表面増強赤外分光法によるクラウンエーテルの金属イオン包接現象の観測

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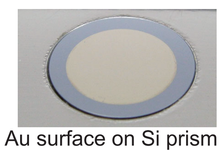
Introduction

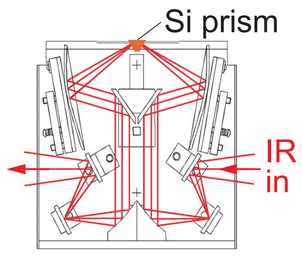
■Crown ethers show ion selectivity in solution.
■Mass spectrometric studies cannot explain ion selectivity, suggesting importance of solvent effect.
■We spectroscopically study metal ion-crown ether complexes on gold surface to discuss dependence of chemical properties such as crown size, chain length, and solvent on ion selectivity.

Experimental

SEIRA (Surface-enhanced IR absorption) spectroscopy with ATR configuration



Au surface on Si prism of ATR (~8 nm thickness)



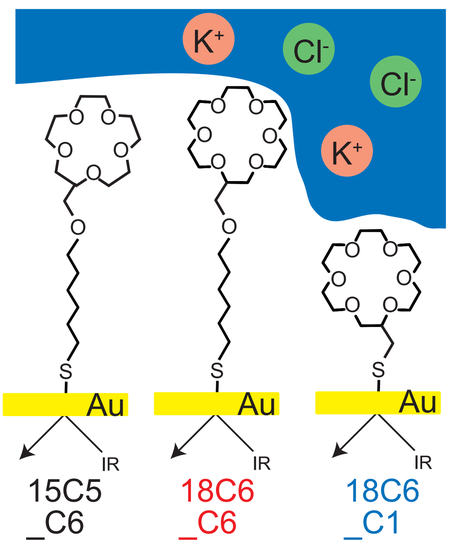
(1) Au surface (~8 nm) is formed on an ATR (attenuated total reflection) element by vacuum deposition.

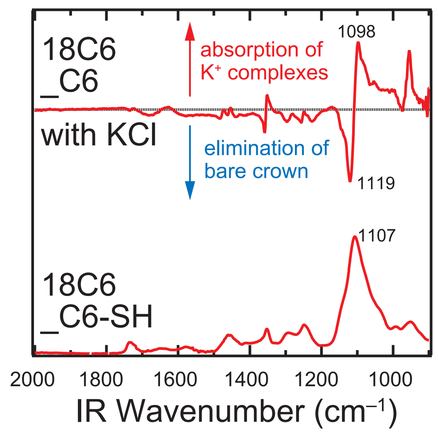
(2) Thiol derivatives of crown ethers are chemisorbed on the Au surface with S–Au bonds.

(3) Aqueous solutions of metal salts are put on it to form complexes.

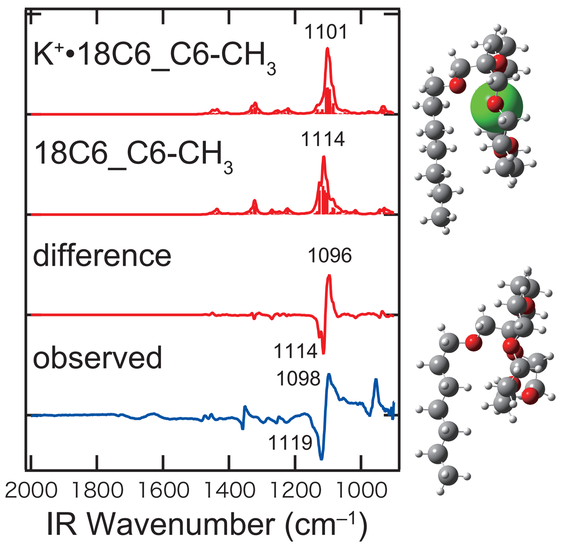
(4) IR spectra are measured with and without the metal salts and we obtain IR difference spectra.

Experimental systems and IR results



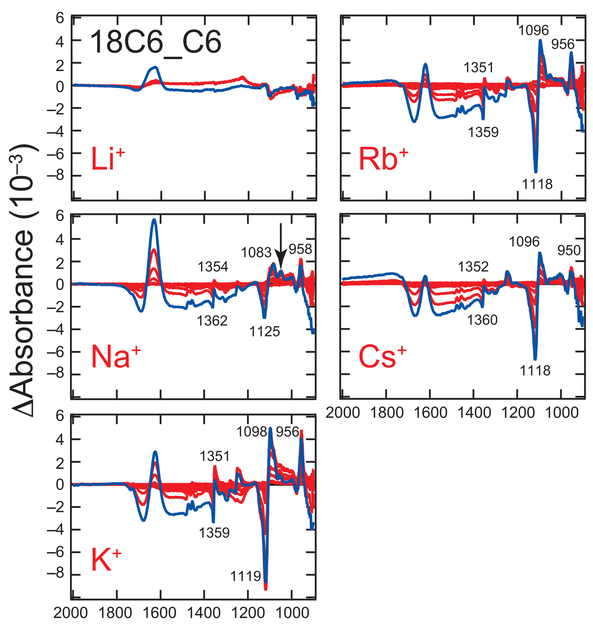


Simulation with DFT calculations

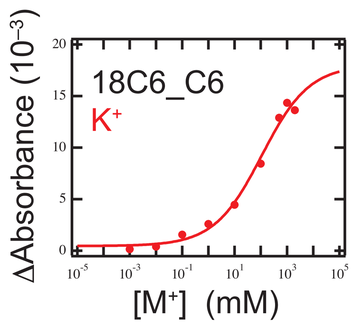


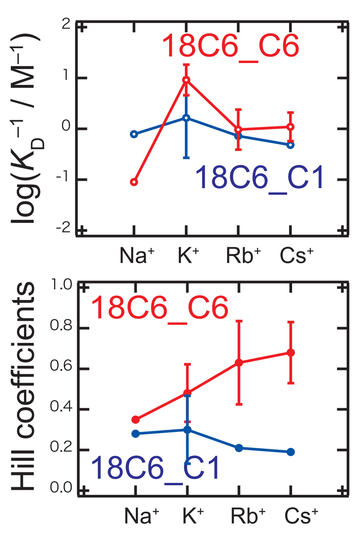
Chain Length Dependence

IR difference spectra



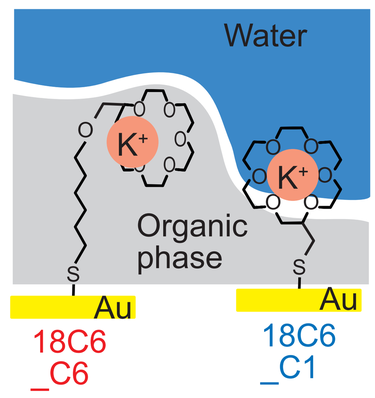
Ion concentration dependence





・Ion selectivity is not so obvious for C1.
・For C1, ion complexes on gold surface inhibit successive complex formation more than C6.

Proposed structure

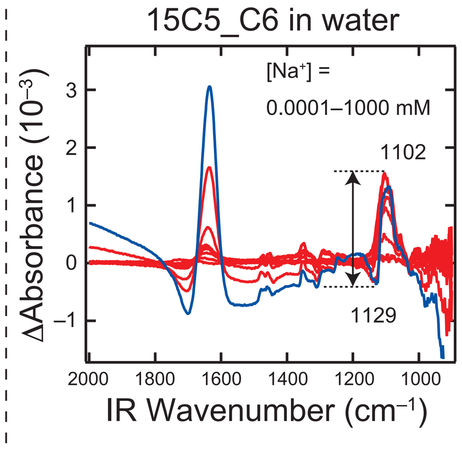


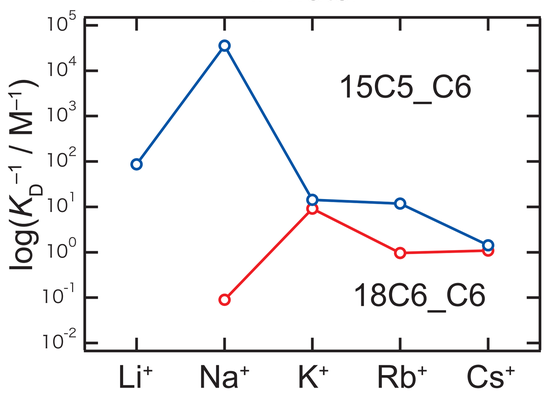
Complexes are isolated from water.

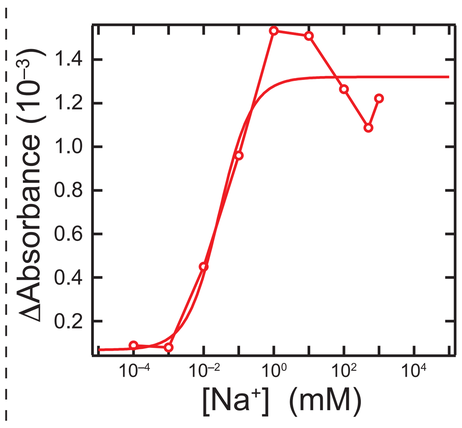
Complexes face to water.

Crown Size Dependence

15C5_C6 in water



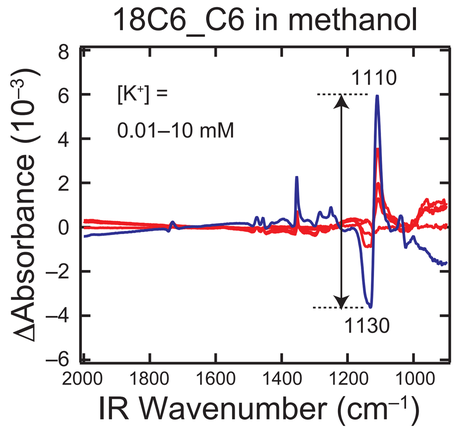


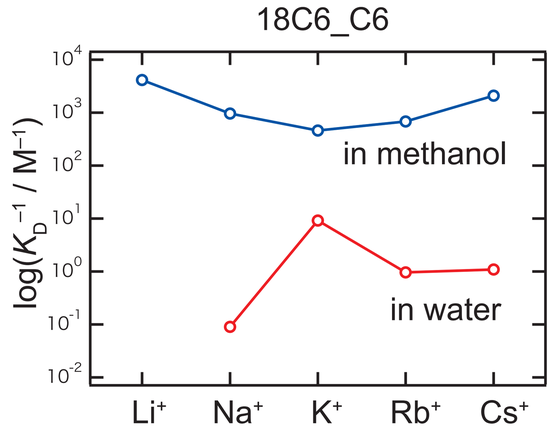


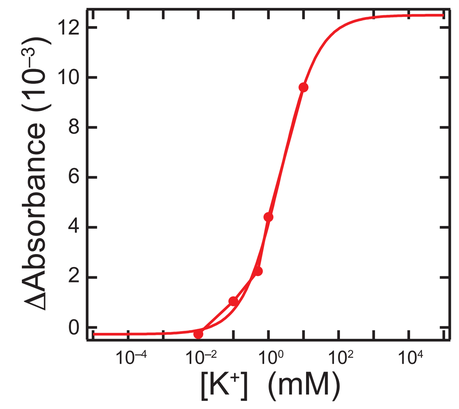
・15C5_C6 shows preference for Na^+, whereas 18C6_C6 shows selectivity for K^+.
・Crown ethers bonded on gold surface have similar properties for ion selectivity with bulk systems.

Solvent Dependence

18C6_C6 in methanol







・18C6_C6 shows selectivity for K^+ in water, but it is not so obvious in methanol.

■We will examine the density dependence of crown ethers on gold surface.
■Now we are synthesizing crown ethers with no S atom in the chain.

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