Supporting Information

Novel Polyvinylimidazolium Nanoparticles as High-performance Binders for Lithium-ion Battery

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Experimental Section

monomer synthesis: Typically, 1,3,5-tris(bromomethyl)benzene (2 g, 5.6 mmol), 10 eq. 1-vinylimidazole (5.26 g, 56 mmol), 2 mol. % (in regard to 1-vinylimidazole) 2,6-di-tert-butyl-4-methylphenol (0.25 g, 1.13 mmol) and DMSO (5 mL) were mixed. The mixture was stirred at 80 °C for 72 h. After cooling down, the mixture was precipitated into ice cooled THF (200 mL). The beige solid product B3VBr was filtered off and washed with THF several times (400 mL in total). Subsequently the product, B3VBr was dried at room temperature under high vacuum ($1 \cdot 10^{-3}$ mbar) till constant weight (yield: 2.82 g, 79 %). The synthesis of other monomers follows the same route.

Polymerization: The purified monomer product B3VBr (2.82 g, 4.4 mmol) was transferred into methanol (15 mL). 1.5 wt% AIBN (40 mg, 0.24 mmol) was then added. The mixture was degassed with argon for 30 min and then stirred at 65 °C for 24 h. After cooling down, the mixture was precipitated into ice cooled THF (200 mL). The beige solid was filtered off and washed with THF several times (400 mL in total). The product was dried at 80 °C under high vacuum till constant weight (yield: 2.62 g, 93 %).

Anion exchange: The purified crosslinked polyvinylimidazolium nanoparticles (2.62 g, 4.1 mmol of monomer units) was dispersed in water (25 mL). 3.70 g (14.9 mmol) of LiTFSI (1.05 eq. for every Br) in water (25 mL) was added dropwise to the stirred dispersion. White precipitate appeared immediately. After filtration and excessive washing with water, the product was dried at 100 °C under high vacuum ($1 \cdot 10^{-3}$ mbar) till constant weight (yield: 4.62 g, 91 %).

Electrochemistry: Binders were tested by electrochemical measurements. The electrodes were made by mixture of high-quality lithium iron phosphate ($LiFePO_4$, supplied by M&T Olivine Co., LTD.) (80 wt.%), conductive additive (acetylene black; 10 wt.%), and binder (10 wt.%) in organic solvents. We used aluminum foils (diameter of 10 mm) as a current collector. 20 µL of cathode mixture in acetonitrile was dropped on Al current collectors, then electrodes were dried first at 60 °C for 3 h and next at 120 °C for overnight. We used the electrode without any additional treatment, such as pressing. The loading mass is ca. 2 mg. We assembled the electrodes in the two-electrode Swagelok-type cells in an argon-filled glove box (M Braun) and tested them on a multichannel potentiostatic-galvanostatic system (VMP-3, Bio-Logic). To calculate a current density, we used 1C as 170 mA/g. We used lithium metal as an anode and 1M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio 1:1) as an electrolyte. Electrochemical impedance spectroscopy measurement was carried out with a frequency range from 100 mHz to 20 kHz with an amplitude of 25 mV. The fitting was carried out by using EC Lab (Bio-logic).

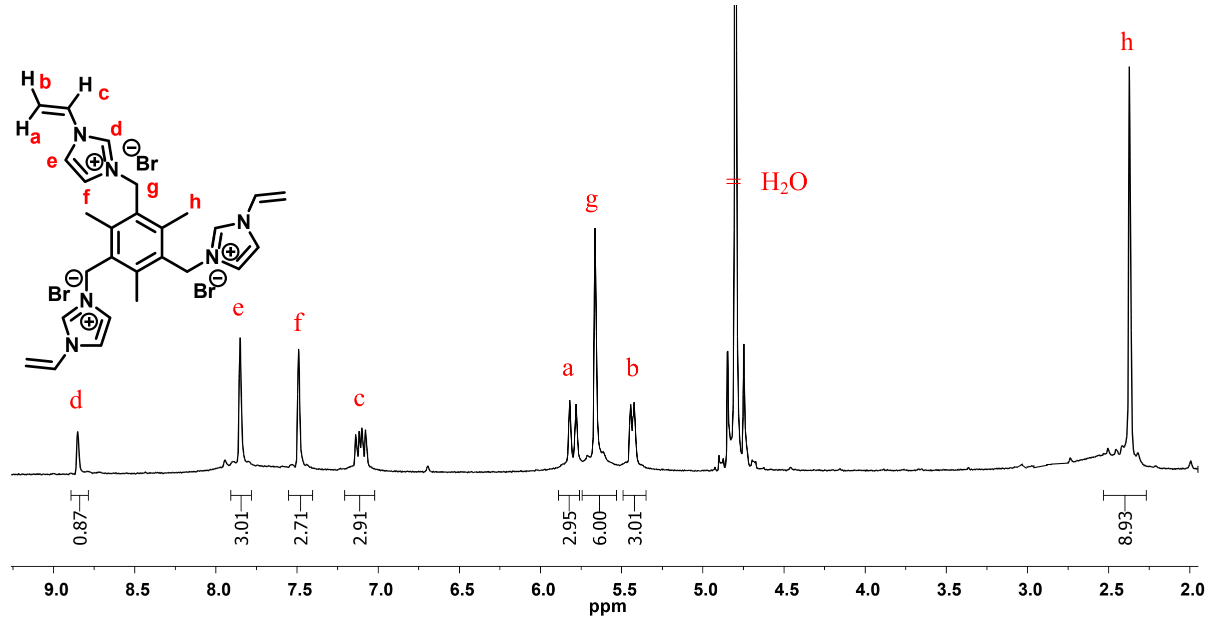


Figure S1. ^{1}H-NMR of Bm3VBr monomer.

^{1}H-NMR (400.1 MHz, D_2O): δ (ppm) = 8.85 (1H), 7.85 (3H), 7.49 (3H), 7.10 (3H), 5.82-5.78 (3H), 5.66 (6H), 5.44-5.42 (3H), 2.37 (9H).

^{13}C-NMR (100.1 MHz, D_2O): δ (ppm) = 142.11, 135.66, 129.33, 123.96, 119.17, 108.72, 48.58, 16.88.

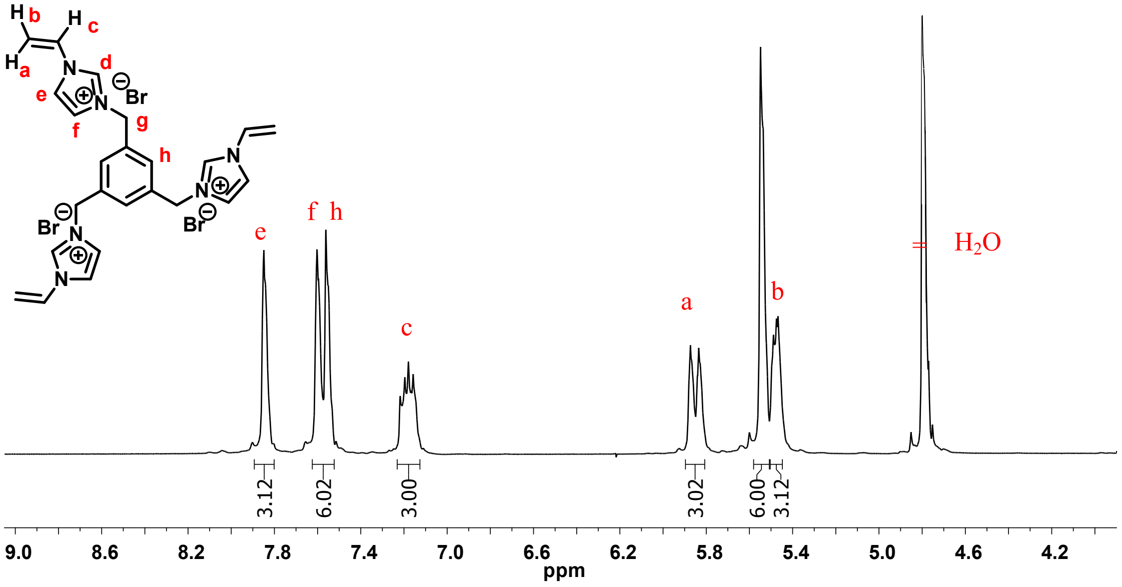


Figure S2. ^{1}H-NMR of B3VBr monomer.

^{1}H-NMR (400.1 MHz, D_2O): δ (ppm) = 7.85 (3H), 7.60 (3H), 7.56 (3H), 7.18 (3H), 5.87-5.83 (3H), 5.55 (6H), 5.47-5.44 (3H).

^{13}C-NMR (100.1 MHz, D_2O): δ (ppm) = 139.07, 127.60, 123.22, 120.10, 111.08, 48.86, 38.78.

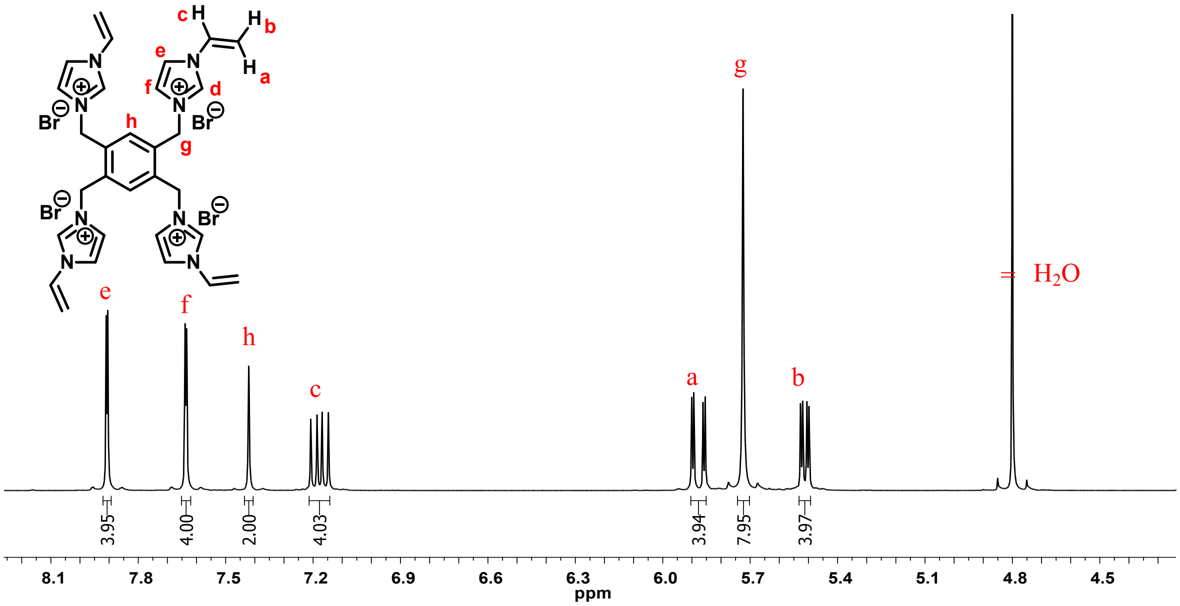


Figure S3. ^{1}H-NMR of B4VBr monomer.

^{1}H-NMR (400.1 MHz, D_2O): δ (ppm) = 7.91 (4H), 7.64 (4H), 7.42 (2H), 7.19 (4H), 5.90-5.85 (4H), 5.72 (8H), 5.52-5.49 (4H).

^{13}C-NMR (100.1 MHz, D_2O): δ (ppm) = 134.03, 132.57, 127.98, 123.24, 119.93, 110.37, 49.83, 38.87.

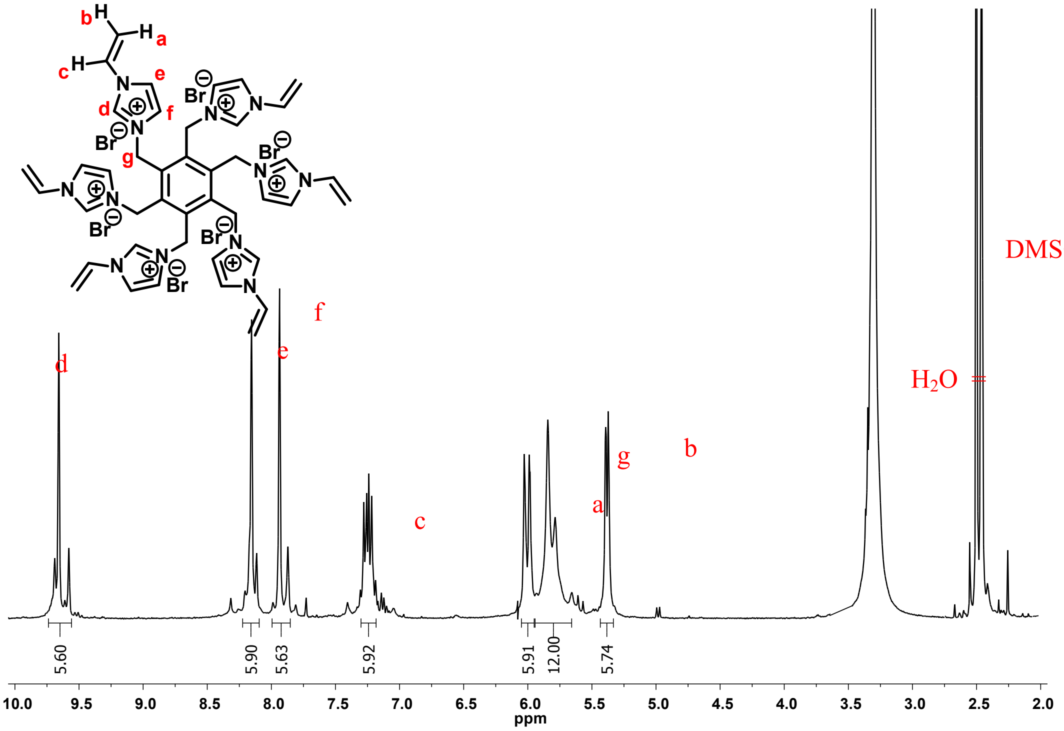


Figure S4. ^{1}H-NMR of B6VBr monomer.

^{1}H-NMR (400.1 MHz, DMSO-d$_6$): δ (ppm) = 9.667.91 (4H), 7.64 (4H), 7.42 (2H), 7.19 (4H), 5.90-5.85 (4H), 5.72 (8H), 5.52-5.49 (4H).

^{13}C-NMR (100.1 MHz, DMSO-D$_6$): δ (ppm) = 139.07, 127.60, 123.23, 120.10, 111.09, 48.16, 38.80 (overlapped peak).

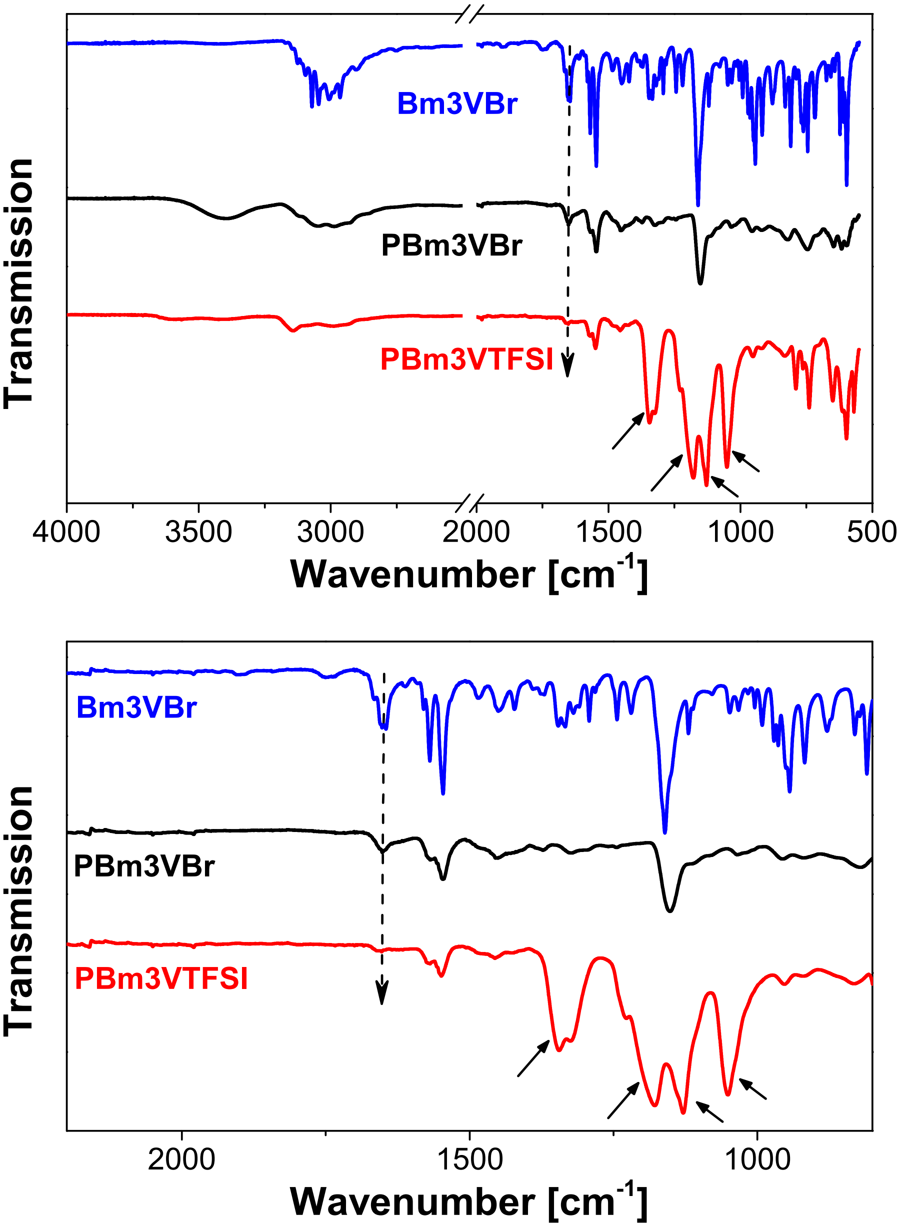
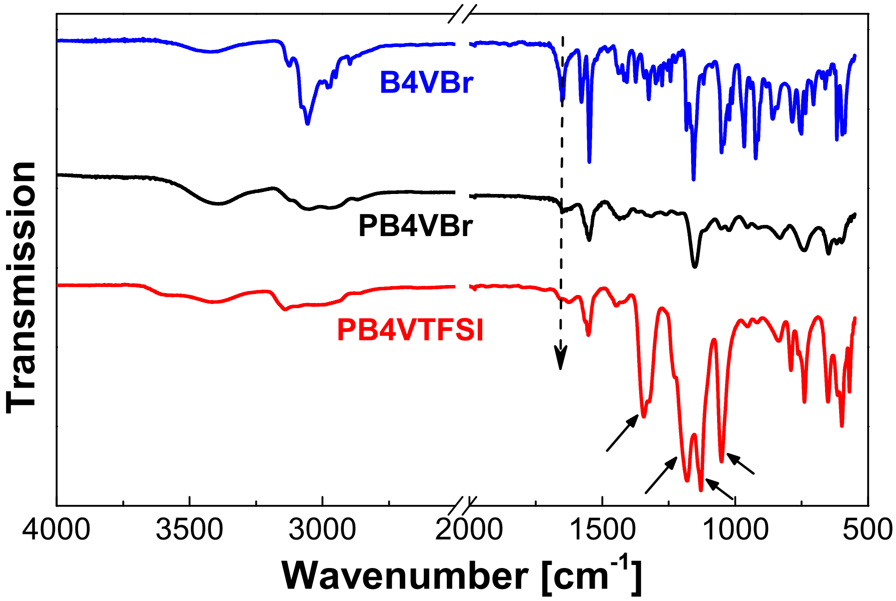


Figure S5. FITR spectra of Bm3VBr, PBm3VBr and PBm3VTFSI. The bottom one is the enlarged view of the upper one.



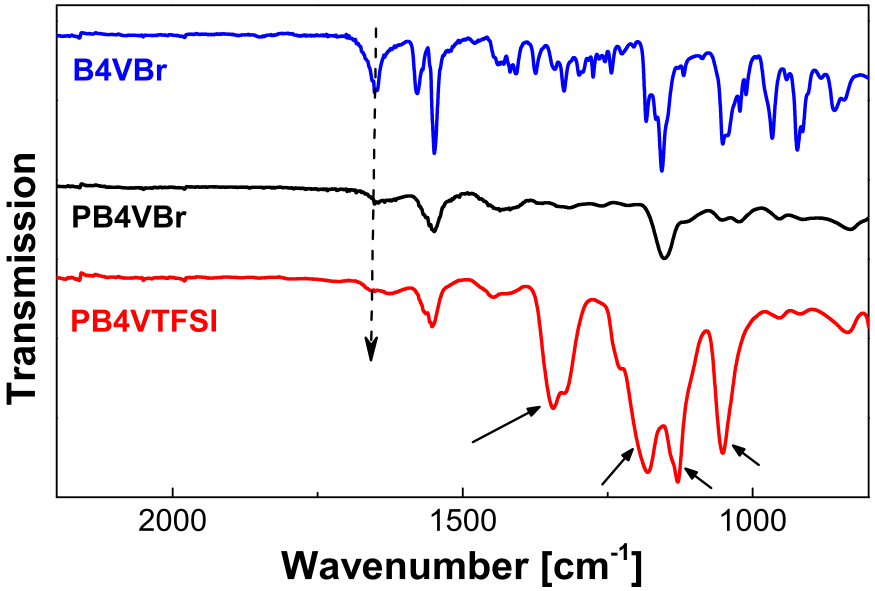


Figure S6. FITR spectra of B4VBr, PB4VBr and PB4VTFSI. The bottom one is the enlarged view of the upper one.

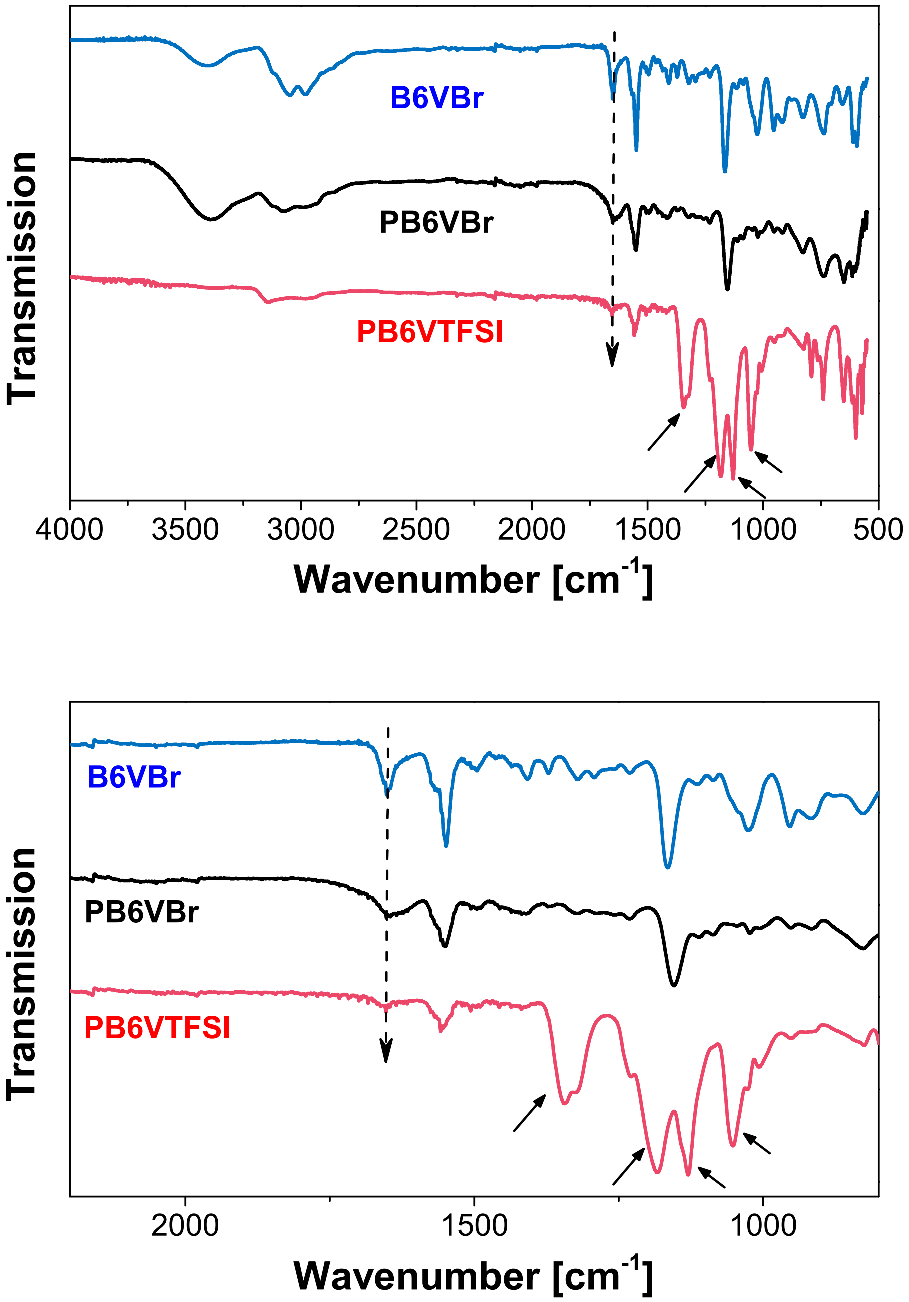


Figure S7. FITR spectra of B6VBr, PB6VBr and PB6VTFSI. The bottom one is the enlarged view of the upper one.

Table S1. Summary of the characterization results of the polyvinylimidazolium nanoparticle binders prepared from 4 different monomers.

Binder samples	Degree of anion exchange (%)	Particle size by DLS / nm (number-averaged)	Standard size deviation
PB3VTFSI	75	28	72%
PBm3VTFSI	75	31	76%
PB4VTFSI	72	31	80%
PB6VTFSI	66	37	68%

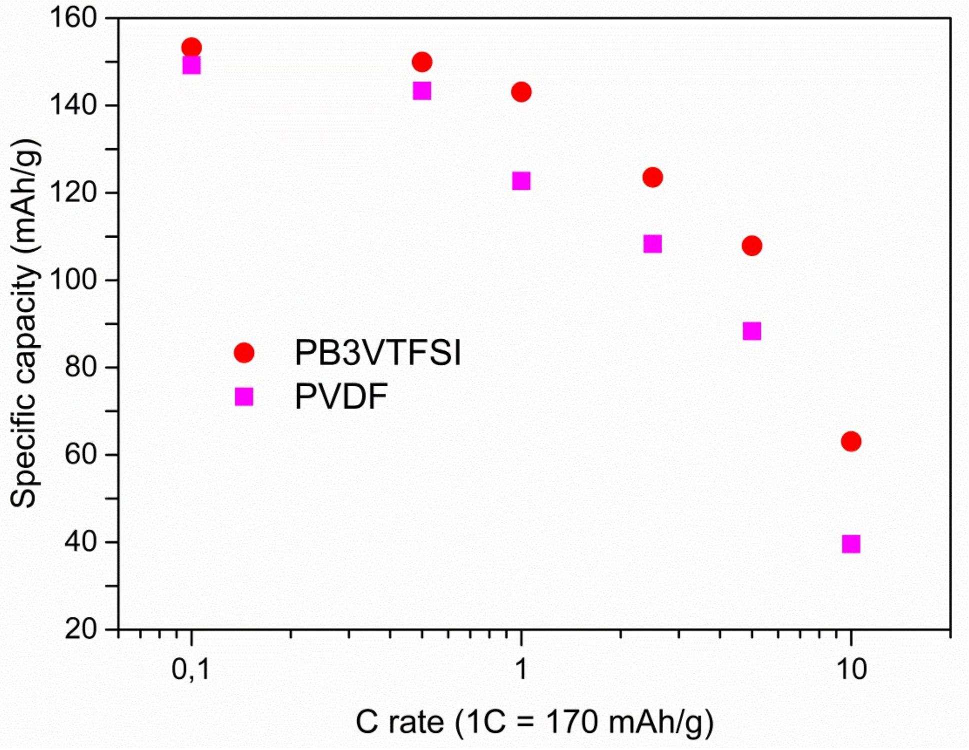


Figure S8. Rate capability of PB3VTHSI and PVDF.

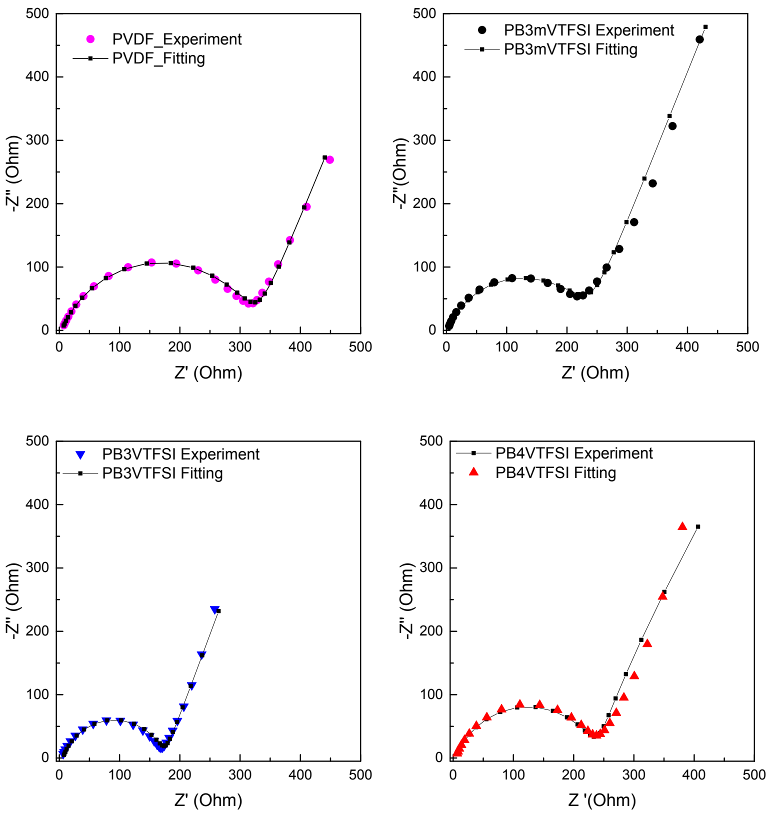


Figure S9. Individual electrochemical impedance spectra for cathode using different binders.

Table S2. Parameters used in EIS for fitting.

Samples	R_s (Ohm)	R_1 (Ohm)	R_2 (Ohm)	T_{CPE1} (μFs^{p-1})	T_{CPE2} (μFs^{p-1})	α_{CPE1}	α_{CPE2}
PVDF	3.67	322.3	64.8	20.56	3.38	0.737	0.743
PBm3VTFSI	2.62	192.3	41.6	18.12	0.874	0.757	0.771
PB4VTFSI	4.09	216.5	33.9	17.16	1.549	0.758	0.893
PB3VTFSI	5.86	188.4	32.2	19.42	5.734	0.783	0.763