From Monomers to Self-Assembled Monolayers: The Evolution of Molecular Mobility with Structural Confinements

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Supporting Information.



Figure SI-1. Chemical formulae of monopolar (a) octadecyltrichlorosilane (OTS), (b) dodecyltrimethoxysilane (DTMS), and bipolar (c) 11-bromoundecyltrimethoxysilane (BUDTMS)



Figure SI-2. Temperature modulated - differential scanning calorimetry (TM-DSC) curves of (red) OTS, (black) DTMS, and (blue) BUDTMS monomers. Heat capacity steps corresponding to glass transitions are observed for each monomer. A rate of 0.5 K.min⁻¹, period of 60 s, and amplitude of 1 K were selected for heating.



Figure SI-3. Temperature modulated - differential scanning calorimetry (TM-DSC) curves of (red) o-OTS, (black) o-DTMS, and (blue) o-BUDTMS. Endothermic peaks correspond to melting transitions of the crystalline phases. A heat capacity step corresponding to the glass transition of o-OTS is observed around 245 K. A rate of 0.5 K.min⁻¹, period of 60 s, and amplitude of 1 K were selected for heating.



Figure SI-4. Dielectric loss (ϵ ") of OTS (a) monomers, (b) oligomers, and (c) self-assembled monolayers as a function of frequency and temperature.



Figure SI-5. Dielectric loss (ϵ ") of DTMS (a) monomers, (b) oligomers, and (c) self-assembled monolayers as a function of frequency and temperature.



Figure SI-6. Dielectric loss (ɛ") of BUDTMS (a) monomers, (b) oligomers, and (c) self-assembled monolayers as a function of frequency and temperature.



Figure SI-7. Variation of activation enthalpy and entropy values as a function of temperature and frequency. The color surface corresponds to the variation of the theoretical activation enthalpy ΔH_0 when $\Delta S^* = 0$. Black squares represent the experimental activation enthalpy ΔH^* , and red circles illustrate the contribution of ΔH_0 to ΔH^* . The difference between the experimental activation enthalpy ΔH^* and theoretical ΔH_0 corresponds to $T\Delta S^*$.