

Supporting Information

Proton conductive cationic nanoporous polymers based on smectic liquid crystal hydrogen-bonded heterodimers

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Synthesis

4-hydroxy-4-stilbazole (ii)

The synthesis of the 4'-hydroxy-4-stilbazole has been carried out according a literature procedure.^{S1,S2} The only change from the procedures was the addition of a small amount of 4 Å molecular sieves to the reaction mixture. Yield: 78.9%. m_p 78 - 80 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.55 (d, 2H), 7.47 (d, 2H), 7.33 (d, 2H), 7.25 (d, 1H), 6.90 (d, 2H), 6.87 (d, 1H), 6.10 (m, 1H), 5.55 (m, 1H), 4.15 (t, 2H), 3.99 (t, 2H), 1.95 (s, 3H), 1.82 (q, 2H), 1.72 (q, 2H), 1.50 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 167.6, 159.7, 150.3, 150.1, 145.0, 136.6, 132.9, 128.8, 128.5, 128.3, 125.4, 125.2, 120.8, 120.5, 114.9, 114.8, 67.9, 64.7, 29.2, 28.6, 25.9, 25.8. FTIR (cm^{-1}): 3071, 3036, 2943, 2899, 2886, 1701, 1594, 1514, 1169, 1023, 873, 545; MS m/z : 198.09 ($\text{M}+\text{H}^+$) (calculated for $\text{C}_{13}\text{H}_{11}\text{NO}$, 197.08).

6-bromohexyl methacrylate (iii)

6-Bromohexan-1-ol (10.05 g, 55.5 mmol) and triethylamine (17 mL, 122 mmol) were dissolved in dichloromethane under an argon atmosphere and cooled down to -20 °C whilst stirring. Methacryloyl chloride (5.69 mL, 58.28 mmol) was slowly added at this temperature. After stirring at -20 °C for 1 h, the mixture was slowly warmed up to room temperature. After 17 h, the mixture was concentrated and the white solid was filtered off. Column chromatography yielded 7.9 g (31.6 mmol, 57 %) of **iii** as a colorless oil (NMR experiments revealed that a small portion of the bromide had been substituted by chloride). In order to avoid premature polymerization of the compound, a small amount of tert-butyl hydroquinone (TBHQ) was added. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H), 3.41 (t, 2H), 1.94 (s, 3H), 1.88 (p, 2H), 1.70 (p, 2H), 1.45 (m, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46,

27.80, 25.23, 18.33. IR (ATR): $\bar{\nu}_{max}$ = 838, 937, 989, 1011, 1139, 1159, 1248, 1294, 1317, 1404, 1418, 1454, 1498, 1582, 1597, 1636, 1716, 2007, 2863, 2940.

4'-(6-methacyloxyhexyloxy-4-stilbazole) (6SzMA)

Under an inert argon atmosphere, 4.60 g (23.3 mmol) of compound **ii** was dissolved in 50 ml dry dimethylformamide (DMF) containing cesium carbonate (22.78 g, 69.9 mmol, 3 eq.) and powdered 4 Å mol. sieves. 6-bromohexyl methacrylate (**iii**, 6.39 g, 25.6 mmol, 1.1 eq.) was added dropwise at 0 °C and the mixture was stirred for 24 h at room temperature. Subsequently, DMF was removed by use of rotary evaporation. The crude mixture purified by column chromatography using 20 vol% EtOAc in heptane to obtain 7.32 g (20.02 mmol) of an off-white solid. Yield: 86 %. ¹H-NMR (400 MHz, CDCl₃) δ: 8.55 (d, 2H), 7.47 (d, 2H), 7.33 (d, 2H), 7.25 (d, 1H), 6.90 (d, 2H), 6.87 (d, 1H), 6.10 (m, 1H), 5.55 (m, 1H), 4.15 (t, 2H), 3.99 (t, 2H), 1.95 (s, 3H), 1.82 (q, 2H), 1.72 (q, 2H), 1.50 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ: 167.6, 159.7, 150.3, 150.1, 145.0, 136.6, 132.9, 128.8, 128.5, 128.3, 125.4, 125.2, 120.8, 120.5, 114.9, 114.8, 67.9, 64.7, 29.2, 28.6, 25.9, 25.8, 18.4; MS *m/z*: 366.13 (M+H⁺) (calculated for C₂₃H₂₇NO₃, 365.20).

Methods

Preparation of LC Cells

30×30 mm glass slides were first wiped clean using ethanol, sonicated in ethanol for 20 minutes, dried under a flow of nitrogen, where after they were exposed 20 minutes to a UV-Ozone treatment. A thin layer of polyimide was applied to the glass slides by spin coating. The coated glass slides were pre-cured at 90 °C for 10 minutes where after they were cured at 180 °C for half an hour. After curing, the glass plates were rubbed using a velvet cloth to induce a homogeneous alignment direction. Subsequently the glass slides were glued together using a photopolymerizable glue

containing 20 μm beads to obtain a well-defined spacing between the glass plates. The glass plates were glued together with their rub-direction antiparallel.

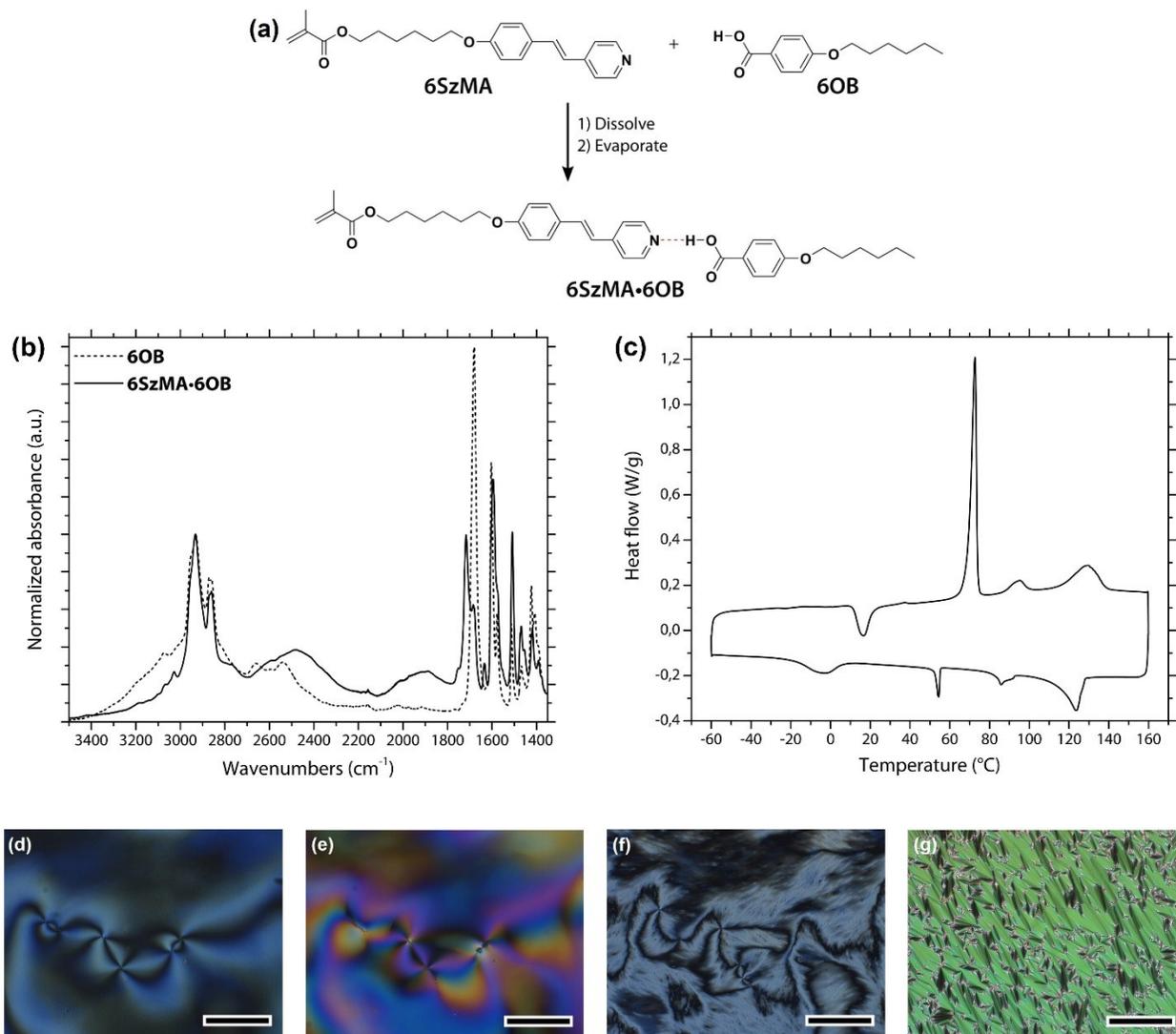


Figure S1. Phase behavior of the **6SzMA•6OB** complex. (a) The **6SzMA•6OB** complex is formed by dissolving **6SzMA** and **6OB** in CH_2Cl_2 and subsequently evaporating the solvent. (b) FTIR spectra of **6OB** (short-dash line), and the **6SzMA•6OB** complex (solid line). (c) DSC trace of the **6SzMA•6OB** complex (exothermal down). (d-g) Polarized light micrographs of the **6SzMA•6OB** complex at 30 $^\circ\text{C}$ (SmX1), 80 $^\circ\text{C}$ (SmX2), and 115 $^\circ\text{C}$ (SmC) under homeotropic boundary conditions, and 130 $^\circ\text{C}$ (SmA) under planer boundary conditions, respectively. Scale bar = 250 μm .

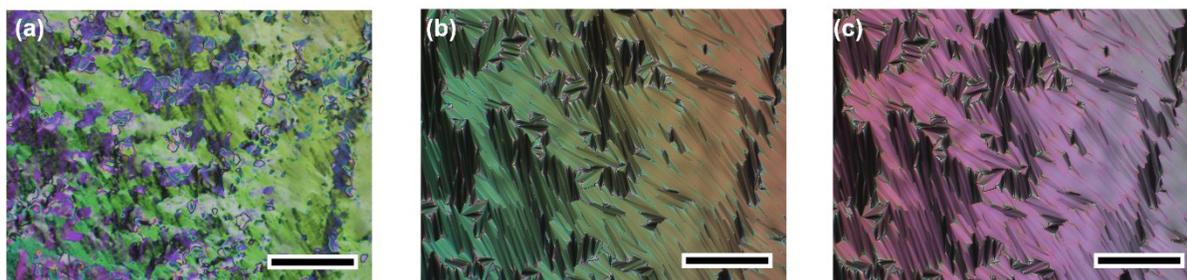


Figure S2. Phase behavior of the **6SzMA•6OB** complex containing 50 wt% CL. (a-c) Polarized light micrographs of the monomer mixture at 118 °C (N), 100 °C (SmA), and 20 °C (SmB), respectively. Scale bar = 250 μm .

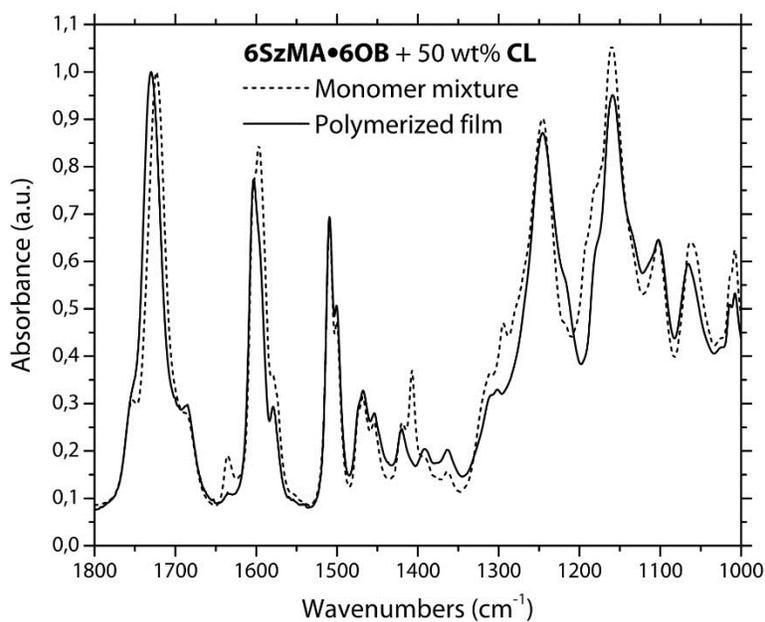


Figure S3. Photopolymerization of the mixture containing **6SzMA•6OB** and 50 wt% CL. ATR-FTIR spectra of the monomer mixture (short-dash line) and the polymer film (solid line).

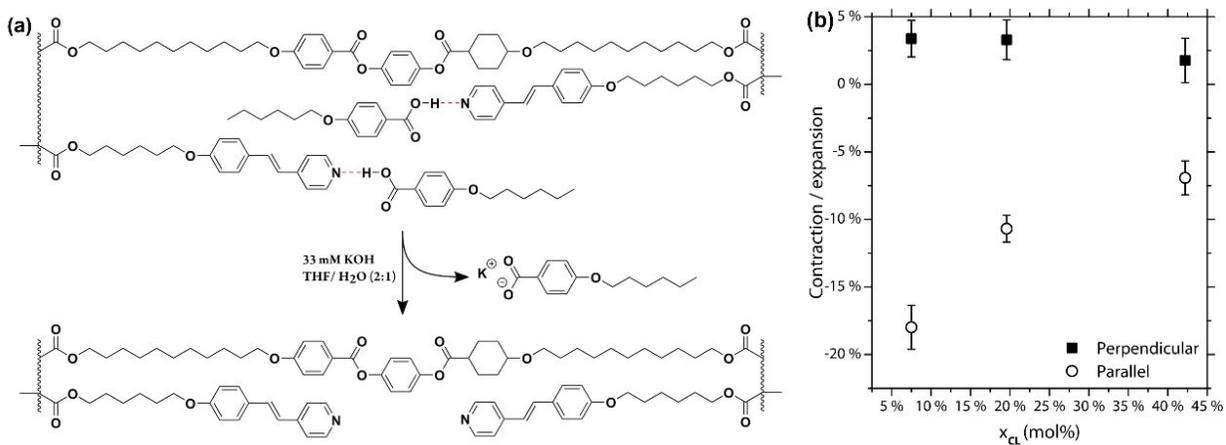


Figure S4. (a) Reaction scheme of the removal of the **6OB** porogen. (b) Macroscopic geometrical changes of the samples containing 10, 25, 50 wt% **CL**, respectively after removal.

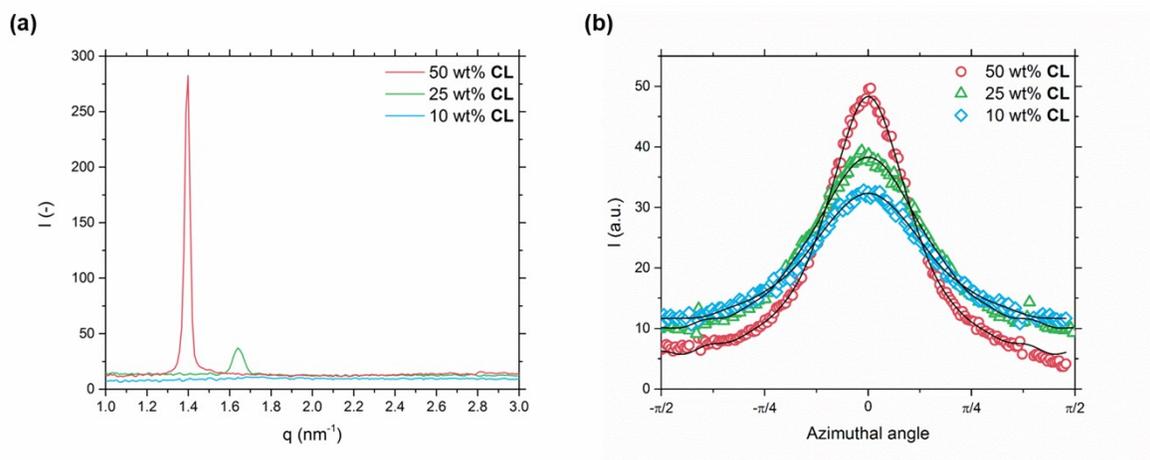


Figure S5. (a) Azimuthal integration of the small angle region of the x-ray diffractograms. (b) Radial integration of the wide angle signal ($q \approx 14$ nm⁻¹).

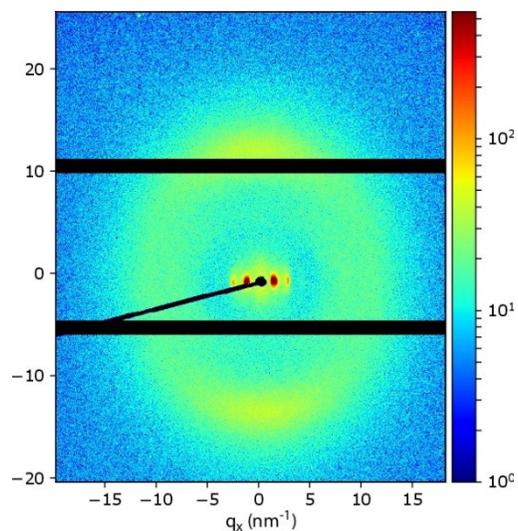


Figure S6. 2D x-ray diffractogram of the HAuCl_4 infiltrated film.

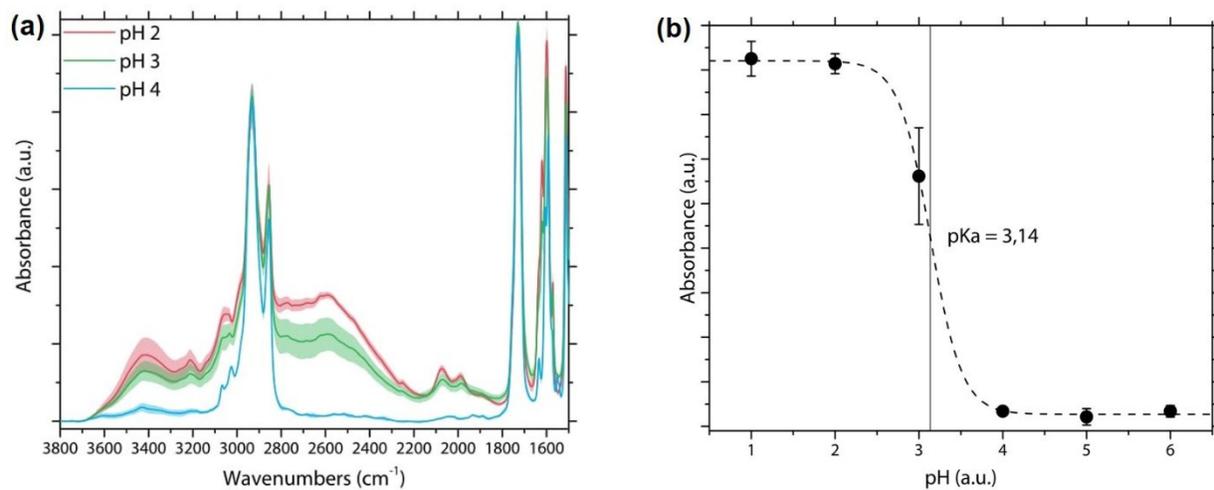


Figure S7. pKa determination of nanoporous LCN containing 25 wt% CL. (a) FTIR spectra of a nanoporous LCN exposed to 1M NaCl (aq.) solutions (red lines), 3 (green line), and 4 (blue line). (b) Estimation of the pKa from the absorbance at 2600 cm^{-1} , for films exposed to 1 M NaCl (aq.) at various pH values.

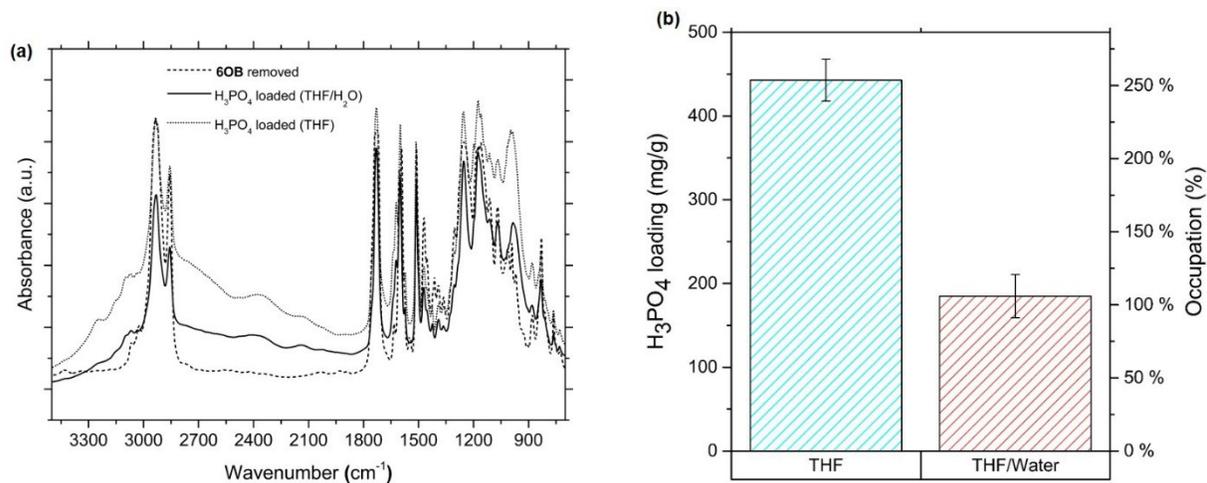


Figure S8. Infiltration of H₃PO₄ in a nanoporous film containing 25 wt% CL. (a) FTIR spectra of nanoporous LCN films: Unexposed (short-dash line), 100 mM H₃PO₄ in 1:1 (v/v) THF/H₂O (dashed line), and 100 mM H₃PO₄ in THF (solid line). (b) Gravimetrically determined H₃PO₄ uptake in films exposed to 100 mM H₃PO₄ in 1:1 (v/v) THF/Water (right column), and 100 mM H₃PO₄ in THF (left column).

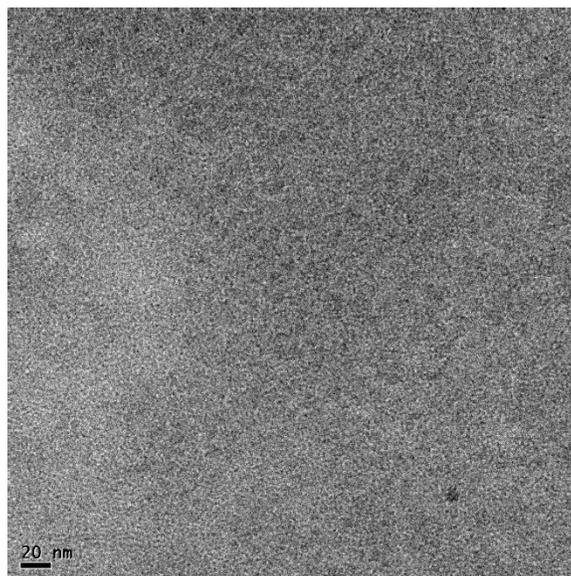


Figure S9 High magnification TEM micrograph of the 2.54 eq. H₃PO₄ infiltrated film.

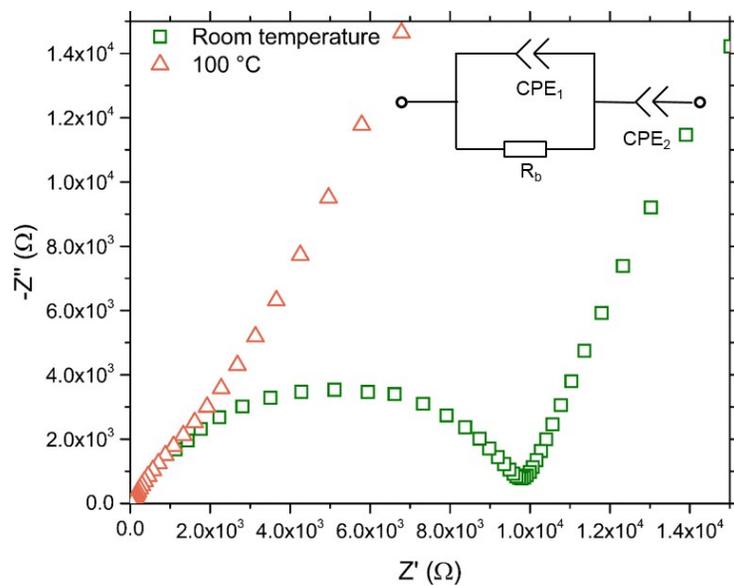


Figure S10. Nyquist plot of films containing 2.54 eq. H_3PO_4 at room temperature and 100 °C. Inset: Equivalent circuit of the test sample.

References

- (S1) B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 1933, **0**, 77–79.
- (S2) M. C. Chiang and W. H. Hartung, *J. Org. Chem.*, 1945, **10**, 21–25.