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**Supplementary information for**

# Proton conductivity enhancement in oriented, sulfonated polyimide thin films

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## Contents

## I. Quantitative information derived from RH dependent FTIR-ATR

Figure S1 shows the time dependent maximum absorption of OH stretching of water molecules (band between 3600 and 3400 cm$^{-1}$) for SPI under both bulk and nanostructured thin film systems. The measurement was conducted from 40% RH to 95% RH with the time interval of 30 min for every 10% RH increment. The absorbance value linearly increases at lower humidity region and the sudden rise in absorbance is observed after 70% RH (as shown in Figure 8). As compared with SPI thin film, the bulk SPI shows the maximum absorbance as function of time. In fact, the maximum absorbance in the bulk SPI at high RH is due to the high hydrogen bond strength, reaches a value as like liquid state of water.

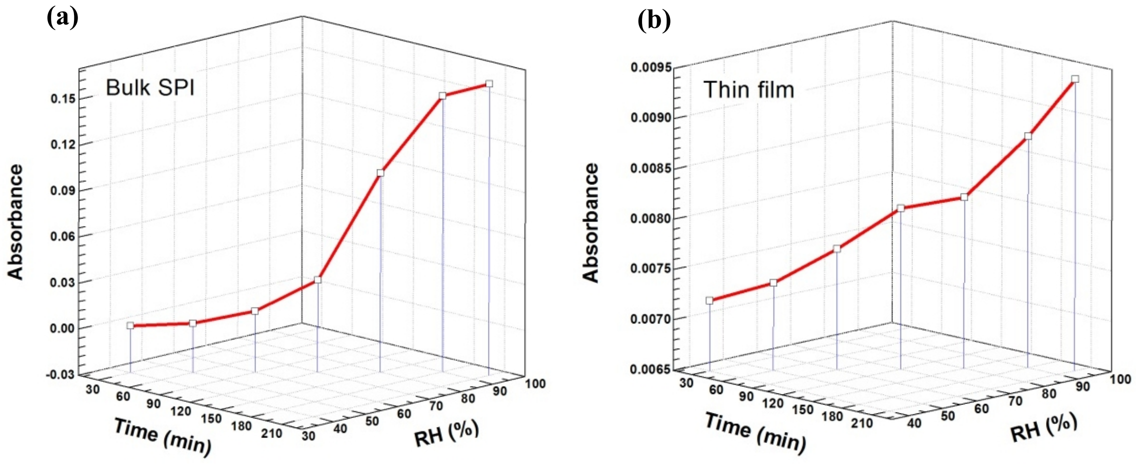

**Figure S1**. Maximum absorption of OH stretching (band between 3600 and 3400 cm$^{-1}$) of water in both (a) bulk and (b) thin film SPI *vs*. time and relative humidity.

In general, the frequency of OH stretching vibrations is known to increase or decrease according to the strength of hydrogen bonding.[1] The frequency of OH stretching vibration tends to decrease linearly with the strength of hydrogen bonding. At high humidity region, the hydrogen bond strength increases and the absorption frequency decreases, implying the state of bonding as like liquid water.[2] Therefore, the RH dependent FTIR-ATR measurement is beneficial to understand the bonding strength of OH stretching vibrations as function of RH. Figure S2 shows the average OH strength of water molecules with various RH for both bulk SPI and nanostructured thin film systems. The quantitative analysis of the average hydrogen bonding strength as function of RH is evaluated by the relation: $[3707 - \nu_s(\mathrm{OH})] / (3707 – 3404)$,[3] where $\nu_s(\mathrm{OH})$ is the stretching frequency of OH group in water. As the fully hydrated region consists of two bands between the gas phase (3707 $\mathrm{cm^{-1}}$) and liquid phase (3404 $\mathrm{cm^{-1}}$) OH (OD) groups of water, which forms the hydrogen bonds. The shift in the peak position of these two bands with respect to the gas or liquid phase value shows that the mean strength of the hydrogen bonds. As compared with the SPI thin film, the average OH bonding strength of bulk SPI is substantially higher. Essentially, the bond strength of bulk SPI increases rapidly until reaching the RH value of 60% and above this humidity region the increase in bond strength is insignificant. Similarly, the significant rise in bond strength is observed for SPI thin film from 40% to 80% RH and the values are quite constant beyond this RH. It is apparent that, the broadening of band in bulk SPI is considered to be due to the increase in hydrogen bond strength caused by the increase in distribution of hydrogen bonding.

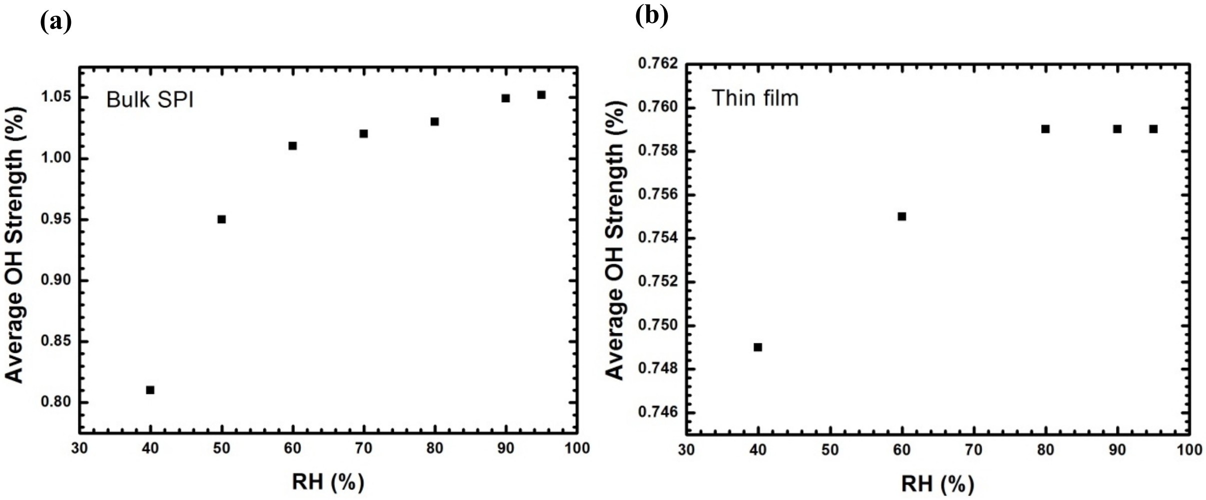

**Figure S2**. The RH dependent average hydrogen bonding strength (band between 3600 and 3400 cm$^{-1}$) of both (a) bulk and (b) thin film SPI, estimated from FTIR absorption data.

The formation of significant ionic clusters makes the stronger hydrogen bond strength in bulk SPI than SPI thin film. During high RH, the increase in water content increases the size of the water clusters, which gives the stronger hydrogen bonds that may occur the coalesced cluster with a continuous phase similar to the pure liquid water.

## II. $^{1}$H NMR Spectrum of SPI in DMSO-$d_6$

$^{1}$H NMR spectrum of SPI is shown in Figure S3. The aromatic protons were detected at 7.4−8.6 ppm and the aliphatic protons were observed at 1.0−4.4 ppm, which could be well matched with the assigned chemical structure.[4] It is important to denote that, there is no other peaks were observed for monomers, solvents and etc,. Integration of proton peaks in $^{1}$H NMR spectrum was in good agreement with the number of hydrogen in both the backbone and side chain of SPI structure.

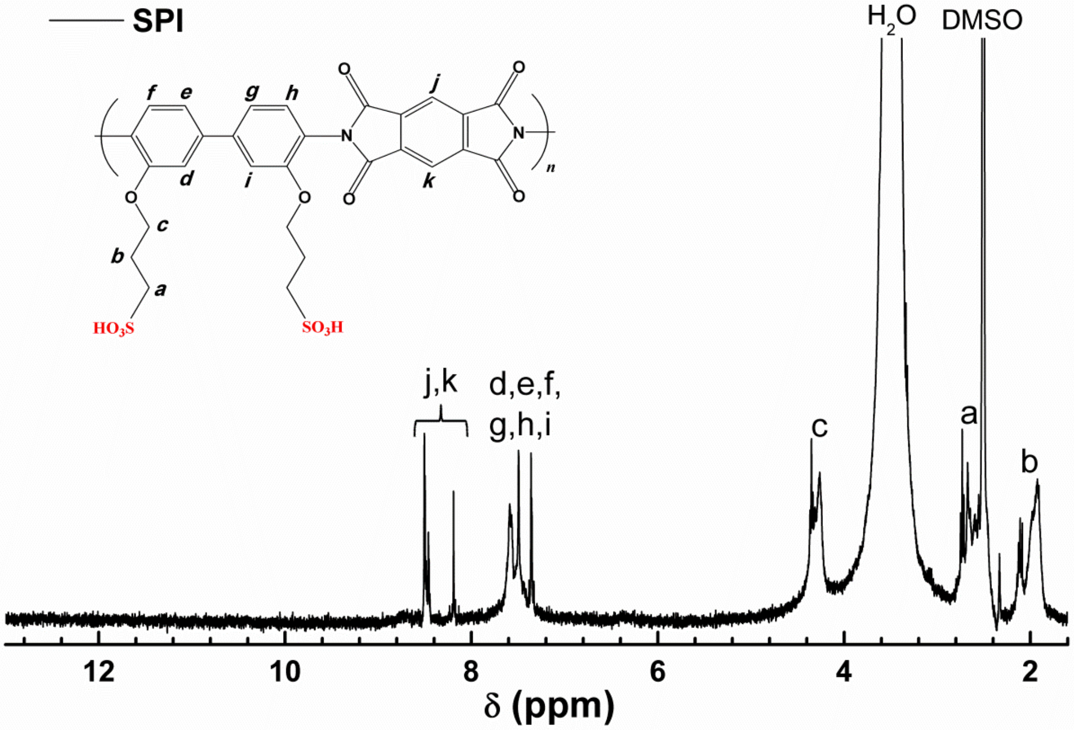

**Figure S3.** $^{1}$H NMR spectrum of SPI sample in DMSO−$d_{6}$.

## Supplementary Information Reference

(1) M. Falk and T. A. Ford, *Can. J. Chem*., 1966, **44**, 1699–1707.

(2) M. Laporta, M. Pegoraro and L. Zanderighi, Phys. Chem. Chem. Phys., 1999, **1**, 4619–4628.

(3) M. Falk, *Can. J. Chem*., 1980, **58**, 1495–1501.

(4) J. Saito, K. Miyatake and M. Watanabe, *Macromolecules*, 2008, **41**, 2415-2420.