UV and IR Spectroscopy of Host-Guest Complexes in the Gas Phase and on Gold Surface

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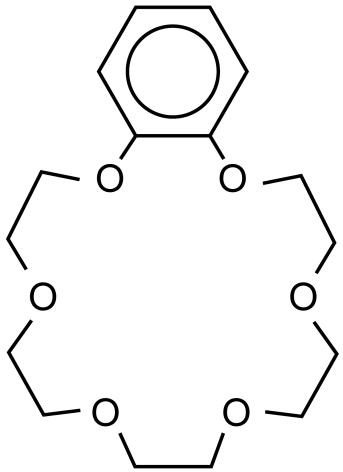
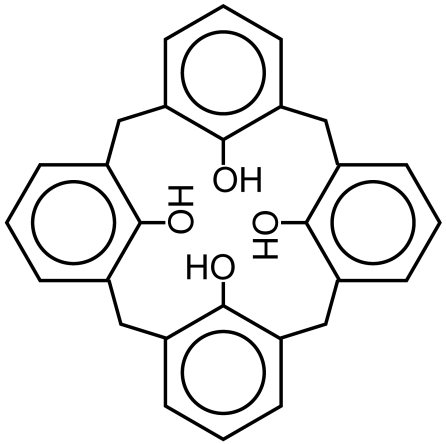
Host Molecules

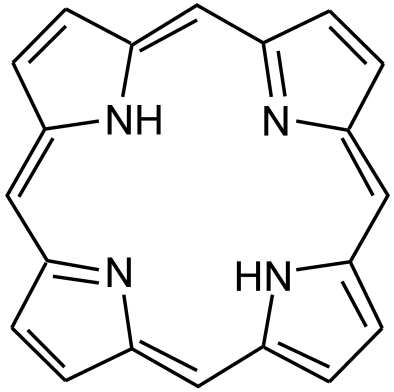
hold other ions and molecules inside



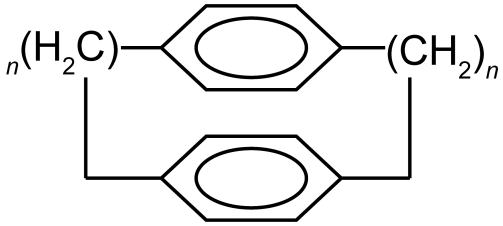
Crown ether



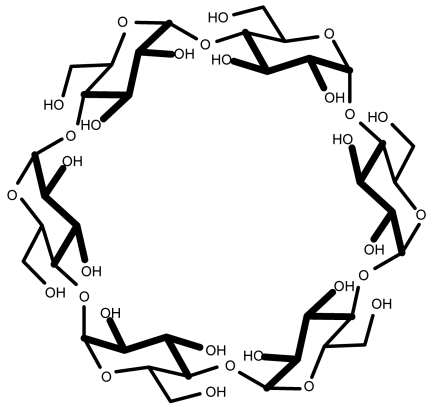
Calix[4]arene



Porphyrin



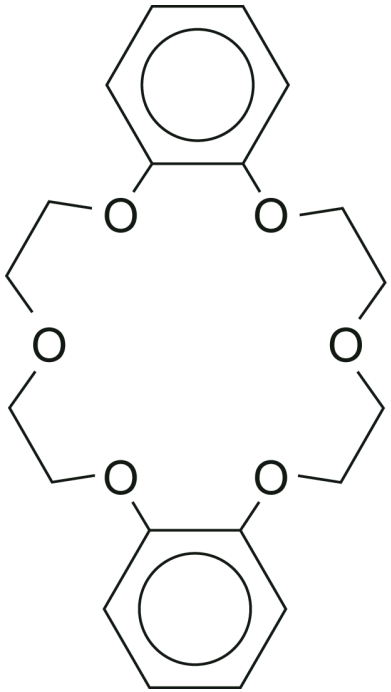
Cyclophane



Cyclodextrin

Crown Ethers (CEs)

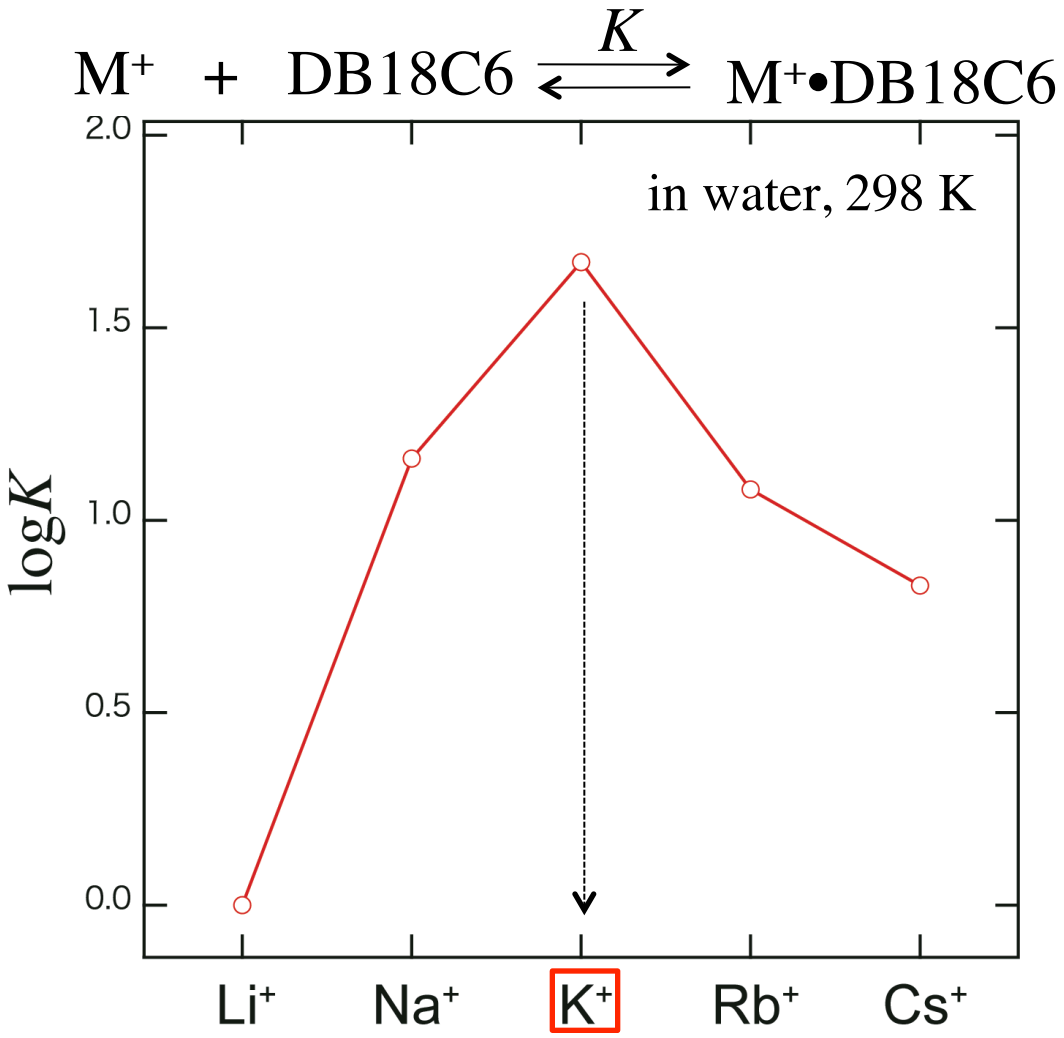
Crown ethers (CEs) show ion selectivity.

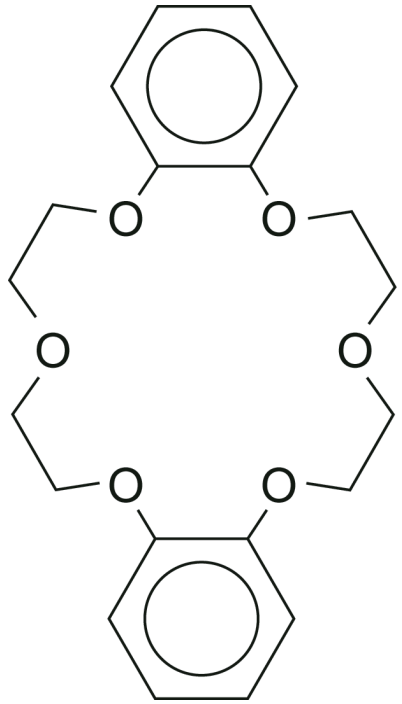


Dibenzo-18-crown-6
(DB18C6)

Ion Selectivity of CE

DB18C6 captures K^+ selectively in water.



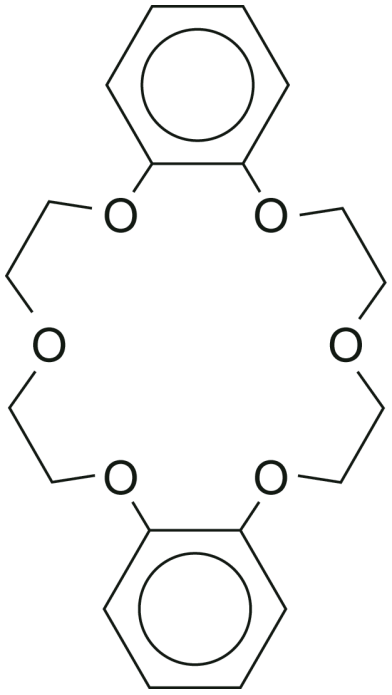


DB18C6

Izatt et al., *Chem. Rev.*, **1985**, *85*, 271.

Our Final Goal

Our final goal is
to reveal the origin of ion selectivity
in terms of quantum chemistry.



Dibenzo-18-crown-6
(DB18C6)

Our Studies

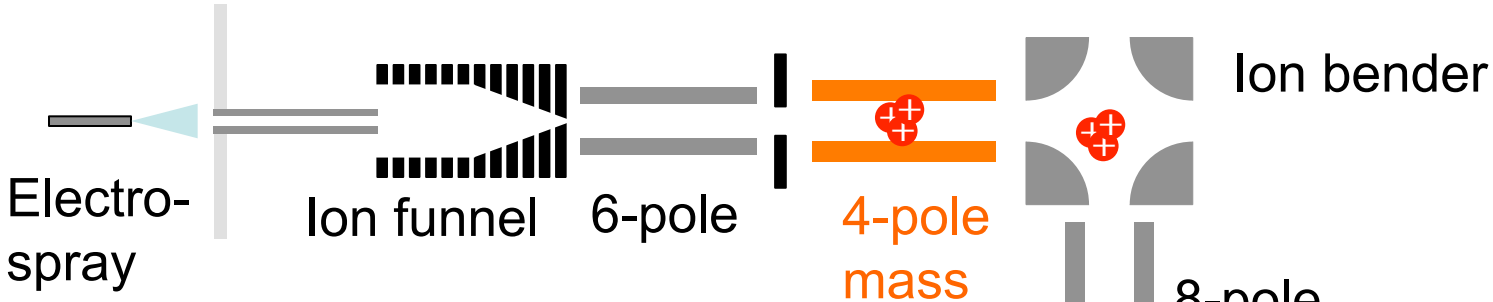

Host-Guest Complexes
IR Spectroscopy on Gold Surface
“Cold” Spectroscopy in the Gas Phase

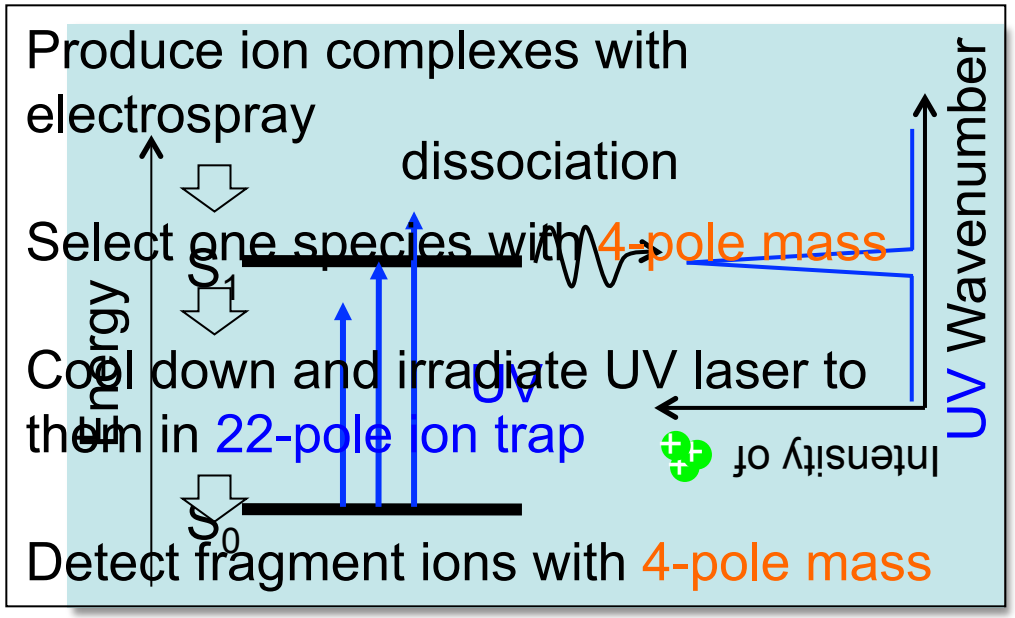
“Cold” Spectroscopy in the Gas Phase

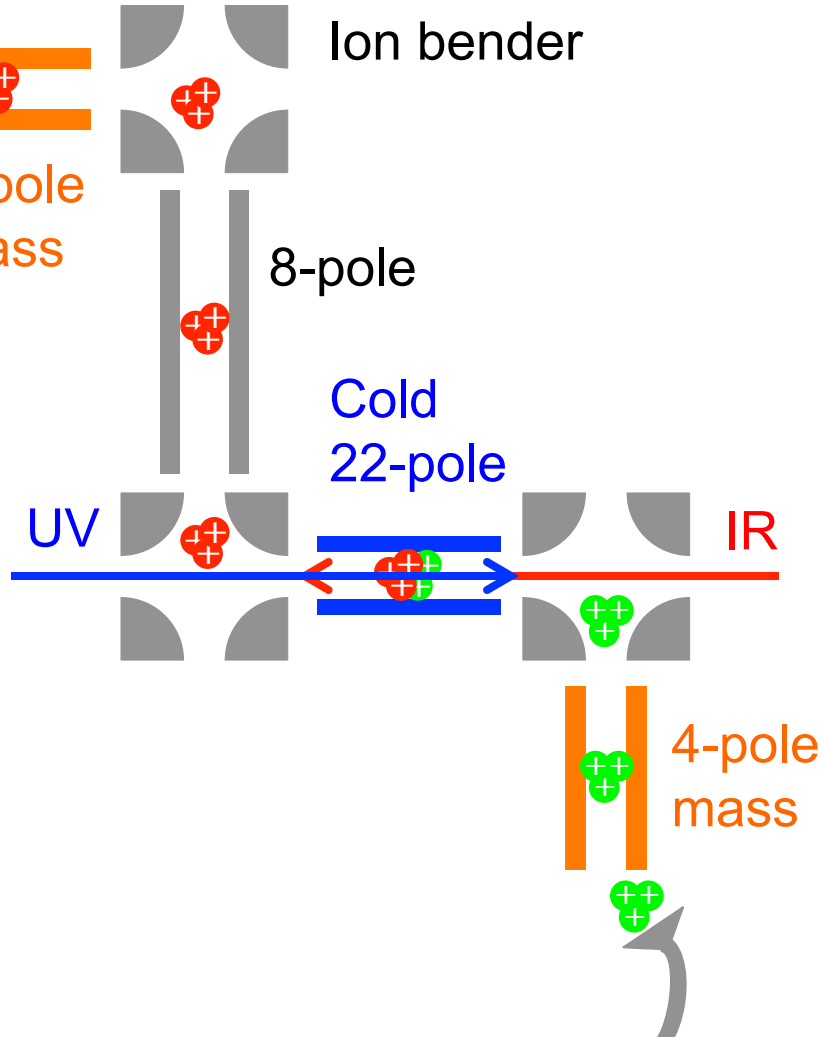
Inokuchi et al., J. Am. Chem. Soc., **2011**, *133*, 12256.
J. Am. Chem. Soc., **2014**, *136*, 1815.
J. Phys. Chem. A, **2015**, *119*, 8512.

Experimental

UV and IR spectra of ions are measured under cold (~10 K) conditions in the gas phase.

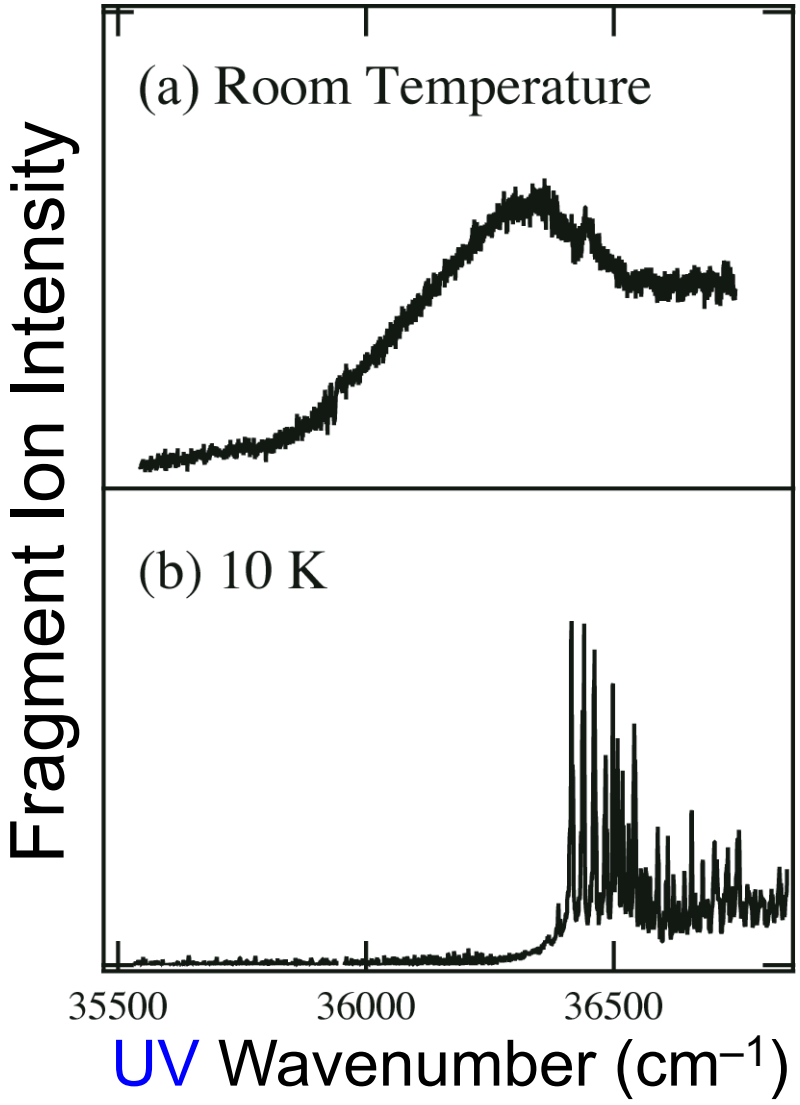


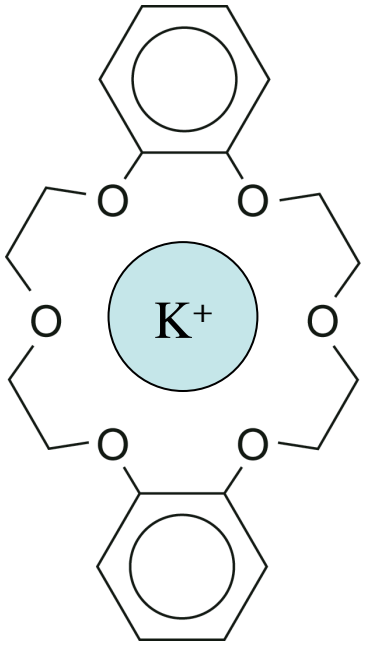




Effect of the Cooling on UV Spectra

Sharp UV bands are observed thanks to the cooling.



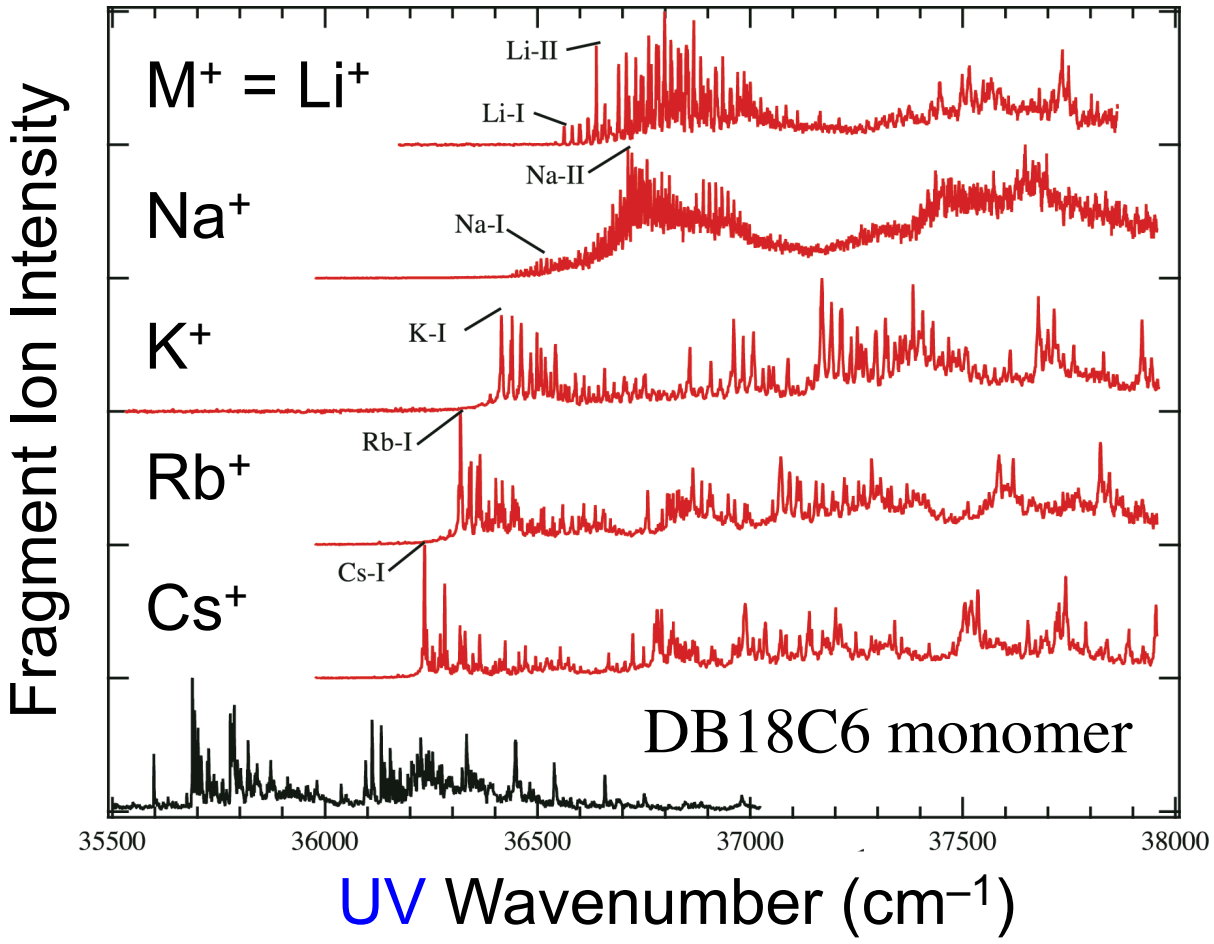


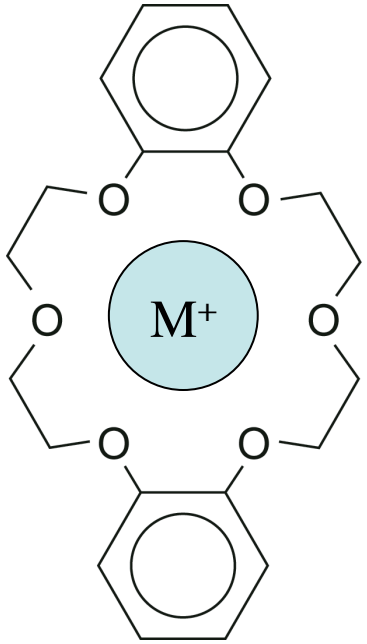
K^+•DB18C6

Inokuchi et al., *JACS*, **2011**, *133*, 12256.

UV Spectra of M^+•DB18C6

All the complexes show sharp UV bands.
Conformer-specific IR spectra can be measured.





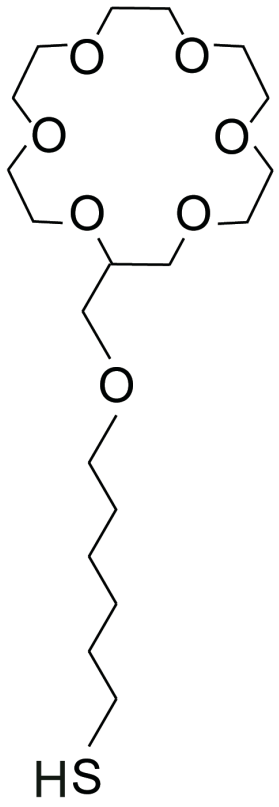
M^+•DB18C6

Inokuchi et al., *JACS*, **2011**, *133*, 12256.

SEIRA Spectroscopy on Gold Surface

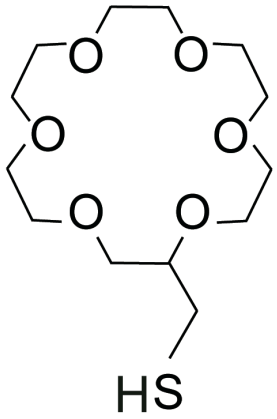
Inokuchi et al., Chem. Phys. Lett., **2014**, *592*, 90.
New J. Chem., **2015**, in press.

Crown Ethers Chemisorbed on Au Surface



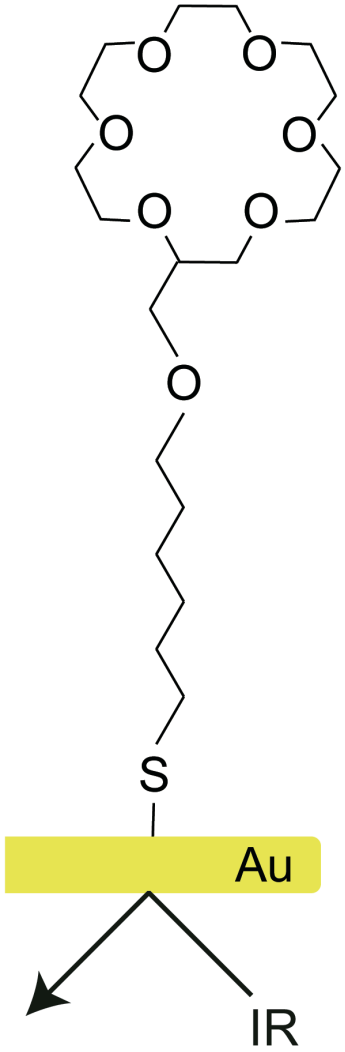
1

(a) 18C6-C_1OC_6-SH

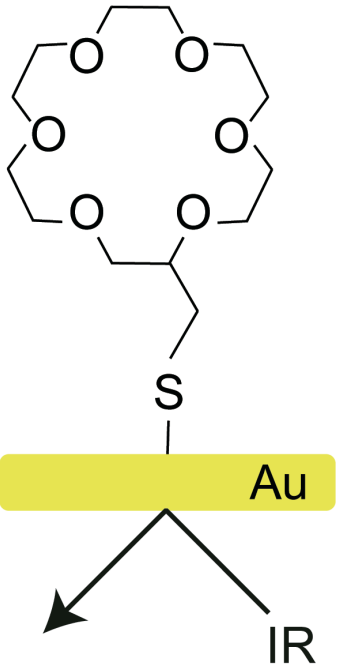


2

(b) 18C6-C_1-SH



(c) 18C6-C_1OC_6

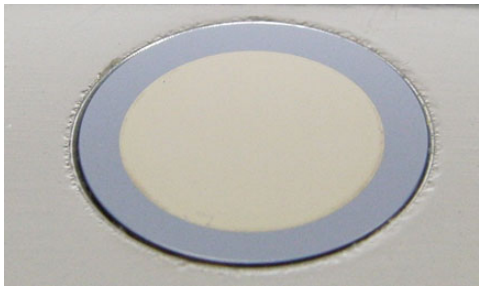


(d) 18C6-C_1

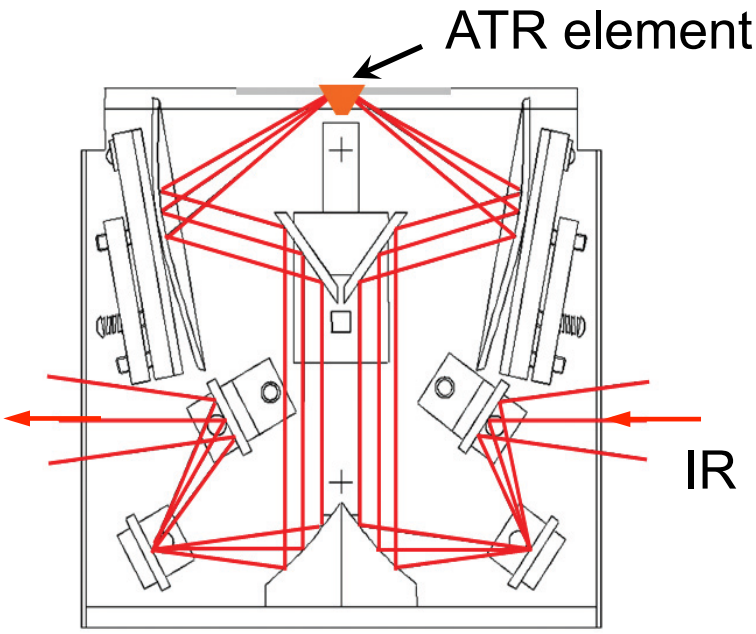
SEIRA with ATR Configuration

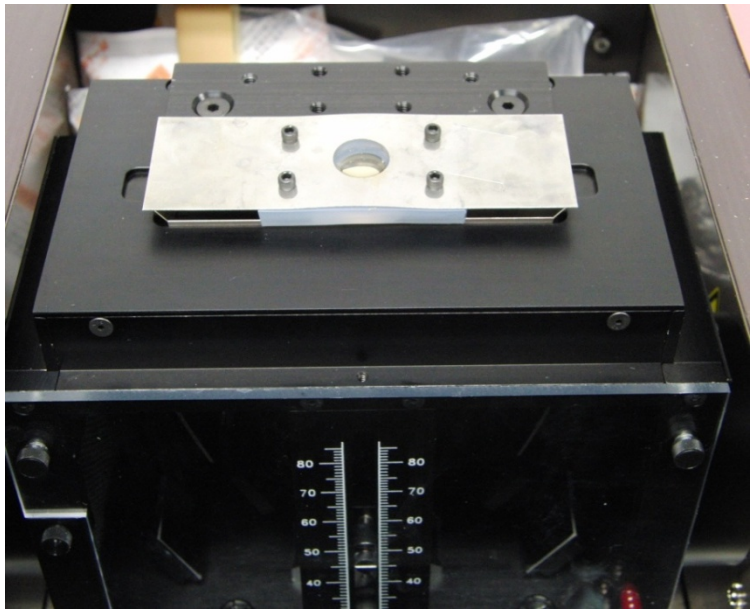
SEIRA (Surface-Enhanced IR Absorption) spectroscopy

(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) Solutions of metal salts are put on it to form complexes.



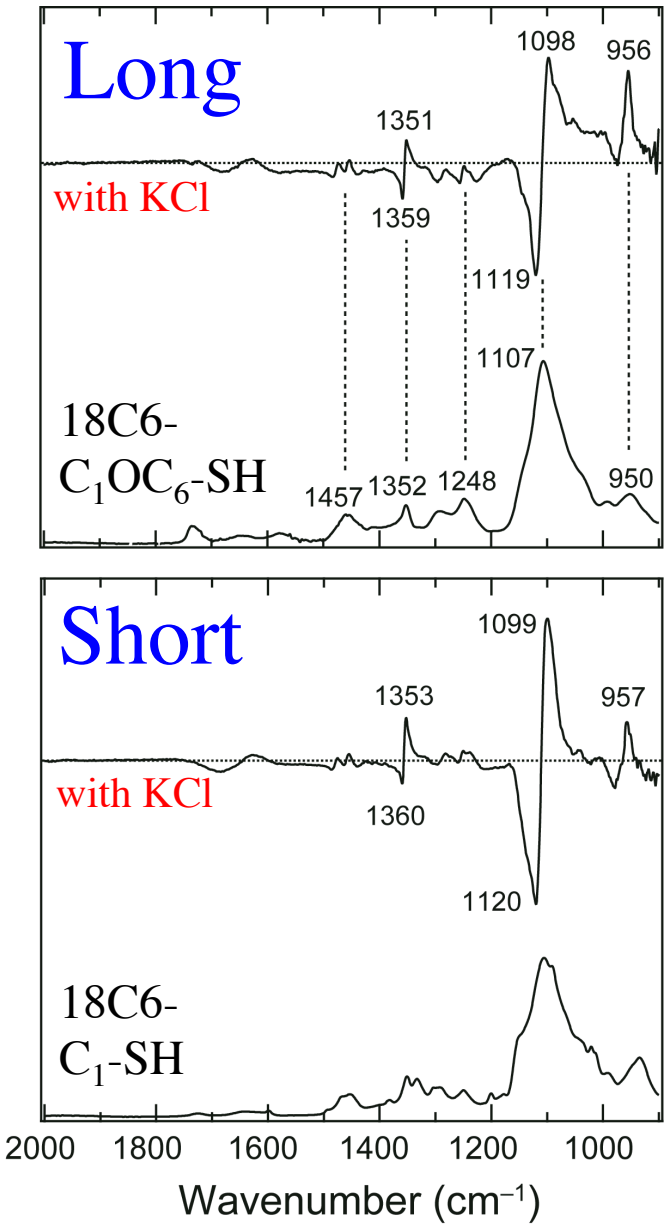
Au surface on Si prism of ATR
~ 8 nm thickness

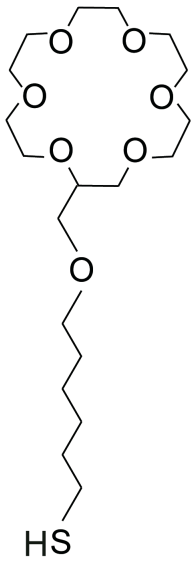




Attenuated total reflection setup

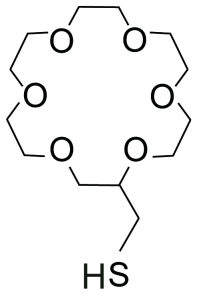
IR Spectra of K^+•18C6 on Au





1

(a) 18C6-C_1OC_6-SH



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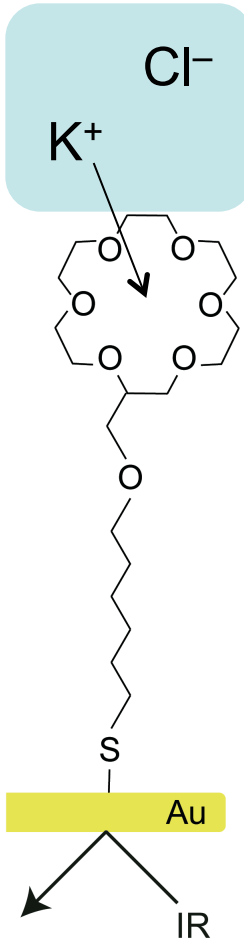
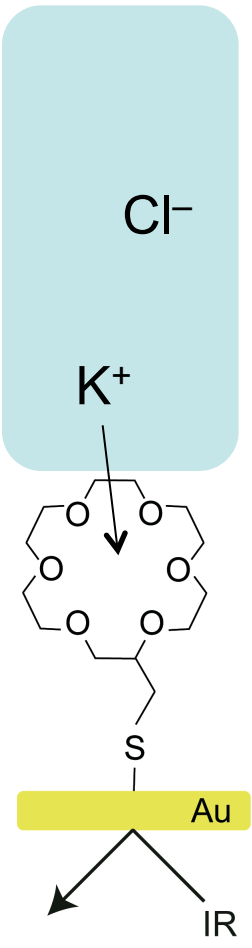
(b) 18C6-C_1-SH



(c) 18C6-C_1OC_6

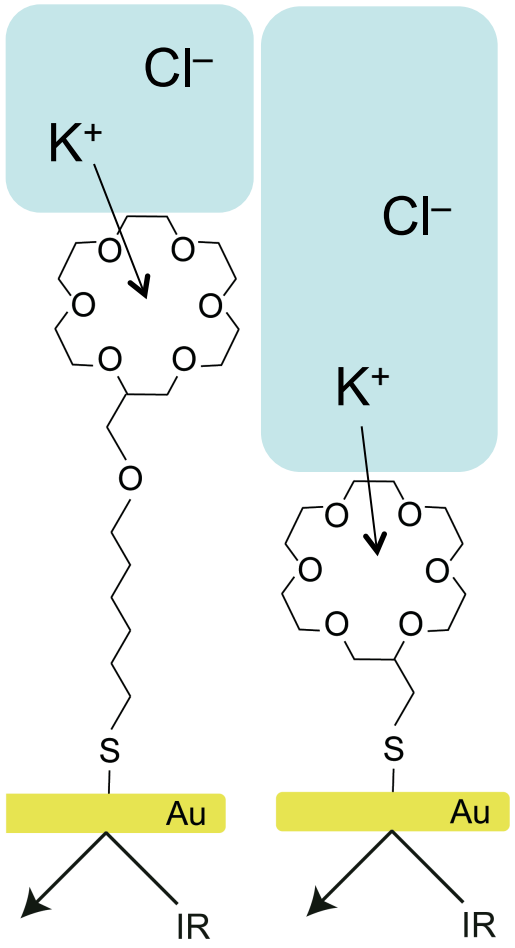


(d) 18C6-C_1

Long Short

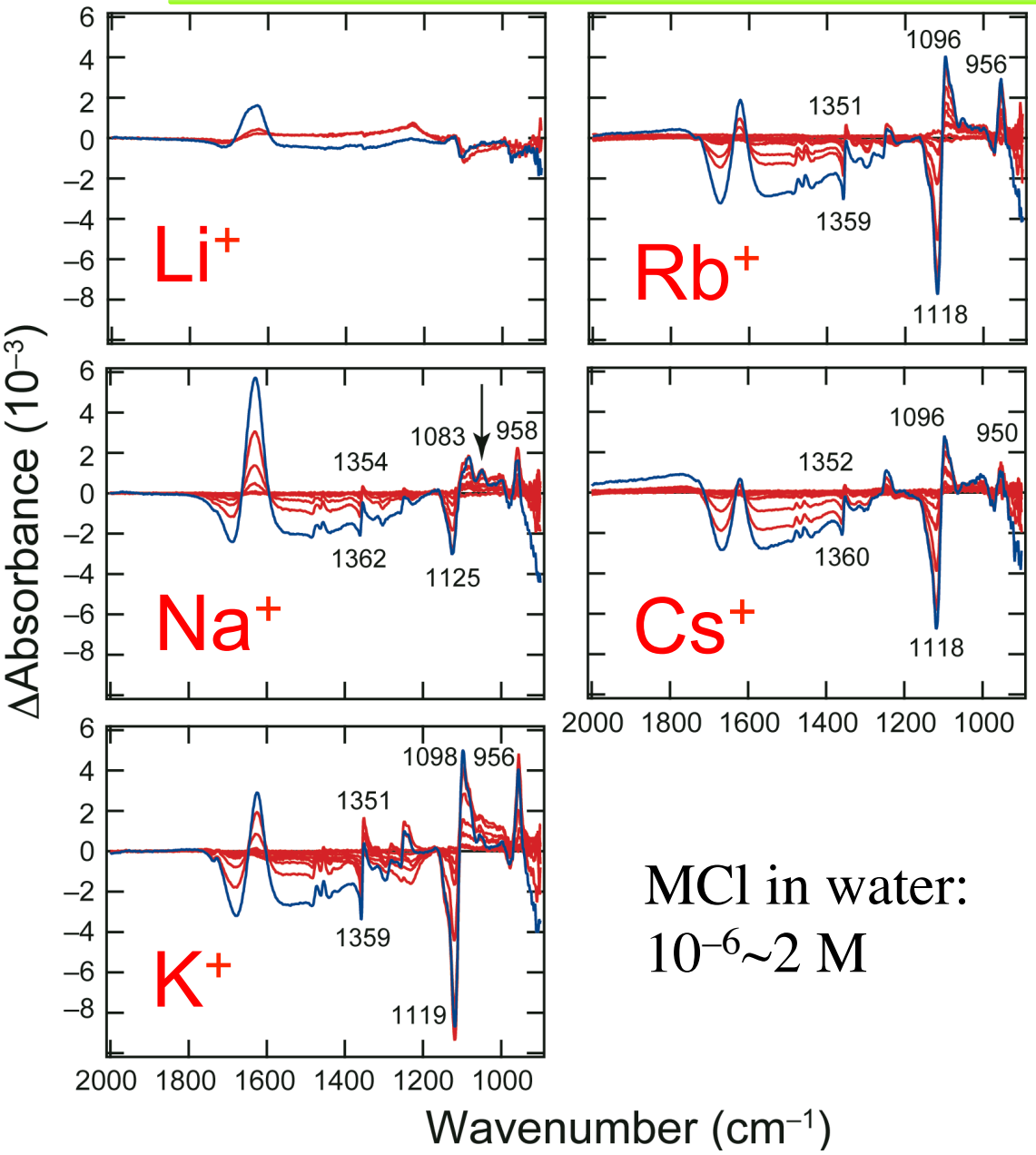
Advantages and Disadvantages

- High sensitivity and selectivity due to Au surface
- Quantitative
- Reusable (washable)
- Condensed phase, interface
- Applications ion filters, sensing devices

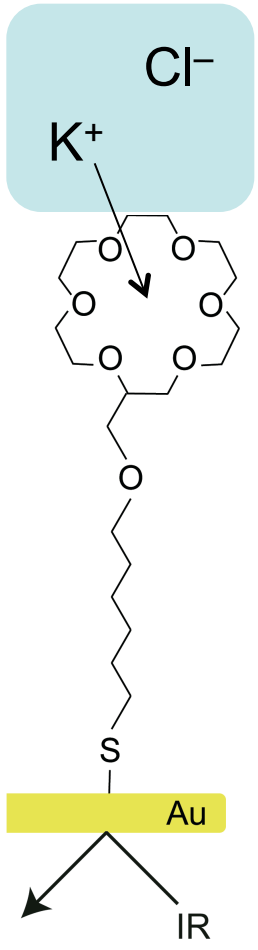


- Necessary to synthesize thiol derivatives
- Effects of Au surface on encapsulation

IR Difference Spectra of M^+•18C6-C_1OC_6

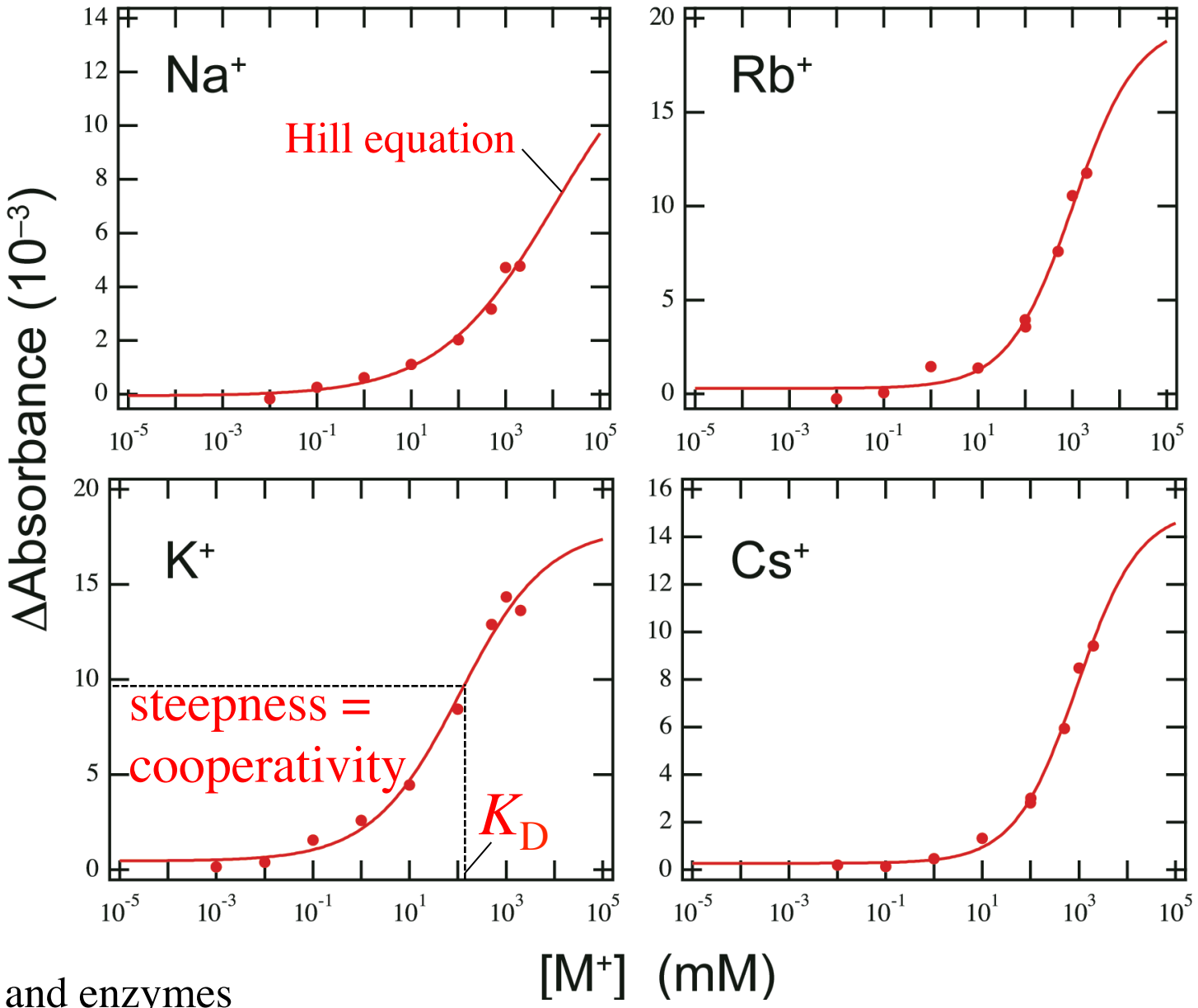


MCl in water:
10^{-6}~2 M



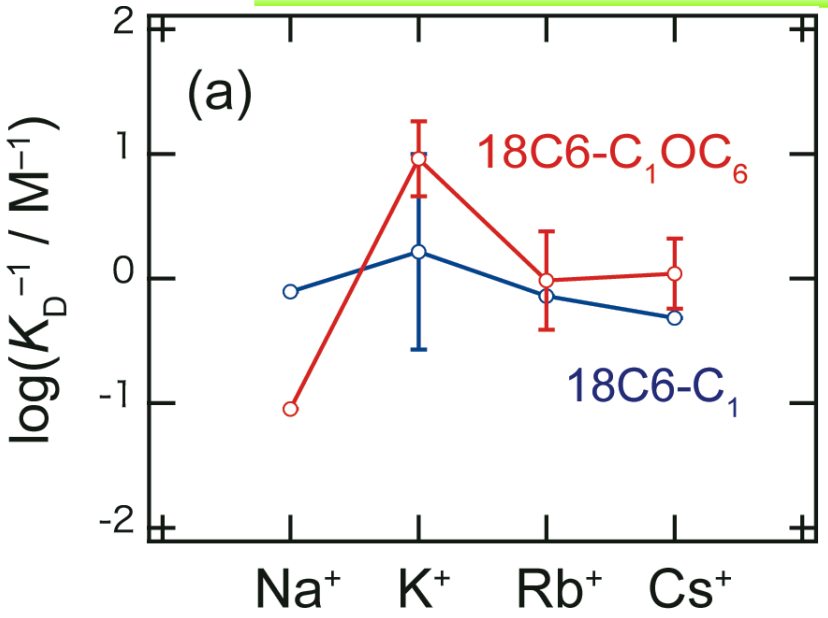
18C6-C_1OC_6

Titration Curves for M^+•18C6-C_1OC_6

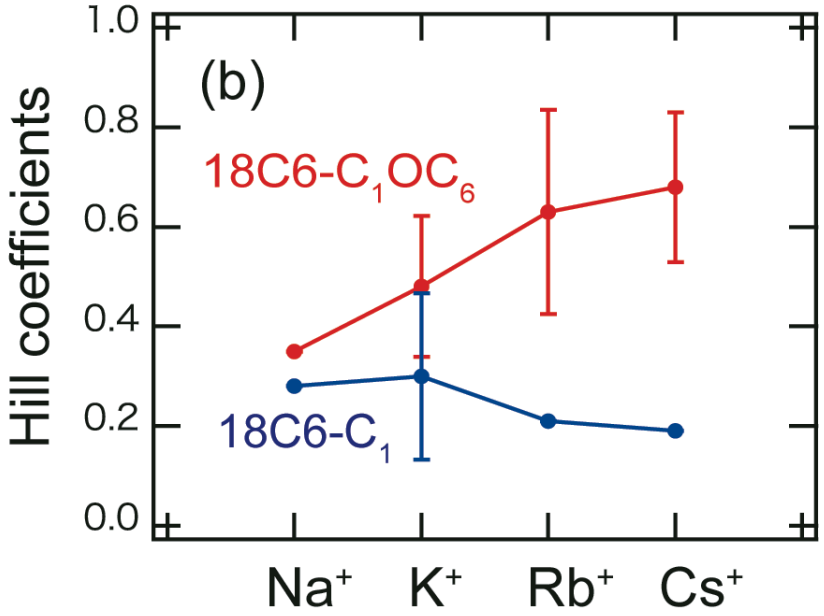


substrates and enzymes

K_D and Hill Coefficients



Ion selectivity for K^+
not so obvious for 18C6-C_1



steepness

18C6-C_1 shows more
negative cooperativity

M^+•18C6-C_1 at interface inhibits
successive encapsulation