Supporting information

Proton transfer in polyamine-P_2Mo_5 model adducts: exploring the effect of polyamine cations on their proton conductivity

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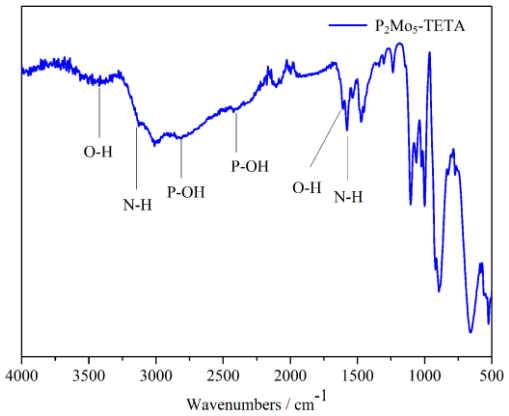

Fig. S1 The IR spectrum of **P_2Mo_5-TETA**.

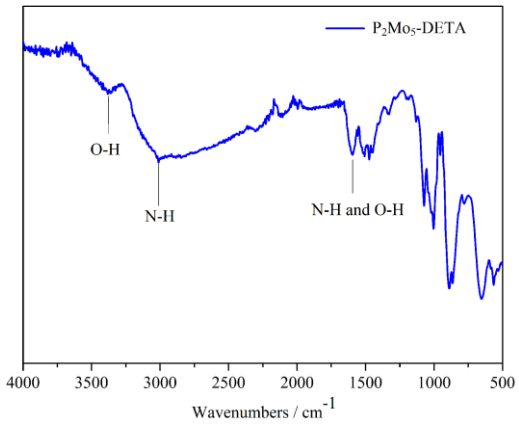

Fig. S2 The IR spectrum of **P_2Mo_5-DETA**.

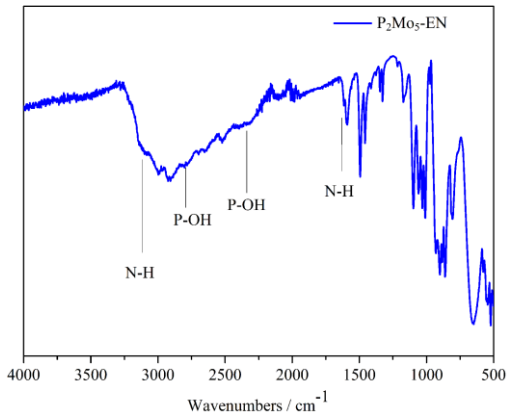

Fig. S3 The IR spectrum of **P_2Mo_5-EN**.

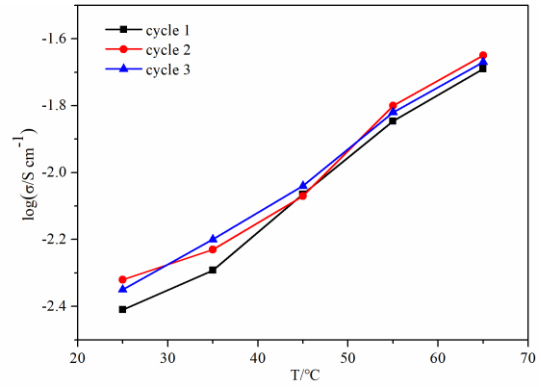

Fig. S4. Arrhenius plots of the proton conductivity of **P_2Mo_5-EN**, cycle 1 (black); cycle 2 (red); cycle 3 (blue).

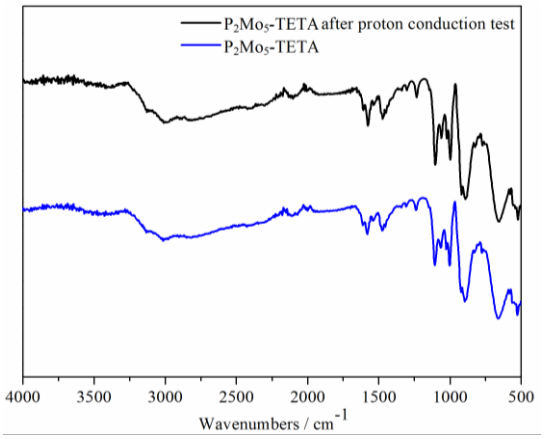

Fig. S5 The original and after proton conduction IR spectra of **P_2Mo_5-TETA**.

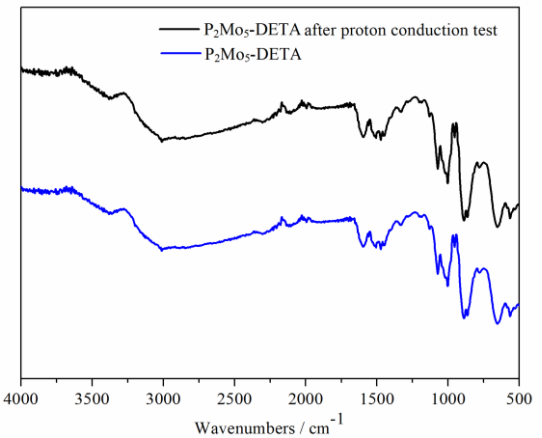

Fig. S6 The original and after proton conduction IR spectra of **P_2Mo_5-DETA**.

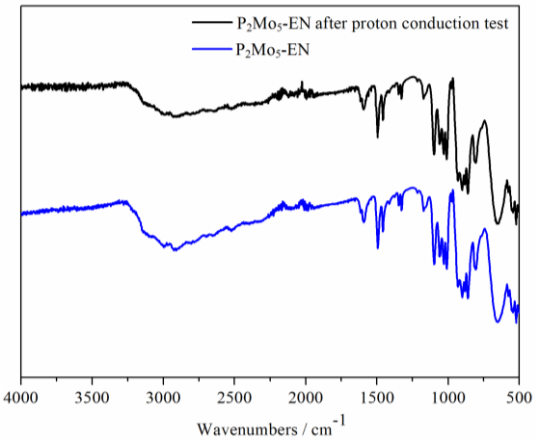

Fig. S7 The original and after proton conduction IR spectra of **P_2Mo_5-EN**.

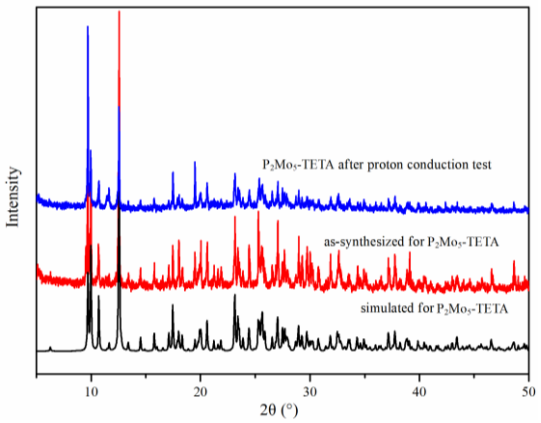

Fig. S8 PXRD profiles of single crystal data simulation for **P_2Mo_5-TETA;** as-synthesized of **P_2Mo_5-TETA**; **P_2Mo_5-TETA** after proton conduction test.

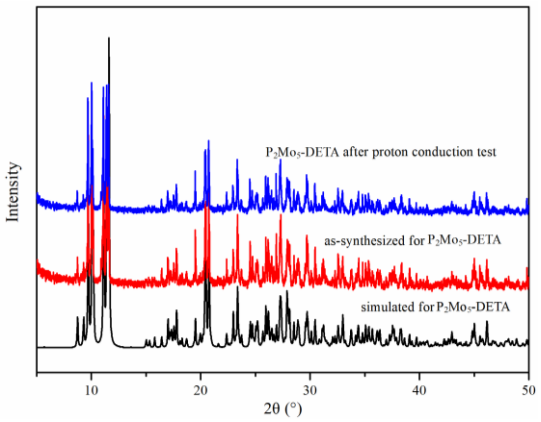

Fig. S9 PXRD profiles of single crystal data simulation for **P_2Mo_5-DETA;** as-synthesized of **P_2Mo_5-DETA**; **P_2Mo_5-DETA** after proton conduction test.

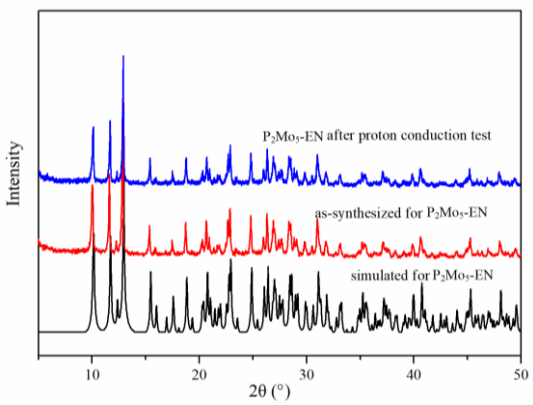

Fig. S10 PXRD profiles of single crystal data simulation for **P_2Mo_5-EN;** as-synthesized of **P_2Mo_5-EN**; **P_2Mo_5-EN** after proton conduction test.

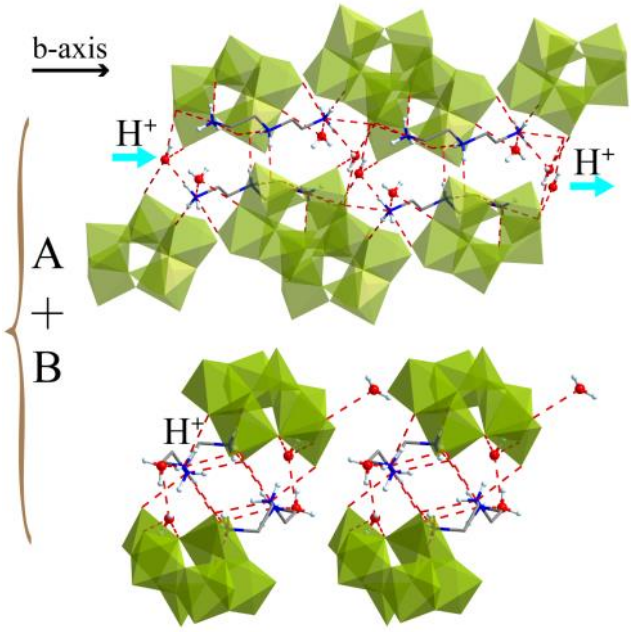

Fig. S11 The possible proton transport pathway of A and B in adduct **P_2Mo_5-DETA** along the b-axis.

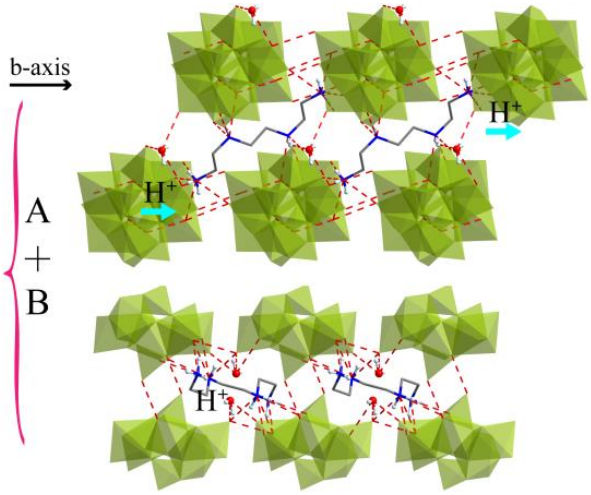

Fig. S12 The possible proton transport pathway of A and B in adduct **P_2Mo_5-TETA** along the b-axis.

Table S1 X-ray crystallographic data for P_2Mo_5-TETA and P_2Mo_5-DETA.

Compound	**P_2Mo_5-TETA**	**P_2Mo_5-DETA**
Empirical formula	$C_6H_{26}Mo_5N_4O_{24}P_2$	$C_8H_{40}Mo_5N_6O_{27}P_2$
Formula weight	1079.95	1194.10
Temperature (K)	238.0	113.0
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.9361(8)	10.3242(14)
b (Å)	10.0331(7)	10.9734(15)
c (Å)	14.4174(12)	15.718(2)
α (°)	84.088(4)	95.654(6)
β (°)	77.796(4)	95.813(5)
γ (°)	65.153(3)	111.470(4)
Volume ($Å^3$)	1274.59(18)	1630.9(4)
Z	2	2
D_{calc}/gcm^{-3}	2.814	2.432
μ/mm^{-1}	2.630	2.076
F(000)	1044	1172
Reflections collected	35964	41817
Independent reflections	8751 [R_{int} = 0.0559]	6454 [Rint = 0.0384]
GOOF	1.023	1.091
Final *R* indexes [I>=2σ (*I*)][ab]	R_1 = 0.0394, wR_2 = 0.0664	R_1 = 0.0255, wR_2 = 0.0622
Final *R* indexes [all data]	R_1 = 0.0798, wR_2 = 0.0767	R_1 = 0.0306, wR_2 = 0.0656

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = \{\Sigma\,[w(F_o^2-F_c^2)^2]/\Sigma\,[w(F_o^2)^2]\}^{1/2}$

Table S2 Hydrogen bond distances (Å) and angles (°) for P_2Mo_5-TETA.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
O1(W)–H1B···O1	0.86	2.737	2.745	141.60
O1(W)–H1A···O6	0.86	2.361	2.922	123.20
O1(W)–H1A···O14	0.86	2.376	2.946	140.56
O8–H8···O12	0.83	2.059	2.816	151.56
N3–H3C···O1(W)	0.90	1.778	2.590	148.78
N1–H1A···O5	0.90	1.991	2.857	160.81
N1–H1C···O2	0.90	2.313	2.977	130.30
N1–H1C···O19	0.90	2.234	3.028	146.80
N1–H1B···O15	0.90	2.076	2.874	147.21
N2–H2A···O7	0.90	1.999	2.842	155.50
N2–H2B···O18	0.90	2.531	2.933	107.74
N2–H2B···O13	0.90	1.957	2.841	166.65
N3–H3D···O11	0.90	2.022	2.777	140.63
N3–H3E···O20	0.90	1.950	2.771	150.80
N3–H3C···O1(W)	0.90	1.778	2.590	148.78
N4–H4B···O20	0.90	2.409	2.968	120.45
N4–H4B···O1	0.90	19.84	2.813	152.46
N4–H1A···O23	0.90	2.042	2.963	164.31

Table S3 Hydrogen bond distances (Å) and angles (°) for P_2Mo_5-DETA.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N1–H1B···O21	1.003	2.092	3.008	150.97
N1–H1C···O2(W)	0.703	2.028	2.739	161.60
N1–H1A···O22	0.934	1.879	2.807	172.26
N2–H2A···O10	0.910	2.068	2.782	134.37
N2–H2A···O22	0.910	2.021	2.893	159.97
N2–H2B···O22	0.910	2.543	2.927	105.89
N3–H3B···O22	0.909	1.808	2.705	168.64
N3–H3A···O12	0.910	2.245	2.859	124.26
N3–H3C···O13	0.911	2.173	2.931	140.20
N4–H4A···O23	0.910	1.850	2.724	160.39
N4–H4B···O16	0.910	2.327	2.984	128.95
N4–H4C···O18	0.910	2.536	2.963	109.22
N5–H5C···O23	0.823	1.871	2.677	166.08
N5–H5D···O6	0.868	1.942	2.808	176.39
N6–H6C···O7	0.909	2.016	2.849	151.61
N6–H6C···O4(W)	0.909	2.586	2.970	106.11
N6–H6D···O14	0.910	2.245	2.848	123.34
N6–H6C···O17	0.911	1.874	2.784	178.14
N6–H6D···O1(W)	0.910	2.234	2.908	130.46
O1W–H1WB···O14	0.869	2.068	2.996	165.77
O1W–H1WA···O13	0.870	2.083	2.877	151.35

O1W–H1WA···O18	0.870	2.485	2.966	115.60
O2(W)–H2WA···O3(W)	0.870	1.847	2.674	158.23
O3W–H3WA···O11	0.870	2.151	2.878	140.78
O3W–H3WB···O20	0.872	2.478	2.880	108.84
O4W–H4WA···O8	0.830	1.939	2.765	173.79

Table S4 Hydrogen bond distances (Å) and angles (°) for P_2Mo_5-EN.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N1–H1A···O12	0.89	1.956	2.085	159.07
N1–H1B···O2	0.89	1.954	2.829	167.58
N1–H1C···O7	0.89	2.495	2.952	112.42
N1–H1C···O11	0.89	2.149	3.017	164.92
N2–H2A···O4	0.89	2.207	2.937	139.12
N2–H2A···O9	0.89	2.169	2.957	147.41
N2–H2B···O11	0.89	2.168	2.912	140.70
N2–H2C···O6	0.89	2.017	2.904	174.18
O1–H1···O4	0.82	1.868	2.26	153.03

Table S5 The short O···O distances between adjacent P_2Mo_5 anions in P_2Mo_5-EN.

Atoms involved	Length (Å)	Atoms involved	Length (Å)
O1···O4	2.626	O11··O11	2.915
O7···O10	2.943		

Table S6 Compare proton conductivity of P_2Mo_5-EN with that of other conductors under similar conditions.

POM-based conductors	**σ (S cm^{-1})**	**Tested conditions**	**Ref.**
P_2Mo_5-EN	1.13×10^{-2}	65 °C and 95% RH	This work
$[H_3O][(VO_2)_3(SeO_3)_2]$	2.95×10^{-2} [100] direction	60 °C and 98% RH	1
$[H_3O][(VO_2)_3(SeO_3)_2]$	4.07×10^{-2} [001] direction	60 °C and 98% RH	1
$[Cu(en)_2(H_2O)]_2\{[Cu(en)]_4[Cu(en)_2]_5\{[Cu(en)_2KNb_{24}O_{72}H_{10}]_2\}\cdot 6en\cdot 70H_2O$	1.35×10^{-3}	85 °C and 98% RH	2
$[Cd(H_2O)_2DABT]_4[Cd(H_7P_4Mo_6O_{31})_2]\cdot 19H_2O$	1.35×10^{-3}	60 °C and 98% RH	3
$(C_2H_5OH)(C_3H_5N_2)_6[Co_3(H_6P_4Mo_6O_{31})_2]\cdot H_2O$	3.78×10^{-3}	60 °C and 98% RH	3
$[Cu_2(H_2O)_2(L1)_3][PMo^{VI}_{11}Mo^{V}O_{40}]$	2.8×10^{-4}	65℃, 95% RH	4
$(H_2L2)_{0.5}[(Cu^{I}L2)_2(PMo_{12}O_{40})]\cdot H_2O$	1.9×10^{-4}	65℃, 95% RH	4
$[Sr(DMPhH_2IDC)_2]n$	0.92 × 10-3 S·cm-1	100 °C and 98% RH	5
$H_3[(CH_3)_4N]_{14}[NaSm(PW_{11}O_{39})_3]\cdot 18H_2O$	4.7×10^{-3}	85℃, 98% RH	6
$(TMA)_{14}H_2[Ce^{III}(H_2O)_6]\{[Ce^{IV}_7Ce^{III}_3O_6(OH)_6(CO_3)(H_2O)_{11}][(P_2W_{16}$-	2.65×10^{-3}	100℃, 98% RH	7

$O_{59})]_3\}\cdot 41H_2O$			
$[\{Cu(pip)_2\}_2\{La_{29}Ge_{10}W_{106}O_{406}(OH)_4(H_2O)_{28}\}]^{49-}$	5.3×10^{-3}	85℃, 98% RH	8
$[Co(4,4'\text{-bipy})(H_2O)_4][Co(4,4'\text{-bipyH})_2(H_2O)_4]\cdot 2(H_3bmt)\cdot 6H_2O$	9.87×10^{-3}	85℃, 98% RH	9
$[Nd_3(H_2O)_{22}][P_2W_{15}Ta_3O_{62}]\cdot nH_2O$	9.88×10^{-3}	95℃, 98% RH	10
JUK13-SO_3H	3.80×10^{-5}	65℃, 90% RH	11
[Zn(Hssa)(1,4-bib)·H_2O]n	3.45×10^{-5}	60℃, 95% RH	12
$(C_5H_{10}NO_2)Ga_4(PO_4)4F\cdot 3H_2O$	8.89×10^{-4}	85℃, 95% RH	13

1 H. Y. Sun, S. H. Sun, B. Hu, L. K. Gong, Y. M. Zou, J. L. Li, M. L. Feng and X. Y. Huang, Anisotropic proton conduction realized by a layered vanadium selenite single crystal, Inorg. Chem. Front., 2020, 7, 1699−1703.

2 Z. K. Zhu, L. D. Lin, J. Zhang, X. X. Li, Y. Q. Sun and S. T. Zhen, A rare 4-connected neb-type 3D chiral polyoxometalate framework based on $\{KNb_{24}O_{72}\}$ clusters, 10.1039/d0qi00927j.

3 Z. Y. Du, Z. Chen, R. K. Kang, Y. M. Han, J. Ding, J. P. Cao, W. Jiang, M. Fang, H. Mei and Y, Xu, Two 2D Layered P_4Mo_6 Clusters with Potential Bifunctional Properties: Proton Conduction and CO_2 Photoreduction, org/10.1021/acs.inorgchem.0c01941.

4 K. Lu, A. L. Pelaez, L. C. Wu, Y. Cao, C. H. Zhu, and H. Fu, Ionothermal Synthesis of Five Keggin-Type Polyoxometalate-Based Metal–Organic Frameworks, *Inorg. Chem*., 2019, **58**, 1794−1805.

5 X. X. Xie, Z. H. Zhang, J. Zhang, L. F. Hou, Z. F. Li and G. Li, Impressive Proton Conductivities of Two Highly Stable Metal−Organic Frameworks Constructed by Substituted Imidazoledicarboxylates, *Inorg. Chem*. 2019, **58**, 5173−5182.

6 Z. Li, L. D. Lin, D. Zhao, Y. Q. Sun, and S. T. Zheng, A Series of Unprecedented Linear Mixed-Metal-Substituted Polyoxometalate Trimers: Syntheses, Structures, Luminescence, and Proton Conductivity Properties, E*ur. J. Inorg. Chem*. 2019, 437−441.

7 P. T. Ma, R. Wan, Y. Y. Wang, F. Hu, D. D. Zhang, J. Y. Niu, and J. P. Wang, Coordination-Driven Self-Assembly of a 2D Graphite-Like Framework Constructed from High-Nuclear Ce_{10} Cluster Encapsulated Polyoxotungstates, *Inorg. Chem*. 2016, **55**, 918−924.

8 Z. Li, X. X. Li, T. Yang, Z. W. Cai, S. T. Zheng, Four-Shell Polyoxometalates Featuring High-Nuclearity Ln_{26} Clusters: Structural Transformations of Nanoclusters into Frameworks Triggered by Transition-Metal Ions, Angew. Chem. 2017, **129**, 2708 – 2713; *Angew. Chem. Int. Ed*. 2017, **56**, 2664.

9 L. Feng, Z. Q. Pan, H. Zhou, M. Zhou and H. B. Hou, Water-mediated proton conduction in Ni(ii) and Co(ii) benzenetriphosphonates, *Dalton Trans*., 2019, **48**, 16493−16496.

10 Q. P. Peng, S. J. Li, R. Y. Wang, S. S. Xia, L. H. Xie, J. X. Zhai, J. Zhang, Q. Y. Zhao and X. N. Chen, Lanthanide derivatives of Ta/W mixed-addendum POMs as proton-conducting materials, *Dalton Trans*., 2017, **46**, 4157−4160.

11 M. Szufla, K. Roztocki, A. Krawczuk and D. Matoga, One-step introduction of terminal sulfonic groups into a proton-conducting metal–organic framework by concerted deprotonation– metalation–hydrolysis reaction, *Dalton Trans*., 2020, **49**, 9953–9956.

12 T. Y. Xu, H. J. Nie, J. M. Li and Z. F. Shi, Highly selective sensing of Fe^{3+}/Hg^{2+} and proton conduction using two fluorescent Zn(ii) coordination polymers, *Dalton Trans*., 2020,**49**, 11129–11141.

13 L. J. Huang, L. Wang, Y. Zhao, L. Huang, J. Bi, G. H. Zou, Z. E. Lin and D. J. Gao, Two amino acid-templated metal phosphates: surfactant-thermal synthesis, water stability, and proton conduction, *Dalton Trans*., 2020, **49**, 5440–5444.

Table S7 The relatively short O···O distances between adjacent P_2Mo_5 anions in the A pathway of P_2Mo_5-TETA, where the oxygen atoms involved can provide potential proton hop sites.

Atoms involved	Length (Å)	Atoms involved	Length (Å)
O1···O20	2.882	O19··O2	2.936
O18···O19	3.025		