

Cite this: *J. Mater. Chem. A*, 2023, **11**, 17550

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

Nan (Louise) Chen, Yunjia Song, Taein Lee, Sasikumar Mayarambakam and Howard E. Katz *

Current thermoelectrics technologies are dominated by inorganic materials that can efficiently harvest low-grade waste heat and realize electrical energy conversion; however, their toxicity, rigidity, rare element-based compositions and energy-intensive processing limit their wide applications. Organic thermoelectrics, with the advantages in mechanical flexibility, material abundance and low-temperature/pressure processing, offer solutions to resolve these limitations. Among organic thermoelectrics, the less well-studied ionic polymers possessing intrinsically high Seebeck coefficients are beneficial for charging supercapacitors or batteries, and hence motivated the present study. Its main purpose is to design and develop air-stable n-type all-ionic thermoelectric polymers with suitable ionic conductivity and high Seebeck coefficients. Our initial focus was on two commercially available, water-processable Cl^- based cationic polyelectrolytes, polydiallyldimethylammonium chloride (PDADMAC) and poly(2-(dimethylamino) ethyl methacrylate) methyl chloride quaternary salt (MADQUAT); however, their instability to moisture led to transient, irreproducible Seebeck coefficients. To tackle this challenge, which is in fact quite common among n-type ionic polymers, we adopted a facile, solution-based anion exchange technique by replacing the smaller and unstable Cl^- ions with bulkier, more hydrophobic tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) ions in the polymer systems. We also conducted comparative experimental studies of the thermoelectric behaviors of post-anion exchanged polyelectrolytes under dry (15% relative humidity) and more humid (40% relative humidity) atmosphere. Results have confirmed that the thermoelectric properties of the post-exchange systems are humidity-dependent. In particular, BF_4^- -based MADQUAT and PF_6^- -based PDADMAC showed good ionic conductivity, reliable, reproducible Seebeck coefficients and outstanding power factors at 40% relative humidity with significant improvement in air stability. This opens up opportunities for the further development of all-ionic polymer systems to be applied in a variety of applications, such as sensors, storage, wearable electronics, and batteries.

Received 11th July 2023
Accepted 4th August 2023DOI: 10.1039/d3ta04091g
rsc.li/materials-a

Introduction

The ongoing search for means of climate-friendly and efficient energy conversion has motivated research and development in thermoelectrics (TEs). The unique capability of TE materials to enable the interconversion of heat and electrical energy allowed them to be applied to a wide range of applications including waste heat harvesting, efficient cooling, and refrigeration, and hence provided potential contributions to solving the climate crisis. The performance of a TE material is determined by a figure of merit $ZT = S^2\sigma T/\kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature in Kelvin,

and κ is the thermal conductivity that comes from both electron and phonon transport. The Seebeck coefficient (S) quantifies the strength of the Seebeck effect, the voltage generated in response to a thermal gradient. S is expressed as $S = \Delta V/\Delta T$ where ΔV is the electrical potential generated and ΔT is the thermal gradient. Conventional TE materials are predominately inorganic semiconductors. The most developed commercialized TE materials, bismuth telluride (Bi_2Te_3) compounds, including their doped forms and the forms with altered stoichiometry, exhibit a ZT of 1–1.5.^{1,2} Despite their great performance, the major issues with inorganic compound semiconductors that hindered further development are their toxicity, rigidity, rare element content, and energy-intensive fabrication processes. Emerging organic semiconductors have attracted great interest due to their mechanical flexibility, material abundance (C, H, O, S, N), facile processing and lower operating temperatures. A well-studied class of organic

Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21210, USA. E-mail: hekatz@jhu.edu

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ta04091g>

semiconductors are the π -conjugated polymers that have been developed for devices for a wide range of applications spanning wearable electronics and photovoltaics.³ One of their characteristic structures is their conjugated core motifs that enable charge transport.^{4,5} There are a great many reported examples of p- and n-type organic thermoelectrics (OTE) such as poly(ethylenedioxythiophene) (PEDOT), poly(3-hexylthiophene) (P3HT), [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and perylene diimide (PDI).³

Ionically conductive polymers are another type of organic material for thermoelectric energy conversion, based on the thermally-induced directional ion migration.⁶ The Soret effect, also known as thermophoresis, describes the mass transport phenomenon of mobile particles in a mixture induced by temperature gradients, which has been applied to both liquid and solid-state polyelectrolyte systems, which are essentially ion-based polymers.^{7,8} In the ionic polymer systems, the voltage is created by a combination of kinetic and thermodynamic factors, the former being the temperature-dependent diffusion coefficients in the short term and the latter being the temperature-dependent stability of ionic polymer structure in the long term.⁹ Theoretically, the current generated by the thermally induced ionic motion is expressed as the following,^{10,11}

$$J_{\pm} = -D_{\pm} \left(\nabla n_{\pm} + 2n_{\pm} \alpha_{\pm} \frac{\nabla T}{T} \mp n_{\pm} \frac{eE}{k_B T} \right).$$

In the equation, D is the Einstein diffusion coefficient, n ion concentration, α is the Soret coefficient, k_B is the Boltzmann constant, e is the elemental charge, and T is the absolute temperature (K), E is the thermoelectric field that is proportional to the applied ∇T . Under steady-state conditions ($J_{\pm} = 0$) and the internal static balance where electric fields from the three terms of the equation compensate each other, the thermopower (S) can be expressed as $S = \frac{(\alpha_+ - \alpha_-)}{k_B/e}$. The equation explains that for ionic conductors, the Soret coefficient, equivalent to the ionic Seebeck coefficient, is attributed to the difference between the thermal distribution of anions and cations. Modern computational tools have been used successfully to analyze and calculate the Soret coefficients of simple atomic salts based on the non-equilibrium molecular dynamics, but predicting the Soret coefficients of ion-based polymers, is far more challenging.^{7,12,13} A helpful simplification arises in systems where the thermodiffusion coefficients of the anions and cations are highly unequal, resulting in a frequently large Seebeck coefficient that can be largely attributed to just one of the ions.¹² Therefore, ionic polymers that comprise nearly immobile cationic/anionic long polymer backbone and their free counter anions/cations that can move much more easily, without complications from hole or electron transport, are likely to generate a large potential difference in response to a heat gradient.

Compared to conjugated polymers, ionic polymers for TE applications are much less studied due to a number of factors.¹⁴ Generally ionic polymers with intrinsically high Seebeck coefficients have correspondingly lower ionic conductivity ($\sim 10^{-1}$ to

10^{-4} S cm⁻¹).⁶ In addition, ionic thermoelectrics cannot produce continuous power because ions do not generally enter the external electrical circuit (making the traditional $S^2\sigma$ power factor inappropriate). However, the ions that are arranged at the electrode surface would result in built-up static voltage, which can be coupled to an electronic circuit where it can be used for charging supercapacitors¹⁵⁻¹⁷ and batteries¹⁸ as well as being used for heat flux sensing.¹³ Furthermore, it is also accepted that effective thermoelectric modules require both p- and n-legs. Literature has reported many p-type polyelectrolytes with ultra-high Seebeck values, such as hydrated polystyrene sulfonic acids (+8 mV K⁻¹),¹⁹ polystyrene sulfonate sodium (up to +4 mV K⁻¹)¹⁷ and ionic liquid polyethylene glycol (+11 mV K⁻¹).¹⁵ There are fewer n-type ionic polymer systems. One of them is the n-type Ag-Nafion with a negative Seebeck coefficient of -1.5 mV K⁻¹ that is generated by an electrochemical reaction based on a thermogalvanic effect.²⁰ N-type ionic thermoelectric polymers based on the Soret effect have not been sufficiently explored and studied.¹³ Hence, developing n-type ionic polymer systems to enable a complete, robust and effective technology for energy conversion and storage applications was our main research direction. In this study, we aimed to design n-type ionically conductive polymeric systems with improved air stability over a prior analogue¹⁶ through a facile solution-processing technique under moderate environmental conditions.

We began our study with two chloride (Cl⁻) based anionic polymers, polydiallyldimethylammonium chloride (PDADMAC) and poly(2-(dimethylamino)ethyl methacrylate) methyl chloride quaternary salt (MADQUAT). These polymers are commercially available, water-processable, environmentally-friendly and have been primarily used in flocculation for water treatment. Their chemical structures as shown in Fig. 1. Cl⁻ ions are the predominant carriers in the polymeric systems that contribute to the ionic conductivity and the n-type Seebeck behavior. However, literature^{12,21} as well as our previous findings⁹ show that properties associated with chloride ions are extremely unstable in air due to their sensitivity to moisture and are dependent on the humidity level. These two polymers are also not stable in an inert environment probably because of their naturally slow polymer relaxation, which commonly exists in most polyelectrolyte gels and solutions.²² These factors make it difficult to obtain consistent conductivity and reliable Seebeck coefficients. In attempt to achieve more stable systems, we

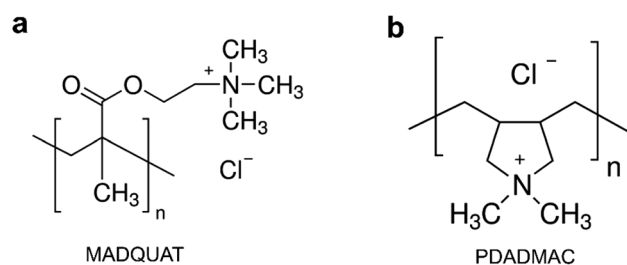


Fig. 1 Chemical structures of two cationic polyelectrolytes (a) poly(2-(dimethylamino)ethyl methacrylate) methyl chloride quaternary salt (MADQUAT) and (b) polydiallyldimethylammonium chloride (PDADMAC).

decided to use the larger sized anions, tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) to replace Cl^- as these polyfluoro ions are more hydrophobic, which make the systems less prone to interact with moisture in the air. It is demonstrated in other studies that PF_6^- -based ionic liquids are chemically stable at moderate temperature and pH levels.²³ Therefore, we conducted a systematic study of the thermoelectric properties of the two ionic polymers, concentrating on their post-anion exchanged forms under dry and humid conditions.

Experimental

Chloride-based PDADMAC and MADQUAT thermoelectric film preparation

Polydiallyldimethylammonium chloride (PDADMAC) (20 wt% in water), poly(2-(dimethylamino)ethyl methacrylate) methyl chloride quaternary salt (MADQUAT), silver tetrafluoroborate (AgBF_4 , 98%), tetrakis (acetonitrile) copper(i) hexafluorophosphate ($[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$, 97%), tetrahydrofuran (THF, anhydrous, >99.9%), and methanol (CH_3OH , 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 thermoelectric sample preparation process was done in an N_2 -filled environment. The two chloride-based polymers were fully dissolved in methanol by heating up the solution (30 mg mL^{-1}) on a hot plate at 50°C for one hour. The polymer ink was spin-coated onto indium tin oxide (ITO)

patterned glass substrates followed by annealing the samples at 100°C for an hour. The thicknesses 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.

$\text{BF}_4^-/\text{PF}_6^-$ - based ionic polymer thermoelectric film preparation *via* anion exchange reaction

To ensure a complete anion exchange, the weights of AgBF_4 and $[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$ as exchange precursors are calculated based on the 1 : 1 molar ratio between $\text{BF}_4^-/\text{PF}_6^-$ and Cl^- . The sample preparation process was also done in an N_2 -filled environment. AgBF_4 was dissolved in methanol in a separate vial – instant dissolution was observed. $[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$ was dissolved in methanol in another vial and the solution was heated for 1 hour to allow for complete dissolution. As illustrated in Fig. 2, each polymer solution was mixed with AgBF_4 and $[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$ solutions, respectively, and cloudy white precipitates formed in each post-mixing solution. The white precipitates were filtered out using a poly(vinylidene fluoride) (PVDF) filter and a clear colorless solution was obtained. The filtered solution was drop-cast onto ITO patterned glass substrates. 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 $\text{MADQUAT}*\text{BF}_4^-$, $\text{MADQUAT}*\text{PF}_6^-$, $\text{PDADMAC}*\text{BF}_4^-$ and $\text{PDADMAC}*\text{PF}_6^-$ films are measured to be 135 nm, 155 nm, 180 nm and 210 nm, respectively. Samples were kept in the

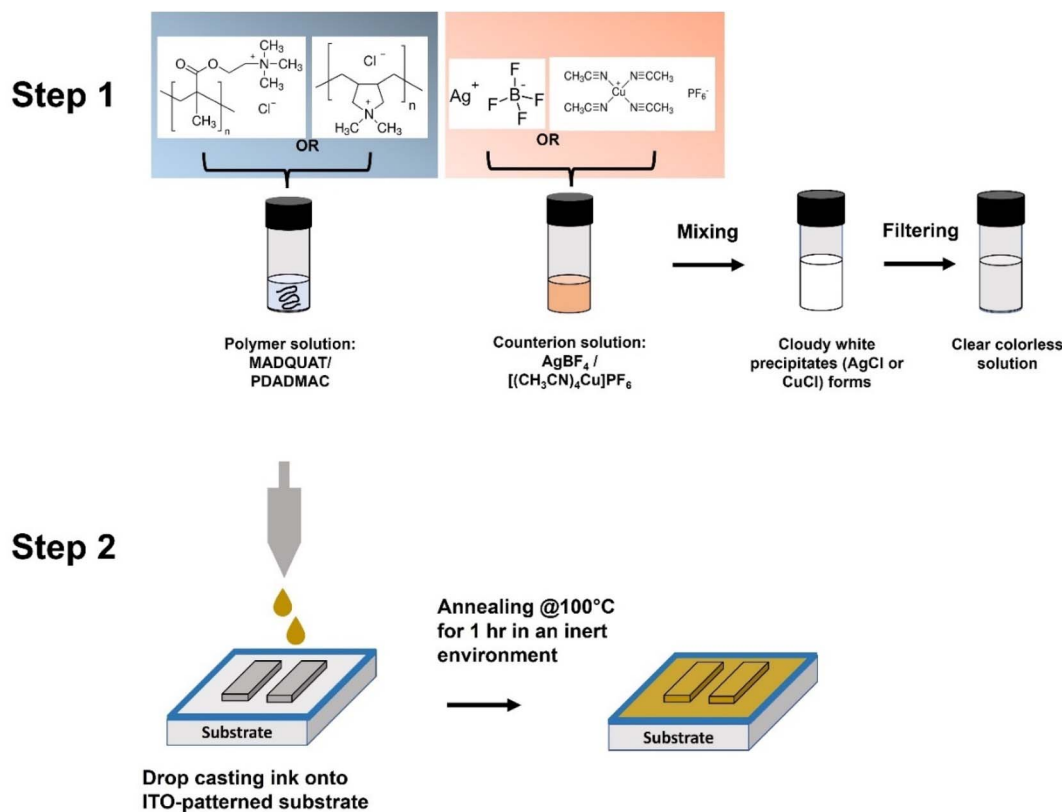


Fig. 2 Schematic illustration of two major procedural steps for the anion exchange reaction.

glovebox before being taken out for thermoelectric measurements. Additional experimental details can be found in Section 1 of the ESI.†

Materials characterizations

The ionic conductivities were obtained using the linear four-point probe resistance measurement set-up, and the Seebeck coefficients were obtained using small Peltier units to induce temperature changes and an electrometer to measure the induced TE voltage created by the temperature gradients across the samples as shown in Fig. S1.† Due to the sensitivity of the samples, the thermoelectric measurements were done within the same day of sample preparation in an environment with controlled humidity. Additional characterizations included scanning electron microscope (SEM), electron-dispersive

spectroscopy (EDX) and profilometer. Details about these characterization techniques can be found in Sections 2 and 3 of the ESI.†

Results and discussion

Equimolar ion-exchanged polymers

The anion exchange mechanisms for both chloride-based polymers are illustrated in Fig. 3. As two exchange precursors were dissolved in methanol, solid AgBF_4 dissociated into Ag^+ and BF_4^- ions while $[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$ dissociated into Cu^+ , PF_6^- and acetonitrile ligands. Each polymer solution was mixed with each exchange solution; a total of four combinations were made, shown as 3a–d. The positively charged metal ions bind with the chloride ions and form AgCl and CuCl , which were

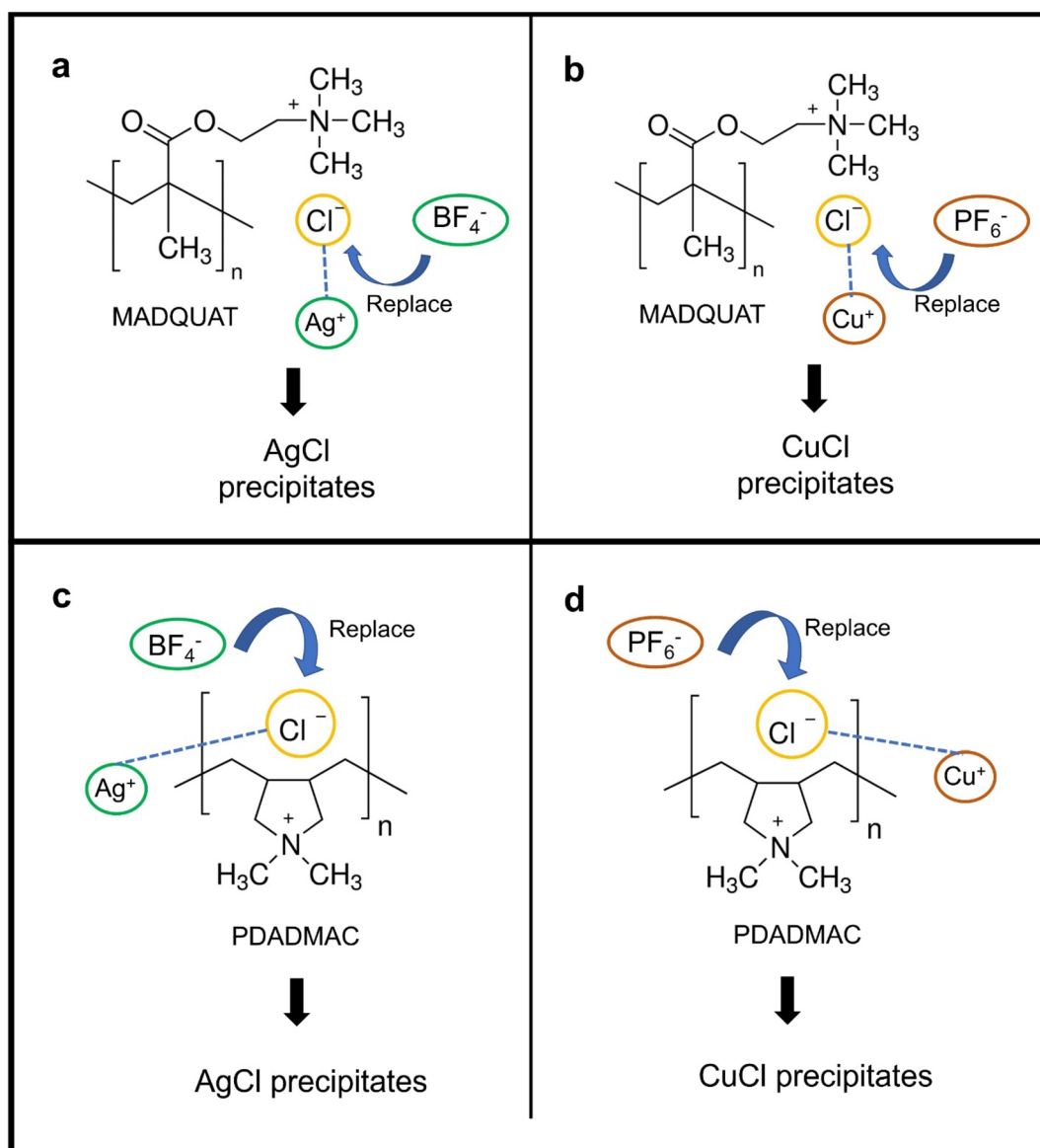


Fig. 3 Anion exchange mechanism of Cl^- ions being exchanged with BF_4^- and PF_6^- ions for both MADQUAT and PDADMAC polymers. Cl^- ions bind with Ag^+ and Cu^+ to form white precipitates which was later filtered out. The backbone of the polymer chains remained the same except that the major anions were BF_4^- and PF_6^- ions after the exchange reaction.

precipitated out instantly from the mixing solutions. In the post-exchange PF_6^- containing polymer systems, the acetonitrile ligands were removed during the annealing process. The anion exchange reaction only exchanged the Cl^- with BF_4^- or PF_6^- meaning that the positively charged main polymer chains remained the same.

Fig. 4 and Table 1 summarize the overall thermoelectric properties of the Cl^- -based polymers and the post anion exchanged BF_4^- and PF_6^- based polymers. All the samples were prepared as solid-state films in the glovebox and went through an annealing process at 100°C to remove the solvent and potentially any water. The samples themselves should have contained very little water in an inert environment. It is expected that they would absorb small amounts of water in air due to their hygroscopicity. Hence, it is worth studying how humidity affects their ionic transport mechanism. We exposed our samples to both dry (15% relative humidity) and humid (40% relative humidity) atmosphere and measured their

thermoelectric properties simultaneously. A discernible difference between thermoelectric properties obtained at 15% relative humidity and at 40% relative humidity for the same type of polymer system was found. Both pristine MADQUAT and PDADMAC exhibit relatively low conductivity at 15% relative humidity. The conductivities of MADQUAT and PDADMAC are $5.1 \times 10^{-4} \pm 1.8 \times 10^{-4} \text{ S cm}^{-1}$ and $3.1 \times 10^{-3} \pm 1.5 \times 10^{-3} \text{ S cm}^{-1}$, respectively, under dry condition. An increase in the ionic conductivities of the two polymers was observed as humidity increased to 40%. As Cl^- is light and very hygroscopic, it is likely that the moisture is absorbed at the polymer film surface, increasing Cl^- mobility and possibly introducing protons into the systems that contributed to ionic conductivity at 40% relative humidity.

The Seebeck coefficient of MADQUAT is negative with a magnitude of $-10600 \pm 7200 \mu\text{V K}^{-1}$ at a 15% humidity level. However, the n-type Seebeck behavior of MADQUAT is transient; we observed that the system failed to reproduce negative S

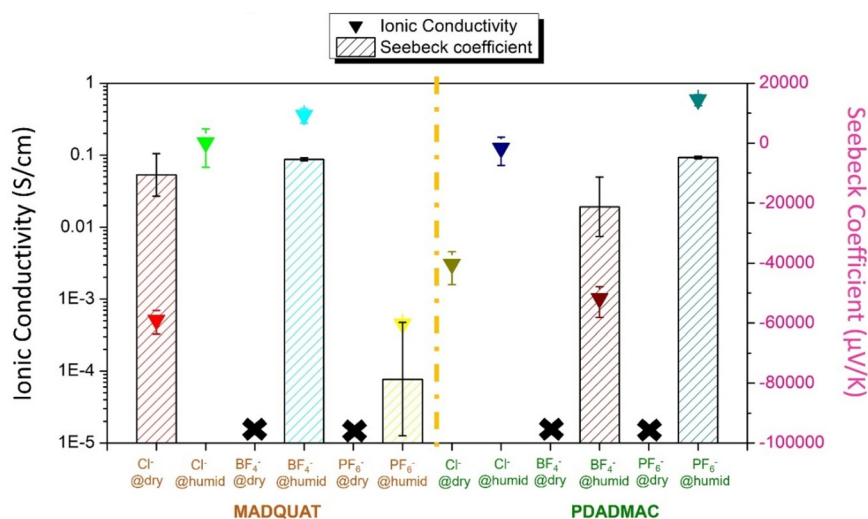


Fig. 4 Thermoelectric properties of the MADQUAT and PDADMAC polymers as well as their post-exchanged systems with BF_4^- and PF_6^- (exchange molar ratio = 1 : 1) under dry and humid conditions; dark cross indicates unmeasurable ionic conductivity and Seebeck coefficient for that specific condition.

Table 1 Numerical representation of Fig. 4; tabular data of thermoelectric properties of the MADQUAT and PDADMAC polymers and their post anion-exchange systems (exchange molar ratio = 1 : 1). At least 12 devices were fabricated and tested for each polymer system at each humidity condition to report the average and standard deviation. N/A means that the property cannot be obtained or determined

Polymer	Counterion	Humidity	Conductivity (S cm^{-1})	Seebeck coefficient ($\mu\text{V K}^{-1}$)
MADQUAT	Cl^-	Dry	$5.1 \times 10^{-4} \pm 1.8 \times 10^{-4}$	-10600 ± 7200
		Humid	0.15 ± 0.08	N/A
	BF_4^-	Dry	N/A	N/A
		Humid	0.360 ± 0.081	-5400 ± 500
	PF_6^-	Dry	N/A	N/A
		Humid	$4.53 \times 10^{-4} \pm 6 \times 10^{-6}$	-79000 ± 19000
PDADMAC	Cl^-	Dry	$3.1 \times 10^{-3} \pm 1.5 \times 10^{-3}$	N/A
		Humid	0.125 ± 0.053	N/A
	BF_4^-	Dry	N/A	N/A
		Humid	$1.02 \times 10^{-3} \pm 4.7 \times 10^{-4}$	-21200 ± 9800
	PF_6^-	Dry	N/A	N/A
		Humid	0.59 ± 0.10	-4800 ± 440

values after being left in air for 5–10 minutes. The S value of MADQUAT reported is the average of the very first set of Seebeck measurements of every fresh sample removed from the glovebox. On the other hand, a Seebeck coefficient cannot be obtained for PDADMAC, giving an unpredictable sign under both dry and humid conditions. Our previous publication reported negative but also transient S values ($S = 0.001\text{--}0.005\text{ V K}^{-1}$ in dry environment)⁹ for PDADMAC where the polymer was processed in water solvent under ambient air instead of in methanol inside the glovebox. We have also previously observed that PDADMAC showed either positive S values or unusable S values with poor ΔV vs. ΔT fitting after leaving samples in ambient air. Additionally, Kim *et al.* has reported extremely large and positive thermopower for PDADMAC ($S = 19\text{ mV K}^{-1}$) under a humid condition.¹⁶ It had been a challenge to explain the reason for not being to obtain measurable, reliable Seebeck coefficients as the tandem thermodiffusion of protons and Cl^- ions exists in these two polycation systems. One of the explanations provided by Kim *et al.* is that the main contribution of the thermal voltage in the ionic polymer is the different water up-taking ability at the hot and cold side of PDADMAC leading to different Cl^- dissociation, rather than the thermodiffusion of Cl^- .¹⁶ In short, the key takeaway is that the unpredictable Seebeck sign and unstable thermoelectric properties add great difficulty in applying the Cl^- based ionic polymers to real world thermoelectric applications, which led us to the study of BF_4^- and PF_6^- ions.

As the BF_4^- and PF_6^- are larger in size and more hydrophobic than Cl^- , the post-anion-exchange polymeric systems are so highly resistant that they almost act like insulators under a dry condition. Reliable Seebeck coefficients were difficult to obtain considering the almost insulating nature of the samples. However, it is again noticeable that the thermoelectric properties of the systems are humidity-dependent. Under 40% relative humidity, the MADQUAT* BF_4^- system works quite well, giving

an ionic conductivity of $5.1 \times 10^{-4} \pm 1.8 \times 10^{-4}\text{ S cm}^{-1}$ and a negative Seebeck coefficient of $-5400 \pm 500\text{ }\mu\text{V K}^{-1}$ with particularly high linearity in ΔV vs. ΔT plots as shown in Fig. 5(a). The MADQUAT* PF_6^- at 40% humidity shows much lower ionic conductivity ($\sigma = 4.53 \times 10^{-4} \pm 6 \times 10^{-6}\text{ S cm}^{-1}$) and displays a negative Seebeck coefficient with an enormous magnitude ($S = -79000 \pm 19\,000\text{ }\mu\text{V K}^{-1}$). We also observe that PDADMAC* BF_4^- and * PF_6^- possess reproducible thermoelectric properties in a more humid atmosphere (40% relative humidity) in contrast to the Cl^- form. Particularly, PDADMAC* PF_6^- is more conductive compared to its BF_4^- form with an ionic conductivity of $0.59 \pm 0.10\text{ S cm}^{-1}$ and Seebeck coefficient of $-4800 \pm 440\text{ }\mu\text{V K}^{-1}$. Its Seebeck value also has outstanding linearity in ΔV vs. ΔT plots as shown in Fig. 5(b). At a higher humidity level, diffused water in the ionic polymers associates with the solvated ions and perturbs the Soret effect, arising from the thermodiffusion of ions.¹² Furthermore, we have assessed our results by comparing them with literature references. There are several examples of BF_4^- and PF_6^- based systems, mostly ionic liquids, reported in literature, such as [EMIn][BF_4^-] ($S = -0.186\text{ mV K}^{-1}$),²⁴ [BMIm][BF_4^-] ($S = -0.609\text{ mV K}^{-1}$),²⁵ [BMIm][PF_6^-] ($S = -0.618\text{ mV K}^{-1}$),²⁶ [HMIm][PF_6^-] ($S = -1.005\text{ mV K}^{-1}$)²⁶ and [OMIm][PF_6^-] ($S = -1.069\text{ mV K}^{-1}$),²⁶ all of which have negative Seebeck coefficients with magnitudes within a similar, reasonable range compared to what we obtained. The differences in ionic conductivity among the four combinations of polymer and counterion could be influenced by multiple factors, *e.g.* different distances, orientations, and charge densities of the fluorine atoms that could change their tendency to be attracted to nitrogens or to water molecules, and the different steric environments around the nitrogens in the two polymers.

Among all the post-exchange polycation samples, MADQUAT* BF_4^- and PDADMAC* PF_6^- are the two better-performing systems which produce reliable conductivity

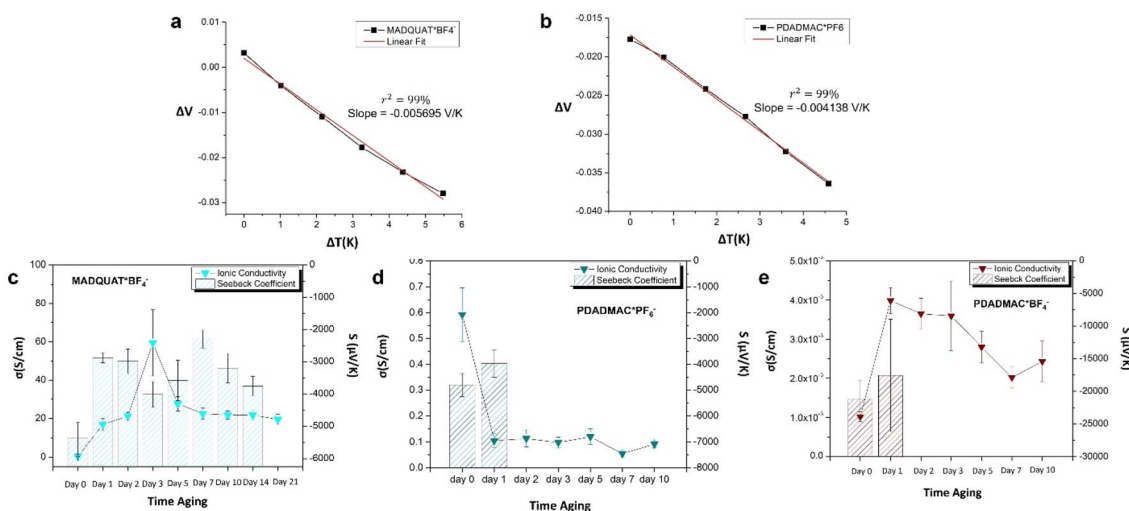


Fig. 5 Linear relationship of ΔT vs. ΔV for two well-behaved polymer systems (a) PDADMAC* PF_6^- and (b) MADQUAT* BF_4^- ; note that (a) and (b) show S values directly obtained from the Seebeck measurement set-up, not the averaged S values for these two ionic polymer systems. Stability test of thermoelectric performance of (c) MADQUAT* BF_4^- within three weeks and (d) PDADMAC* PF_6^- & (e) PDADMAC* BF_4^- within 10 days.

measurements as well as consistent n-type Seebeck coefficients with reasonable magnitudes ranging from -1000 to $-9000 \mu\text{V K}^{-1}$. To evaluate the stability of the BF_4^- and PF_6^- ion-containing polymers, we conducted a stability test by leaving the samples in air under 40–50% relative humidity for extended times, and their ionic conductivity and Seebeck coefficients were measured after each time interval. MADQUAT* BF_4^- demonstrated the best stability out of all other polycation combinations. As shown in Fig. 5(c), MADQUAT* BF_4^- showed an increase in ionic conductivity along with a decrease in the Seebeck coefficient after day 0, which may be attributed to the fact that the samples continued to absorb moisture from air over time. However, MADQUAT* BF_4^- overall produced reliable, measurable and reasonably consistent Seebeck coefficients for a span of two weeks. Even though the S was no longer

measurable after three weeks, the samples still remained conductive. The other better-performing polycation, PDADMAC* PF_6^- was able to produce measurable, reliable and comparable S values in the second day (day 1) but the S behavior started to become inconsistent and eventually unmeasurable after two days as shown in Fig. 5(d). However, the samples showed a slight decrease in σ but still stayed significantly conductive for a much longer period of time (up until 10 days of our stability study). The stability of the much less conductive PDADMAC* BF_4^- was also examined. After day 0, the n-type Seebeck behavior was not changed as most S values were negative, but the Seebeck values varied considerably as reflected by the much larger error bar on day 1 than in day 0 shown in Fig. 5(e). The σ of the samples stayed within the same order of magnitude within 10 days of our stability measurements. Lastly,

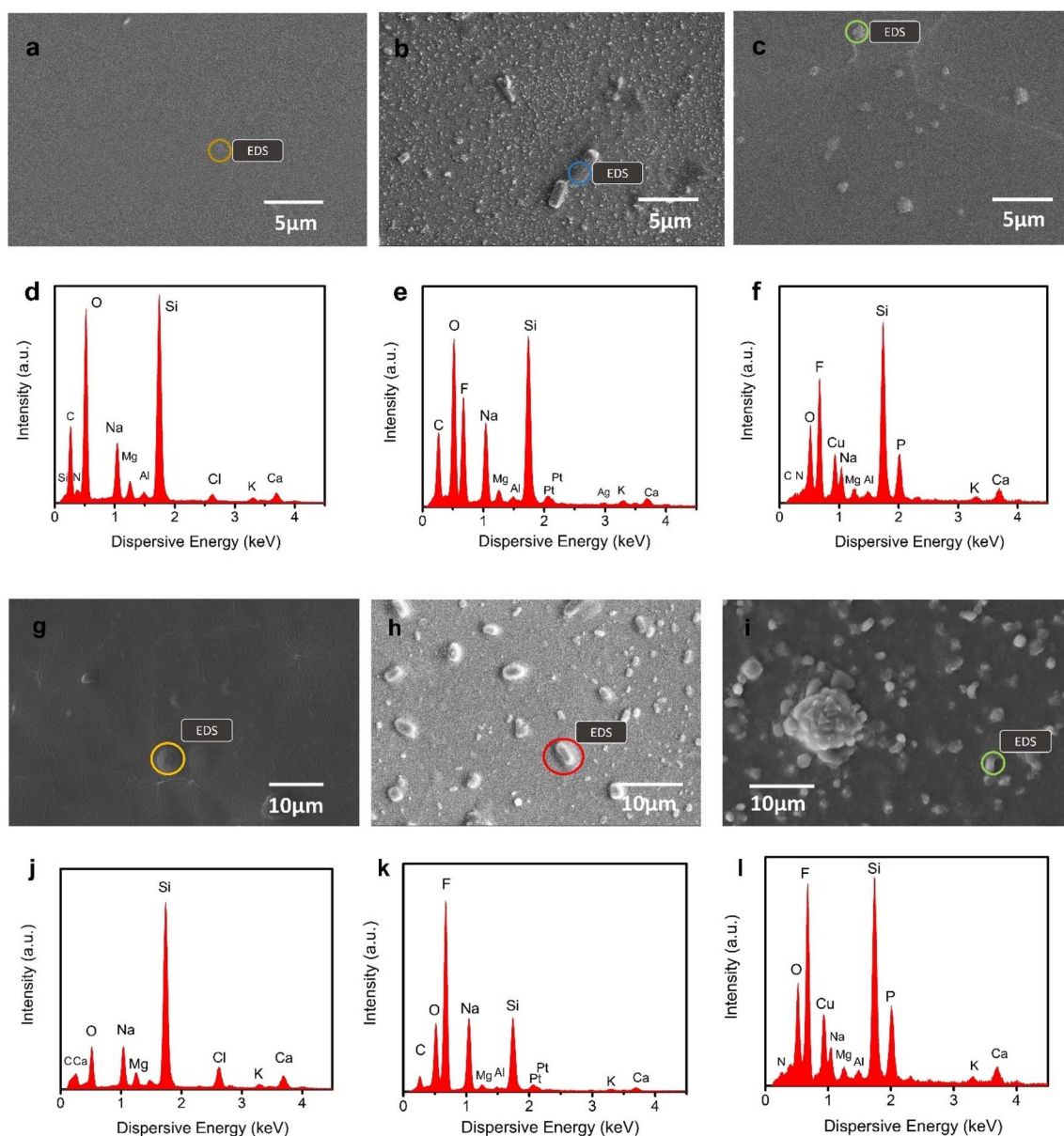


Fig. 6 Scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDX) of (a) and (d): MADQUAT, (b) and (e): MADQUAT* BF_4^- , (c) and (f): MADQUAT* PF_6^- , (g) and (j): PDADMAC, (h) and (k): PDADMAC* BF_4^- , (i) and (l): PDADMAC* PF_6^- .

for the least conductive MADQUAT*PF₆⁻, as expected, the samples became resistant with unmeasurable Seebeck coefficients the next day under 40% relative humidity. Overall, we have successfully transformed the original Cl⁻ based polymers that are not chemically stable at all (stability time scale within 5–10 minutes) to new polymer systems that shows largely improved stability (stability time scale >24 h, with one composition lasting two weeks) where we can obtain meaningful thermoelectric performance with good conductivity and reproducible Seebeck coefficients, which is the key takeaway from the stability study.

There has been very little work on solid state electronic properties of ionic polymers and the majority of the ionic thermoelectrics reported in literature have poor stability under ambient conditions.^{12,27,28} Therefore, the novelty of our work is that the simple ion exchange approach that we are introducing here provided a route to more stable all-ionic thermoelectric polymers than had been reported before. Furthermore, we employed readily available polymer structures as starting materials, and as will be seen in a later section, further tuning of properties is possible by fine adjustments of the ionic stoichiometry.

An additional parameter that could be calculated from our data is the power factor. While some of ours are numerically high, as stated above, they would not be applicable to electronically conductive systems. For readers' reference, a brief tabulation of power factors from this work and the literature is presented in the ESI.†

To determine whether or not the anion exchange was complete, electron dispersive X-ray spectroscopy (EDX) was performed on the pre- and post-anion exchanged polymer samples. For polymer samples it is ideal to coat them with metals or any conductive materials before EDX, otherwise sample burning would occur; therefore, in our case, MADQUAT*BF₄⁻ and PDADMAC*BF₄⁻ were coated with Pt as shown on Fig. 6(e) and (k), and the rest of the samples were coated with Cr to avoid having conflicting peaks with P. The Cl peaks located at 2.6 eV can be seen in the pre-anion-exchange polymers and disappeared after the exchange as we expected, confirming the completion of the anion exchange. For the BF₄⁻ exchanged polymer samples, the F peak appeared at 0.6 eV, but B is too light to be picked up by EDX. For the PF₆⁻ based

polymer samples, P and F peaks emerged at 2.013 eV and 0.6 eV, respectively. Fig. 6(e) and (l) show that there was a trace amount of Ag residue in MADQUAT*BF₄⁻ as well as a small amount of Cu in PDADMAC*PF₆⁻ but consistent n-type Seebeck behavior from both samples would be consistent with the Ag and Cu elements not having any significant impact on their thermoelectric properties that were dominated by the BF₄⁻ and PF₆⁻. The rest of the elements such as O, Ca, Mg, Na, K and Al come from the glass substrates. Tables S1–S6† showcase the detailed elemental breakdown in weight% and atomic% for each ion-polymer system.

Ion exchange with excess counterions

The thermoelectric properties of post-exchange polymeric systems with an excess of exchanged counterions were also studied. We added 10 wt% (also equivalent to 10 mol%) more AgBF₄ and [(CH₃CN)₄Cu]PF₆ into each of the polymers and measured their properties under dry and humid conditions. Results in Table 2 and Fig. 7 show that BF₄⁻ ions work better than the PF₆⁻ ions for the same type of polymer chain. The MADQUAT*-excess BF₄ system exhibits an ionic conductivity of 0.099 ± 0.017 S cm⁻¹ and consistent Seebeck coefficients ($S = -3100 \pm 1100 \mu\text{V K}^{-1}$) under dry conditions, in contrast to what we observed for the MADQUAT*BF₄ system with a one-to-one exchange ratio as discussed previously. This can be explained by the fact that there are more mobile BF₄⁻ ions present, leading to measurable, consistent ionic conductivity and Seebeck coefficients under dry conditions. Humidity has contributed to the increase in the ionic conductivity of the same system ($\sigma = 3.7 \pm 2.0 \text{ S cm}^{-1}$) but not so much difference in the Seebeck coefficients ($S = -3140 \pm 1120 \mu\text{V K}^{-1}$). Similarly, at 15% humidity level, 10 wt% more BF₄⁻ has made the BF₄⁻-based PDADMAC system conductive with an ionic conductivity of $8.9 \times 10^{-2} \pm 1.8 \times 10^{-2} \text{ S cm}^{-1}$ and a reliable negative Seebeck coefficient of $-3200 \pm 700 \mu\text{V K}^{-1}$. This is again consistent with BF₄⁻ ions being the dominant carriers in the post-exchange system, despite the existence of Ag⁺ ions. At 40% humidity level, the ionic conductivity of the PDADMAC*BF₄ has increased to $1.7 \pm 1.4 \text{ S cm}^{-1}$; however, the Seebeck coefficient remains about the same.

On the other hand, PF₆⁻ ion-containing polymers behave differently compared to the BF₄⁻ ion-containing polymers. With

Table 2 Thermoelectric properties of post-anion-exchanged MADQUAT and PDADMAC with excess BF₄⁻ and PF₆⁻. At least 12 devices were made and measured to report the average ionic conductivity and Seebeck coefficient at each ion-polymer combination at each humidity condition

Polymer	Counterion (10 wt% in excess)	Humidity	Conductivity (S cm ⁻¹)	Seebeck coefficient (μV K ⁻¹)
MADQUAT	BF ₄ ⁻	Dry	$9.9 \times 10^{-2} \pm 1.7 \times 10^{-2}$	-3100 ± 1100
	BF ₄ ⁻	Humid	3.7 ± 2.0	-3140 ± 1120
	PF ₆ ⁻	Dry	N/A	N/A
	PF ₆ ⁻	Humid	N/A	N/A
PDADMAC	BF ₄ ⁻	Dry	$8.9 \times 10^{-2} \pm 1.8 \times 10^{-2}$	-3200 ± 700
	BF ₄ ⁻	Humid	1.7 ± 0.49	-3550 ± 550
	PF ₆ ⁻	Dry	N/A	N/A
	PF ₆ ⁻	Humid	N/A	N/A

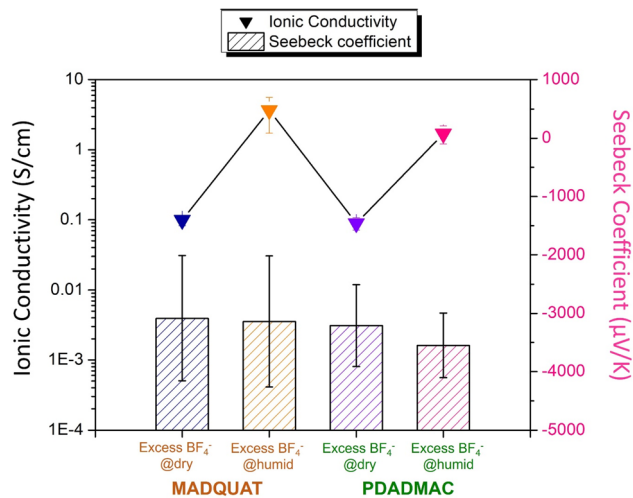


Fig. 7 Data visualization of well-behaved ionic polymer systems from Table 2. Ionic conductivity and Seebeck coefficient of BF₄⁻ based MADQUAT and PDADMAC with excess BF₄⁻ each measured in dry and humid environments.

excess of [(CH₃CN)₄Cu]PF₆ being added into MADQUAT and PDADMAC, the post-exchange systems are not conductive under the dry condition shown in Table 2. This is similar to the results of post-exchange polymer systems with one-to-one exchange ratio at the same humidity level. It can be seen that the excess amount of PF₆⁻ ions present in the system cannot compensate for the ionic conductivity inhibition due to the bulky structure of PF₆⁻ resulting in the impediment of ionic movement across the polymer chains. Furthermore, a more humid environment does not contribute much to increasing the ionic conductivity or obtaining good Seebeck coefficients, which is opposite to what we observed for PDADMAC*PF₆⁻ (at 1 : 1 exchange ratio). It is suspected that the extra 10 wt% of Cu⁺ ions being added introduce barriers or aggregation, further hindering the movement of PF₆⁻ ions. In contrast, Ag⁺ ions seem to have less infringement in the ionic movement of BF₄⁻ ions, so even if 10 wt% more AgBF₄ is added to the pristine polymer, the effect of excess BF₄⁻ ions dominates. Another possible explanation for humidity failing to increase the conductivity of excess PF₆⁻ containing polymer systems is that the moisture is more prone to react with excess Cu⁺ ions and form copper hydroxides than creating percolation channels in the polymers. However, further experiments would need to be performed to understand the carrier transport in this more complicated system.

Conclusions

We have successfully designed and developed relatively air-stable n-type ionic thermoelectric polymers based on the chloride based MADQUAT and PDADMAC polymers. The issue of stability in MADQUAT and PDADMAC polymers, also common among most polyelectrolytes, was ameliorated by exchange the light-weight, hygroscopic Cl⁻ ions with BF₄⁻ and PF₆⁻ ions that are larger in size and more hydrophobic. A comparative humidity test has shown that as expected, the resulting polymer

systems behaved poorly under dry condition but showed significantly improved thermoelectric behavior at a higher humidity level. More specifically, MADQUAT*BF₄⁻ and PDADMAC*PF₆⁻ have demonstrated high ionic conductivity and consistent, reproducible Seebeck coefficients at 40% relative humidity. Another important and surprising discovery is that both MADQUAT*BF₄⁻ and PDADMAC*BF₄⁻ with excess BF₄⁻ exhibit good thermoelectric performance under both dry and humid conditions.

We acknowledge that to integrate our ionic thermoelectric polymers into real applications such as energy conversion devices, stability on a much larger time scale is needed, and remains a goal of our future work. Also, because conductivities seemed to be more stable than Seebeck coefficients, possible origins of Seebeck coefficient instabilities, such as contact effects or surface voltages, will need to be probed. However, our study expands the library of n-type ionic thermoelectric polymers showing definitive Soret effects and represents a new pathway towards ionically conductive polymers suitable for flexible electronics devices, sensors and battery chargers for energy applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors acknowledge the financial support from the National Science Foundation, Division of Chemistry, Grant number 2107360 and the Johns Hopkins University Department of Materials Science and Engineering.

References

- H. Mamur, M. R. A. Bhuiyan, F. Korkmaz and M. Nil, *Renewable Sustainable Energy Rev.*, 2018, **82**, 4159–4169.
- Z. Soleimani, S. Zoras, B. Ceranic, S. Shahzad and Y. Cui, *Sustainable Energy Technol. Assess.*, 2020, **37**, 100604.
- B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyk and R. A. Segalman, *Nat. Rev. Mater.*, 2016, **1**, 16050.
- V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Brédas, *Chem. Rev.*, 2007, **107**, 926–952.
- J. Mei and Z. Bao, *Chem. Mater.*, 2014, **26**, 604–615.
- X. Wu, N. Gao, H. Jia and Y. Wang, *Chem.-Asian J.*, 2021, **16**, 129–141.
- R. Piazza, *Soft Matter*, 2008, **4**, 1740–1744.
- D. Niether and S. Wiegand, *J. Phys.: Condens. Matter*, 2019, **31**, 503003.
- N. Chen, J. Pino and H. E. Katz, *Appl. Phys. Lett.*, 2021, **119**, 060503.
- A. Majee and A. Würger, *Phys. Rev. E*, 2011, **83**, 061403.
- A. Majee and A. Würger, *Phys. Rev. Lett.*, 2012, **108**, 118301.
- D. Zhao, A. Würger and X. Crispin, *J. Energy Chem.*, 2021, **61**.
- D. Zhao, A. Martinelli, A. Willfahrt, T. Fischer, D. Bernin, Z. U. Khan, M. Shahi, J. Brill, M. P. Jonsson, S. Fabiano and X. Crispin, *Nat. Commun.*, 2019, **10**, 1093.

- 14 Y. He, Q. Zhang, H. Cheng, Y. Liu, Y. Shu, Y. Geng, Y. Zheng, B. Qin, Y. Zhou, S. Chen, J. Li, M. Li, G. O. Odunmbaku, C. Li, T. Shumilova, J. Ouyang and K. Sun, *J. Phys. Chem. Lett.*, 2022, **13**, 4621–4627.
- 15 D. Zhao, H. Wang, Z. U. Khan, J. C. Chen, R. Gabrielsson, M. P. Jonsson, M. Berggren and X. Crispin, *Energy Environ. Sci.*, 2016, **9**, 1450–1457.
- 16 S. L. Kim, J.-H. Hsu and C. Yu, *Org. Electron.*, 2018, **54**, 231–236.
- 17 H. Wang, D. Zhao, Z. U. Khan, S. Puzinas, M. P. Jonsson, M. Berggren and X. Crispin, *Adv. Electron. Mater.*, 2017, **3**, 1700013.
- 18 N. S. Hudak and G. G. Amatucci, *J. Electrochem. Soc.*, 2011, **158**, A572.
- 19 S. L. Kim, H. T. Lin and C. Yu, *Adv. Energy Mater.*, 2016, **6**, 1600546.
- 20 W. B. Chang, C. M. Evans, B. C. Popere, B. M. Russ, J. Liu, J. Newman and R. A. Segalman, *ACS Macro Lett.*, 2016, **5**, 94–98.
- 21 S. Sowmiah, V. Srinivasadesikan, M. C. Tseng and Y. H. Chu, *Molecules*, 2009, **14**, 3780–3813.
- 22 J. Li, T. Ngai and C. Wu, *Polym. J.*, 2010, **42**, 609–625.
- 23 M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho and A. M. Fernandes, *J. Phys. Chem. A*, 2010, **114**, 3744–3749.
- 24 X. Wu, N. Gao, X. Zheng, X. Tao, Y. He, Z. Liu and Y. Wang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 27691–27699.
- 25 E. Laux, S. Uhl, L. Jeandupeux, P. P. López, P. Sanglard, E. Vanoli, R. Marti and H. Keppner, *J. Electron. Mater.*, 2018, **47**, 3193–3197.
- 26 H. Jia, X. Tao and Y. Wang, *Adv. Electron. Mater.*, 2016, **2**, 1600136.
- 27 B. Kim, J. U. Hwang and E. Kim, *Energy Environ. Sci.*, 2020, **13**, 859–867.
- 28 H. Wang, J.-H. Hsu, S.-I. Yi, S. L. Kim, K. Choi, G. Yang and C. Yu, *Adv. Mater.*, 2015, **27**, 6855–6861.