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When do defectless alkanethiol SAMs in ionic liquids become penetrable? A molecular dynamics study

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Fig. S2. Dihedral angle distributions in hexadecanethiol $SC_{16}H_{33}$ (a) and hexanethiol $SC_{6}H_{13}$ (b) molecules. The distribution of C4-C5-C6-C7, C5-C6-C7-C8, etc. angles in $SC_{16}H_{33}$ are very similar to the distributions presented in Figure 2a and therefore are not shown for clarity.

On the permeability of real alkanethiol SAMs.

The experimentally determined potential range of alkanethiol monolayers impermeability in aqueous media doesn't exceed 1 V. Therefore we can take 1 V as an upper boundary of the voltage across a monolayer. Since the monolayer thickness of the shortest alkanethiols, where a threshold effect for permeability is observed,¹ is ca. 1 nm, we get an estimation of the critical electric field E \sim 1 V·nm⁻¹ (vs. E \sim 3–6 V·nm⁻¹ obtained for defectless monolayers in MD simulations). Experimental value of the critical surface charge density in aqueous electrolytes can de deduced from the data in ref 2, according to which undecanethiol monolayers are highly permeable to ions once the electrode potential is increased above U=+500 mV vs Ag/AgCl. Potential of zero charge for the undecanethiol monolayer is U_{PZC}= -500 mV vs Ag/AgCl.³ Since the monolayer capacitance, C_{SAM} at the critical potential ($U^* = +500 \text{ mV}$) amounts to ~ 4 μ F·cm⁻ ², we obtain the critical surface charge $\sigma = C_{SAM} (U^* - U_{PZC}) \sim 4 \ \mu C \cdot cm^{-2}$ that is 2-3 times less then values for the defectless SC_6H_{13} and $SC_{16}H_{33}$ monolayers (Fig. 3). This discrepancy may be explained by numerous defects (such as pinholes, domain boundaries, vacancy Au islands etc.) in a real monolayer, which significantly reduce the energy barrier for the penetration of ions inside the monolayer and result in a decrease of the critical electric field and surface charge density values.







Figure S4. Snapshots demonstrating the changes in the $SC_{16}H_{33}$ monolayer structure at the permeation of anions (a) and cations (c) as compared with the monolayer at the neutral Au (111) surface (b).

References

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