Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
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Supplementary information for

Ionic Conductivity of Ni(II)-Based Metallo-Supramolecular Polymers: Effect of the Ligand Modification

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1. Characterization data of polyNiL1-4.

Molecular weight (M_w):

The molecular weight (M_w)[1] were determined by a SEC-viscometry–RALLS (size exclusion chromatography-viscometry-right angle laser light scattering) system. The eluent was acetonitrile at a flow speed of 1 mL/min. The column temperature was 30 °C. Polyethylene oxide-PEO-22K was used as standard, when 20 μL of an acetonitrile solution of **polyNiL1-4** (c = 1.0 mg/mL) was injected. The M_w was obtained by automatic program calculation taking account of viscosity and RALLS factor into consideration.

[1] M. Chiper, M. A. R. Meier, J. M. Johannes, U. S. Schubert, *Macromol. Chem. Phys.* **2007**, *208*, 679.

PolyNiL1: pink solid; yield: 92%; weight-average molecular weight: 1.24 × 10^5 Da; IR (KBr) : ν_{max}/cm^{-1} 2928, 2843, 1493, 1423, 1366, 1292, 1088 (strong peak, uncoordinated perchlorate anion), 891, 833, 748, 621. ESI-MS (m/z): 430.203 [**L1**Ni^{II}]$^{2+}$, 959.447 [**L1**Ni^{II}, ClO_4^-]$^+$, 558.301 [**L1(**$Ni^{II})_2$, $2ClO_4^-$]$^{2+}$, 831.452 [(**L1)$_2$**Ni^{II}]$^{2+}$.

PolyNiL2: pink solid; yield: 95%; weight-average molecular weight: 1.05 × 10^5 Da; IR (KBr) : ν_{max}/cm^{-1} 2924, 2855, 1616, 1585, 1520, 1454, 1427, 1092 (strong peak, uncoordinated perchlorate anion), 891, 833, 810,733, 625. ESI-MS (m/z): 402.234 [**L2**Ni^{II}]$^{2+}$, 903.372 [**L2**Ni^{II}, ClO_4^-]$^+$, 530.207 [**L2(**$Ni^{II})_2$, $2ClO_4^-$]$^{2+}$, 775.464 [(**L2)$_2$**Ni^{II}]$^{2+}$.

PolyNiL3: pink solid; yield: 90%; weight-average molecular weight: 1.28 × 10^5 Da; IR (KBr) : ν_{max}/cm^{-1} 2967, 2866, 1593, 1497, 1435, 1377, 1292, 1142, 1115, 1092 (strong peak, uncoordinated perchlorate anion), 895, 837, 783, 748, 633. ESI-MS (m/z): 236.057 [**L3**Ni^{II}]$^{2+}$, 571.102 [**L3**Ni^{II}, ClO_4^-]$^+$, 364.026 [**L3(**$Ni^{II})_2$, $2ClO_4^-$]$^{2+}$, 443.159 [(**L3)$_2$**Ni^{II}]$^{2+}$.

PolyNiL4: pink solid; yield: 93%; weight-average molecular weight: 1.03 × 10^5 Da; IR (KBr) : ν_{max}/cm^{-1} 2920, 2851, 1620, 1520, 1423, 1146, 1115, 1092 (strong peak, uncoordinated perchlorate anion), 941, 814, 733, 629. ESI-MS (m/z): 208.023 [**L4**Ni^{II}]$^{2+}$, 515.037 [**L4**Ni^{II}, ClO_4^-]$^+$, 335.969 [**L4(**$Ni^{II})_2$, $2ClO_4^-$]$^{2+}$, 387.069 [(**L4)$_2$**Ni^{II}]$^{2+}$.

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2. Determination of the film thickness of polyNiL1-3

Film preparation:

PolyNiL1-3 films were prepared on conductivity measuring electrodes (CME) by casting the MeCN/EtOH (1:1) solution. The CME has a precisely fixed distance between the electrodes for conductivity measurements. Prior to casting a film, the electrode was cleaned with isopropanol using an ultrasonic cleaner and then washed in Millipore water to remove any ionic impurity. The electrode was then again cleaned in isopropanol to remove any dust or water residue and kept for drying in a closed container. Immediately before casting the polymer solution, nitrogen gas was blown on the electrode surface. A MeCN/EtOH solution (10 µl) of **polyNiL1-3** (1.0 mg/mL) was carefully cast on the electrode surface. After the polymer films had formed, they were stored in a closed airtight container until they were used in the experiments.

The electrode without any polymer film:

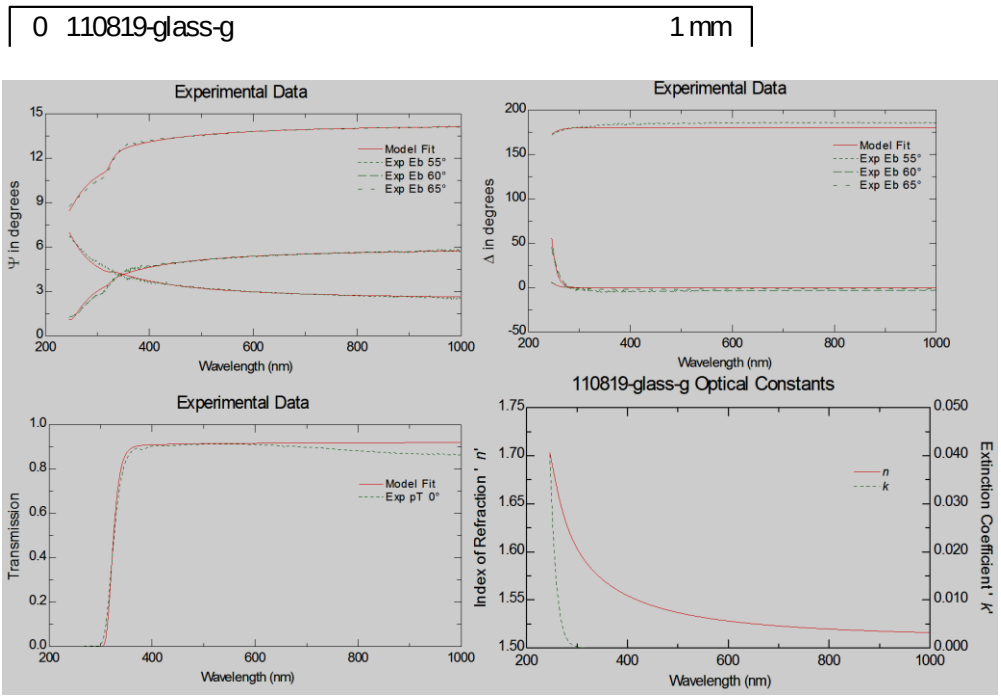

Figure S1. Ellipsometry data of a bear electrode.

General Oscillator model, thick film sample (an unknown very high concentration of a metallo-supramolecular polymer): Since the optical constants of such kind of metallo-supramolecular polymers were not available in the literature, we carried out an

experiment to measure the optical constant of such polymers. The model can be used for a variety of metallo-supramolecular polymer films.

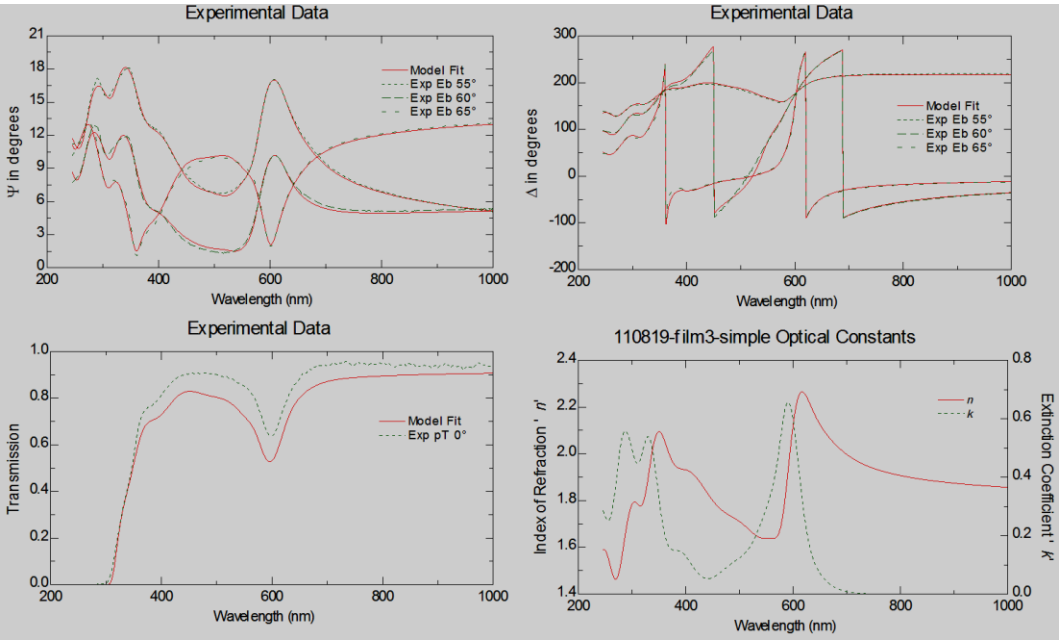

Figure S2. Ellipsometry data of a thick polymer film on the electrode.

Thickness measurement of polyNiL1-3 films:

The experiments were carried out at different angles and a nice fitting data was obtained for the polymer films.

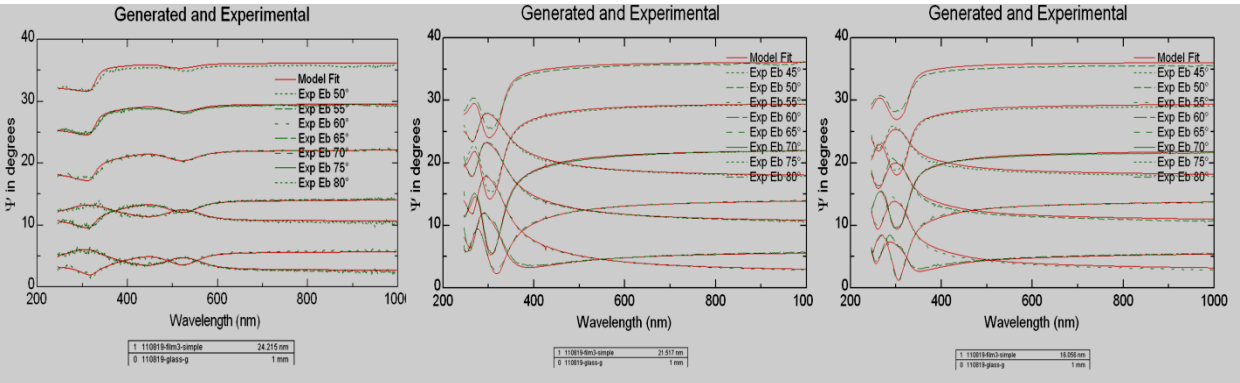

Figure S3. Ellipsometry data of **polyNiL1-3** films. The thicknesses were 24.2, 21.5 and 16.0 nm for **polyNiL1-3** films, respectively.

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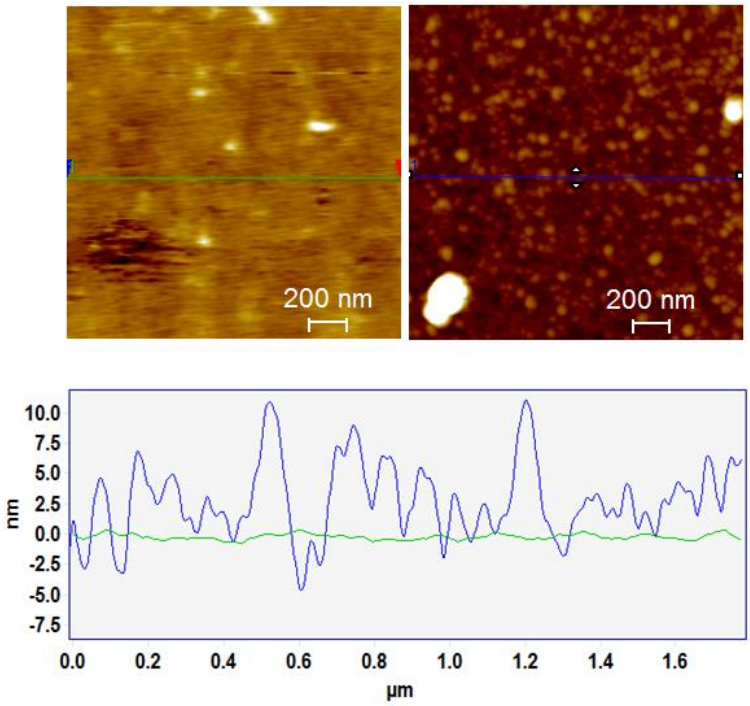

Figure S4. AFM images of a **polyNiL3** film. (Left) an AFM image of the electrode surface (the green line profile in the cross section). (Right) an AFM image of a **polyNiL3** film on the electrode (the blue line profile in the cross section).

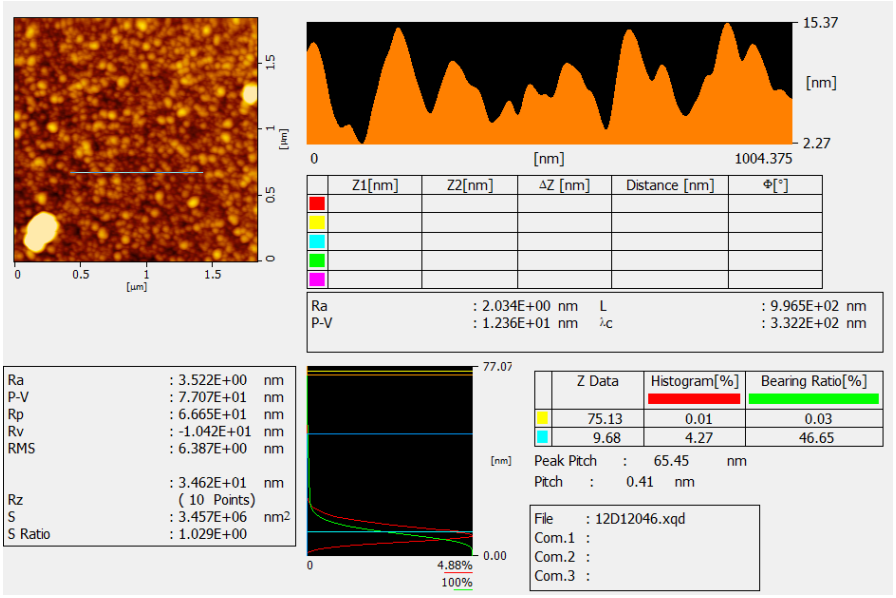

Figure S5. A cross section of an AFM image of a **polyNiL3** film. The average roughness was about 4.5 nm.

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3. Ionic conductivity measurements of the polymer films

Humidity cum temperature control chamber from ESPEC Japan (model no. SH-221) was used to keep the sample under ambient and high humidity during the measurements. In order to avoid water droplets formation on the electrode, only the polymer film was firstly warmed up to the measurement temperature and kept for an hour. Then temperature and humidity in the chamber were operated together. The ionic conductivity was measured using Solartron SI 1260 Impedance/Gain-Phase Analyzer and 1296 Dielectric Interface. A frequency range of 50 Hz to 5 MHz of 10 mV amplitude ac was used to determine the resistance of the film. The real axis intercept of the Nyquist plot was used for the calculation of resistance. *I–V* characteristics of the polymer films were measured by using a standard semiconductor characterization system (Keithley 4200-SCS). Even though the polymers are absolutely insoluble in water, nevertheless when studying the electrical response of the polymer film inside a humidity chamber, it is crucial that dew does not wet the specimen. Dew formation on the specimen surface (polymer film) takes place especially when we increase the temperature. At that point surface temperature of the specimen is less than the dew point of the test region i.e. inside the chamber.

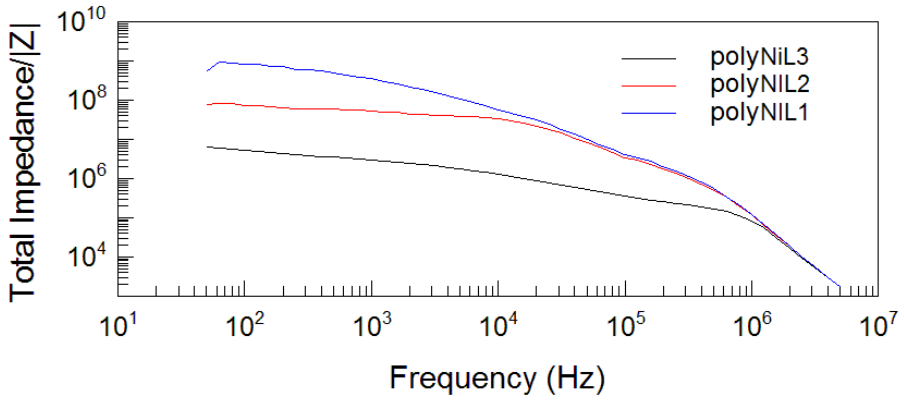

Figure S6. Total impedance Bode plots for **polyNiL1**-**3** films at 98 % RH.

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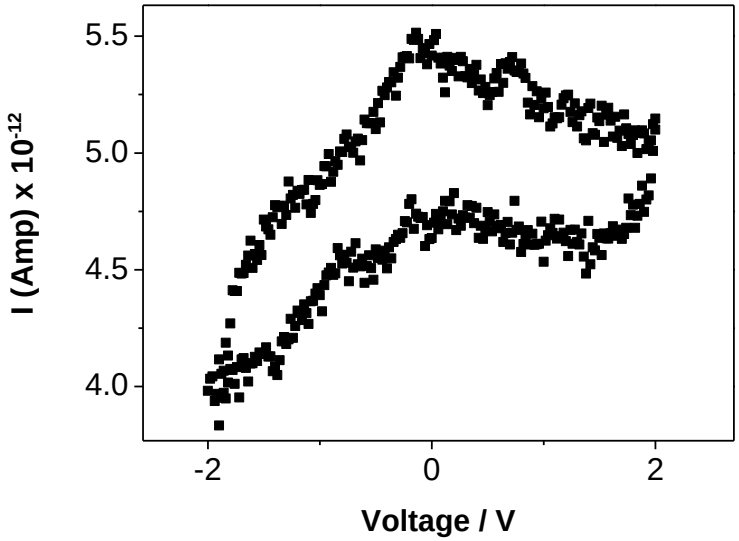

Figure S7. The dc current measurement of a **polyNiL3** film in vacuum. The negligible low currents indicate very low electronic conductivity of the polymer film.

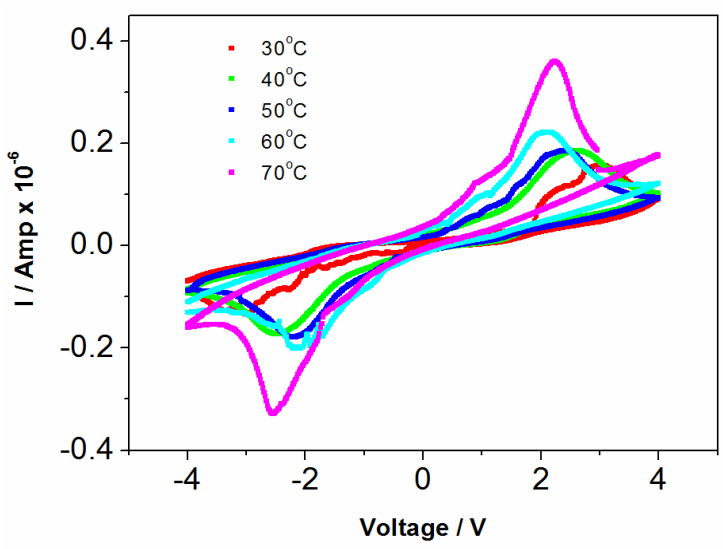

Figure S8. *I-V* characteristics for **polyNiL3** at different temperatures and 98% RH.

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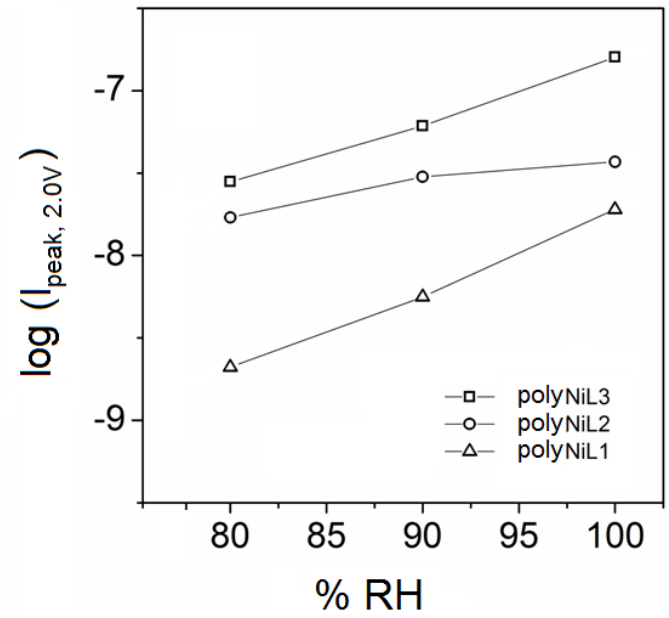

Figure S9. Logarithm of peak current response in **polyNiL1-3** films as a function of humidity (please note that peak current only appears prominently at higher humidities). A slope value of 0.04 was calculated for the **polyNiL3** film, which is apparently equal to the slope obtained in the plot of log(conductivity) vs. % RH at higher humidities (Figure 1d).