Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials for

Molecular dynamics simulations of proton conducting mediums containing phosphoric acid

Ryosuke Jinnouchi

Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

Contents

S1 Size consistency

The radial distribution functions (RDFs), diffusion coefficients of hydrogen atoms, lifetimes of $H_nPO_4^{-(3-n)}$ ions, and rotational time calculated by the 200 ps MD simulations on the proton conductive $48H_3PO_4$ and $32CsH_2PO_4$ systems are compared with those calculated by the 200 ps MD simulations on $96H_3PO_4$ and $64CsH_2PO_4$ systems in Figs. S1 and S2, respectively.

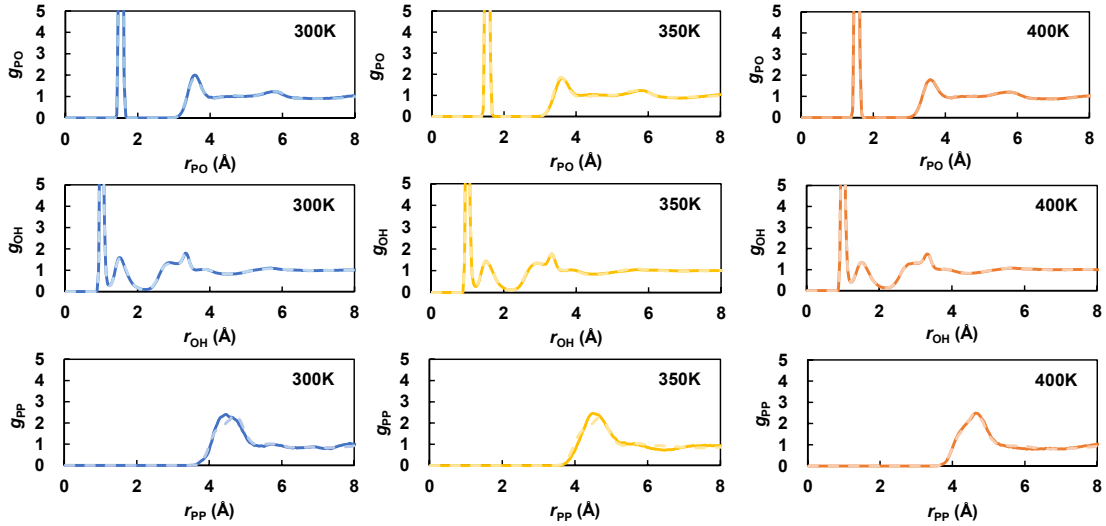

Fig. S1 Radial distribution functions of $48H_3PO_4$ (solid lines) and $96H_3PO_4$ (dashed lines) at 300, 350 and 400 K.

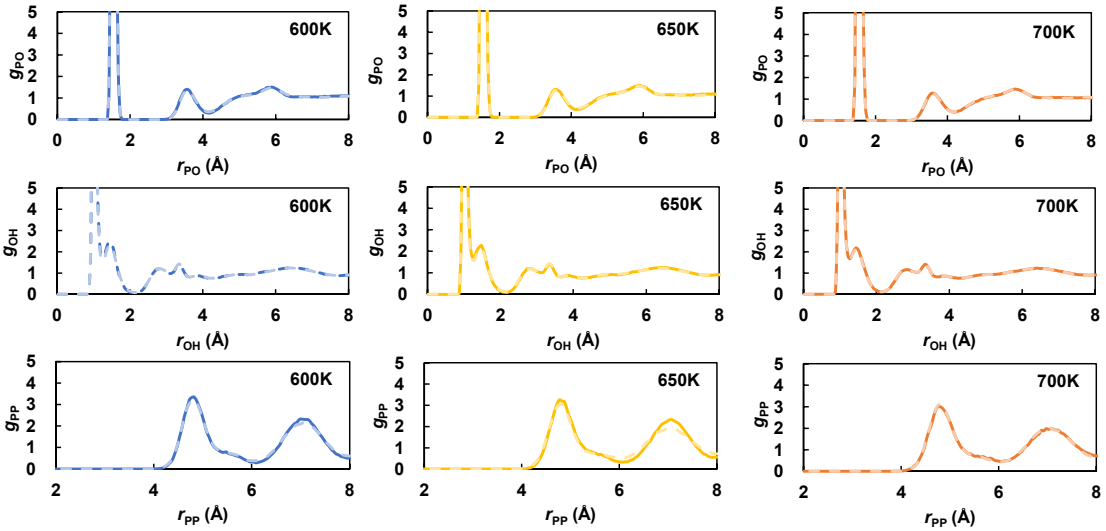

Fig. S2 Radial distribution functions of $32CsH_2PO_4$ (solid lines) and $64CsH_2PO_4$ (dashed lines) obtained by 200 ps MD simulations at 600, 650 and 700 K.

Table S1 Diffusion coefficients of hydrogen atoms ($m^2\ s^{-1}$) in $48H_2PO_4$ and $96\ H_2PO_4$ obtained by 200 ps MD simulations.

Temperature (K)	$48H_2PO_4$	$96\ H_2PO_4$
300	0.21×10^{-10}	0.34×10^{-10}
350	0.76×10^{-10}	0.73×10^{-10}
400	2.33×10^{-10}	2.45×10^{-10}
Temperature (K)	$32CsH_2PO_4$	$64CsH_2PO_4$
600	0.54×10^{-10}	0.68×10^{-10}
650	1.17×10^{-10}	1.09×10^{-10}
700	1.21×10^{-10}	1.73×10^{-10}

Table S2 Lifetimes of $H_nPO_4^{(3-n)-}$ (fs) in $48H_2PO_4$ and $96\ H_2PO_4$ obtained by 200 ps MD simulations.

Temperature (K)	*n*	$48H_2PO_4$	$96\ H_2PO_4$
300	2	56	60
	3	116	109
	4	46	56
350	2	41	44
	3	118	95
	4	44	45
400	2	40	33
	3	71	76
	4	42	36
Temperature (K)	*n*	$32CsH_2PO_4$	$64CsH_2PO_4$
600	1	15	16
	2	36	42
	3	15	17
650	1	14	16
	2	34	40
	3	15	16
700	1	13	14
	2	33	34
	3	14	15

Table S3 Reorientation time of $H_nPO_4^{(3-n)-}$ (ps) in $48H_2PO_4$ and 96 H_2PO_4 obtained by 200 ps MD simulations.

Temperature (K)	$48H_2PO_4$	$96H_2PO_4$
300	1065	931
350	305	453
400	110	107
Temperature (K)	$32CsH_2PO_4$	$64CsH_2PO_4$
600	140	103
650	123	70
700	64	67

S2 MD simulation time

In order to verify the MD simulation times, the correlation times of the three computational systems were examined by the statistical inefficiencies obtained by the method suggested in Refs. 39, 42 and 43. To calculate the statistical inefficiency, the MD trajectory is broken down into a series of N_{block} blocks of size M_{block}. The average of the property A, which is the potential energy similarly to Refs. 42 and 43, is calculated for each block as:

$$\langle A\rangle_b = \frac{\sum_{i=1}^{M_{\text{block}}} A_i}{M_{\text{block}}}. \quad \text{(S1)}$$

The block averages become increasingly uncorrelated as the number of steps M_{block} in each block increases. The variance of the block averages, $\sigma^2(<A>_b)$, becomes inversely proportional to N_{block}:

$$\sigma^2(\langle A\rangle_b) = \frac{\sum_{b=1}^{N_{\text{block}}}(\langle A\rangle_b - \langle A\rangle_{\text{total}})^2}{N_{\text{block}}}, \quad \text{(S2)}$$

where $<A>_{\text{total}}$ is the average of the property A for the entire trajectory. The statistical inefficiency, s, is calculated as:

$$s = \lim_{M_{\text{block}}\to\infty} \frac{M_{\text{block}}\Delta t\sigma^2(\langle A\rangle_b)}{\sigma^2(\langle A\rangle_{\text{total}})}. \quad \text{(S3)}$$

The statistical inefficiency is related to the correlation time, τ, as $s = 2\tau$ in a Markovian process. In actual computations, the convergency of the statistical inefficiency is examined increasing the block size M_{block} up to 10^5. The computed statistical inefficiencies of the liquid PA, CsH_2PO_4 and CP are summarized in Fig. S3. In all three systems, the correlation times are estimated to be much shorter than the MD simulation times. Accordingly, the correlations in the errors of MSDs are expected to be small.

The calculated MSDs of hydrogen atoms in the three materials are shown in Fig. S4, and the dependence of the computed diffusion coefficients of hydrogen atoms on the MD simulation time is summarized in Fig. S5. Here, the diffusion coefficients were calculated from the slopes of MSDs after 10 ps relaxations. For both liquid PA and cubic CsH_2PO_4, the simulation time of 200 ps is judged to be sufficiently long while for the monoclinic CsH_2PO_4 and CP, considerably longer simulations will be required to quantitatively compute the diffusion coefficients.

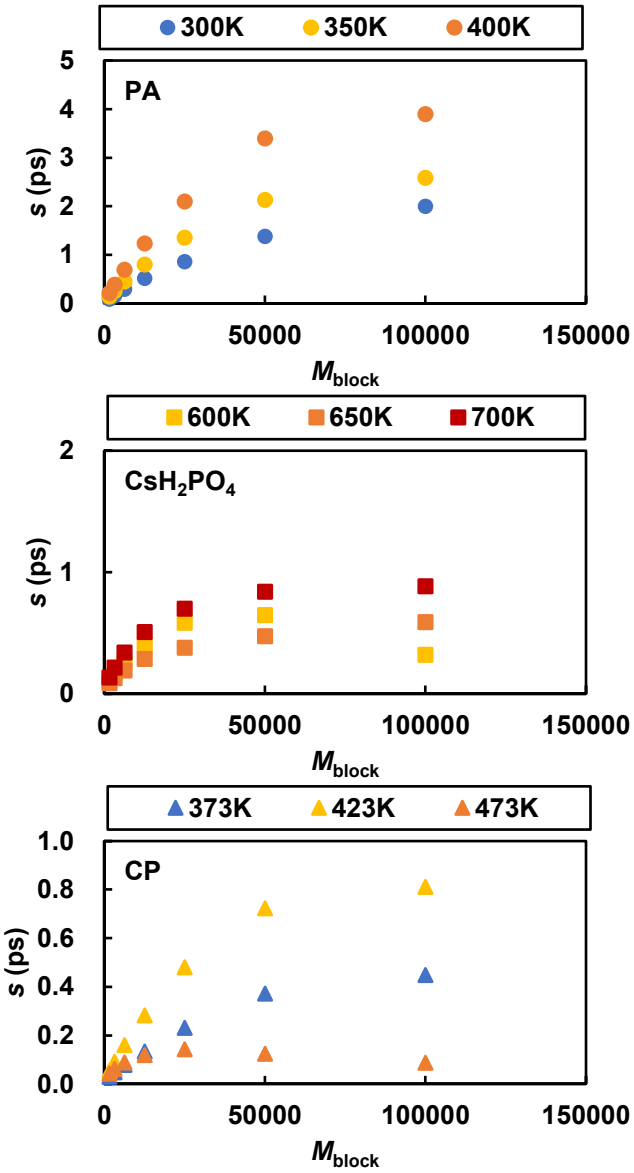

Fig. S3 Statistical inefficiencies, *s*, of the liquid PA ($48H_3PO_4$), cubic CsH_2PO_4 ($32CsH_2PO_4$) and CP (4 formula units of $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$) as functions of the block size, M_{block}.

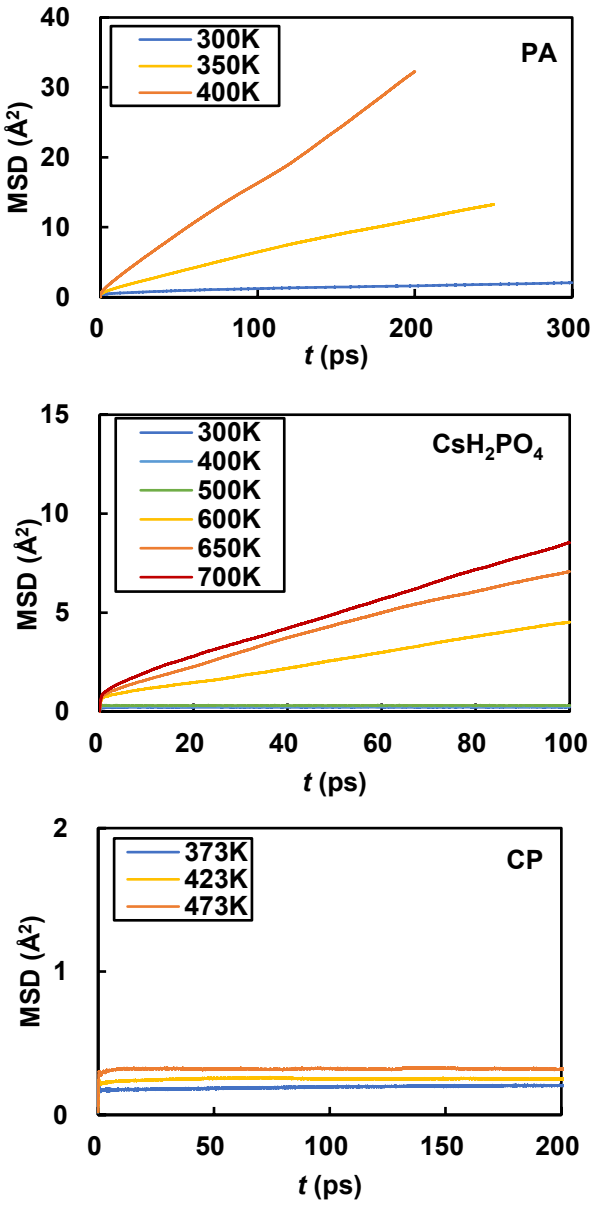

Fig. S4 Mean square displacements (MSDs) of hydrogen atoms in the liquid PA ($48H_3PO_4$), CsH_2PO_4 ($32CsH_2PO_4$) and CP (4 formula units of $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$).

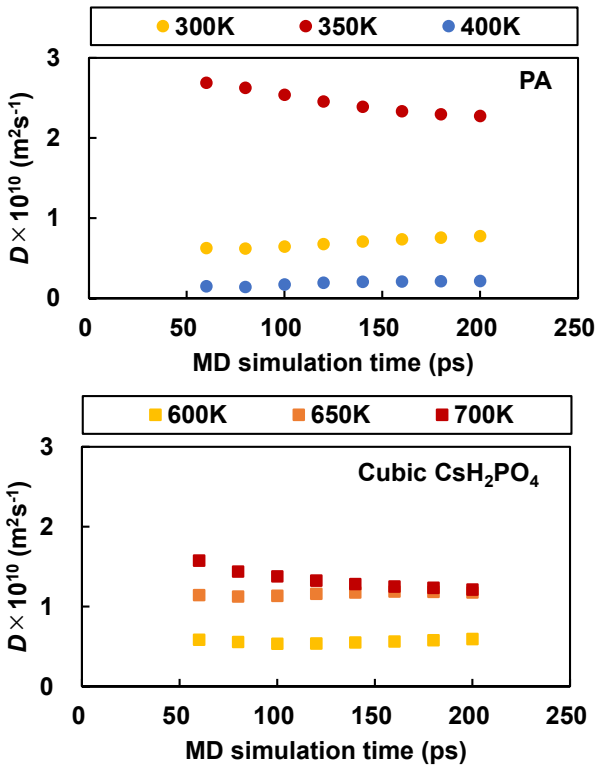

Fig. S5 Dependence of the computed diffusion coefficients of hydrogen atoms in the liquid PA and cubic CsH_2PO_4 on the MD simulation time.