# Supplementary Information

# Suitable acid groups and density in electrolytes to facilitate proton conduction

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**Contents**

## I. The order of acidity

Table S1 Experimental pKa (25°C) of the acid molecules[S1]

| | $C_6H_5PO_3H_2$ | $C_6H_5SO_3H$ | $CF_3CF_2PO_3H_2$ | $CF_3CF_2SO_3H$ | $CH_3PO_3H_2$ |
|---|---|---|---|---|---|
| pKa | 1.83 (pK1) | 0.7 | - | −14 ($CF_3SO_3H$) | 2.38 (pK1) |

We evaluate the order of acidity among five molecules here. The stronger acidity is, the lower pKa becomes. Then, we referred to pKas of some acids. However, we could not obtain the experimental pKas of $CF_3CF_2PO_3H_2$ and $CF_3CF_2SO_3H$. When we take a look at the pKas of $CF_3SO_3H$, −14, as a reference of $CF_3CF_2SO_3H$, it is noted that fluorine withdraws electrons to make the sulfonic acid group much stronger. In addition, sulfonic acid is stronger than phosphoric acid. Therefore, the order of acidity is as follows: $CF_3CF_2SO_3H$ > $CF_3CF_2PO_3H_2$ > $C_6H_5SO_3H$ > $C_6H_5PO_3H_2$ > $CH_3PO_3H_2$. We can roughly estimate the quantitative difference of pKa among the acids based on Table S2 (see section III).

## II. The comparison of hopping and reorientation

The hopping and reorientation frequencies are compared here, which confirm that reorientation is still the rate-determining step. According to a previous report,[S2] the activation energy of hopping, $E_{a:hop}$, is described as:

$$E_{a:hop} = 381.21r^2 - 1783.0r + 2083.4,$$

where r = $Roo^{1st}$ [Å], and the unit for $E_{a:hop}$ is kJ mol$^{-1}$. The reorientation frequency in H-bonds in all ranges of $Roo^{1st}$ at each $WN$, represented as $f_{hop}(WN)$, is derived as well as $f_{reor}(WN)$.[S1] The $f'x(WN)$ (x= hop or reor) values are shown in Fig. S1. The hopping in $WN = 0$, for example, in the case with $CH_3PO_3H_2$, which indicates hopping from $CH_3PO_3H_2$ to $CH_3PO_3H_2$, which results in $CH_3PO_3H^-$ and $CH_3PO_3H_3^+$. Because this phenomenon should rarely occur, $f'_{hop}(0)$ was excluded. All $f'_{hop}(WN)$ values are higher than those of $f'_{reor}(WN)$, which indicates that reorientation is the rate-determining step in all cases.

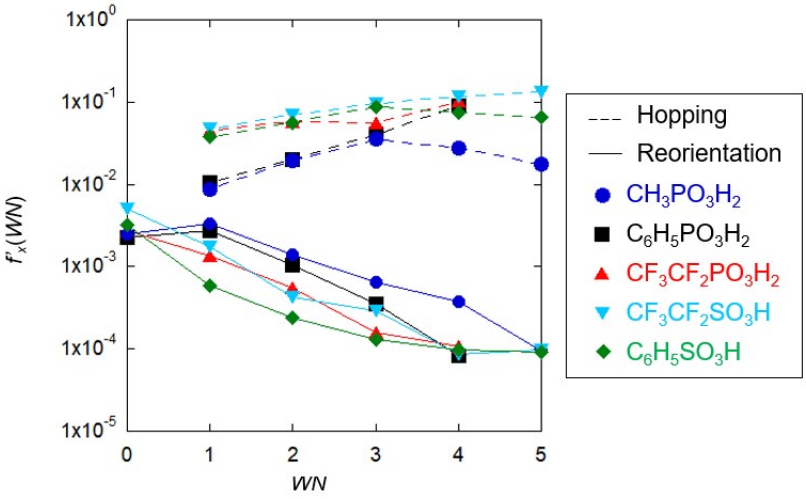


Figure S1 $f'x(WN)$ (x = hop and reor) associated with $WN$

## III. The relation of $f'_{reor}(WN)$ and electropolarization between water and acid molecules

We investigated the relation of $f'_{reor}(WN)$ and electropolarization between water and acid molecules. Partial atomic electrostatic charges were computed with the Mulliken scheme. To calculate the Mulliken charge of each atom, the basis set of hydrogen, DZP, was changed to the double-ζ split-valence basis set (DZ) while fixing the structure calculated with the DZP basis set. This change gives reasonable values for the charge calculation of a water molecule.[S3]

The average charges on two acid molecules in the models with each λ are shown in Table S2. The order of polarization, from largest to smallest, is $CF_3CF_2SO_3H > CF_3CF_2PO_3H_2 > C_6H_5SO_3H > C_6H_5PO_3H_2 \gtrsim CH_3PO_3H_2$, which is the same to the order of acidity in section I. It is reasonable because acidity means how strong acids tend to be polarized in water, resulting in the dissociation of $H^+$. Therefore, we can roughly estimate the quantitative difference of acidity (pKa) among the acids based on Table S2. Small λ induces low polarization, and large λ does vice versa, which is reasonable because many water molecules can facilitate dielectric responses with their dipoles.

Figure S2 shows $f'_{reor}(WN)$s associated with λ in the models composed of acid molecules. As a general tendency, the $f'_{reor}(WN)$s of phosphates hardly depends on λ although λ changes polarization a lot. Therefore, the electropolarization of acid molecules does not directly influence the $f'_{reor}(WN)$. Meanwhile, the $f'_{reor}(WN)$s of sulfates depends on λ, and a large λ enhances the $f'_{reor}(WN)$. This paper proposes a suitable acid group that facilitates acid-acid interactions and improves proton conductivity at low RH, *i.e.,* low λ. Therefore, phosphates are more suitable than sulfates. The conclusion is the same in the main text.

The different tendency on λ seems to be derived from the nature of phosphates and sulfates, as discussed in Section 4.2 in the main text. Generally, an acid forms a strong H-bond, which can be diluted by water molecules to form a weak H-bond network and a large electropolarization, as shown in Table S2, although a more polarized negative charge should form a strong H-bond. The weak H-bond, regardless of the large polarized negative charge, should be interpreted to indicate that a positive charge exists on a water molecule distant from the acid. In the case of sulfates, the single -OH bond is simply diluted by water molecules and facilitates reorientation when λ is large. Instead, the two -OH bonds in phosphates influence the H-bond network of water molecules in two ways, which makes it difficult for the positive charge to exist at a distance from the phosphates. Therefore, far more water molecules are required for phosphates to increase $f'_{reor}(WN)$s like sulfates. Actually, $f'_{reor}(WN)$s with λ =15 in phosphates show different tendencies from other λs, and more λ might enhance $f'_{reor}(WN)$. However, the focus in this paper is on the proton conductivity at low RH, and thus, we did not further investigate the cases with larger values of λ.

Table S2 Average charges on two acid molecules in the models with each λ.

| λ | $C_6H_5SO_3H$ | $CF_3CF_2SO_3H$ | $C_6H_5PO_3H_2$ | $CF_3CF_2PO_3H_2$ | $CH_3PO_3H_2$ |
|---|---|---|---|---|---|
| 2 | –0.30 | –0.53 | –0.16 | –0.32 | –0.15 |
| 3 | –0.43 | –0.79 | –0.18 | –0.42 | –0.17 |
| 4 | –0.41 | –0.84 | –0.21 | –0.50 | –0.20 |
| 5 | –0.51 | –0.91 | –0.23 | –0.56 | –0.20 |
| 15 | –0.78 | –1.18 | –0.34 | –0.82 | –0.31 |

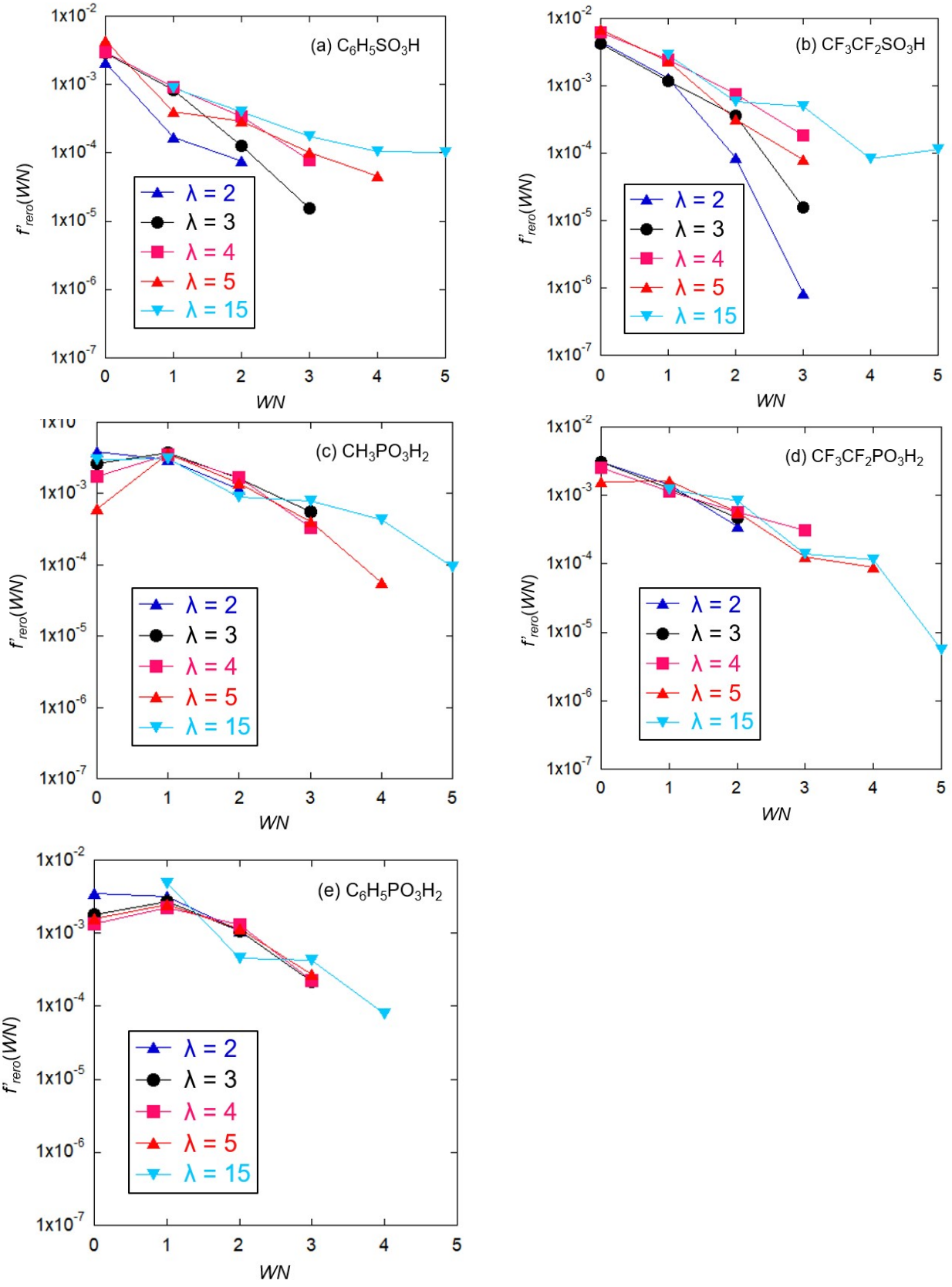


Figure S2 $f'_{reor}(WN)$ in the model with each λ, composed of (a) $C_6H_5SO_3H$, (b) $CF_3CF_2SO_3H$, (c) $CH_3PO_3H_2$, (d) $CF_3CF_2PO_3H_2$, and (e) $C_6H_5PO_3H_2$.

**References**

S1. Chemistry Book (https://www.chemicalbook.com)

S2. T. Ogawa, H. Ohashi, T. Tamaki and T. Yamaguchi, *Chem. Phys. Lett.*, 2019, **731**, 136627.

S3. T. Ogawa, H. Ushiyama, J. M. Lee, T. Yamaguchi and K. Yamashita, *J. Phys. Chem. C*, 2011, **115**, 5599-5606.