Lecture XXX: Anion Binding, Ion Pair Binding

1. Biological relevance of anion binding
2. Binding of ion pairs
   - cascade approach / separate binding sites / zwitterion binding
3. A fluorescent sensor for anions

- Arginine has a guanosine moiety in it:

\[
\text{HN-} \quad \text{HN} \quad \text{NH}_2 \quad \text{CO}_2\text{H} \quad \text{H}^+ \quad \text{HN} \quad \text{HN} \quad \text{NH}_2 \quad \text{CO}_2\text{H}
\]

remains protonated over large pK_a=13.5 pK_a ranges

Very common anion-binding motif

But other parts of protein can also help in anion recognition:

[Diagram showing various amino acids and their roles in anion recognition]

These come into play in SO_4^{2-} and PO_4^{3-} binding proteins (Quiocho, Rice U Phil Trans RSC. 1999 326, 341)

H-bond donors needed
(b) Separate binding sites

The crown binds KF, KCN, KI, Me but not KBr or KCN. It can dissolve all KF in CH₂Cl₂.

There is certainly a cooperative effect relative to the mixture of the crown and the boron ester.

David Reinholdt:

Cl⁻ cannot bind here, since urea is blocked

Na⁺ contracts the lower rim and breaks up the H-bond of urea \( \Rightarrow \) Cl⁻ can now bind

(c) Binding 2-witersious

Early primitive systems:

Not too selective bhr:
A fluorescent sensor for anions

Sensing = binding + measurable (optical, electrochemical) response

Sensor for $\text{Na}^+$
- If CO$_3^-$ groups are esterified, this sensor can pass through cell membranes

Sensor for anions (Eric Anslyn):

Sensor for citrate
- Citrate displaces and fluorescence is restored;
- Poor, but fluorescent guest is quenched in the cavity.