

## **Electronic Supporting Information**

# **Acid-Base Bi-functionalized, Large-pored Mesoporous Silica Nanoparticles for Cooperative Catalysis of One-Pot Cellulose-to-HMF Conversion**

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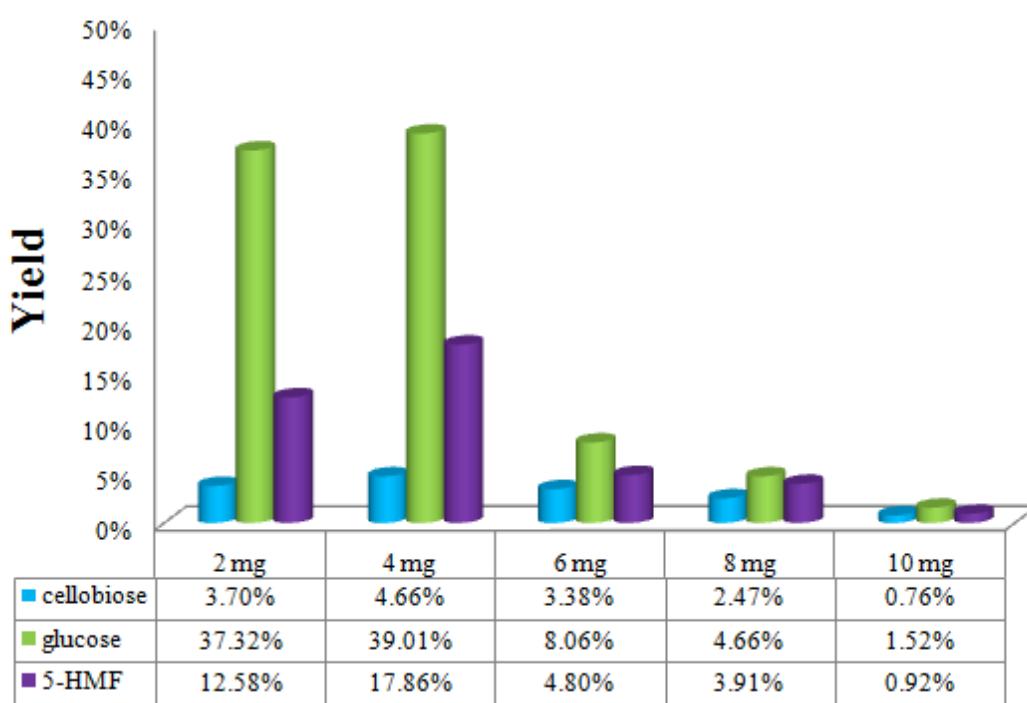
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**Table S1.** Indicators used in the study.

| Indicator            | Color alkaline form | Color acid form | pKa value |
|----------------------|---------------------|-----------------|-----------|
| Crystal violet       | Blue                | Yellow          | +0.8      |
| Fast Garnet GBC base | Yellow              | Red             | +2        |
| Methyl red           | Yellow              | Red             | +4.8      |
| Neutral red          | Yellow              | Red             | +6.8      |
| Phenol red           | Red                 | Yellow          | +7.65     |
| Phenolphthalein      | Red                 | Colorless       | +9.3      |
| 2,4-Dinitroaniline   | Violet              | Yellow          | +15       |

### Effect of the amount of catalysts on the conversion efficiency

The effect of different amount of catalysts on the yields of final products converted from cellulose was investigated with the range from 2 to 10 mg using LPMSN-Both as the catalyst. The result was shown in **Fig. S1** the optimal amount of catalyst was carried out with 4 mg of LPMSN-Both. With the presence of 4 mg LPMSN-Both catalysts, the yields of cellobiose, glucose and 5-HMF were the highest. When the amount of the catalyst exceeded 4 mg, the yield of each product was suddenly dropped down. We suggested it was because the inefficient stir and further decomposition of final products when too many catalysts were added in the reaction mixture.

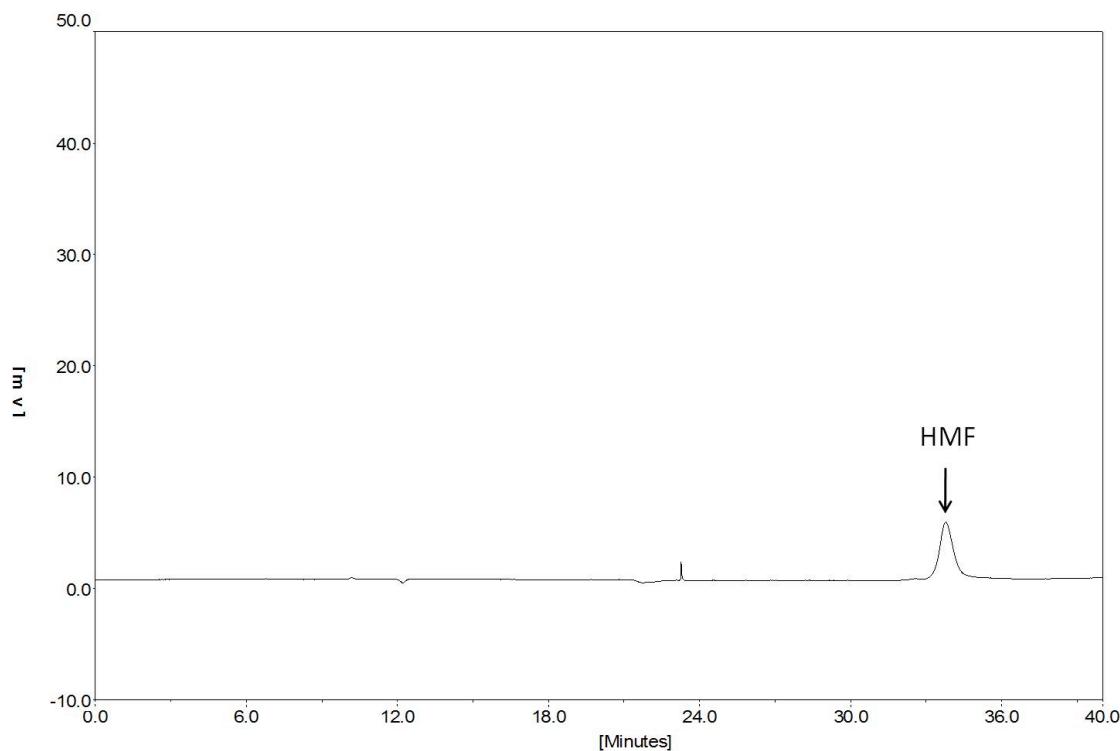


**Fig. S1** Effect of the amount of catalyst on the product yields

### Definition of yield

$$Y = \left( \frac{\text{Moles of product}}{\text{Moles of starting materials}} \right) \times 100 \%$$

All the calculation of final product yield was based on the glucose unit.

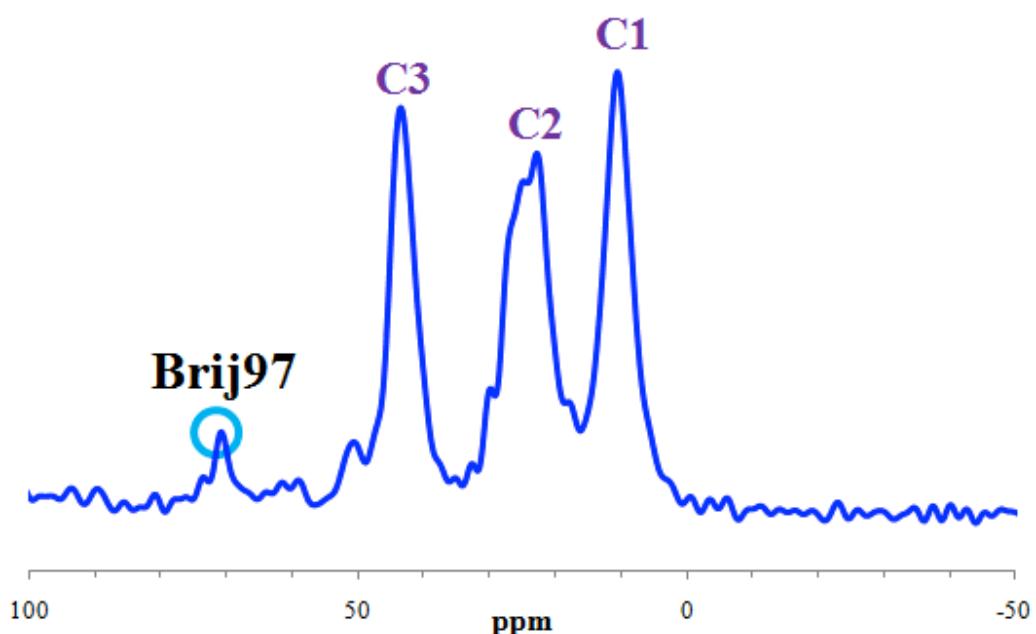


**Fig S2.** A typical HPLC spectrum of HMF standard. The position of the HMF peak is located at 33.76 min.

### Solid-state NMR results

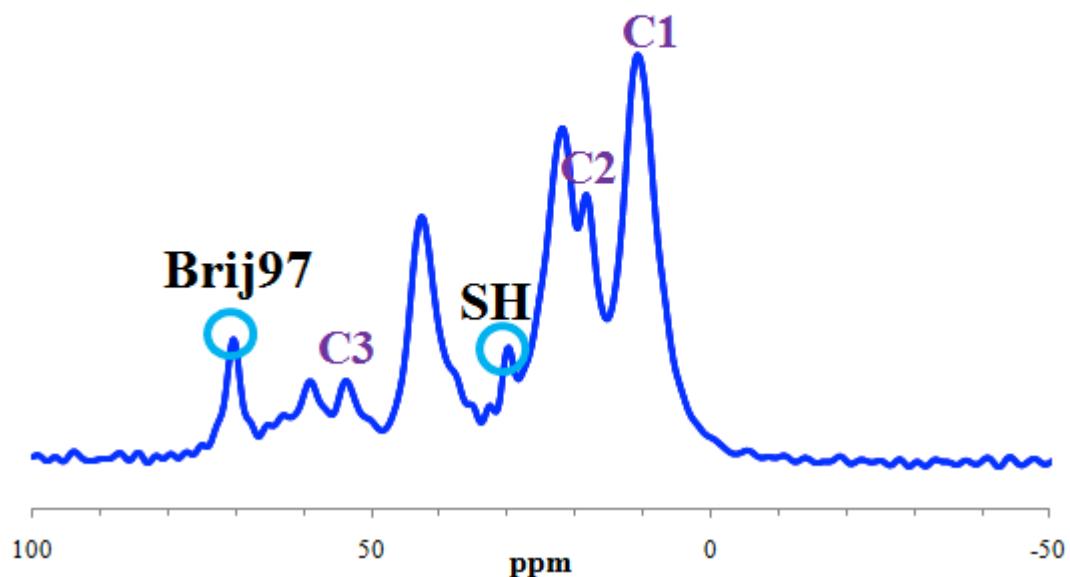
We qualitatively and quantitatively investigated the functional groups on the LPMSN using  $^{13}\text{C}$  and  $^{29}\text{Si}$  CPMAS solid state nuclear magnetic resonance (NMR). As shown in **Fig. S3.1**, there were three distinct peaks at approximately 11, 22 and 42 ppm corresponding to the carbons on the Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> from left to right. This result indicates that the amine groups were grafted onto the LPMSN surface and exhibit the functionality of alkaline. In **Fig. S3.2**, three individual peaks at 11, 18 and 54 ppm also correspond to the carbons on the Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub>H from left to right. This data proved that the sulfonic group were grafted onto the LPMSN surface and exhibited the acid functionality. However, this result also exhibited the peak of incomplete oxidation of thiol group. Besides that, the peaks of amine group were also appeared in the spectrum. In both figures there was a peak at 71 ppm due to the presence of the surfactant Brij-97. The amount of functional and hydroxyl group were listed in **Table 1**. The amount of silanol group of LPMSN, LPMSN-NH<sub>2</sub>, LPMSN-SO<sub>3</sub>H and LPMSN-Both are 6.12, 7.28, 5.14 and 2.51 mmol/g LPMSN. The amount of functional group of LPMSN, LPMSN-NH<sub>2</sub>, LPMSN-SO<sub>3</sub>H and LPMSN-Both are 1.06, 1.67, 1.35 and 2.32 mmol/g LPMSN. The incorporation and loading amount of functional group onto the LPMSN could be identified and calculated by CPMAS  $^{29}\text{Si}$  NMR. As shown in **Fig. S3.3-S3.6**, there were five individual peaks corresponding to Q<sup>4</sup> (Si(OSi)<sub>4</sub>), Q<sup>3</sup> (Si(OSi)<sub>3</sub>OH), Q<sup>2</sup> (Si(OSi)<sub>2</sub>(OH)<sub>2</sub>), T<sup>3</sup> (RSi(OSi)<sub>3</sub>) and T<sup>2</sup> (RSi(OSi)<sub>2</sub>OH). So the presence of T<sup>2</sup> and T<sup>3</sup> were also the evidence to prove both amine and sulfonic group are on the LPMSN. The percentage of Q<sup>4</sup>, Q<sup>3</sup>, Q<sup>2</sup>, T<sup>3</sup> and T<sup>2</sup> were summarized in **Table S2**.

**$^{13}\text{C}$  LPMSN-NH<sub>2</sub>**

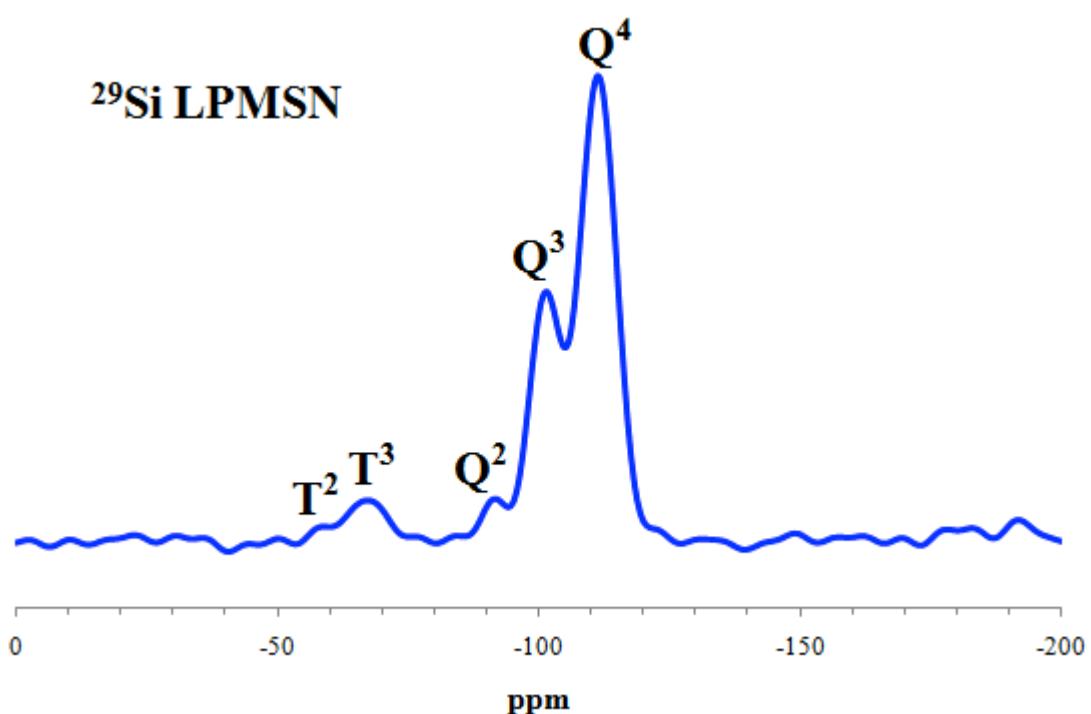


**Fig. S3.1** Solid-state NMR  $^{13}\text{C}$  spectrum of LPMSN-NH<sub>2</sub>

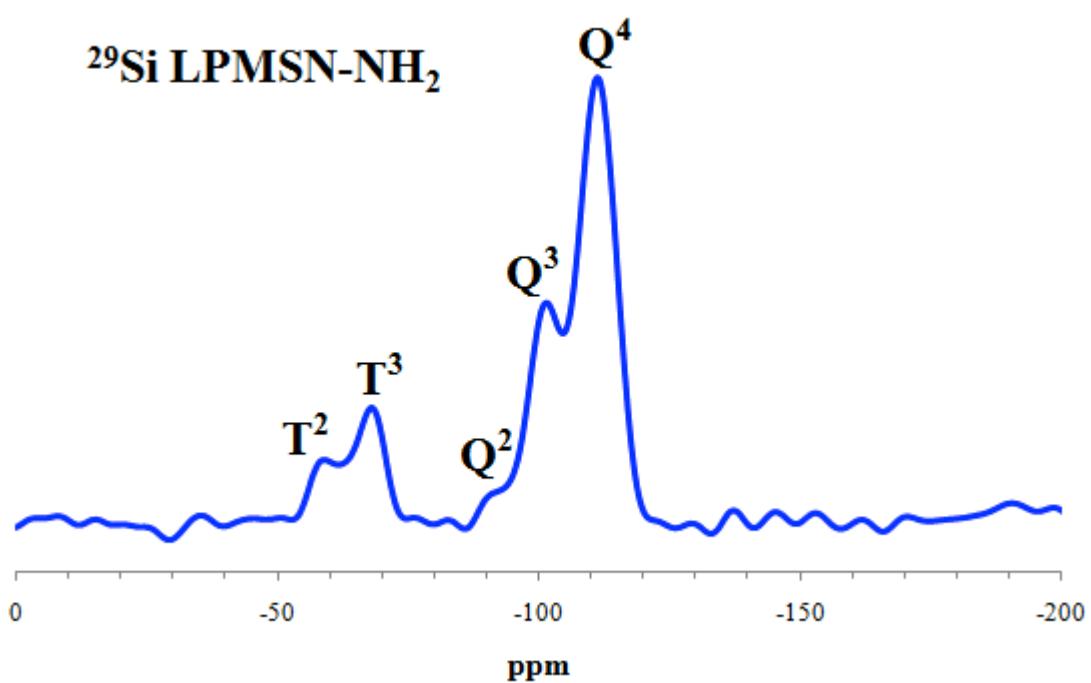
**$^{13}\text{C}$  LPMSN-SO<sub>3</sub>H**



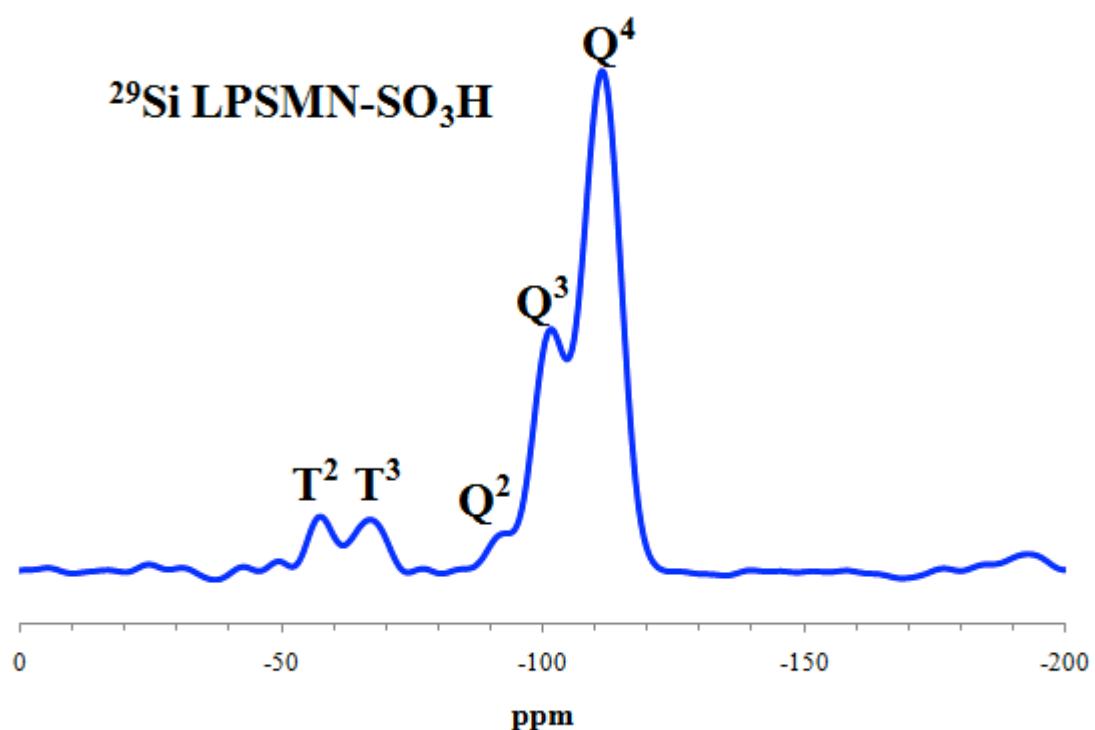
**Fig. S3.2** Solid-state NMR  $^{13}\text{C}$  spectrum of LPMSN-SO<sub>3</sub>H



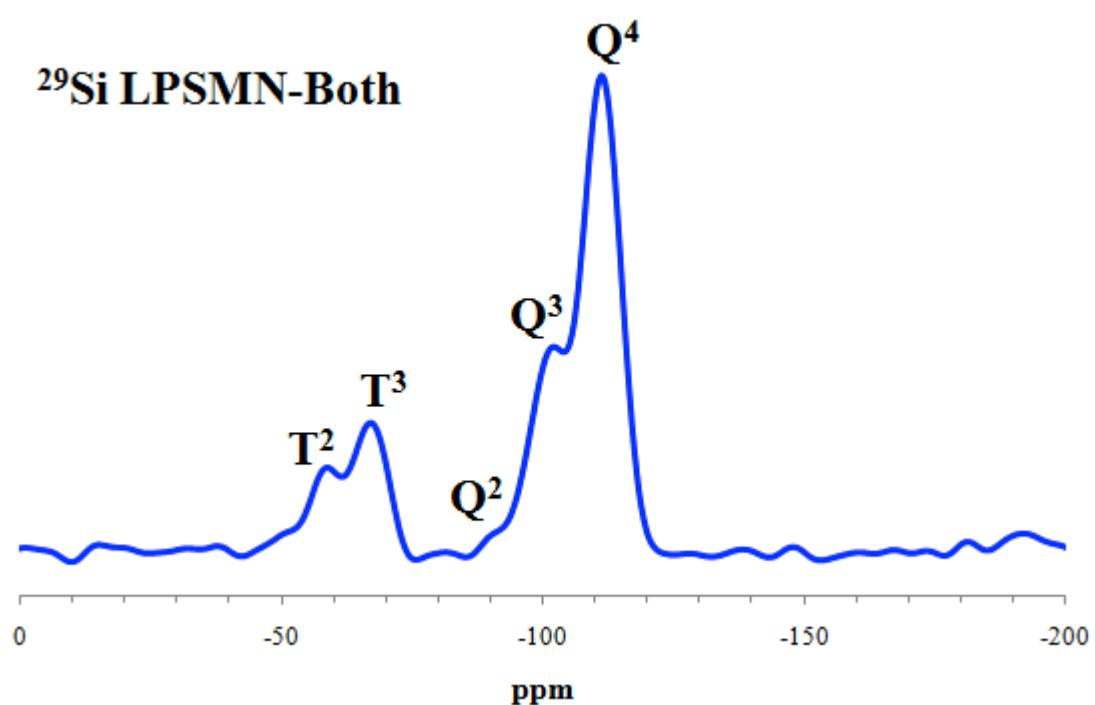
**Fig. S3.3** Solid-state NMR  $^{29}\text{Si}$  spectrum of LPMSN



**Fig. S3.4** Solid-state NMR  $^{29}\text{Si}$  spectrum of LPMSN-NH<sub>2</sub>



**Fig. S3.5** Solid-state NMR  $^{29}\text{Si}$  spectrum of LPMSN-SO<sub>3</sub>H

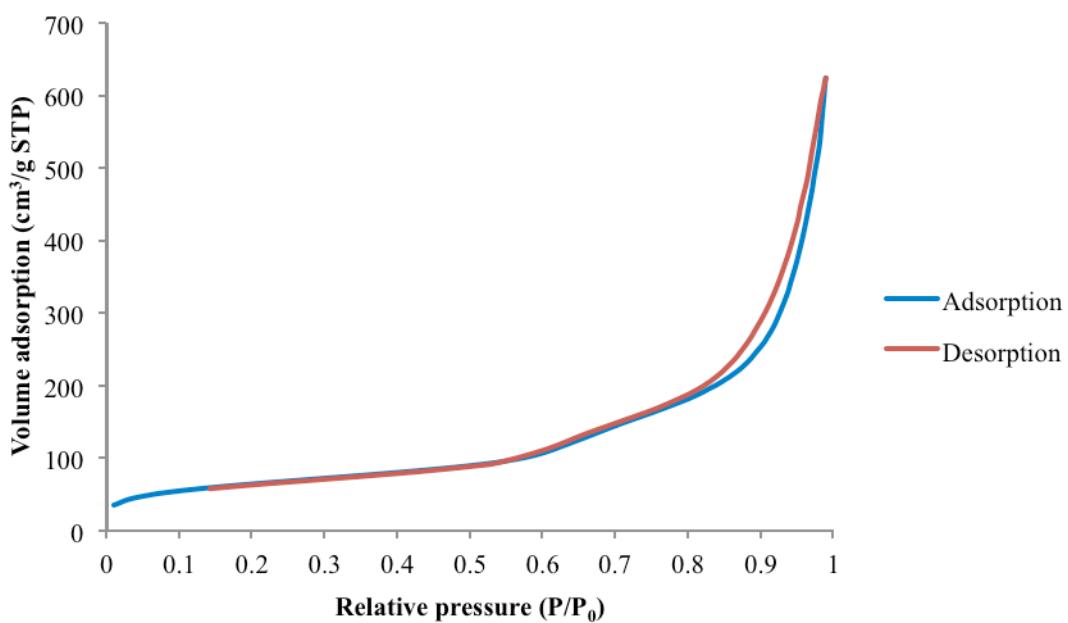


**Fig. S3.6** Solid-state NMR  $^{29}\text{Si}$  spectrum of LPMSN-Both

**Table S2.** Percentage of each characteristic peak of  $^{29}\text{Si}$  solid state NMR of LPMSN, LPMSN-NH<sub>2</sub>, LPMSN-SO<sub>3</sub>H and LPMSN-Both

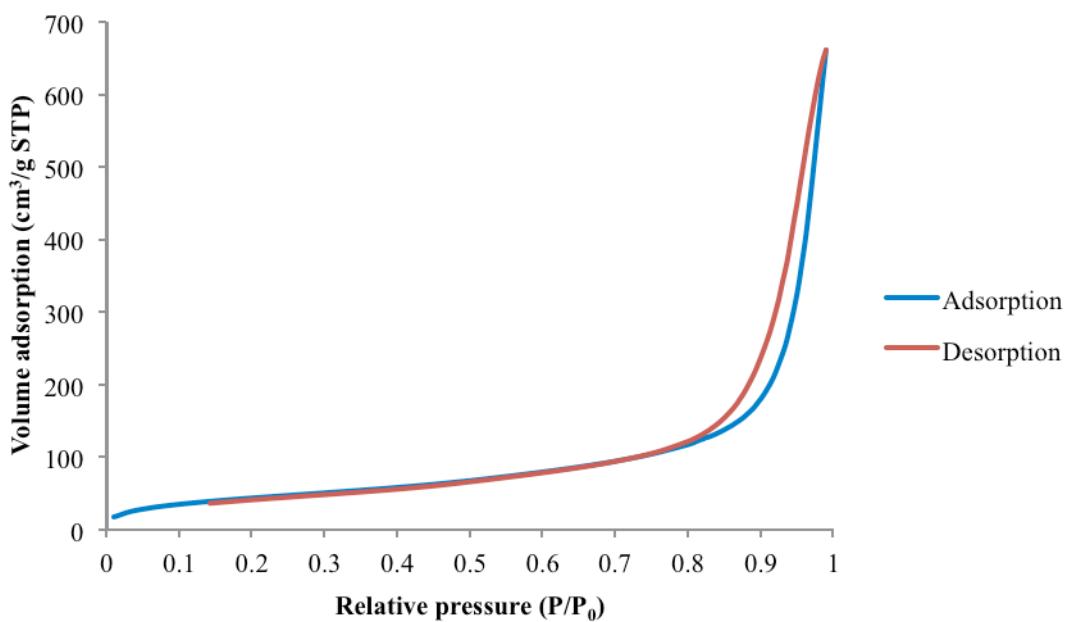
| Sample                  | Q <sup>4</sup> (%) | Q <sup>3</sup> (%) | Q <sup>2</sup> (%) | T <sup>3</sup> (%) | T <sup>2</sup> (%) |
|-------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| LPMSN                   | 56.86              | 30.59              | 5.39               | 5.17               | 1.98               |
| LPMSN-NH <sub>2</sub>   | 49.78              | 24.97              | 13.38              | 7.62               | 4.25               |
| LPMSN-SO <sub>3</sub> H | 56.58              | 27.35              | 5.81               | 6.18               | 4.08               |
| LPMSN-Both              | 50.87              | 21.33              | 2.85               | 15.09              | 9.85               |

## LPMSN



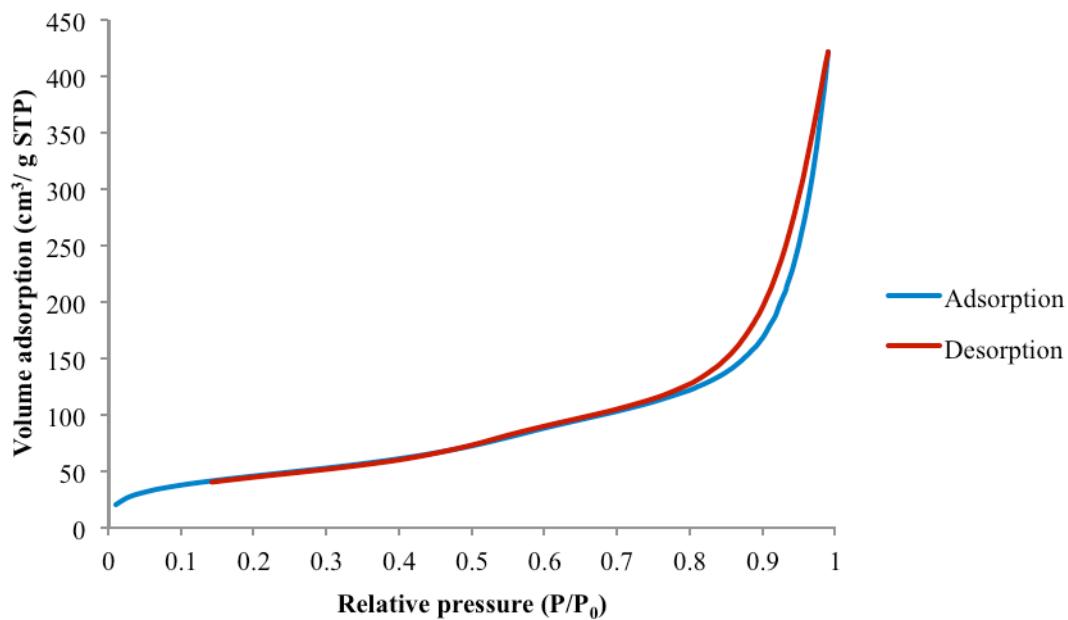
**Fig S4.1** Nitrogen adsorption/desorption isotherm of LPMSN

## LPMSN-NH<sub>2</sub>

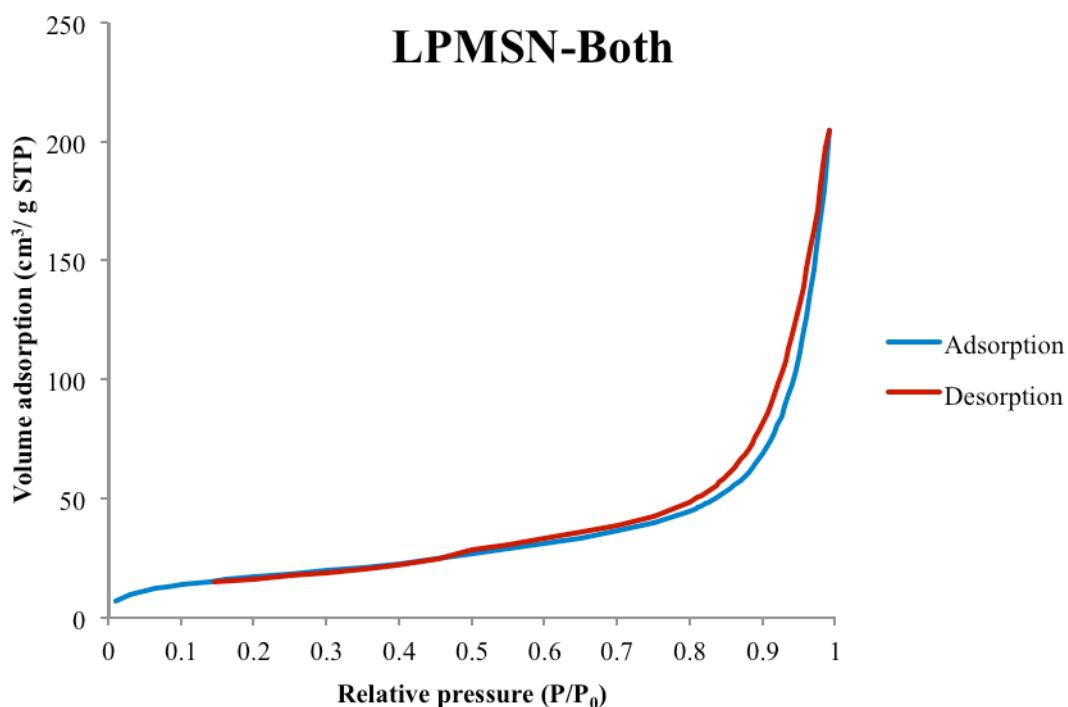


**Fig S4.2** Nitrogen adsorption/desorption isotherm of LPMSN-NH<sub>2</sub>

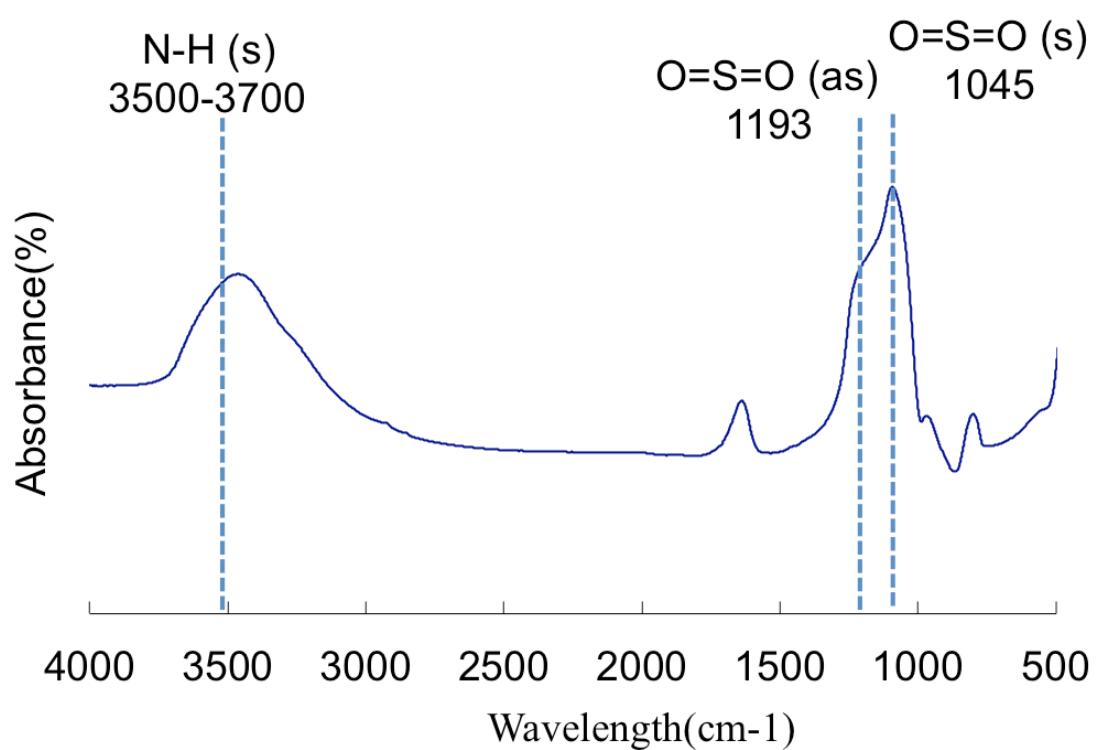
### LPMSN-SO<sub>3</sub>H



**Fig S4.3** Nitrogen adsorption/desorption isotherm of LPMSN-SO<sub>3</sub>H



**Fig S4.4** Nitrogen adsorption/desorption isotherm of LPMSN-Both



**Fig S5** FT-IR spectrum of LPMSN-Both