SUPPLEMENTARY MATERIAL

The Role of Anions in Adsorbate-induced Anchoring Transitions of Liquid Crystals on Surfaces with Discrete Cation Binding Sites

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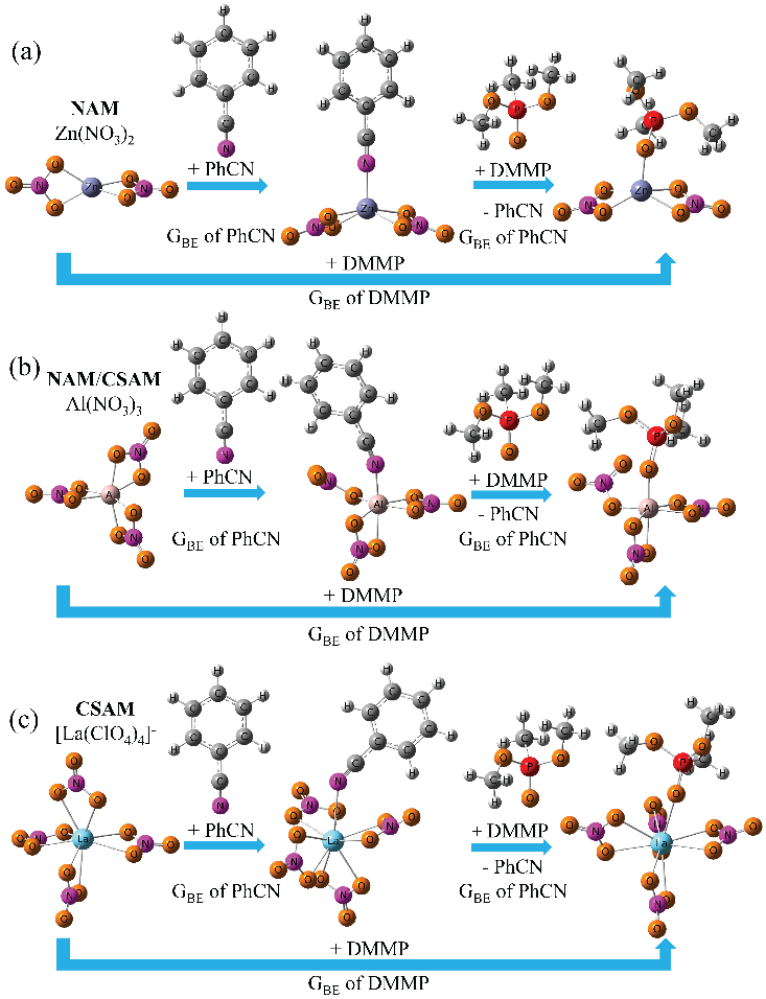

Figure S1. Representative structures from which G_{BE} and G_{DE} were calculated. (a) NAM structure for $Zn(NO_3)_2$ (left structure), its interaction with PhCN (middle structure), and DMMP (right structure). (b) CSAM and NAM structure for $Al(NO_3)_3$ (left structure), its interaction with PhCN (middle structure), and DMMP (right structure). (c) CSAM structure for $[La(NO_3)_4]^-$ (left structure), its interaction with PhCN (middle structure), and DMMP (right structure).

The NAM consists of a metal cation, in its most stable oxidation state, and anions are added to neutralize the cluster model. A model structure of $Zn(NO_3)_2$ and $Al(NO_3)_3$ is shown in Figure S1a and S1b, respectively. The NAM describes the right global composition of the metal salt while the metal cations are relatively under-coordinated. We previously hypothesized that this under-coordination can be present on metal salt surfaces thus NAM can be very useful to predict homeotropic ordering.

The CSAM model also contains a metal cation and anions are added to fill the coordination shell of the metal cation. Examples for CSAM, $Al(NO_3)_3$ and $[La(NO_3)_4]^-$, are shown in Figure S1b and S1c, respectively. We note that the definition of NAM and CSAM results in the same structure for Al^{3+}, Fe^{3+}, and Ga^{3+}. Also, the CSAM model structures can be negatively charged as shown in Figure S1c for $[La(NO_3)_4]^-$. CSAM provides somewhat over-coordinated metal cations which may be good candidates to describe the metal cation environment after homeotropic ordering thus predict response properties.

Table S1. Calculated G_{BE} of PhCN using NAM and CSAM. All energy values are in eV. Dashed lines indicate the lack of a stable bound structure.

Anion	ClO_4^-		NO_3^-	
Model	NAM	CSAM	NAM	CSAM
Ni^{2+}	-1.04	0.09	-0.77	---
Zn^{2+}	-0.84	0.03	-0.65	---
La^{3+}	-0.84	-0.20	-0.62	-0.07
Co^{2+}	-0.76	0.40	-0.47	---
Fe^{3+}	-0.43	-0.43	-0.33	-0.33
Ga^{3+}	-0.54	-0.54	-0.03	-0.03
Al^{3+}	-0.40	-0.40	0.08	0.08

Table S2. Calculated G_{DE} of PhCN using NAM and CSAM. All energy values are in eV. Dashed lines indicate the lack of a stable bound structure of PhCN and metal nitrate model cluster during energy minimization. 'x' signifies the lack of homeotropic ordering.

Anion	ClO_4^-		NO_3^-	
Model	NAM	CSAM	NAM	CSAM
Ni^{2+}	-0.47	-0.27	-0.41	---
Zn^{2+}	-0.57	-0.38	-0.50	---
La^{3+}	-0.64	-0.55	-0.57	-0.44
Co^{2+}	-0.66	-0.58	-0.66	---
Fe^{3+}	-0.66	-0.66	-0.40	-0.40
Ga^{3+}	-0.66	-0.66	x	x
Al^{3+}	-0.74	-0.74	x	x

Table S2 shows the calculated G_{DE} of DMMP for all studied metal salts. Dashed lines indicate the lack of G_{DE} of DMMP. This is because of the absence of a stable bound structure of PhCN for those metal salts (see Table S1). For the rest of the metal salts, the calculations predict negative G_{DE} values, but it is important to remember that because of the model-dependent threshold, (see Methods section) this does not necessarily mean that an experimental response would be observed.

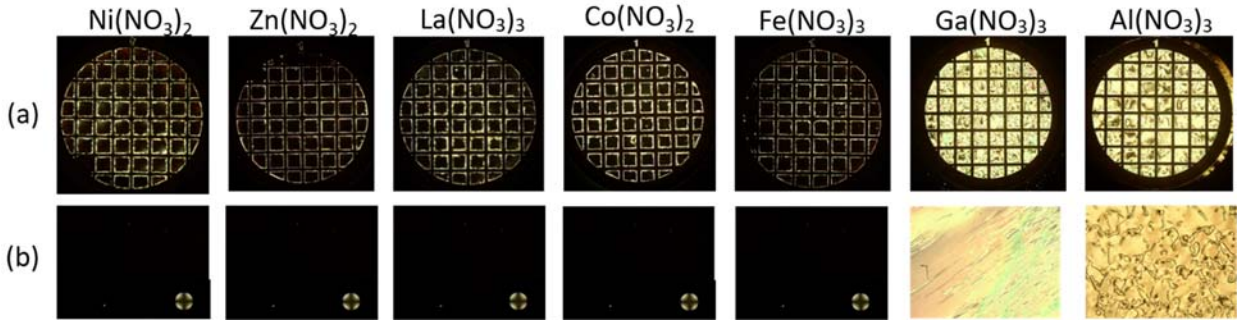

Figure S2. Cross-polarized images of 5CB films (a) in the experiment setup a and (b) in the experiment setup b in Figure 2 on the metal nitrate salts-decorated glasses.

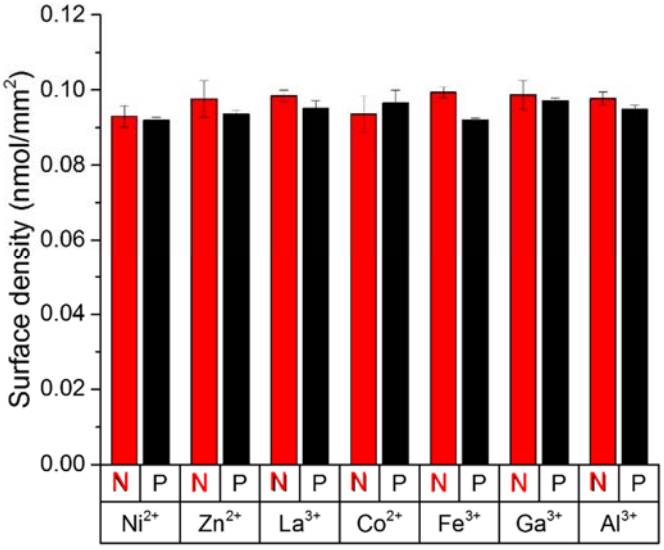

Figure S3. Surface density of metal salts coated on glass surface measured using ICP-OES. The concentration of metal salts is 10 mM in ethanolic solution. "N" and "P" on the x axis refer to nitrate and perchlorate anions, respectively.

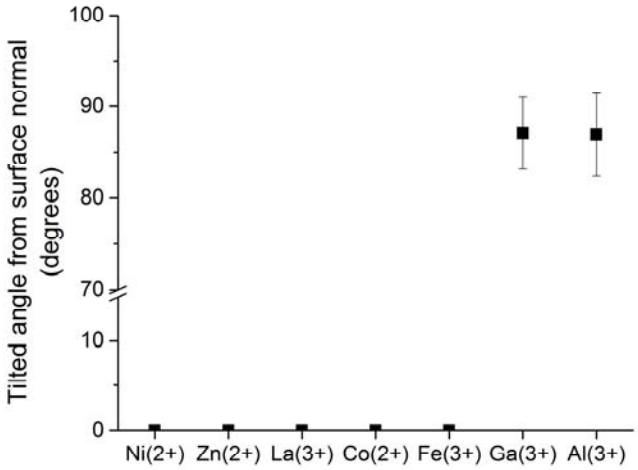

Figure S4. Tilt angle with respect to the surface normal for 5CB in experimental setup b in Figure 2 using retardance measurements.

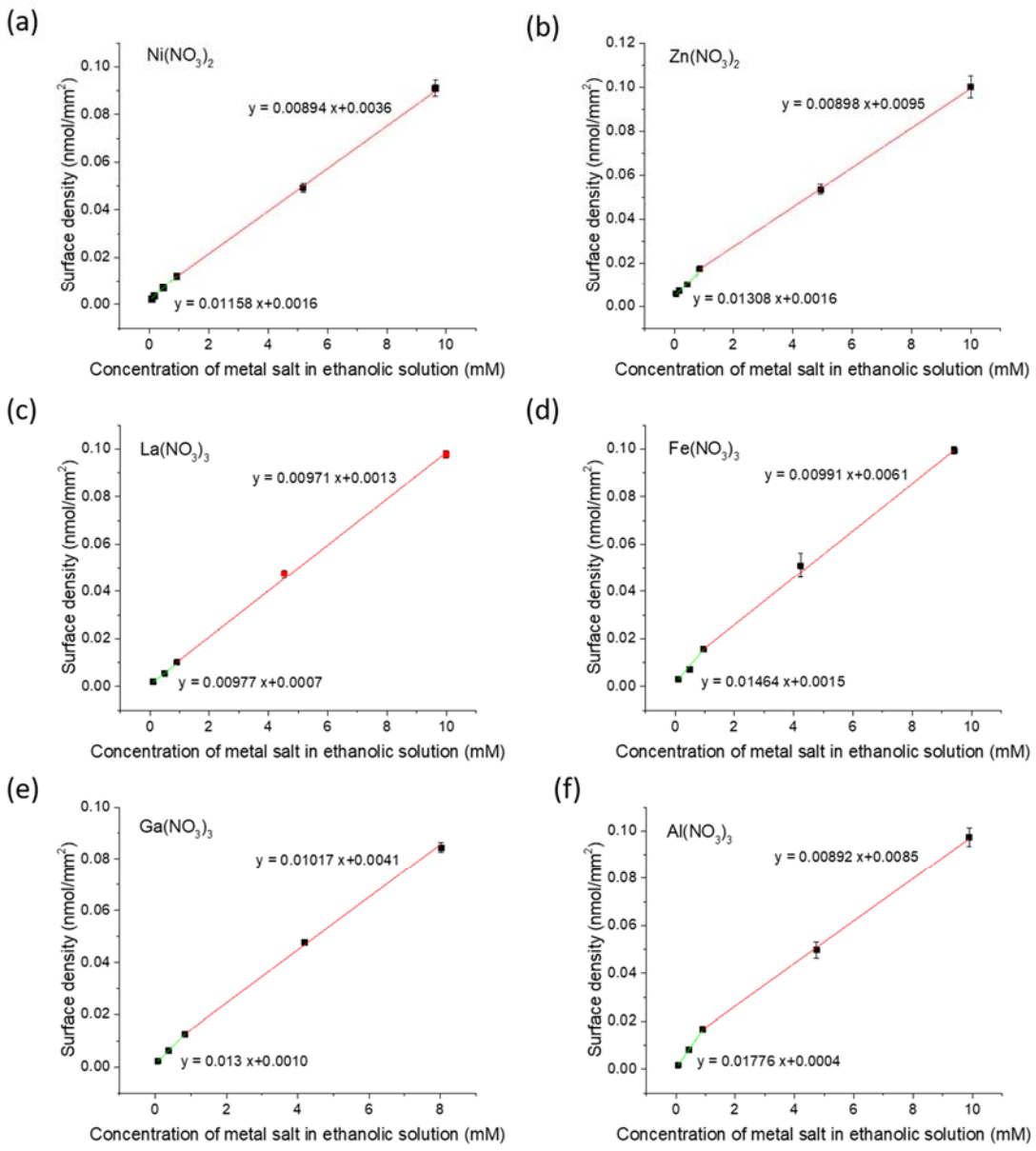

Figure S5. Surface density of metal nitrate salts coated on glass surface as a function of its concentration in ethanolic solution as coating solution. There are two fitting regions for each metal salt: one is from 1 mM to 10 mM (x axis); the other is from 0.1 mM to 1 mM. Metal salts: (a) $Ni(NO_3)_2$ (b) $Zn(NO_3)_2$ (c) $La(NO_3)_3$ (d) $Fe(NO_3)_3$ (e) $Ga(NO_3)_3$ (f) $Al(NO_3)_3$.

Two fitting regions (1 mM to 10 mM, and 0.1 mM to 1 mM) were decided based on fitting correlations. In these six plots, the slop of the region with lower concentration is always larger than that of the region with higher concentration. This could be due to different viscosities. The viscosity of coating solution is a key factor in spin-coating process: thicker coating can be obtained using solutions with higher viscosity under the same coating condition. So, if we suppose that the viscosity of coating solution in lower concentration region (0.1 mM to 1 mM) is constant and lower, the surface density should be smaller than what we get based on red linear fitting lines.

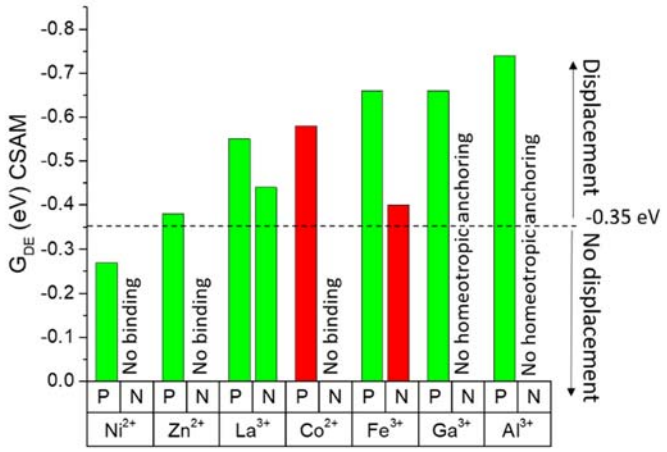

Figure S6. Comparison of experimental response to DMMP and calculated G_{DE} of PhCN using the CSAM. Displacement is predicted to occur when the displacement free energy is more negative than -0.35 eV. "N" and "P" on the x axis refer to nitrate and perchlorate anions, respectively. Green bars represent agreement between theoretical predictions and experimental observations, whereas red bars show disagreement.

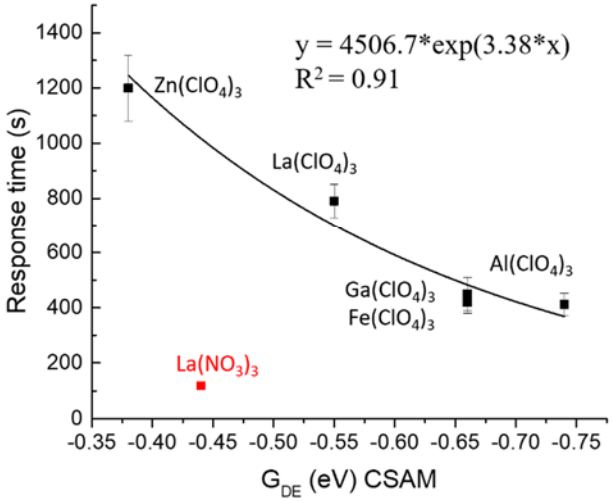

Figure S7. Experimental response time of 5CB anchored to various metal salts upon exposure to DMMP as a function of the calculated G_{DE} using CSAM. Exponential curve fitted using only perchlorate salt results.

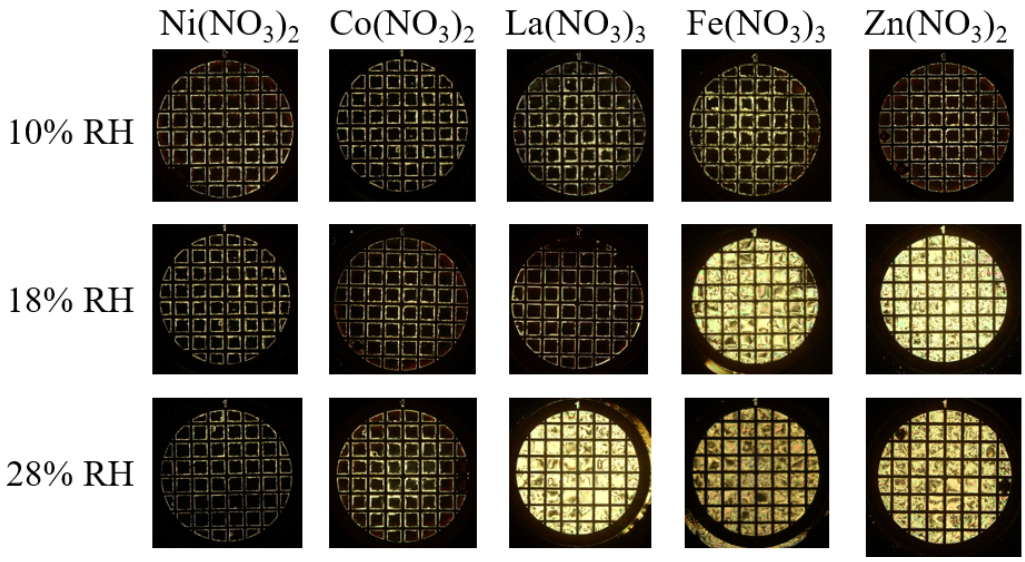

Figure S8. Cross-polarized images of 5CB films on the metal nitrate salts-decorated glasses in the experiment setup a in Figure 2 The samples were made in three separate days with ambient humidity of 10%, 18% and 28% RH.

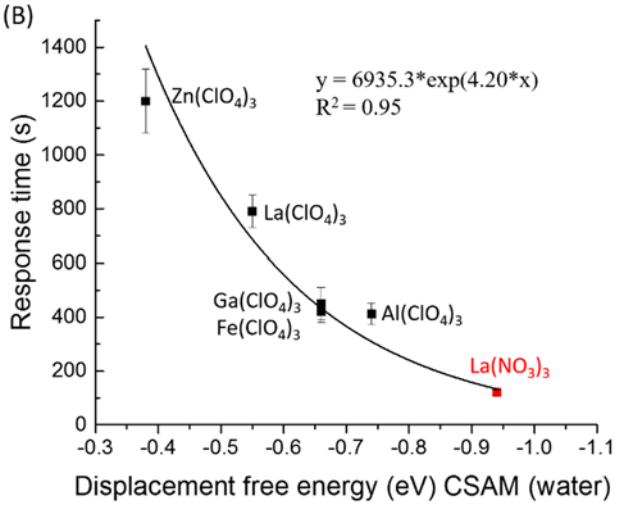

Figure S9. Experimental response time of 5CB anchored to various metal salts upon exposure to DMMP as a function of the calculated G_{DE}. Exponential curve fitted using all metal salt results after correction using water correction on $La(NO_3)_3$.