

Phosphate Enriched Polyoxometalate Based Ionic Salts for Proton Conduction

(Supporting Information: 28 pages)

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Section S1	Synthesis of $[\text{NiMo}_{12}\text{O}_{30}(\text{PO}_4)_8]^{n-}$ POM anion and organic cation based ionic composites	S-2
Section S2	Single crystal X-ray diffraction data collection, structure solution and refinement procedures	S-4
Section S3	Thermal stability of Ni-POM-EN and thermal gravimetric analysis (TGA) data	S-17
Section S4	Scanning Electron Microscopy (SEM) imaging of Ni-POM-EN	S-18
Section S5	IR Spectroscopy of Ni-POM-EN	S-19
Section S6	Proton conductivity measurement of Ni-POM-EN	S-21

Section S1. Synthesis of $[\text{NiMo}_{12}\text{O}_{30}(\text{PO}_4)_8]^{n-}$ POM anion and organic cation based ionic composites

All reagents and solvents for synthesis and analysis were commercially available and used as received. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a *PERKIN ELMER FT-IR SPECTRUM* (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PNAlytical diffractometer for Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ . Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25–700 °C on a SDT Q600 TG-DTA analyzer under N_2 atmosphere at a heating rate of $10^\circ \text{ C min}^{-1}$.

Synthesis of Ni-POM-EN, $[\text{H}_2\text{EN}]_5[\text{NiMo}_{12}\text{O}_{30}(\text{PO}_4)_8] \cdot 5.5\text{H}_2\text{O}$: The brown crystals of Ni-POM-EN was obtained by heating the mixture of 20% wt solution of phosphomolybdic acid in ethanol (1ml), ethylene diamine (0.6 ml), 85% H_3PO_4 (0.5 ml), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.21mmol) and H_2O (8ml) at 150 °C for 96 hours. **FT-IR:** (KBr 4000-450 cm^{-1}): 2354(w), 2320(w), 2014(b), 1606(w), 1519(w), 1469(w), 1107(w), 999(m), 894(s), 818(s), 780(m), 716(s), 667(s), 606(s). **Elemental Analysis:** Found (%) C= 4.04, H= 2.23, N= 4.84; Calc. (%) C= 4.21, H= 1.76, N= 4.92.

Synthesis of Ni-POM-44BP: The yellow block shaped crystals of Ni-POM-44BP were synthesized by heating the mixture of 20% wt solution of phosphomolybdic acid in ethanol (1ml), 4,4'-bipyridyl (0.16 mmol), 85% H_3PO_4 (0.5 ml), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.21mmol) and H_2O (8ml) at 150 °C for 96 hours.

Synthesis of Ni-POM-44DP: The red block shaped crystals of Ni-POM-44BP were synthesized by heating the mixture of 20% wt solution of phosphomolybdic acid in ethanol (1ml), 4,4'-dimethyl 2,2'-bipyridyl (0.14 mmol), 85% H_3PO_4 (0.5 ml), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.21mmol) and H_2O (8ml) at 150 °C for 96 hours.

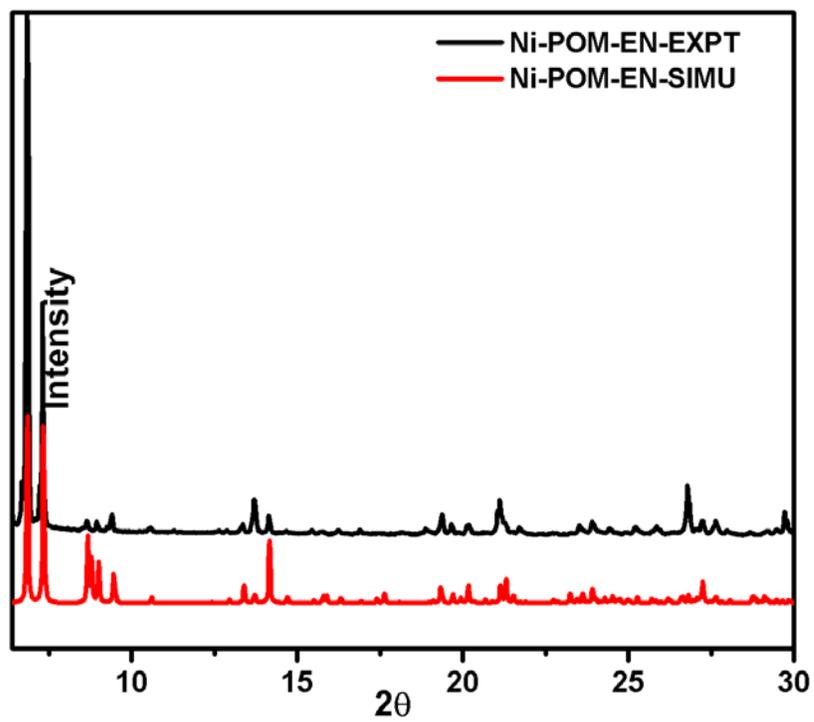


Figure S1: Simulated (bottom) and experimental (top) PXRd pattern of Ni-POM-EN.

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

General Data Collection and Refinement Procedures:

Data was collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. The crystals reported in this paper were mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research).

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. *Bruker SMART*¹ software was used suite to carry out overlapping ϕ and ω scans at detector (2θ) settings ($2\theta = 28$). Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using *CELL_NOW*². In no data collection was evidence for crystal decay encountered. Following exhaustive review of collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT³ software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program SADABS⁴. The space group determination and tests for merohedral twinning were carried out using *XPREP*³.

The structure was solved by direct methods and refined using the *SHELXTL 97*⁵ software suite. Atoms were located from iterative examination of difference F-maps

following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. The structure was examined using the *Adsym* subroutine of PLATON⁷ to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 30% probability level unless noted otherwise. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No. CCDC 1014850, 1014852, and 1014854. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax: þ 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk].

1. Bruker (2005). *APEX2*. Version 5.053. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2004). *CELL_NOW*. University of Göttingen, Germany.
- Steiner, Th. (1998). *Acta Cryst.* B54, 456–463.
3. Bruker (2004). *SAINTE-Plus* (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA.
4. Sheldrick, G. M. (2002). *SADABS* (Version 2.03) and *TWINABS* (Version 1.02). University of Göttingen, Germany.
5. Sheldrick, G. M. (1997). *SHELXS '97* and *SHELXL '97*. University of Göttingen, Germany.
6. WINGX
7. A. L. Spek (2005) *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

Ni-POM-EN (TRICLINIC)

Experimental and Refinement Details for Ni-POM-EN

A yellow needle like crystal ($0.34 \times 0.29 \times 0.21 \text{ mm}^3$) of Ni-POM-EN was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K in a liquid N₂ cooled stream of nitrogen. A total of 21120 reflections were collected of which 8341 were unique. The range of θ was from 1.58 to 28.24. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *P*-1 space group, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0587$ ($F > 2\sigma F$) and $wR_2 = 0.1719$ (all data) with GOF = 1.013.

Table S1. Crystal data and structure refinement for Ni-POM-EN

Identification code	Ni-POM-EN
Empirical formula	$C_{10}H_{50}Mo_{12}N_{10}NiO_{67.5}P_8$
Formula weight	2848.19
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.874(8)
b/Å	13.373(9)
c/Å	13.817(10)
$\alpha/^\circ$	87.199(12)
$\beta/^\circ$	69.838(11)
$\gamma/^\circ$	65.002(11)
Volume/Å ³	1854(2)
Z	1
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	2.5503
μ/mm^{-1}	2.501
F(000)	1353.3
Crystal size/mm ³	0.34 × 0.29 × 0.21
Radiation	Mo K α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.16 to 56.48
Index ranges	-14 ≤ h ≤ 15, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	21120
Independent reflections	8341 [$R_{\text{int}} = 0.0833$, $R_{\text{sigma}} = 0.1143$]
Data/restraints/parameters	8341/0/482
Goodness-of-fit on F ²	1.013
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0587$, $wR_2 = 0.1601$
Final R indexes [all data]	$R_1 = 0.0870$, $wR_2 = 0.1719$
Largest diff. peak/hole / e Å ⁻³	5.92/-1.75

Ni-POM-44BP (MONOCLINIC)

Experimental and Refinement Details for Ni-POM-44BP

A yellow needle like crystal ($0.38 \times 0.31 \times 0.27 \text{ mm}^3$) of Ni-POM-44BP was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K in a liquid N₂ cooled stream of nitrogen. A total of 90583 reflections were collected of which 18817 were unique. The range of θ was from 1.72 to 28.38. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic $P2_1/c$ space group using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0657$ ($F > 2\sigma F$) and $wR_2 = 0.2004$ (all data) with GOF = 1.082.

Table S2. Crystal data and structure refinement for Ni-POM-44BP

Identification code	Ni-POM-BP
Empirical formula	$C_{10}H_{18}Mo_{12}N_2NiO_{67}P_8$
Formula weight	2695.99
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.559(6)
b/Å	23.664(9)
c/Å	23.421(9)
$\alpha/^\circ$	90
$\beta/^\circ$	92.441(6)
$\gamma/^\circ$	90
Volume/Å ³	8062(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	2.2211
μ/mm^{-1}	2.292
F(000)	5045.0
Crystal size/mm ³	$0.38 \times 0.31 \times 0.27$
Radiation	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.44 to 56.76
Index ranges	$-18 \leq h \leq 18, -30 \leq k \leq 30, -31 \leq l \leq 30$
Reflections collected	90583
Independent reflections	18817 [$R_{\text{int}} = 0.1095, R_{\text{sigma}} = 0.0643$]
Data/restraints/parameters	18817/3/884
Goodness-of-fit on F^2	1.082
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0657, wR_2 = 0.1892$
Final R indexes [all data]	$R_1 = 0.0801, wR_2 = 0.2004$
Largest diff. peak/hole / e Å ⁻³	4.73/-1.49

The Detail of SQUEEZE Material for Ni-POM-BP

Details about the Squeezed Material

loop_

_platon_squeeze_void_nr

_platon_squeeze_void_average_x

_platon_squeeze_void_average_y

_platon_squeeze_void_average_z

_platon_squeeze_void_volume

_platon_squeeze_void_count_electrons

_platon_squeeze_void_content

1 0.000 0.500 0.000 838 37''

2 0.000 0.000 0.500 838 37''

_platon_squeeze_details

;

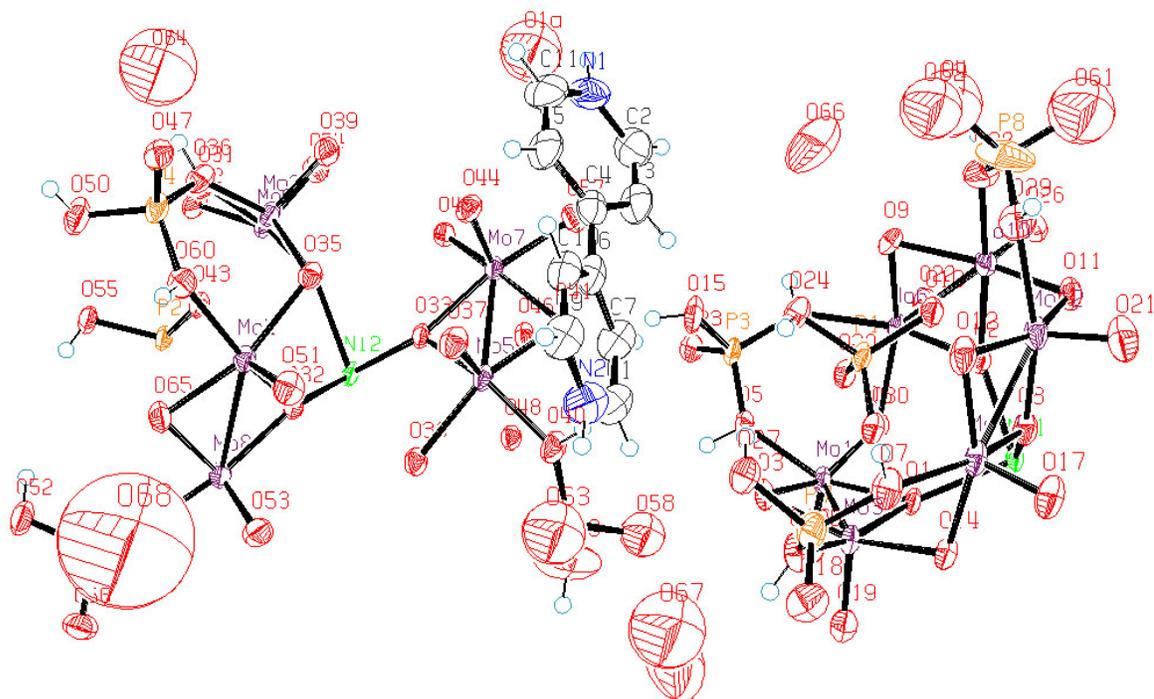


Figure S3: ORTEP drawing of the asymmetric unit of **Ni-POM-44BP**. [Color code: blue:C, Red:O, Black:Mo, Orange:P, Yellow:Cu, White:H]

Ni-POM-44DP (TRICLINIC)

Experimental and Refinement Details for Ni-POM-44DP

A yellow needle like crystal ($0.32 \times 0.23 \times 0.21 \text{ mm}^3$) of Ni-POM-44DP was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K in a liquid N₂ cooled stream of nitrogen. A total of 17676 reflections were collected of which 9034 were unique. The range of θ was from 1.70 to 28.21. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *P*-1 space group, with *Z* = 2, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0508$ ($F > 2\sigma F$) and $wR_2 = 0.1371$ (all data) with GOF = 1.009

Table S3. Crystal data and structure refinement for Ni-POM-44DP

Identification code	Ni-POM-DP
Empirical formula	C ₂₄ H ₂₈ Mo ₁₂ N ₄ NiO ₇₀ P ₈
Formula weight	2950.23
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.891(10)
b/Å	13.743(10)
c/Å	14.234(11)
α/°	111.029(12)
β/°	109.293(12)
γ/°	101.693(13)
Volume/Å ³	2069(3)
Z	1
ρ _{calc} /g/cm ³	2.3681
μ/mm ⁻¹	2.247
F(000)	1393.3
Crystal size/mm ³	0.32 × 0.23 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.4 to 56.42
Index ranges	-14 ≤ h ≤ 16, -17 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	17676
Independent reflections	9034 [R _{int} = 0.0697, R _{sigma} = 0.0935]
Data/restraints/parameters	9034/0/516
Goodness-of-fit on F ²	1.009
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0508, wR ₂ = 0.1291
Final R indexes [all data]	R ₁ = 0.0648, wR ₂ = 0.1371
Largest diff. peak/hole / e Å ⁻³	4.87/-1.58

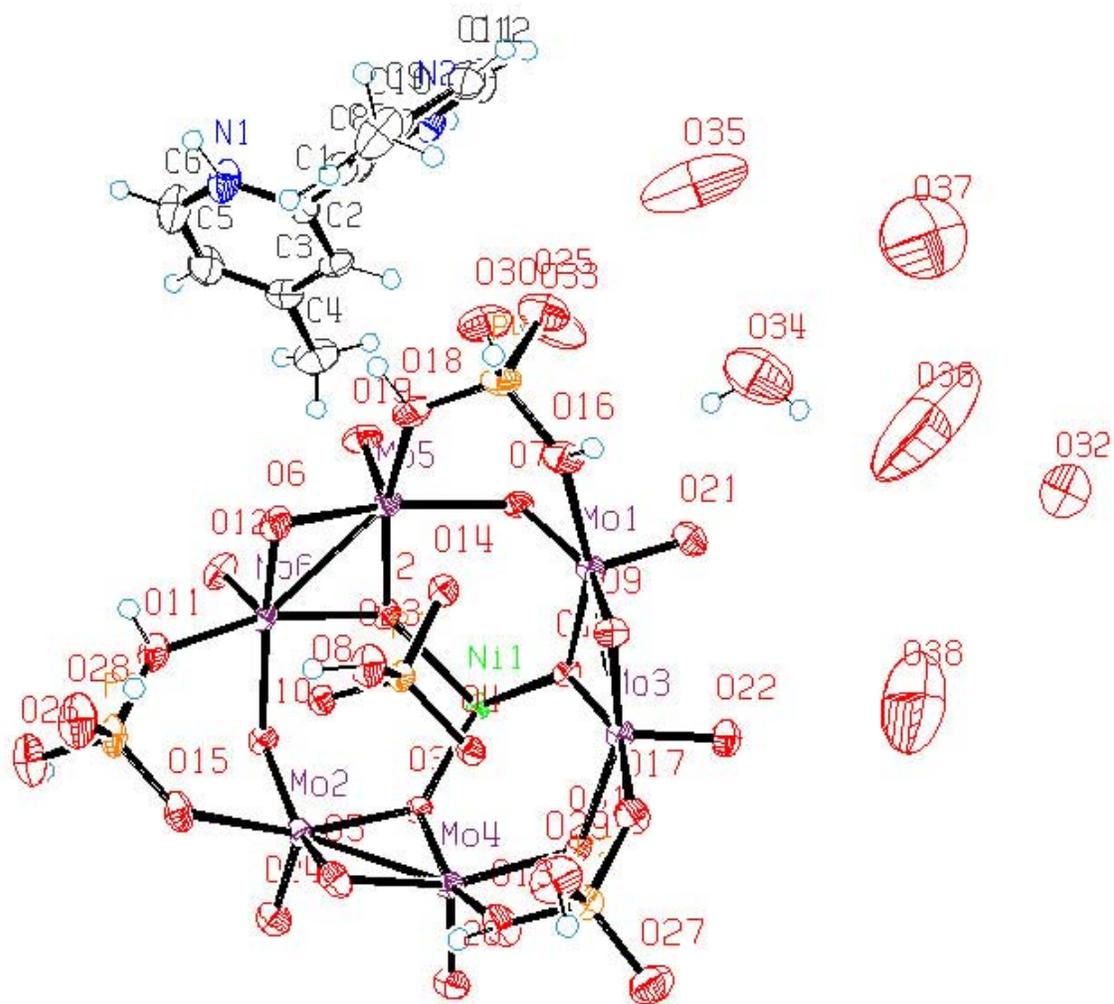


Figure S4: ORTEP drawing of the asymmetric unit of **Ni-POM-44DP**. [Color code: blue:C, Red:O, Black:Mo, Orange:P, Yellow:Cu, White:H]

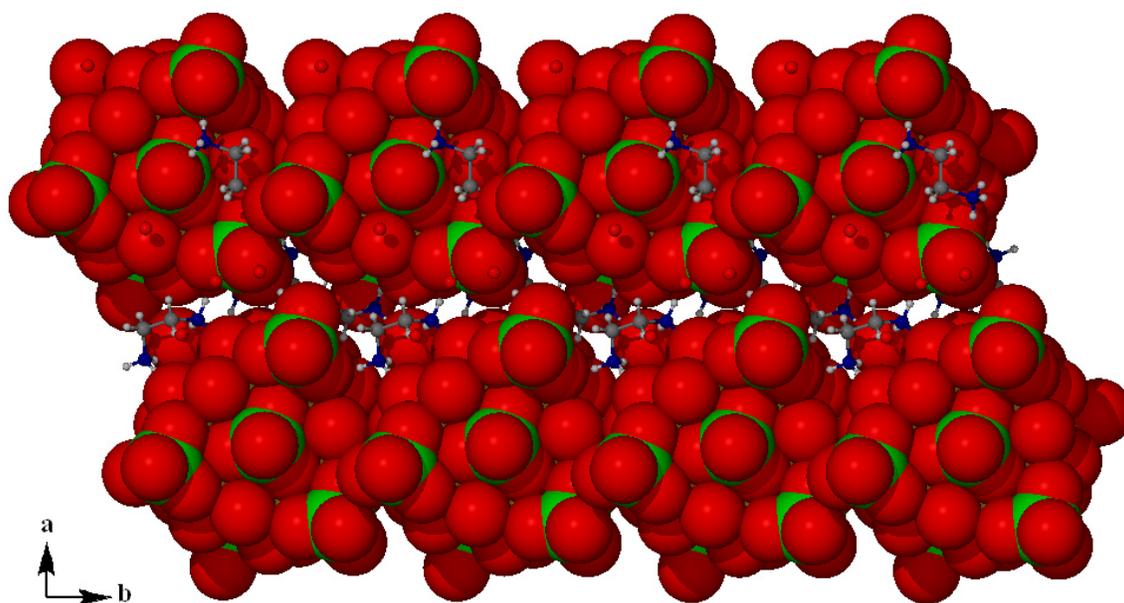


Figure S5: Space fill model of Ni-POM-EN showing the floating cationic counterpart and solvent molecules in-between two layers which create proton conducting pathway. Red: O, Green: Mo, Grey: C, Blue: N, White: C.

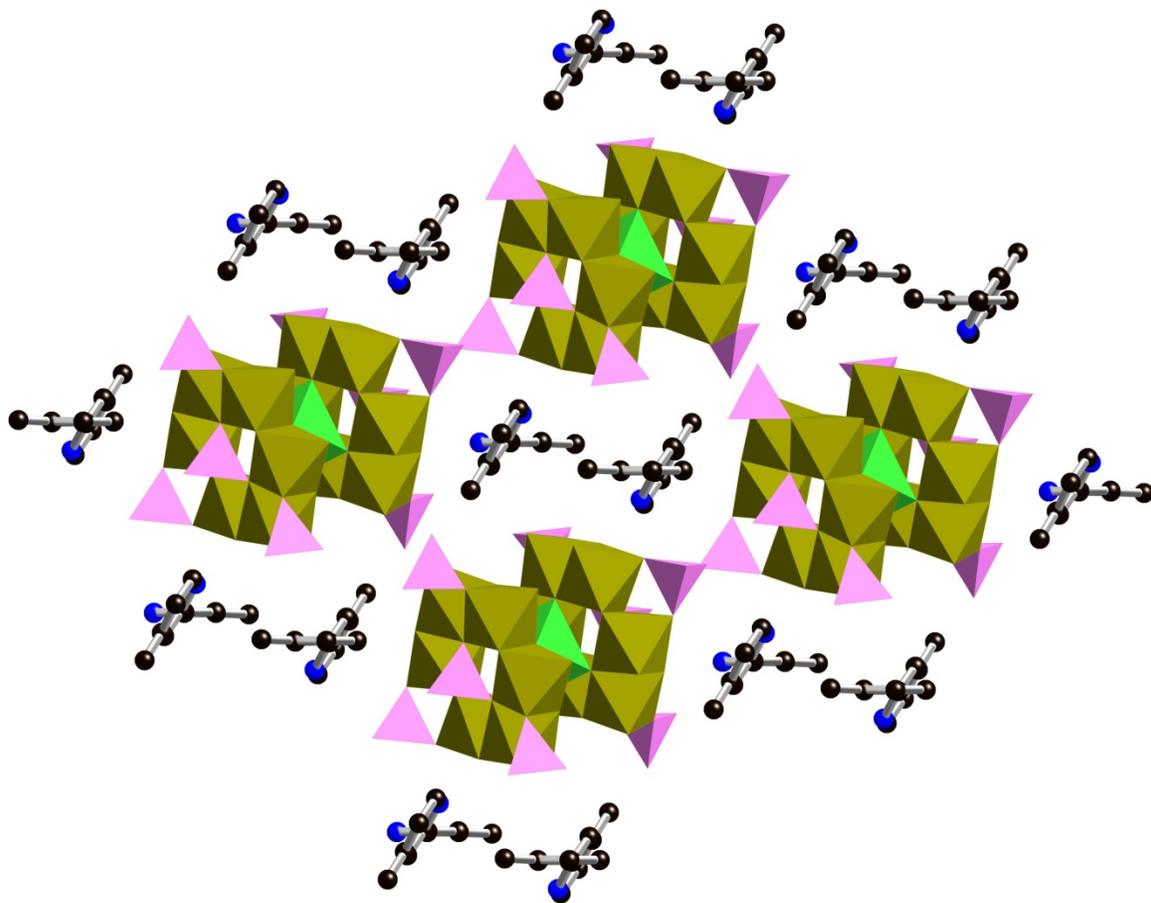


Figure S6: Crystal structure of Ni-POM-44DP. [Color Code: Golden Yellow: Mo, Pink: P, Green: Ni, Blue: N, Grey: C]. Oxygen and hydrogen atoms have been removed for clarity.

Section S3. Thermal stability of Ni-POM-EN and the thermal gravimetric analysis (TGA) data

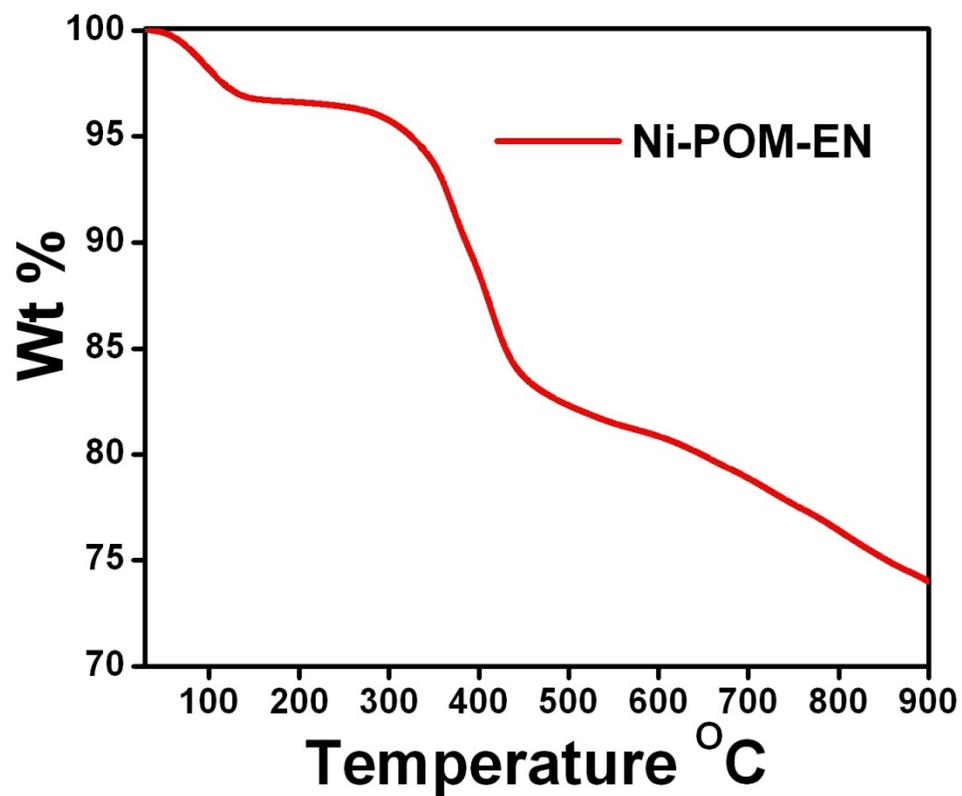


Figure S7. Thermal Gravimetric Analysis curve for Ni-POM-EN.

Section S4. Scanning Electron Microscopy (SEM) imaging of Ni-POM-EN

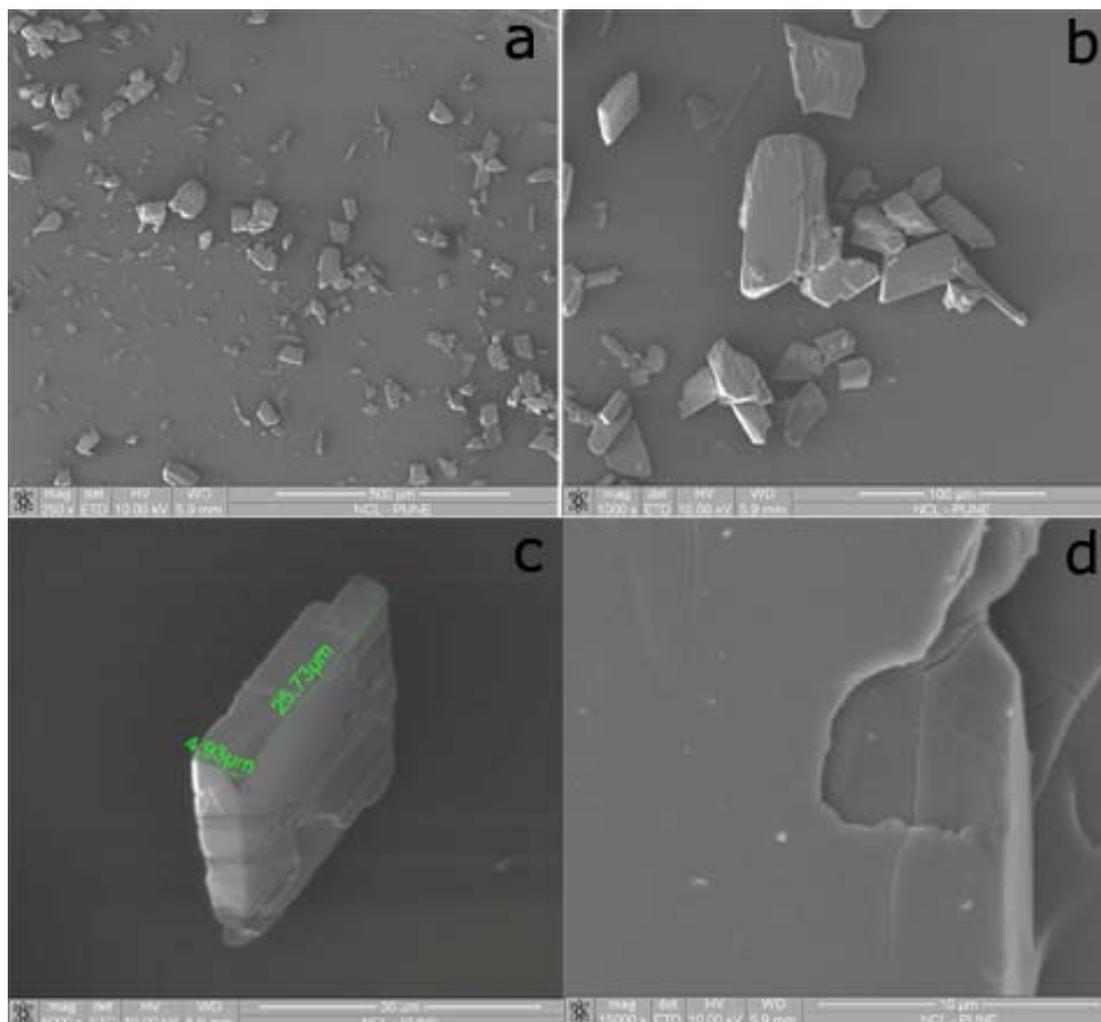


Figure S8 : (a) SEM image of as-synthesised Ni-POM-EN showing bulk morphology. (b) Zoomed SEM image of as-synthesised Ni-POM-EN showing bulk morphology. (c) SEM image single crystal of Ni-POM-EN. (d) SEM image of Ni-POM-EN showing crystalline edges.

Section S5. IR Spectroscopy of Ni-POM-EN

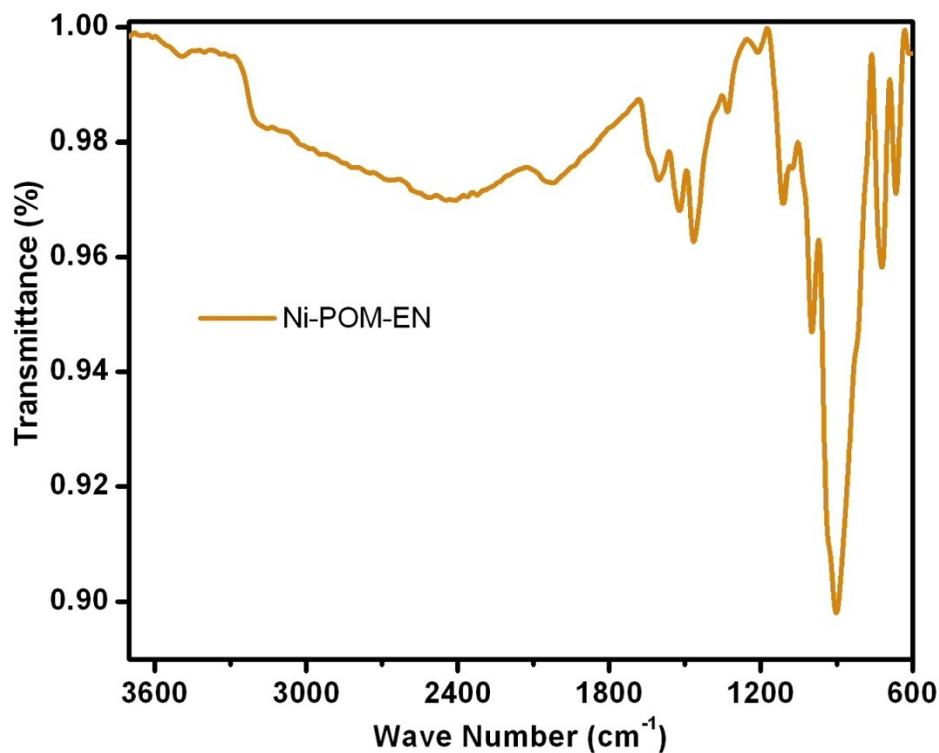


Figure S9: IR Spectroscopy of as-synthesized Ni-POM-EN. The Ni-POM-EN shows characteristic IR frequencies for $[\text{NiMo}_{12}\text{O}_{30}(\text{PO}_4)_8]^{11-}$ POM units at 1117($\nu_{\text{asym}}\text{P-O}_a$), 998($\nu_{\text{asym}}\text{P-O}_b$), 897($\nu_{\text{asym}}\text{Mo=O}$), 819 ($\nu_{\text{asym}}\text{Mo-O}_a$), 725($\nu_{\text{asym}}\text{Mo-O}_b$) and 668 ($\nu_{\text{asym}}\text{Mo-O}_c$) cm^{-1} .

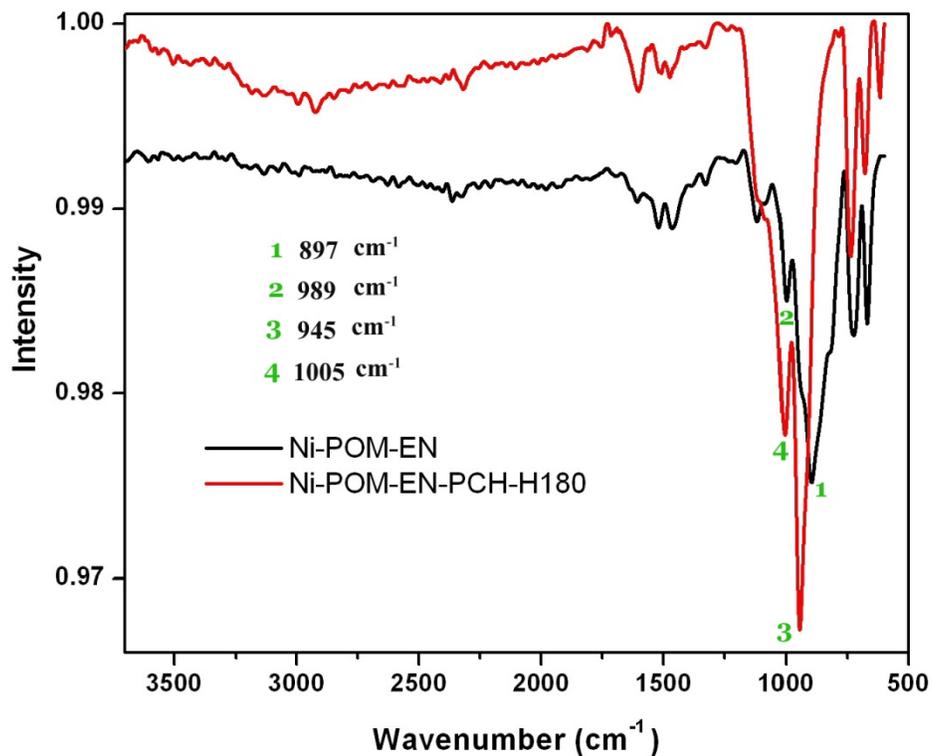


Figure S10: Comparison of IR Spectroscopy of as-synthesized Ni-POM-EN (black) and heated (180 °C) sample after proton conductivity measurement (red). The IR spectroscopic analysis of sample, Ni-POM-EN-180 shows shift from 897 (1) to 945 cm⁻¹ (3) and 989 (2) to 1005 cm⁻¹(4). The shift could be due to the removal of hydrogen bonded water molecules from the structure.

Section S6. Proton Conductivity measurement of Ni-POM-EN

Proton Conductivities were measured using Solartron 1287 Electrochemical Interface with 1255B frequency response analyzer via quasi-four-probe method. ~120mg of as-synthesized samples were pressed in a pellet maker to obtain uniform pellets of 0.37-0.38 mm, which was subject to humidification for 24h and subsequently measured the proton conductivity. Resistances were measured from the semicircle of the Nyquist plots. Proton conductivity was measured by the following equation; $\sigma = L/(R.A)$, where σ = proton conductivity, L = thickness of the pellet, R = resistance of the pellet and A = area of the pellet = $4\pi r^2$, where r = radius of the pellet. For high-temperature proton conductivity measurements, the pellets were inserted within a humidification chamber, which was encircled with a controlled heating coil attached with an automated temperature controller. The heat flow within the temperature controller was controlled by a dimmerstat accordingly. The temperature of the chamber was measured by an infrared temperature sensor attachment, having a sensing accuracy of ± 0.5 °C. For low temperature proton conductivity measurements, the pellets were inserted within a humidification chamber, which was encircled with a water circulation coil attached with a chiller integrated with an automated temperature controller. The heat flow within the chamber was controlled by the chiller accordingly. The temperature of the chamber was measured by an infrared temperature sensor attachment, having a sensing accuracy of ± 0.5 °C.

Amplitude of the potential perturbation = 5 mV

Frequency interval = 1 MHz to 1Hz

Number of points per frequency decade = total 140 points

Time to stabilize the electrode/solution interface = 2 h

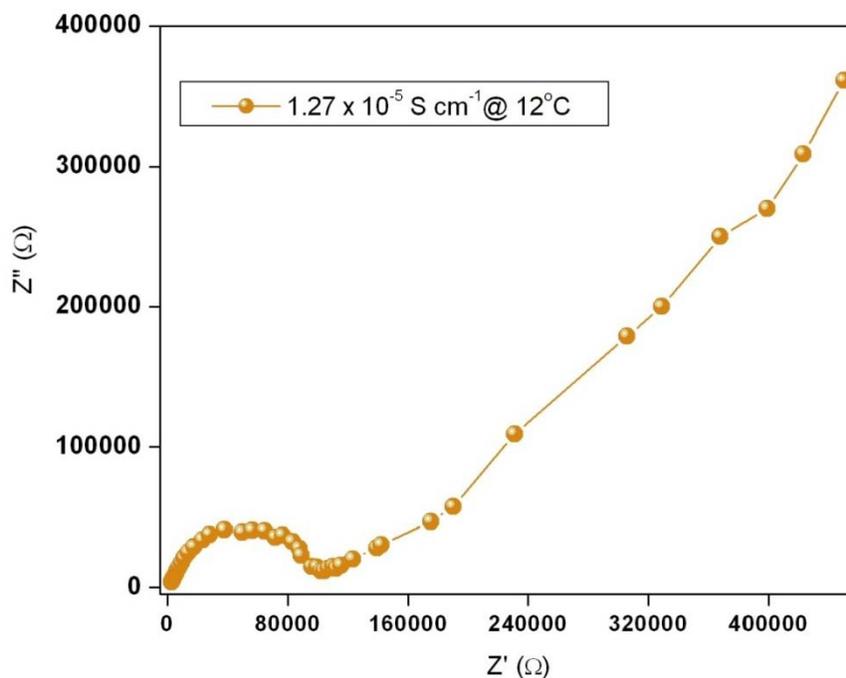


Figure S11: Proton conductivity plot at 285 K [$\sigma = 1.27 \times 10^{-5} \text{ Scm}^{-1}$].

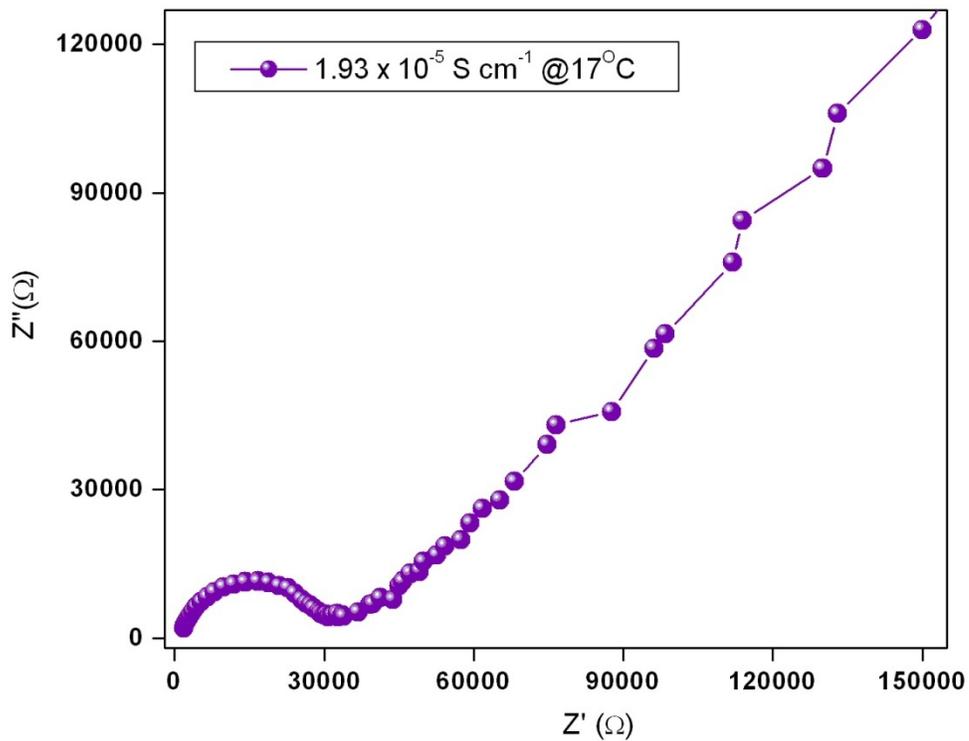


Figure S12: Proton conductivity plot at 290 K [$\sigma=1.93 \times 10^{-5} \text{ Scm}^{-1}$].

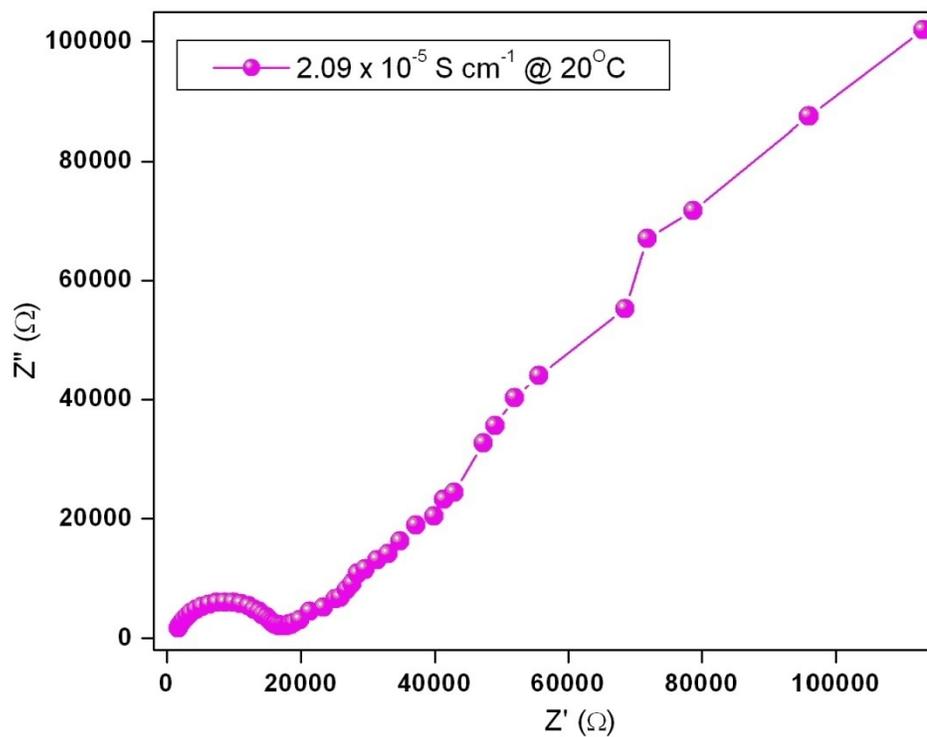


Figure S13: Proton conductivity plot at 293 K [$\sigma=2.09 \times 10^{-5} \text{ Scm}^{-1}$].

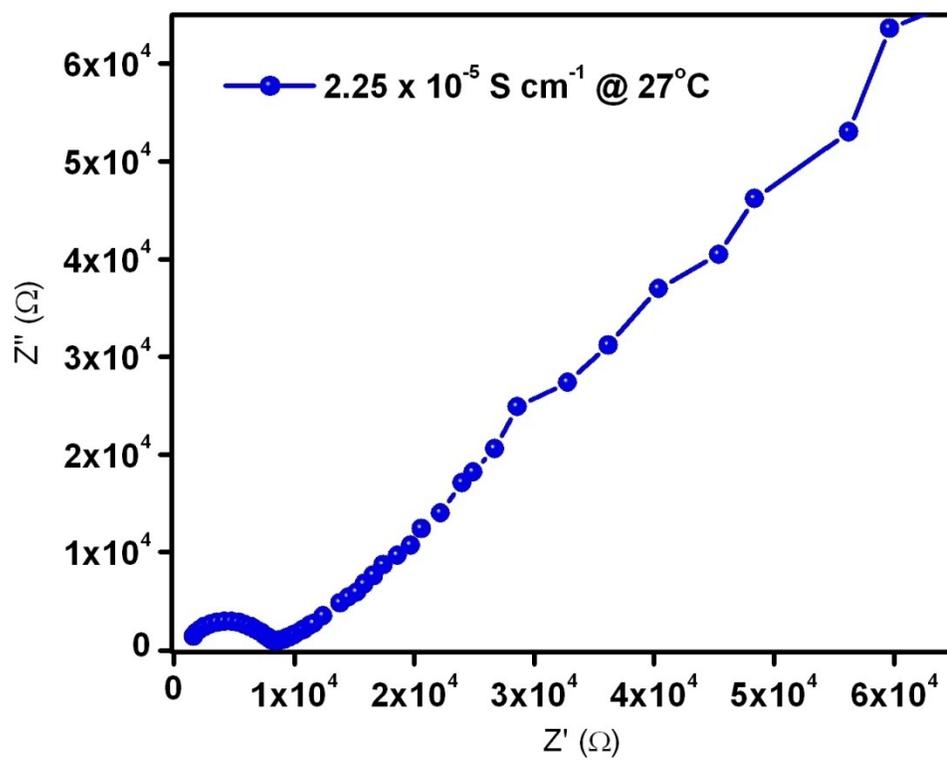


Figure S14: Proton conductivity plot at 300 K showing highest proton conductivity value for Ni-POM-EN at room temperature [$\sigma=2.25 \times 10^{-5} \text{ Scm}^{-1}$].

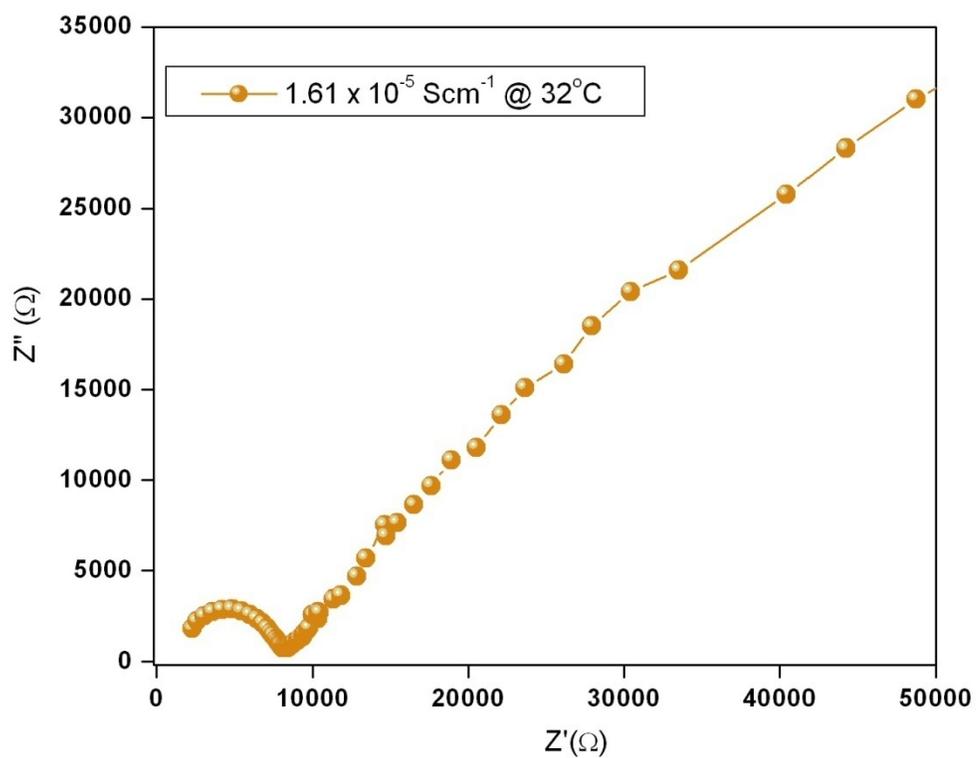


Figure S15: Proton conductivity plot at 305 K showing decrease in proton conductivity with respect to room temperature [$\sigma=1.61 \times 10^{-5} \text{ Scm}^{-1}$].

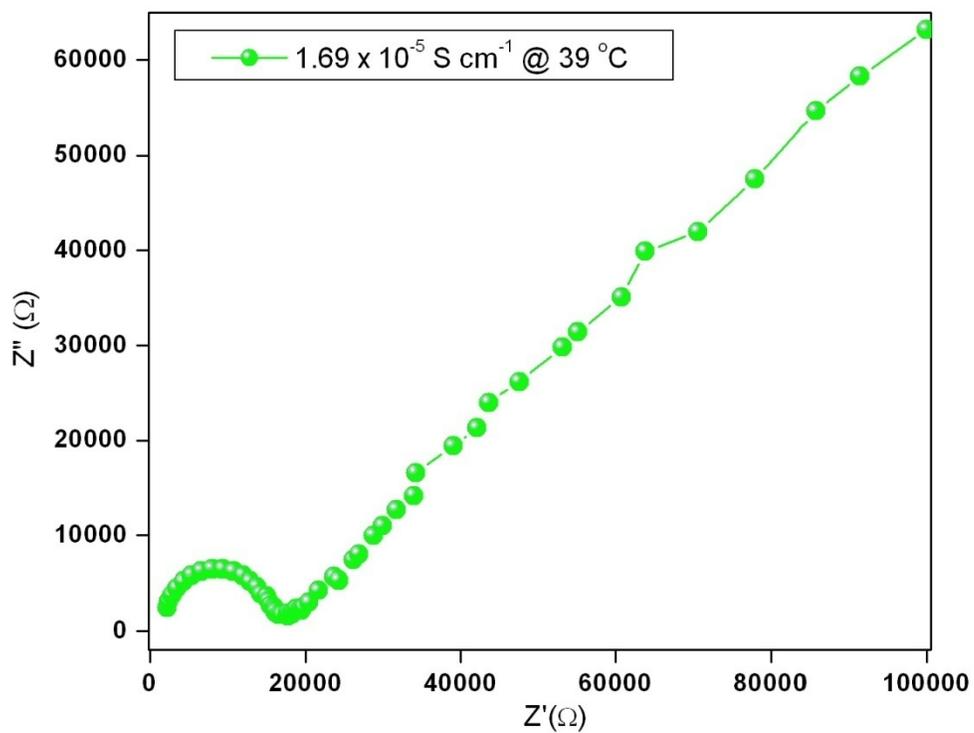


Figure S16: Proton conductivity plot at 312 K showing decrease in proton conductivity with respect to room temperature [$\sigma=1.69 \times 10^{-5} \text{ Scm}^{-1}$].

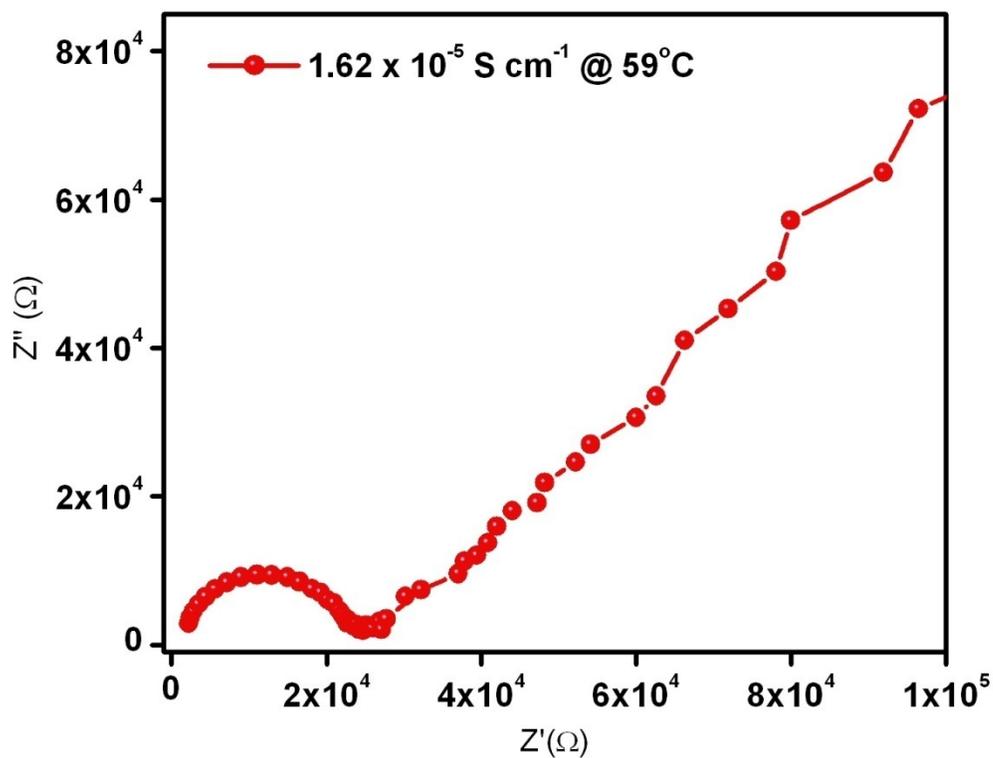


Figure S17: Proton conductivity plot at 332 K showing decrease in proton conductivity with respect to room temperature [$\sigma=1.62 \times 10^{-5} \text{ Scm}^{-1}$].

Calculation of Activation Energy:

The activation energy was calculated using *Arrhenius equation*

$$\sigma = \sigma_0 \exp(-E/kT)$$

where, σ = ionic conductivity
 σ_0 = material constant
 E = Activation energy
 k = Boltzmann constant
 T = Temperature

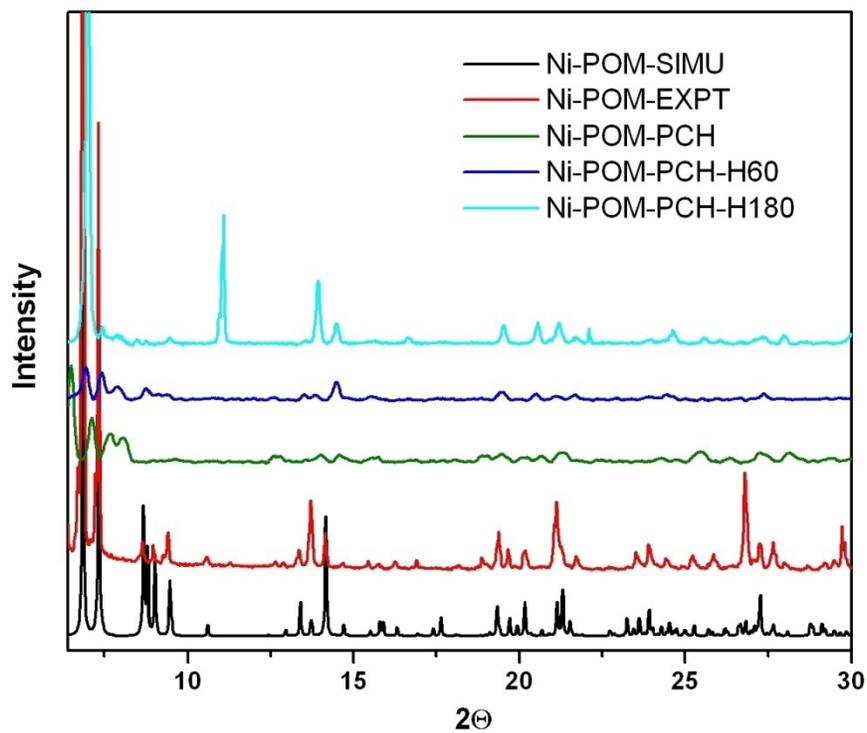


Figure S18: The PXRD pattern of the sample obtained after proton conductivity measurement shows a different crystalline phase (green) whereas heating at 60 °C causes the regeneration of parent phase (blue). Heating of the sample at 180 °C (Ni-POM-EN-180) generate a completely new phase due to the removal of all solvent molecules (cyan).