1	SUPPORTING INFORMATION
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3	Metal Speciation in Complexing Soft Film Layer :
4	A Theoretical Dielectric Relaxation Study of Coupled Chemodynamic and
5	Electrodynamic Interfacial Processes
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13	Determination of the criterion for the detection of coupled chemodynamic and electrodynamic
14	interfacial processes at a soft ligand film/reactive electrolyte interphase by dielectric relaxation
15 16	speciroscopy (DKS).
17	As detailed in the main text, we consider a DRS experiment for the analysis of metal speciation in
18	a complexing soft film layer supporting a ligand concentration c_{i}^{*} and an ionic solution containing a
10	z z indifferent electrolyte and reactive metal ions of concentration c^* and c^* respectively. A stability
20	K > 0 is associated to the complex formed between the ligands L distributed throughout the
20	film layer and free metal ions M. The thickness of the film layer is taken here large enough ($\kappa d >>1$)
22	so that, at equilibrium. Donnan potential v^{D} is reached in the bulk film layer. For the sake of
23	comprehensiveness, a typical dielectric spectrum corresponding to the above situation is represented in
24	Figure S1 (curve (i) therein, detailed interpretation of the spectra is given in the main text). The impact
25	of chemodynamic processes is in particular reflected by the presence of a maximum in the permittivity
26	increment $\Delta \varepsilon'(\omega)$ and the presence of a low magnitude permittivity plateau at low frequencies (see
27	main text for details).
28	In order to construct a quantitative criterion for the appropriate detection of such a maximum and
29	low frequency limit for the permittivity as a function of the key relevant parameters K, $c_{\rm L}^*$, c^* and $c_{\rm M}^*$,
30	we adopt the following strategy based on the separate analysis of two distinct situations. First, we
31	assume that metal ions M do not interact with ligands L ($K \rightarrow 0$) while all others parameters
32	(including ionic strength and ligand concentration) are kept unchanged. The resulting Donnan
33	potential is then denoted as $y^{D,o}$. Because the formation of complex ML leads to a decrease in the
34	magnitude of the equilibrium potential distribution across the EDL, it comes $ y^{D,o} > y^{D} $. The
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resulting frequency-dependent permittivity increment, $\Delta \varepsilon'_{K\to 0}(\omega)$, is displayed in Figure S1 (curve (ii) therein). The second situation considered provides the 'reference dielectric spectrum' defined in §3.2.3. of the main text. The frequency-dependent permittivity increment corresponding to this reference is denoted as $\Delta \varepsilon'_{ref}(\omega)$. An example is given in Figure S1 (curve (iii) therein). Briefly, for this reference, the interconversion of M into ML is not taken into account ($K \to 0$), but, contrarily to the previous situation, the Donnan potential in the bulk film layer is set to y^D via appropriate adjustment of the ligand concentration (see details in §3.2.3. of the main text).

42 Conformably to the results discussed in §3.1.2, $\Delta \varepsilon'_{ref}(\omega)$ is lower than $\Delta \varepsilon'_{K\to 0}(\omega)$ at low 43 frequency, in agreement with the drop (in magnitude) of the equilibrium Donnan potential following 44 metal complexation in the film layer. Consequently, the searched detection criterion may be written in 45 the form

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$$\left| \frac{\Delta \varepsilon_{K \to 0}' \left(\omega \to 0 \right) - \Delta \varepsilon_{\text{ref}}' \left(\omega \to 0 \right)}{\Delta \varepsilon_{\text{ref}}' \left(\omega \to 0 \right)} \right| > \theta,$$
(S1)

47 where θ is a scalar that must be sufficiently large for metal complexation kinetics to affect the low-48 frequency limit of the dielectric permittivity increment. Because there is no interaction between M and 49 L in both situations considered above, $\Delta \varepsilon'_{K \to 0}(\omega \to 0)$ and $\Delta \varepsilon'_{ref}(\omega \to 0)$ may be written using eqn 50 (37) in the main text

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$$\Delta \varepsilon'_{\rm ref} (\omega \to 0) = \varepsilon_{\rm r} (\kappa_{\rm m} H / 2 - 1)$$

$$\Delta \varepsilon'_{K \to 0} (\omega \to 0) = \varepsilon_{\rm r} (\kappa_{\rm m,o} H / 2 - 1),$$
(S2a,b)

52 with
$$\kappa_{\rm m,o} = \left[\kappa_{\pm}^2 \cosh\left(zy^{\rm D,o}\right) + \kappa_{\rm A}^2 \exp\left(y^{\rm D,o}\right) + \kappa_{\rm M}^2 \exp\left(-z_{\rm M} y^{\rm D,o}\right)\right]^{1/2},\tag{S3}$$

and $\kappa_{\rm m}$ given by eqn (38) in the main text. Combining Eqns (S1) and (S2a,b) provides the following criterion for the detection of chemodynamic processes by DRS:

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$$\left|\frac{\kappa_{\rm m,o} - \kappa_{\rm m}}{\kappa_{\rm m}}\right| > \theta , \qquad (S4)$$

recalling that $\kappa_{\rm m}H >> 2$ under conditions of practical interest. Donnan potentials $y^{\rm D}$ and $y^{\rm D,o}$ are then determined *via* solving the Poisson-Boltzmann equation (eqn (8) in the main text) applied at $\tilde{x} = 0$ or $\tilde{x} = \kappa H$. When the interconversion of ML into M is accounted for, the Donnan potential, $y^{\rm D}$, satisfies

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$$2z c^* \sinh(zy^{\rm D}) + z_{\rm M} c_{\rm M}^* \left(e^{y^{\rm D}} - e^{-z_{\rm M} y^{\rm D}} \right) - z_{\rm L} c_{\rm L}^* - z_{\rm M} c_{\rm L}^* \left(1 + \frac{1}{K c_{\rm M}^* e^{-z_{\rm M} y^{\rm D}}} \right)^{-1} = 0.$$
(S5)

60 Unfortunately, an explicit analytical solution of eqn (S5) is not possible. However, in the limit of low 61 potentials, *i.e.* $y^{D} < 1$, eqn (S5) may be linearized and y^{D} is then given by

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$$y^{\mathrm{D}} = \left[\frac{z_{\mathrm{M}}c_{\mathrm{L}}^{*}}{\lambda} + z_{\mathrm{L}}c_{\mathrm{L}}^{*}\right] \cdot \left[\gamma + \frac{z_{\mathrm{M}}^{2}c_{\mathrm{L}}^{*}}{Kc_{\mathrm{M}}^{*}\lambda^{2}}\right]^{-1}$$
(S6)

63 where $\gamma = \sum_{i} z_i^2 c_i^*$ and $\lambda = 1 + 1/Kc_M^*$. In the absence of metal complexation in the soft ligand film, 64 *i.e.* for $K \rightarrow 0$, the chemical source term in eqn (S5) vanishes and the equilibrium Donnan potential $y^{D,o}$

then satisfies the relationship

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$$2z c^* \sinh\left(z \cdot y^{D,o}\right) + z_M c_M^* \left(e^{y^{D,o}} - e^{-z_M y^{D,o}}\right) - z_L c_L^* = 0.$$
(S7)

This equation may be linearized for low potentials ($y^{D,o} < 1$) and yields

$$y^{\mathrm{D},\mathrm{o}} = \frac{z_{\mathrm{L}} c_{\mathrm{L}}^*}{\gamma} \quad . \tag{S8}$$

The evaluation of the detection criterion is then performed by combining eqns (S3), (S4), (S6), (S8) and eqn (38) in the limit of low Donnan potentials, *i.e.* $y^{D,o} < 1$ and $y^{D} < 1$. When the two latter conditions are not satisfied, eqns (S5) and (S7) must be solved numerically, using standard numerical solvers for that purpose.¹ In case Donnan condition is not satisfied (*i.e.* $\kappa d < 1$ or $\kappa d \sim 1$), the above strategy may be adopted *albeit* with reasoning in terms of the equilibrium surface potential $y_{o} = y^{e}(\tilde{x} = 0)$ instead of the Donnan potential. Procedures for evaluation of y_{o} were detailed by Ohshima.² The acquisition of numerous dielectric spectra was performed for various sets of K, $c_{\rm L}^*$, c^* and $c_{\rm M}^*$ under the condition $\kappa d >>1$. The data showed a strong sensitivity of the dielectric response with respect to the intra-film formation/dissociation of ML complex, even at low values of K and c_{M}^{*} . As a result, we estimated $\theta \approx 10^{-4}$ for $1 \text{ mM} \le c^* \le 10 \text{ mM}$ and $\theta \approx 10^{-5}$ for $10 \text{ mM} \le c^* \le 100 \text{ mM}$ with $c_{\rm M}^*/c^*$ and $K' = Kc_{\rm L}^*$ in the range 10⁻³ to 0.1.



Figure S1. Dielectric permittivity increment for a soft ligand film as a function of field frequency with 107 $\omega_{\rm d} = 10 \, {\rm s}^{-1} \, \Box \, \omega_{\rm diff}$, (i) K' = 1, Donnan potential $y^{\rm D}$; (ii) $K \to 0$, Donnan potential $y^{\rm D,o}$; (iii) 108 $K \rightarrow 0$ and Donnan potential y^{D} (reference spectrum, see text for further details). The film is 109 homogeneous $(\alpha/d \rightarrow 0)$ with a thickness d = 50 nm and ligand concentration $c_{\rm L}^* = 10$ mM (i, ii) 110 and $c_{\rm L}^* = 7.4 \text{ mM}$ (iii). The medium includes free metal ions M and counter-ion A with $c_{\rm M}^* = 0.1 \text{ mM}$ 111 and indifferent electrolyte with $c^* = 1 \text{ mM}$. Numerical resolution of eqns (S5-S7) provides 112 $y^{D,o} = -1.6$ and $y^{D} = -1.4$. Other model parameters: $H = 1 \ \mu m$, $D_{M} = D_{\pm} = 10^{-9} \ m^{2} \ s^{-1}$, $z_{M} = 2$ 113 114 and $z_{\rm L} = -1$.

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116 **References.**

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