Supporting Information for

Functional Group-Dependent Proton Conductivity of Phosphoric Acid-Doped Ion-pair Coordinated Polymer Electrolyte: A Molecular Dynamics Study

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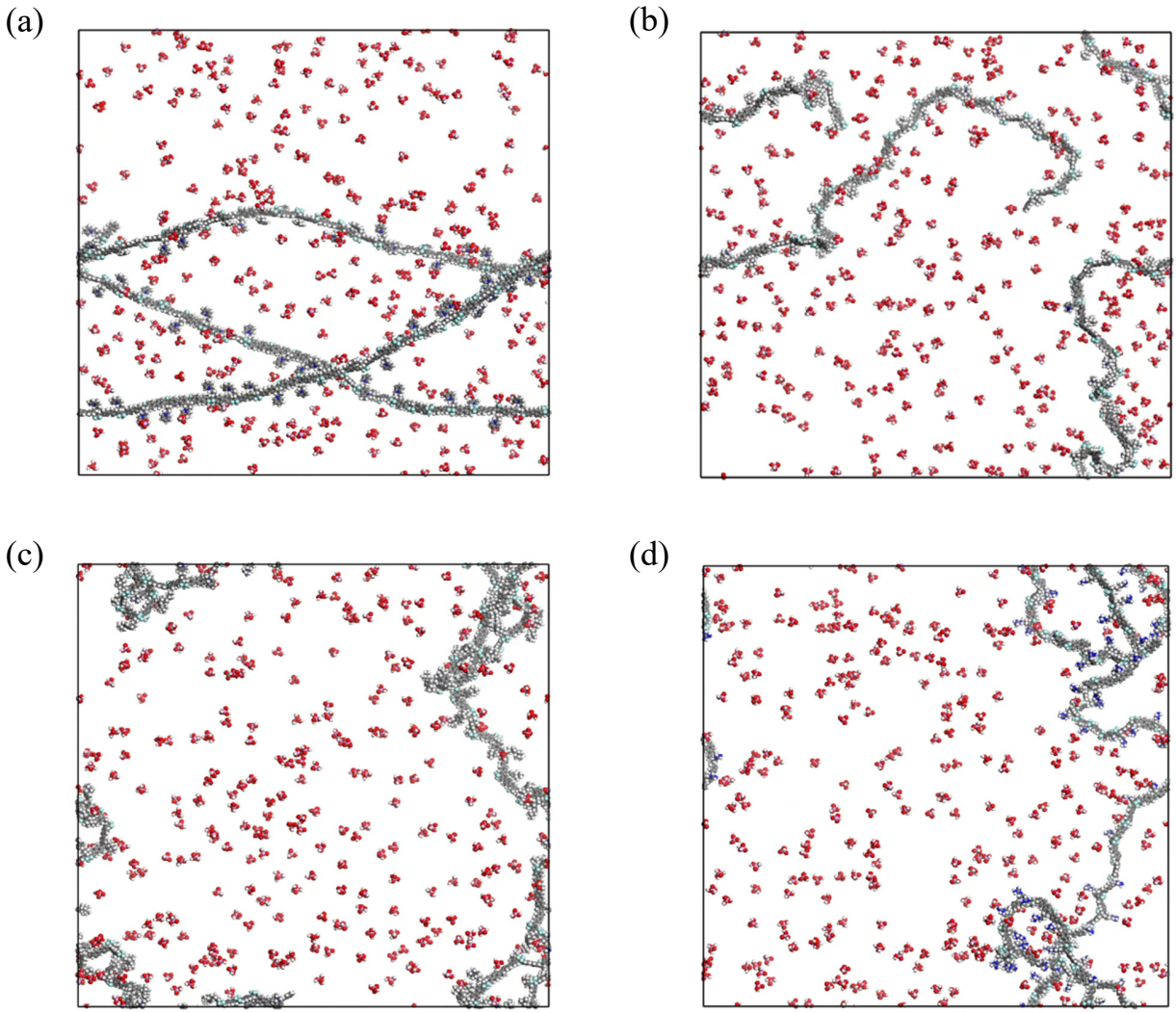


Figure S1. Initial structures of (a) PB-PP-PY(0.9), (b) PB-PP-TMA(0.9), (c) PB-PP-BTMA(0.9), and (d) PB-PP-GN(0.9), which were obtained after the polymer growth step in a large cubic simulation boxes with a cell volume of 200×200×200 $Å^3$.

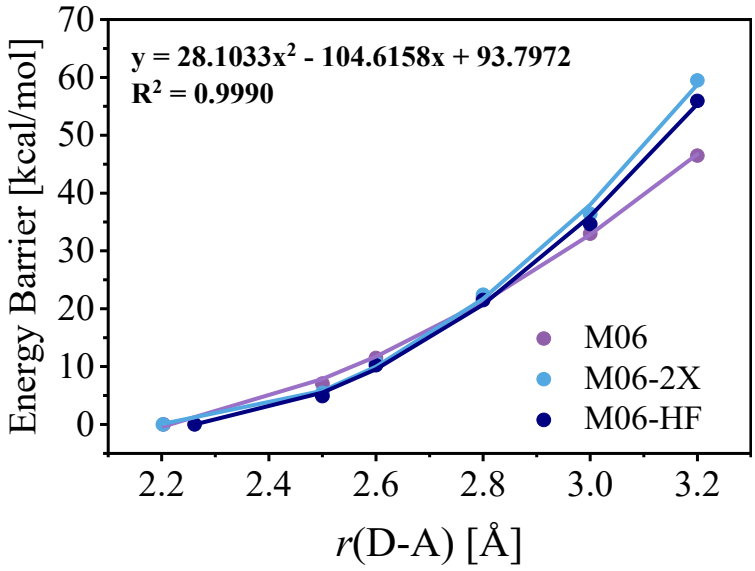


Figure S2. Comparison of donor-acceptor distance, *r*(D-A) dependent proton hopping barriers calculated using three different functionals of M06, M06-2X and M06-HF having different amount of Hartree-Fock exchange ratio.

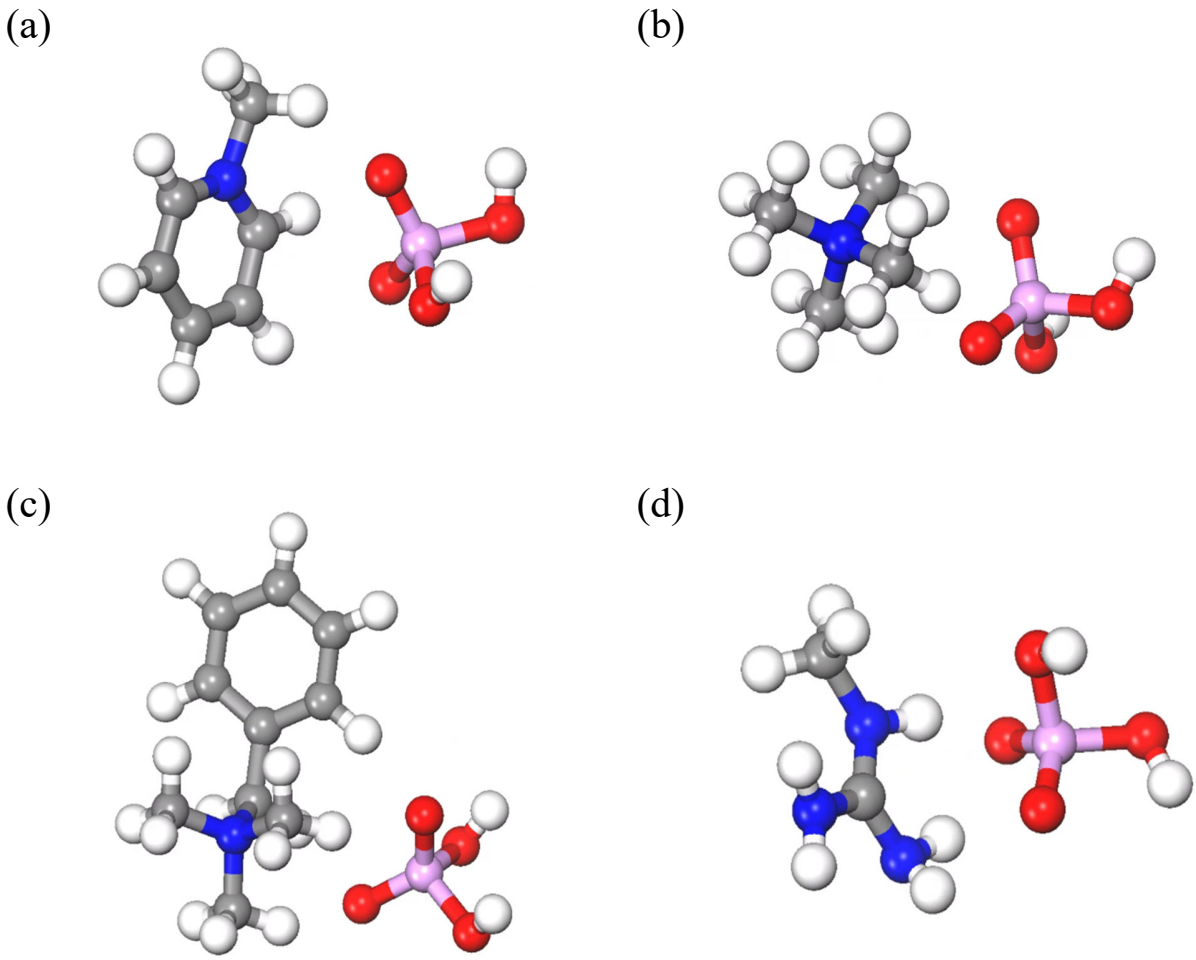


Figure S3. DFT-optimized structures for the ion-pair complexes consisting of anionic PS and cationic functional group moieties of (a) PY, (b) TMA, (c) BTMA and (d) GN. Binding energy is calculated under B3LYP-D3 and 6-31G* level. O, H, N, C, and P atoms are shown in red, white, blue, grey, and pink, respectively.

Conversion [%]	N_{group}	N_{PA}	N_{total}			
			PA-PB-PY	PA-PB-TMA	PA-PB-BTMA	PA-PB-GN
10	8	296	4782	4798	4902	4766
20	15	289	4908	4938	5133	4878
30	23	281	5052	5098	5397	5006
50	38	266	5322	5398	5892	5246
70	53	251	5592	5698	6387	5486
90	68	236	5862	5998	6882	5726

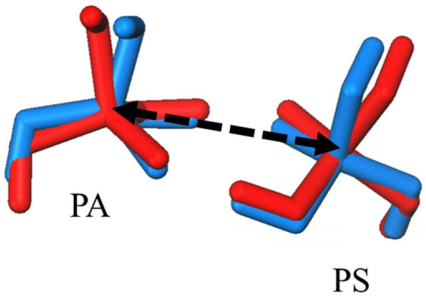
Table S1. Composition of simulation cell as a function of conversion ratio. The number of cationic functional groups, N_{group}, is equal to the number of anionic PSs to maintain the cell neutrality. The number of PAs, N_{PA}, and the number of total atoms, N_{total}, are provided.

(a)

	R_0 [Å]	D_0 [kcal/mol]
P	4.30	0.28
O in P = O	3.40	0.07
O in P – O – H	3.70	0.0957
H	1.00E-4	0.00

	K [kcal/mol]	θ [°]
O in P – O – H	100	115.00

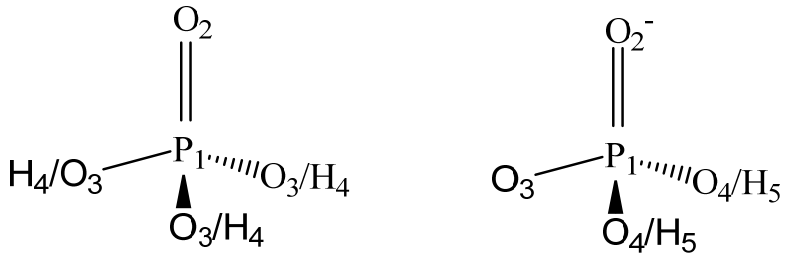
(b)



	QM	FF
ΔE_b [eV]	-1.35	-0.89
r [Å]	4.05	3.97

Table S2. (a) Force field (FF) parameters modified to describe the PA-PS interaction. (b) Comparison of DFT- and FF-optimized structures, binding energy (ΔE_b), and distance (r) between PA and PS. The DFT- and FF-optimized structures are shown in red and blue, respectively.

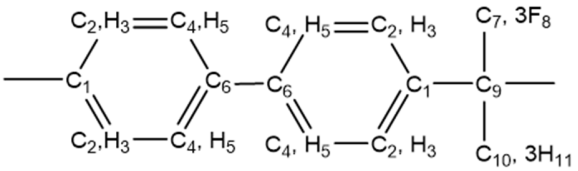
(a) (b)



PA PS

i	PA	PS
1	0.9487	1.0311
2	-0.6094	-0.7670
3	-0.5251	-0.6911
4	0.4120	-0.6329
5	-	0.3464

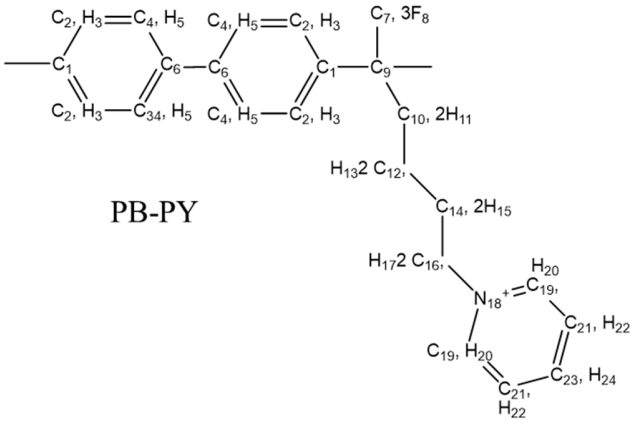
Table S3. Atomic partial charges assigned to (a) PA and (b) PS. The index number *i* is written next to the element in molecular structures.



PB

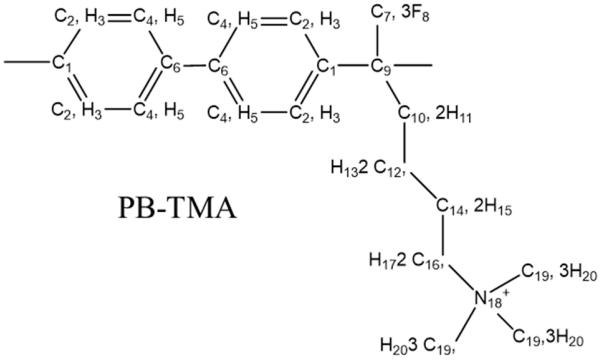
i	*q*	*i*	*q*
1	0.1830	7	0.1830
2	-0.1730	8	0.4170
3	0.1240	9	-0.1460
4	-0.1470	10	-0.1620
5	0.1190	11	-0.3970
6	0.0600	12	0.1340

Table S4. Atomic partial charges assigned to PB, Electrostatic potential (ESP) charges obtained from DFT calculations at B3LYP-D3/6-31G* level was used. The index number *i* is written next to the element in molecular structure.



i	*q*	*i*	*q*	*i*	*q*
1	0.3470	9	-0.7100	17	0.1570
2	-0.1600	10	0.0180	18	0.2460
3	0.1310	11	0.0710	19	-0.0300
4	-0.1740	12	0.0100	20	0.1810
5	0.1260	13	0.0360	21	-0.1500
6	0.0780	14	0.0130	22	0.1870
7	0.4510	15	0.0410	23	0.0520
8	-0.1300	16	-0.3740	24	0.1560

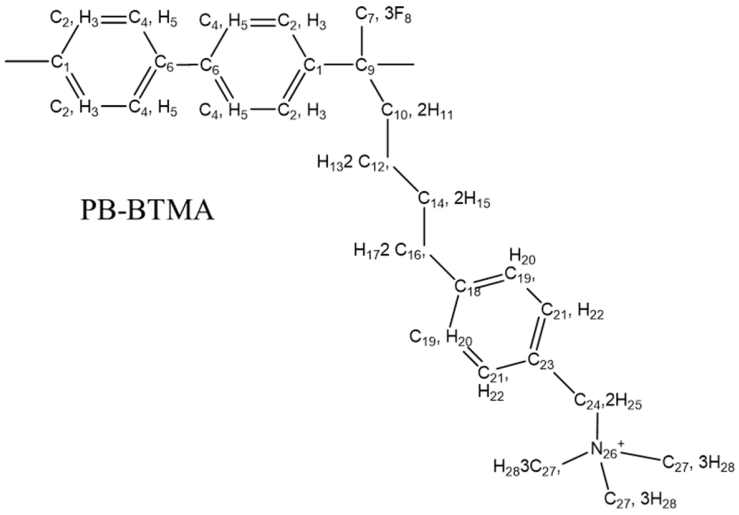
Table S5. Atomic partial charges assigned to PB-PY, Electrostatic potential (ESP) charges obtained from DFT calculations at B3LYP-D3/6-31G* level was used. The index number *i* is written next to the element in molecular structure.



PB-TMA

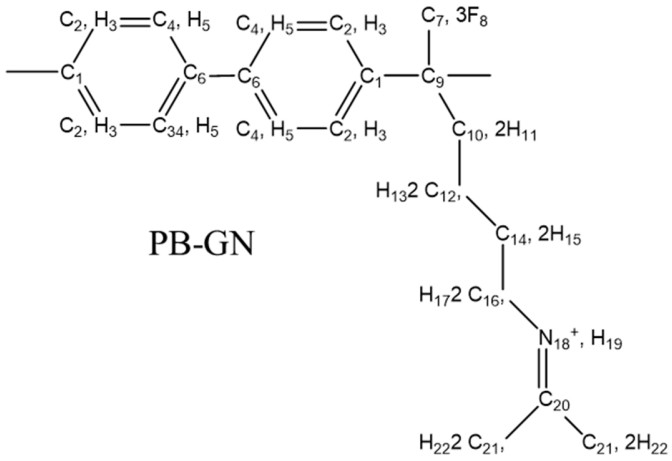
i	*q*	*i*	*q*
1	0.3200	11	0.0720
2	-0.1610	12	-0.1620
3	0.1400	13	0.0800
4	-0.1620	14	0.0810
5	0.1200	15	0.0300
6	0.0700	16	-0.2460
7	0.4610	17	0.1520
8	-0.1290	18	0.1730
9	-0.7030	19	-0.4060
10	0.0200	20	0.1970

Table S6. Atomic partial charges assigned to PB-TMA, Electrostatic potential (ESP) charges obtained from DFT calculations at B3LYP-D3/6-31G* level was used. The index number *i* is written next to the element in molecular structure.



i	*q*	*i*	*q*	*i*	*q*	*i*	*q*
1	0.2710	8	-0.1430	15	0.0140	22	0.1260
2	-0.1450	9	-0.5280	16	-0.3480	23	0.1930
3	0.1270	10	-0.0860	17	0.1170	24	-0.3500
4	-0.1620	11	0.0790	18	0.2240	25	0.1620
5	0.1210	12	-0.1320	19	-0.2080	26	0.1320
6	0.0990	13	0.0440	20	0.1540	27	-0.3510
7	0.4840	14	0.1169	21	-0.1570	28	0.1790

Table S7. Atomic partial charges assigned to PB-BTMA, Electrostatic potential (ESP) charges obtained from DFT calculations at B3LYP-D3/6-31G* level was used. The index number *i* is written next to the element in molecular structure.



PB-GN

i	*q*	*i*	*q*	*i*	*q*
1	0.2880	9	-0.5500	17	0.0790
2	-0.1600	10	0.0810	18	-0.5410
3	0.1290	11	0.0650	19	0.3510
4	-0.1790	12	-0.1100	20	0.8520
5	0.1290	13	0.0380	21	-0.900
6	0.0800	14	0.0600	22	0.4520
7	0.4730	15	-0.1100		
8	-0.1380	16	0.0640		

Table S8. Atomic partial charges assigned to PB-GN, Electrostatic potential (ESP) charges obtained from DFT calculations at B3LYP-D3/6-31G* level was used. The index number *i* is written next to the element in molecular structure.

Conversion [%]	ρ_{eq}			
	PA-PB-PY	**PA-PB-TMA**	**PA-PB-BTMA**	**PA-PB-GN**
10	1.408	1.4015	1.405	1.4158
20	1.407	1.4135	1.394	1.4188
30	1.404	1.4180	1.386	1.4215
50	1.403	1.4207	1.370	1.4189
70	1.393	1.4199	1.361	1.4248
90	1.378	1.4121	1.339	1.4162

Table S9. Equilibrium densities (ρ_{eq}) of PA-PB-PY, PA-PB-TMA, PA-PB-BTMA, and PA-PB-GN calculated using isobaric-isothermal (NPT) ensemble simulations as a function of conversion ratio.

(a)

D_{hop} [cm^2/s]			
M06	**M06-2X**	**M06-HF**	**Exp.**
9.35×10^{-5} ($\pm 3.42 \times 10^{-6}$)	3.94×10^{-4} ($\pm 1.35 \times 10^{-5}$)	1.29×10^{-11} ($\pm 3.98 \times 10^{-13}$)	-

σ_{hop} [S/cm]			
M06	**M06-2X**	**M06-HF**	**Exp.**[1]
5.63×10^{-1} ($\pm 2.06 \times 10^{-2}$)	2.37 ($\pm 8.12 \times 10^{-2}$)	7.77×10^{-8} ($\pm 2.39 \times 10^{-9}$)	3×10^{-1}

(b)

Species	D_{veh} [cm^2/s]		σ_{veh} [S/cm]	
	Result	**Exp.**[1]	**Result**	**Exp.**[1]
$H_2PO_4^-$	1.13×10^{-6} ($\pm 7.52 \times 10^{-8}$)	2.5×10^{-6}	6.81×10^{-3} ($\pm 4.53 \times 10^{-4}$)	2×10^{-2}
H_3O^+	1.23×10^{-6} ($\pm 1.07 \times 10^{-7}$)	6.25×10^{-6}	7.40×10^{-3} ($\pm 6.46 \times 10^{-4}$)	4.95×10^{-2}

Table S10. (a) D_{hop} and σ_{hop} in 12.5% water content PA solution evaluated using the DFT-calculated barriers from three different functionals, M06, M06-2X, and M06-HF, combined with ensemble structures sampled from MD simulations. (b) D_{veh} and σ_{veh} calculated based on the mean-squared-displacements (MSDs) obtained from the MD trajectories. The proton hopping barriers calculated using the M06 functional accurately predicts both hopping and vehicular diffusivities as combined with MD simulation trajectories.

References

1. Melchior, J. P., Kreuer, K. D. & Maier, J. Proton conduction mechanisms in the phosphoric acid-water system ($H_4P_2O_7$-$H_3PO_4 \cdot 2H_2O$): A ^{1}H, ^{31}P and ^{17}O PFG-NMR and conductivity study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 587–600.