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Self-assembled monolayers (SAM) allow simple and easy manipulation of solid surface properties. A SAM consists of a head part, an alkyl chain part, and a functional part. The head part is bound to a solid substrate through a hydrolysis reaction and dehydration-condensation reaction, the alkyl chain part forms a monolayer aligned by the van der Waals interaction of the long chains of SAM, and the functional part has a functional group. Among the three parts of SAM, we investigated the properties of the alkyl chain in this study. (3,3,3-trifluoropropyl)-trimethoxysilane ( $\text{CF}_3(\text{CF}_2)(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ), having the shortest chain length, showed the smallest contact angle. Heptadecafluoro-(1,1,2,2-tetrahydrodecyl)triethoxysilane ( $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$ ), having the longest chain length, showed the largest contact angle. This indicated that SAM with a longer chain length was more hydrophobic. The SAM with the shortest chain length showed a disordered molecular arrangement due to a weak van der Waals interaction. The SAM with the longest chain length showed good molecular arrangement due to a strong van der Waals interaction. However, when the film was formed sufficiently, the contact angle was not greatly dependent on the chain length. The slight difference in the contact angle was considered to be the result of the offset between the carbon and fluorine in the middle of the alkyl chain. The interfacial properties of SAM depending on the alkyl chain length was investigated in detail.