDADMAC*PF_6^- films are measured to be 135 nm, 155 nm, 180 nm and 210 nm, respectively. Samples were kept in the glovebox before being taken out for thermoelectric measurements.

It is generally known that drop casting may create coffee-ring effect on the samples; however, the coffee-ring effect is not typical in our case. 70-80% of the films are overall smooth and uniform while the rest of samples display some coffee-ring patterns due to surface tension. As for sheet resistance measurement, when the coffee-ring effect occurred, the uniform part of the film was selected for measurement, and profilometry was conducted on the same area for thickness measurement for calculating the ionic conductivity. On the other hand, Seebeck coefficient (S) was not affected by a coffee ring effect because S generally depends on the carrier concentration and energetics instead of the thickness/volume of the film.
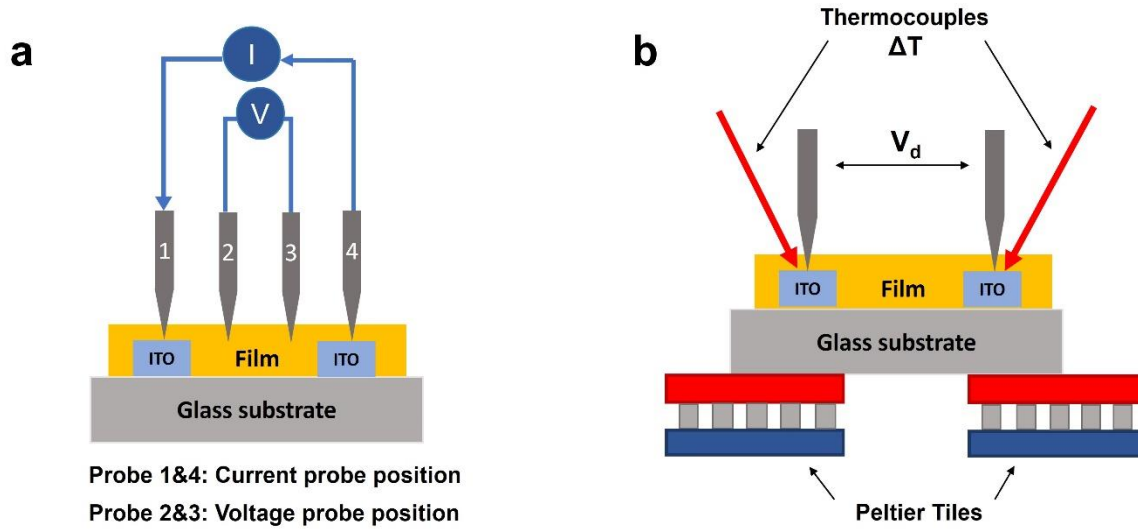
2. Thermoelectric characterizations

Figure S1: Schematic illustrations of configurations of (a) four-point probe sheet resistance measurement and (b) Seebeck coefficient measurement.[1]

Conductivity measurements were performed by using a standard four-point probe measurement method with an Agilent B1500A Semiconductor Parameter Analyzer with a channel length of 1000 µm and a channel width of 140 µm.

Seebeck coefficient measurements were performed using a homemade set-up consisting of a pair of small Peltier units to measure the induced thermoelectric voltage created by various temperature gradients across the sample. The configuration is shown in **Figure S1(b)** above. The system was monitored via a LabVIEW program along with a Keithley 2400 source meter and a Keithley 2000 multimeter. Seebeck coefficient can be calculated by $S = \Delta V/\Delta T$ with a channel length of 2000 µm and width of 8000 µm. ΔV is thermally induced voltage obtained between the two electrodes of the device subject to a temperature gradient $\Delta T = 1.5$ °C. A total of six ΔT were imposed on each sample.

At least 12 devices were fabricated and tested for each ion-polymer system at each humidity level to obtain an average and a standard error of ionic conductivity and Seebeck coefficient respectively.

### 3. Additional Characterizations

SEM and EDS characterizations were completed through the Helios[TM] G4 PFIB UXe DualBeam[TM] from Thermo Scientific[TM] at 5-10 keV and at 15 keV, respectively. The following tables show the EDS elemental analysis for MADQUAT, PDADMAC and their post anion exchange polymer systems with an exchange ratio of 1:1.
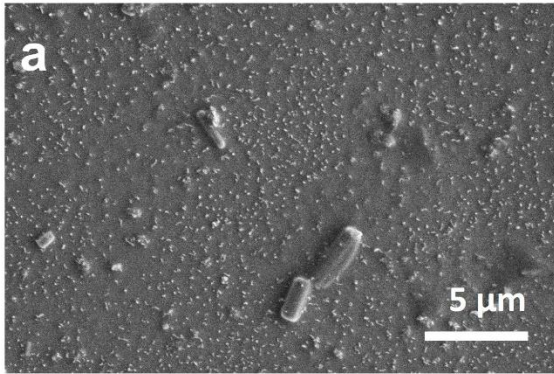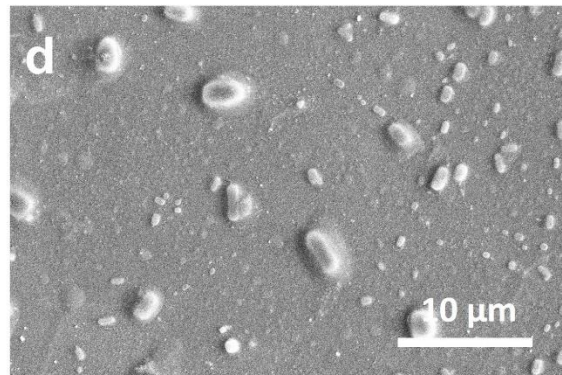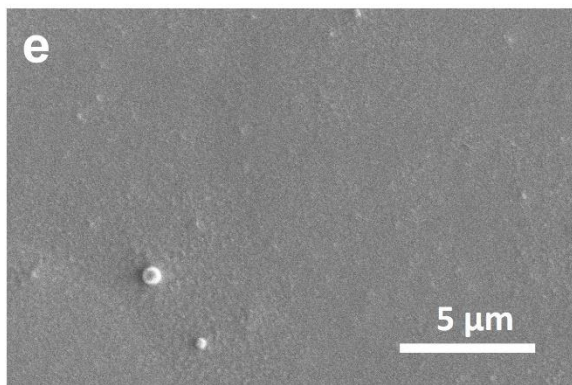
MADQUAT*BF$_4^-$
@ 40% relative humidity
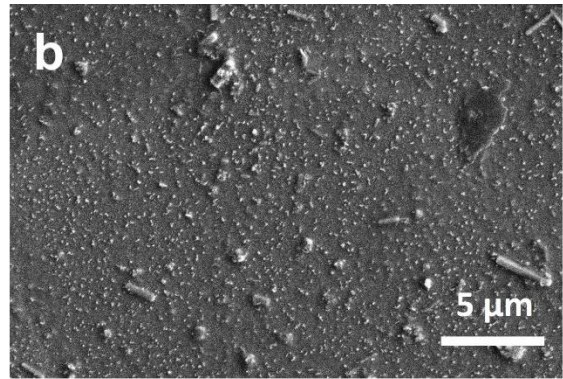
MADQUAT*BF$_4^-$
@ 15% relative humidity
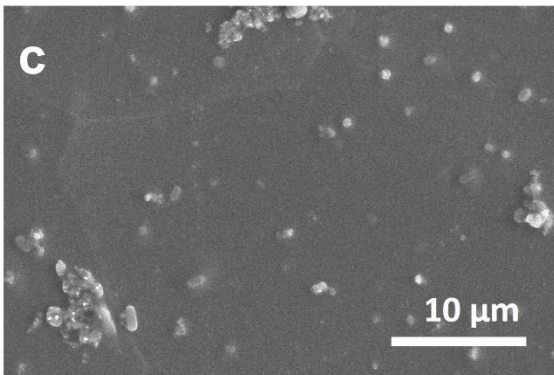
PDADMAC*BF$_4^-$
@ 40% relative humidity

PDADMAC*BF$_4^-$
@ 15% relative humidity

e MADQUAT*PF$_6^-$ @ 40% relative humidity — 5 μm
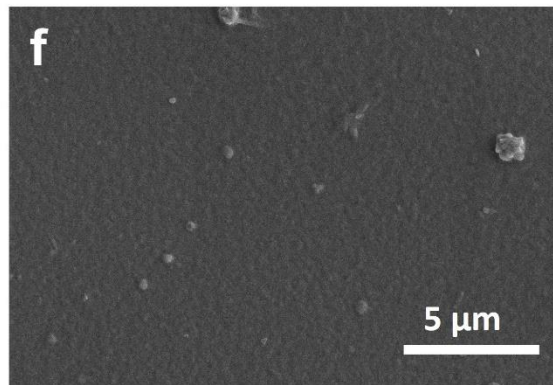
f MADQUAT*PF$_6^-$ @ 15% relative humidity — 5 μm
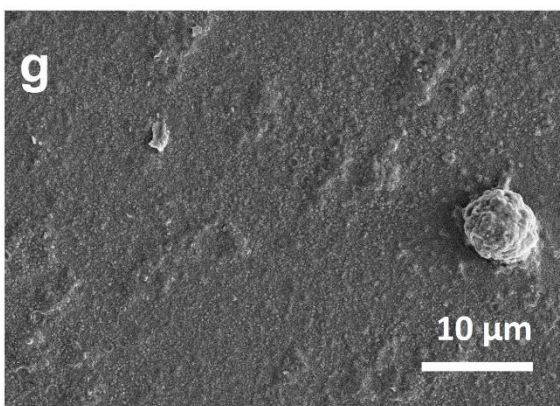
g PDADMAC*PF$_6^-$ @ 40% relative humidity — 10 μm
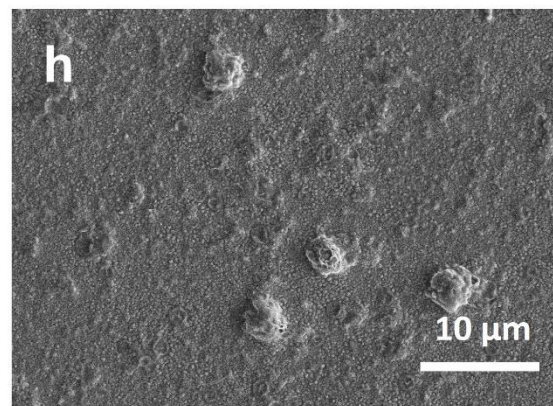
h PDADMAC*PF$_6^-$ @ 15% relative humidity — 10 μm

Figure S2: SEM images of film surfaces of MADQUAT*BF$_4^-$ under (a) 40% and (b) 15% relative humidity, PDADMAC*BF$_4^-$ under (c) 40% and (d)15% relative humidity, MADQUAT*PF$_6^-$ under (e) 40% and (f)15% relative humidity, and PDADMAC*PF$_6^-$ under (g) 40% and (h) 15% relative humidity.

We have previously performed scanning electron microscopy (SEM) analysis on our sample films that were measured in dry and humid conditions. As shown in Figure S2, there is no significant variation in the morphologies of the same polymer-ion combination under 16% relative humidity and 40 relative humidity and hence we do not have sufficient evidence to say that humidity level has strong impact on the film morphology, or that a higher humidity level would alter the film morphology.

Table S1: EDS element analysis of polymer MADQUAT

Element	Weight %	Atomic %
C K	13.19	20.99
N K	3.17	4.32
O K	35.45	42.34
Na K	8.00	6.65
Mg K	2.22	1.75
Al K	1.18	0.83
Si K	26.55	18.06
Cl K	2.30	1.24
K K	2.46	1.20
Ca K	5.49	2.62

Table S2: EDS element analysis of polymer PDADMAC

Element	Weight %	Atomic %
C K	16.7	28.23
O K	22.92	29.09
Na K	9.07	8.01
Mg K	2.64	2.2
Al K	1.41	1.06
Si K	32.19	23.27
S K	0.48	0.31
Cl K	6.36	3.64
K K	1.79	0.93
Ca K	6.44	3.26

Table S3: EDS elemental analysis of MADQUAT*BF$_4^-$

Element	Weight %	Atomic %
C K	24.48	30.27
N K	2.26	2.87
O K	29.05	32.31
F K	8.70	8.15
Na K	8.36	6.47
Mg K	1.29	0.94
Al K	0.62	0.41
Si K	15.72	9.96
K K	1.31	0.60
Ca K	3.27	1.45
Ag L	1.60	0.27
Pt M	3.33	0.30

Table S4: EDS elemental analysis of PDADMAC*BF$_4^-$

Element	Weight %	Atomic %
C K	6.39	10.93
N K	1.16	1.71
O K	16.85	21.63
F K	34.97	37.80
Na K	15.30	13.66
Mg K	1.08	0.91
Al K	0.73	0.56
Si K	12.72	9.30
Cl K	0.64	0.37
K K	1.58	0.83
Ca K	3.17	1.62
Ag L	1.40	0.27
Pt M	4.00	0.42

Table S5: EDS elemental analysis of MADQUAT*PF$_6^-$

Element	Weight%	Atomic%
C K	2.34	4.39
N K	10.16	15.05
O K	20.04	25.99
F K	23.82	26.02
Na K	4.35	3.92
Mg K	1.04	0.88
Al K	0.90	0.69
Si K	18.98	14.03
P K	6.07	4.07
Cl K	0.15	0.09
K K	1.09	0.58
Ca K	3.45	1.79
Cu K	7.63	2.50

Table S6: EDS elemental analysis of PDADMAC*PF$_6^-$

Element	Weight%	Atomic%
C K	1.82	3.45
N K	10.54	15.64
O K	19.06	24.75
F K	28.41	31.07
Na K	2.05	1.85
Mg K	0.39	0.34
Al K	0.68	0.52
Si K	17.63	13.05
P K	6.28	4.21
Cl K	0.06	0.03
K K	1.07	0.57
Ca K	3.14	1.62
Cu K	8.87	2.90

Power factor analysis

We provide a graphical illustration of power factors calculated for our own systems in **Figure S3** and a representative table of power factors reported for high-performing n-type electronic and mixed conductors from the literature along with analogous numerical values from the present work. Because ionic thermoelectrics could not generate continuous power unless a complete ionic circuit were constructed, the "power factor" concept has limited utility for ionic thermoelectrics and is essentially irrelevant for comparing ionic thermoelectrics with electronic ones. Thus, the information shown below, and the accompanying explanation are provided as a courtesy to readers.
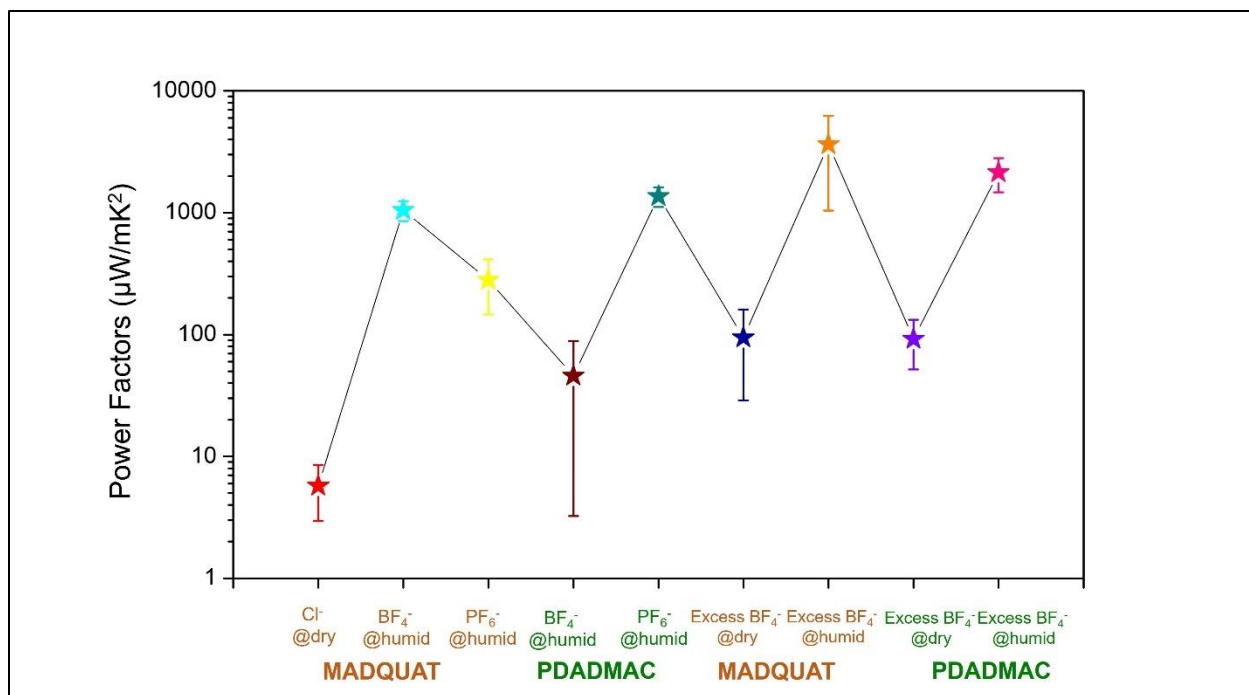

Figure S3: Calculated power factors of selected ionic polymer systems with various anions under dry and humid conditions

N-type ionic thermoelectric polymer system	$\mu W/mK^2$	Ref
poly[K_x(Ni-ett)]	66	Sun et.al. [2]
Hybrids of single-walled carbon nanotubes and PEDOT:$FeCl_4$ treated by tetrakis(dimethylamino)ethylene (TDAE)	1050	Wang et.al [3]
Benzyl viologen-doped CNT webs	3103	An et. al. [4]
TiS_2/[(hexylammonium)$_x$(H_2O)$_y$(DMSO)]	450	Wan et. al. [5]
Mixed ionic-electronic PEDOT:PSS-$CuCl_2$ at 80% RH with 40wt% $CuCl_2$	1700	Kim et. al. [6]
MADQUAT*BF_4^- (40% RH)	1050	Our work (cyan)
MADQUAT*PF_6^- (40% RH)	280	Our work (yellow)
PDADMAC*BF_4^- (40% RH)	46	Our work (wine red)
PDADMAC* PF_6^- (40% RH)	1400	Our work (dark green)
MADQUAT*excess BF_4^- (15% RH)	95	Our work (indigo)
MADQUAT*excess BF_4^- (40% RH)	3600	Our work (orange)
PDADMAC*excess BF_4^- (15% RH)	92	Our work (purple)
PDADMAC*excess BF_4^- (40% RH)	2100	Our work (pink)

Table S7: Power factors of selective recently reported n-type ionic thermoelectric polymer systems in literature and our work. The table provides an overview of the performance of the n-type ionic thermoelectric materials. Since these representative ionic thermoelectric devices are intended for various applications, they would not be evaluated based on the same criteria.

The power factors ($PF = S^2\sigma$) are calculated and plotted only for the ionic polymer systems with measurable ionic conductivity and Seebeck coefficients, as shown in **Figure S3**. It can be seen that the post anion-exchange polymer systems perform much better than any of the chloride-based polymers, MADQUAT ($PF = 5.7 \pm 2.0 \, \mu W/mK^2$) or PDADMAC (Its PF cannot be determined). The following systems showed better stability and reproducible results: MADQUAT* BF_4^-, PDADMAC*PF_6^-, MADQUAT*excess BF_4^- and PDADMAC*excess BF_4^- under humid condition have displayed outstanding power factors of over $1000 \mu W/mK^2$: each of their PFs (respectively) is $1000 \pm 200 \, \mu W/mK^2$, $1400 \pm 250 \, \mu W/mK^2$, $3600 \pm 2600 \, \mu W/mK^2$, $2100 \pm 700 \, \mu W/mK^2$, which far exceeds the PFs of many conjugated polymers as well as inorganics.[7] Out of all post anion-exchange polymers measured at dry condition, only two BF_4^- containing polymer systems have derivable PFs: the PF of MADQUAT*excess BF_4^- is 95 ± 66

$\mu W/mK^2$ and PDADMAC*excess BF_4^- is $92 \pm 40 \, \mu W/mK^2$, approximately 38 times and 23 times, respectively, lower than the same systems measured in humid environment. **Table S7** lists power factors of selective ionic thermoelectrics or mixed-conductor thermoelectrics from literature as well as our work. Notable examples include benzyl viologen-doped CNT webs [4] with a PF of 3103 $\mu W/mK^2$, mixed ionic-electronic PEDOT:PSS- $CuCl_2$ with 40wt% $CuCl_2$ [6]under 80% RH with a PF of 1700 $\mu W/mK^2$ and a hybrid material consisting SWCNTs and PEDOT:$FeCl_4$ treated by TDAE with a PF of 1050 $\mu W/mK^2$. As compared to the generally poor stability in most of the literature examples, the PEDOT:PSS-$CuCl_2$ mixed conductor systems are reported to have over 30 days of stability. In our study, the TE performance of some of the ionic polymer systems are similar to or higher than the abovementioned literature examples and one of them demonstrated a two-week stability. Hence, the ultra-high PFs obtained from our ionic thermoelectric polymer systems under humid condition would be a breakthrough in the field of stable n-type organic thermoelectrics if it could be integrated with an all-ionic power circuit.

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