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Supporting Information

CD Stretching Modes are Sensitive to the Microenvironment in Ionic Liquids
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S1 Deconvolution of IR spectra of the [C18C1Im-\textit{d}_{37}][X] SAIL

The IR Spectra were fitted using OPUS v5.5 (Bruker, Germany) by employing Lorentzian-Gaussian sum functions with a Lorentzian-to-Gaussian ratio of 80 % for the ATR IR spectrum and 40 % for the surface spectra. Based on the second derivative of the ATR IR spectrum, six bands were used to fit the following modes (from high to low wavenumbers): \( \nu_{\text{as}}(\text{CD}_3) \), \( \nu_{\text{as}}(\text{CD}_2) \), \( \text{FR} \ [\nu_{\text{s}}(\text{CD}_2)] \), \( \text{FR} \ [\nu_{\text{s}}(\text{CD}_3)] \), \( \nu_{\text{s}}(\text{CD}_2) \), \( \nu_{\text{s}}(\text{CD}_3) \). For surface spectra, another IR absorption mode around 2183 cm\(^{-1}\) and 2230 cm\(^{-1}\) were added. No further constraints in the deconvolution procedure were employed. The deconvoluted spectra of pure the SAIL and monolayer films on the Au(111) are shown in figure S1.

\begin{center}
\includegraphics[width=\textwidth]{figureS1.png}
\end{center}

\textbf{Figure S1.} Deconvolution of IR spectra: a) ATR spectrum of [C18C1Im-\textit{d}_{37}][\text{TfO}] powder, b) [C18C1Im-\textit{d}_{37}][X] LB film on Au(111) in air (ex situ), c) [C18C1Im-\textit{d}_{37}][X] LB film on Au(111) in 0.1 M KClO\(_4\) (in situ, averaged over all potentials), and d) [C18C1Im-\textit{d}_{37}][X] LB film on Au(111) in 0.1 M KCl (in situ, averaged over all potentials). The solvent for the latter two was H\(_2\)O. Residuals (\(\mathcal{R}\)) are shown below spectra.
S2 Raw spectra of \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\}[X]:[\text{C}18\text{C}1\text{Im}-\text{h}_{43}]\}[X]\) SAIL Monolayer

Figure 1 shows original, raw PM IRRA spectra of the pure \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\][X] and of a mixed \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\][X]:[\text{C}18\text{C}1\text{Im}-\text{h}_{43}]\][X] = 1:10 molar ratio LB monolayer. Both amphiphilic cations have the same structure, with the difference that in the mixed \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\)^+ cation the H atoms in the octadecyl chains were substituted by D. Amphiphilic molecules containing the same in length and degree of saturation hydrogenated and deuterated chains form uniform monolayers. No phase segregation was observed.

![Figure S2. Raw PM IRRA spectra of the \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\][X] and mixed \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\][X]:[\text{C}18\text{C}1\text{Im}-\text{h}_{43}]\][X] in 1:10 molar ratio LB monolayers on the air|gold interface.](image)

In the isotopic dilution experiment, only 9% consist the IL with the perdeuterated alkyl chain: \([\text{C}18\text{C}1\text{Im}-\text{d}_{37}]\][X]. Thus, the spectral intensity of the CD absorption modes is very low (absorbance maximum of the \(\text{CD}_2\) stretching mode is close to \(2 \times 10^4\)). The signal to noise ratio changes between these two spectra. However, a close look at the original spectra shows in both cases the presence of the IR absorption band around 2182 \(\text{cm}^{-1}\) (Figure S2).
S3. Electrochemical Characterization of the [C18C1Im][X] SAIL Monolayer

Figure S3 shows capacitance of the [C18C1Im-h43][X] monolayer as a function of the electrode potential. Electrochemical characterization of the monolayer films was described by Sieling and Brand in [1].

![Figure S3](image)

**Figure S3.** Capacitance – potential curves of the [C18C1Im-h43][X] LB monolayer on the Au(111) surface in 0.1 M KClO4. Arrows show the directions of potential scan.

S4. Differential Reflectivity and Difference in situ PM IRRA Spectra of the [C18C1Im-d37][X] Monolayer

The raw PM IRRA signal $S_{raw}$ (equation S1) consists of p- and s-polarized reflectivity $R$, the second-order Bessel function $J_2$, and the gain factor $g$ for different electronic treatments during two-channel acquisition. Background-corrected differential reflectivity spectra are displayed with $\Delta S$ (equation S2).

$$
S_{raw} = \left( \frac{\Delta R}{\langle R \rangle} \right)_{exp} \approx g \frac{|R_p - R_s|}{(R_p + R_s)/2} \quad (S1)
$$

$$
\Delta S = \left( \frac{\Delta R}{\langle R \rangle} \right)_{exp} - \left( \frac{\Delta R}{\langle R \rangle} \right)_{background} \quad (S2)
$$

In case of monolayer films, the IR absorption modes of the analyte molecules are sometimes very poorly resolved from the non-linear background of the PM IRRA spectrum. For this reason, difference spectra $\Delta S_{raw,E}$ can be used to track intensity changes (equation S3) without the need of background correction.

$$
\Delta S_{raw,E} = S_{raw}(E) - S_{raw}(E_{ref}) \quad (S3)
$$

$\Delta S_{raw}(E)$ corresponds to a raw spectrum at one of the measured potentials and is referenced to the raw spectrum of a selected electrode potential, $\Delta S_{raw}(E_{ref} = -0.80 \text{ V})$. 

4
Background corrected differential reflectivity spectra $\Delta S$ and the difference spectra $\Delta S_{raw,E}$ of in situ experiments are shown in figures S4 and S5. Due to small changes in the background, a vertical offset procedure was used.

Figure S4. In situ PM IRRA spectra as function of the applied potential for the [C18C1Im-$d_{37}$][X] film in aqueous 0.1 M KClO₄ solution onto the Au(111) surface. Left - background-corrected differential reflectivity spectra. Right – differences of raw spectra with respect to $E_{ref} = -0.80$ V.
Figure S5. In situ PM IRRA spectra as function of the applied potential for the [C18C1Im-\textit{d}_{37}][X] film in aqueous 0.1 M KCl solution onto the Au(111) surface. Left - background-corrected differential reflectivity spectra. Right – differences of raw spectra with respect to $E_{\text{ref}} = -0.80$ V.
S5. Quantum Chemical Calculation of the Frequencies of the CD Stretching Modes of the [C18C1Im-d37][ClO4] SAIL in a Liquid State of the Alkyl Chain

All optimized geometries and frequencies were calculated on PBE0-D3BJ/def2-TZVP level of theory. Tables S1-3 show cartesian coordinates of the [C18C1Im-d37][ClO4] complex in vacuum, heptane, and water.

Table S1. Cartesian coordinates of the [C18C1Im-d37][ClO4] complex in vacuum ($E = -1733.515394$ hartree).

| Symbol | $x$ / Å | $y$ / Å | $z$ / Å |
|-------|--------|--------|--------|
| C     | -7.775663 | 0.923799 | -1.30422 |
| C     | -7.838711 | -0.26591 | -0.65833 |
| C     | -6.375262 | 0.997203 | 0.385907 |
| N     | -6.859397 | 1.694431 | -0.63375 |
| H     | -8.293051 | 1.281207 | -2.17741 |
| H     | -8.420863 | -1.14843 | -0.85785 |
| H     | -5.582737 | 1.307391 | 1.06141 |
| N     | -6.962475 | -0.1952  | 0.395137 |
| C     | -6.416661 | 3.02201  | -1.02311 |
| H     | -5.558782 | 3.30355  | -0.41365 |
| H     | -6.096414 | 2.994047 | -2.06344 |
| H     | -7.233988 | 3.73252  | -0.89386 |
| C     | -6.639769 | -1.27663 | 1.327153 |
| D     | -7.359391 | -2.07284 | 1.127205 |
| D     | -6.819649 | -0.90907 | 2.339092 |
| C     | -5.213361 | -1.76915 | 1.170522 |
| D     | -5.06134  | -2.54361 | 1.930588 |
| D     | -4.527357 | -0.95298 | 1.411349 |
| C     | -4.908113 | -2.32783 | -0.20948 |
| D     | -5.665593 | -3.07775 | -0.47331 |
| D     | -4.982129 | -1.5231  | -0.94927 |
| C     | -3.522652 | -2.95436 | -0.30793 |
| D     | -3.413975 | -3.4046  | -1.30113 |
| D     | -3.446414 | -3.78217 | 0.409129 |
| C     | -2.384702 | -1.97185 | -0.08246 |
| D     | -2.509783 | -1.11326 | -0.74931 |
| D     | -2.433202 | -1.56021 | 0.931167 |
| C     | -1.012745 | -2.5858  | -0.2967 |
| D     | -0.939438 | -2.96395 | -1.32482 |
| D     | -0.892307 | -3.46124 | 0.355343 |
| C     | 0.117166  | -1.60367 | -0.03861 |
| D     | -0.026234 | -0.71513 | -0.66332 |
| D     | 0.052899  | -1.2434  | 0.99489 |
| C     | 1.495602  | -2.19002 | -0.28724 |
| D     | 1.561628  | -2.53693 | -1.32659 |
| D     | 1.631814  | -3.08322 | 0.336418 |
Table S2. Cartesian coordinates of the [C18C1Im-<sub>d7</sub>][ClO₄] complex in heptane

(E = -1733.526935 hartree).

| Symbol | x / Å   | y / Å   | z / Å  | Symbol | x / Å   | y / Å   | z / Å  |
|--------|---------|---------|--------|--------|---------|---------|--------|
| C      | -7.94528| 0.80038 | -1.16587| C      | 2.651555| -1.21444| -0.02602|
| C      | -7.95476| 0.37432 | -0.49893| D      | 2.610723| -0.93984| 1.035332|
| C      | -6.40575| 0.907067| 0.396918| D      | 2.500582| -0.28141| -0.58242|
| N      | -6.97251| 1.581517| -0.59525| C      | 4.025636| -1.77658| -0.34739|
| H      | -8.53607| 1.140548| -1.99832| D      | 4.071469| -2.03552| -1.41283|
| H      | -8.55472| -1.25827| -0.617  | D      | 4.169263| -2.71827| 0.197688|
| H      | -5.56937| 1.240252| 1.001613| C      | 5.162364| -0.8262  | -0.01247|
| N      | -6.99079| -0.28329| 0.482776| D      | 5.119828| -0.57359| 1.054419|
| C      | -6.59237| 2.914731| -1.02882| D      | 5.015795| 0.118378| -0.55087|
| H      | -5.68007| 3.21014 | -0.51418| C      | 6.53638 | -1.38403| -0.34158|
| H      | -6.39686| 2.895115| -2.09958| D      | 6.58395 | -1.62226| -1.41172|
| H      | -7.39896| 3.613966| -0.80976| D      | 6.677374| -2.3363 | 0.185281|
| C      | -6.60845| -1.33689 | 1.423911| C      | 7.673559| -0.44131| 0.013435|
| D      | -7.30436| -2.1601 | 1.255628| D      | 7.635775| -0.21591| 1.087071|
| D      | -6.77357| -0.95967 | 2.434582| D      | 7.518623| 0.513222| -0.50142|
| C      | -5.17196| -1.7866 | 1.235407| C      | 9.044571| -1.00164| -0.33097|
| D      | -4.97808| -2.54971 | 1.996933| D      | 9.103282| -1.17093| -1.41373|
| D      | -4.50197| -0.9509 | 1.453519| D      | 9.147636| -1.98333| 0.135552|
| C      | -4.88657| -2.34782 | -0.14813| C      | 10.21031| -0.1241 | 0.104789|
| D      | -5.64047| -3.10695 | -0.39214| D      | 11.14964| -0.65781| -0.08433|
| D      | -4.98898| -1.54944 | -0.89147| D      | 10.15684| 0.022659| 1.189474|
| C      | -3.49755| -2.96002 | -0.27489| C      | 10.26898| 1.224585| -0.5979 |
| D      | -3.39875| -3.3941  | -1.27628| D      | 9.384882| 1.818317| -0.33952|
| D      | -3.40423| -3.79705 | 0.428993| D      | 10.21806| 1.057453| -1.68058|
| C      | -2.36222| -1.97436 | -0.04934| C      | 11.51769| 2.036745| -0.2788 |
| D      | -2.50908| -1.09878 | -0.68992| D      | 11.53116| 2.928652| -0.91394|
| D      | -2.39017| -1.59382 | 0.977438| D      | 12.40512| 1.45417 | -0.55372|
| C      | -0.99194| -2.57316 | -0.31311| C      | 11.62119| 2.462465| 1.177151|
| D      | -0.93613| -2.90572 | -1.35775| D      | 11.70403| 1.602982| 1.84617 |
| D      | -0.85962| -3.47566 | 0.298275| D      | 12.49756| 3.093122| 1.343983|
| C      | 0.142496| -1.6029  | -0.03138| D      | 10.73817| 3.032921| 1.480514|
| D      | -0.01338| -0.68572 | -0.61035| Cl     | -3.11773| 1.948824| 0.215585|
| D      | 0.101394| -1.29612 | 1.020722| O      | -3.7518 | 1.236435| -0.87329 |
| C      | 1.515914| -2.17378 | -0.33825| O      | -3.48343| 3.34187 | 0.140261 |
| D      | 1.562592| -2.45781 | -1.39743| O      | -1.69965| 1.796168| 0.151181 |
| D      | 1.660834| -3.10243 | 0.229031| O      | -3.61614| 1.405262| 1.469781 |
Table S3. Cartesian coordinates of the \([\text{C}18\text{C}1\text{Im-d}2\text{7}]\)[ClO\textsubscript{4}] complex in water \((E = -1733.549094\) hartree). 

| Symbol | \(x / \text{Å}\) | \(y / \text{Å}\) | \(z / \text{Å}\) | Symbol | \(x / \text{Å}\) | \(y / \text{Å}\) | \(z / \text{Å}\) |
|--------|----------------|----------------|----------------|--------|----------------|----------------|----------------|
| C      | -7.87177       | 0.844612       | -1.39194       | C      | 2.575246       | -1.26941       | -0.02331       |
| C      | -7.9497        | -0.33619       | -0.72999       | D      | 2.487674       | -0.81959       | 0.973704       |
| C      | -6.39155       | 0.875878       | 0.230092       | D      | 2.454844       | -0.44608       | -0.73855       |
| N      | -6.8935        | 1.582347       | -0.77488       | C      | 3.960851       | -1.87166       | -0.18122       |
| H      | -8.42161       | 1.218397       | -2.23791       | D      | 4.050011       | -2.31844       | -1.17948       |
| H      | -8.58048       | -1.19354       | -0.88748       | D      | 4.080244       | -2.69692       | 0.532065       |
| H      | -5.58629       | 1.185853       | 0.880524       | C      | 5.083356       | -0.86829       | 0.021176       |
| N      | -7.0207        | -0.29354       | 0.277498       | D      | 4.994105       | -0.42231       | 1.019785       |
| C      | -6.4733        | 2.918117       | -1.15701       | D      | 4.963537       | -0.0424        | -0.69126       |
| H      | -5.64093       | 3.220876       | -0.52693       | C      | 6.469481       | -1.46932       | -0.13688       |
| H      | -6.15273       | 2.909442       | -2.19722       | D      | 6.560577       | -1.9107        | -1.13741       |
| H      | -7.30594       | 3.608849       | -1.03359       | D      | 6.587998       | -2.29854       | 0.572004       |
| C      | -6.73805       | -1.36183       | 1.236406       | C      | 7.591317       | -0.4664        | 0.072242       |
| D      | -7.44566       | -2.16147       | 1.017874       | D      | 7.50726        | -0.03251       | 1.077045       |
| D      | -6.95716       | -0.98221       | 2.235049       | D      | 7.460792       | 0.364813       | -0.62951       |
| C      | -5.30739       | -1.85653       | 1.14053        | C      | 8.975182       | -1.0746        | -0.09348       |
| D      | -5.18024       | -2.61094       | 1.923516       | D      | 9.077747       | -1.46444       | -1.11428       |
| D      | -4.62681       | -1.03711       | 1.388264       | D      | 9.058681       | -1.94125       | 0.572766       |
| C      | -4.96075       | -2.45452       | -0.21334       | C      | 10.12217       | -0.11552       | 0.195686       |
| D      | -5.69911       | -3.22632       | -0.45827       | D      | 11.0677        | -0.67052       | 0.168403       |
| D      | -5.04932       | -1.68569       | -0.9899        | D      | 10.01925       | 0.261004       | 1.219714       |
| C      | -3.56443       | -3.05899       | -0.27196       | C      | 10.21737       | 1.049874       | -0.77871       |
| D      | -3.43805       | -3.55357       | -1.24151       | D      | 9.320634       | 1.675207       | -0.70163       |
| D      | -3.47952       | -3.84767       | 0.485912       | D      | 10.2247       | 0.65079        | -1.80019       |
| C      | -2.43864       | -2.0545        | -0.08388       | C      | 11.44706       | 1.926687       | -0.57901       |
| D      | -2.56236       | -1.23325       | -0.79969       | D      | 11.49766       | 2.655709       | -1.39458       |
| D      | -2.50431       | -1.59715       | 0.909479       | D      | 12.3477       | 1.307396       | -0.66734       |
| C      | -1.05914       | -2.66783       | -0.25078       | C      | 11.46763       | 2.666483       | 0.749306       |
| D      | -0.98          | -3.11845       | -1.24818       | D      | 11.50732       | 1.977777       | 1.596371       |
| D      | -0.938         | -3.49109       | 0.464675       | D      | 12.3357       | 3.326078       | 0.821423       |
| C      | 0.067827       | -1.66737       | -0.06021       | D      | 10.57053       | 3.28218        | 0.865803       |
| D      | -0.05351       | -0.84549       | -0.77673       | C      | -2.91991       | 2.113397       | 0.44953        |
| D      | -0.01645       | -1.2138        | 0.935276       | O      | -3.36809       | 1.508749       | -0.78014       |
| C      | 1.451625       | -2.27269       | -0.21992       | O      | -3.26965       | 3.512435       | 0.449722       |
| D      | 1.537893       | -2.72268       | -1.217         | O      | -1.49579       | 1.965696       | 0.579289       |
| D      | 1.571979       | -3.09576       | 0.49575        | O      | -3.57576       | 1.461907       | 1.564875       |
Calculated harmonic frequencies in vacuum and solvent models are listed in Tables S4-S6. Based on the deflection, most participating groups were assigned (for relative weights ≥ 5.0 %) according to the numbering in Figure 5 in the manuscript.

**Table S4.** Harmonic CD stretching vibrations of the [C18C1Im-δ₂][ClO₄] complex in vacuum.

| No. | ν / cm⁻¹ | ν_scaled / cm⁻¹ | I_R / km mol⁻¹ | Stretching vibration: participating group position in the alkyl chain (relative weight in %) |
|-----|----------|-----------------|----------------|-----------------------------------------------------------------------------------|
| 168 | 2188.1   | 2095.1          | 2.43           | ν_s(CD₂): 6 (25.5), 8 (14.7), 4 (5.1)                                               |
| 169 | 2188.9   | 2095.9          | 11.82          | ν_a(CD₃): 18 (62.0); ν_s(CD₂): 17 (5.4)                                             |
| 170 | 2191.7   | 2098.5          | 4.41           | ν_a(CD₂): 8 (13.8), 10 (13.0), 6 (8.6), 12 (5.0)                                    |
| 171 | 2193.5   | 2100.3          | 7.67           | ν_s(CD₂): 12 (11.0), 3 (10.6), 4 (8.2), 10 (6.8)                                    |
| 172 | 2194.0   | 2100.8          | 14.78          | ν_a(CD₂): 3 (11.1), 12 (9.1), 4 (6.4), 6 (5.3), 8 (5.3)                              |
| 173 | 2195.8   | 2102.5          | 4.01           | ν_a(CD₂): 14 (8.6), 11 (8.4), 8 (7.5), 13 (7.3), 10 (7.4)                           |
| 174 | 2198.0   | 2104.6          | 1.62           | ν_a(CD₂): 11 (15.2), 14 (11.3), 9 (9.4), 15 (7.1)                                  |
| 175 | 2198.5   | 2105.0          | 12.94          | ν_a(CD₂): 10 (9.9), 12 (9.9), 13 (8.4)                                              |
| 176 | 2201.7   | 2108.1          | 34.46          | ν_a(CD₂): 4 (21.4), 3 (15.1)                                                        |
| 177 | 2202.0   | 2108.5          | 3.61           | ν_a(CD₂): 9 (15.0), 13 (12.3), 14 (6.0), 15 (5.7)                                  |
| 178 | 2202.8   | 2109.2          | 17.16          | ν_a(CD₂): 16 (17.3), 17 (10.3), 14 (8.5)                                            |
| 179 | 2204.3   | 2110.7          | 48.32          | ν_a(CD₂): 13 (11.0), 11 (10.9), 9 (10.4), 15 (8.8)                                 |
| 180 | 2206.0   | 2112.3          | 41.82          | ν_a(CD₂): 15 (17.6), 14 (11.0), 13 (6.5), 16 (8.0), 12 (5.0)                        |
| 181 | 2209.5   | 2115.6          | 14.56          | ν_a(CD₂): 17 (27.2), 16 (15.3)                                                      |
| 182 | 2211.6   | 2117.6          | 16.99          | ν_a(CD₂): 7 (32.5), 9 (7.2), 5 (5.4)                                                |
| 183 | 2221.7   | 2127.2          | 12.57          | ν_a(CD₂): 5 (26.1), 2 (14.7)                                                       |
| 184 | 2223.7   | 2129.2          | 5.27           | ν_a(CD₂): 2 (26.7), 5 (15.3)                                                        |
| 185 | 2242.2   | 2146.9          | 17.31          | ν_a(CD₂): 1 (42.7), 2 (6.3)                                                        |
| 186 | 2249.6   | 2154.0          | 4.25           | ν_a(CD₂): 8 (9.6), 9 (8.1), 10 (8.7), 11 (6.1)                                     |
| 187 | 2250.8   | 2155.1          | 4.47           | ν_a(CD₂): 6 (10.5), 11 (6.6), 12 (6.9), 7 (5.2), 10 (5.2), 8 (5.1)                |
| 188 | 2252.5   | 2156.8          | 2.67           | ν_a(CD₂): 6 (10.3), 8 (6.8), 12 (7.3)                                               |
| 189 | 2256.6   | 2160.6          | 0.41           | ν_a(CD₂): 10 (8.1), 13 (7.8), 8 (7.1), 12 (6.6), 14 (6.0)                          |
| 190 | 2261.8   | 2165.7          | 4.54           | ν_a(CD₂): 14 (10.1), 15 (8.7), 16 (5.8)                                             |
| 191 | 2264.2   | 2168.0          | 6.46           | ν_a(CD₂): 4 (13.6), 3 (6.6)                                                        |
| 192 | 2264.6   | 2168.4          | 2.98           | ν_a(CD₂): 16 (7.9), 15 (6.0), 4 (5.5)                                               |
| 193 | 2272.4   | 2175.8          | 1.58           | ν_a(CD₂): 17 (7.6), 11 (7.7), 9 (7.6), 14 (5.1)                                    |
| 194 | 2274.0   | 2177.4          | 4.73           | ν_a(CD₂): 17 (13.6), 15 (6.3), 9 (5.0)                                              |
| 195 | 2275.1   | 2178.4          | 15.73          | ν_a(CD₂): 3 (18.6), 4 (8.4)                                                        |
| 196 | 2280.2   | 2183.3          | 2.80           | ν_a(CD₂): 10 (9.8), 9 (9.7), 7 (7.7), 11 (7.4), 13 (6.8), 14 (5.9)                |
| 197 | 2284.7   | 2187.6          | 30.93          | ν_a(CD₂): 16 (18.7), 15 (16.2), 17 (8.8)                                            |
| 198 | 2285.2   | 2188.1          | 22.13          | ν_a(CD₂): 13 (12.4), 7 (9.4), 12 (8.8), 14 (8.2), 11 (6.1)                         |
| 199 | 2286.6   | 2189.5          | 83.34          | ν_a(CD₂): 7 (13.4), 9 (7.9), 8 (7.7), 10 (5.5), 13 (5.5), 11 (5.3)                |
| 200 | 2298.1   | 2200.4          | 25.53          | ν_a(CD₂): 5 (26.7), 4 (8.5), 6 (7.1)                                               |
| 201 | 2305.4   | 2207.4          | 1.64           | ν_a(CD₂): 2 (28.4), 3 (6.5), 1 (6.3)                                               |
| 202 | 2306.5   | 2208.5          | 19.56          | ν_a(CD₂): 18 (50.0); ν_a(CD₂): 17 (9.1)                                             |
| 203 | 2313.4   | 2215.1          | 18.75          | ν_a(CD₃): 18 (48.5); ν_a(CD₂): 17 (7.1)                                             |
| 204 | 2327.0   | 2228.1          | 3.62           | ν_a(CD₂): 1 (49.0), 2 (7.9)                                                        |
| No. | $\tilde{v}$ / cm$^{-1}$ | $\tilde{v}_{\text{scaled}}$ / cm$^{-1}$ | $I_{\text{IR}}$ / km mol$^{-1}$ | Stretching vibration: participating group position in the alkyl chain (relative weight in %) |
|-----|------------------------|-------------------------|------------------|-------------------------------------------------|
| 168 | 2188.0 | 2095.0 | 14.48 | $v_6$(CD$_3$): 18 (62.3); $v_8$(CD$_2$): 17 (5.9) |
| 169 | 2189.0 | 2096.0 | 2.01 | $v_6$(CD$_2$): 6 (23.8), 8 (16.2) |
| 170 | 2191.8 | 2098.7 | 4.64 | $v_6$(CD$_2$): 10 (14.5), 8 (11.2), 6 (9.9), 12 (7.0) |
| 171 | 2193.5 | 2100.2 | 4.41 | $v_6$(CD$_2$): 12 (14.2), 8 (8.1), 14 (6.6), 11 (6.3), 6 (5.0) |
| 172 | 2195.4 | 2102.1 | 1.03 | $v_6$(CD$_2$): 14 (8.4), 8 (7.6), 11 (7.5), 10 (6.9), 13 (6.9) |
| 173 | 2196.9 | 2103.5 | 21.14 | $v_6$(CD$_2$): 4 (15.3), 3 (14.0) |
| 174 | 2197.3 | 2103.9 | 1.38 | $v_6$(CD$_2$): 11 (14.7), 9 (10.5), 14 (10.3), 15 (5.9) |
| 175 | 2198.1 | 2104.6 | 29.33 | $v_6$(CD$_2$): 10 (8.9), 12 (8.7), 13 (6.3) |
| 176 | 2200.9 | 2107.3 | 3.85 | $v_6$(CD$_2$): 9 (15.9), 13 (11.7), 14 (5.9), 10 (5.2) |
| 177 | 2202.2 | 2108.6 | 33.35 | $v_6$(CD$_2$): 16 (16.7), 17 (9.7), 14 (8.0) |
| 178 | 2203.2 | 2109.5 | 46.07 | $v_6$(CD$_2$): 13 (12.6), 11 (9.8), 9 (7.2), 15 (7.0) |
| 179 | 2203.8 | 2110.1 | 38.95 | $v_6$(CD$_2$): 3 (21.8), 4 (18.9) |
| 180 | 2205.4 | 2111.6 | 43.04 | $v_6$(CD$_2$): 15 (20.8), 14 (11.9), 16 (8.5) |
| 181 | 2208.3 | 2114.5 | 26.71 | $v_6$(CD$_2$): 7 (20.1), 9 (8.1) |
| 182 | 2209.0 | 2115.1 | 16.86 | $v_6$(CD$_2$): 17 (26.0), 16 (14.9) |
| 183 | 2223.4 | 2128.9 | 12.67 | $v_6$(CD$_2$): 5 (28.3), 2 (15.5) |
| 184 | 2225.6 | 2131.0 | 6.81 | $v_6$(CD$_2$): 2 (28.0), 5 (15.6) |
| 185 | 2246.5 | 2151.1 | 17.08 | $v_6$(CD$_2$): 1 (42.5), 2 (5.5) |
| 186 | 2249.3 | 2153.7 | 3.17 | $v_{as}$(CD$_2$): 10 (9.3), 9 (9.1), 8 (8.4), 11 (7.1) |
| 187 | 2250.9 | 2155.2 | 3.66 | $v_{as}$(CD$_2$): 6 (8.0), 8 (7.2), 7 (5.4), 12 (6.7), 11 (6.3) |
| 188 | 2253.1 | 2157.3 | 4.96 | $v_{as}$(CD$_2$): 6 (11.4), 12 (6.5) |
| 189 | 2256.7 | 2160.8 | 0.42 | $v_{as}$(CD$_2$): 13 (7.3), 10 (7.4), 8 (7.3), 14 (6.2), 12 (5.3) |
| 190 | 2261.4 | 2165.3 | 5.75 | $v_{as}$(CD$_2$): 14 (9.6), 15 (8.5), 16 (6.0) |
| 191 | 2264.2 | 2168.0 | 0.45 | $v_{as}$(CD$_2$): 16 (8.7), 15 (6.6) |
| 192 | 2265.0 | 2168.8 | 9.45 | $v_{as}$(CD$_2$): 4 (15.8), 3 (7.6) |
| 193 | 2271.8 | 2175.2 | 1.37 | $v_{as}$(CD$_2$): 9 (8.0), 11 (7.8), 17 (6.7), 12 (5.3), 14 (5.2) |
| 194 | 2273.6 | 2176.9 | 7.10 | $v_{as}$(CD$_2$): 17 (15.2), 15 (6.9) |
| 195 | 2275.8 | 2179.1 | 16.35 | $v_{as}$(CD$_2$): 3 (19.3), 4 (8.2), 2 (5.3) |
| 196 | 2279.1 | 2182.3 | 3.67 | $v_{as}$(CD$_2$): 10 (9.6), 9 (8.8), 7 (8.0), 11 (7.6), 13 (6.2), 14 (5.6) |
| 197 | 2283.8 | 2186.8 | 3.85 | $v_{as}$(CD$_2$): 7 (11.5), 13 (10.8), 12 (7.0), 14 (6.5), 8 (6.0) |
| 198 | 2284.0 | 2186.9 | 42.61 | $v_{as}$(CD$_2$): 16 (21.5), 15 (19.3), 17 (10.1) |
| 199 | 2285.0 | 2187.9 | 128.02 | $v_{as}$(CD$_2$): 7 (9.9), 13 (8.3), 9 (7.3), 12 (6.6), 8 (6.5), 11 (6.5), 10 (5.8) |
| 200 | 2297.6 | 2200.0 | 33.86 | $v_{as}$(CD$_2$): 5 (27.2), 4 (8.9), 6 (7.1) |
| 201 | 2305.1 | 2207.1 | 2.91 | $v_{as}$(CD$_2$): 2 (19.0), 3 (7.2), 5 (6.1), 1 (5.0) |
| 202 | 2305.5 | 2207.5 | 23.23 | $v_{as}$(CD$_2$): 18 (49.9); $v_{as}$(CD$_2$): 9 (2.2) |
| 203 | 2312.3 | 2214.0 | 21.96 | $v_{as}$(CD$_2$): 18 (48.5); $v_{as}$(CD$_2$): 7 (6.0) |
| 204 | 2331.8 | 2232.7 | 4.44 | $v_{as}$(CD$_2$): 1 (39.9), 2 (6.3) |
Table S6. Harmonic CD stretching vibrations of the [C18C1lm-d2][ClO4] complex in water.

| No. | $\tilde{\nu}$ / cm$^{-1}$ | $\tilde{\nu}_{\text{scaled}}$ / cm$^{-1}$ | $I_{\text{IR}}$ / km mol$^{-1}$ | Stretching vibration: participating group position in the alkyl chain (relative weight in %) |
|-----|------------------|------------------|------------------|------------------------------------------------------------------------------------------------|
| 168 | 2186.2           | 2093.3           | 22.05            | $\nu_S$(CD$_2$): 18 (62.3); $\nu_S$(CD$_3$): 17 (6.7) |
| 169 | 2192.3           | 2099.1           | 0.30             | $\nu_S$(CD$_2$): 8 (10.2), 6 (10.0), 9 (10.0), 11 (9.2), 12 (6.1) |
| 170 | 2192.6           | 2099.4           | 0.17             | $\nu_S$(CD$_2$): 10 (15.4), 12 (12.9), 8 (9.6), 9 (5.4) |
| 171 | 2193.8           | 2100.6           | 6.70             | $\nu_S$(CD$_2$): 6 (11.6), 11 (9.2), 14 (7.4), 10 (5.0) |
| 172 | 2195.0           | 2101.7           | 0.74             | $\nu_S$(CD$_2$): 9 (11.0), 12 (10.0), 11 (7.8), 7 (7.3), 14 (6.5), 8 (6.4) |
| 173 | 2195.8           | 2102.4           | 2.01             | $\nu_S$(CD$_2$): 14 (9.3), 6 (6.9), 8 (6.8), 13 (5.9), 15 (5.7), 12 (5.1) |
| 174 | 2197.3           | 2103.9           | 1.48             | $\nu_S$(CD$_2$): 11 (11.2), 9 (8.0), 7 (7.5), 6 (6.6), 14 (6.2), 10 (5.9) |
| 175 | 2198.0           | 2104.6           | 36.00            | $\nu_S$(CD$_2$): 10 (11.0), 12 (7.7), 8 (6.8), 7 (5.5) |
| 176 | 2199.1           | 2105.6           | 100.04           | $\nu_S$(CD$_2$): 7 (14.8), 9 (10.6), 8 (9.1) |
| 177 | 2200.0           | 2106.5           | 121.21           | $\nu_S$(CD$_2$): 13 (13.9), 16 (10.5), 14 (7.3), 11 (6.4), 12 (5.8), 17 (5.0) |
| 178 | 2201.1           | 2107.6           | 35.53            | $\nu_S$(CD$_2$): 4 (15.1), 3 (8.6), 16 (6.1) |
| 179 | 2201.4           | 2107.8           | 12.46            | $\nu_S$(CD$_2$): 16 (10.5), 13 (9.4), 17 (7.3), 4 (6.0) |
| 180 | 2204.5           | 2110.8           | 47.56            | $\nu_S$(CD$_2$): 15 (25.1), 14 (12.6), 16 (7.1) |
| 181 | 2207.6           | 2113.8           | 26.40            | $\nu_S$(CD$_2$): 3 (17.8), 4 (14.7) |
| 182 | 2208.1           | 2114.3           | 23.72            | $\nu_S$(CD$_2$): 17 (24.1), 16 (13.5) |
| 183 | 2208.3           | 2114.4           | 39.15            | $\nu_S$(CD$_2$): 5 (33.3) |
| 184 | 2226.4           | 2132.2           | 10.42            | $\nu_S$(CD$_2$): 2 (42.4) |
| 185 | 2248.5           | 2152.9           | 0.27             | $\nu_{as}$(CD$_2$): 10 (8.5), 9 (8.3), 11 (7.2), 8 (7.0), 12 (5.0) |
| 186 | 2250.6           | 2154.9           | 0.12             | $\nu_{as}$(CD$_2$): 7 (7.1), 12 (6.8), 8 (6.5), 11 (6.5), 6 (6.0) |
| 187 | 2253.8           | 2158.0           | 3.94             | $\nu_{as}$(CD$_2$): 6 (7.7), 12 (6.3), 9 (5.8), 13 (5.1) |
| 188 | 2254.2           | 2158.4           | 17.80            | $\nu_S$(CD$_2$): 1 (36.2) |
| 189 | 2257.8           | 2161.9           | 0.99             | $\nu_{as}$(CD$_2$): 14 (7.4), 13 (6.3), 6 (6.0), 8 (5.8), 11 (5.0) |
| 190 | 2261.3           | 2165.1           | 10.90            | $\nu_{as}$(CD$_2$): 15 (7.7), 14 (6.6), 16 (6.5) |
| 191 | 2263.4           | 2167.2           | 0.31             | $\nu_{as}$(CD$_2$): 16 (7.4), 15 (5.5) |
| 192 | 2266.4           | 2170.0           | 6.68             | $\nu_{as}$(CD$_2$): 4 (9.7) |
| 193 | 2270.1           | 2173.6           | 1.95             | $\nu_{as}$(CD$_2$): 9 (6.3), 11 (5.4), 4 (5.2), 12 (5.0) |
| 194 | 2272.4           | 2175.8           | 11.33            | $\nu_{as}$(CD$_2$): 17 (18.1), 15 (7.7) |
| 195 | 2274.6           | 2177.9           | 14.40            | $\nu_{as}$(CD$_2$): 3 (11.6), 11 (5.6), 8 (5.0) |
| 196 | 2276.5           | 2179.7           | 4.92             | $\nu_{as}$(CD$_2$): 3 (8.7), 10 (7.0), 11 (6.2), 7 (6.1), 6 (5.2), 4 (5.0) |
| 197 | 2279.3           | 2182.4           | 70.58            | $\nu_{as}$(CD$_2$): 8 (10.6), 9 (10.2), 7 (9.3), 10 (7.6) |
| 198 | 2281.4           | 2184.5           | 175.05           | $\nu_{as}$(CD$_2$): 13 (14.1), 14 (10.3), 12 (9.7), 15 (7.8), 11 (6.6), 16 (5.5) |
| 199 | 2282.2           | 2185.2           | 61.81            | $\nu_{as}$(CD$_2$): 16 (16.2), 15 (13.2), 13 (8.7), 17 (7.4), 12 (5.7) |
| 200 | 2286.5           | 2189.3           | 101.49           | $\nu_{as}$(CD$_2$): 5 (23.9), 4 (15.1), 6 (10.5), 3 (5.8) |
| 201 | 2302.5           | 2204.7           | 14.94            | $\nu_{as}$(CD$_2$): 2 (32.5), 3 (9.3) |
| 202 | 2303.4           | 2205.5           | 33.22            | $\nu_{as}$(CD$_2$): 18 (50.3); $\nu_{as}$(CD$_2$): 17 (9.1) |
| 203 | 2310.6           | 2212.4           | 29.33            | $\nu_{as}$(CD$_2$): 18 (48.9); $\nu_{as}$(CD$_2$): 17 (6.6) |
| 204 | 2341.0           | 2241.5           | 5.96             | $\nu_{as}$(CD$_2$): 1 (41.5) |
S6. XP Spectra of the [C18C1Im-h43][Cl] SAIL on the Au Surface

Survey and a high-resolution Cl 2p XP spectra of the [C18C1Im-h43][X] SAIL monolayer on a polycrystalline gold surface were recorded using an ESCALAB 250 Xi spectrometer (Thermo Fisher Scientific, East Grinstead, UK). The XPS instrument was operated using monochromatic Al Kα X-ray radiation source ($h\nu = 1486.6$ eV, 288 W). The samples were grounded by connecting carbon tape to the surface and the sample holder. Survey spectra were recorded at a pass energy of 100 eV and a dwell time of 50 ms. High-resolution Cl 2p XP spectra were recorded at pass energy of 20 eV and dwell time of 1000 ms. Thus, acquisition time was kept rather low to avoid radiation damage of the sample. The binding energy scale was referenced to the Au 4f7/2 line at 84.0 eV. The spectra were fitted using Avantage v5.982 software (Thermo Fisher Scientific, East Grinstead, UK) by employing Gaussian-Lorentzian functions with a fixed ratio after Shirley-type background subtraction. For the fit of Cl 2p lines the doublet splitting of 1.60 eV was fixed and the full width at half maxima (fwhm) were constrained to be the same.

Figure S6. XP spectra of the [C18C1Im-h43][X] LB film transferred from aqueous 0.1 M NaCl solution onto the Au(poly) surface. a) Survey and b) Cl 2p spectra are shown. Residuals ($R$) are shown below spectrum.

References:

[1] T. Sieling, B. I., ChemElectroChem 2020, 7, 3233-3243.