Electronic supplementary information (ESI)

**Proton conduction in Mo(II)-based metallo-supramolecular polymer films**

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1. Synthetic procedure

The synthetic procedure for polyMo is as follows. L1 (0.03 mmol) was dissolved in CH2Cl2 (5 mL) under a nitrogen atmosphere. MoO2(acac)2 (0.03 mmol) dissolved in CH3CN (5 mL) was added to the ligand solution drop by drop over a period of 30 min. The mixture was stirred for 12 h at 40 °C. After the reaction, the solvent was slowly evaporated from the pink solution by leading a stream of nitrogen over the reaction mixture. The precipitate was rinsed thoroughly with Et2O (20 mL), filtered off, then dried in vacuo at room temperature to afford polyMo in a 90% yield.

For polyMo-C synthesis, a two-neck flask fitted with a stirrer bar and an oxygen gas inlet and outlet was charged with polyMo (0.0123 mmol) and anhydrated DMF (2 mL). A solution of t-BuOK (0.125 mmol) in DMF (2 mL) was added dropwise and the yellow mixture was stirred at r.t. for 1 h. Oxygen was then purged into the reaction mixture for 6 h. The solvent was slowly evaporated from the orange solution by leading a stream of nitrogen over the reaction mixture. The precipitate was rinsed thoroughly with H2O (20 mL), filtered off, then dried in vacuo at room temperature to afford orange colored polyMo-C in a 85% yield.

2. Characterization details of polyMo and polyMo-C

SEC-viscometry–RALLS (size exclusion chromatography-viscometry-right angle laser light scattering) measurement

SEC-viscometry–RALLS system consists of a pump, solvent degasser, liquid chromatograph, refractive index detector, column oven, viscotek 270 dual detector. The eluent was acetonitrile at a flow speed of 1 mL/min. The column temperature was 30 °C. The synthesized Mo polymer (c =1.0 mg/mL) show weight-average molecular weight of polyMo using polyethylene oxide-PEO-22K as standard, when 20 μL of acetonitrile solution was injected. The molecular weight was obtained by automatic program calculation taking account of viscosity and RALLS factor into consideration.

PolyMo: yellow solid; yield: 90%; IR (KBr) : $\nu_{\text{max}}$/cm$^{-1}$ 3432, 2927, 2853, 1627, 1509, 1493, 1462, 1407, 1383, 1124, 1034, 916, 837, 708. $^1$H NMR (300 MHz, DMSO) 8.93 (br, s), 8.42 (br, m), 8.13 (br, m), 7.93 (s), 7.67-7.47 (br, m), 3.15 (m), 2.99 (s), 2.27 (br, m), 1.47-1.07 (m), 0.83-0.72 (m). $[M^+]$, weight-average molecular weight: 1.13 × 10$^5$ Da.

PolyMo-C: Orange solid: 85%; IR (KBr) : $\nu_{\text{max}}$/cm$^{-1}$ 3436, 3072, 2956, 1675 (C=O acid), 1681, 1614, 1557, 1488, 1447, 1387 (O-H acid), 1262 (O-H acid), 1108, 1075, 1020, 899, 863, 822, 792. $^1$H NMR (300 MHz, DMSO) $\delta$ = 11.97 (br, s), 8.91 (br, s), 8.39 (br, m), 8.11 (br, m), 7.92 (s), 7.67-7.56 (br, m), 3.05 (m), 2.81 (s), 2.09 (br, m), 1.46-1.06 (m), 0.83-0.69 (m), weight-average molecular weight: 1.02 × 10$^5$ Da.
Fig. S1. $^1$H NMR spectra of (a) L1, (b) polyMo and (c) polyMo-C measured in DMSO-d$_6$ at room temperature.

Fig. S2. FTIR spectra of (blue) polyMo and (black) polyMo-C, in ambient conditions, inset shows the presence of –C=O stretching peak in polyMo-C at 1675 cm$^{-1}$. 
Fig. S3. Dynamic mode AFM topographic images of polyMo on an HOPG substrate; (a) large area image showing several individual polymer chains and (b) height analysis from the AFM image of two polymer chains, bottom left side of the image shows the structure of a single unit of polyMo.

Fig. S4. Nyquist plot for impedance measurement at very low humidity for polyMo and the schematic of the conductivity measurement setup.

Note: the sample holder used in the experiments consists of an electrode with attached micrometer and another fix electrode with a guard ring on the electrode, which reduces the effect of stray field lines existing at the edge of the sample. The guard ring ensures that the electric field lines remain parallel all over the sample. In addition to this the impedance results were also normalized using the empty cell measurements by carrying out the experiment in an air-gap created with the help of the attached
micrometer. This procedure eliminates the errors due to connection and instrumentation etc. thus making the measurement more reliable.

**Fig. S5.** FTIR spectra of the polyMo-C at two different %RHs (blue: 50 %RH and red: 95 %RH).

**Fig. S6.** (a) FTIR spectra of the polyMo (dried sample), recorded after the experiment at 90 % RH and (b) FTIR spectra of the polyMo at 90 % RH after (a), suggesting a reversible trend and no damage to the polymer.
Fig. S7. Activation energy determination at three different %RHs (40, 70, 95 %RH) for polyMo. Comparable Eₐ values suggest the presence of an identical mechanism at different level of hydration in the polymer.

References

