Supporting Information

Polymer of Intrinsic Microporosity based Macroporous Membrane with High Thermal Stability as Li-ion Battery Separator

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Supplemental Figures

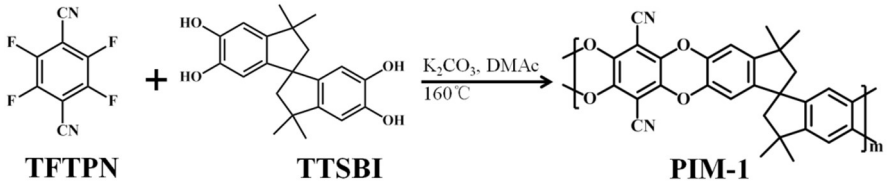

Figure S1. Synthesis route of PIM-1.

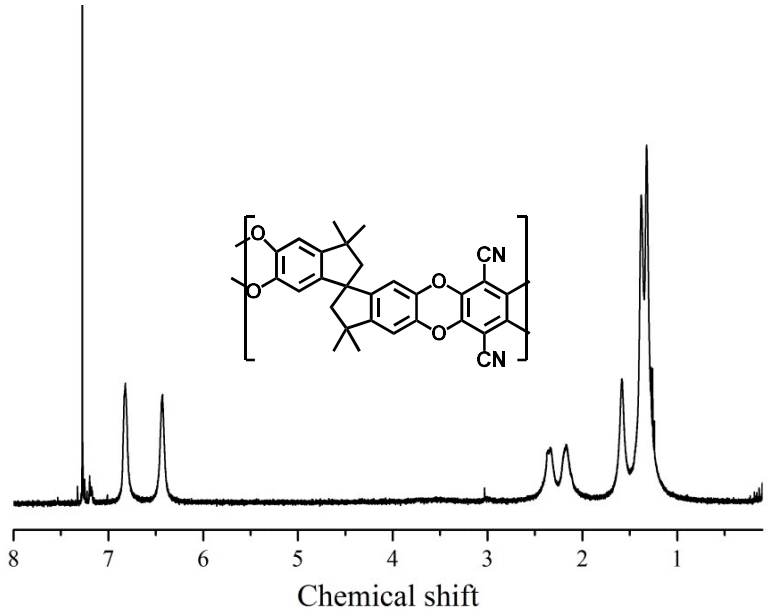

Figure S2. ^{1}H NMR analysis of PIM-1 chemical structure.

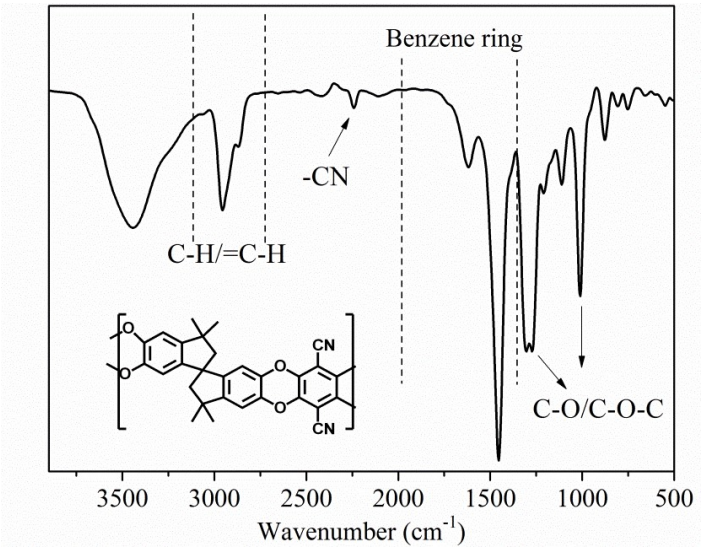

Figure S3. FT-IR spectrum of PIM-1.

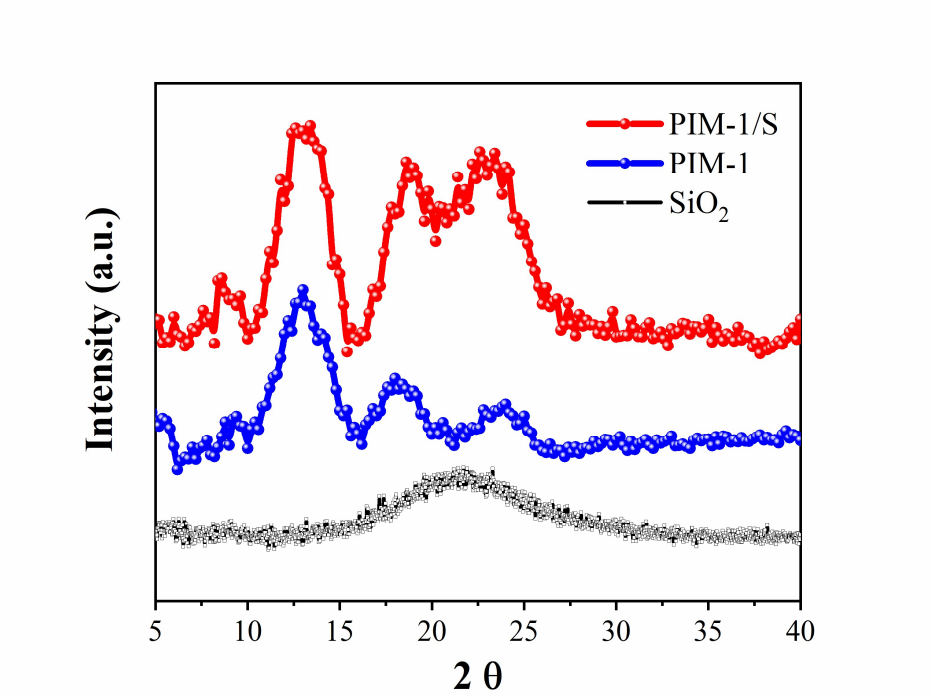

Figure S4. XRD pattern of PIM-1, PIM/S membrane and SiO_2 powder.

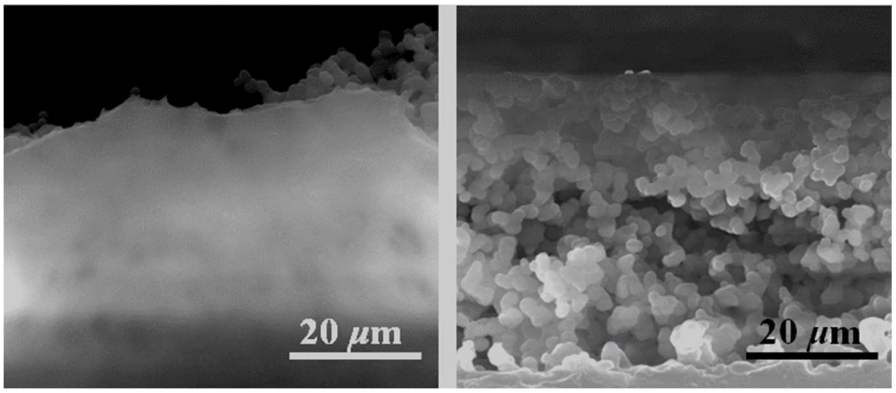

Figure S5. Surface (left) and cross-sectional (right) SEM images of PIM-1 membrane prepared by dry phase transition process without the addition of SiO_2 nanoparticles.

As shown in the above figures, the pure PIM-1 membrane without addition of SiO_2 nanoparticle demonstrates dense surface morphology. The phase transition phenomenon only occurs inside the membrane. Ultra-small size and -OH functionalized SiO_2 nanoparticle could furthermore slow down the non-solvent n-butyl alcohol evaporation. After the fast evaporation of $CHCl_3$, the adsorbed n-butyl

alcohol still exists inside the membrane. With temperature increase, the adsorbed n-butyl alcohol starts to evaporate and porous surface layer is successfully formed.

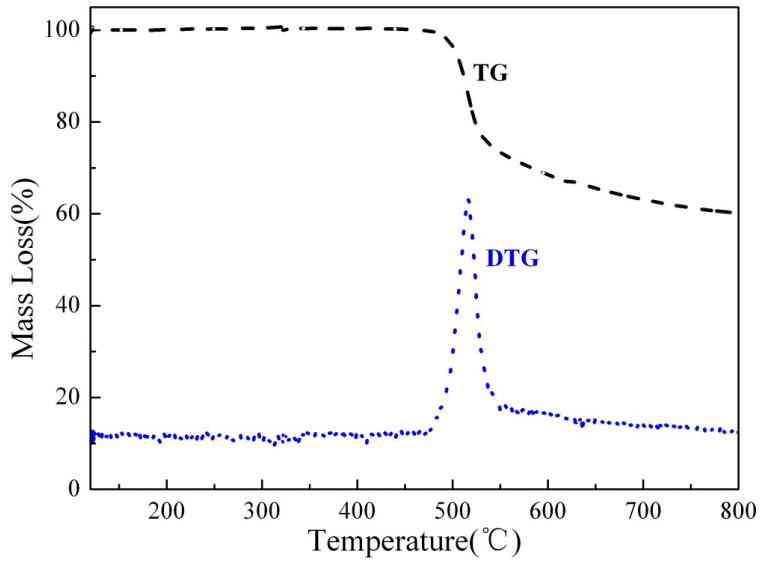

Figure S6. TGA and DTG curves of PIM-1.

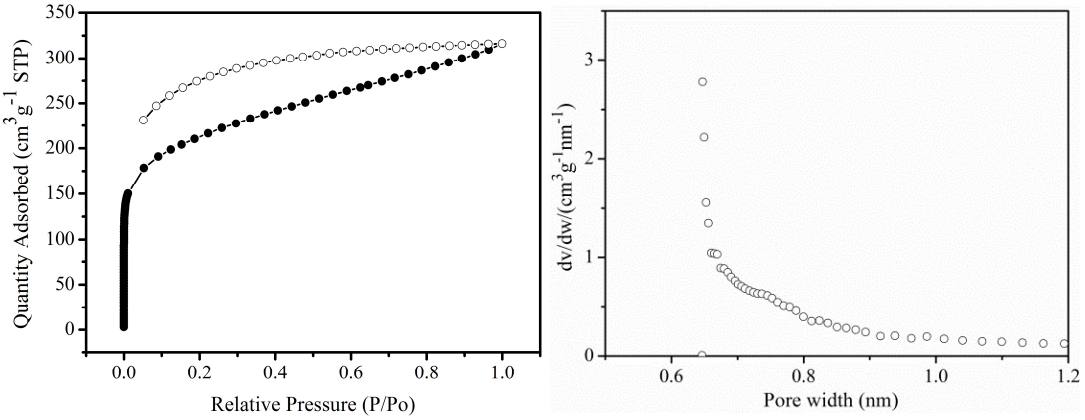

Figure S7. (a) N_2 adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K for PIM-1; (b) pore width distribution obtained by analysis of N_2 adsorption by the Horvath-Kawazoe method.

The BET surface area of PIM-1 is 770 m^2/g. Micropore around 0.7 nm is observed in the figure of pore width distribution.

Table S1. Physical properties of PP and PIM-1/S separators with different SiO_2 weight contents.

Sample	Porosity [%]	Electrolyte uptake [%]	Li-ion conductivity of cell [10^{-4} S cm^{-1}, 25°C]
PIM-1/S-0%	~39	~90	0.2
PIM-1/S-5%	~55	~150	3.2
PIM-1/S-10%	~67	~190	6.0
PIM-1/S-15%	~75	~240	8.2
PIM-1/S-20%	~81	~260	9.0
PP	~37	~110	5.1

The porosity was measured by immersing separators into isobutyl alcohol. After saturated adsorption, the solvent on the surface was wiped and then the weight of wet separator was recorded. The porosity was calculated following the equation (1):

$$\text{Porosity}(\%) = 100 \times \frac{\rho_m \times (M_s - M_d)}{\rho_m \times (M_s - M_d) + \rho_i \times M_d} \qquad (1)$$

where ρ_m and ρ_i represent the density of the separator matrix and isobutyl alcohol. Ms and M_d represent the weight of the saturated and dry separator.

As shown in the table, the Li-ion conductivity and the electrolyte uptake capacity increase greatly with the increase of SiO_2 content. However, high SiO_2 content in the separator will sacrifice the mechanical strength of membrane. In our work, 15% SiO_2 content was chosen under the consideration of both the Li-ion conductivity and the electrolyte uptake and membrane strength.

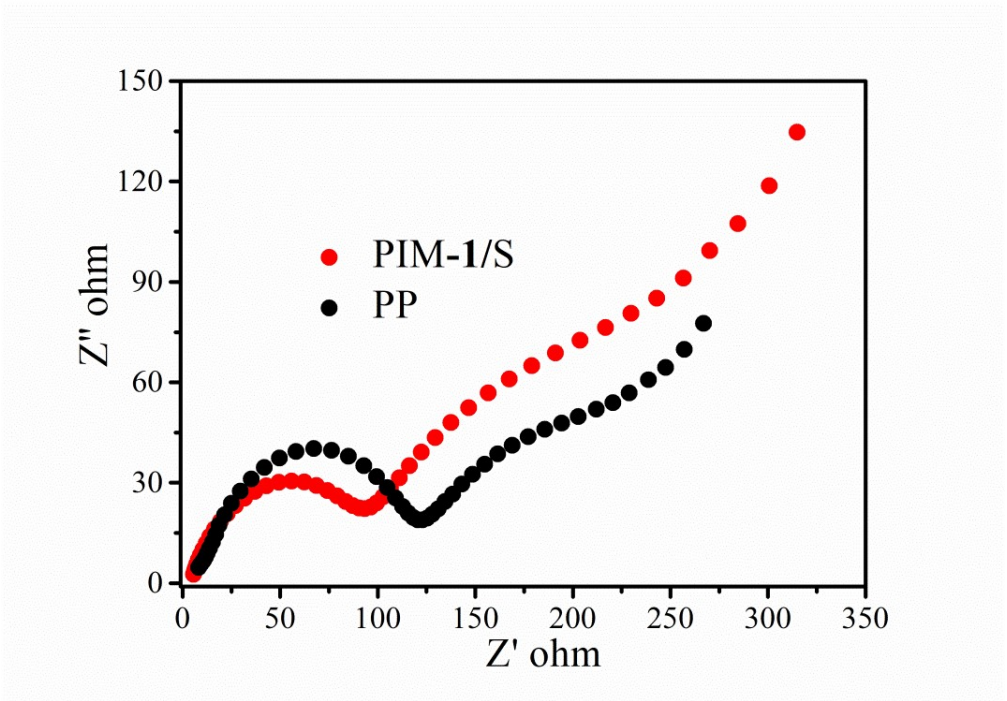

Figure S8. Nyquist plots of PIM-1/S and PP cells.