

# Supporting Information

for

## Cation exchange improves the efficiency and stability of the n-doping of $\pi$ -conjugated polymers

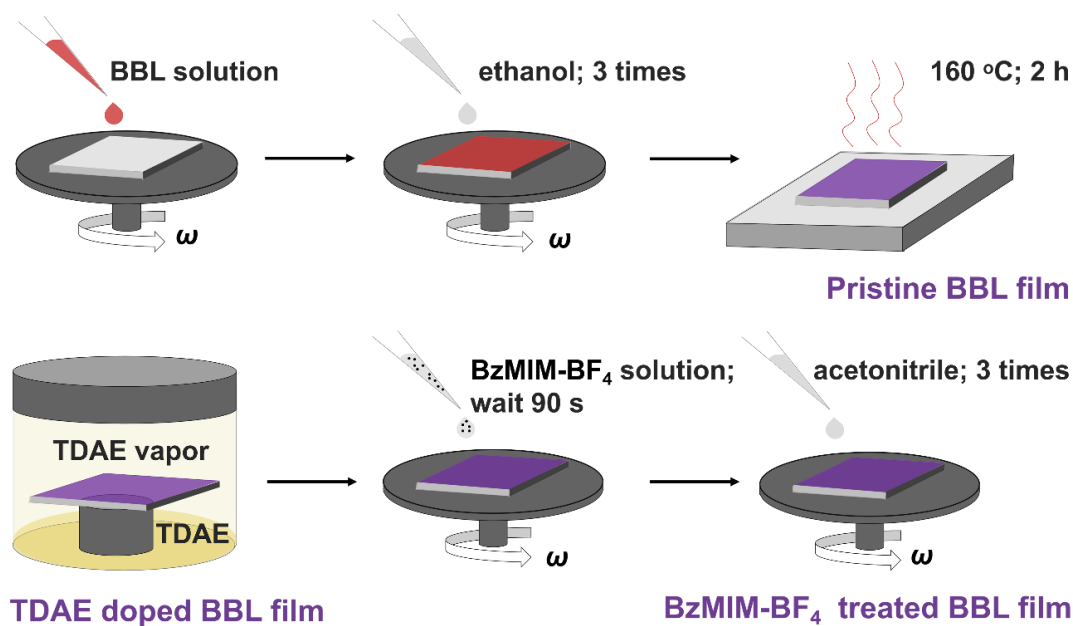
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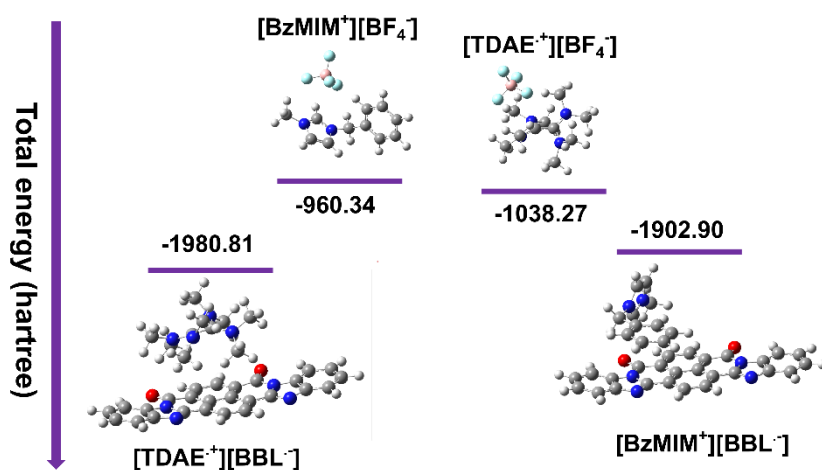
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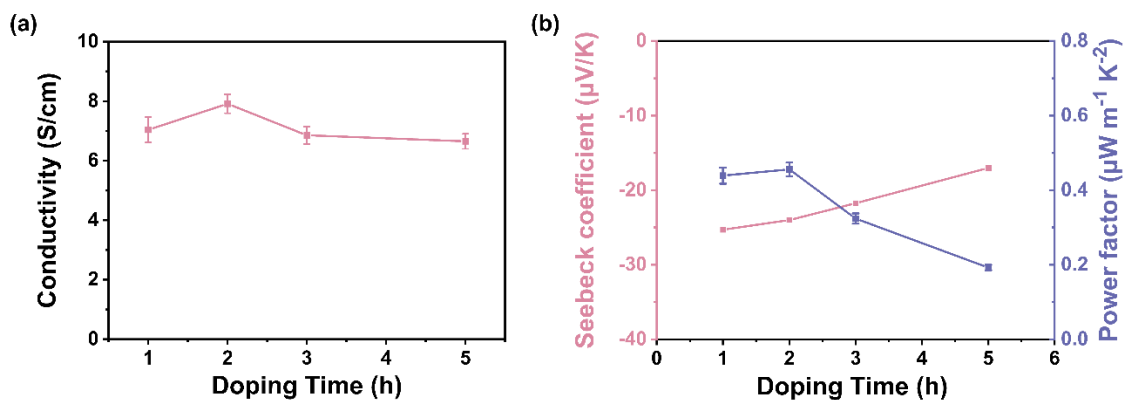
\* Corresponding author at [hujl100@nenu.edu.cn](mailto:hujl100@nenu.edu.cn).



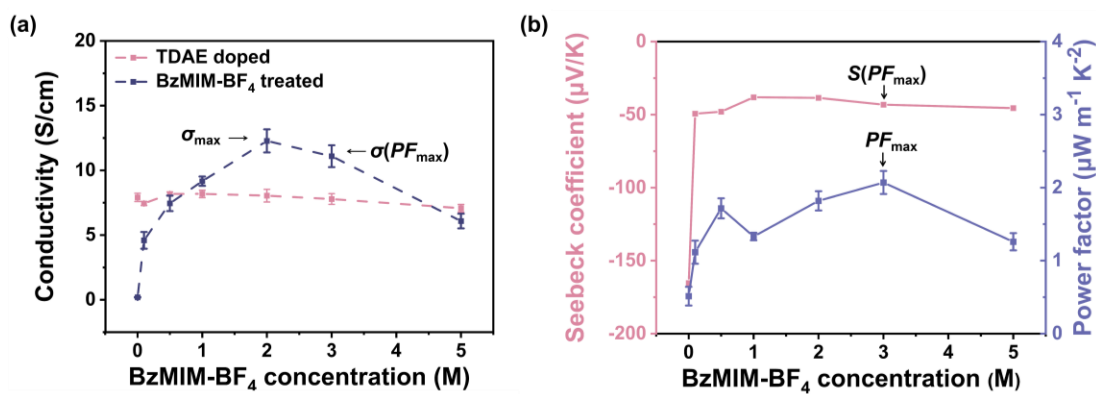
**Figure S1.** Schematic illustration of the processes of device fabrication.



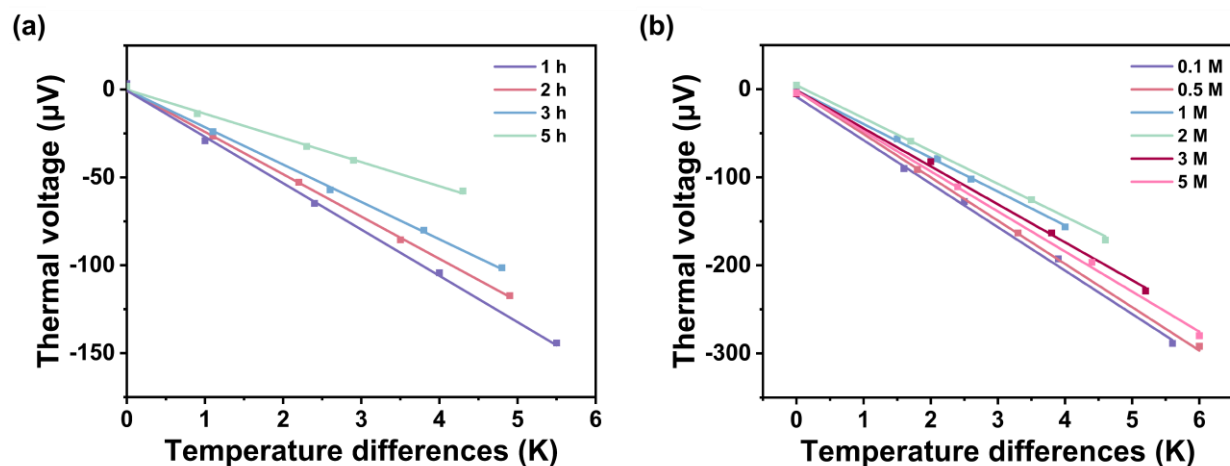
**Figure S2.** The optimized structures and total energy of different ion pairs. The total energy values for ion pairs as calculated using the B3LYP functional and the def2-SVP basis set.



**Figure S3.** The effect of doping time of TDAE on (a) the conductivity and (b) the thermoelectric performance of the BBL film.



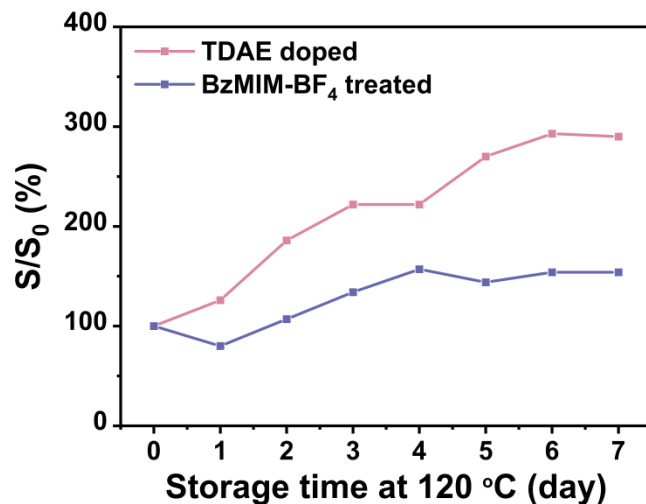
**Figure S4.** (a) Conductivity and (b) thermoelectric performance of the BBL films treated with BzMIM-BF<sub>4</sub> solution of different concentrations. The concentration of 0 M implies pure acetonitrile treatment.



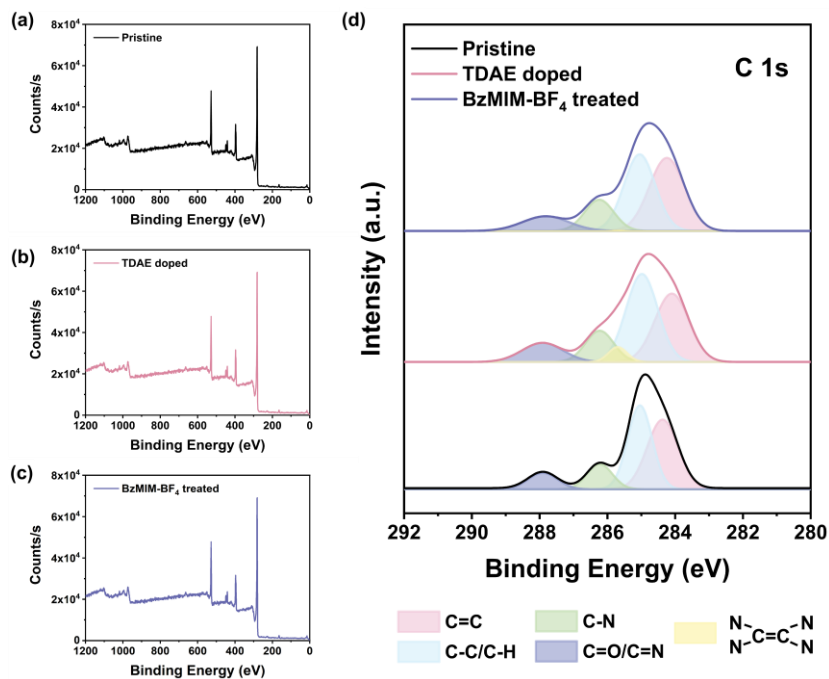
**Figure S5.** Temperature difference dependent thermal voltage of a) TDAE doped BBL films at different doping times and b) BzMIM- $\text{BF}_4$  treated BBL films at different concentrations.

**Table S1.** Summary of conductivity of BBL films reported in literatures.

Polymer: dopant	Doping method	$\sigma_{\text{max}}$ (S/cm)	Ref
BBL: TDAE: BzMIM- $\text{BF}_4$	Cation exchange	12.3	This work
BBL: N-DMBI	Sequential doping	4.4	32
	Sequential doping	11.0	47
BBL: PEI	Blending doping	8.0	40
BBL: $\text{BV}^{++}$	Sequential doping	1.6	44
BBL: P(g42T-T)	Blending doping	0.2	42
BBL: TDAE	Vapor doping	1.7	39

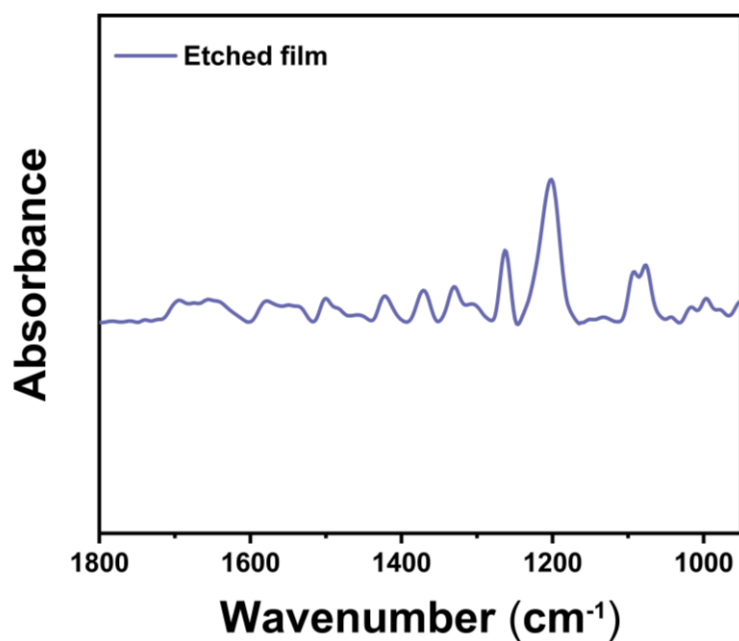


**Figure S6.** The change of the normalized Seebeck coefficient of the TDAE doped and BzMIM-BF<sub>4</sub> treated BBL films during the storage at 120 °C under nitrogen atmosphere.

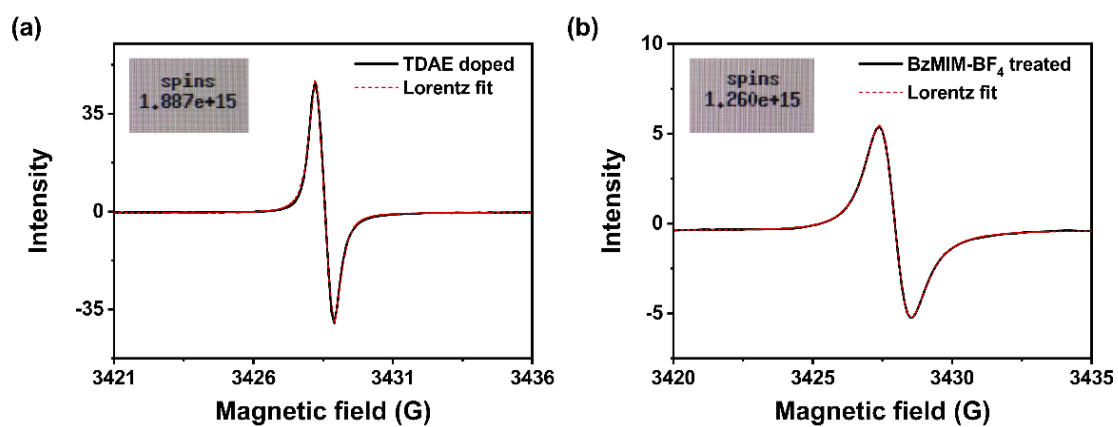


**Figure S7.** The XPS spectra of the (a) pristine, (b)TDAE doped and (c) BzMIM-BF<sub>4</sub> treated BBL films.

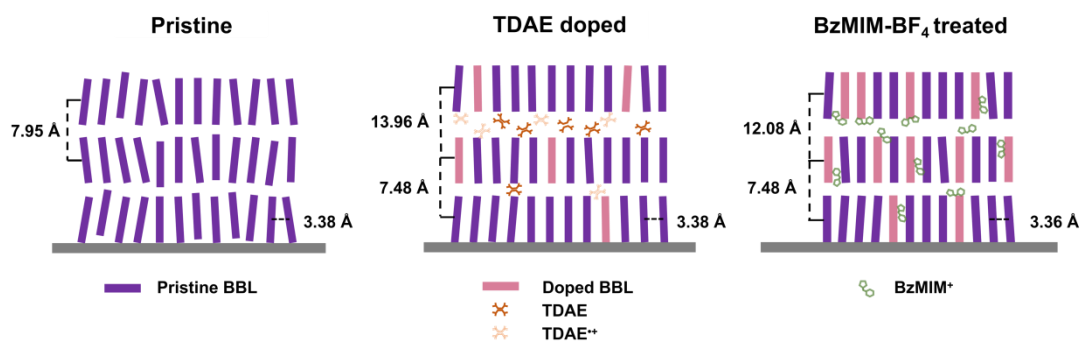
(d)The XPS spectra analysis of C 1s for the pristine, TDAE doped and BzMIM-BF<sub>4</sub> treated BBL films.



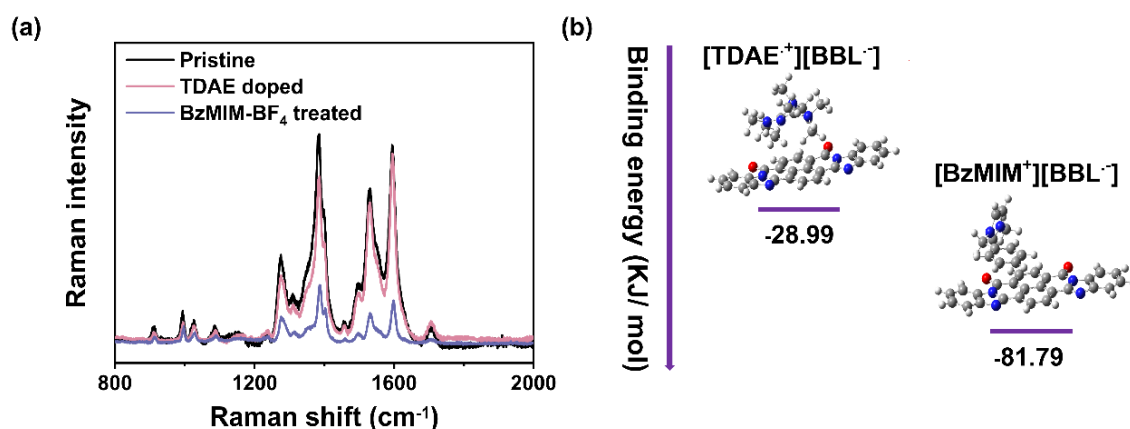
**Figure S8.** The FTIR spectra of BzMIM-BF<sub>4</sub> treated BBL film etched by nitrogen plasma. The thickness of the etched film was 28 nm.



**Figure S9.** The spins calculation and the Lorentz fit of EPR curves of (a) the TDAE doped and (b) the BzMIM-BF<sub>4</sub> treated BBL films.



**Figure S10.** Schematic illustration of the microstructure of the BBL films.



**Figure S11.** (a) The Raman spectra of the BBL films. (b) The binding energy between different cations and polarons.

**Table S2.** The GIWAXS analysis of the pristine, TDAE doped and BzMIM-BF<sub>4</sub> treated BBL films.

Coherence length, and paracrystallinity in in-plane (010) diffraction.

Sample	Coherence length (Å)	Paracrystallinity (%)
Pristine BBL film	35.12	3.43
TDAE doped BBL film	44.87	3.04
BzMIM-BF <sub>4</sub> treated BBL film	43.83	3.05