

## Supporting Information:

### **Insight into Proton Transfer in Phosphotungstic Acid Functionalized Mesoporous Silica based Proton Exchange Membrane Fuel Cells**

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**Table S1.** Calculated Proton Affinity (eV) and  $R_{P-H}$  Distance (pm) for the  $[PW_{12}O_{40}]^{3-}$  Anion.

| binding site    | PA     | $R_{P-H}$ |
|-----------------|--------|-----------|
| O <sub>b1</sub> | -16.66 | 430       |
| O <sub>b2</sub> | -16.74 | 370       |
| O <sub>t</sub>  | -16.10 | 565       |

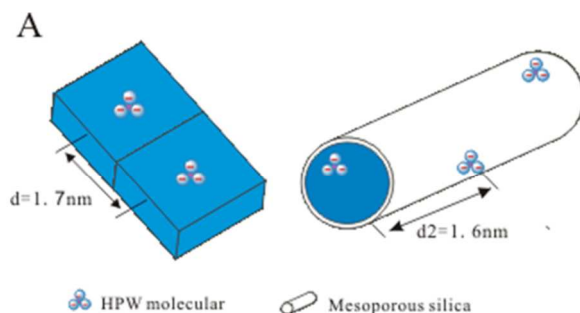
**Note 1:** Assumption on Calculation models:

Firstly, we proposed the distributions of HPW on silica are uniform. At a given concentration of HPW,  $c$ , we can get the average distance,  $d$ , between two nearest HPW molecules in HPW/meso-silica electrolyte by using the followed eq.1 and eq.2:

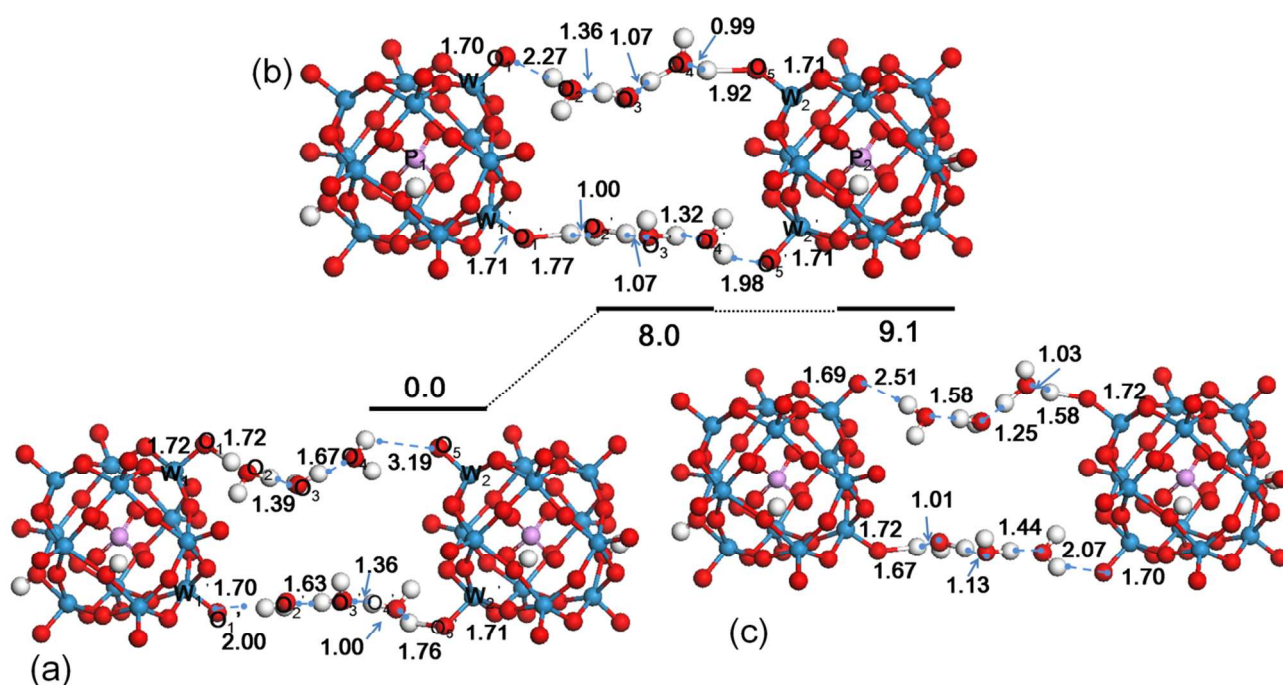
$$d = \sqrt{\frac{A \cdot m_{silica}}{m_{HPW} / M_{HPW}}} \quad (1)$$

$$c = \frac{m_{HPW} / M_{HPW}}{A \cdot m_{silica}} \times \frac{1}{2\pi r} \quad (2)$$

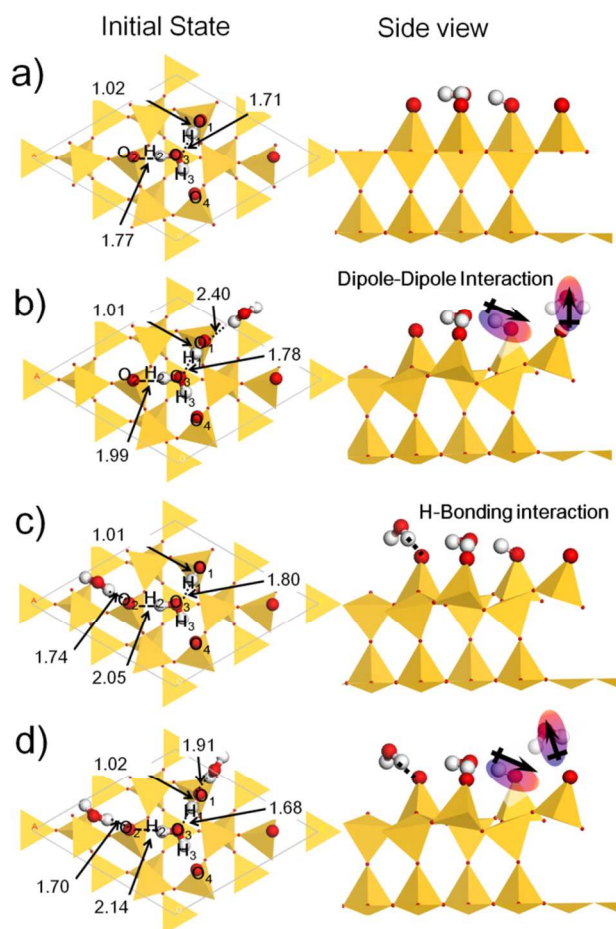
Where  $M_{HPW}$  is the molecular weight of HPW,  $A$  and  $r$  stand for surface area and pore diameter of siliceous host, respectively. For sample Ia3d-60-67,  $m_{HPW}/m_{silica} = 2:1$ ,  $A = 935 \text{ m}^2\text{g}^{-1}$ ,  $r = 2.5 \text{ nm}$ ,  $M_{HPW} = 3808$ , thus  $d$  is calculated to be 1.7 nm, which is in good consistent with the value of 1.5 nm from TEM results in experiment. The value of  $c$  is 1/1.6 nm, which means there was one HPW existence every 1.6nm in length inside the nanochannels. We secondly proposed the HPW adsorbed on silica stably and fixed the distance between the neighboring HPW during the process of proton transferring from one HPW to another one in our model as shown in Figure S1.

**Table S2.** DFT optimized interatomic distances and angles of the reactant ( $R_1$ ), Transition-State (TS) and product ( $P_1$ ) structures for proton transferring from O<sub>b1</sub> to O<sub>t</sub> on anhydrous HPW.

|                                            | R (H <sup>+</sup> on O <sub>b1</sub> ) | TS    | P(H <sup>+</sup> on O <sub>t</sub> ) |
|--------------------------------------------|----------------------------------------|-------|--------------------------------------|
| ∠O <sub>b1</sub> -W-O <sub>t</sub> (deg)   | 94.5                                   | 72.1  | 98.3                                 |
| ∠H-O <sub>b1</sub> -W-O <sub>t</sub> (deg) | 19.6                                   | 1.0   | 1.6                                  |
| O <sub>b1</sub> -H (Å)                     | 0.985                                  | 1.263 | 2.886                                |
| O <sub>t</sub> -H (Å)                      | 2.804                                  | 1.253 | 0.975                                |
| O <sub>b1</sub> -W (Å)                     | 2.109                                  | 2.129 | 1.883                                |
| O <sub>t</sub> -W (Å)                      | 1.679                                  | 1.768 | 1.833                                |
| H-W (Å)                                    | 2.677                                  | 2.069 | 2.531                                |
| W-P (Å)                                    | 3.501                                  | 3.334 | 3.422                                |
| ∠O <sub>b1</sub> -H-O <sub>t</sub> (deg)   |                                        | 133.4 |                                      |



**Figure S1.** DFT calculated equilibrium states and transition state for **three-water-assisted** proton-hopping reactions between two phosphotungstic acid molecules. (a) scheme of the proton transfer between two nearest HPW molecules inside the nanochannel of meso-silica; (b) Equilibrium structure (reactant) with H<sup>+</sup> bound to O<sub>1</sub> and O<sub>4</sub>' atoms; (c) Transition state for water-assisted proton-hopping reaction between two neighboring phosphotungstic acid molecules; (d) Equilibrium structure (product) with H<sup>+</sup> bound to O<sub>4</sub> and O<sub>1</sub>' atoms. The estimated activation energy for movement of proton between the two units is about **8.0 kJ/mol**.



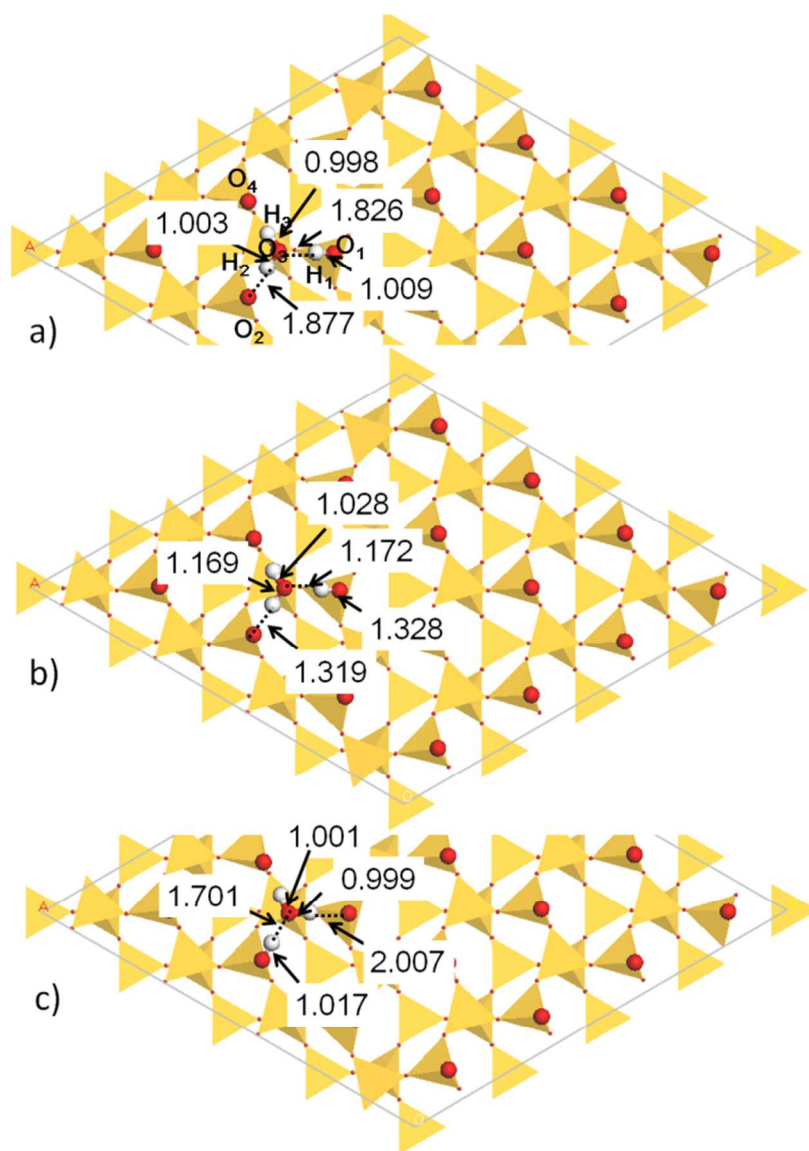
**Figure S2.** The water-concentration dependent proton transfer on the silica surface.

To account for the delicate water-concentration dependent proton transfer on silica surface, we present detailed illustrations in Figure S2. When the amount of water increases, the second adsorbed water affects the polar bond ( $O_1$ - $H_1$ ) by the dipole-dipole coupling interaction as shown in Figure S2(b) (c.f. Figure 8(b) in the manuscript). Water has a molecular polarity. The polarization of the second water promotes the charge transfer in the  $O_1$ - $H_1$  bond. Thus, the more electronegative atom ( $O_1$ ) has more negative charge and the other atom has more positive charge ( $H_1$ ). Therefore, bond-length ( $O_1$ - $H_1$ ) is decreased by 1 pm, with respect to the structure of Figure 6a. The increase of the strength of  $O_1$ - $H_1$  bond impedes the transfer of  $H_1$  to  $O_3$ , which provides the microscopic origin to address the increase of the proton transfer barrier with the presence of the second water on the silica surface.

For the same amount of water, there is another alternative configuration, namely, the second water is adsorbed near  $O_2$  atom, as shown in Figure S2(c) (c.f. Figure 8c in the manuscript), it forms a direct H-Bonding interactions with  $O_2$  with a distance of 1.74 Å to stabilize this configuration with respect to the

structure of Figure S2(a). The stabilization of such H-Bonding interaction will hinder the process of proton transfer, and lead to a higher activation barrier.

When the amount of water increases further, the additional water molecules can have both the polarization effect in Figure S2(b) and the H-bonding interaction in Figure S2(c), as presented in Figure S2(d). In this case, the proton transfer process will be impeded with the synergized effects of both configurations as described above. Thus, the activation barrier will be the highest in all models shown in Figure S2.



**Figure S3.** DFT calculated equilibrium states and transition state for water-assisted proton-hopping reactions on SiO<sub>2</sub>(111) surface. (a) Equilibrium structure (reactant) with H bound to O<sub>1</sub>; (b) Transition state for water-assisted proton-hopping reaction: H<sub>1</sub> transfer from O<sub>1</sub> to O<sub>3</sub>; H<sub>2</sub> transfer from O<sub>3</sub> to O<sub>2</sub>; (c) Equilibrium structure (product) with H<sub>2</sub> bound to O<sub>2</sub>. The estimated activation energy for movement of proton on SiO<sub>2</sub>(111) is about 51.5 kJ/mol.

**Table S3.** DFT optimized interatomic distances and angles of the reactant, Transition-State (TS) and product structures for proton transferring from O<sub>1</sub> to O<sub>2</sub> on SiO<sub>2</sub>(111) surface using 3x3 unit cell (distance in Å, angle in °).

|                                                     | Reactant | TS    | Product |
|-----------------------------------------------------|----------|-------|---------|
| O <sub>1</sub> ···H <sub>1</sub>                    | 1.009    | 1.328 | 2.007   |
| H <sub>1</sub> ···O <sub>3</sub>                    | 1.826    | 1.172 | 0.999   |
| O <sub>3</sub> ···H <sub>2</sub>                    | 1.003    | 1.169 | 1.701   |
| H <sub>2</sub> ···O <sub>2</sub>                    | 1.877    | 1.319 | 1.017   |
| O <sub>3</sub> ···H <sub>3</sub>                    | 0.998    | 1.028 | 1.001   |
| H <sub>3</sub> ···O <sub>4</sub>                    | 1.997    | 2.066 | 1.928   |
| ∠O <sub>1</sub> ···H <sub>1</sub> ···O <sub>3</sub> | 164.8    | 168.5 | 163.8   |
| ∠H <sub>1</sub> ···O <sub>3</sub> ···H <sub>2</sub> | 115.7    | 127.3 | 117.5   |
| ∠O <sub>3</sub> ···H <sub>2</sub> ···O <sub>2</sub> | 166.8    | 170.3 | 175.0   |
| ∠H <sub>1</sub> ···O <sub>3</sub> ···H <sub>3</sub> | 117.0    | 109.8 | 106.4   |
| ∠O <sub>3</sub> ···H <sub>3</sub> ···O <sub>4</sub> | 167.1    | 162.7 | 167.0   |
| ∠H <sub>2</sub> ···O <sub>3</sub> ···H <sub>3</sub> | 106.1    | 107.5 | 118.7   |