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Supporting Information

New Approach of Blending Polymeric Ionic Liquid with Polybezimidazole (PBI) for Enhancing Physical and Electrochemical Properties

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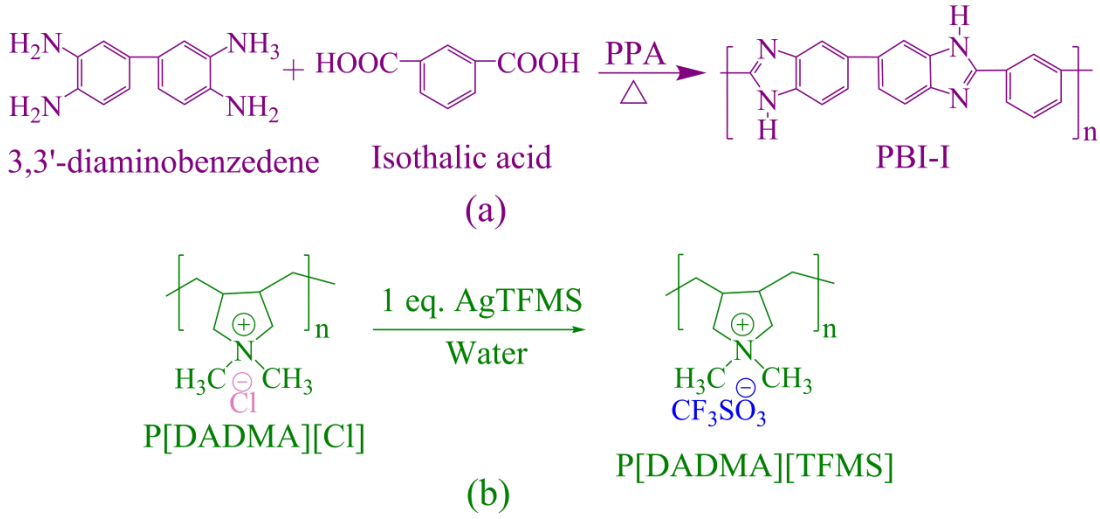
1. Synthesis of polybenzimidazole (PBI) and polymeric ionic liquid (PIL)

Polybenzimidazole was synthesized by polycondensation reaction of DAB and isophthalic acid, (PBI-I) as reported earlier [SCK JMS 2006] (Scheme S1a). A three-necked flask equipped with a mechanical stirrer, N_2 inlet and $CaCl_2$ drying tube was charged with 300 g of PPA, 10 g (0.04667 mol) of DAB and temperature was elevated to 140 ºC. After dissolution of DAB, 0.04667 mol of isophthalic acid was added; temperature was slowly raised to 170 ºC and maintained for 5 h under constant flow of N_2. The temperature was further raised to 210 ºC and maintained for 12 h. The polymer was obtained by precipitation in water. It was crushed, thoroughly washed with water, kept in 10% $NaHCO_3$ for 16 h; followed by water wash until filtrate was neutral to pH. The polymer was then soaked in acetone for 16 h, filtered and dried in vacuum oven at 100 ºC for 7 days. Further purification by dissolving in DMAc (3% w/v) and reprecipitation in water yielded yellow colored fibrous polymer.

The PIL, viz., P[DADMA][TFMS] was prepared by anion exchange of a commercially available polymer, P[DADMA][Cl] (Scheme S1b). The 8% (w/v) solution of P[DADMA][Cl] was prepared in water and an equimolar quantity of Ag salt of trifluoromethanelsulphonate was added to the solution while stirring at ambient. As the replacement of Cl^- with the anion progressed, AgCl precipitated out. In view of polymeric nature of the cation, stirring continued for 24 h in order to ensure maximum possible exchange. The resulting mixture was centrifuged at 12000 rpm for 30 min to separate AgCl in precipitate form. To remove silver salt, centrifugation was repeated 5 times. In order to recover the product polymer, supernatant solution was poured on to a flat teflon surface and dried at 60 °C for 24 h and finally in vacuum oven at 60 °C for 7 days. The chloride

remained in the formed PIL was estimated by Volhard's method[25], in which 0.1 g of PIL was stirred in 20 ml of 0.01 M $AgNO_3$ solution for 24 h. Excess of unreacted $AgNO_3$ was titrated with 0.01 M KSCN, in order to assess chloride content in PIL.



Scheme S1. Synthesis of (a) polybenzimidazoles and (b) P[DADMA][TFMS].

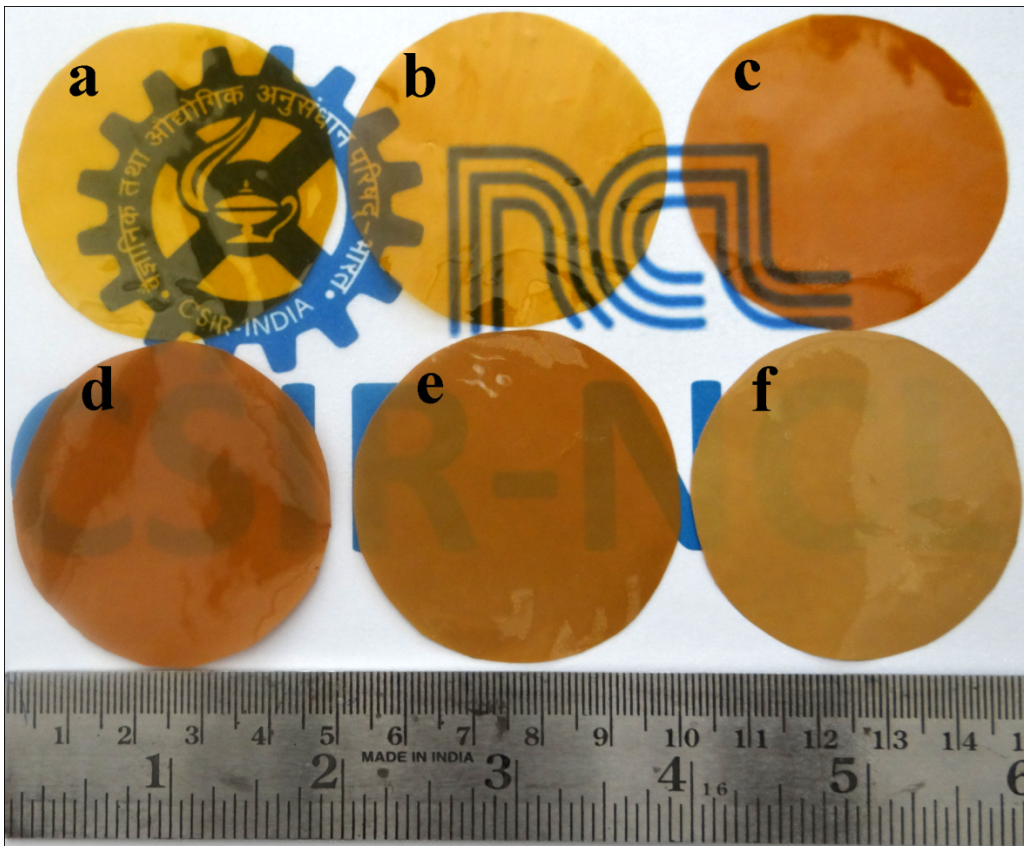


Fig S1. Photographs of PBI-PIL blend membranes (a) PBI, (b) PBI-PIL_5, (c) PBI-PIL_{15}, (d) PBI-PIL_{25} (e) PBI-PIL_{35}, (f) PBI-PIL_{45}.

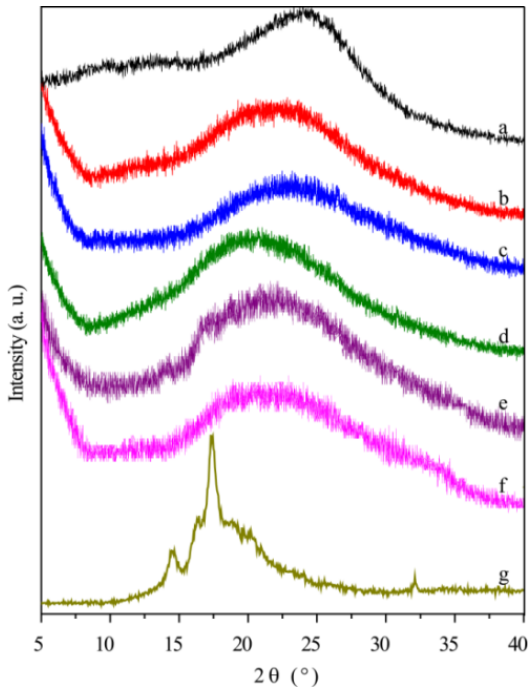


Fig. S2. WAXD pattern of PBI-PIL blend membranes (a) PBI, (b) PBI-PIL$_5$, (c) PBI-PIL$_{15}$, (d) PBI-PIL$_{25}$ (e) PBI-PIL$_{35}$, (f) PBI-PIL$_{45}$, (g) PIL.

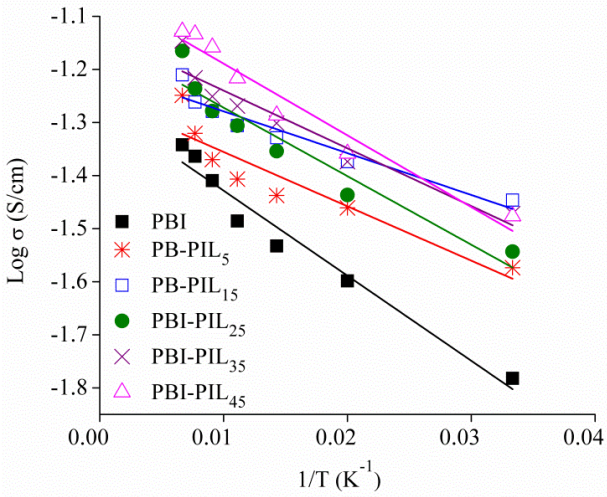


Fig. S3. Proton conductivity of PBI-PIL blends membrane at different temperatures.

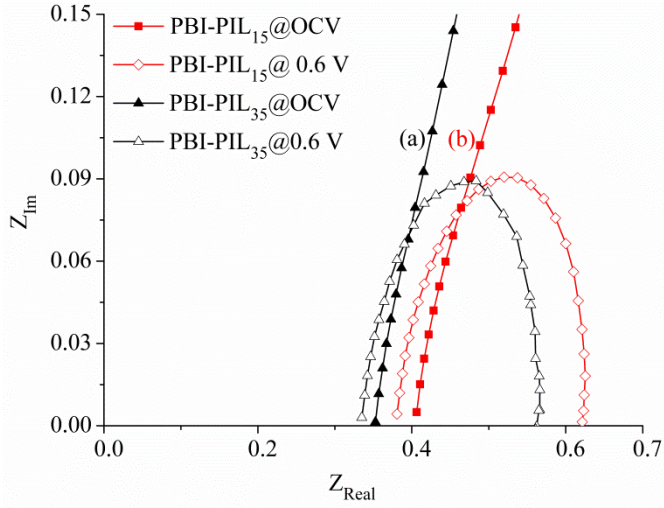


Fig. S4. MEA impedance curve of PBI-PIL$_{35}$ and PBI-PIL$_{15}$ blend membranes.

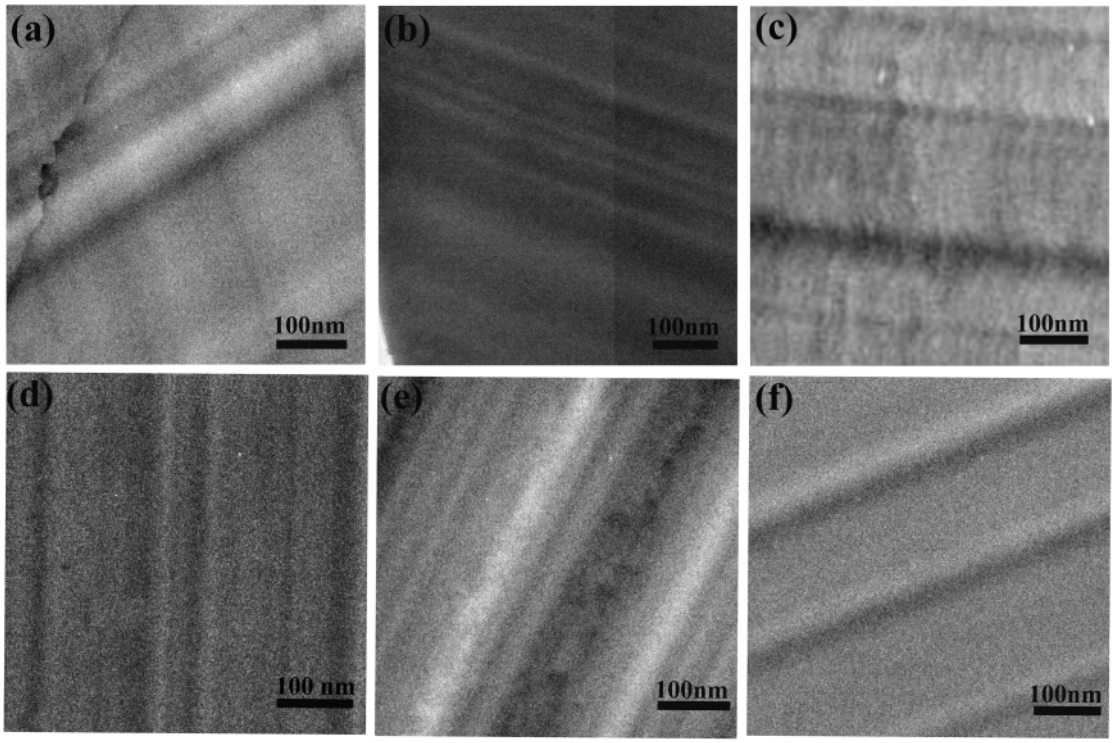


Fig. S5. TEM images of PBI-PIL blend membranes (a) PBI, (b) PBI-PIL$_5$, (c) PBI-PIL$_{15}$, (d) PBI-PIL$_{25}$ (e) PBI-PIL$_{35}$, (f) PBI-PIL$_{45}$. These figures do not show inhomogeneity in any of the blend composition. This further supports homogeneous blend formation.