B903509E: Supporting data

Modulation of electroactive polymer film dynamics by metal ion complexation and redox switching

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Figure S1: Acoustic admittance spectra acquired during the potentiodynamic electropolymerisation of [Ni(3-Mesalophen-b15-c5)] at v = 0.02 V s^{-1}: ▬ bare electrode in deposition solution; ─ film-coated electrode at the end of successive deposition cycles (sequence denoted by arrow). Minimal decrease in peak admittance with increasing coverage (decreasing peak frequency) signifies an acoustically thin ("rigid") film. End of deposition sequence corresponds to film **A**, Γ = 18.3 nmol cm^{-2}.

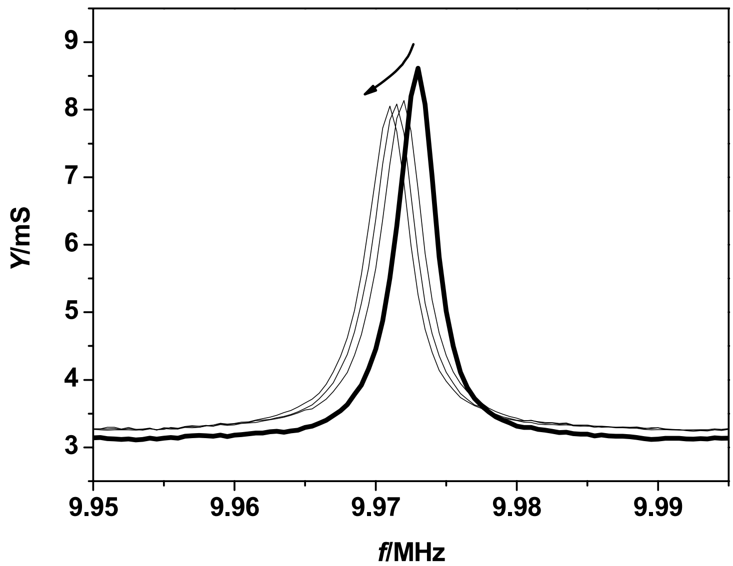


Figure S2: Voltammetric responses for film **B** before (full line) and after (dashed line) addition of Ba^{2+} ions. Solution: 0.1 mol dm^{-3} TBAP / CH_3CN (full line); 0.1 mol dm^{-3} TBAP / CH_3CN / 2 mmol dm^{-3} Ba^{2+} (dashed line). Scan rate: 10 mV s^{-1}.

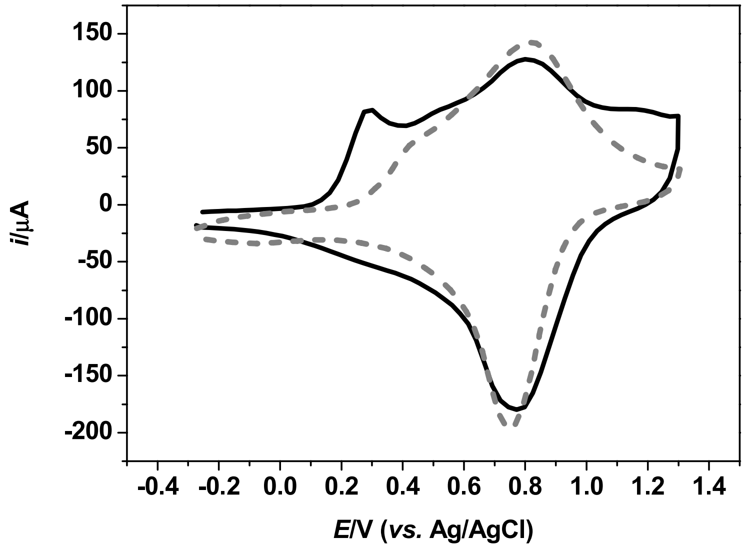
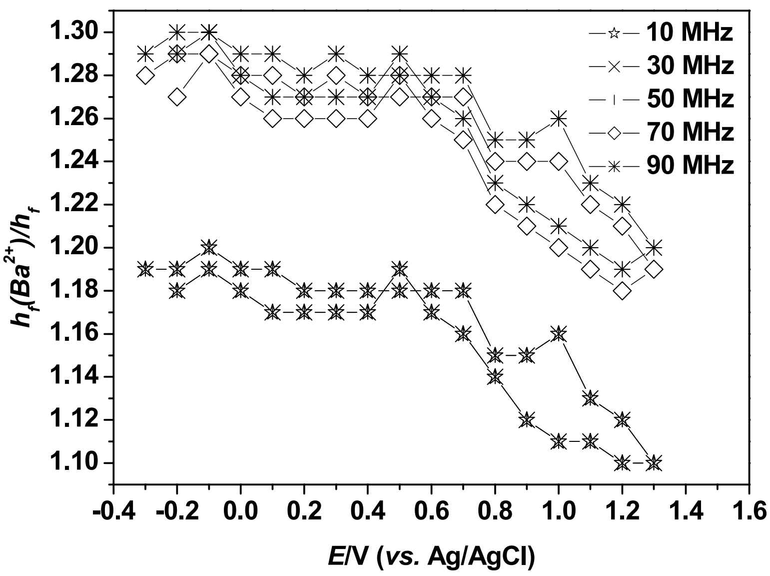


Figure S3: Ratio of $h_f(Ba^{2+})/h_f$ for acoustically sensed inner region, where individual film thickness values were determined from acoustic admittance spectra at different frequencies, as indicated. Data for film **B**.



Supplementary Material (ESI) for Soft Matter

Equivalent circuit models

The electrical equivalent circuit used in this work is the *lumped-element* or Butterworth van Dyke (BvD) model[1]. The presence of a film loading on the resonator generates an additional contribution $Z_e = R_2 + j\omega L_2$ to the crystal impedance, which accounts for all the system components (bulk fluid, rigidly coupled mass layer and viscoelastic film). Except in the special case of acoustically thin ("rigid") layers, the combination of the impedances associated with each of these physical components is non-linear, due to the accumulation of phase shifts across the surface loading. In the case of a surface loading consisting of a semi-infinite Newtonian fluid with impedance Z_L and a uniform viscoelastic layer with Z_0, the overall impedance is given by:

$$Z_s = Z_0\left[\frac{Z_L \cosh(\gamma h_f) + Z_0 \sinh(\gamma h_f)}{Z_0 \cosh(\gamma h_f) + Z_L \sinh(\gamma h_f)}\right] \qquad \text{(S1)}$$

where the wave propagation constant, $\gamma = j\omega(\rho_f / G)^{1/2}$. In the case of additional layers, the procedure for the generalization of equation (S1) has been described elsewhere[2].

The mechanical equivalent circuits that can be used to represent the viscoelastic behaviour of a polymer consist of combinations of springs and dashpots[3,4]: springs represent purely elastic deformation (with energy storage) and dashpots represent purely viscous flow (with energy dissipation). The two simplest models, each comprising a single spring and dashpot, are the Voigt and Maxwell models. In the Voigt model the spring and dashpot are in parallel, so the strains (S) are equal across the two elements and the stresses (T) are additive. The shear modulus is then:

$$G = \frac{T}{S} = \mu_f(1 + j\omega\tau) \qquad \text{(S2)}$$

where μ_f is the material stiffness, η_f the viscosity, and the relaxation time, $\tau = \eta_f/\mu_f$. Conversely, in the Maxwell model the spring and dashpot are in series, so the strains are additive and the stress across the elements are the same. The shear modulus is then:

$$G = \mu_f \left(\frac{(\omega\tau)^2}{1+(\omega\tau)^2} + j\frac{\omega\tau}{1+(\omega\tau)^2} \right) \qquad \text{(S3)}$$

These models predict distinct dependences of G on ω. In the Voigt model, G' is independent of frequency and G'' increases linearly with frequency. In the Maxwell model G' increases monotonically with frequency to a limiting value of μ_f, when $\omega\tau >> 1$, and G'' rises to a maximum of $\mu_f/2$ at $\omega\tau = 1$. In the low frequency range. Additionally, when $\omega\tau << 1$, the Maxwell model has limiting forms for the shear modulus components, $G' \approx \mu_f, \omega^2\tau^2$ *and* $G'' \approx \mu_f, \omega\tau$.

References

1. J. F. Rosenbaum, in *Bulk Acoustic Wave Theory and Devices*, Artech, Boston, 1988.
2. H. L. Bandey, S. J. Martin, R. W. Cernosek and A. R. Hillman, *Anal. Chem.*, 1999, **71**, 2205.
3. M. J. Brown, A. R. Hillman, S. J. Martin, R. W. Cernosek and H. L. Bandey, *J. Mater. Chem.*, 2000, **10**, 115.
4. J. J. Aklonis and W. J. MacKnight, in *Introduction to Polymer Viscoelasticity*, Wiley, New York, 1983.