Electrostatic Mechanisms for Shape Selection in Charged Chiral Molecular Assemblies

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Northwestern University

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Outline

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I. Introduction to charged chiral amphiphile assemblies

a) C_nK molecule

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II. Chapter 1: Characterization of C_nK assemblies in different ionic environments, shape selection dictated by electrostatics

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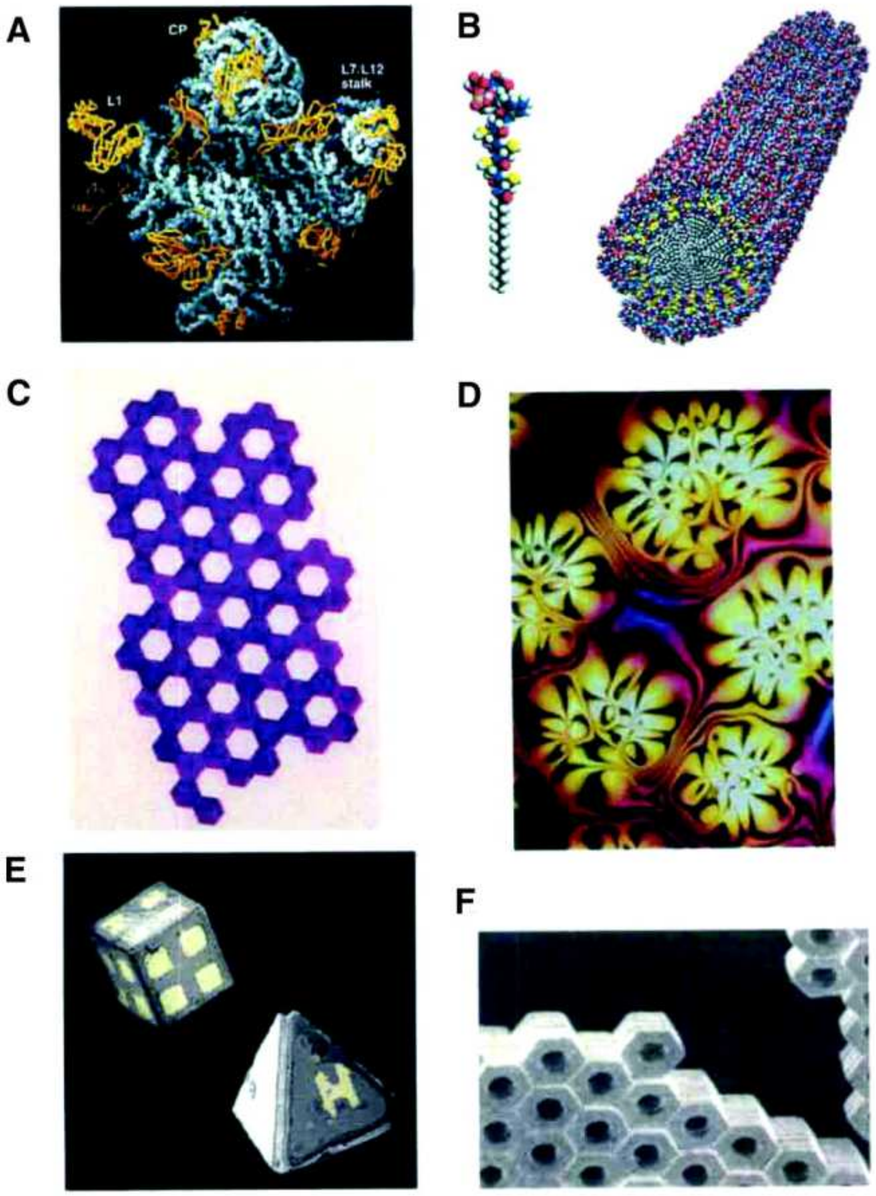
Self-Assembly

- Molecules (building blocks) arrange themselves in supra-molecular structures



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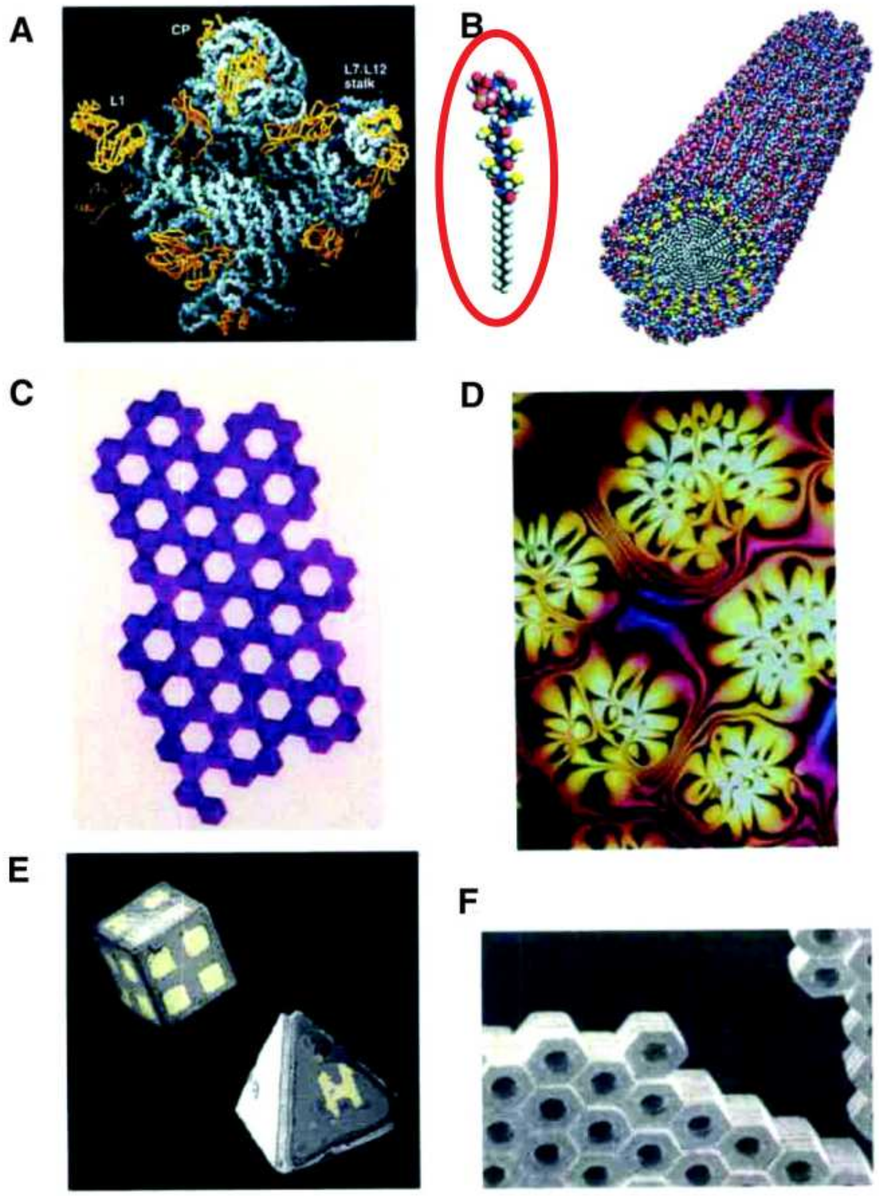

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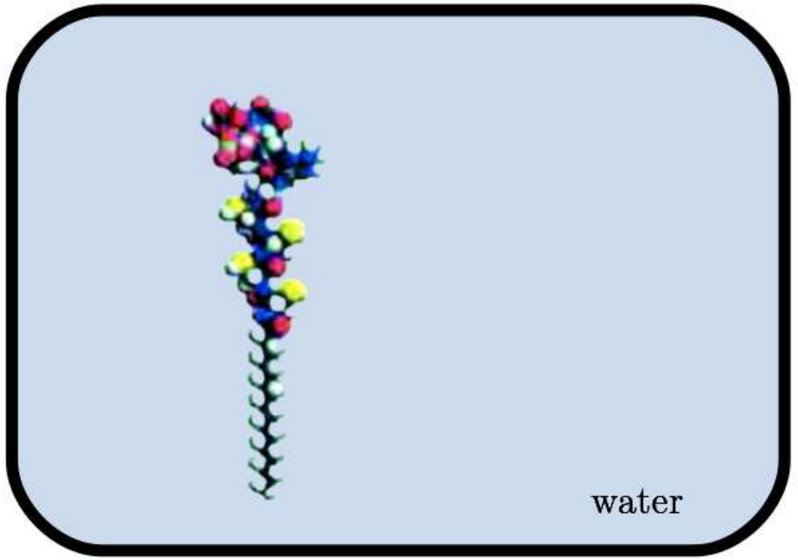

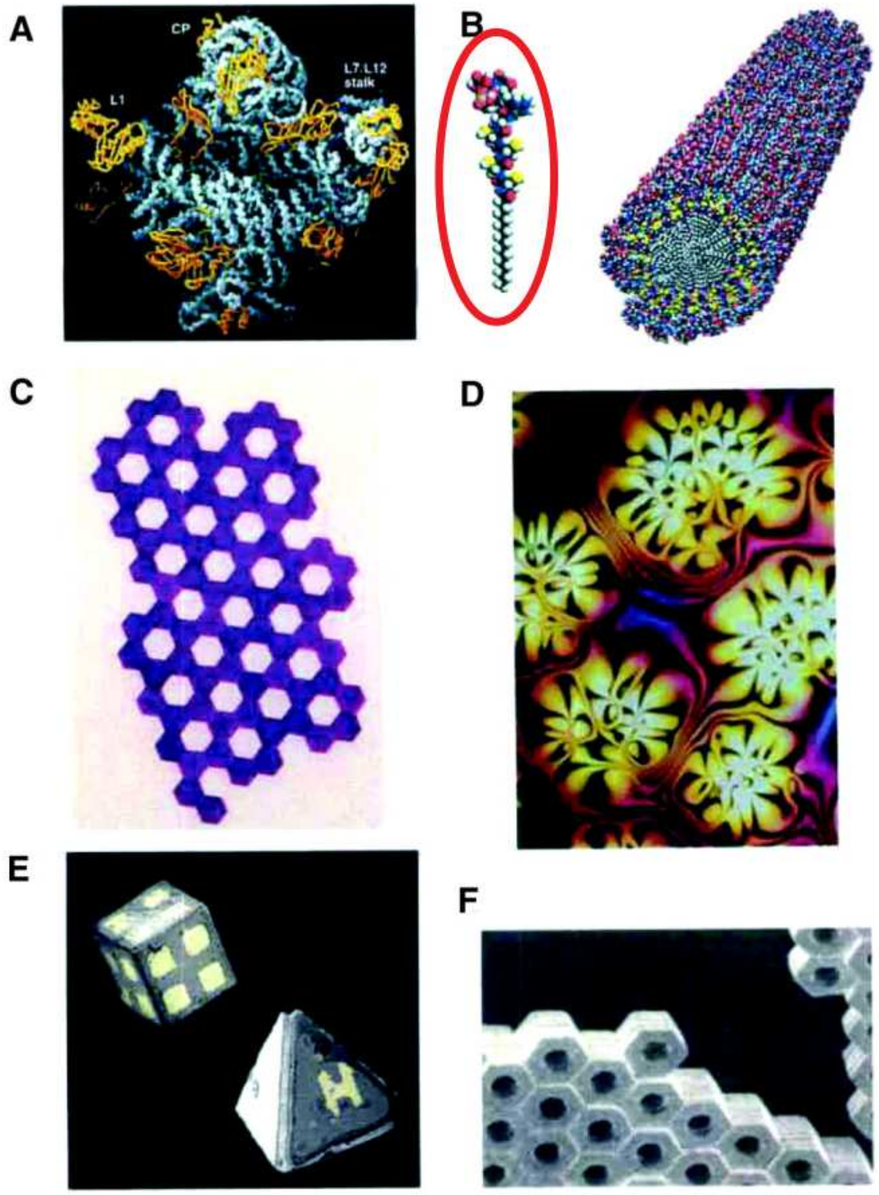

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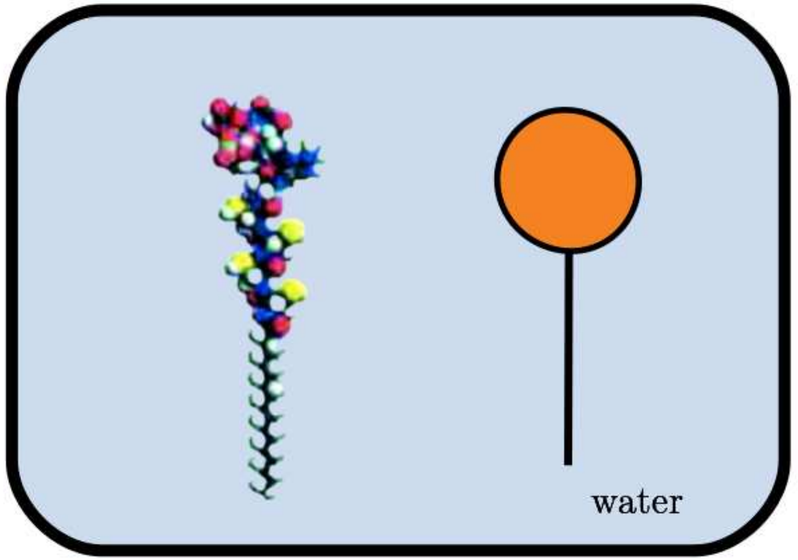

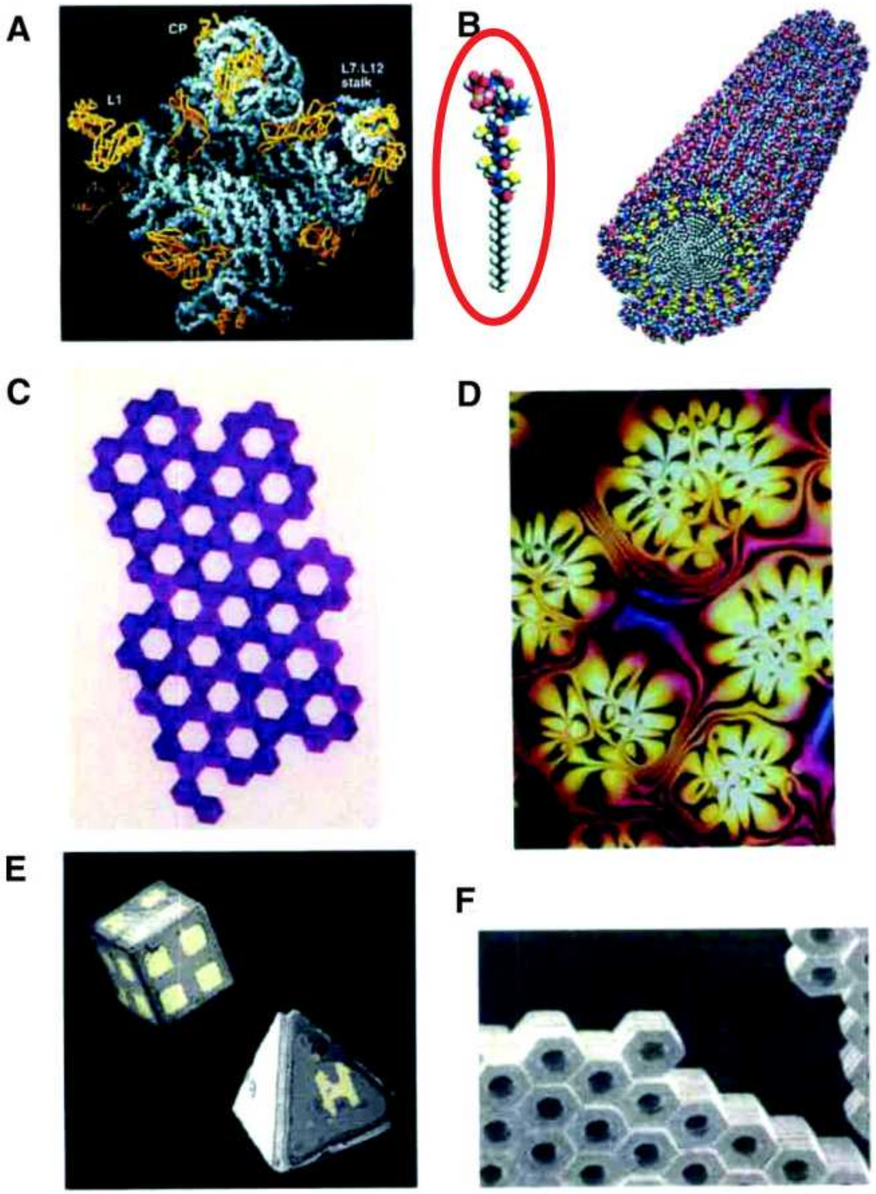

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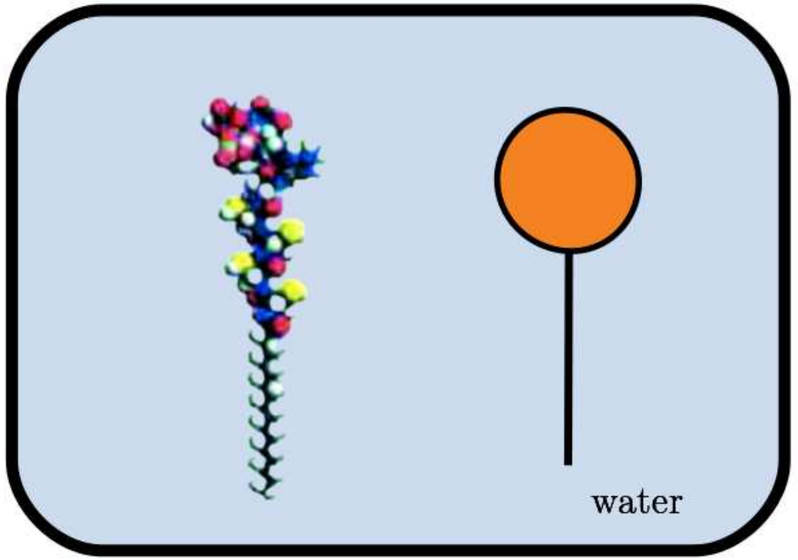
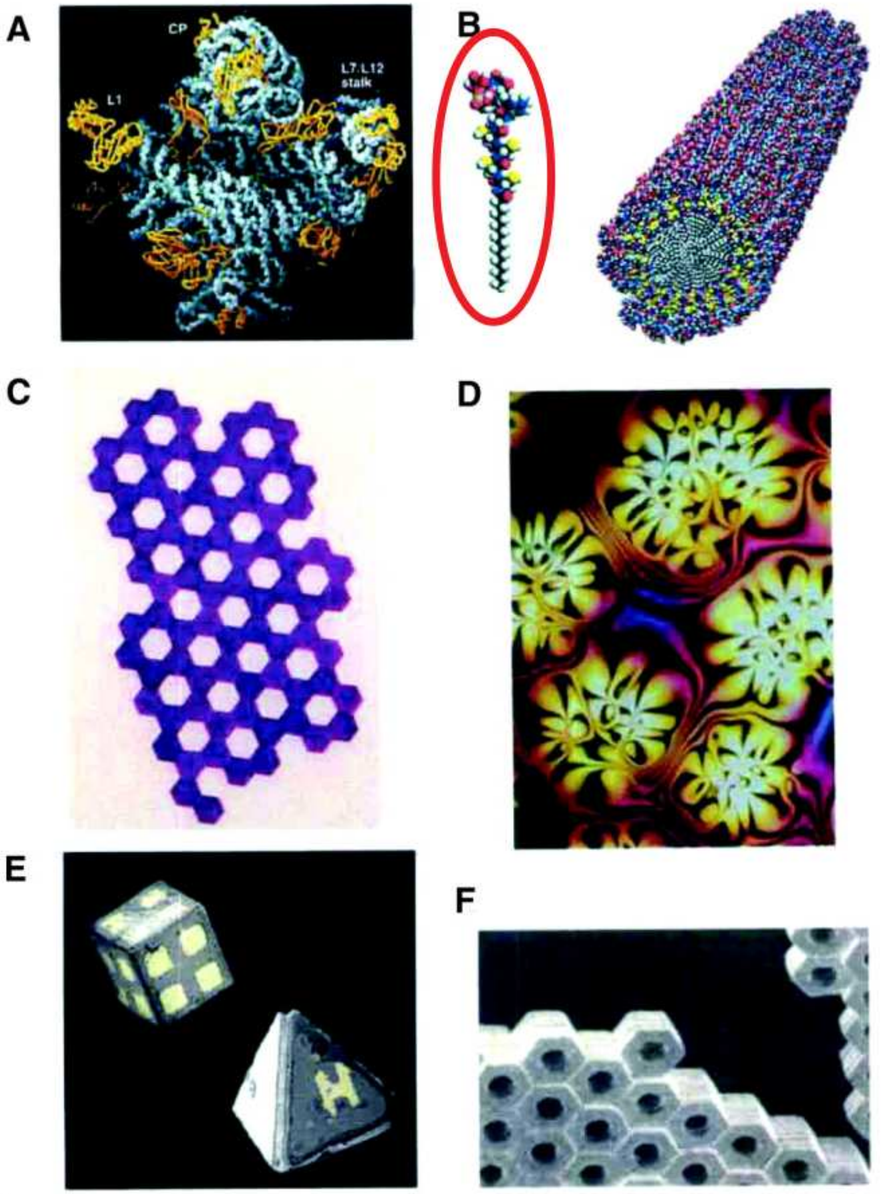
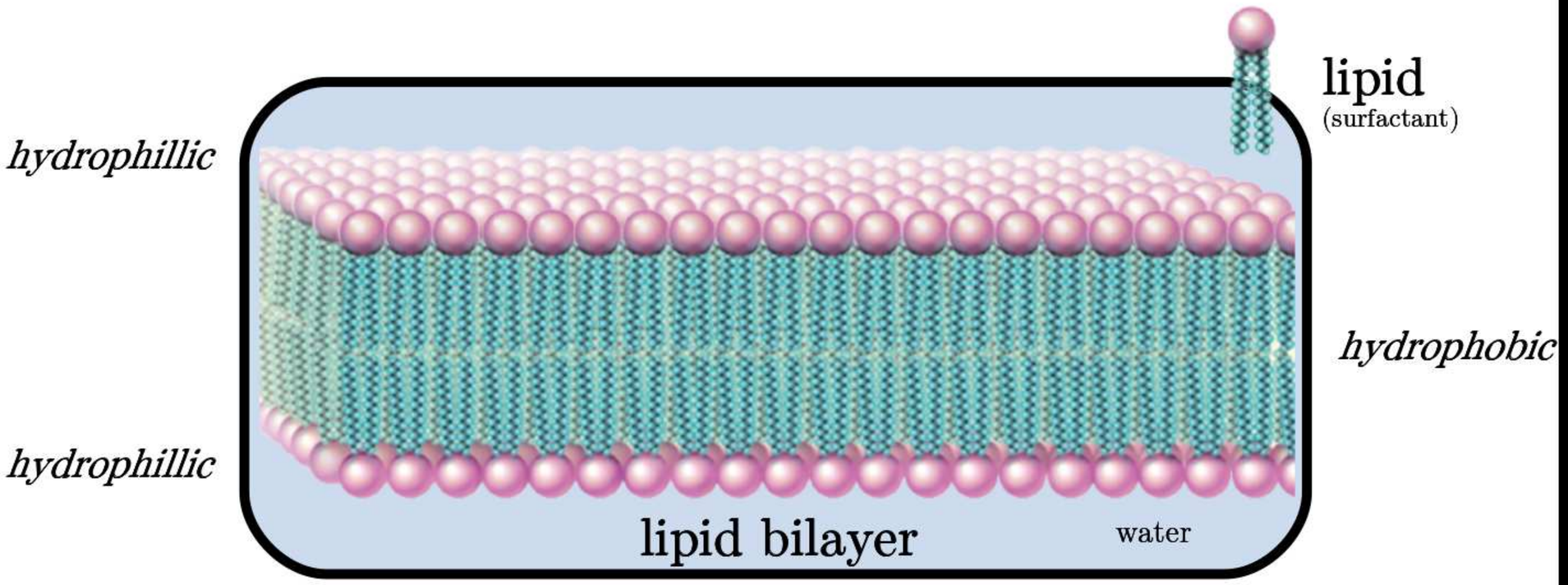


Most common self-assembling objects

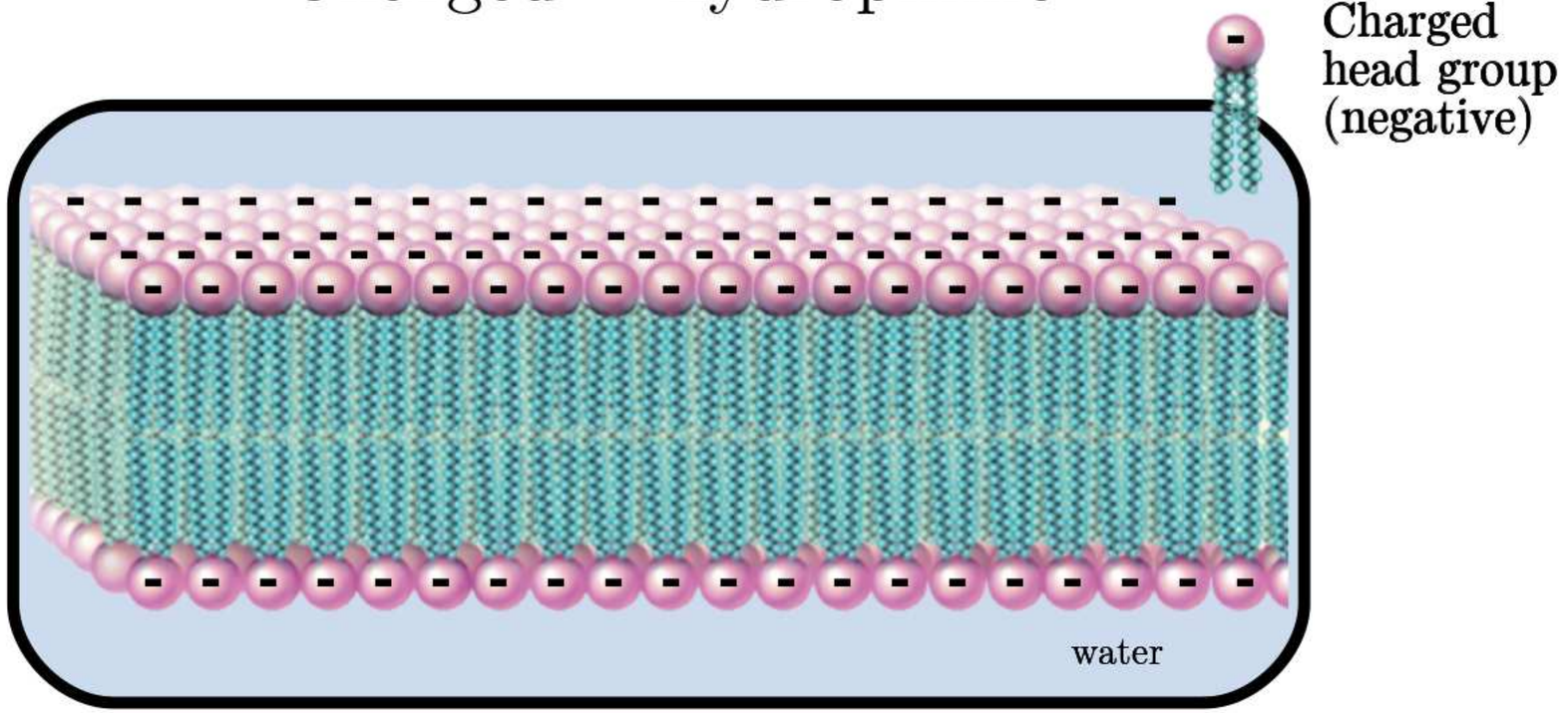


Amphiphiles and Charged Soft Matter

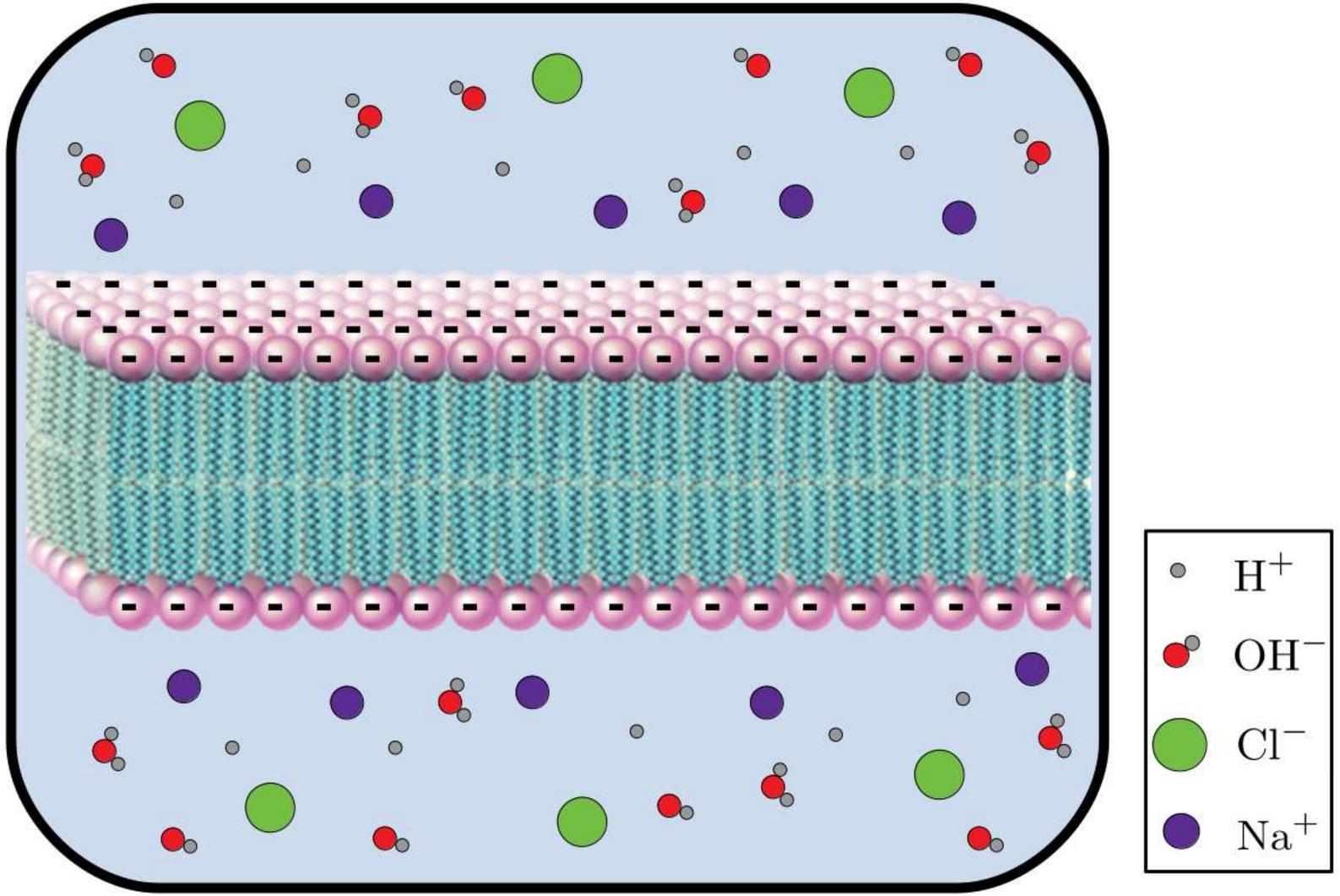


Amphiphiles and Charged Soft Matter

Charged = hydrophillic



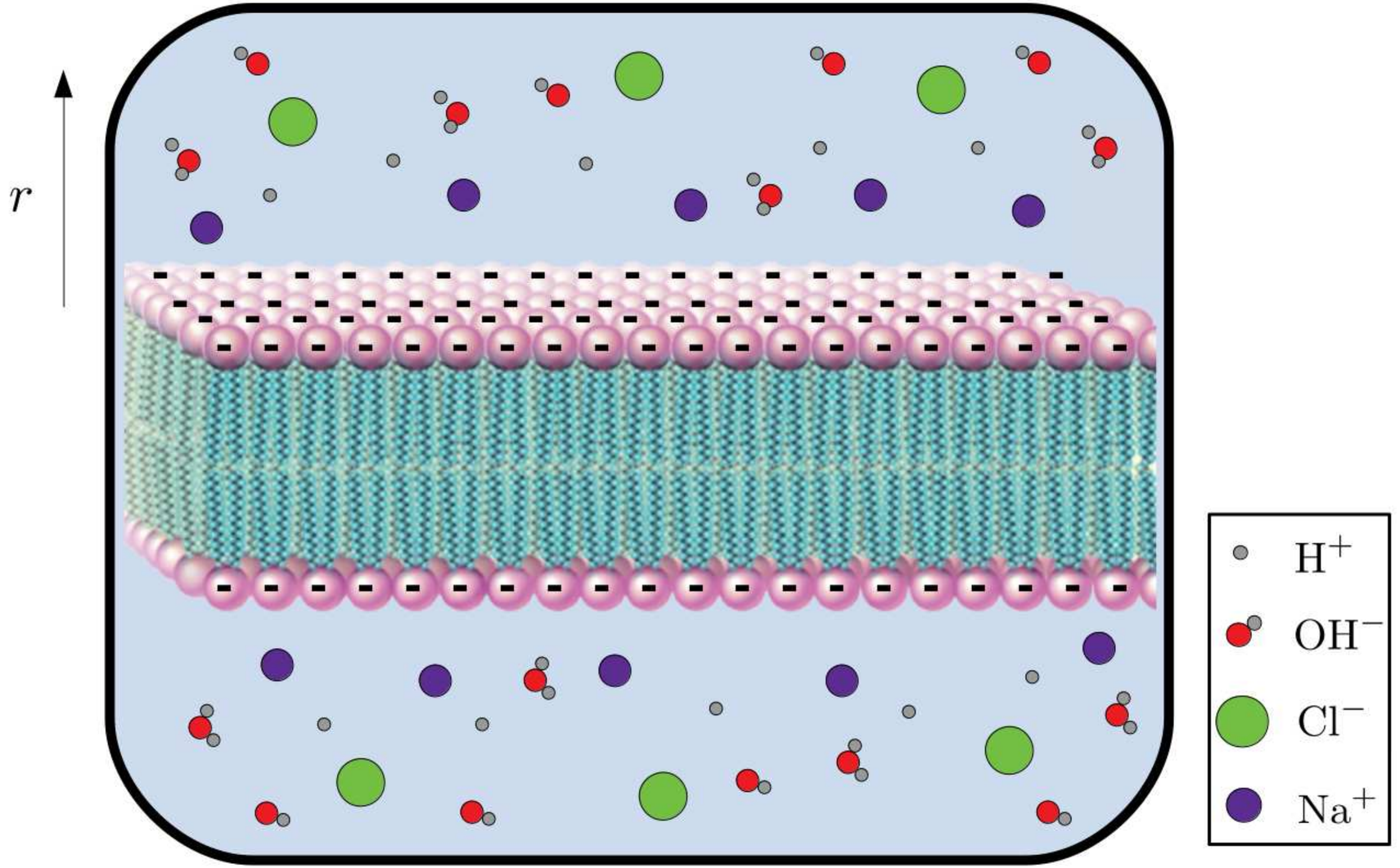
How do *charge interactions* affect assembly?


H^+
OH^-
Cl^-
Na^+

Poisson Boltzmann

$$\frac{d^2\psi(r)}{dr^2} \simeq \frac{1}{\lambda_D^2}\psi(r)$$

$$\psi(r) \sim e^{-r/\lambda_D} \qquad \lambda_D \sim \frac{1}{\sqrt{[\mathrm{NaCl}]}}$$



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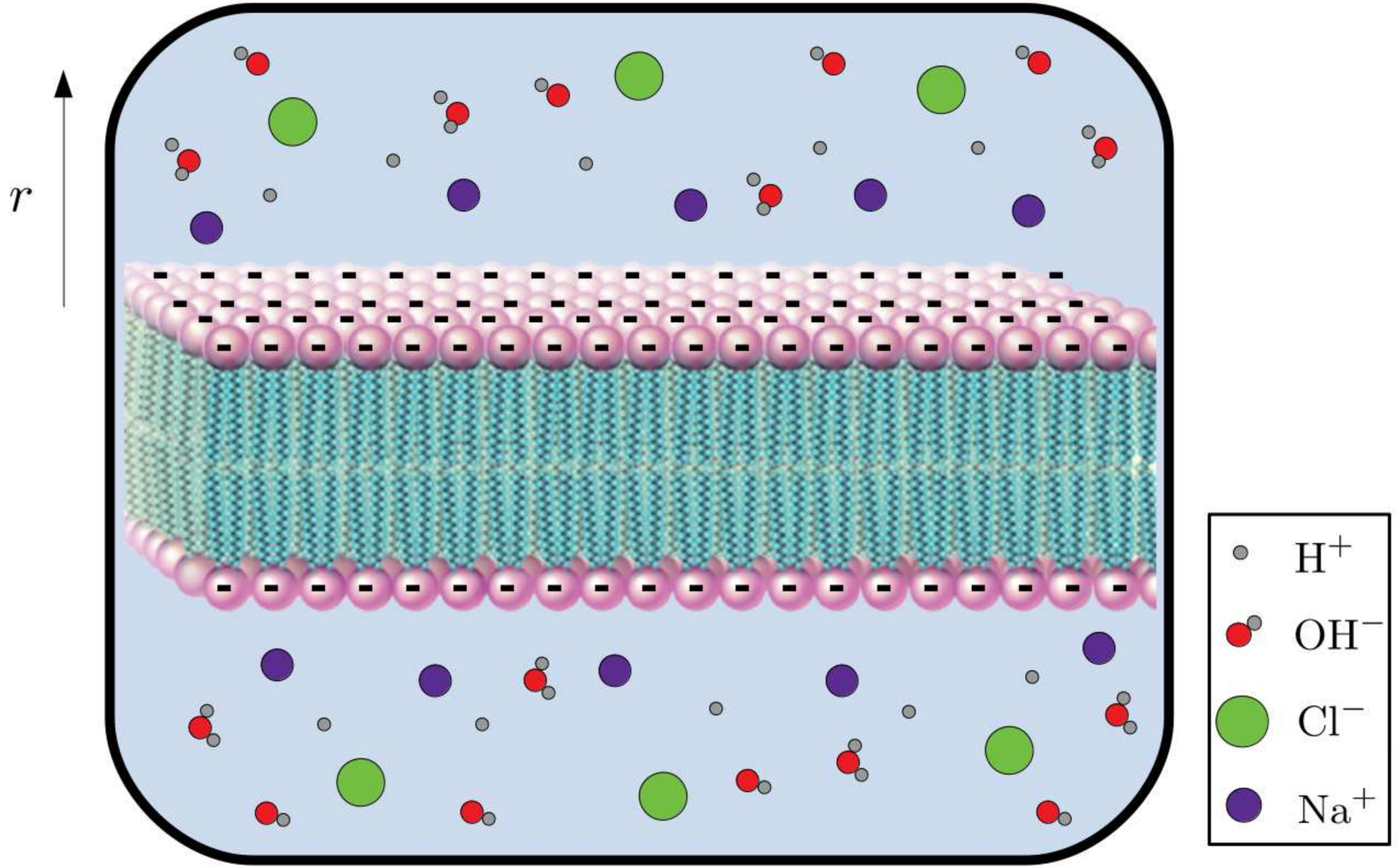
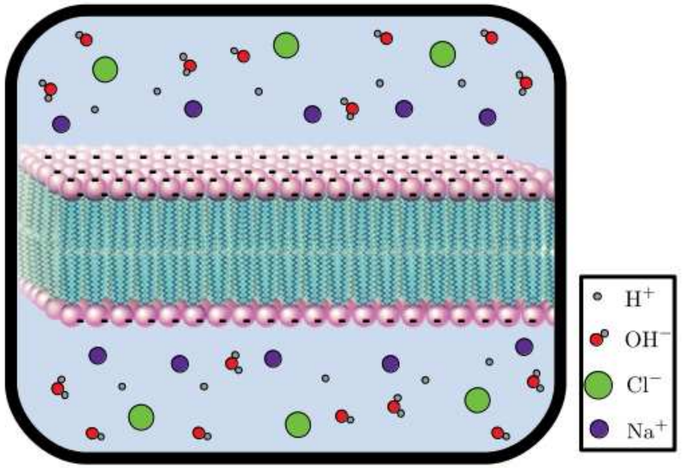
$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$$

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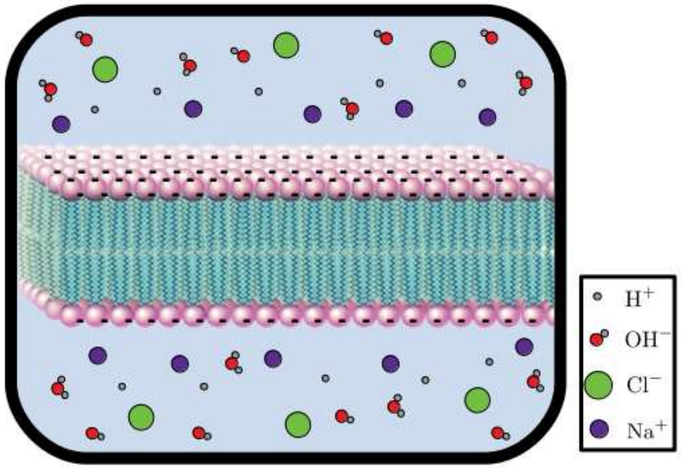
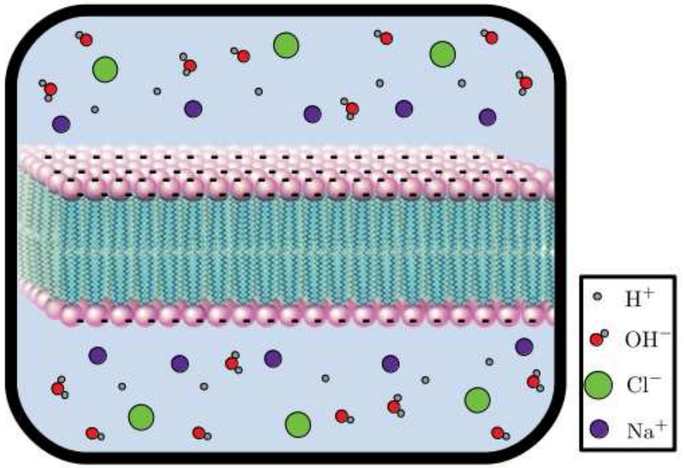


Bilayer



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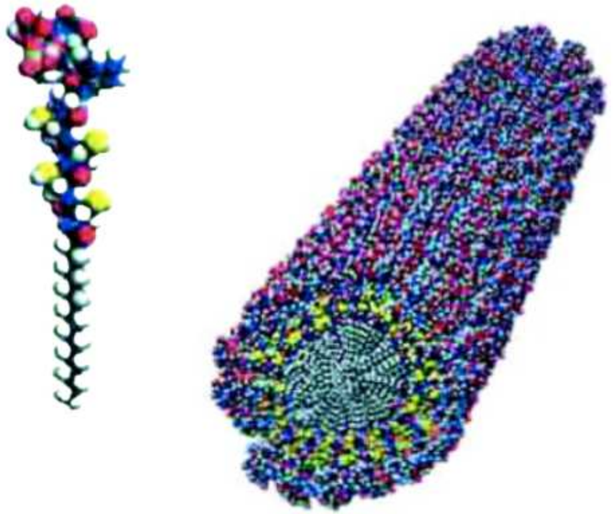
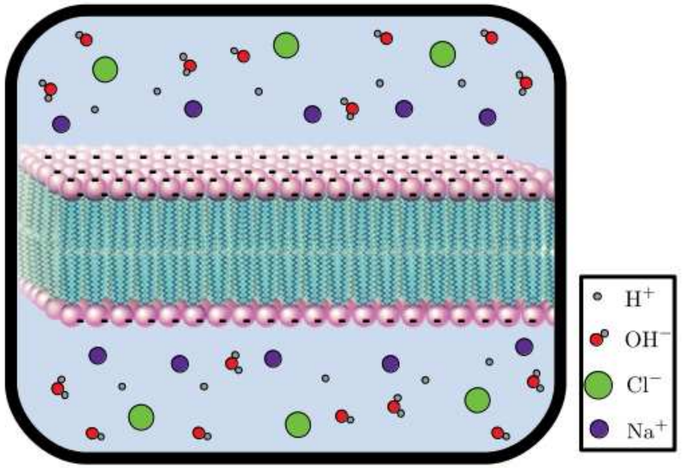


Cylindrical Micelle



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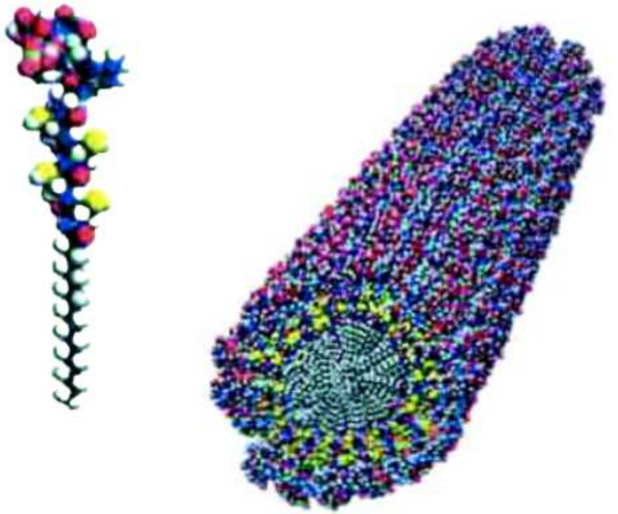

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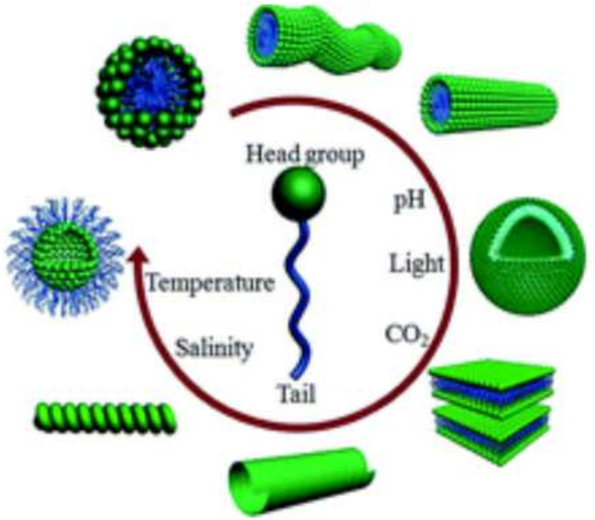
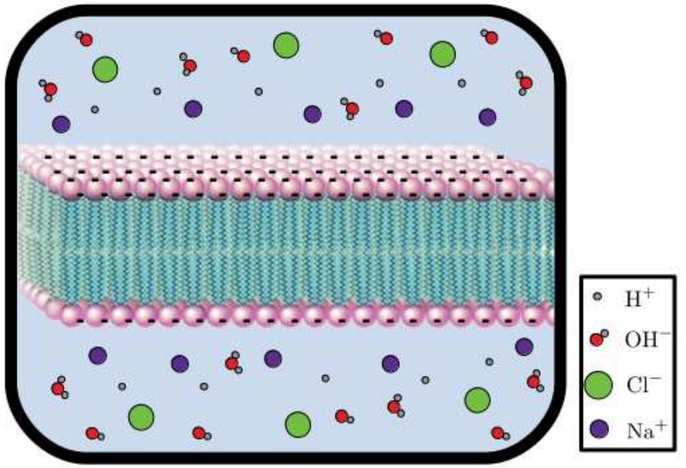


Driving transformations with external stimuli



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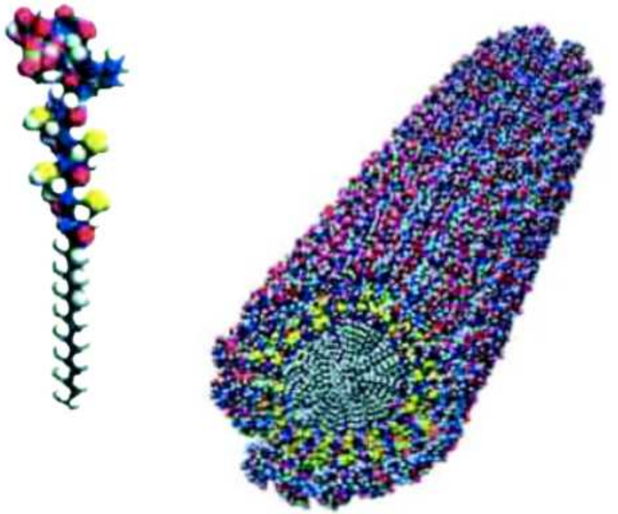

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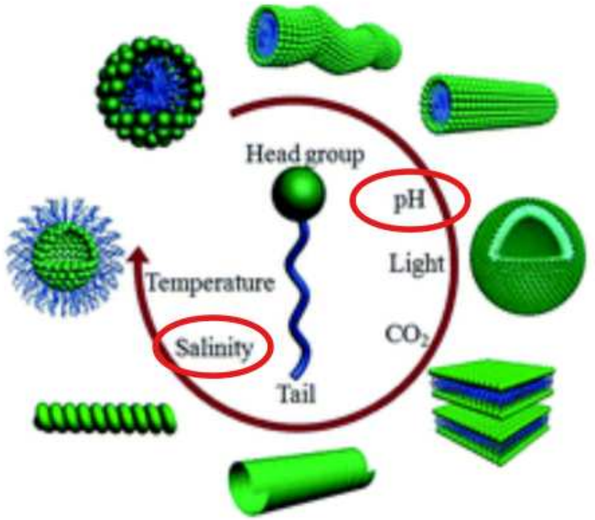
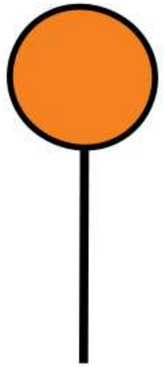


Driving transformations with external stimuli

Chiral Assemblies



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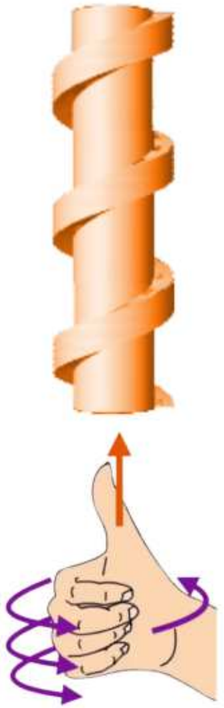

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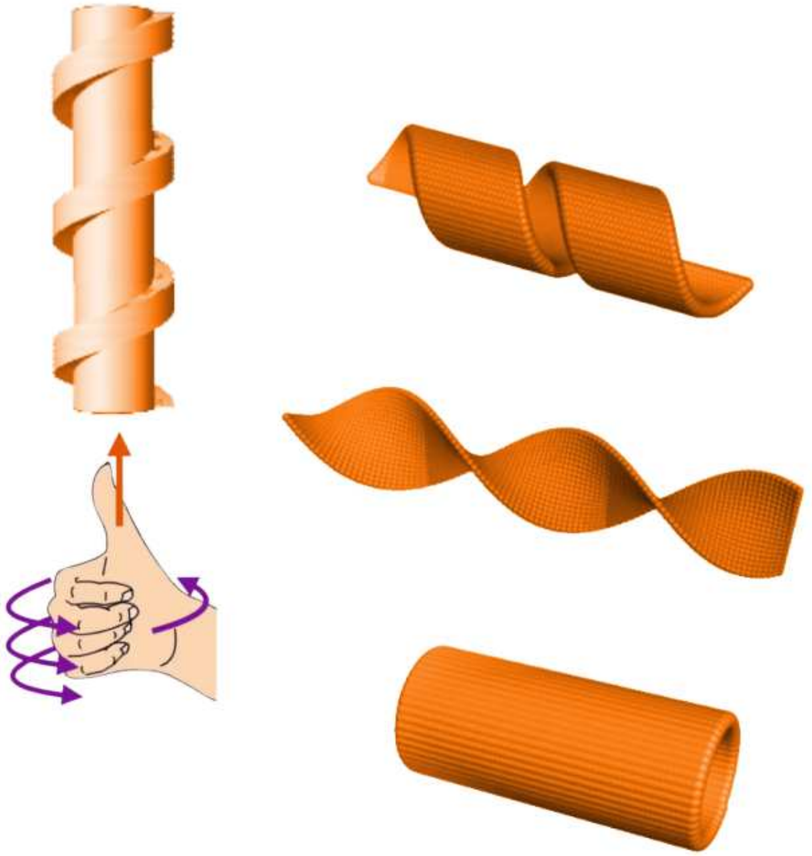

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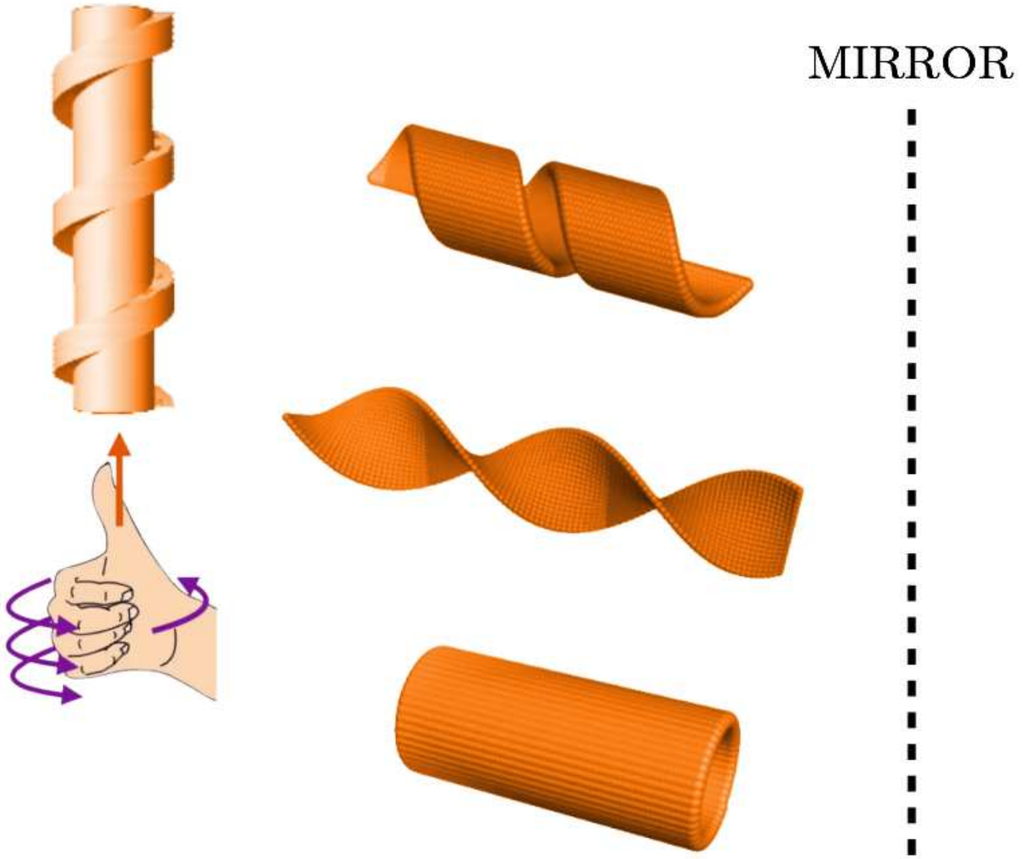

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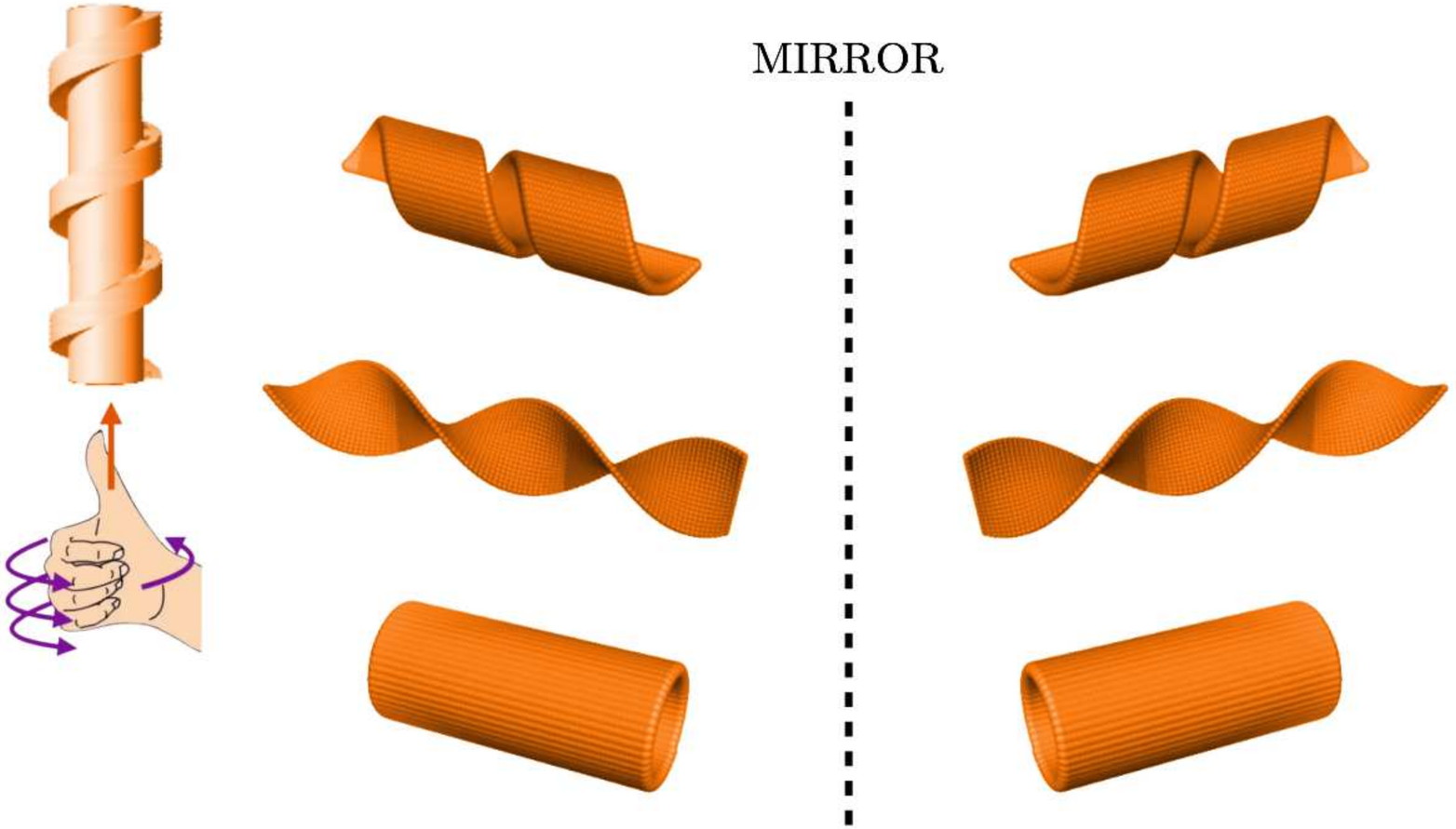

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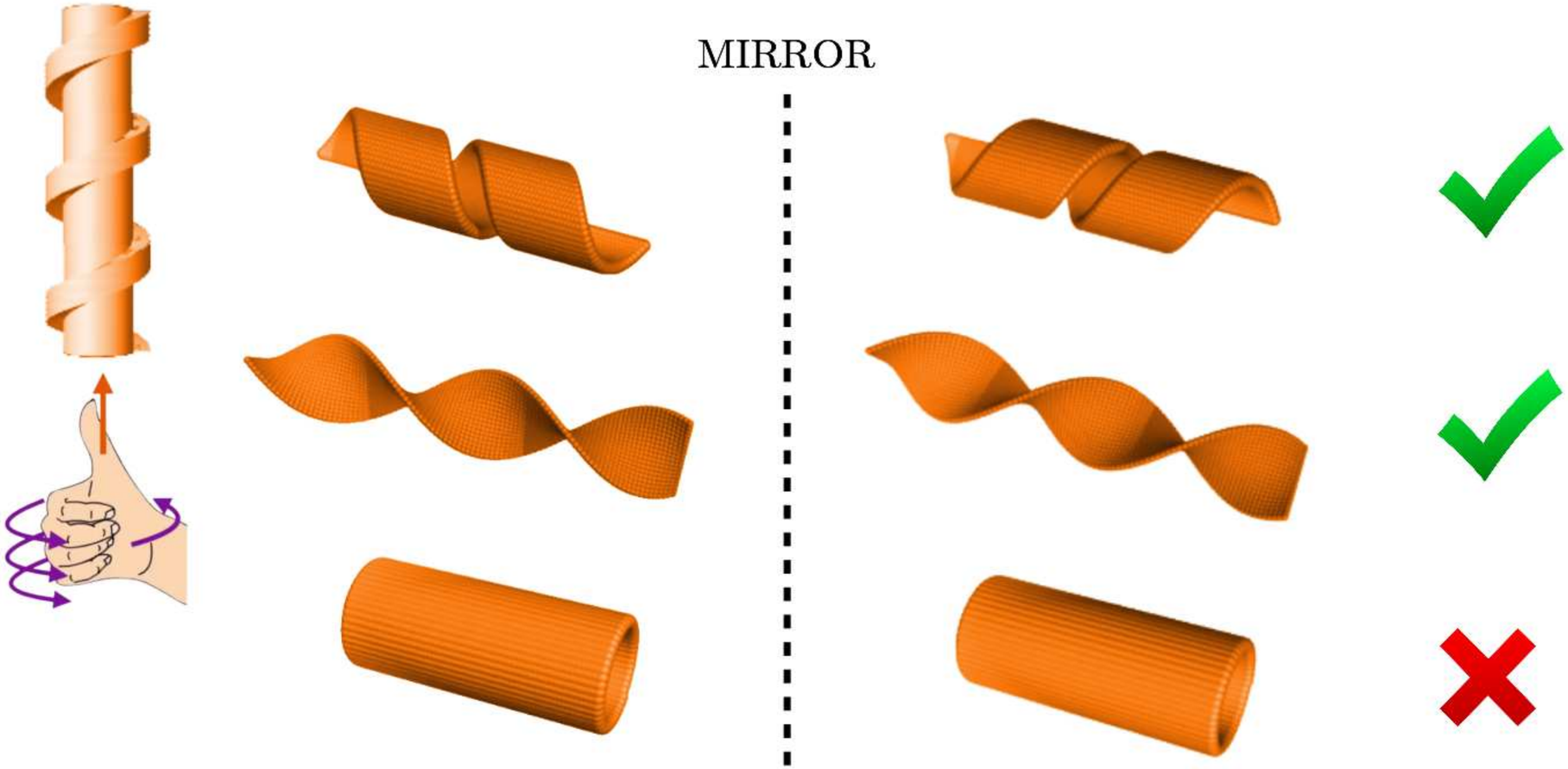

Not superimposable on mirror image (axial handedness)

Driving Chiral Assemblies with Electrostatics

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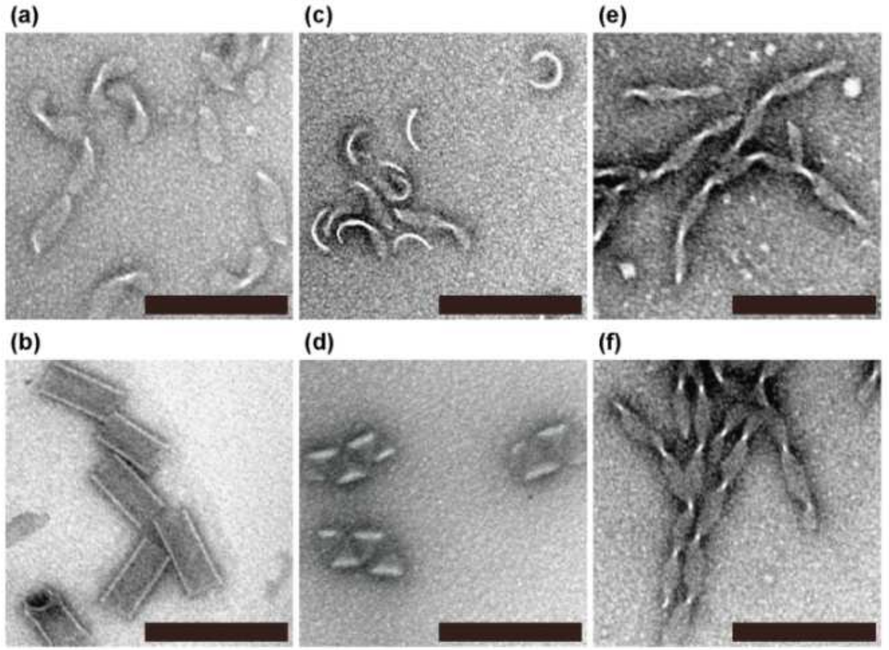

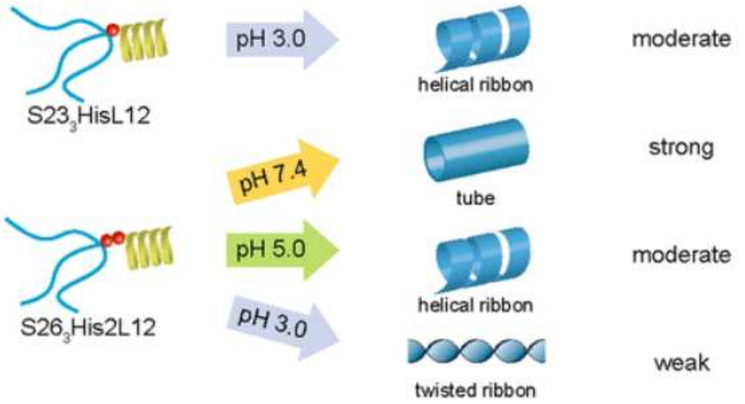

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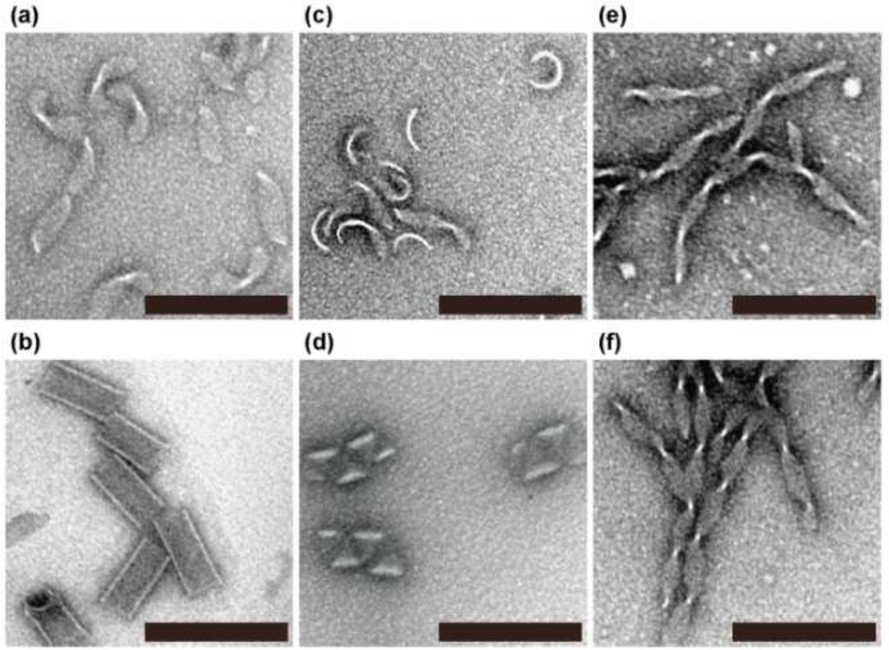

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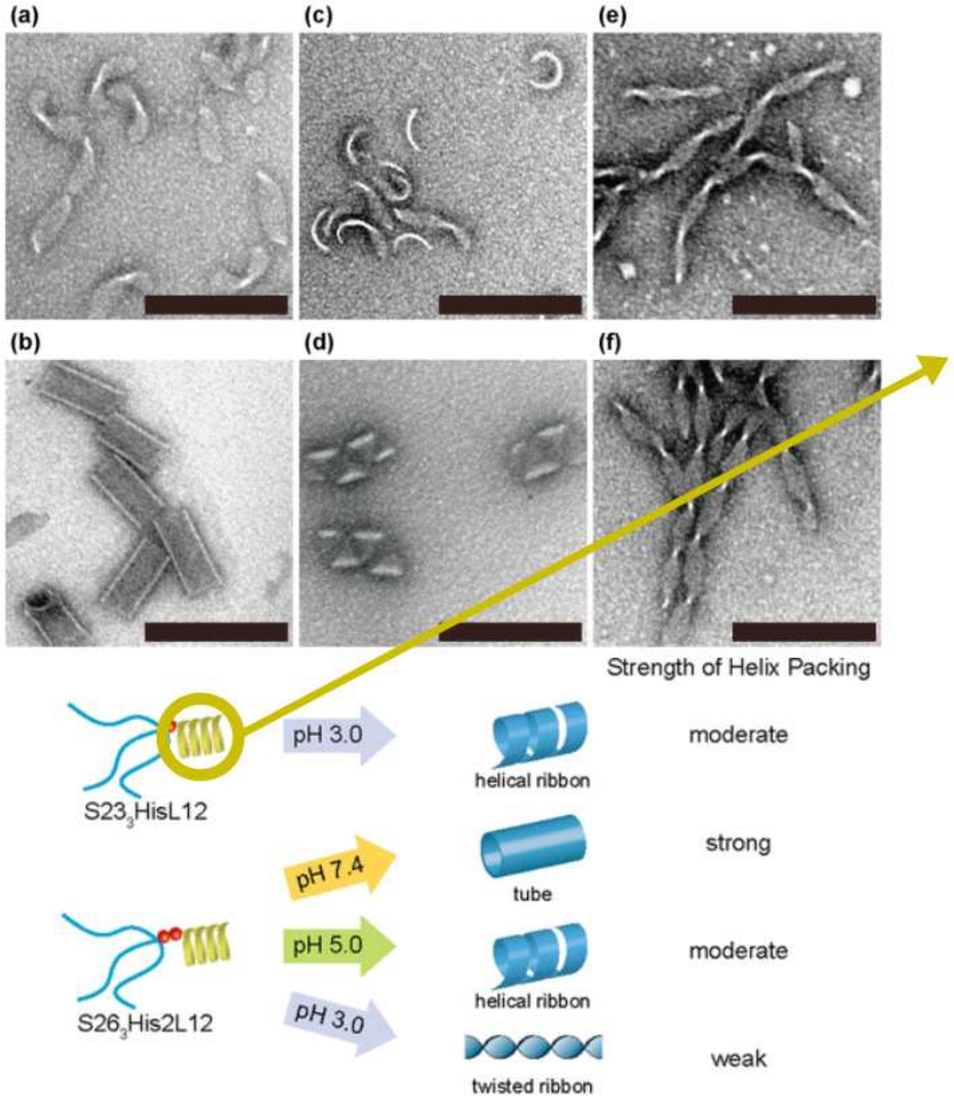

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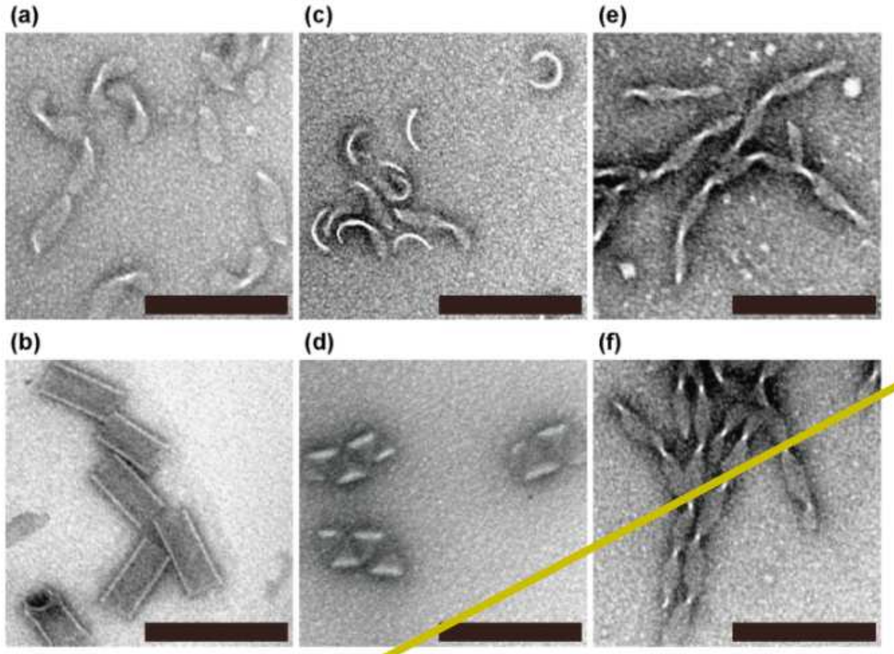

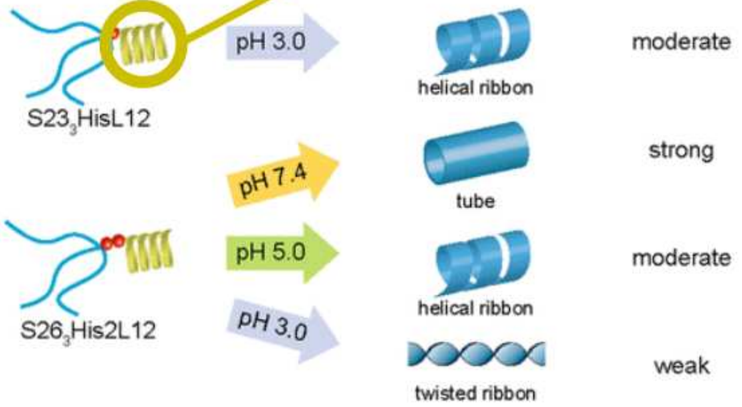

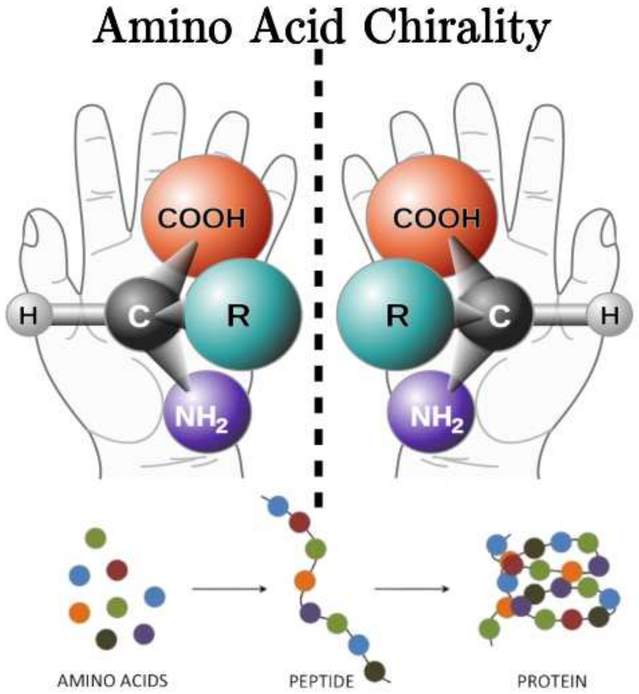

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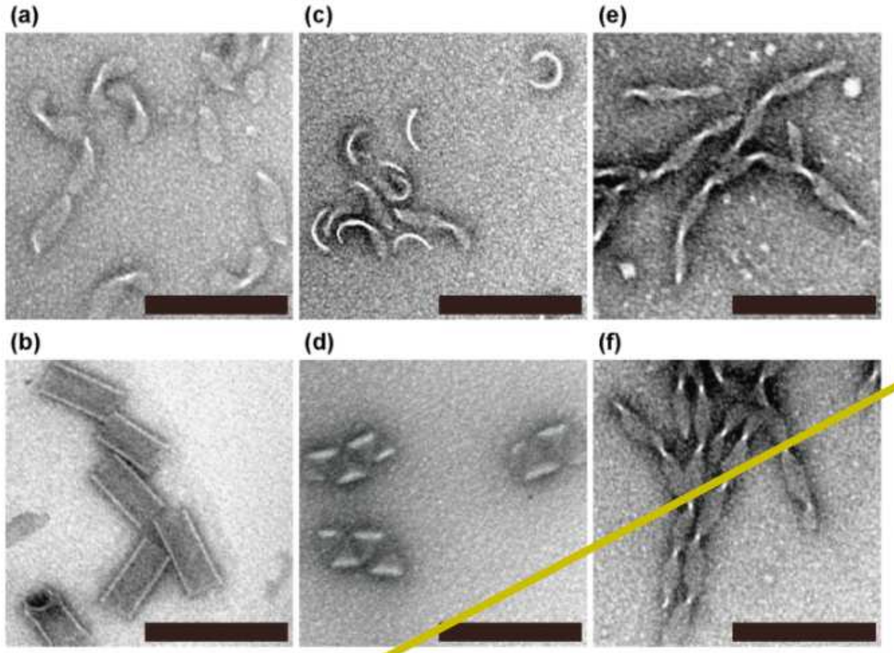
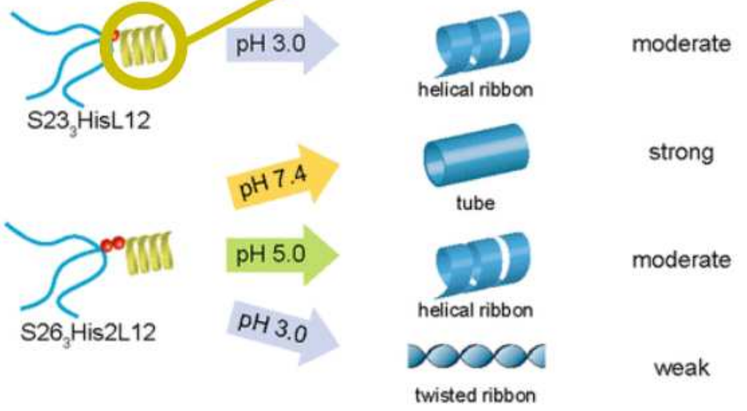
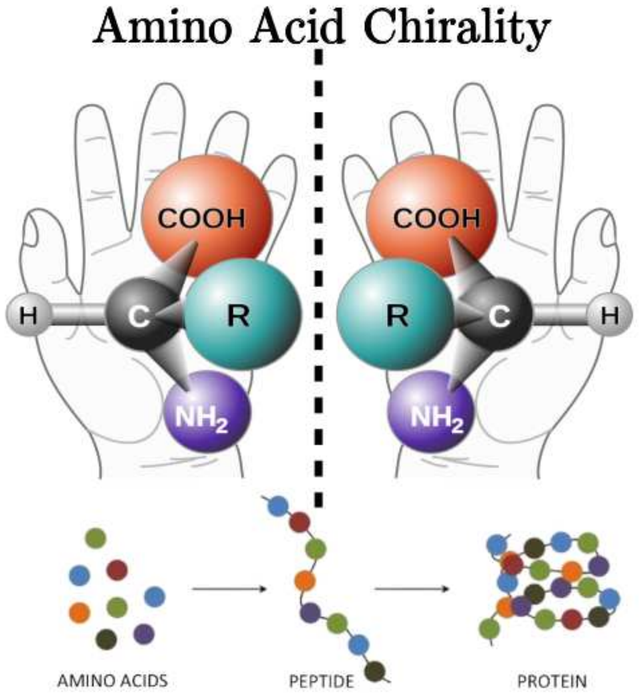
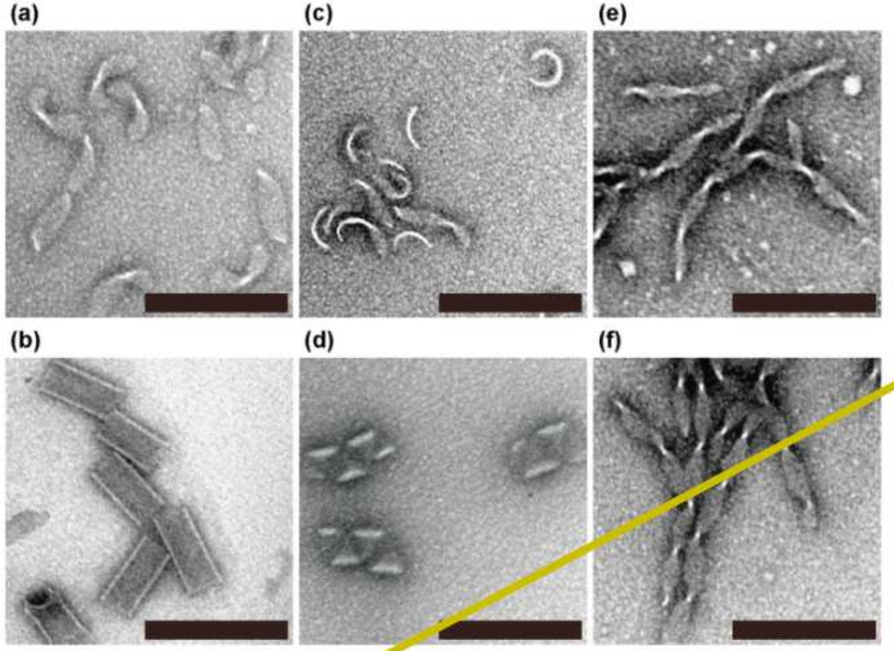


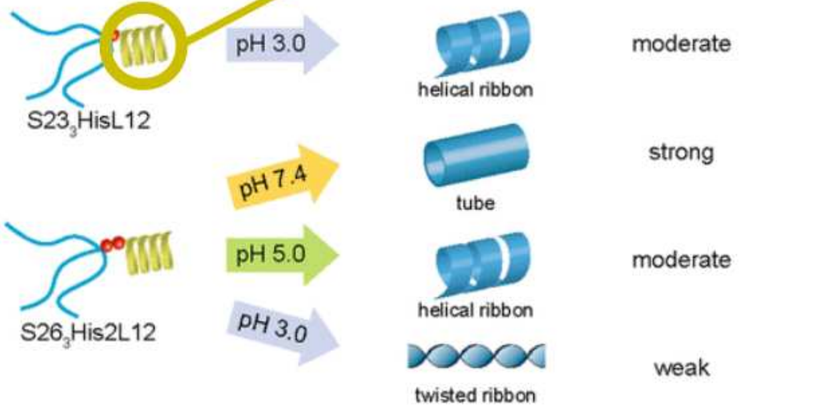


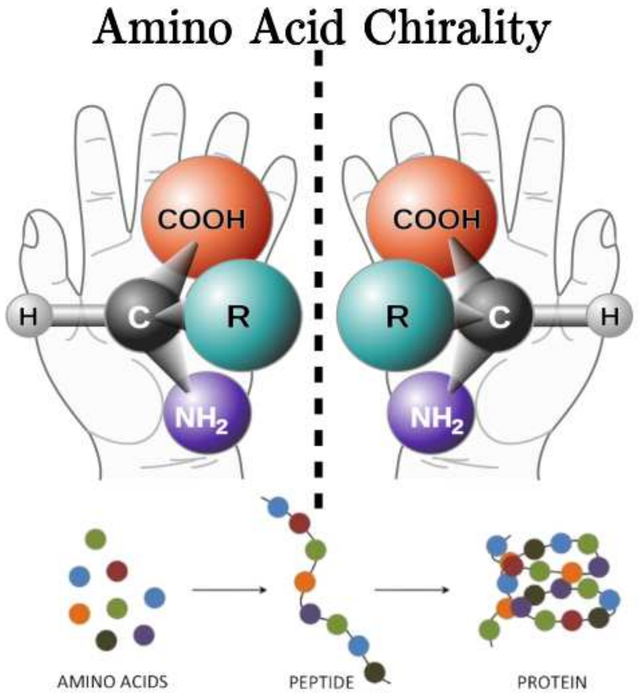


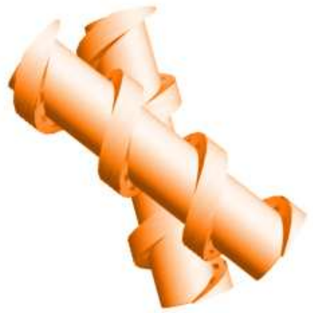
pH dependent charge

Driving Chiral Assemblies with Electrostatics









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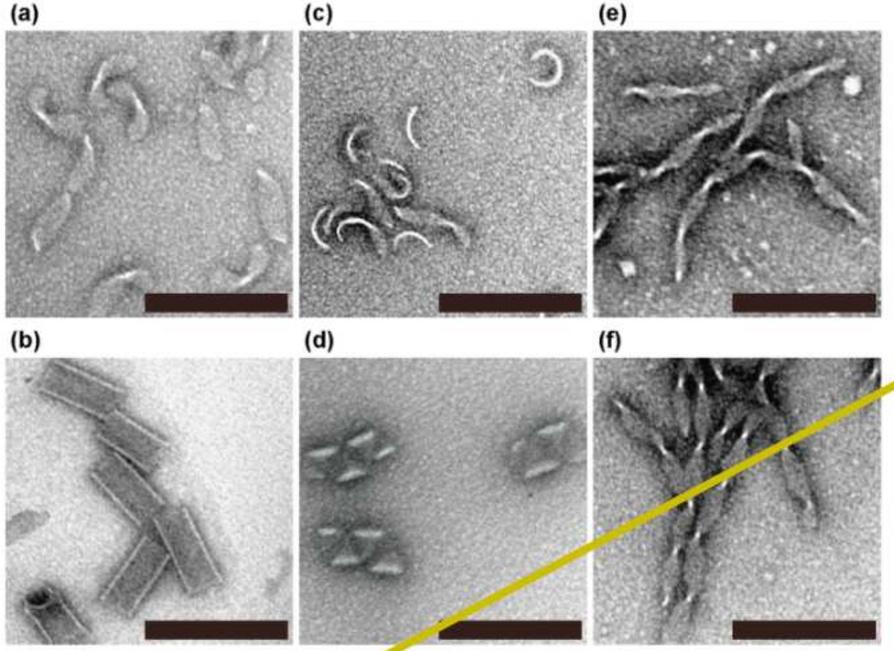
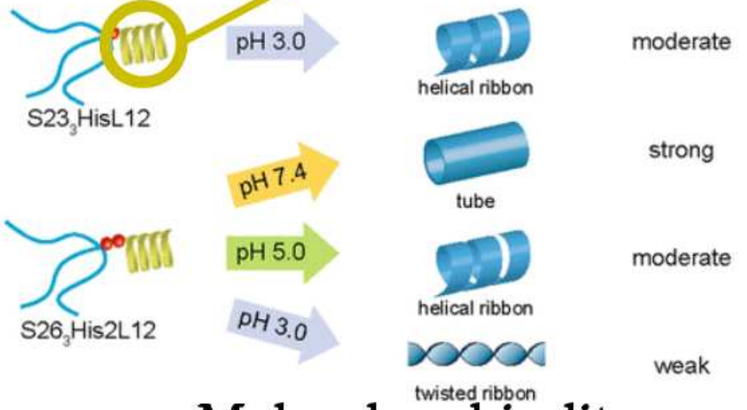
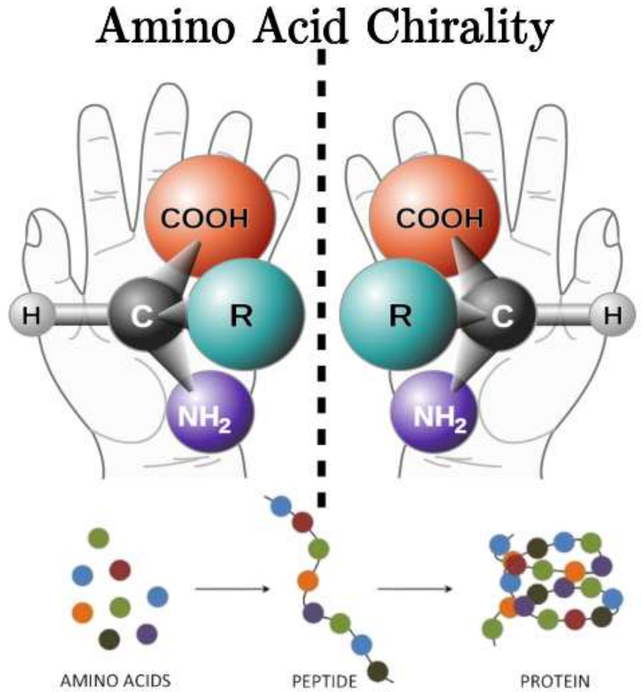
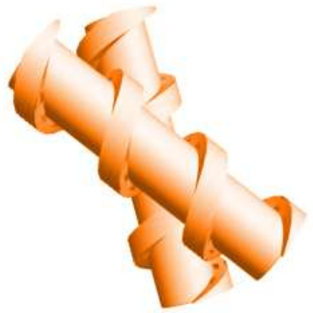


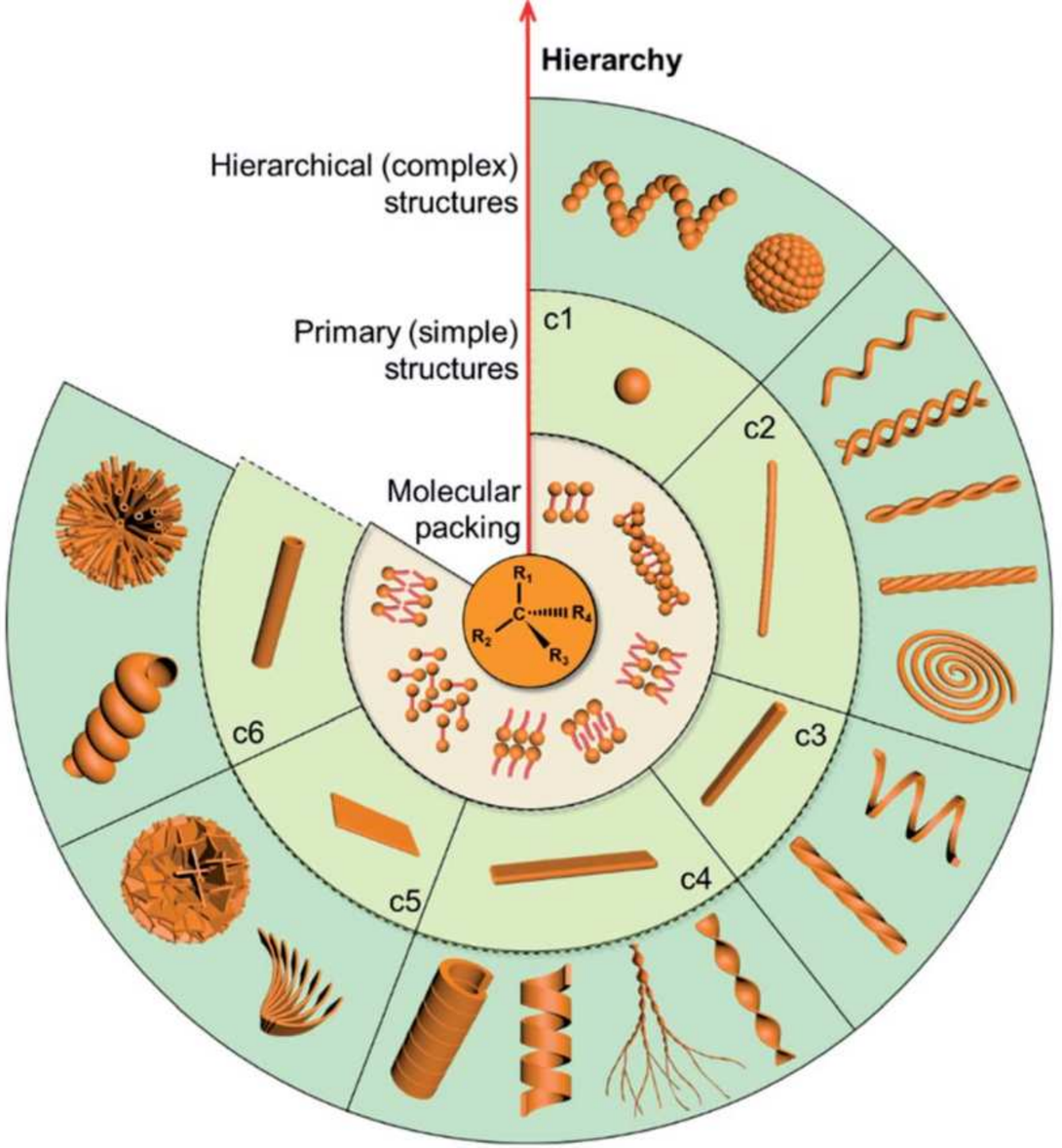


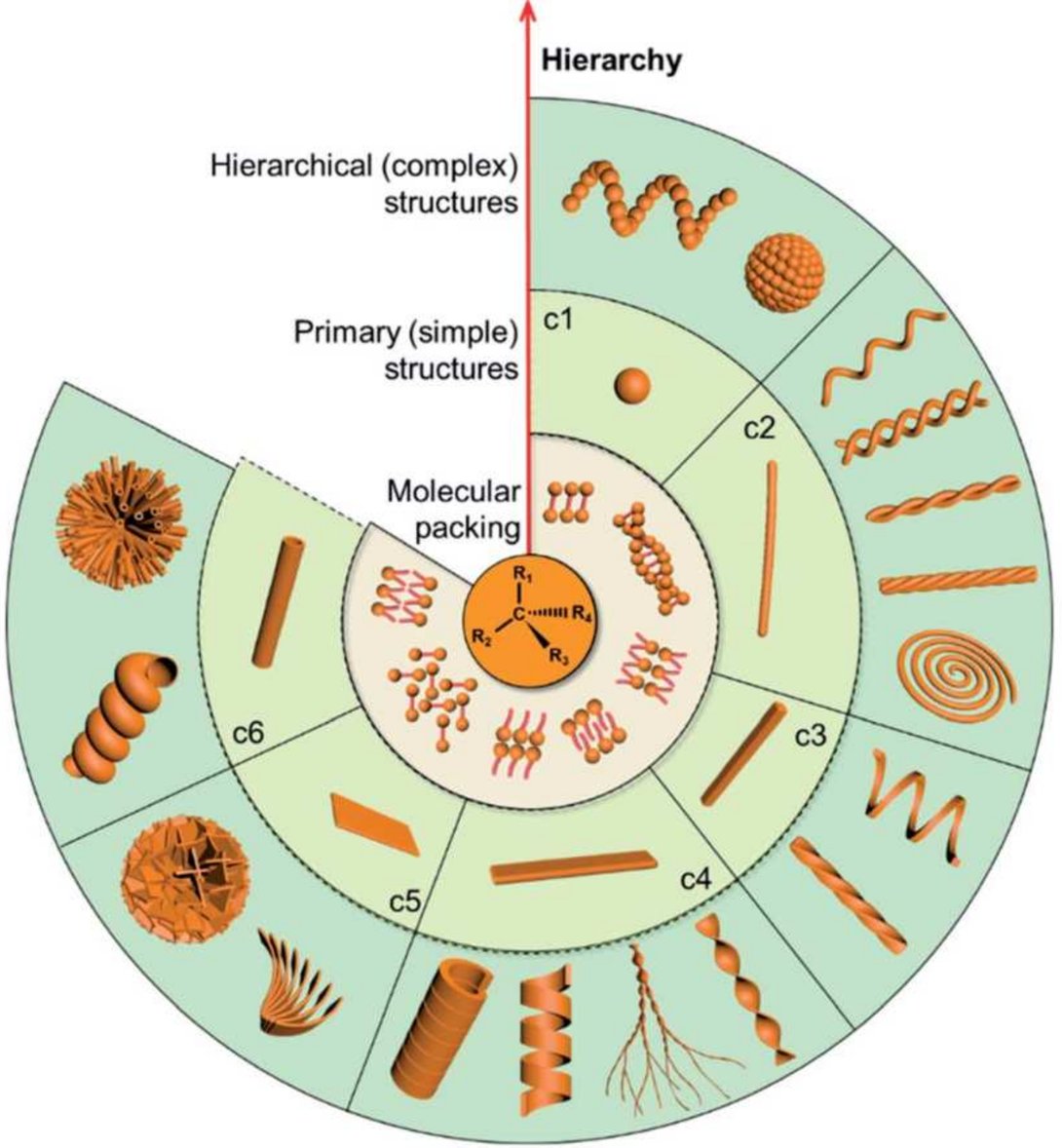




pH dependent charge

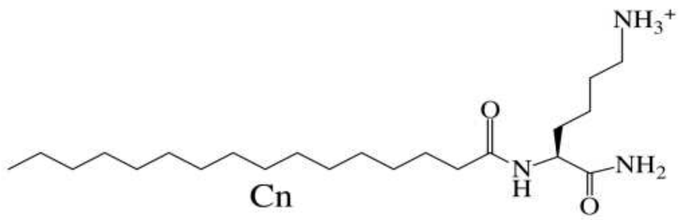
Molecular chirality manifests at the supramolecular level


Hierarchy
Hierarchical (complex) structures
Primary (simple) structures
Molecular packing
c1
c2
c3
c4
c5
c6
R1
R2
R3
R4
C



Electrostatic-based bottom-up design principles for chiral assemblies and interconversion mechanisms

Charged Chiral Assemblies: C_nK



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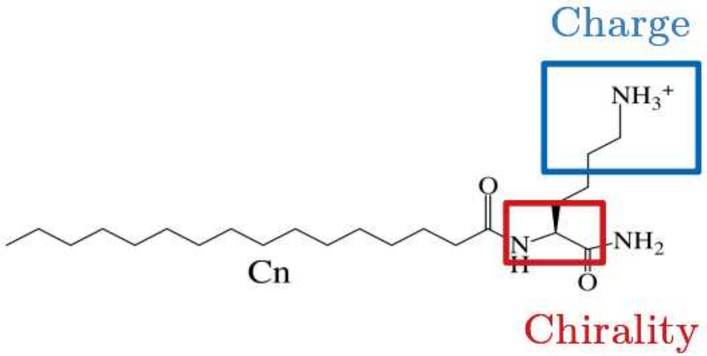
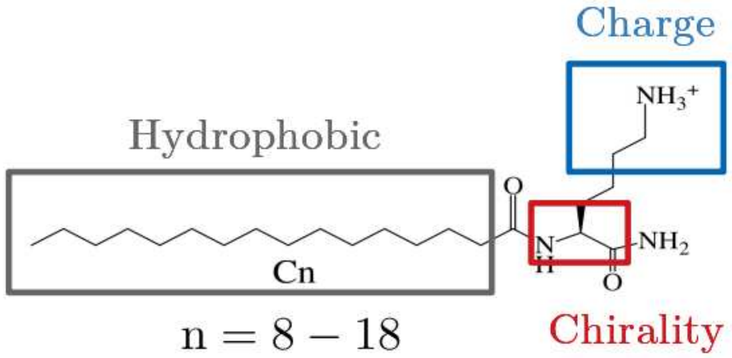


Lysine (L / D)

Charged Chiral Assemblies: C_nK



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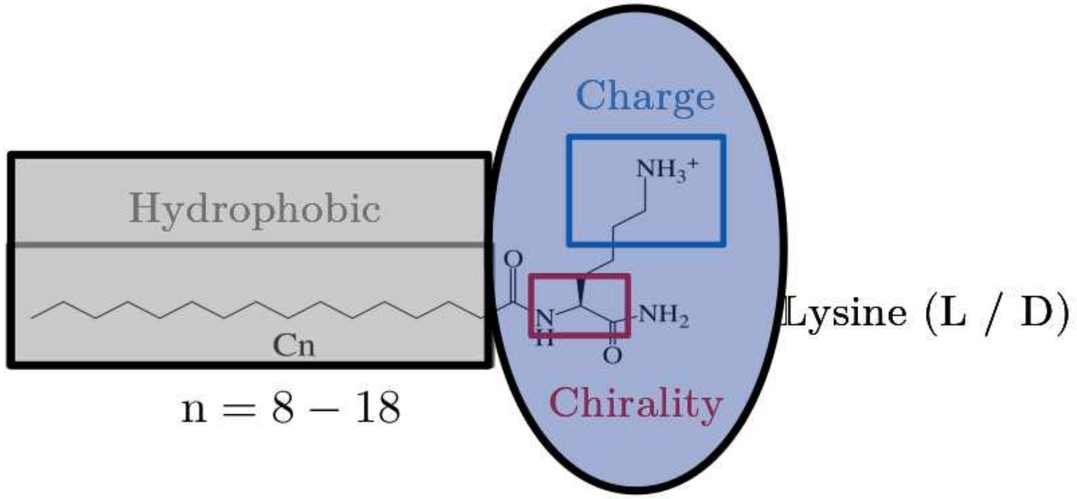
Charged Chiral Assemblies: C_nK



Simplest Charged, Chiral, Assembling Molecule

Outline

I. Introduction to charged chiral amphiphile assemblies
   a) C_nK molecule

II. Chapter 1: Characterization of C_nK assemblies in different ionic environments, shape selection dictated by electrostatics

III. Chapter 2: Charge regulation in ionizable assemblies

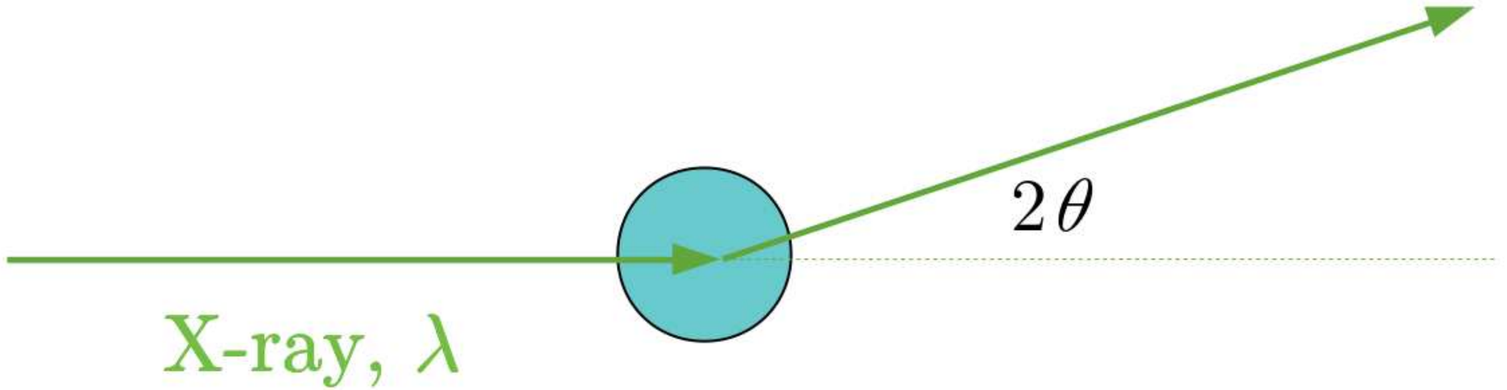
IV. Conclusion: summary, outlook, and acknowledgements

Northwestern

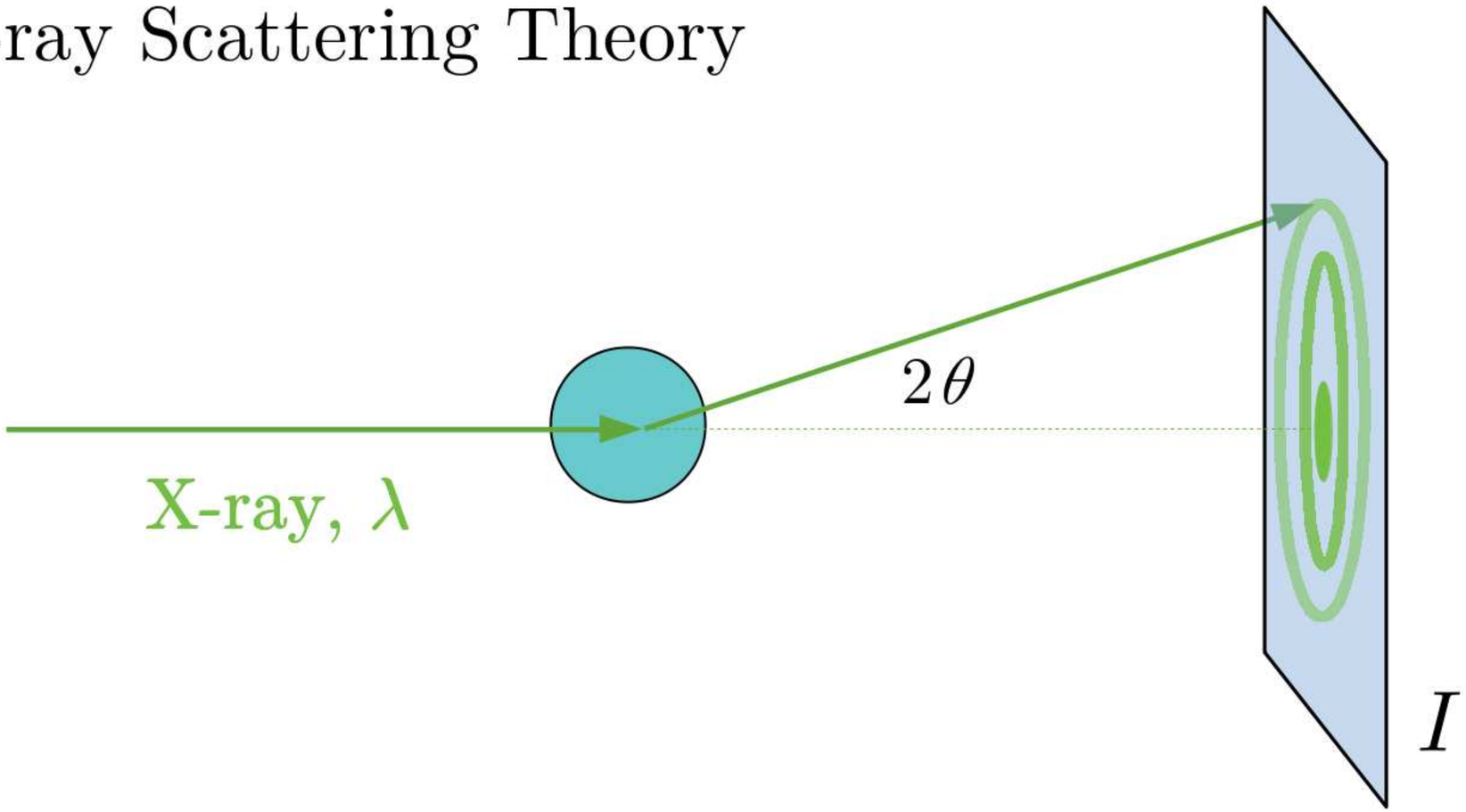
X-ray Scattering Theory

X-ray Scattering Theory

X-ray Scattering Theory



X-ray Scattering Theory



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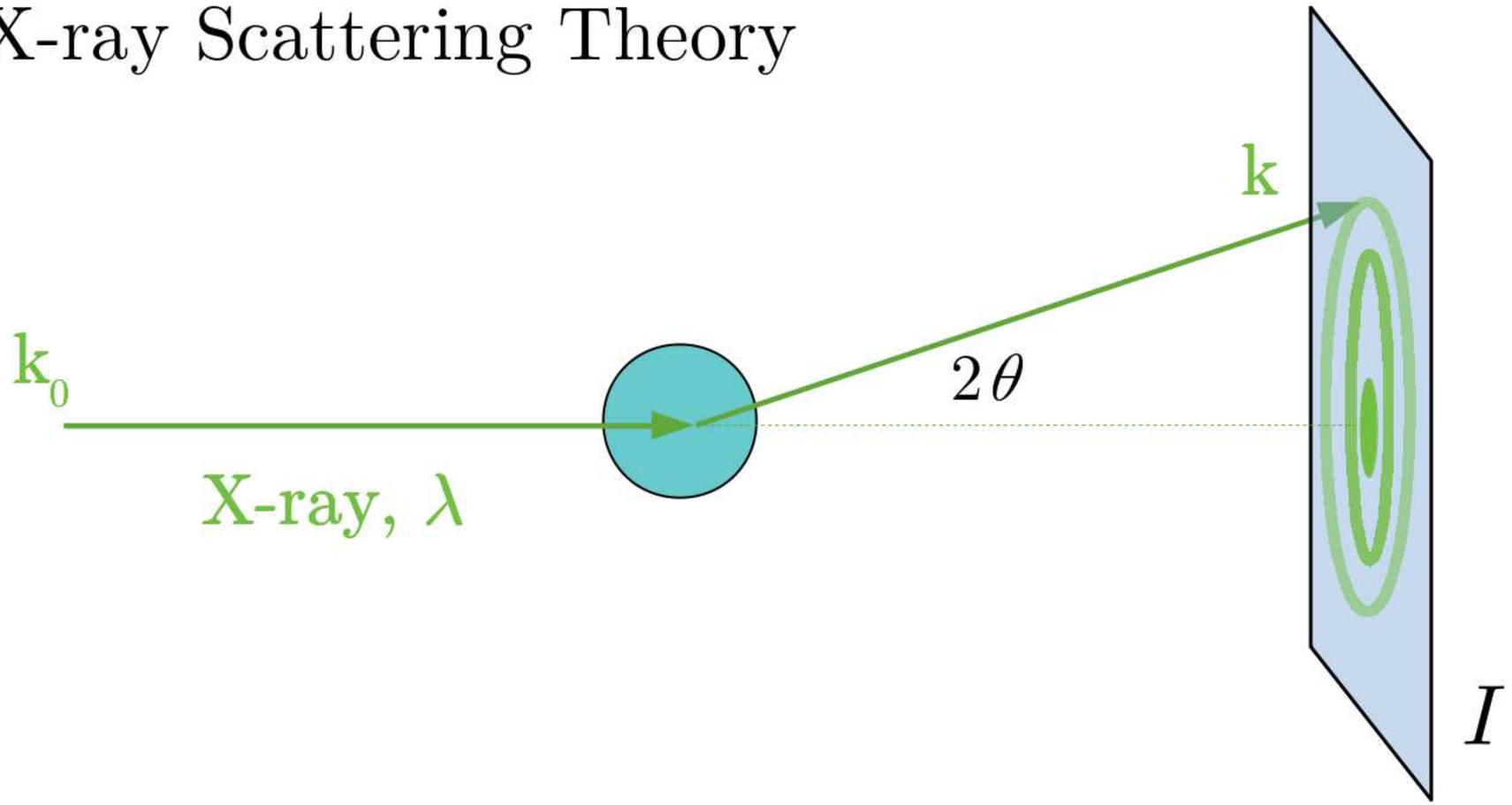
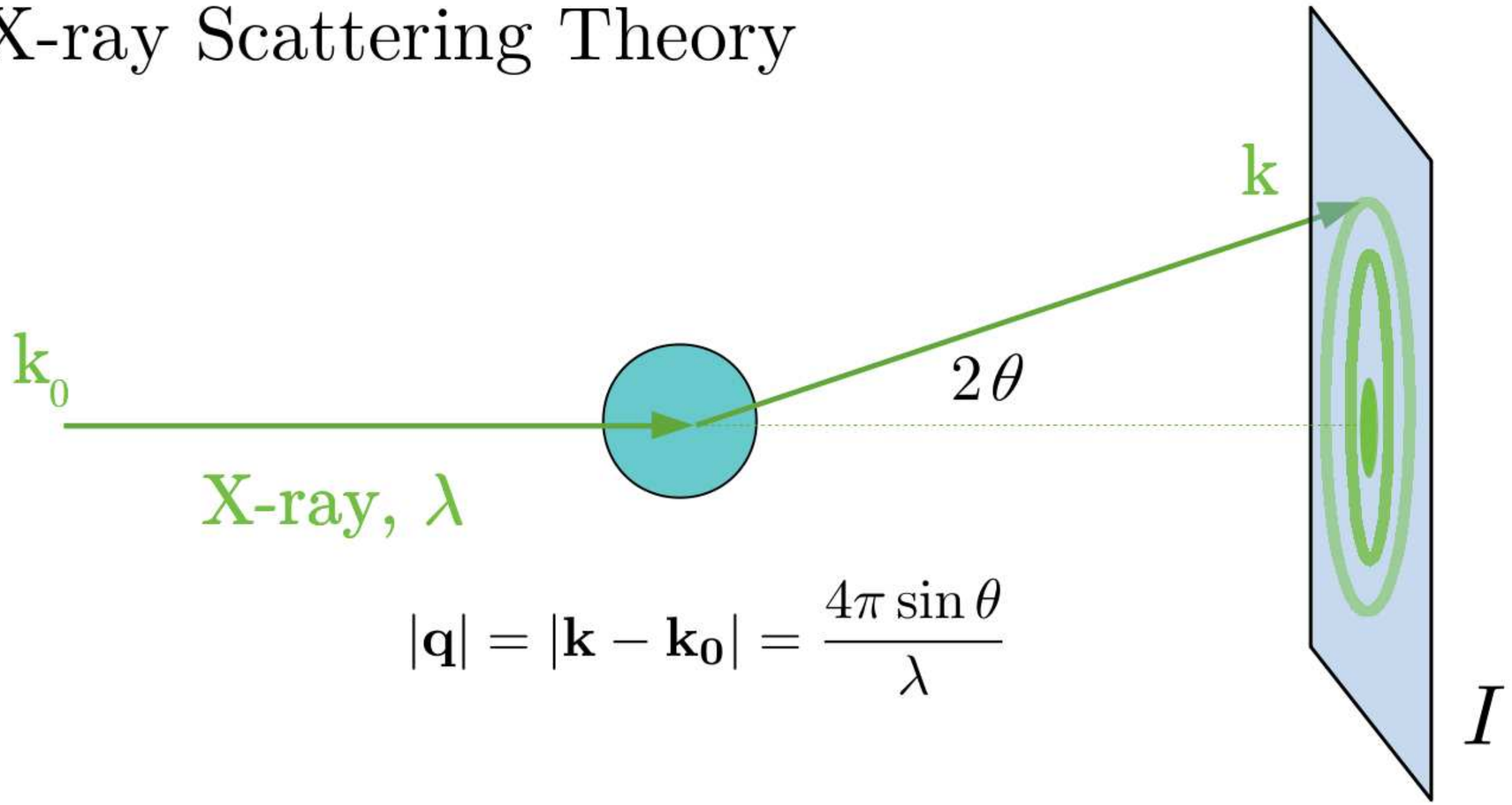
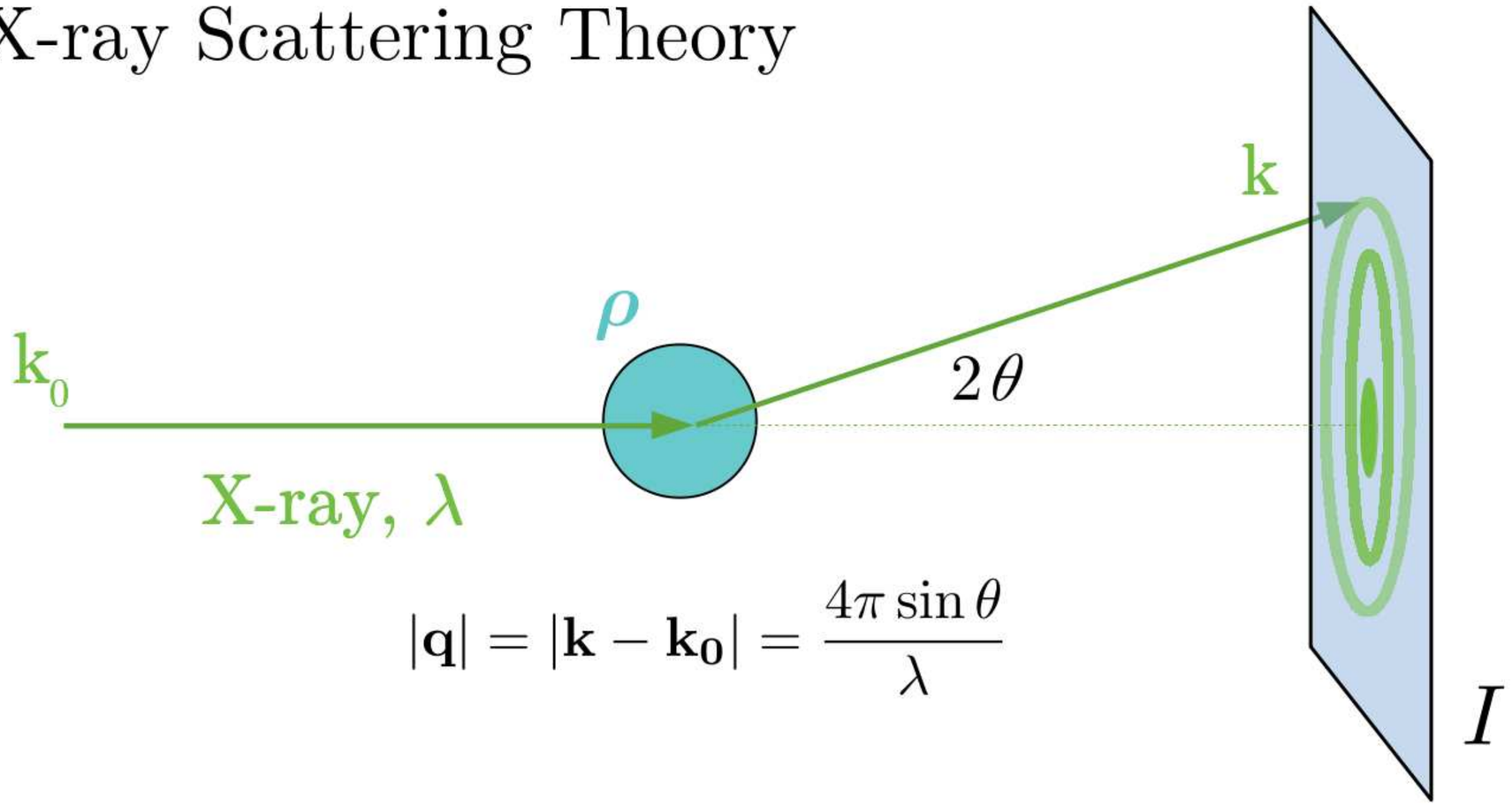


X-ray Scattering Theory



$$|\mathbf{q}| = |\mathbf{k} - \mathbf{k_0}| = \frac{4\pi \sin\theta}{\lambda}$$

X-ray Scattering Theory



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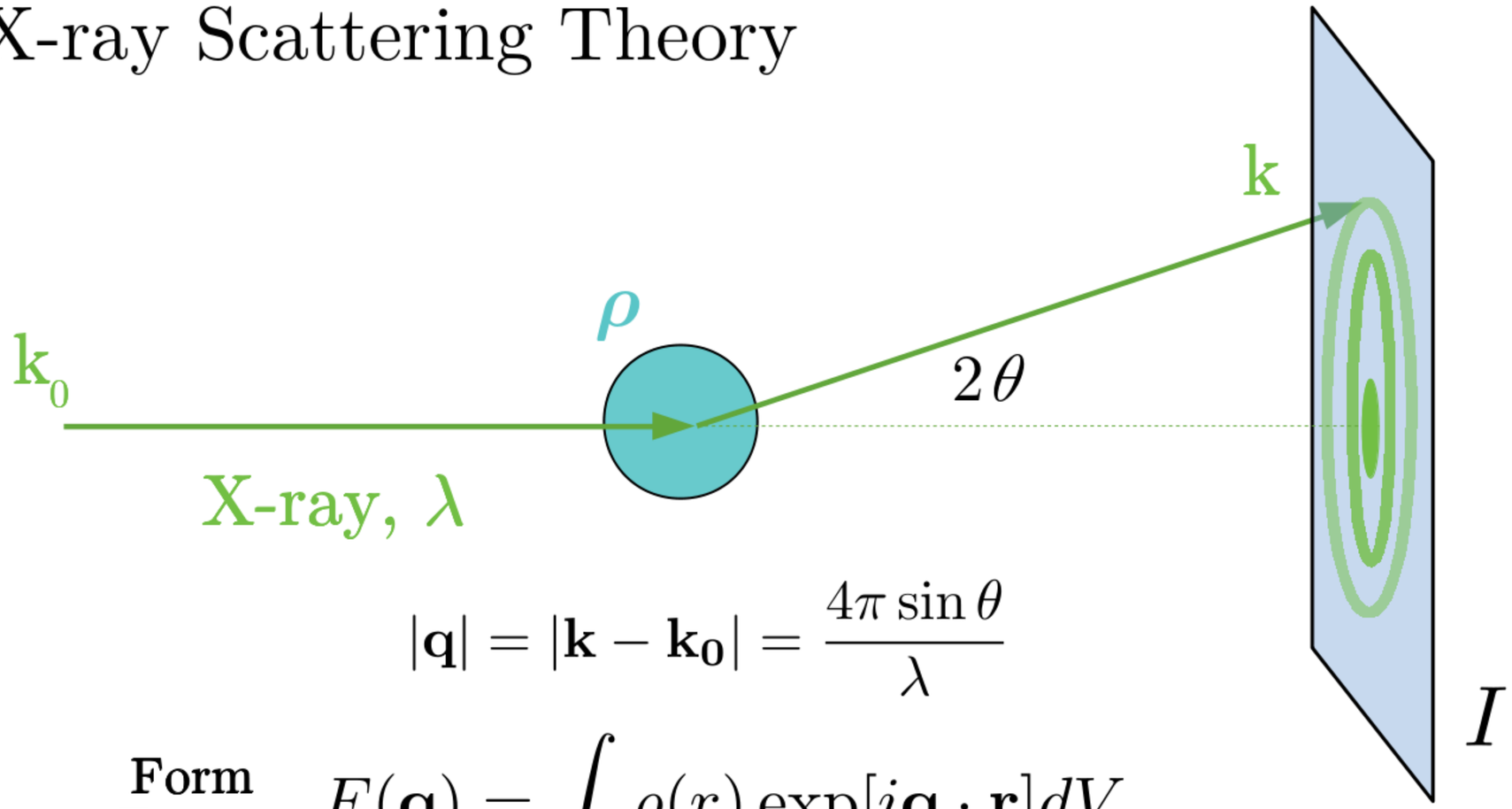
X-ray Scattering Theory



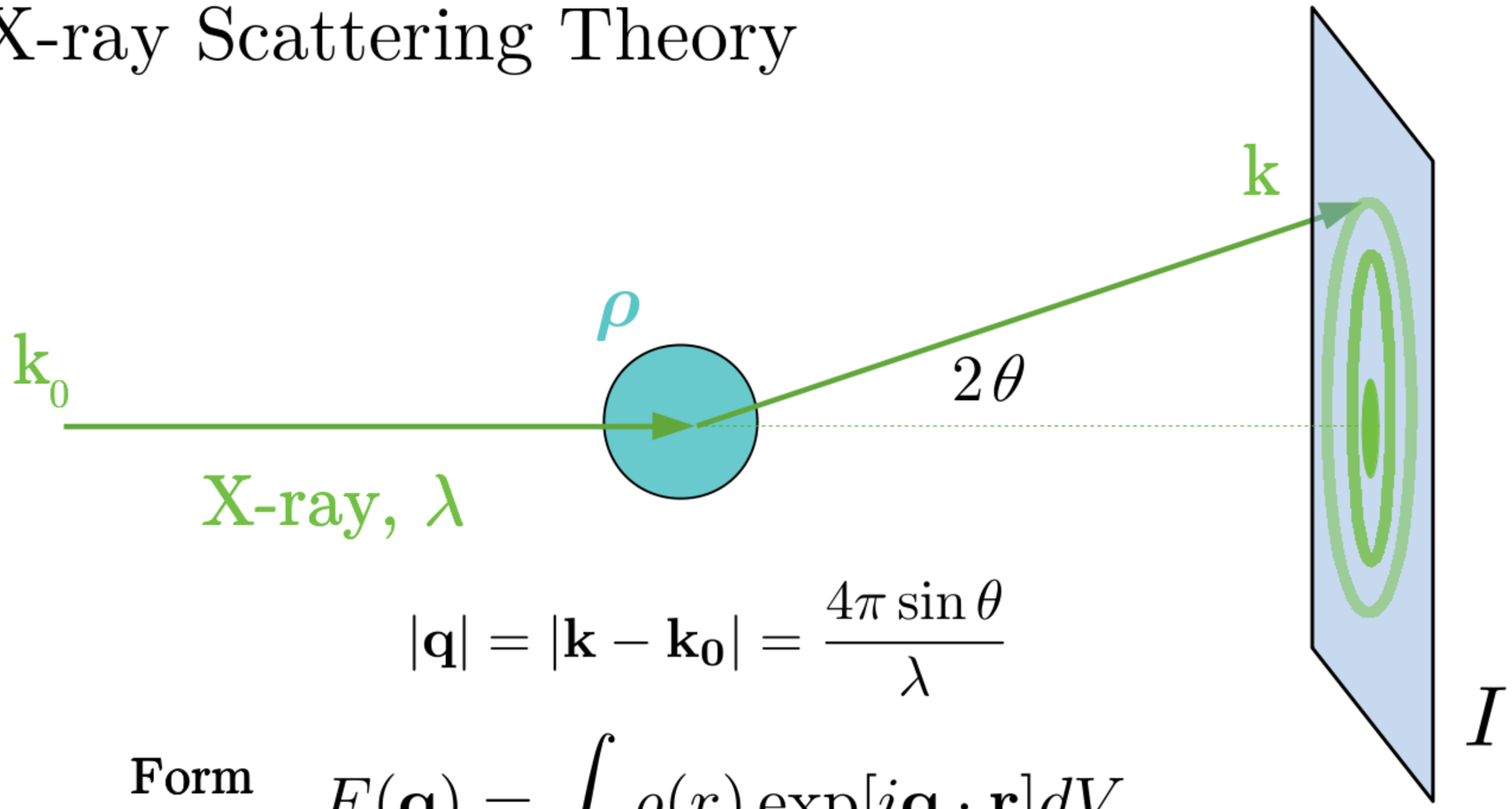
$$|\mathbf{q}| = |\mathbf{k} - \mathbf{k_0}| = \frac{4\pi \sin\theta}{\lambda}$$

Form Factor

$$F(\mathbf{q}) = \int \rho(r) \exp[i\mathbf{q} \cdot \mathbf{r}] dV$$

$$I(q) = \langle |F(\mathbf{q})|^2 \rangle_{\text{orientations}}$$

X-ray Scattering Theory



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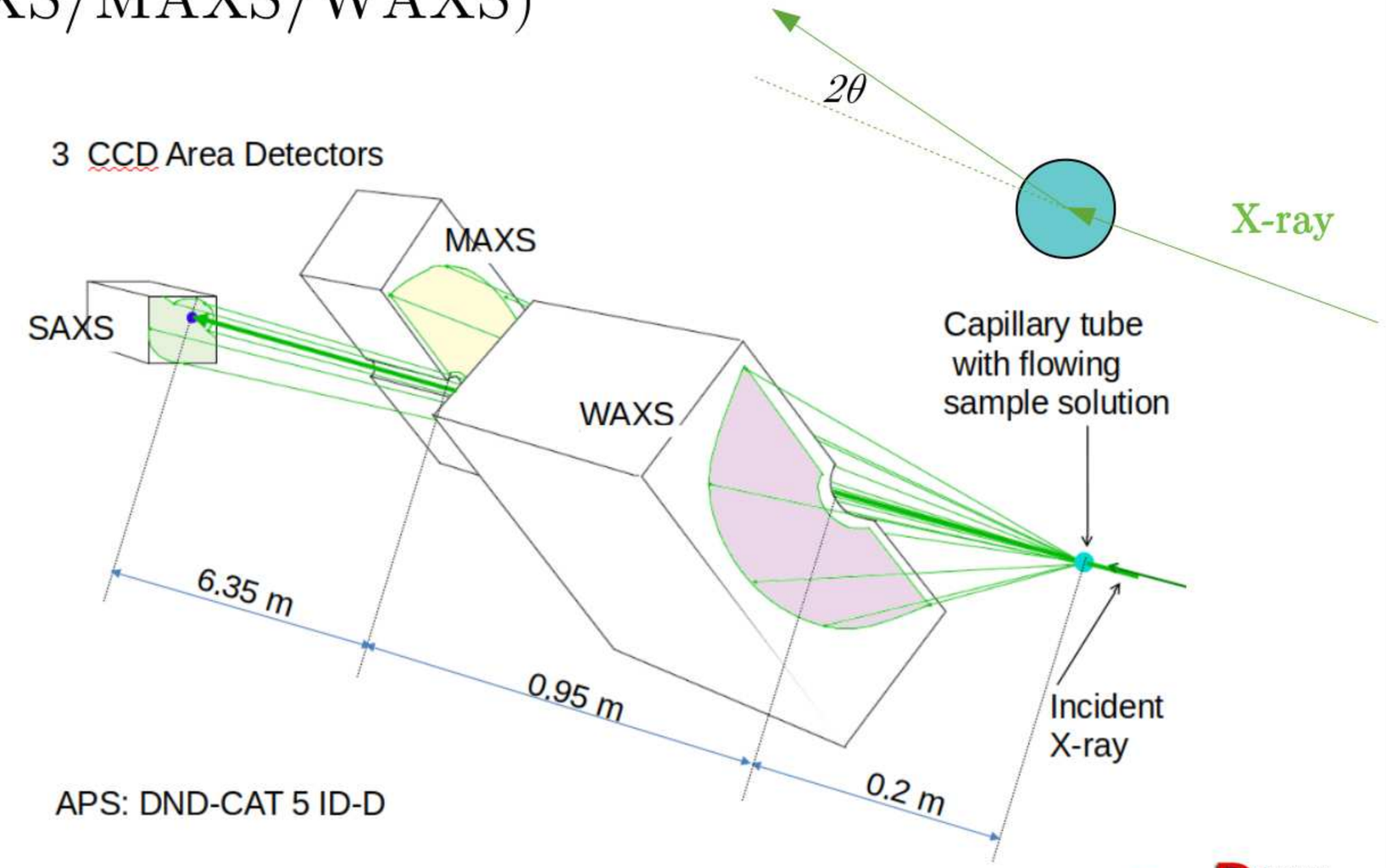
Geometry of object determines scattering profiles (*form factor*)

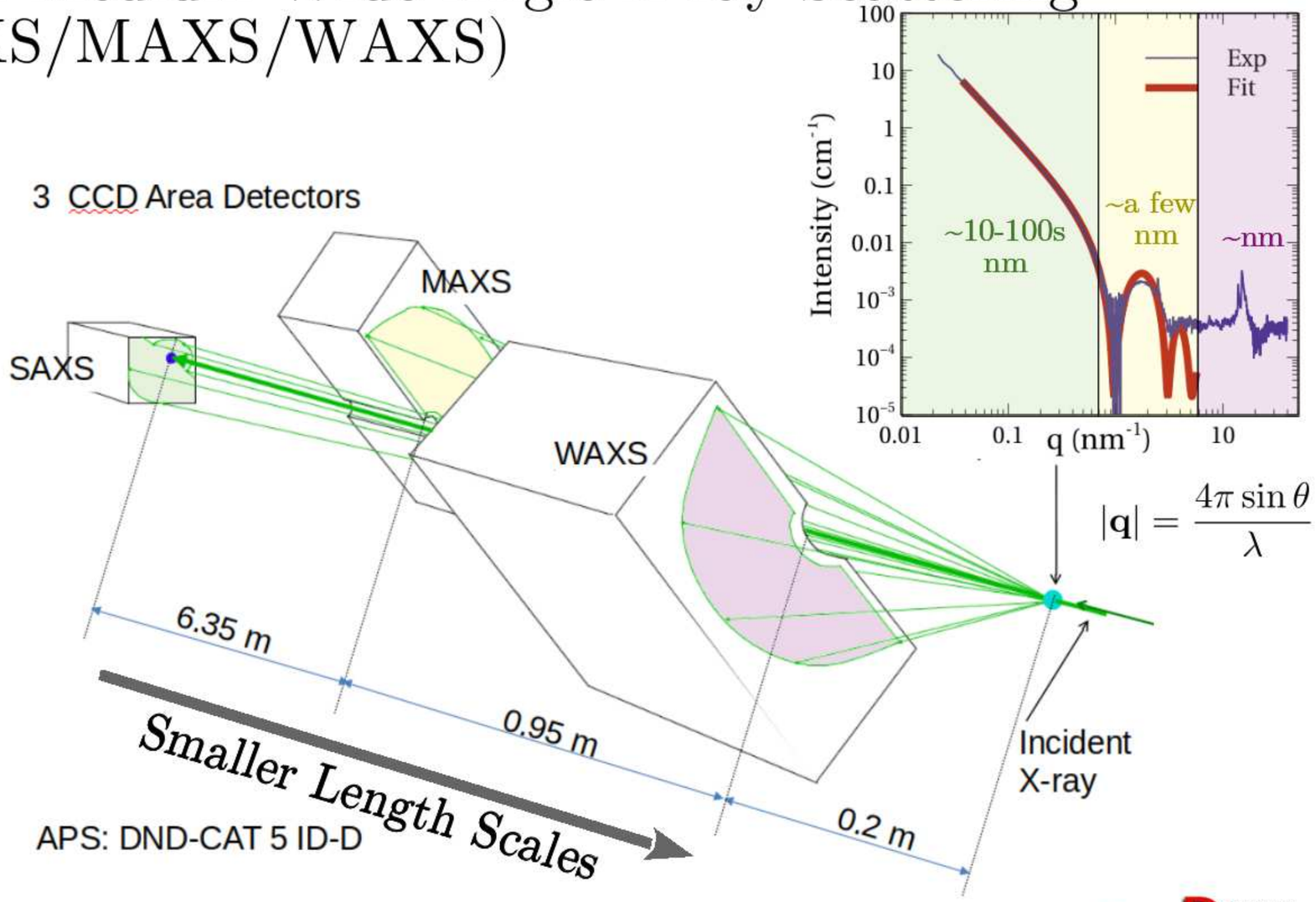
Small Medium Wide-Angle X-ray Scattering (SAXS/MAXS/WAXS)



Argonne NATIONAL LABORATORY

DND Collaborative Access Team Synchrotron Research Center

Small Medium Wide-Angle X-ray Scattering (SAXS/MAXS/WAXS)

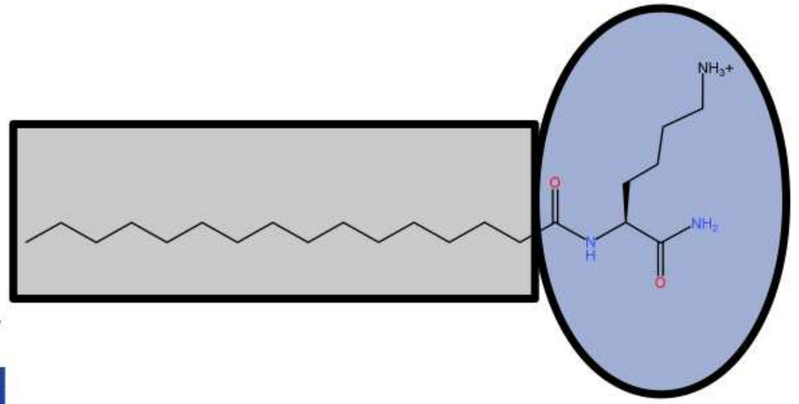


$C_{16}K$ in water

C_nK

carbon tail

lysine head



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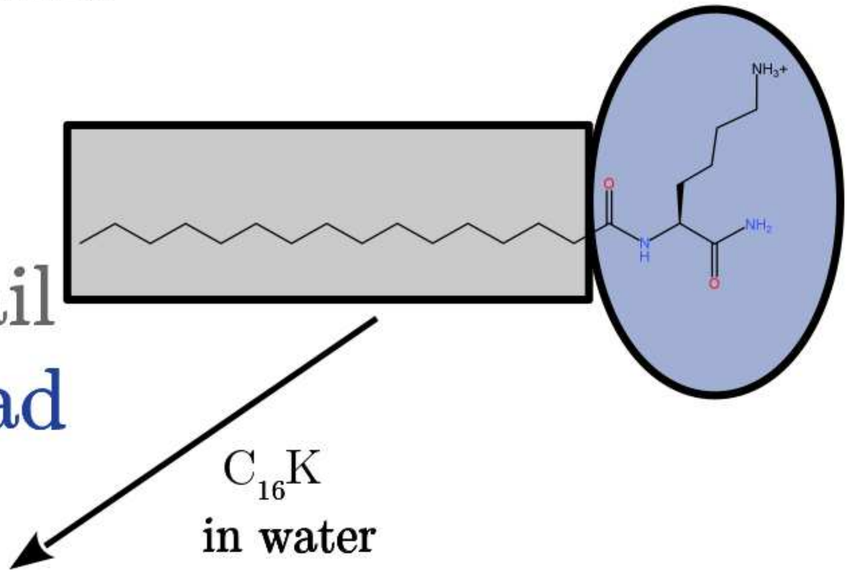

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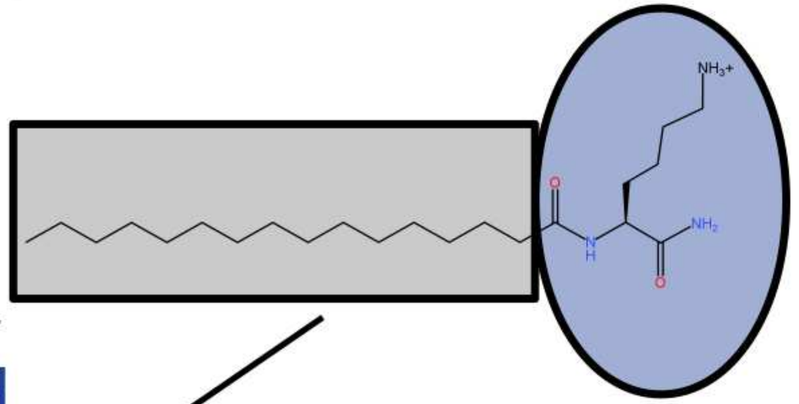
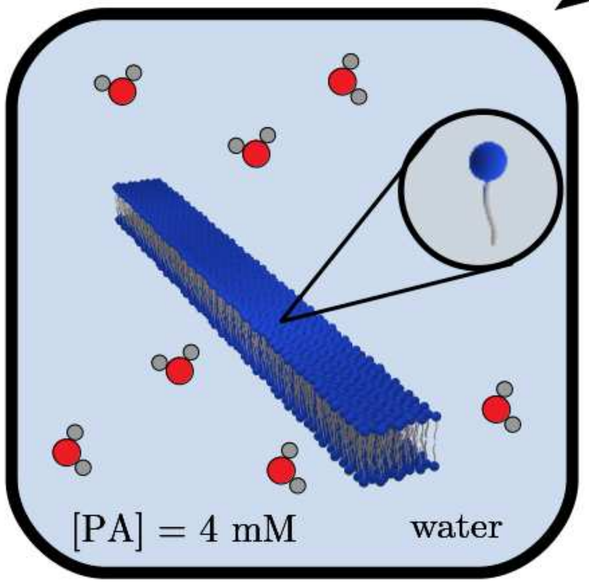
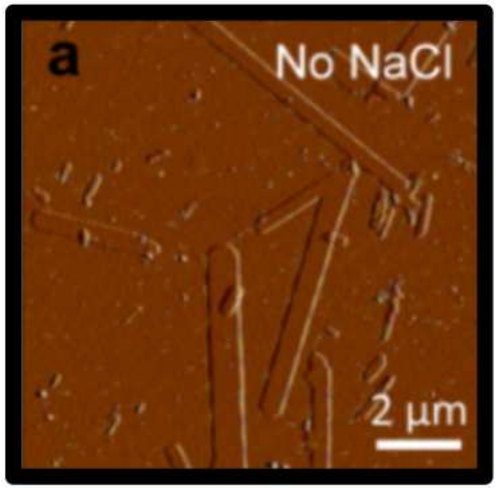


$C_{16}K$
in water





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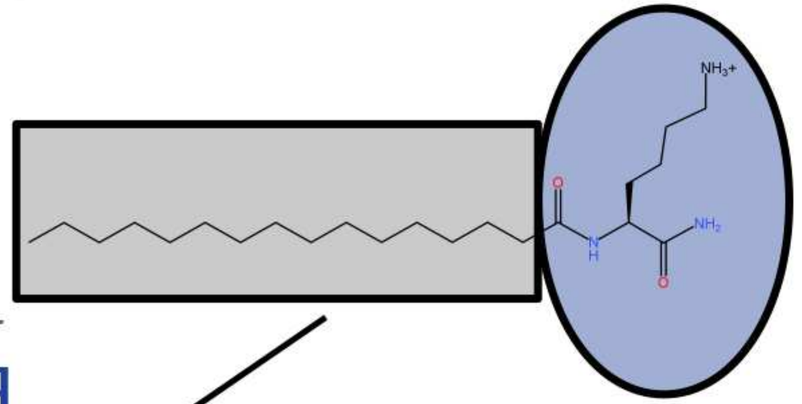

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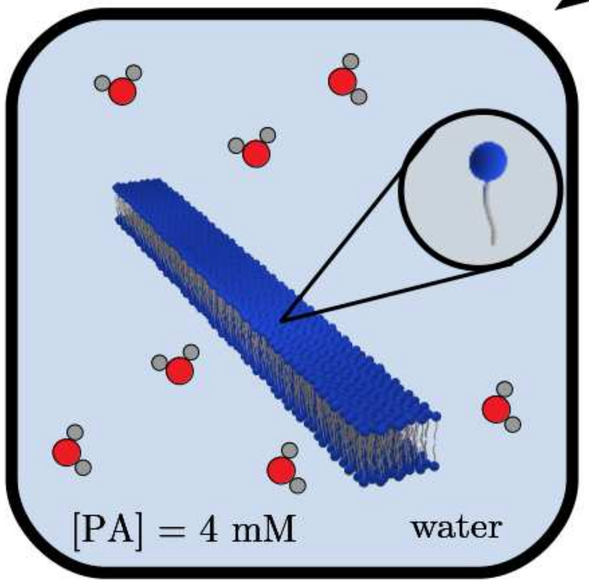

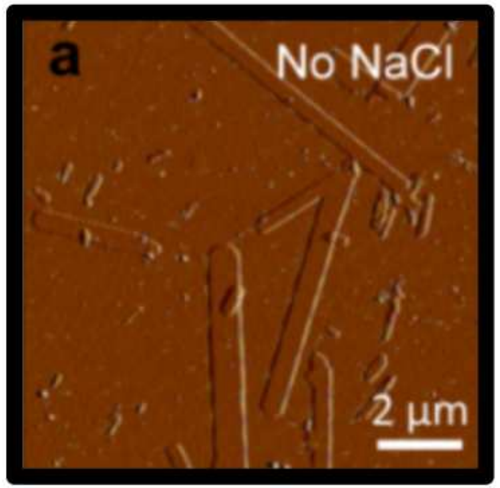

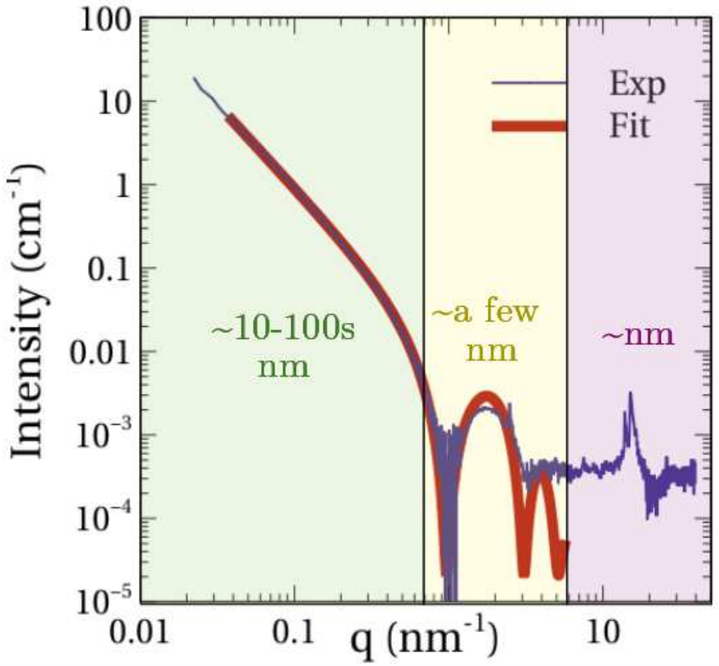

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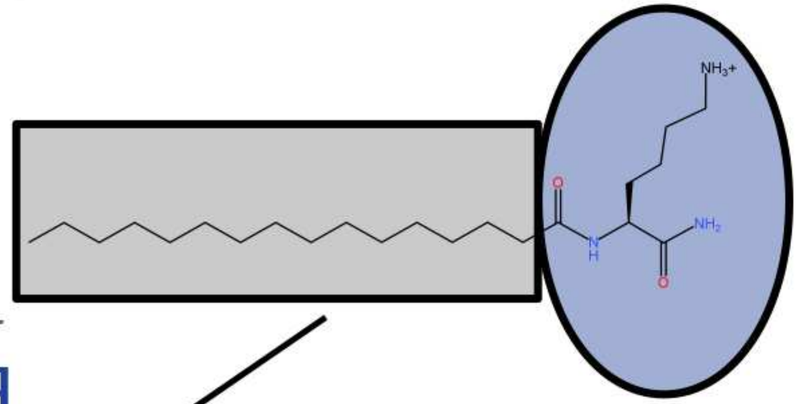

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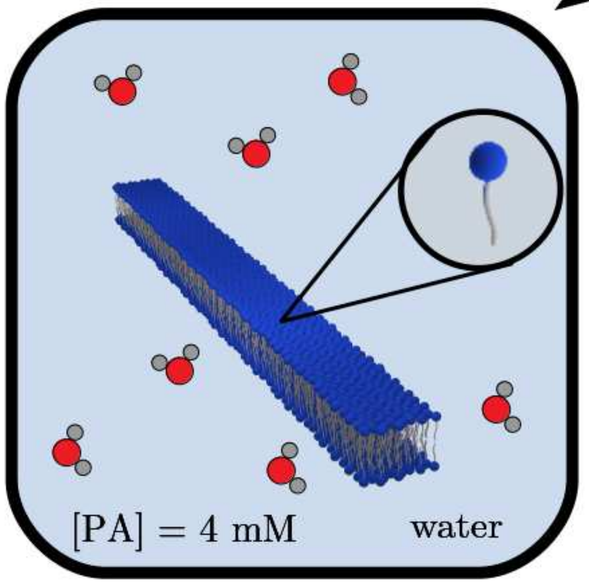
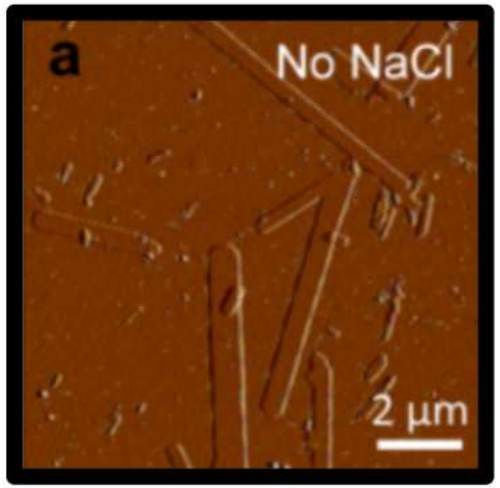
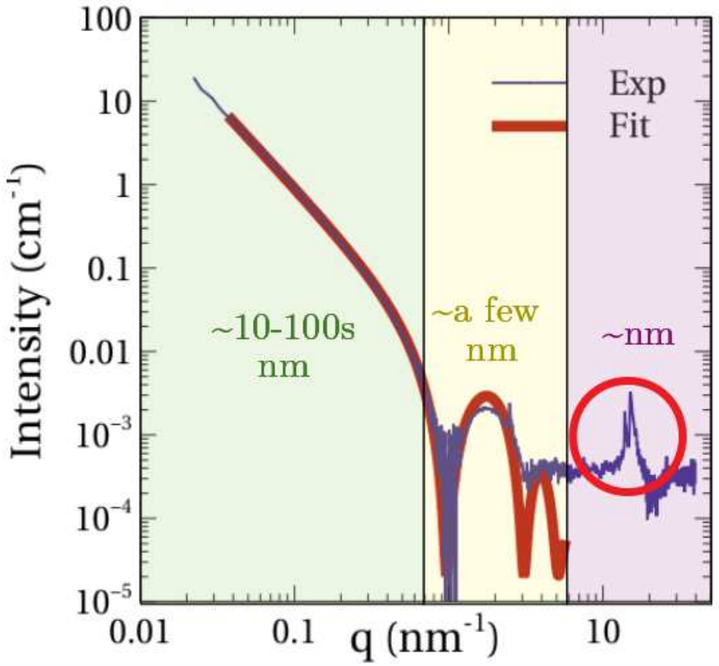
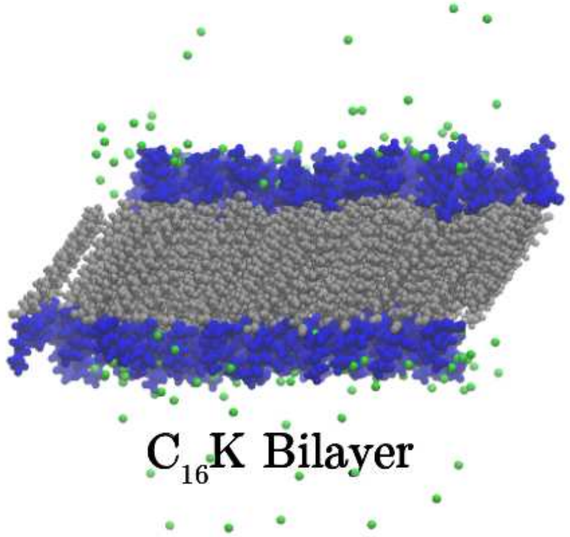




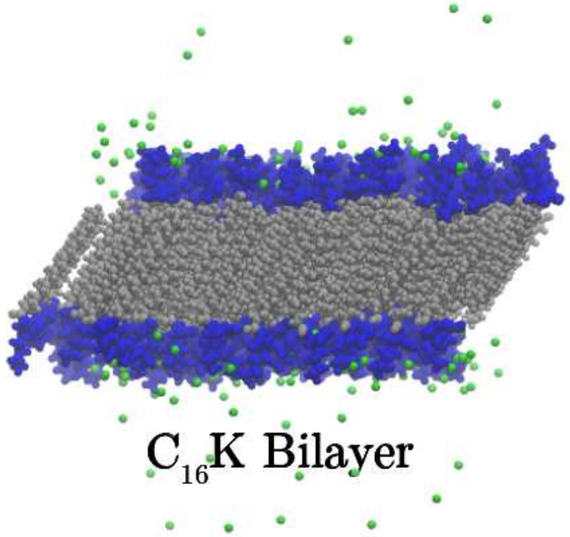


Tilt and Molecular Dynamics (MD) Simulations



$C_{16}K$ Bilayer

Tilt and Molecular Dynamics (MD) Simulations



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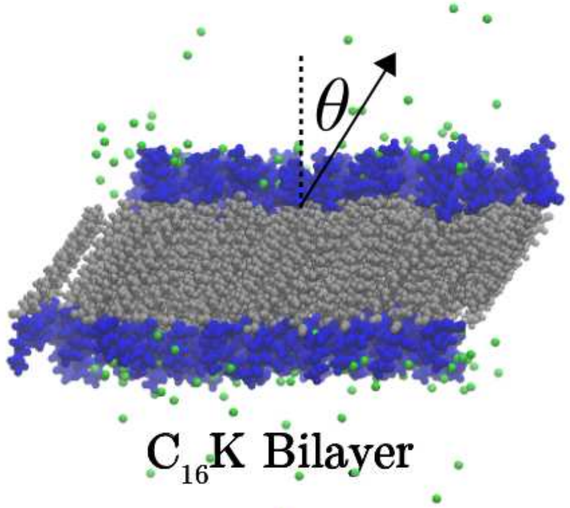
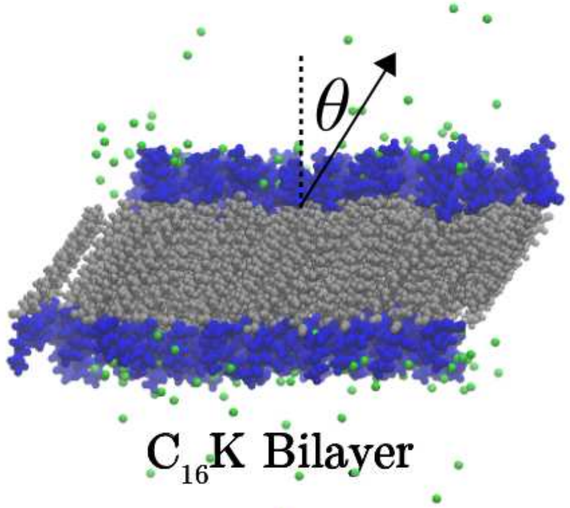


$C_{16}K$ Bilayer

$\theta \simeq 40°$

Tilt and Molecular Dynamics (MD) Simulations



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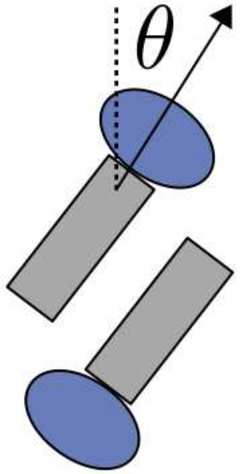

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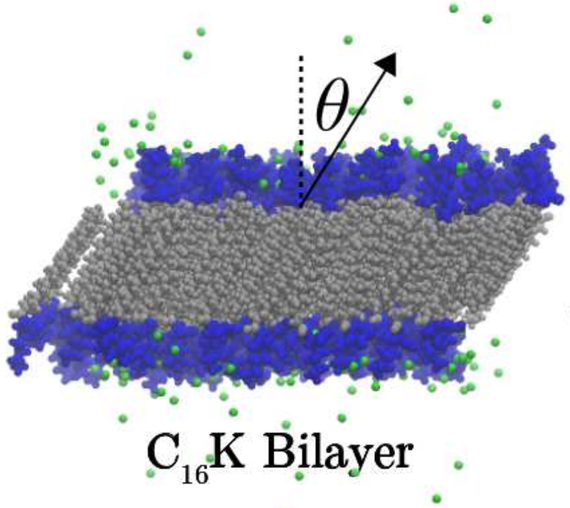

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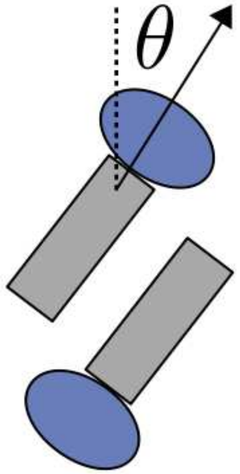
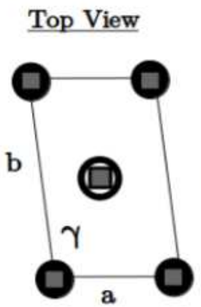
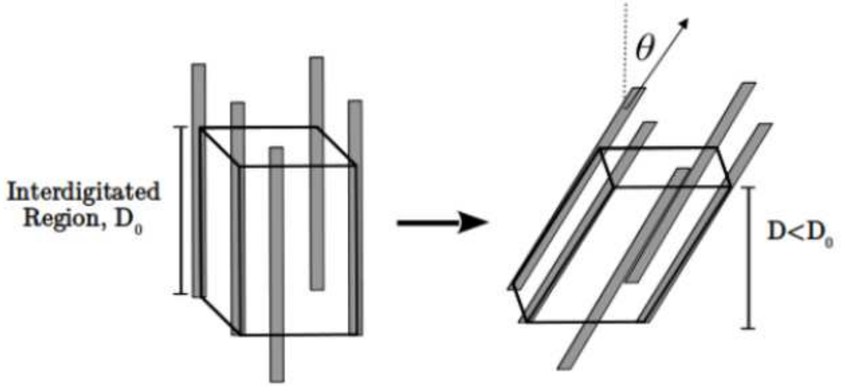




a = 0.494 nm
b = 0.851 nm
γ = 100°



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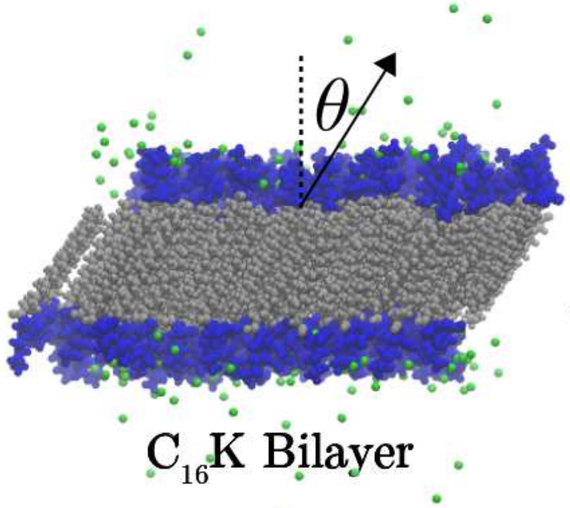

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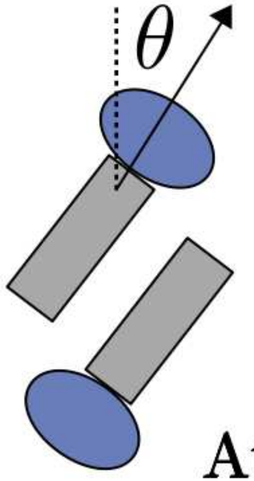
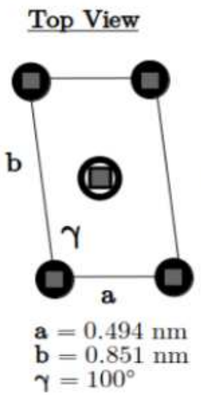
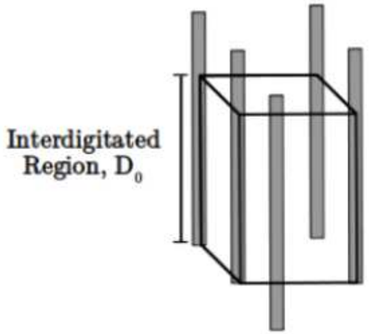
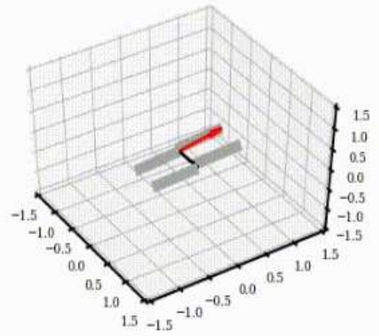
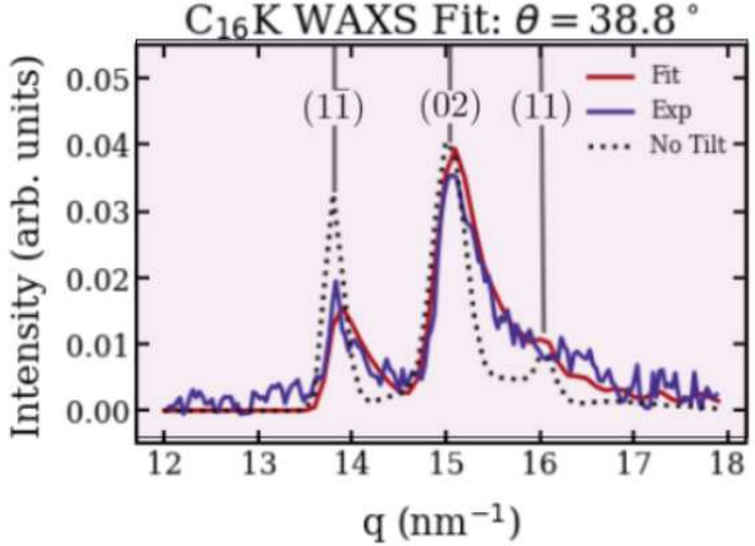






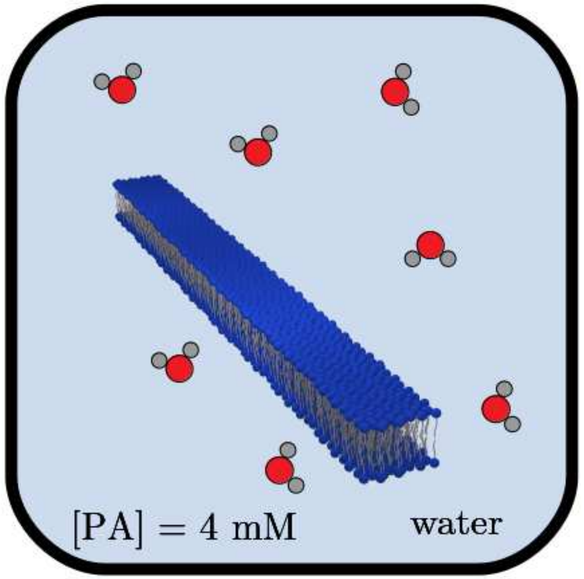


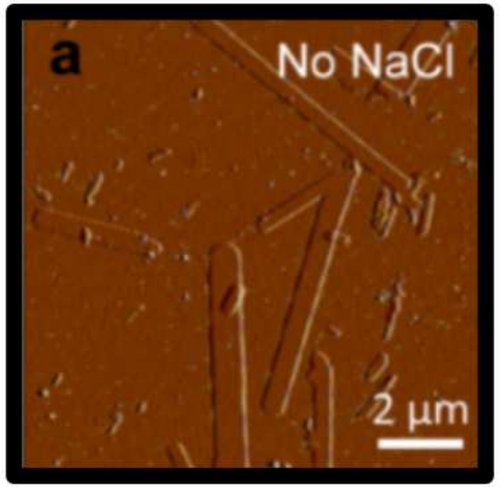


Atomistic MD simulations in conjunction with SAXS reveal *tilt order*

McCourt et al., *ACS Central Science*, **2022**, 8, 8, 1169–1181
Harutyunyan et al., *J. Phys. Chem. C.*, **2017**, 121, 1047–1054

$C_{16}K$, Ribbon to Sheet with Added NaCl





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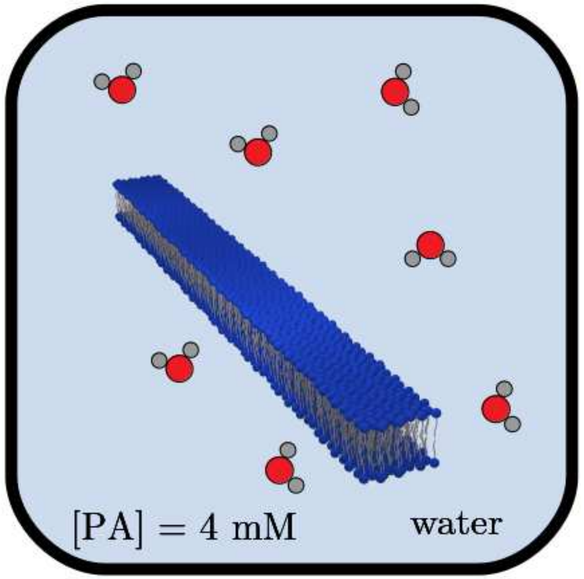
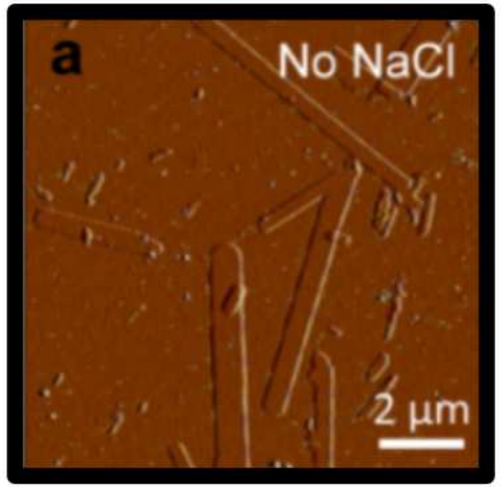
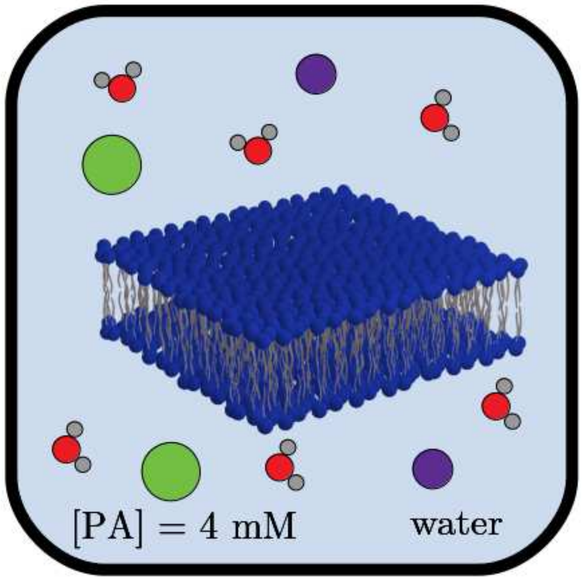
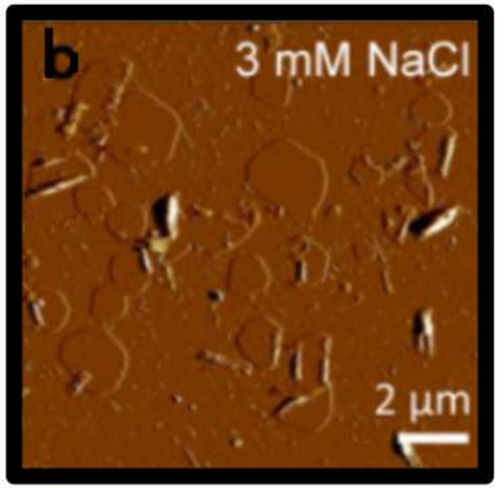
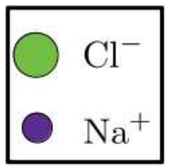








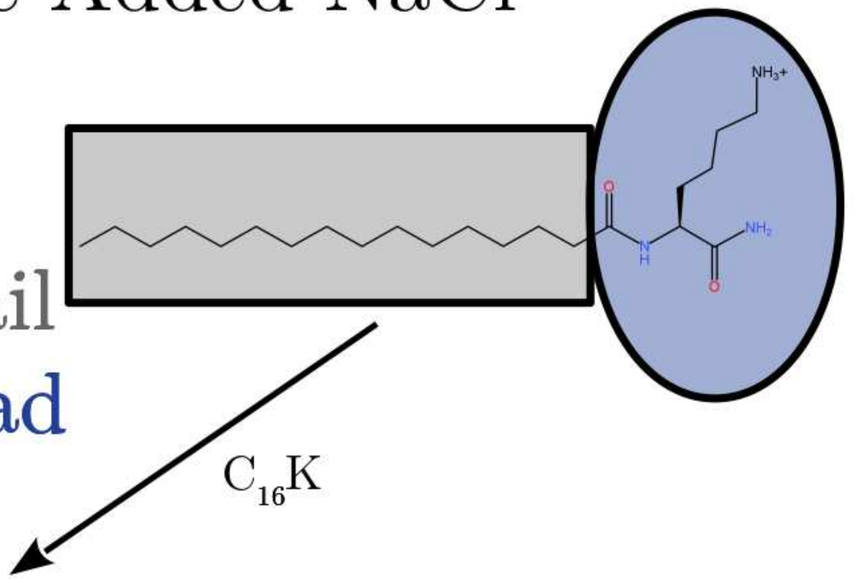


With More Added NaCl

C_nK

carbon tail

lysine head



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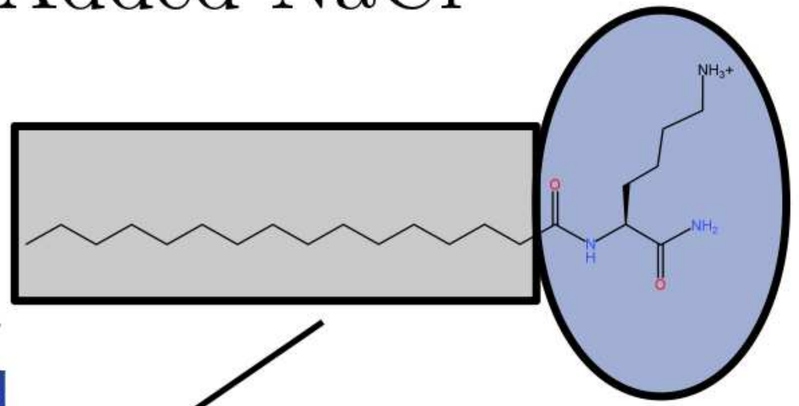

$C_{16}K$

Add More NaCl

With More Added NaCl

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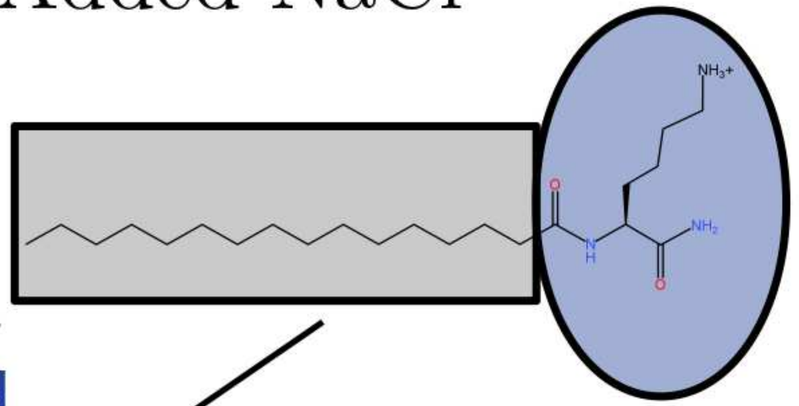
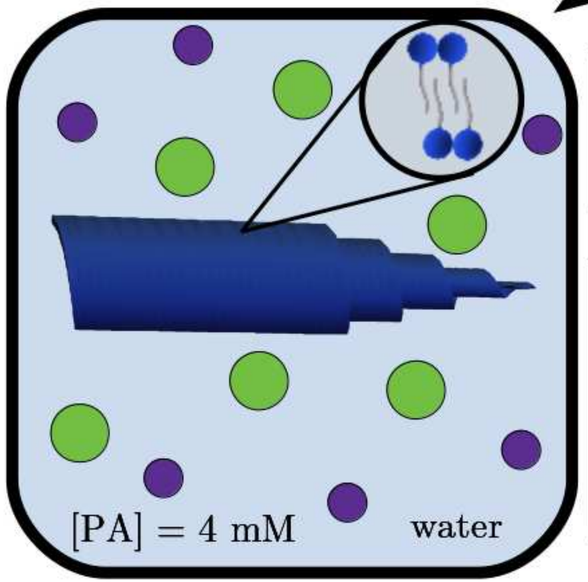
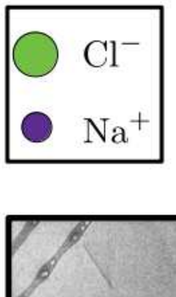
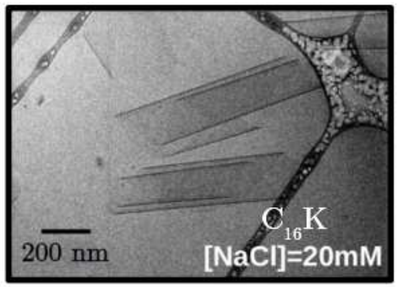


$C_{16}K$

Add More NaCl







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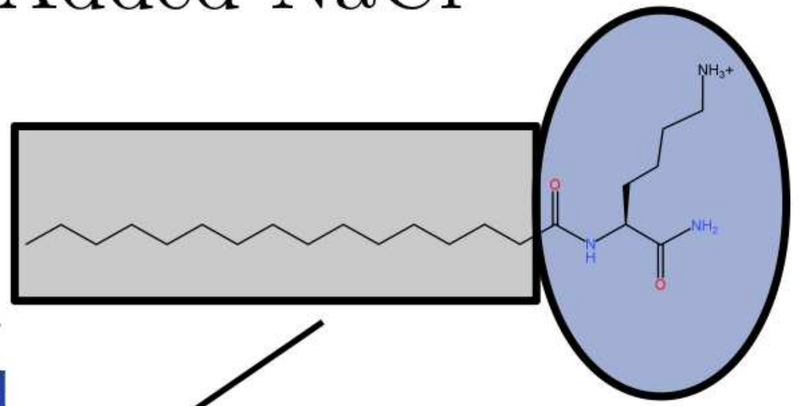

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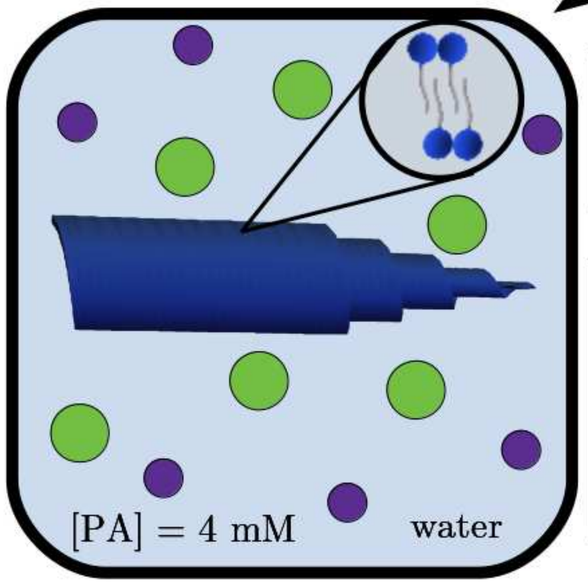
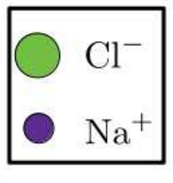
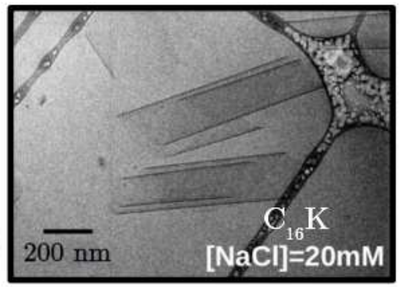
Add More NaCl





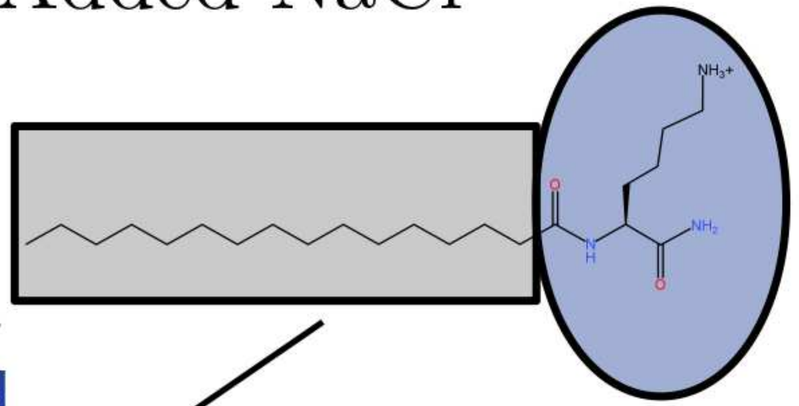


With More Added NaCl

C_nK

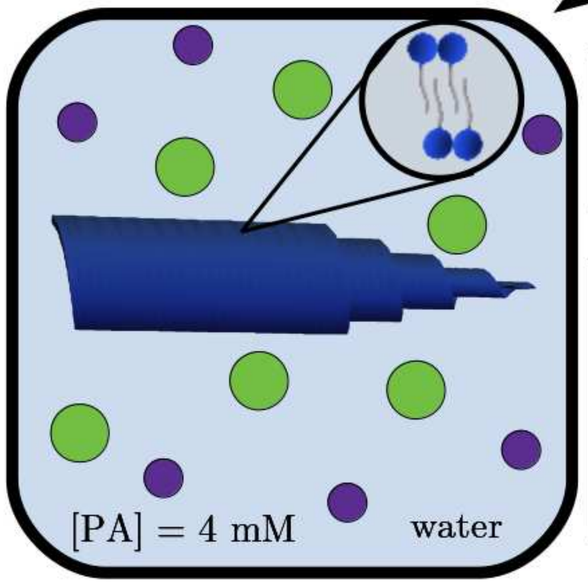
carbon tail

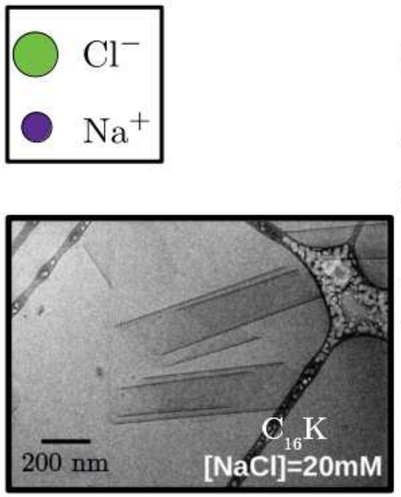
lysine head



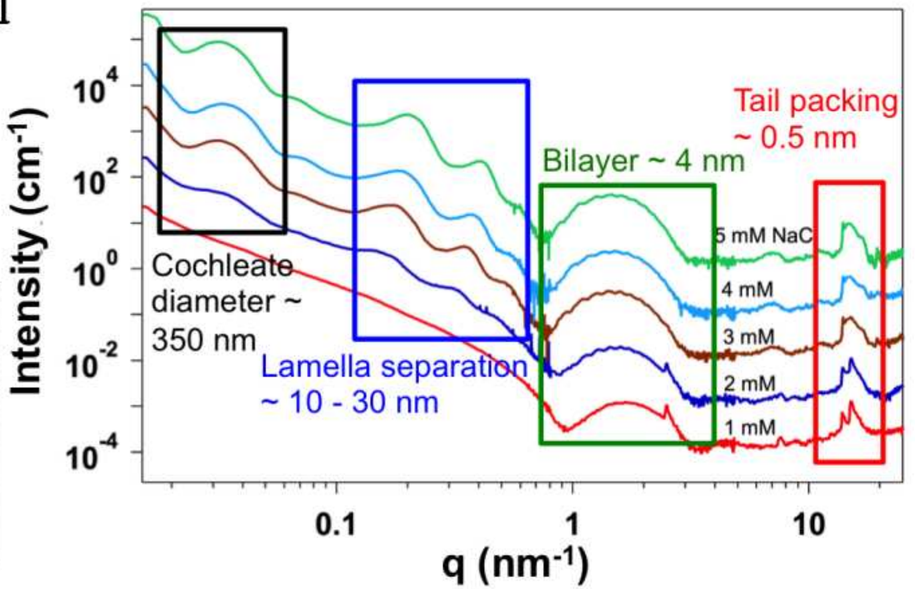
$C_{16}K$

Add More NaCl



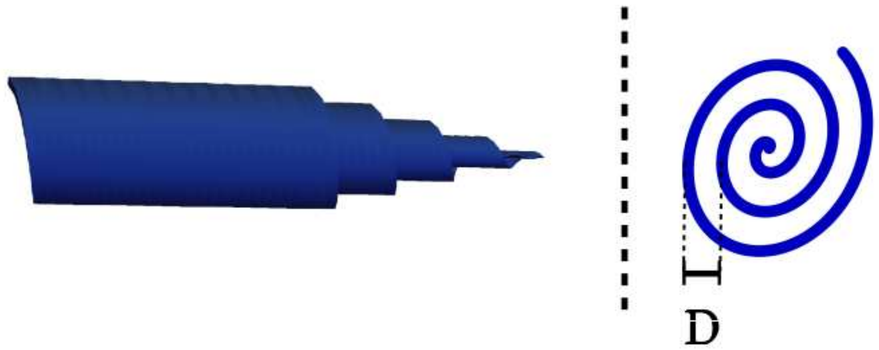


Scroll-like/Cochleate

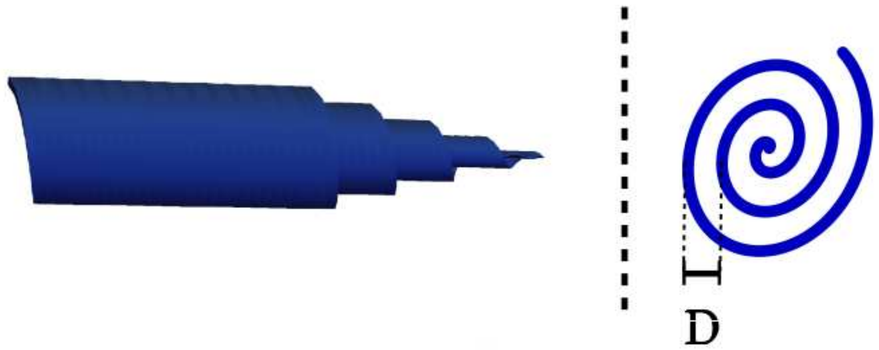


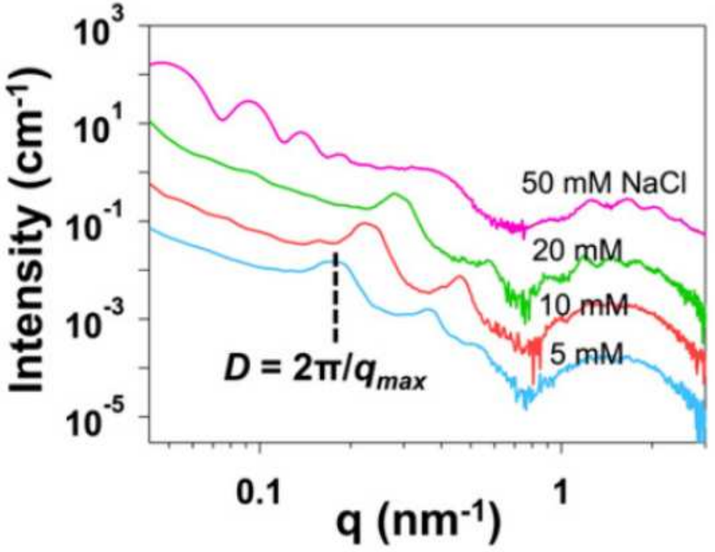
Drug Delivery Applications

Drug Delivery Applications

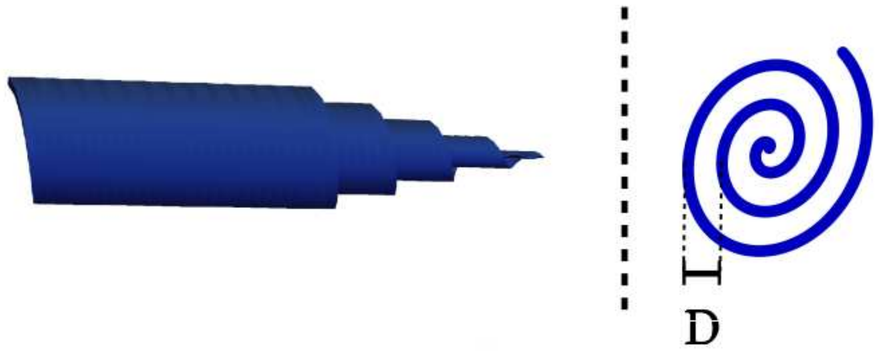


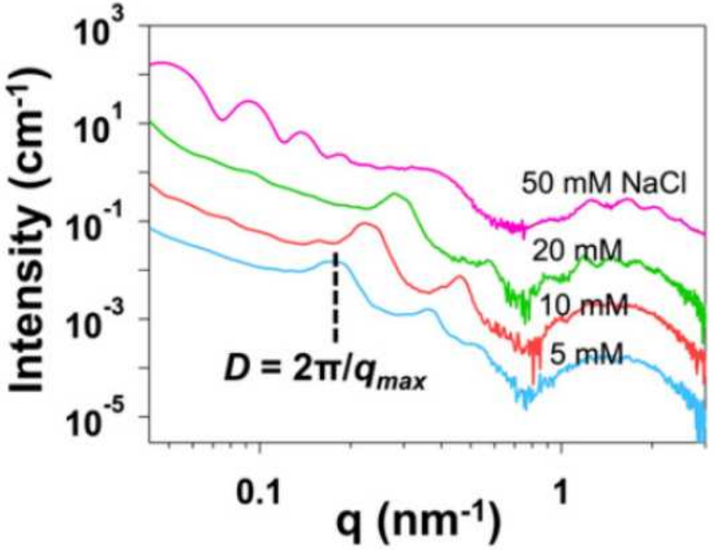
Drug Delivery Applications

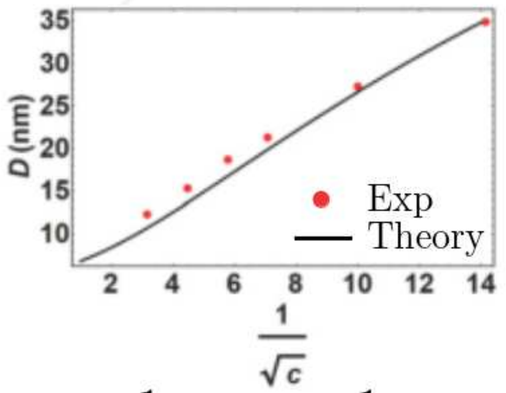




Drug Delivery Applications

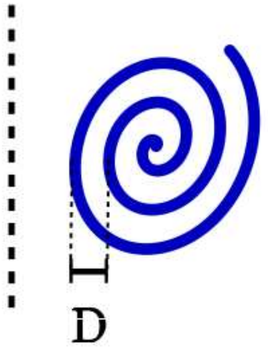


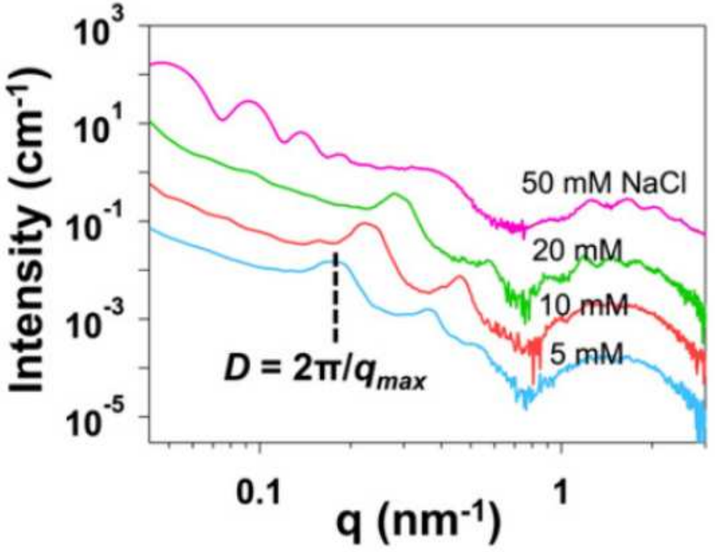


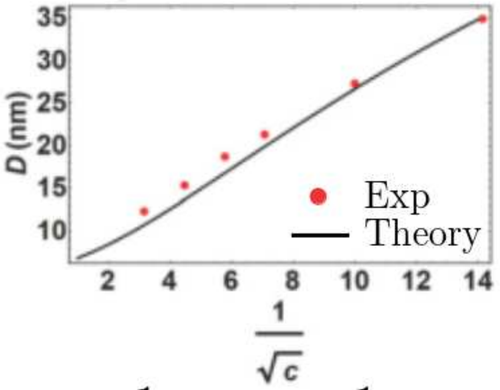


$$\frac{1}{\sqrt{c}} = \frac{1}{\sqrt{[\mathrm{NaCl}]}}$$

Drug Delivery Applications







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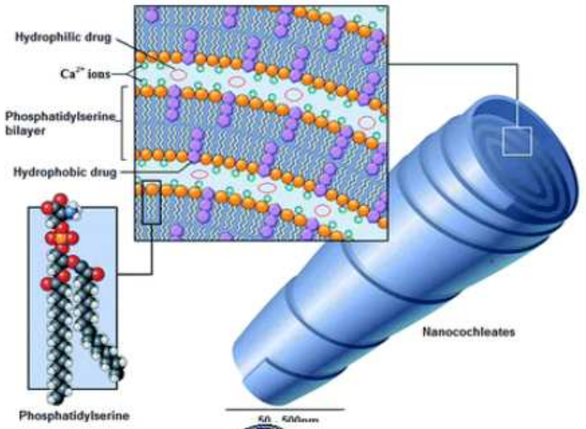
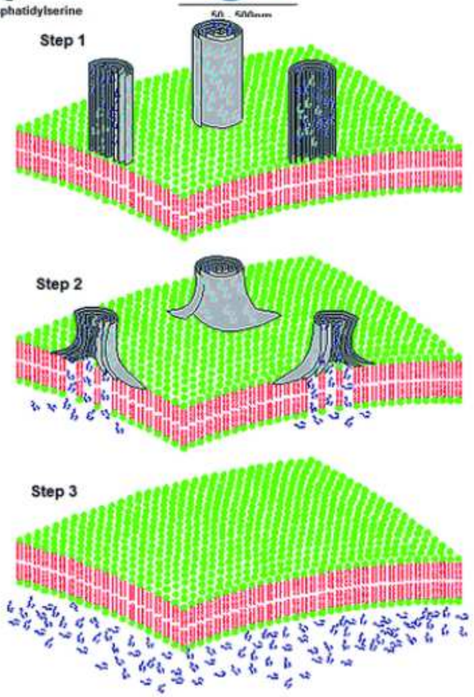
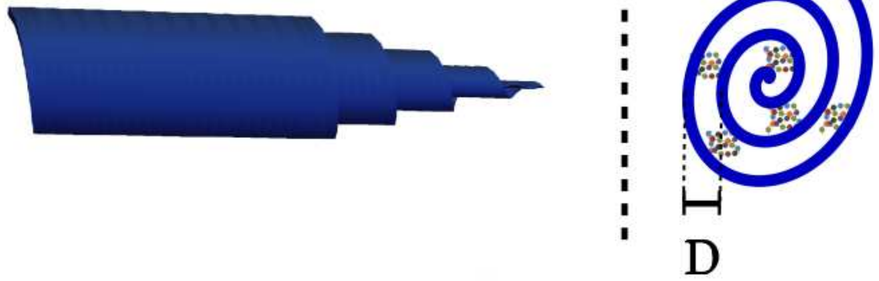
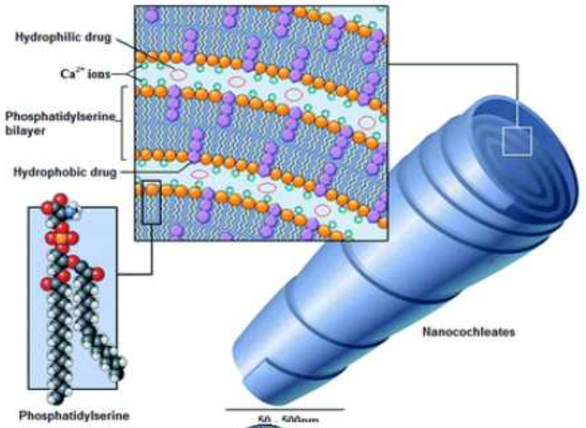
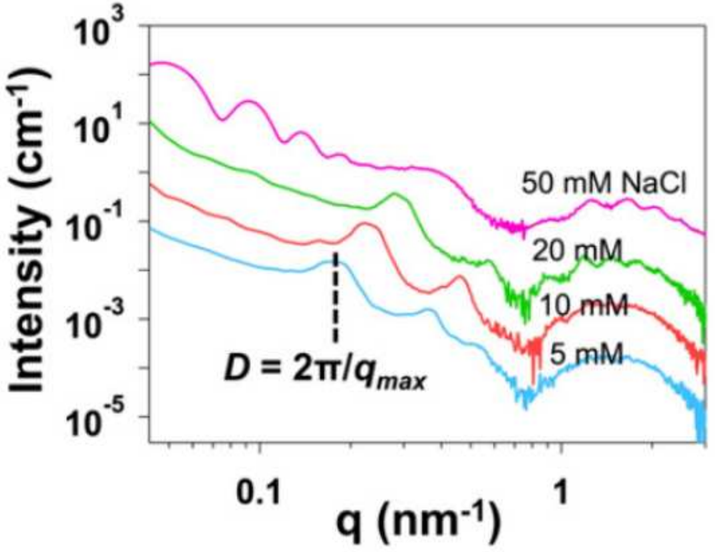


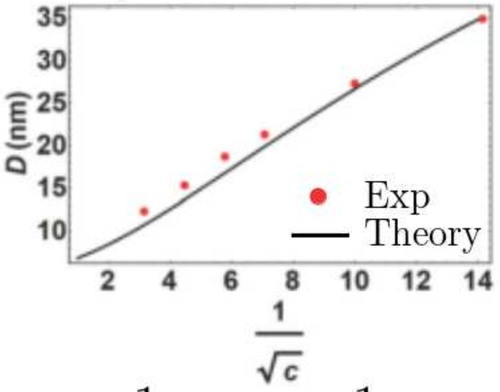


Drug Delivery Applications









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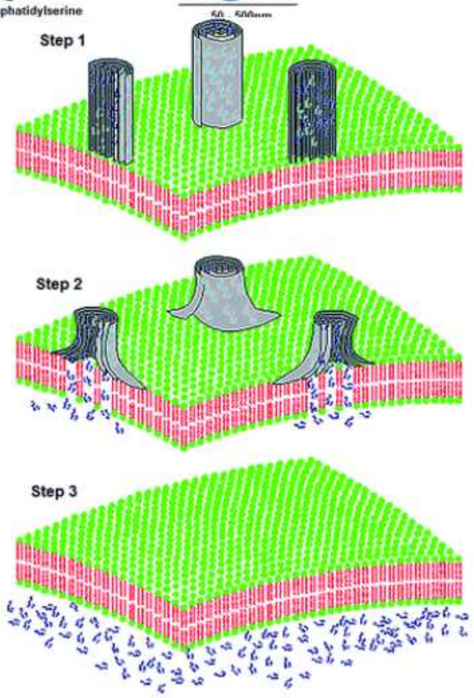
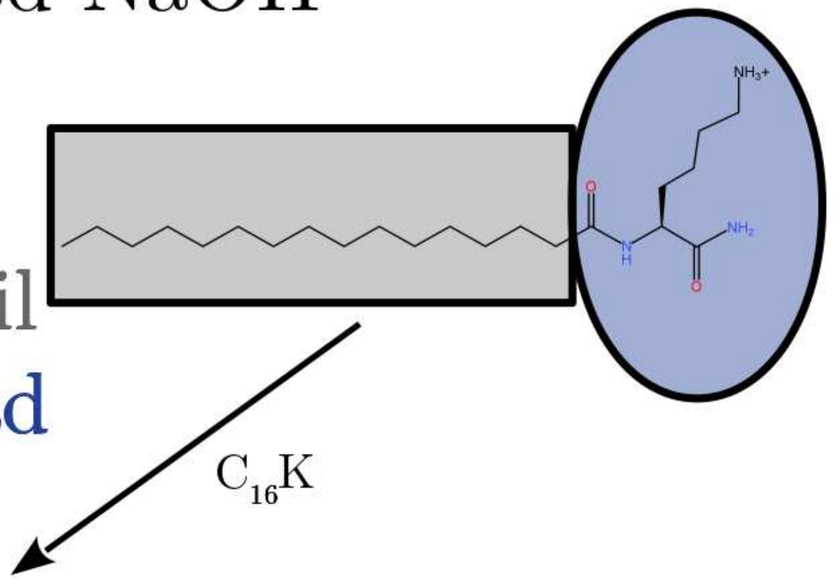


With Added NaOH

C_nK

carbon tail

lysine head

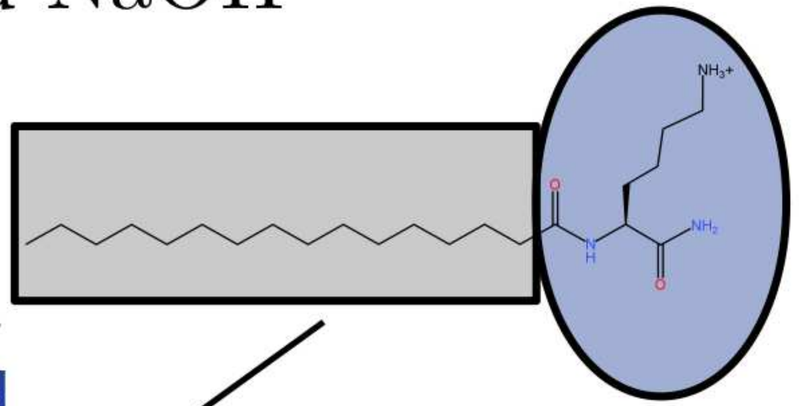


With Added NaOH

C_nK

carbon tail

lysine head



$C_{16}K$

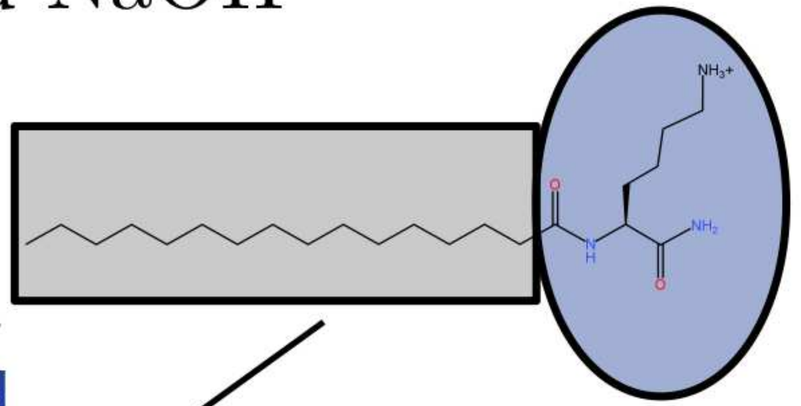
Add NaOH

With Added NaOH

C_nK

carbon tail

lysine head



$C_{16}K$

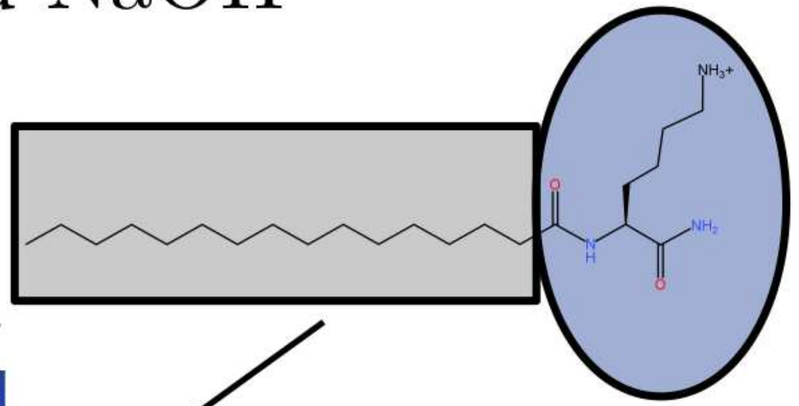
Add NaOH
(increase pH)

With Added NaOH

C_nK

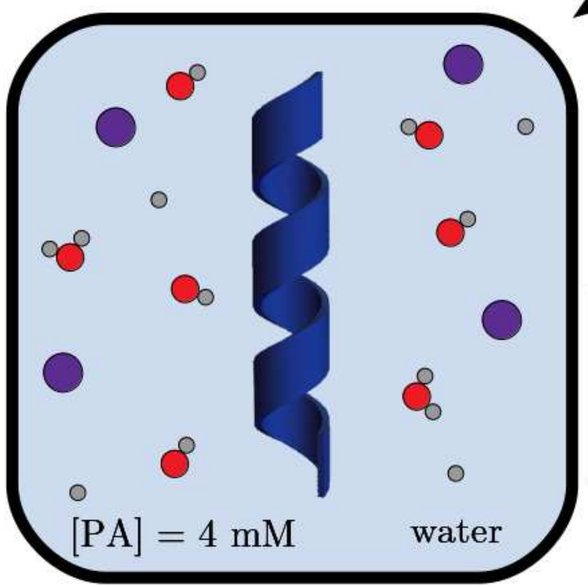
carbon tail

lysine head



$C_{16}K$

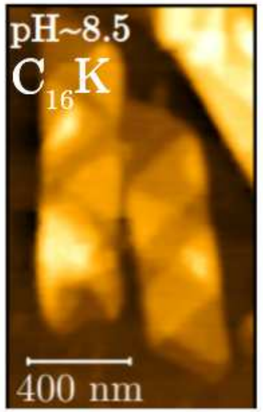
Add NaOH (increase pH)



H^+

OH^-

Na^+

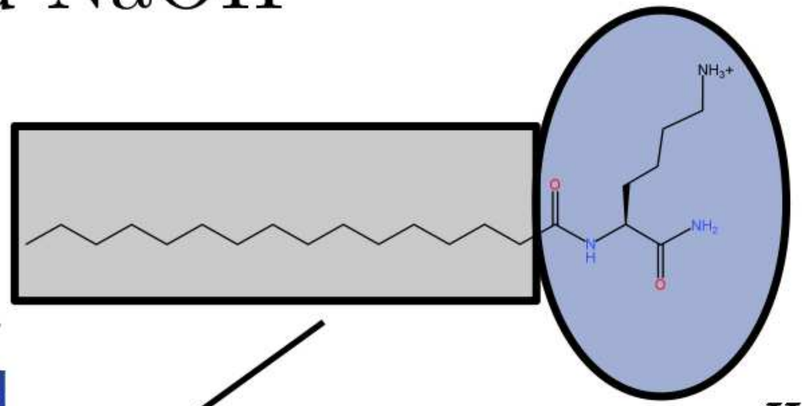


With Added NaOH

C_nK

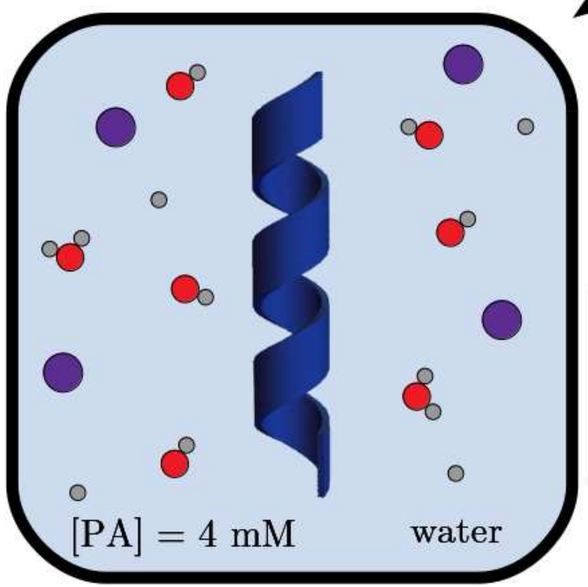
carbon tail

lysine head



$C_{16}K$

Add NaOH (increase pH)



H^+

OH^-

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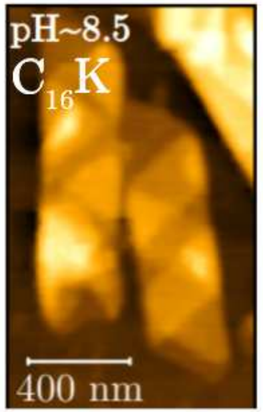
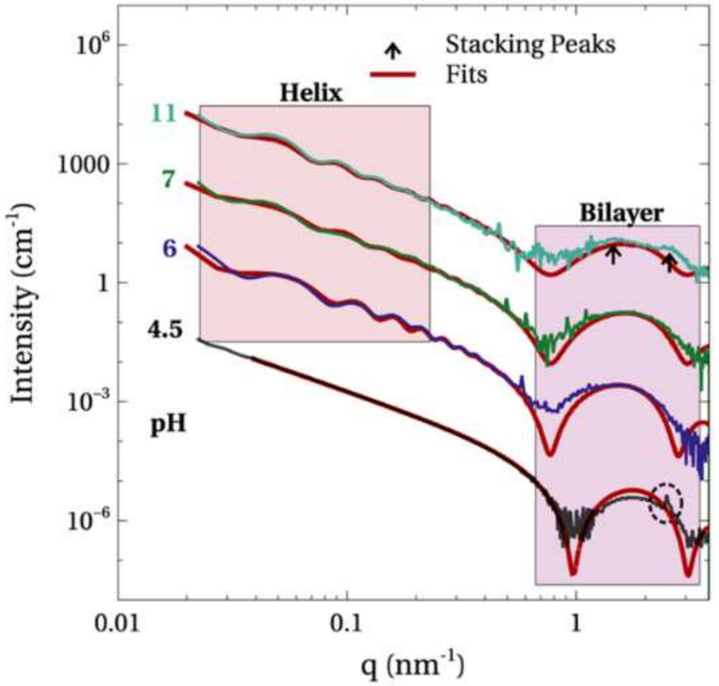


Helical Ribbon



Templated Materials

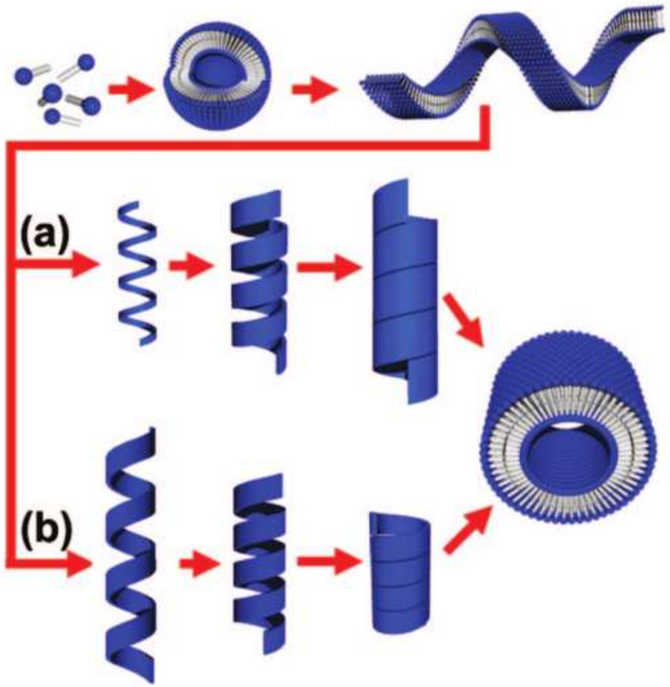
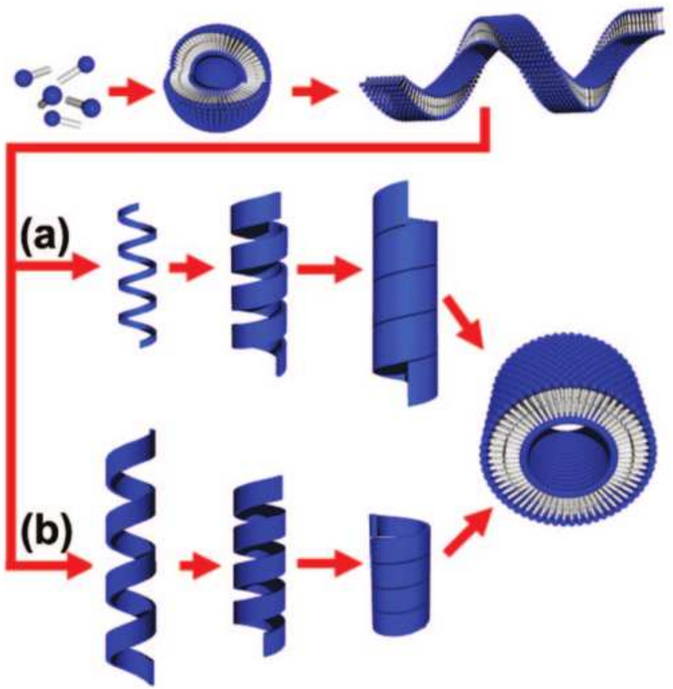


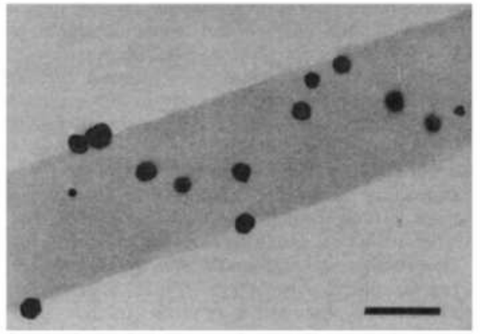
Table 1. LNT Templating and the Location for Diverse 1-D Nanostructures with Potential Applications

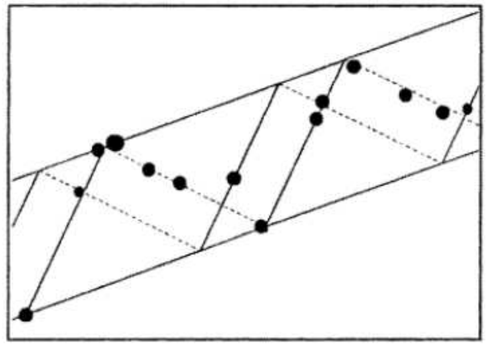
chemical phenomena	location of occurrence	templated materials	applications
1. surface modification	outer and inner surfaces	Cu,[31–33,39a] Ni,[31–33,39b] Au,[36,41,43] Ag,[40] ZnS[42]	controlled release, sensor, nanocircuit, etc.
2. sol–gel reaction	outer and inner surfaces	aluminum carbonate,[44] silica,[45,48–50,53,58] Fe_3O_4,[46] silicate clay,[47] TiO_2,[51,52b] Ta_2O_5,[51] V_2O_5[51]	photocatalysis, reinforcement of materials, etc.
3. crystallization and deposition	bilayer membrane walls	CdS,[54] Pt[57]	fluorescence tracer in biological systems, catalysis, etc.
4. helical organization	outer and inner surfaces	Au,[70] silica,[71] Cu,[73] Pd,[74] CdS,[75] Ppy,[76,77] PEDOT,[77] poly(aniline),[77] streptavidin,[78,79] ferritin[79]	catalysts, helical sensors, optical materials, springs and inductors for microelectronic devices, etc.
5. confinement	hollow cylinder	Fe_3O_4,[84,85,91] Au,[54,88,93] Ag[88,92] CdS,[89] ferritin,[14b,c,54,90] polymer beads,[14b] DNA,[14c]	nanochannel, metal nanowire, storage nanovessel, nanoreactor, capacitor, fundamental study of electrical transport and optical phenomena, etc.

Templated Materials

Burkett, S.L.; Mann, S., *Chem. Commun.*, **1996**, 321-322







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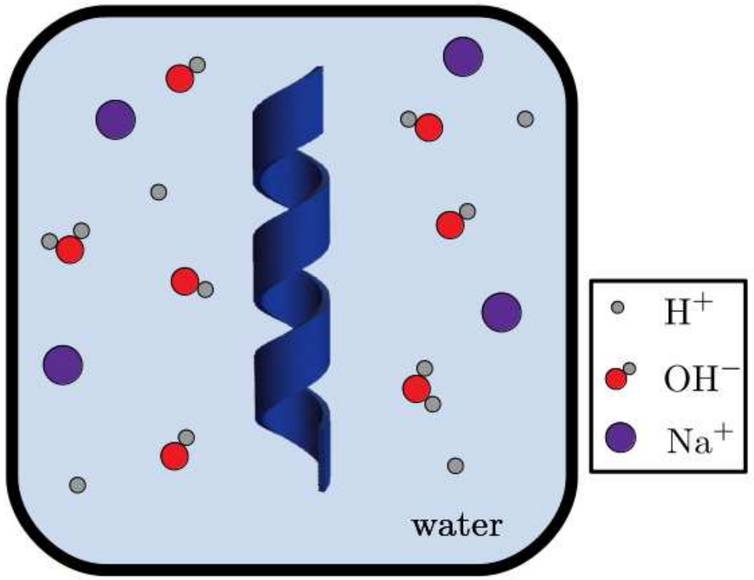
Electrostatic Effects

Electrostatic Effects

Assembly
(solution)

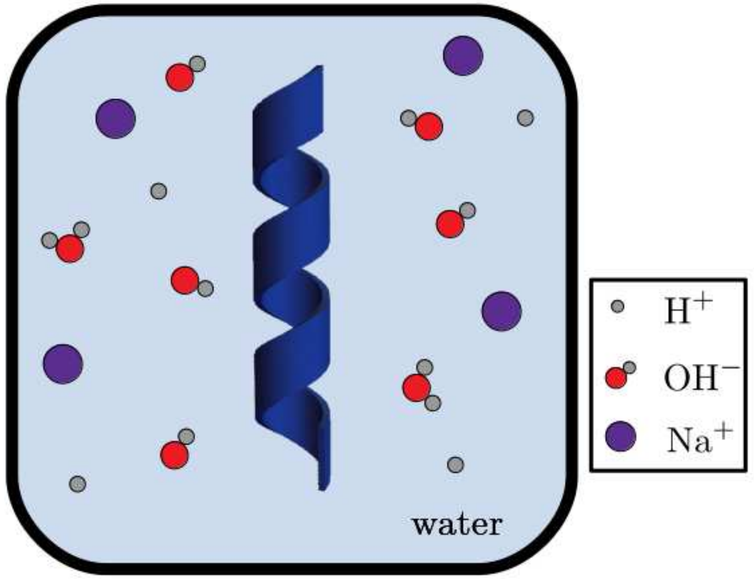
Electrostatic Effects

Assembly (solution)

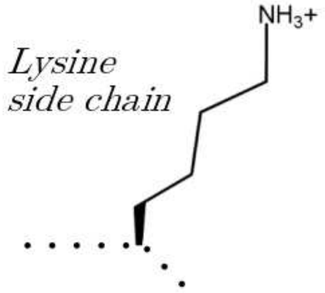


Electrostatic Effects

Assembly (solution)

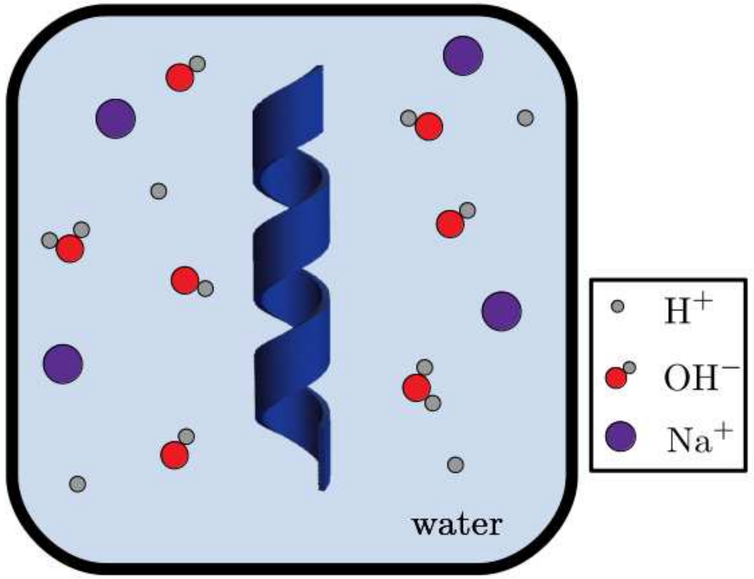


Mechanism $NH_3^+ + OH^- \overset{K_a}{\rightleftharpoons} NH_2 + H_2O$



Electrostatic Effects

Assembly (solution)



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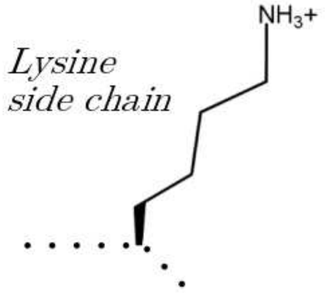
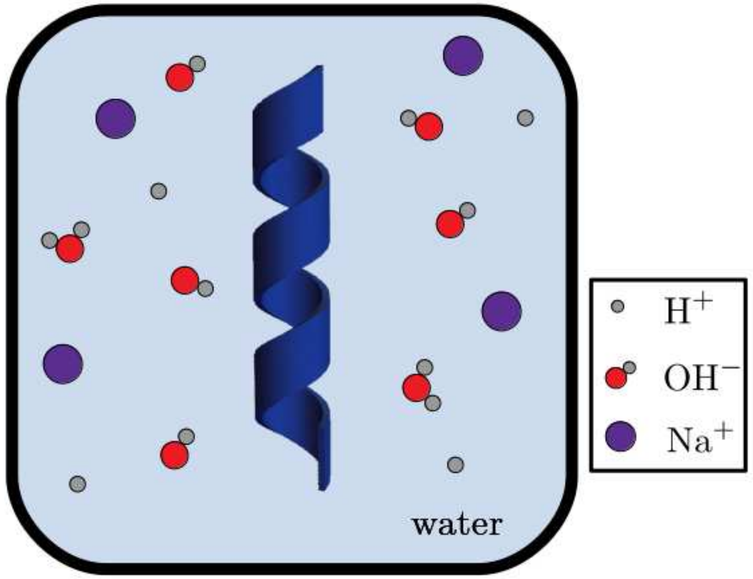


$$\alpha \equiv \frac{[NH_3^+]}{[NH_2] + [NH_3^+]}$$

= Degree of Ionization

Electrostatic Effects

Assembly (solution)



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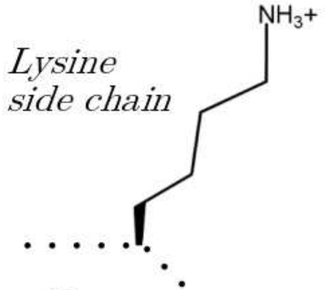


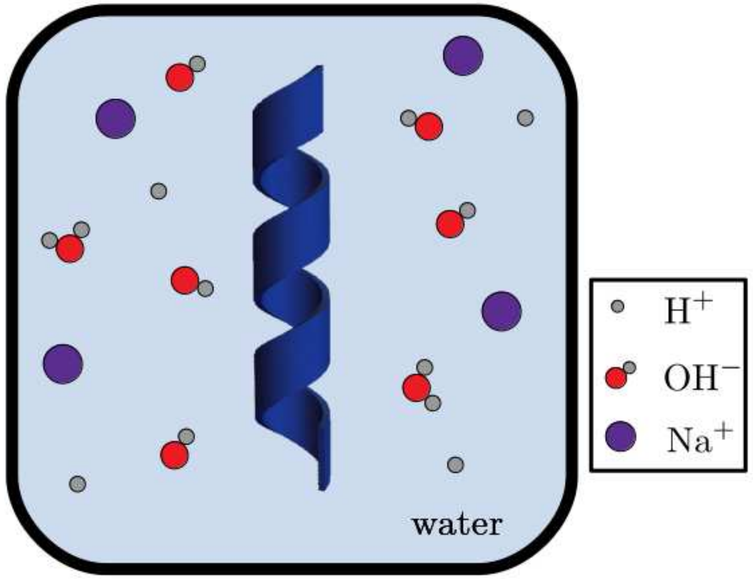
Effect on Interaction

$$\alpha \equiv \frac{[NH_3^+]}{[NH_2] + [NH_3^+]}$$

$$= \text{Degree of Ionization}$$

Electrostatic Effects

Assembly (solution)



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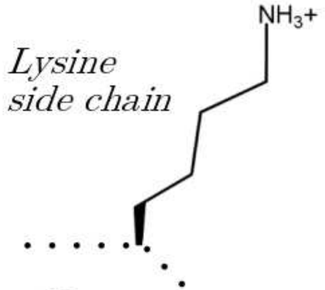


$$\alpha \equiv \frac{[NH_3^+]}{[NH_2] + [NH_3^+]}$$

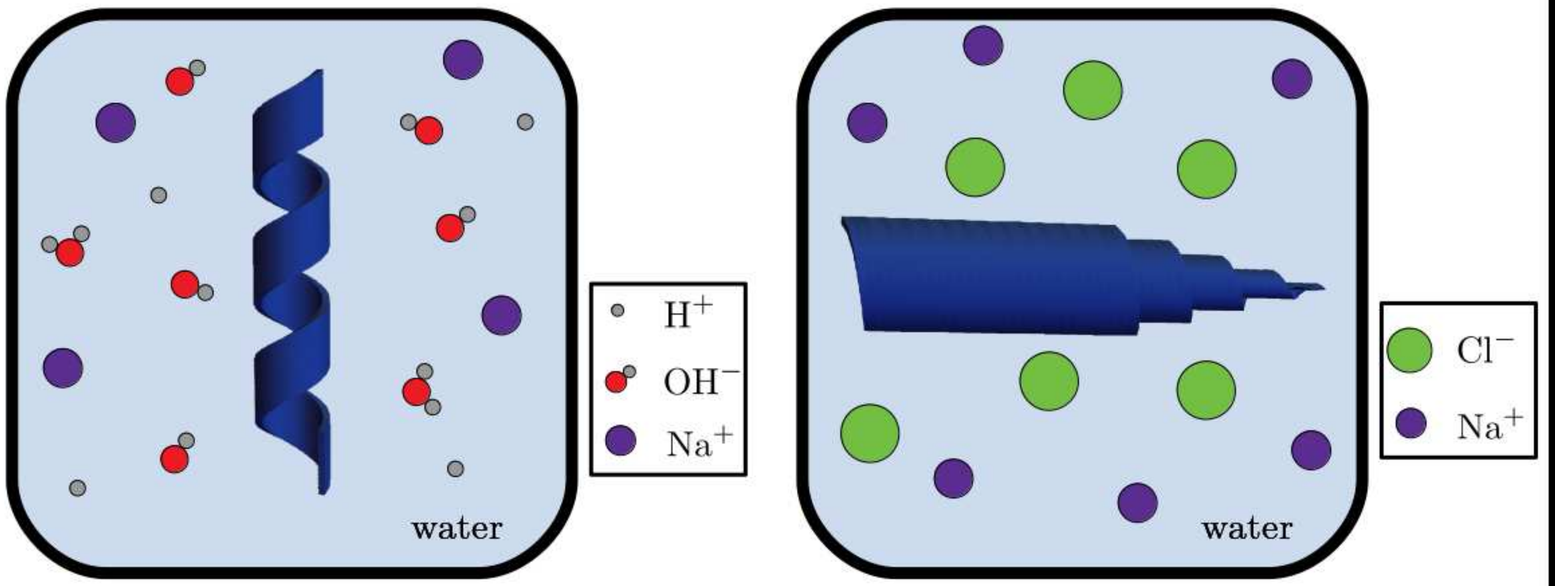
$$= \text{Degree of Ionization}$$

Effect on Interaction

Reduces Magnitude

Electrostatic Effects

Assembly (solution)



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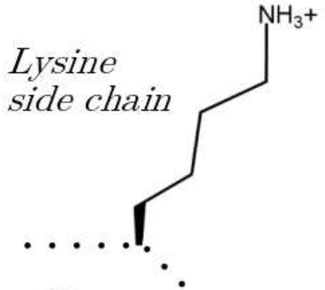

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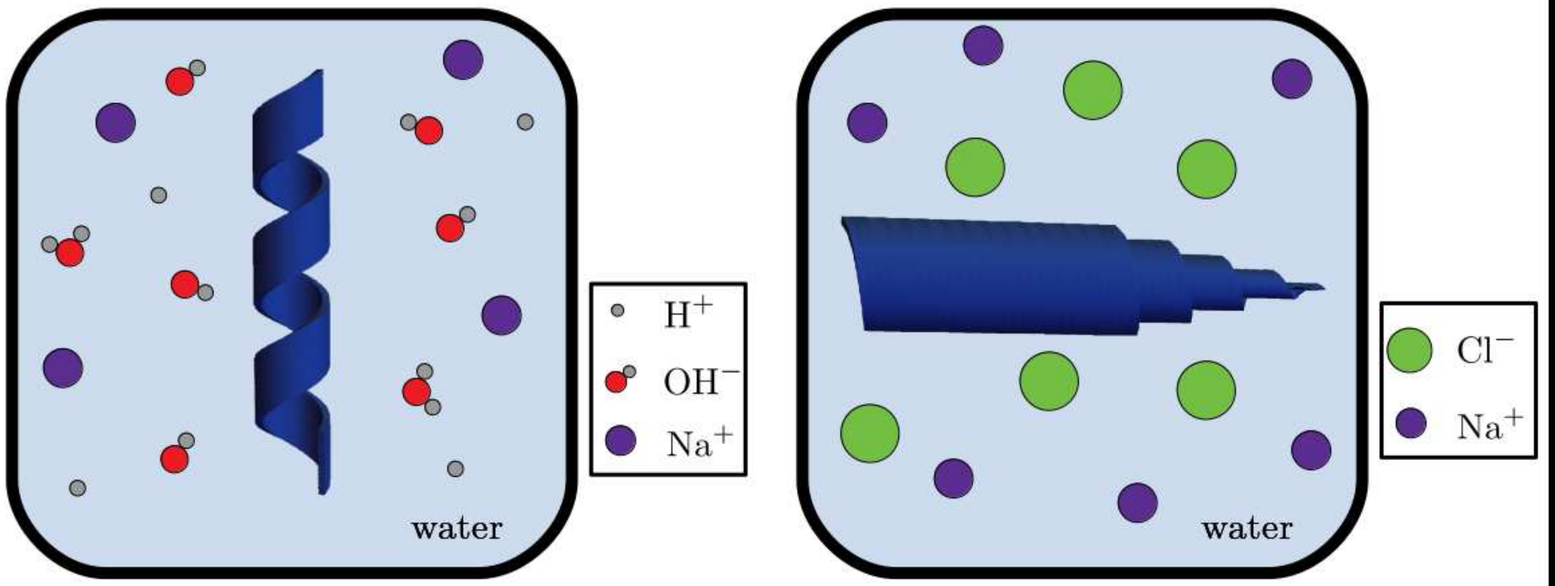
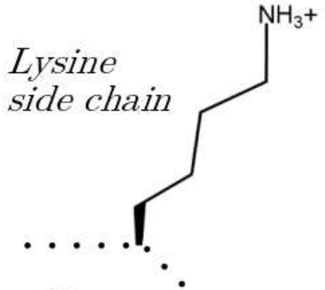
Assembly (solution)



Mechanism $\mathrm{NH_3^+ + OH^- \overset{K_a}{\rightleftharpoons} NH_2 + H_2O}$

$$\psi(r) \sim e^{-r/\lambda_D}$$



$$\alpha \equiv \frac{[NH_3^+]}{[NH_2] + [NH_3^+]}$$

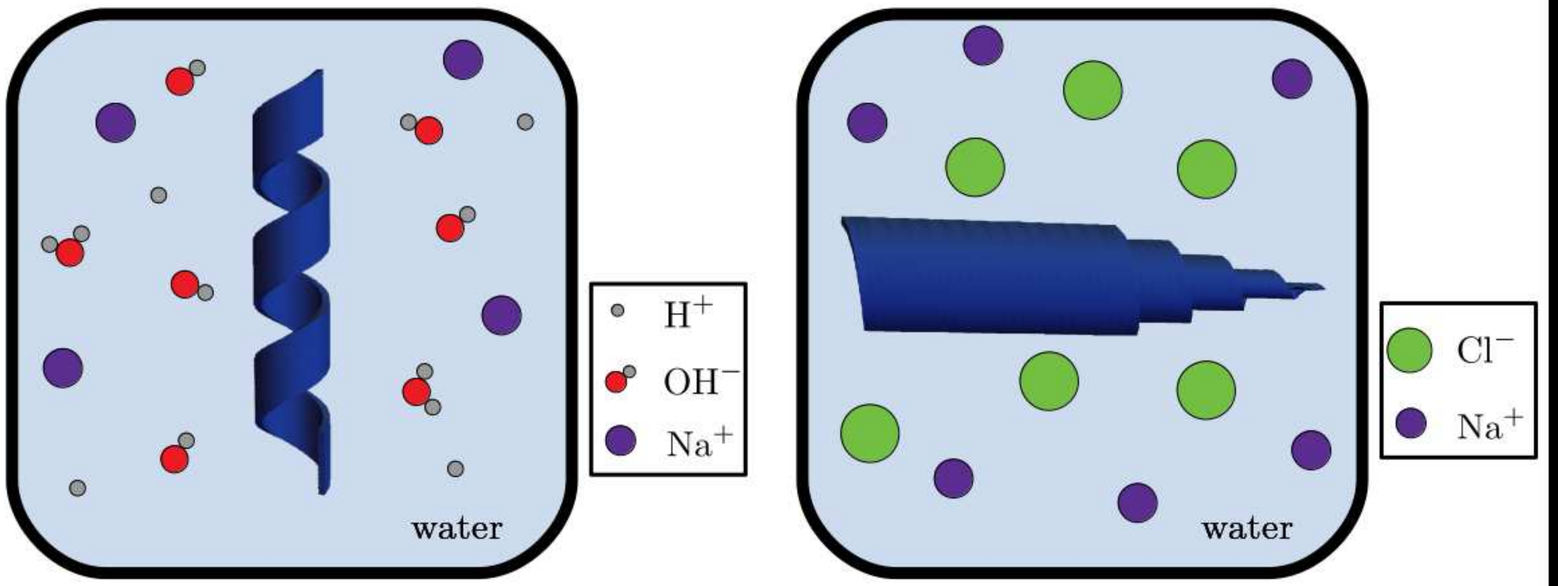
$$= \text{Degree of Ionization}$$

Effect on Interaction

<u>Reduces Magnitude</u>

Electrostatic Effects

Assembly (solution)



Mechanism

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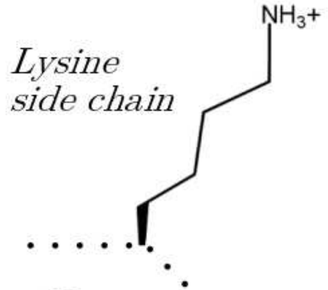


$$\alpha \equiv \frac{[NH_3^+]}{[NH_2] + [NH_3^+]}$$

$$= \text{Degree of Ionization}$$

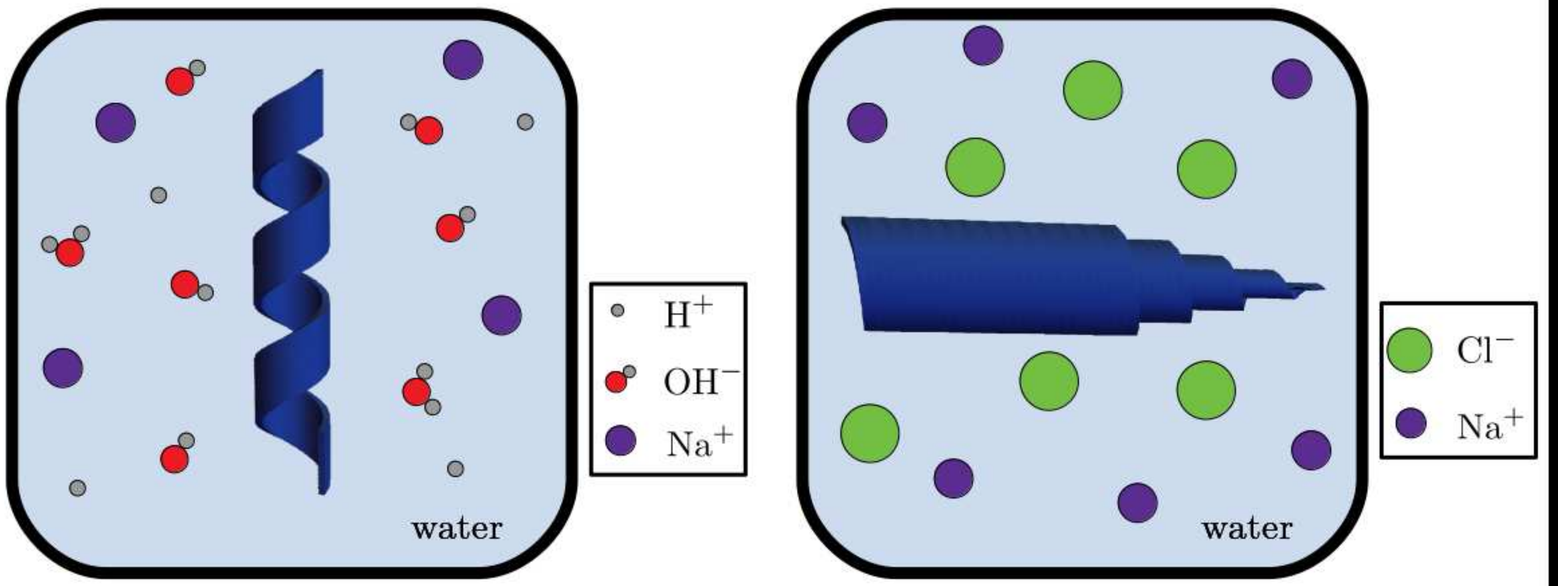
$$\lambda_D \sim \frac{1}{\sqrt{\text{NaCl}}}$$

Effect on Interaction

<u>Reduces Magnitude</u>

Electrostatic Effects

Assembly (solution)



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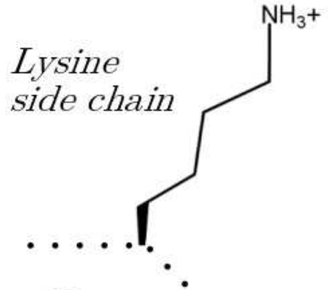

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$$= \text{Degree of Ionization}$$

$$\lambda_D \sim \frac{1}{\sqrt{\text{NaCl}}}$$

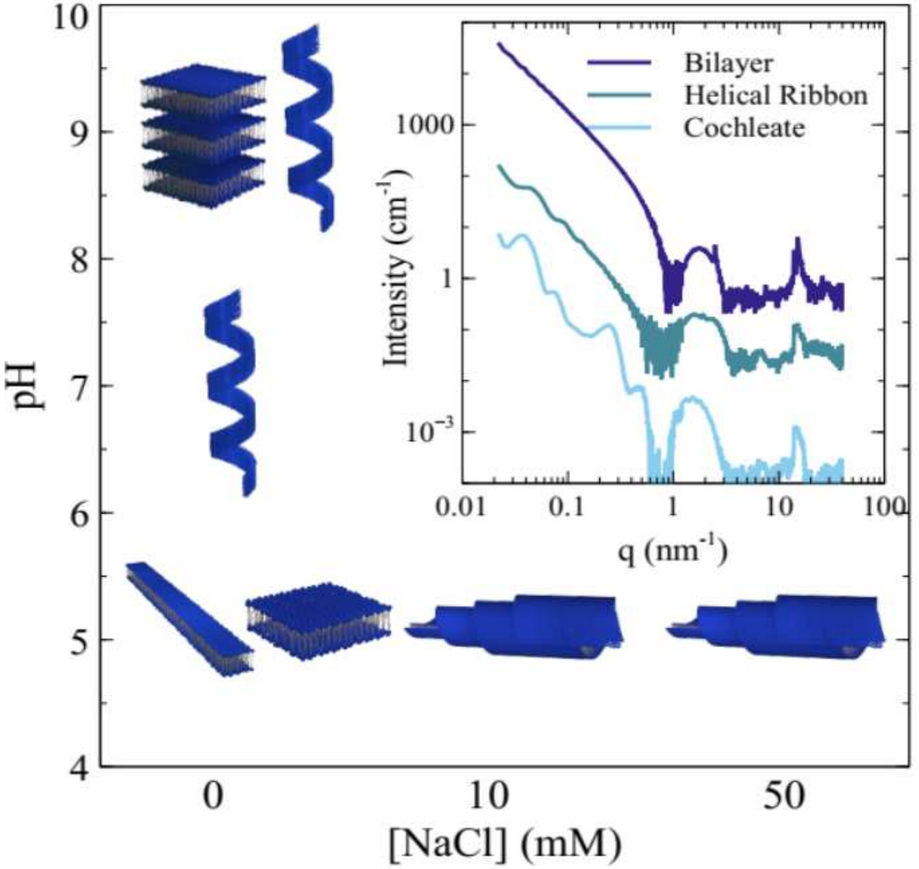
Effect on Interaction

Reduces Magnitude

Reduces Range

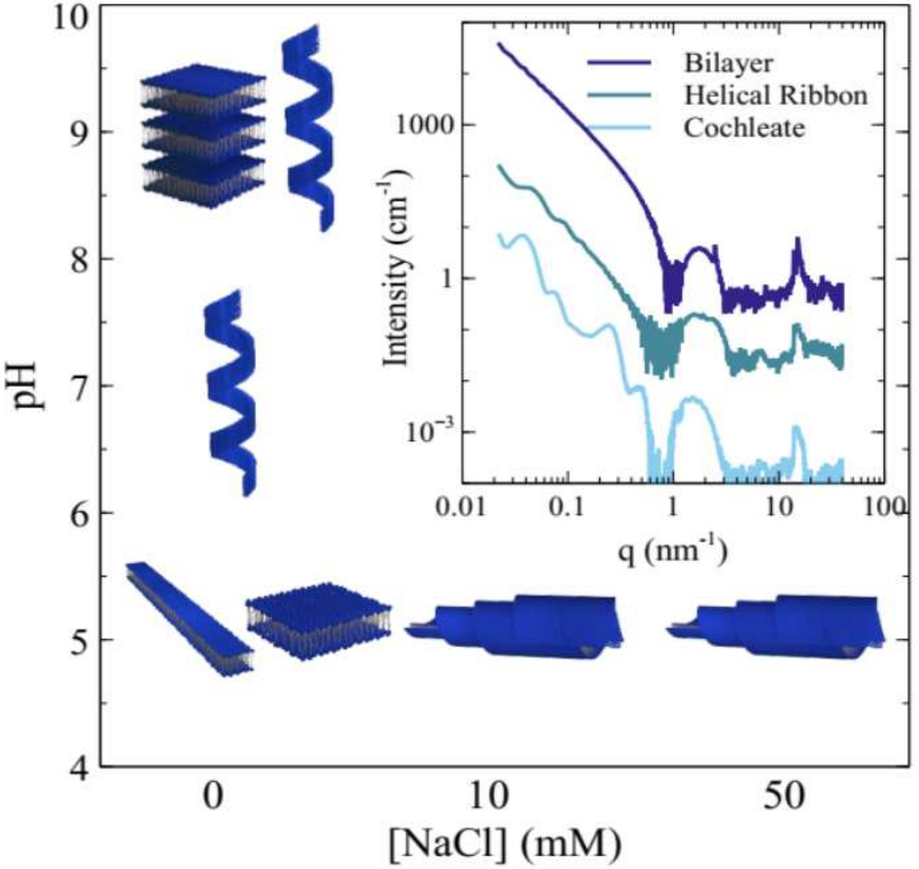
$C_{16}K$ Electrostatic Pathways Summary

X-ray Scattering

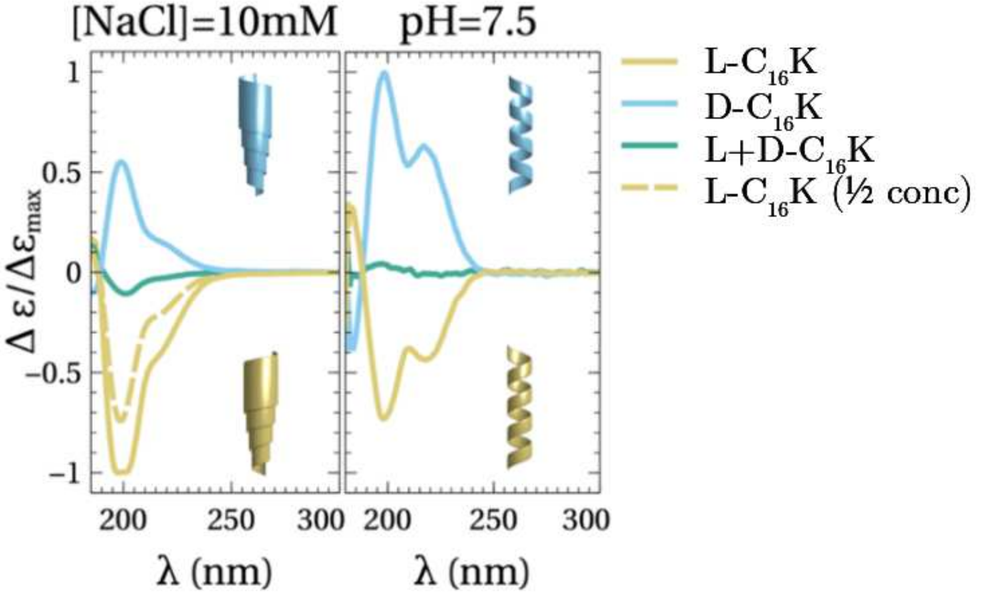


$C_{16}K$ Electrostatic Pathways Summary

X-ray Scattering

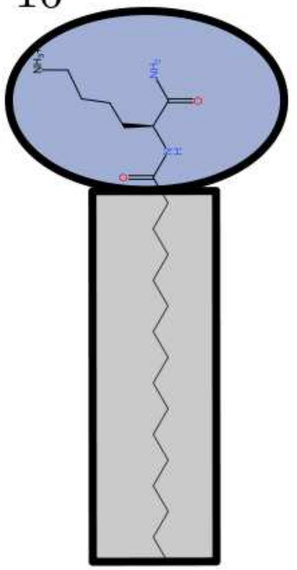


Circular Dichroism (CD)

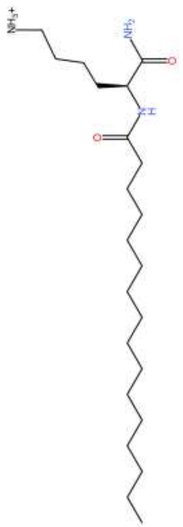


Chiral assemblies preferentially absorb (left or right) circularly polarized light

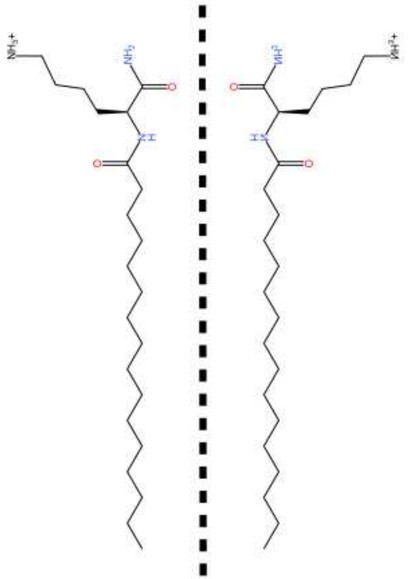
$C_{16}K$, Reducing Chiral Interaction



$C_{16}K$, Reducing Chiral Interaction



$C_{16}K$, Reducing Chiral Interaction



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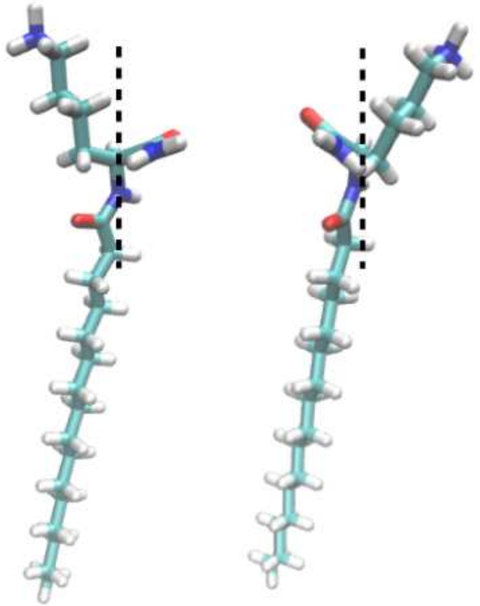

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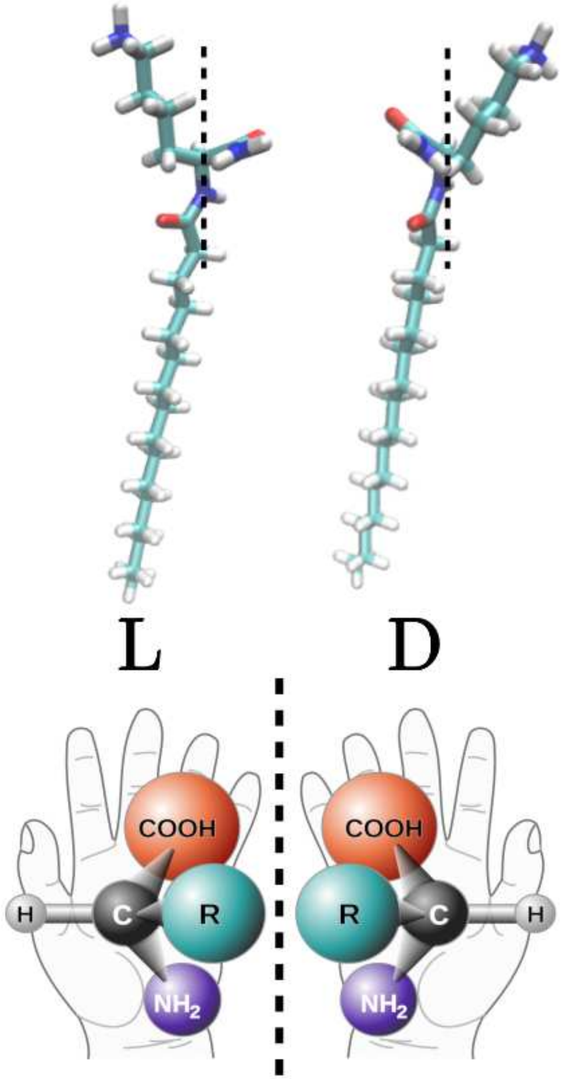
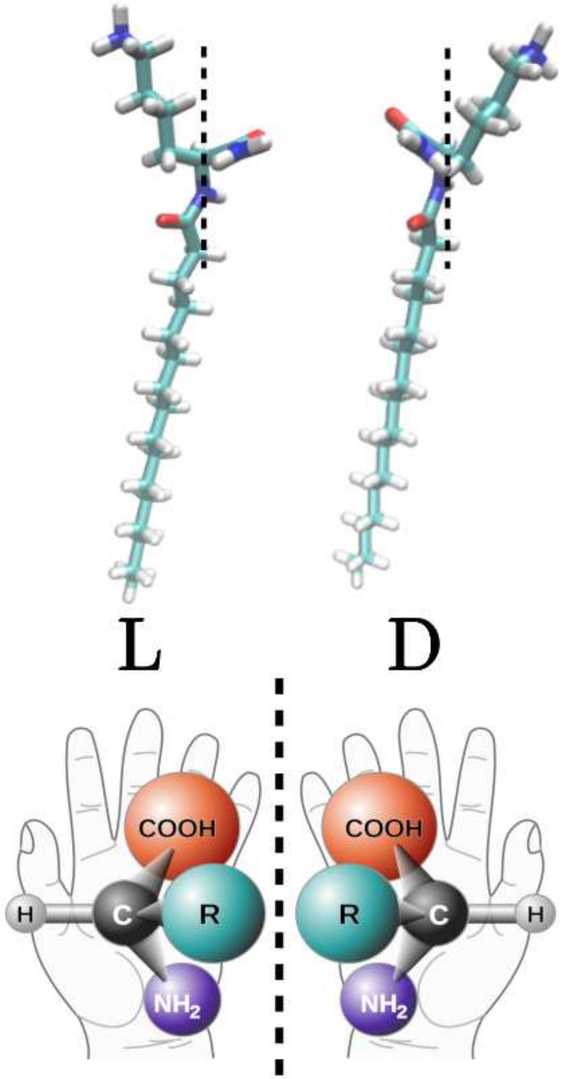
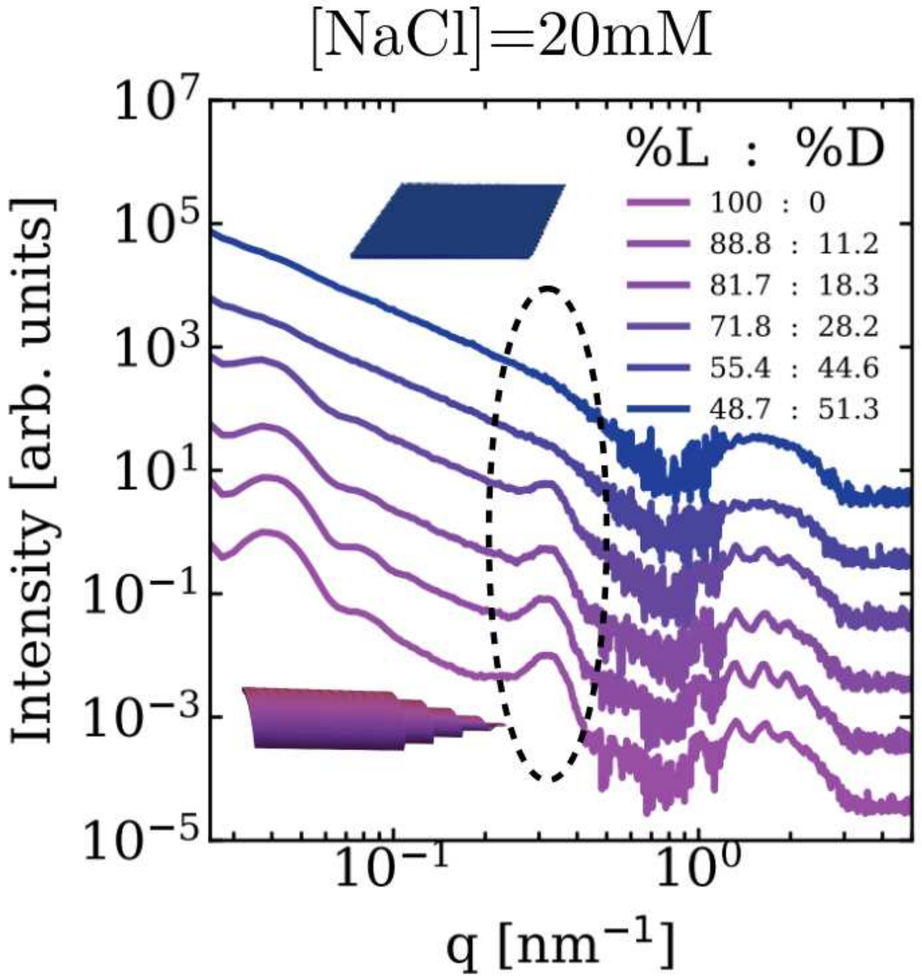


$C_{16}K$, Reducing Chiral Interaction





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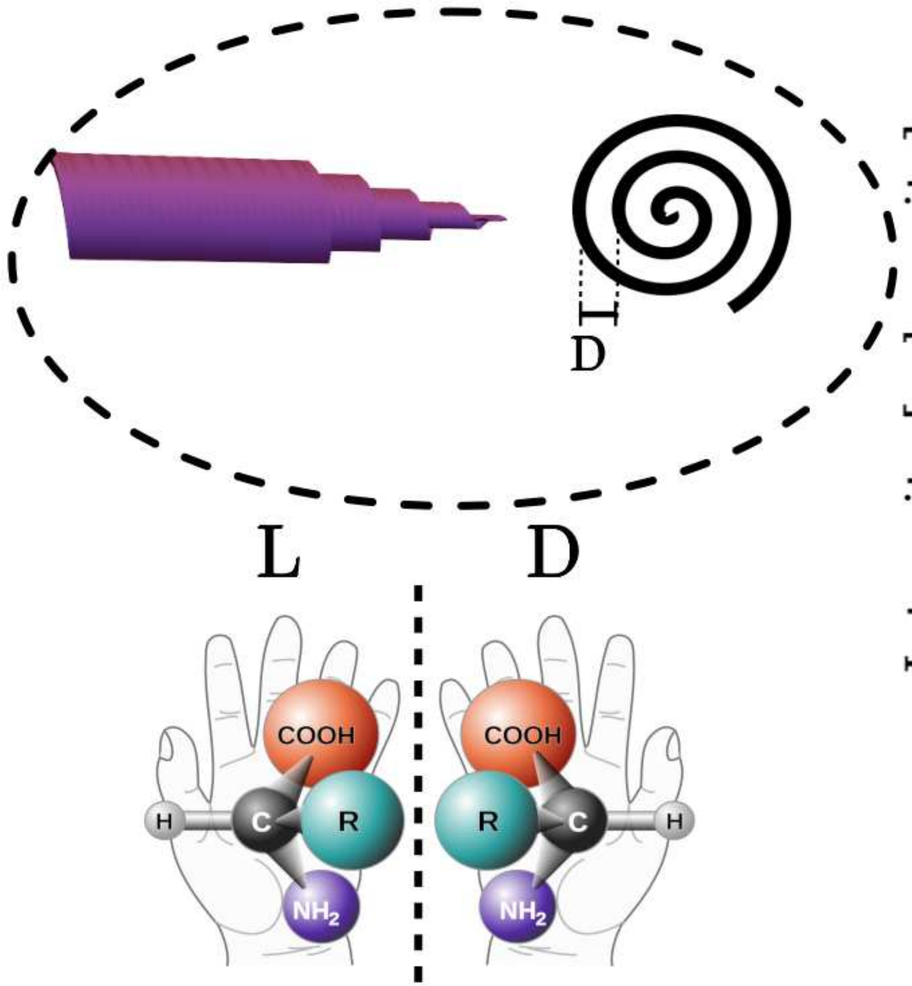

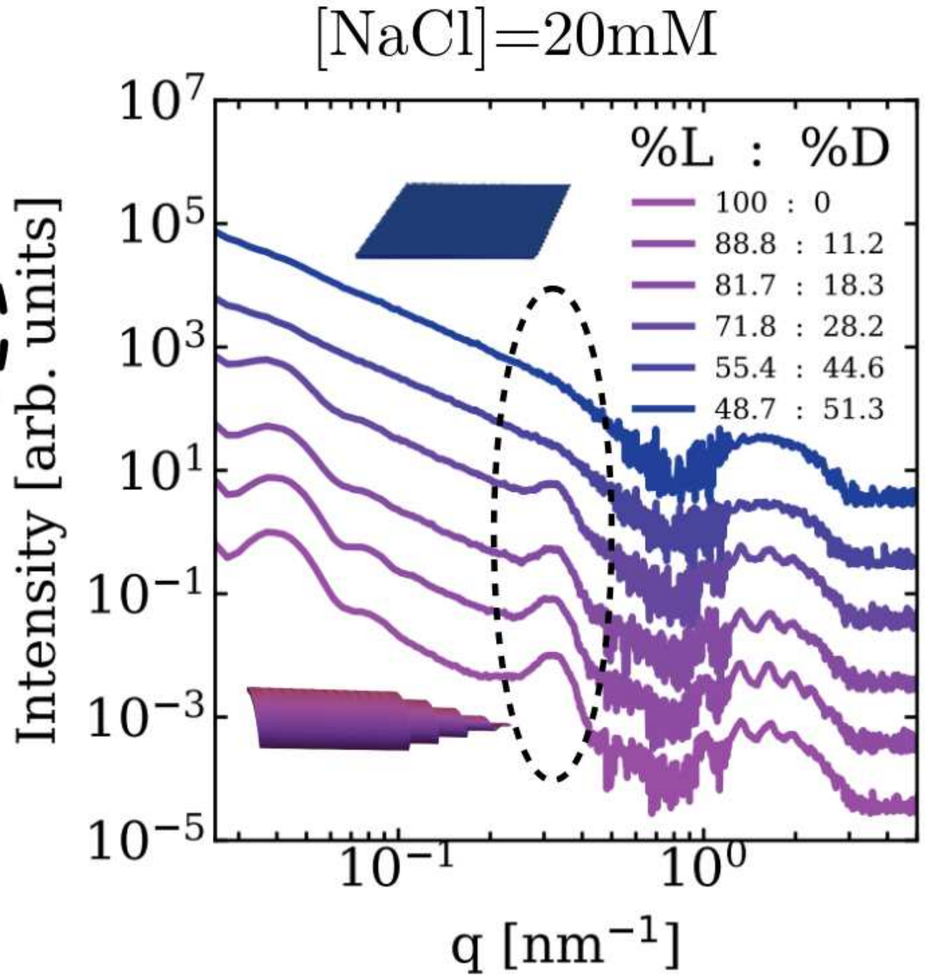

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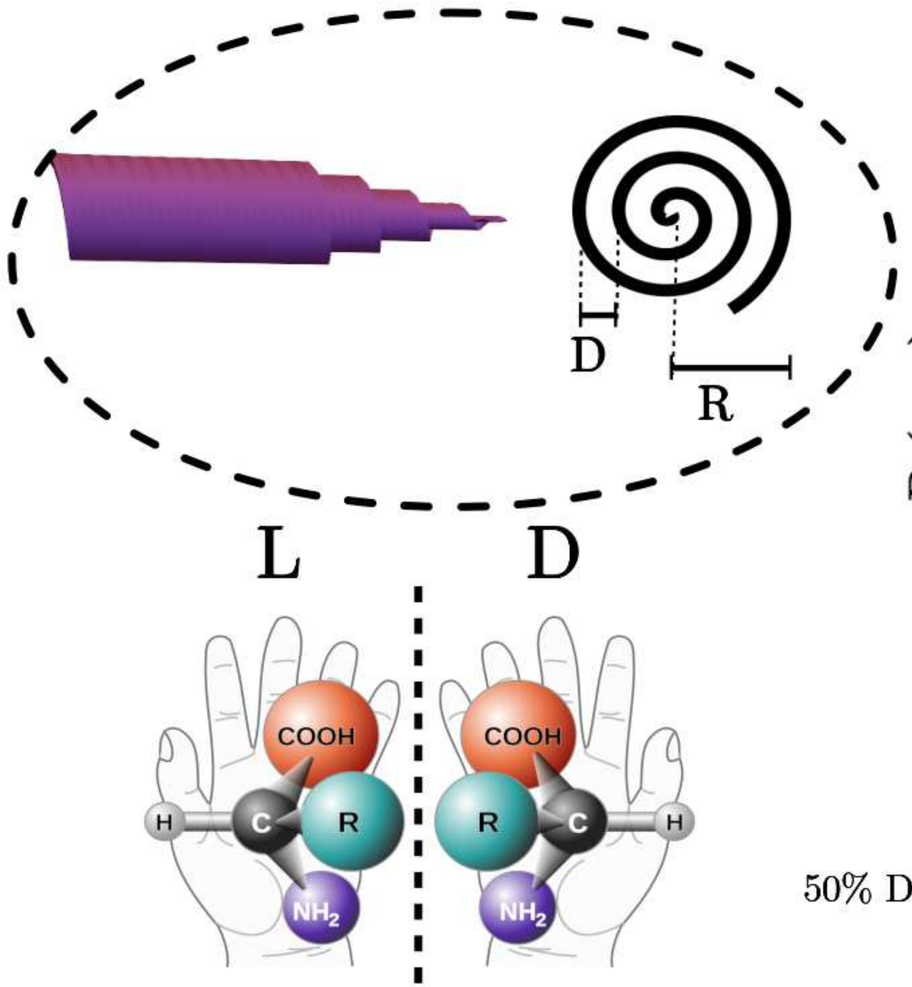
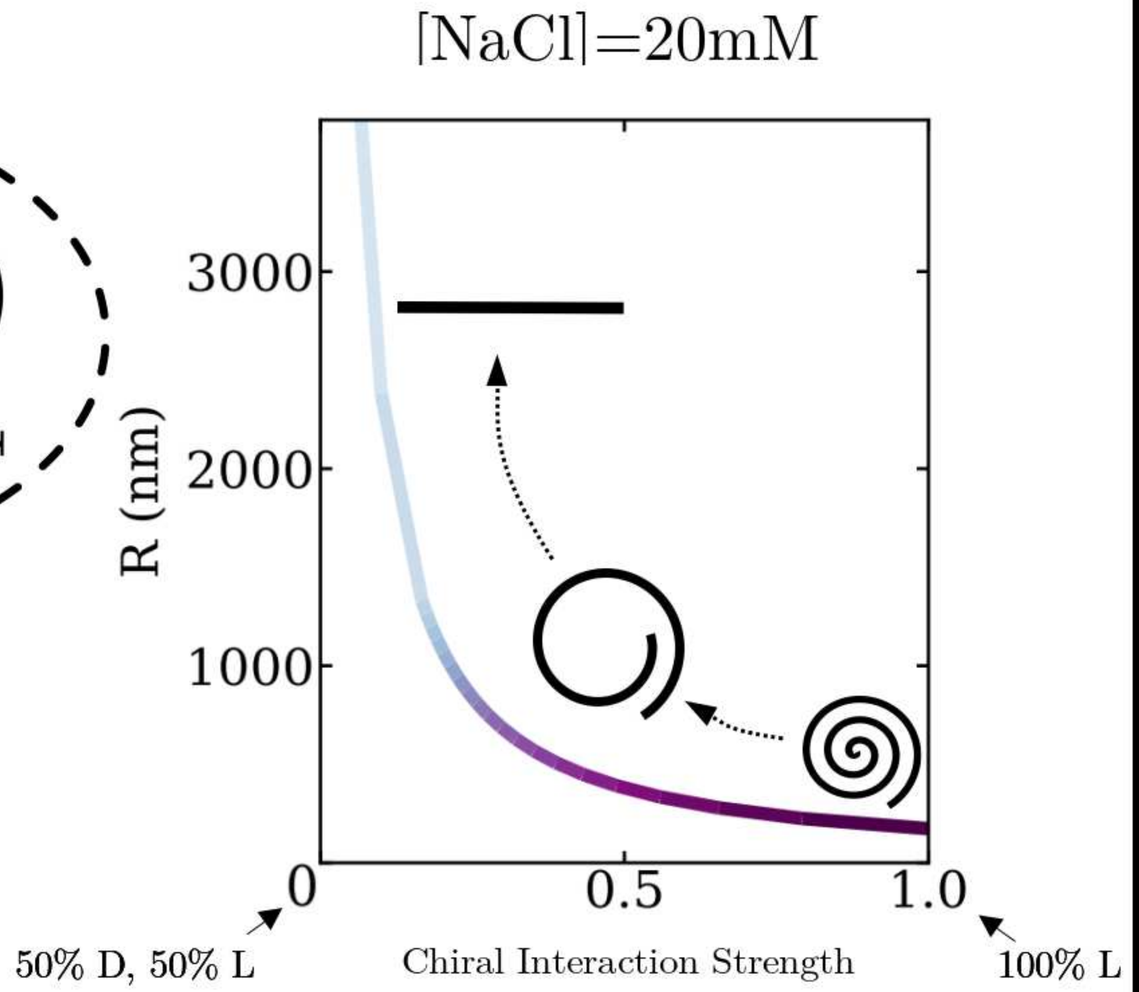


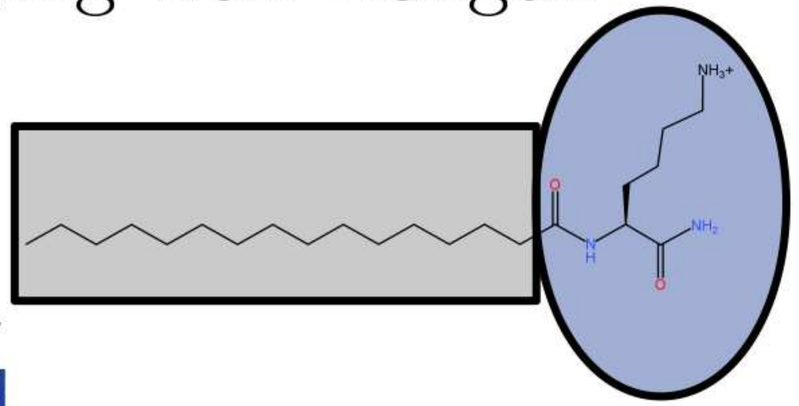


C_nK, Changing Tail Length

C_nK

carbon tail

lysine head



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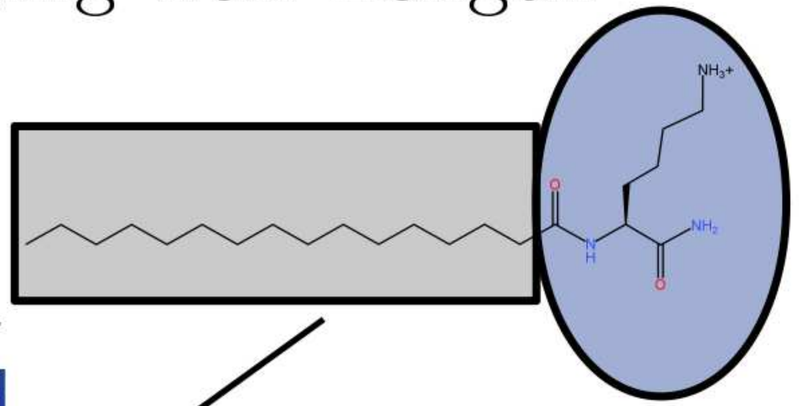


C_nK
$n<16$

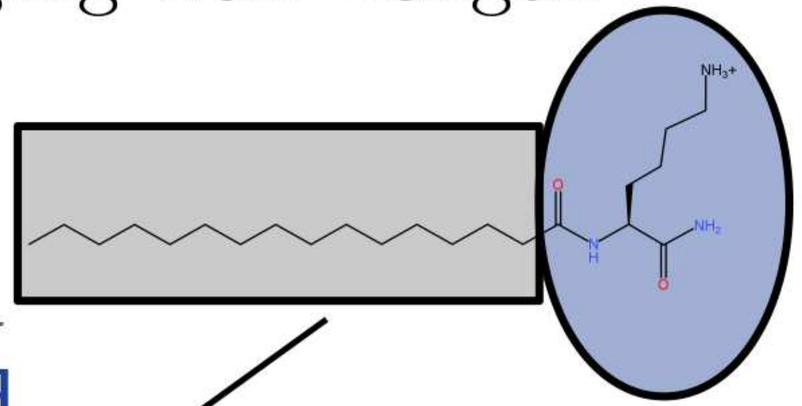
?

C_nK, Changing Tail Length

C_nK

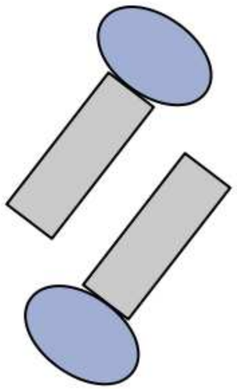
carbon tail

lysine head



C_nK
$n<16$

?



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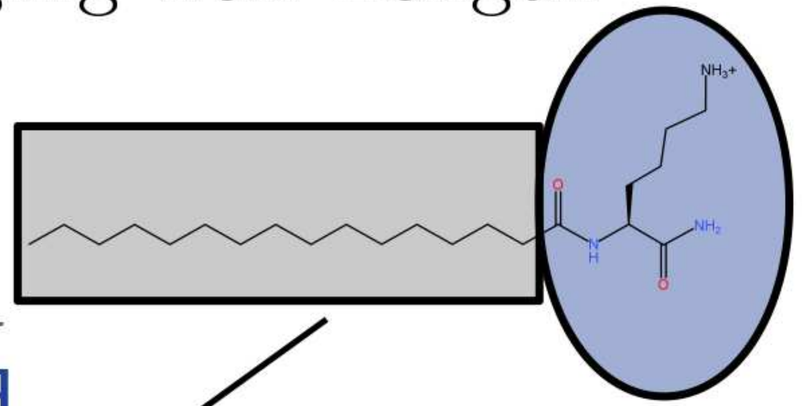

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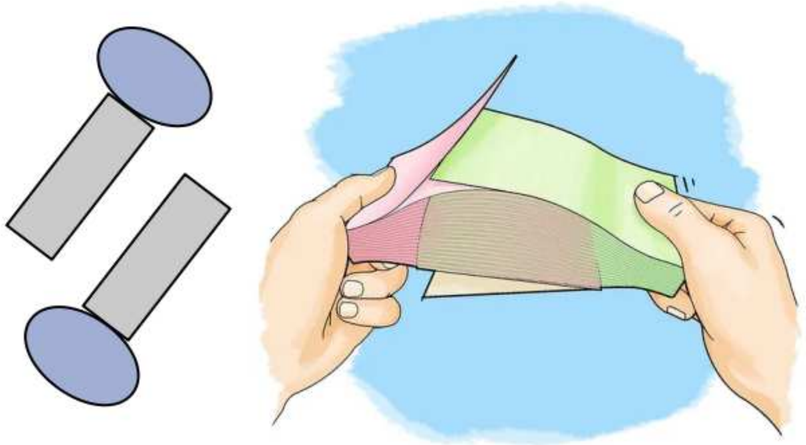
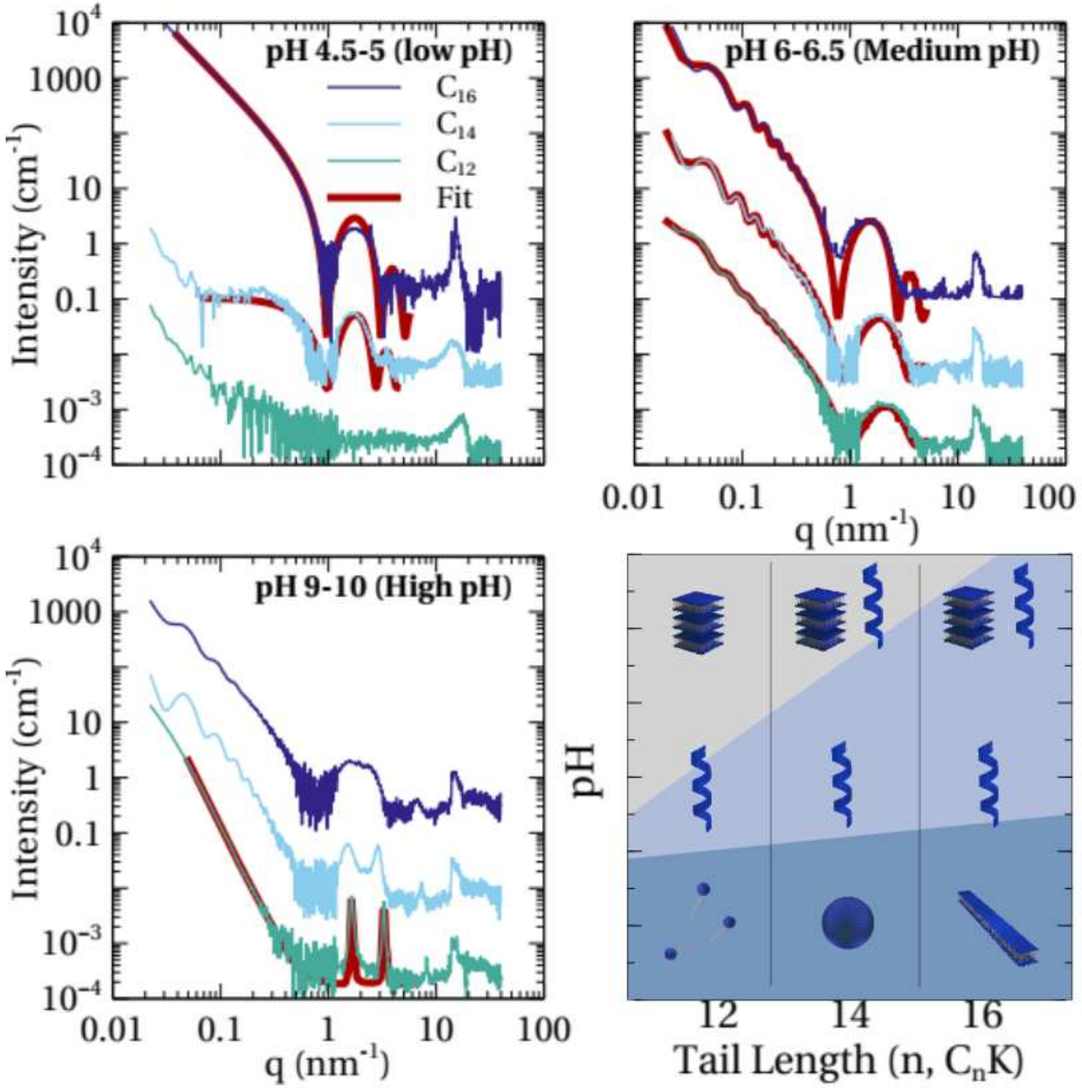
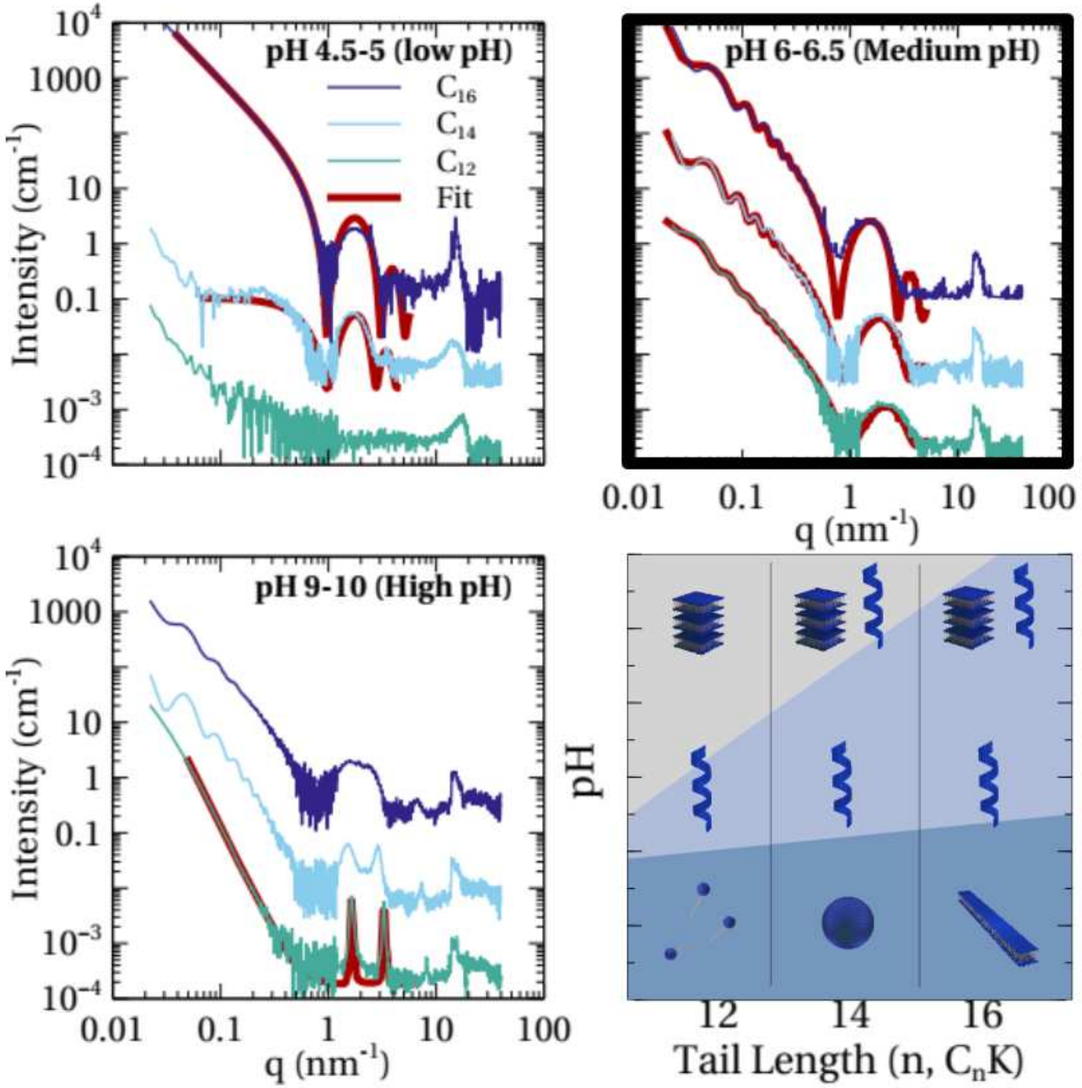
?

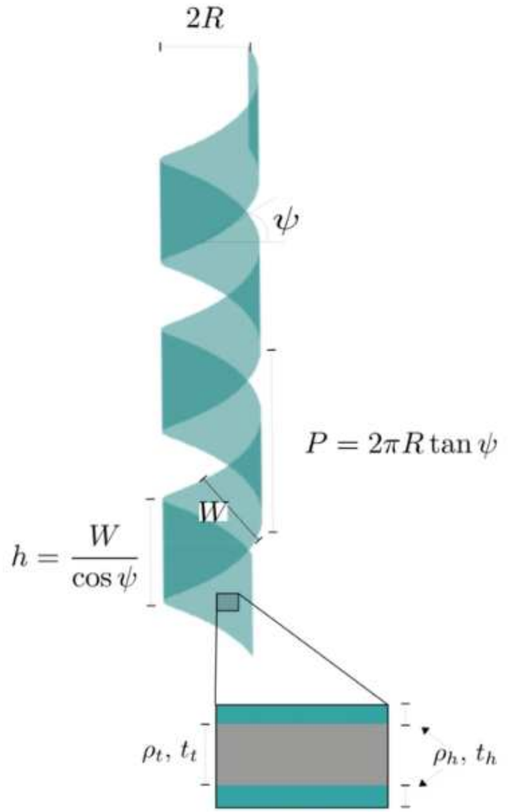


C_nK Assemblies, n=12,14,16

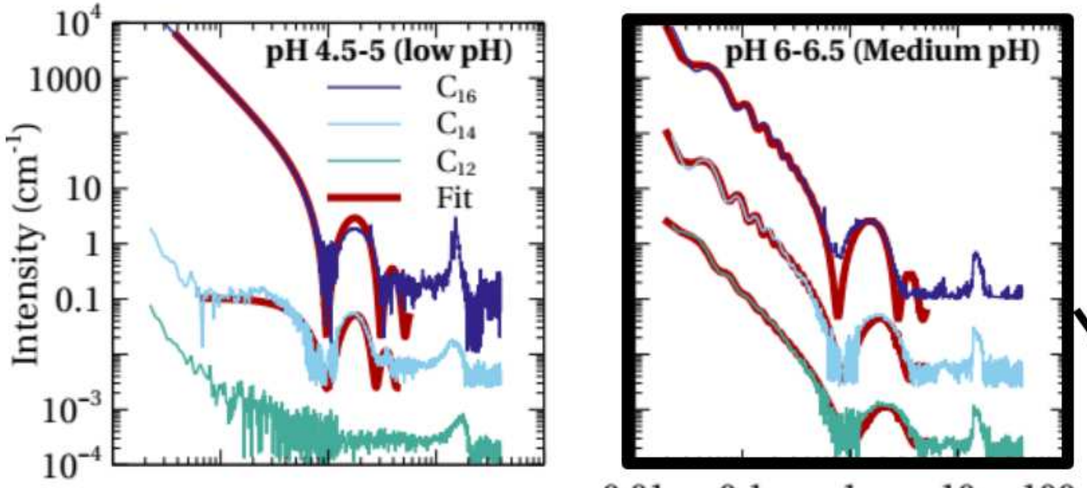


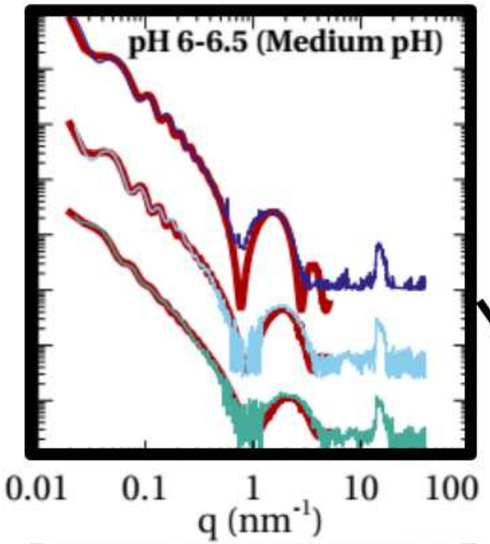
C_nK Assemblies, n=12,14,16

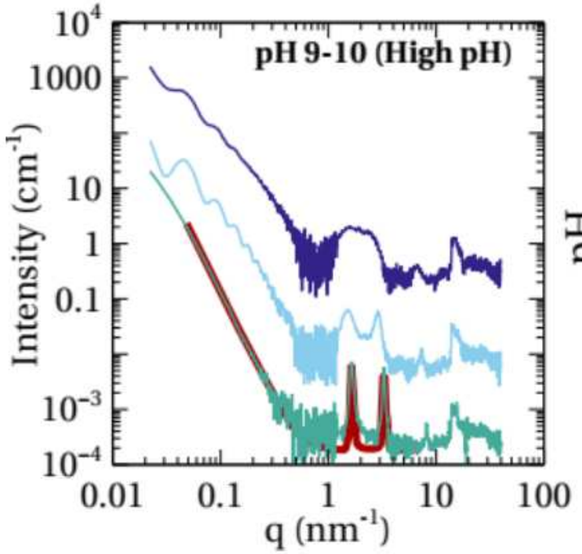


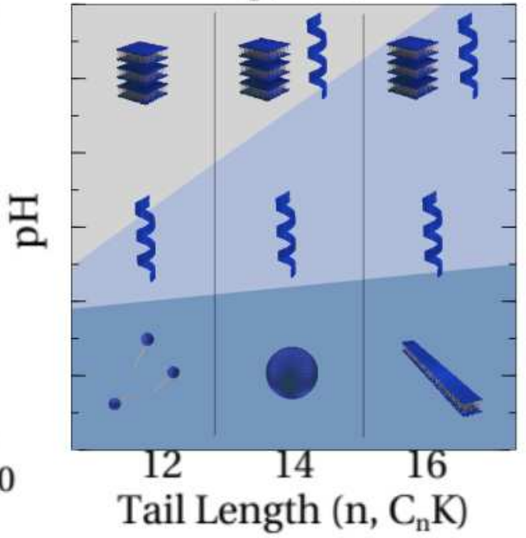


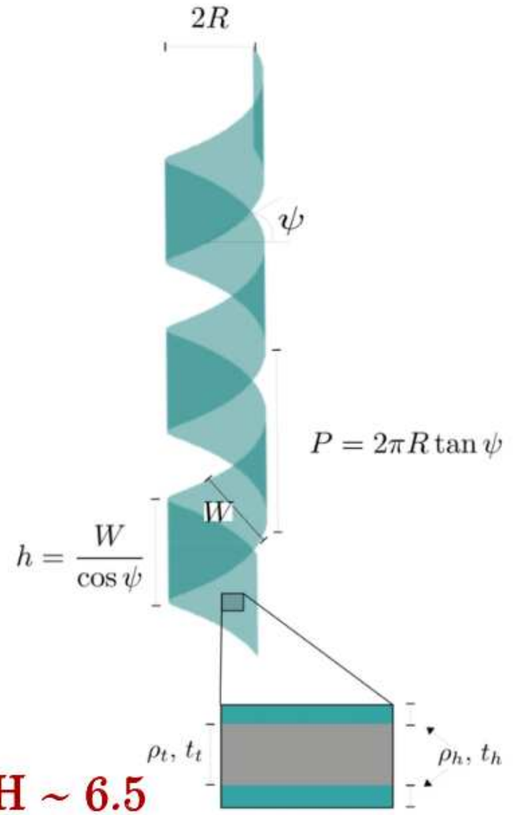
C_nK Assemblies, n=12,14,16



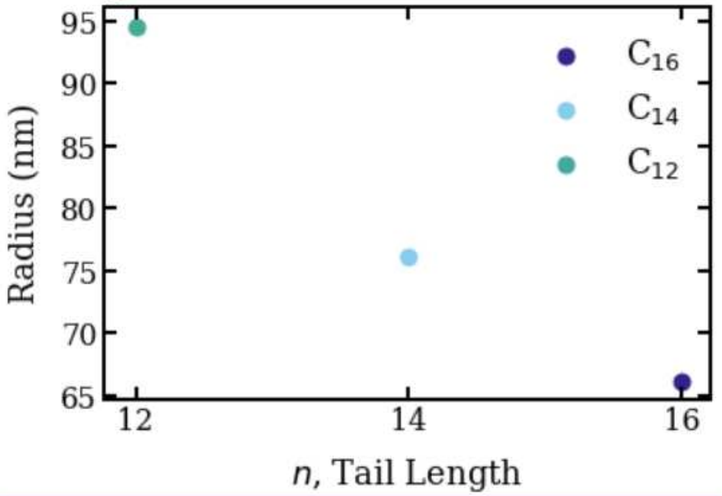








pH ~ 6.5



$C_{10}K$ Assemblies

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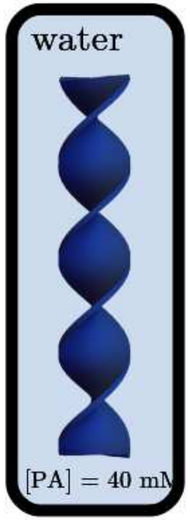
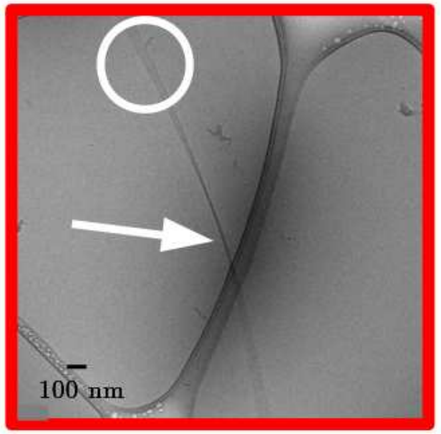
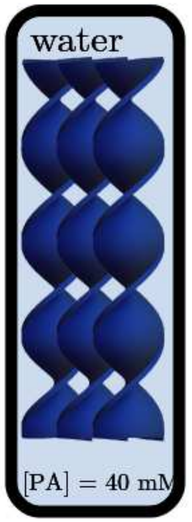


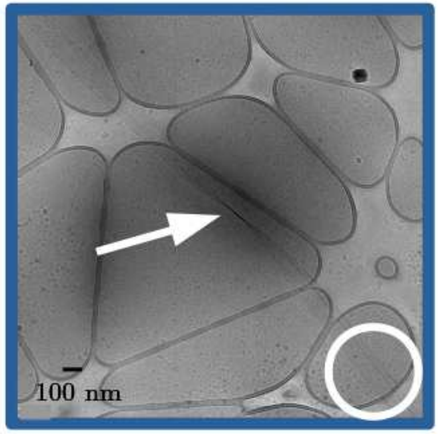
pH 8.8

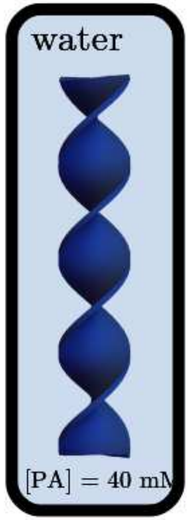


$C_{10}K$ Assemblies

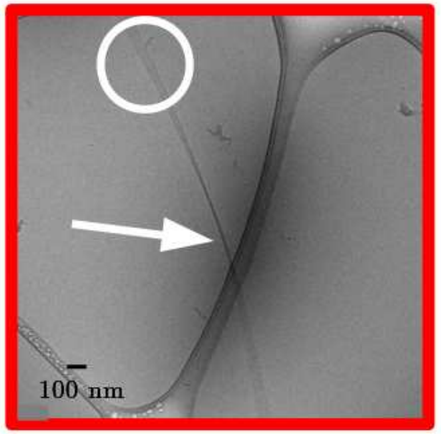


pH 9.3

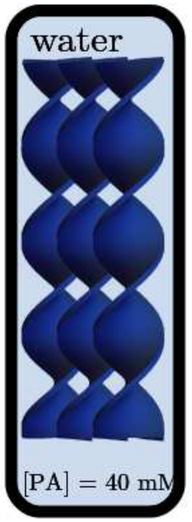




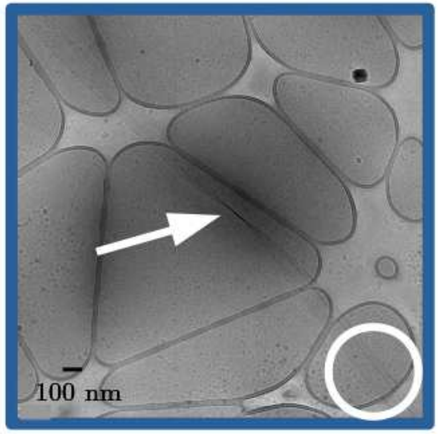
pH 8.8

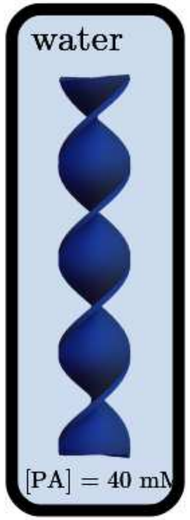


$C_{10}K$ Assemblies

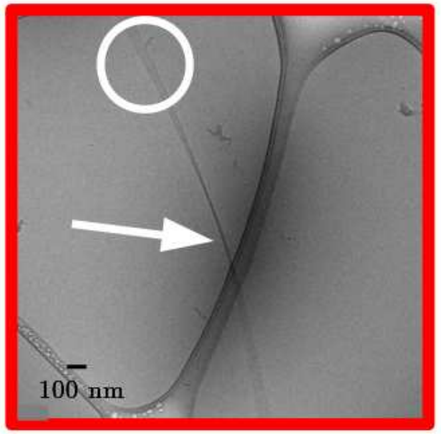


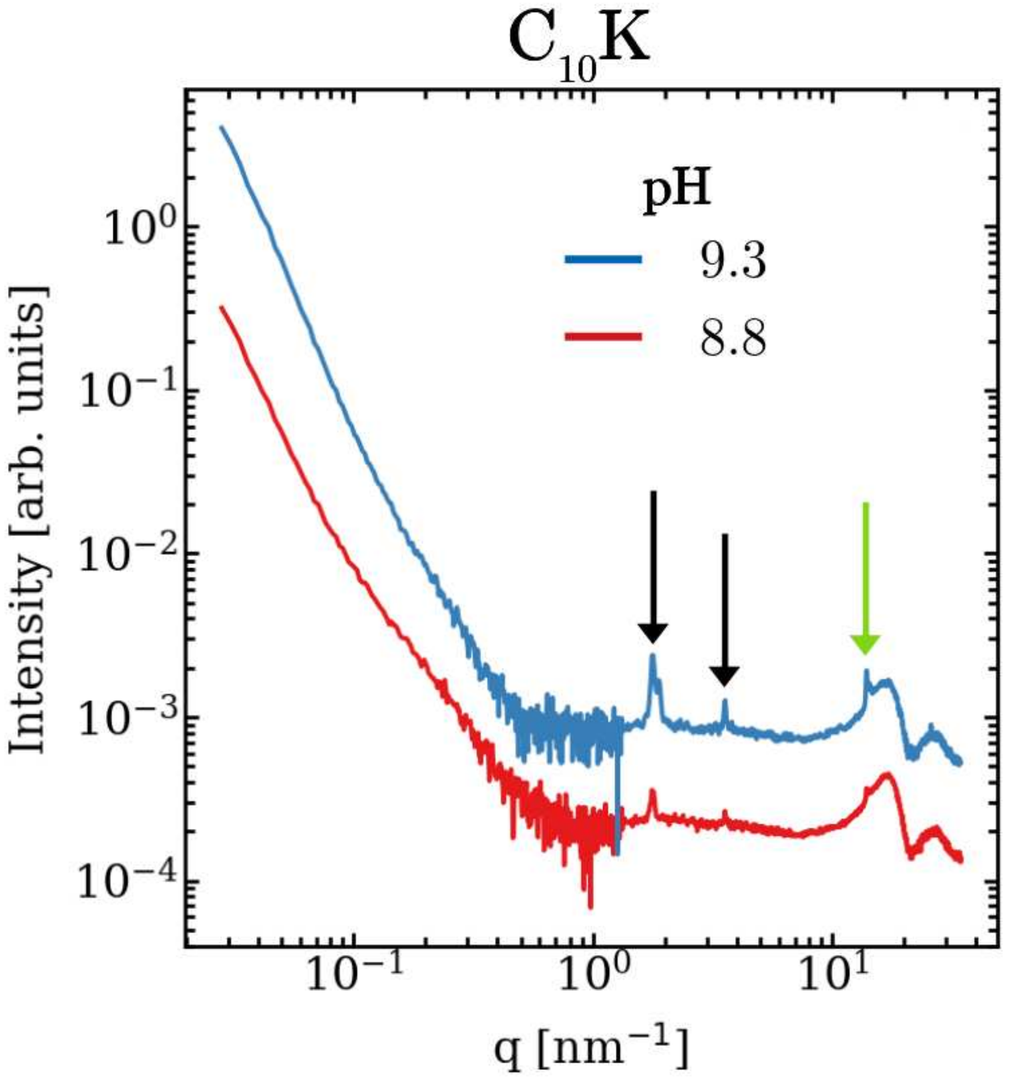
pH 9.3





pH 8.8

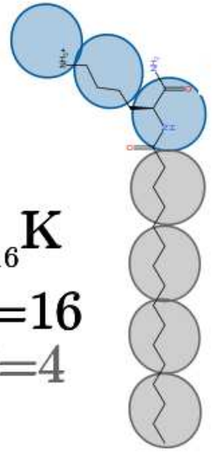




C_nK Bilayer Elastic Properties

$C_{16}K$

C_nK Bilayer Elastic Properties



$C_{16}K$

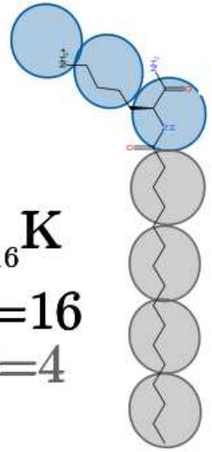
n=16

N=4

MARTINI 2.2P

Marrink et al., *J. Phys. Chem. B* 2007, 111, 27, 7812–7824
Monticelli et al., *J. Chem. Theory and Comput.* 2008, 4, 5, 819–834

C_nK Bilayer Elastic Properties



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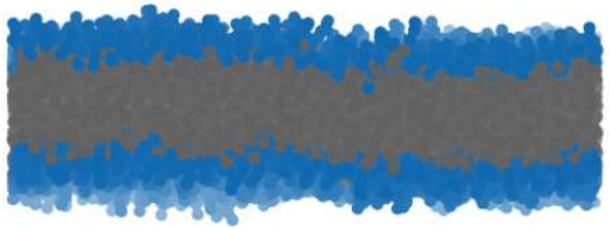
MARTINI 2.2P



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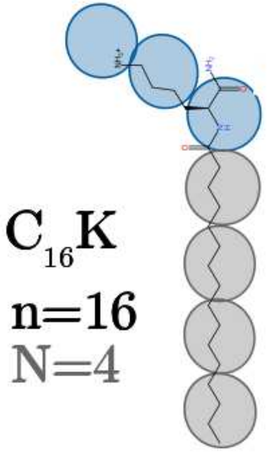
C_nK Bilayer Elastic Properties



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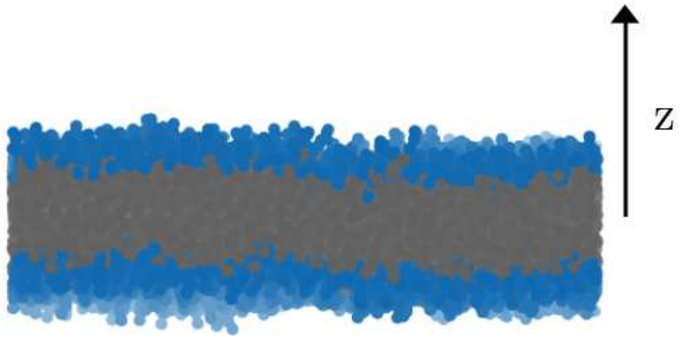
MARTINI 2.2P



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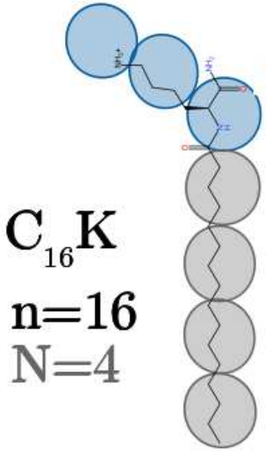
C_nK Bilayer Elastic Properties



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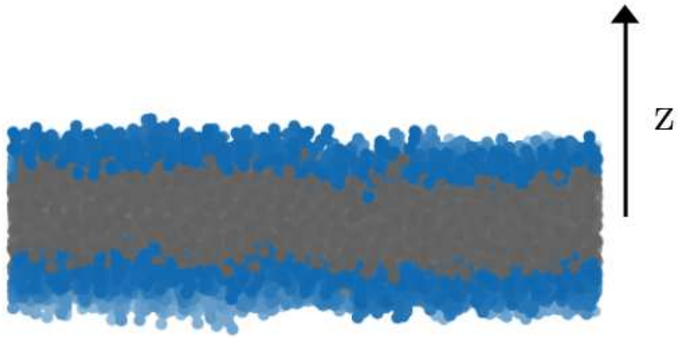
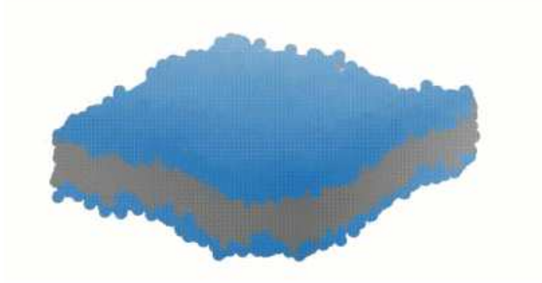
N=4

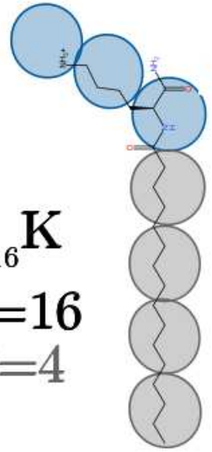
MARTINI 2.2P





Marrink et al., *J. Phys. Chem. B* 2007, 111, 27, 7812–7824
Monticelli et al., *J. Chem. Theory and Comput.* 2008, 4, 5, 819–834

C_nK Bilayer Elastic Properties

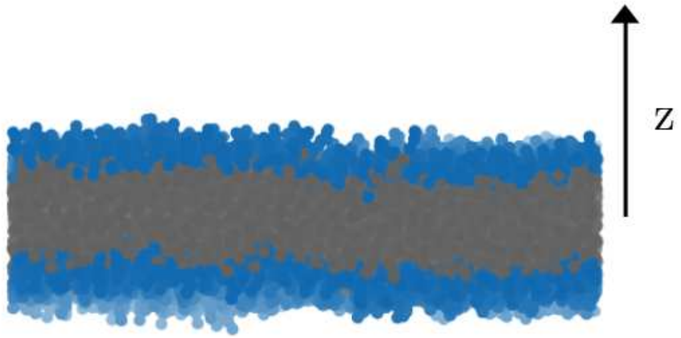


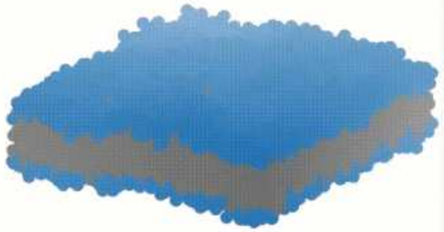
$C_{16}K$

n=16

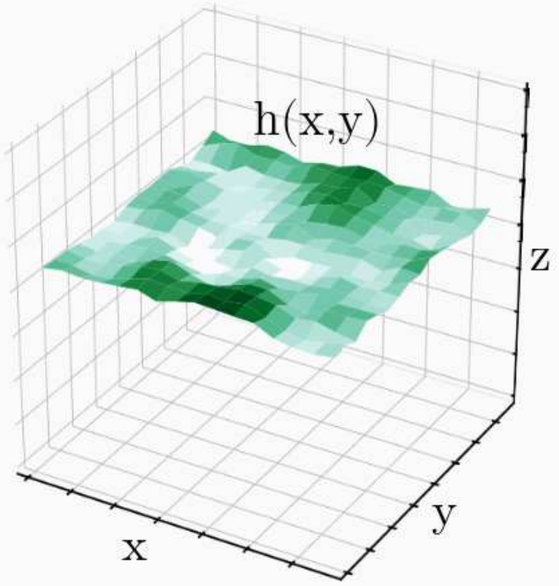
N=4

MARTINI 2.2P





10 nm



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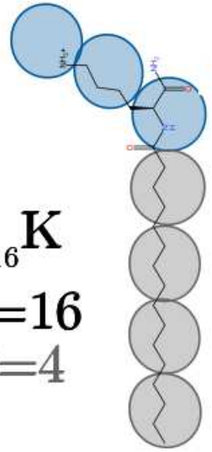
C_nK Bilayer Elastic Properties

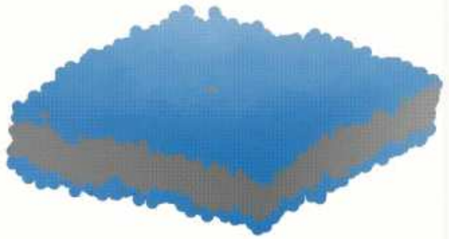


$C_{16}K$

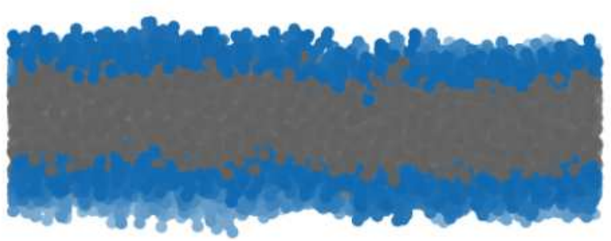
n=16

N=4

MARTINI 2.2F

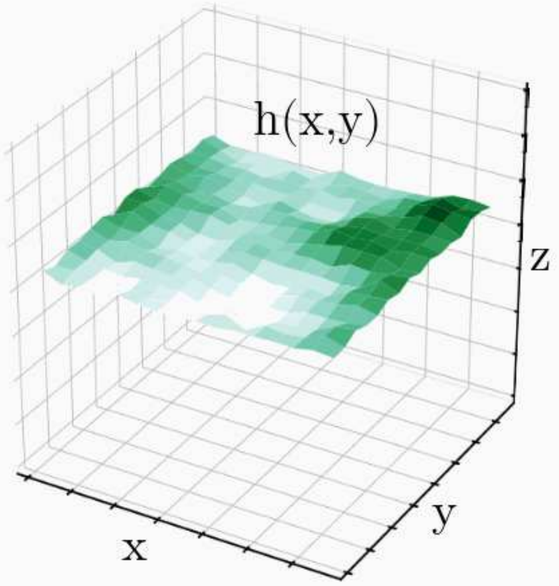


10 nm



z

$$h(x,y) = \sum_{q_x,q_y} h_{q_x,q_y} e^{i(q_x x + q_y y)}$$



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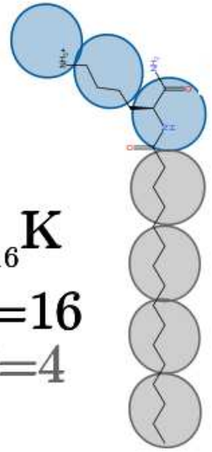
C_nK Bilayer Elastic Properties

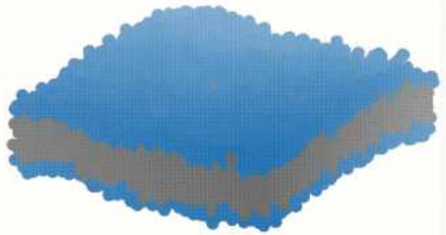


$C_{16}K$

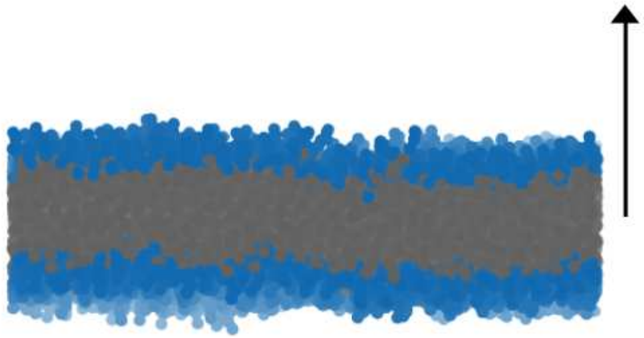
n=16

N=4

MARTINI 2.2F



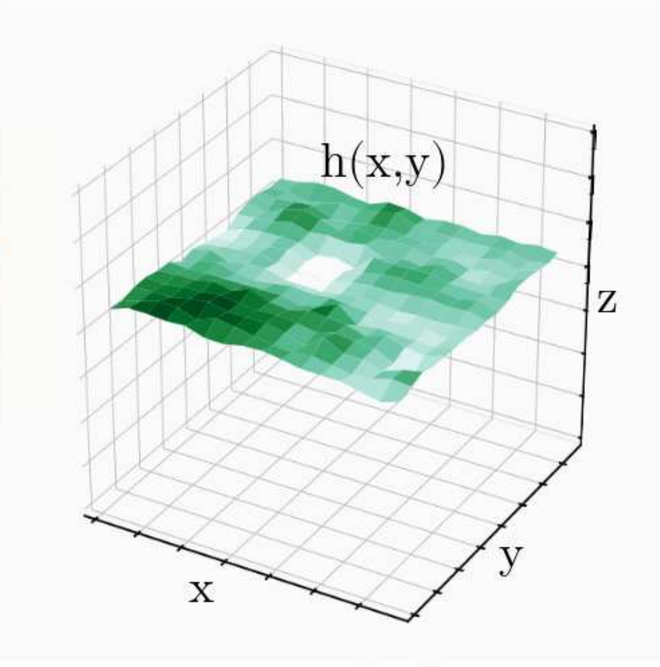
10 nm



z

$$h(x,y) = \sum_{q_x,q_y} h_{q_x,q_y} e^{i(q_x x + q_y y)}$$

$$L_x L_y \langle |h_q|^2 \rangle = \frac{k_B T}{\kappa q^4}$$



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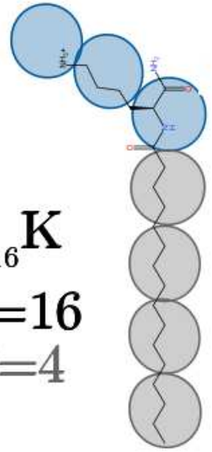
C_nK Bilayer Elastic Properties

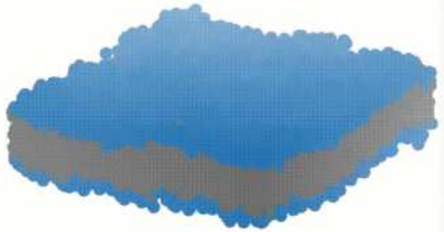


$C_{16}K$

n=16

N=4

MARTINI 2.2F



10 nm

z

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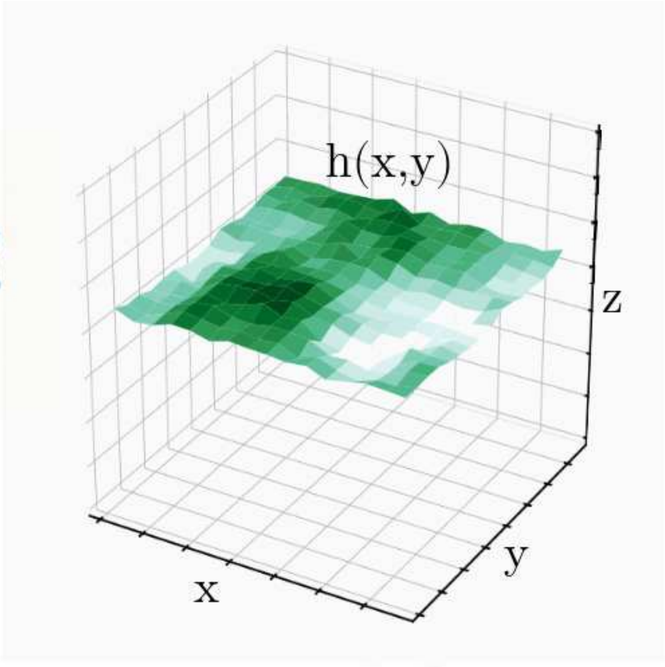

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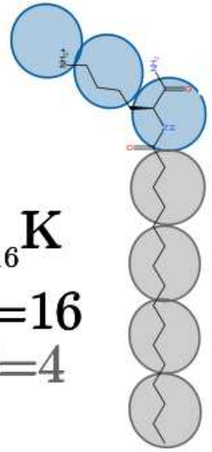
C_nK Bilayer Elastic Properties

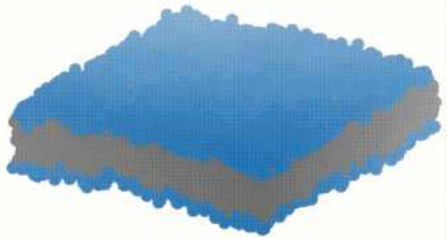


$C_{16}K$

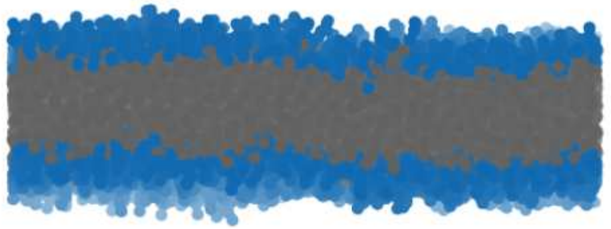
n=16

N=4

MARTINI 2.2P



10 nm



z

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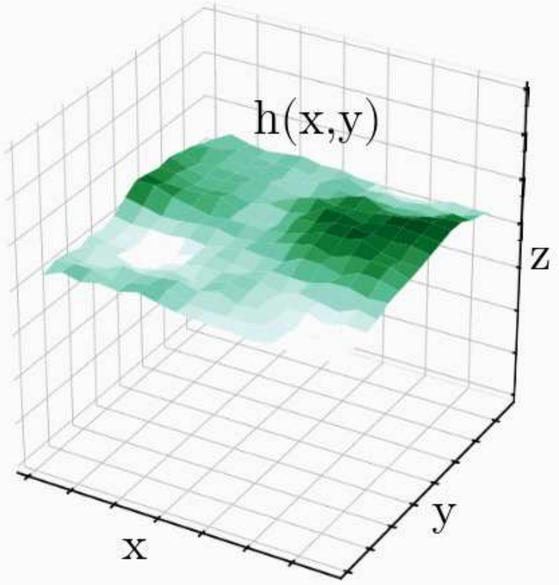

Tail Length, n	Tail Beads, N	Bending Rigidity (kT) (40% charge)
8	2	18.4
12	3	49.5
16	4	83.7
20	5	122.0

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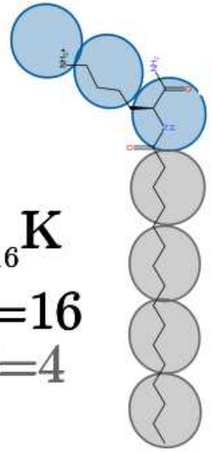
C_nK Bilayer Elastic Properties

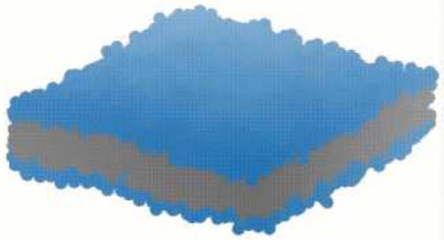


$C_{16}K$

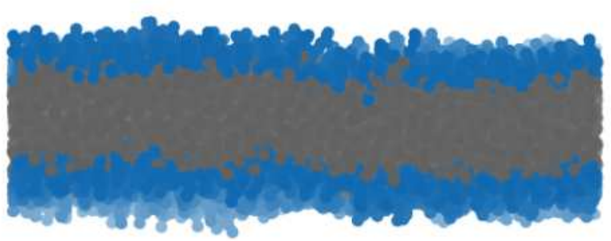
n=16

N=4

MARTINI 2.2F



10 nm



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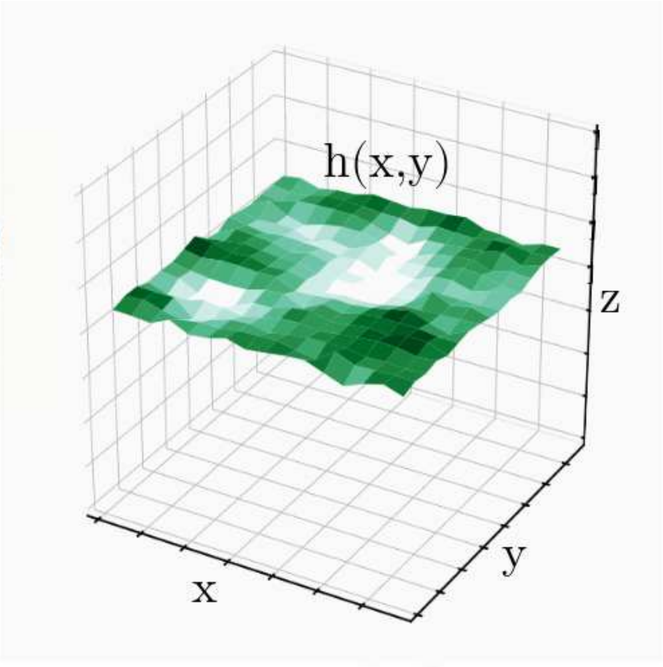
$$L_x L_y \langle |h_q|^2 \rangle = \frac{k_B T}{\kappa q^4}$$



Tail Length, n	Tail Beads, N	Bending Rigidity (kT) (40% charge)
8	2	18.4
12	3	49.5
16	4	83.7
20	5	122.0

Increasing tail length leads to more rigid bilayers

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Outline

I. Introduction to charged chiral amphiphile assemblies
    a) C_nK molecule

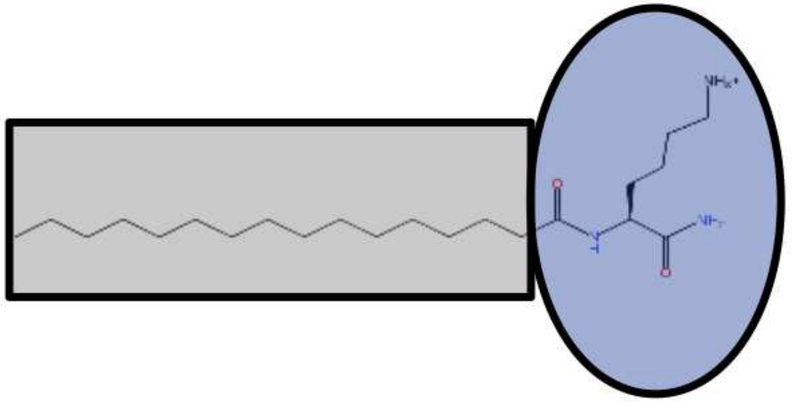
II. Chapter 1: Characterization of C_nK assemblies in different ionic environments, shape selection dictated by electrostatics

III. Chapter 2: Charge regulation in ionizable assemblies

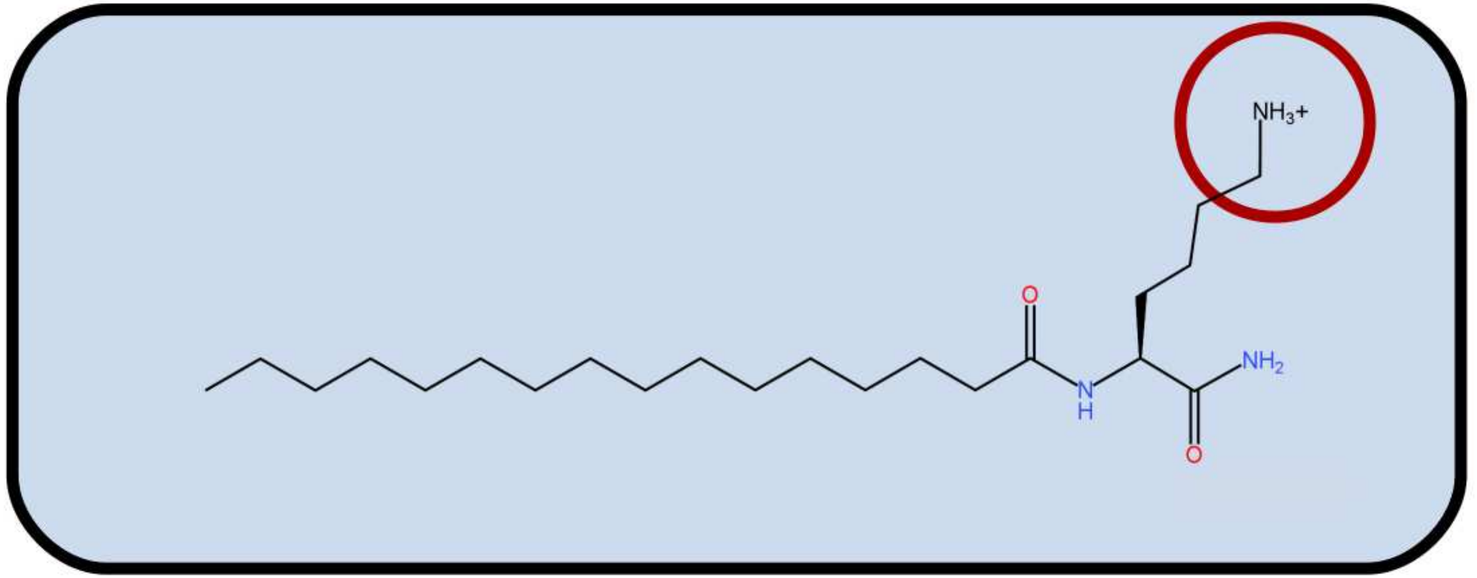
IV. Conclusion: summary, outlook, and acknowledgements

Northwestern

A Closer Look at the Electrostatics

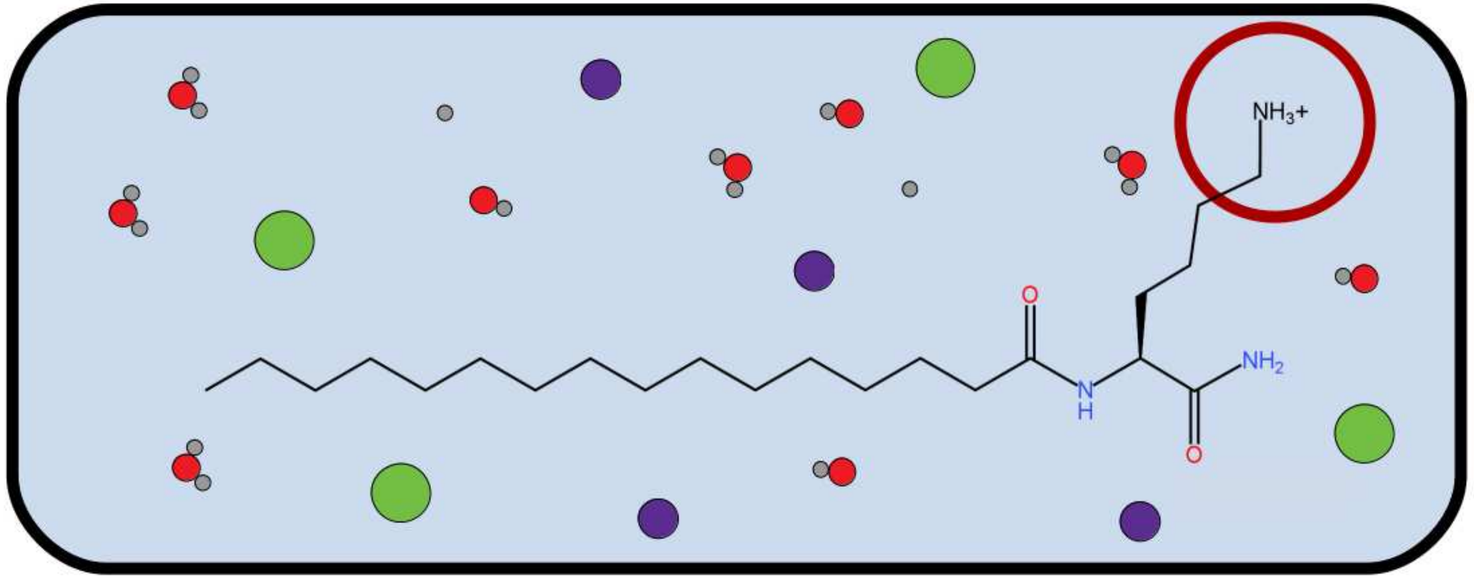


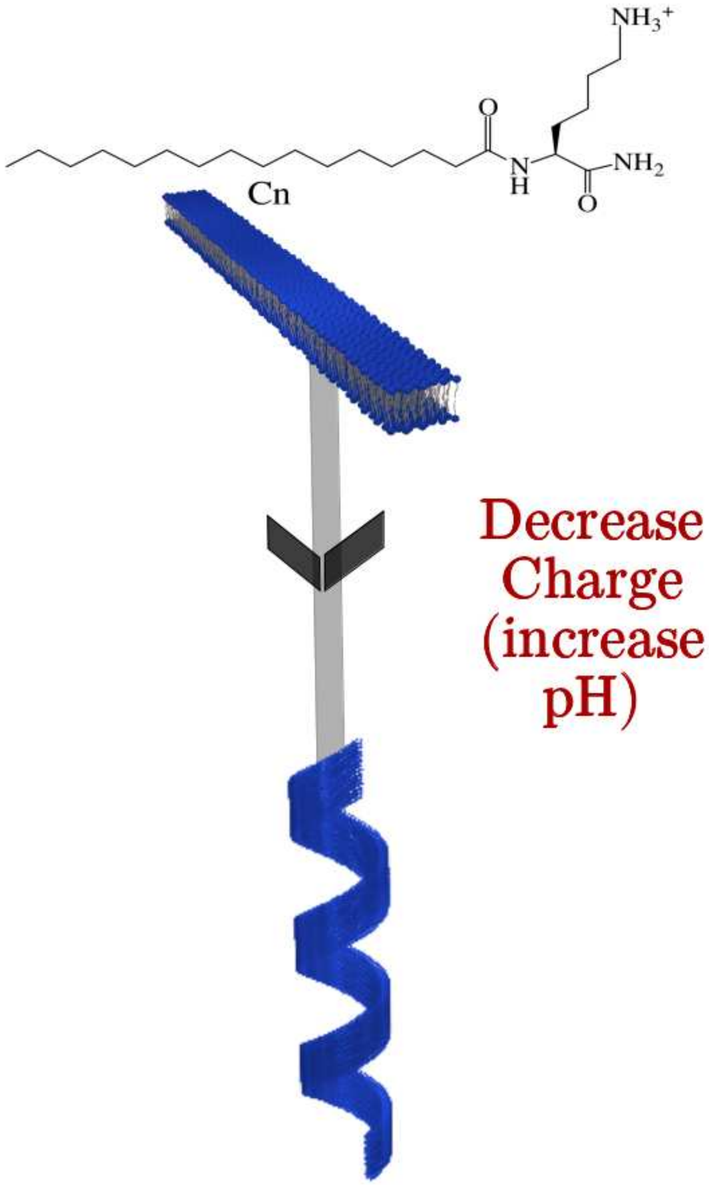
A Closer Look at the Electrostatics



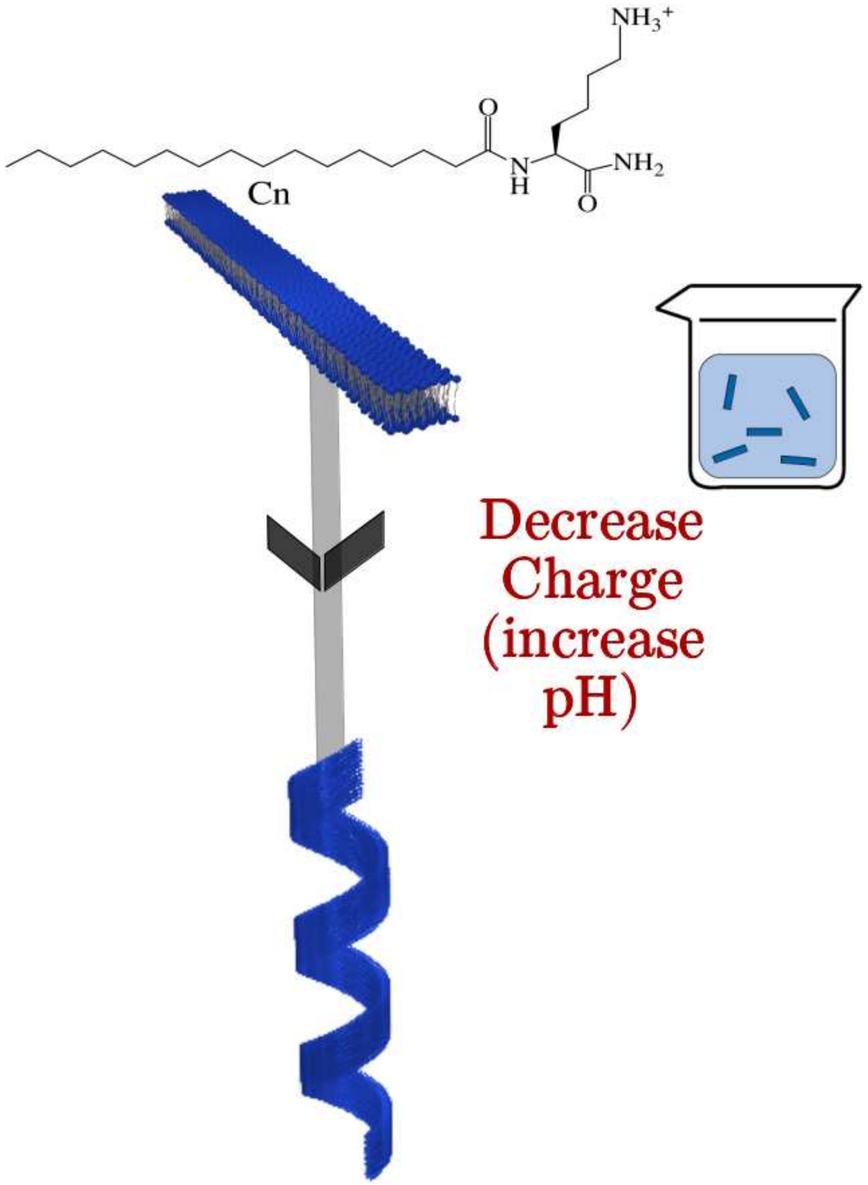
A Closer Look at the Electrostatics

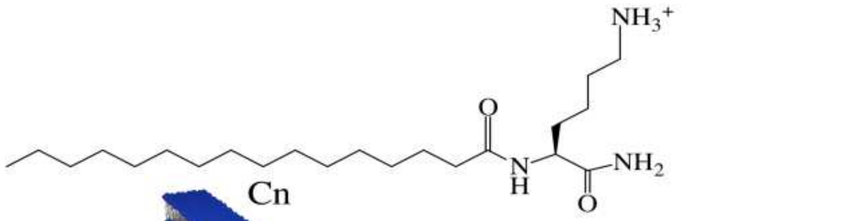
Ionization behavior of lysine headgroup: charge regulation effects

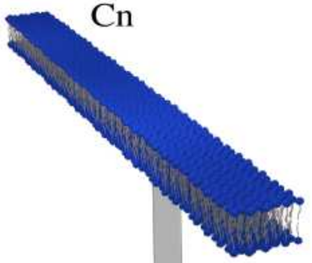


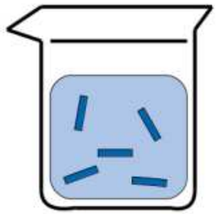


Decrease Charge (increase pH)

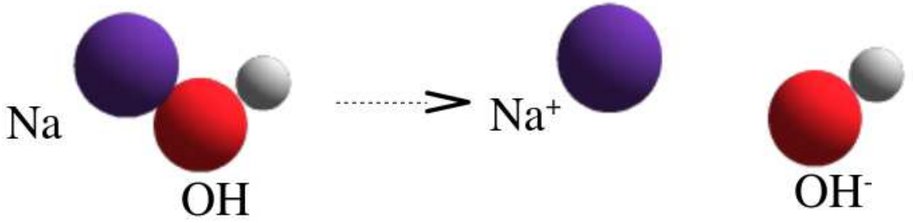

NH_3^+
O
N
H
NH_2
O
Cn
Decrease
Charge
(increase
pH)

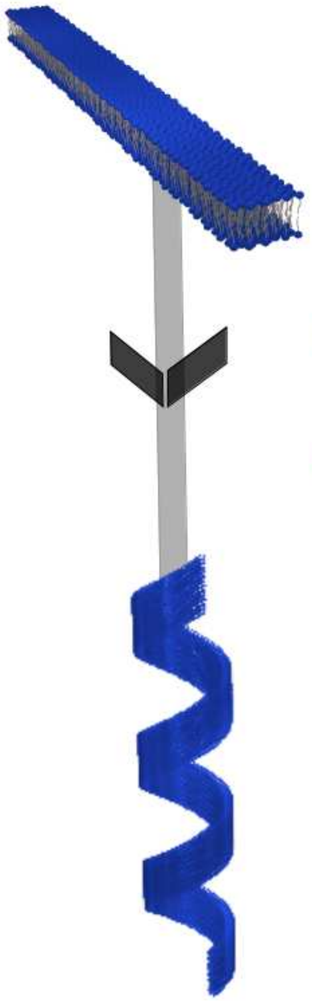


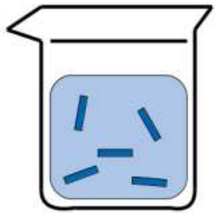




Decrease Charge (increase pH)







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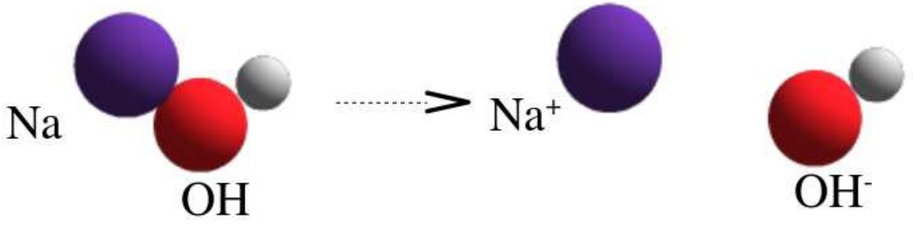

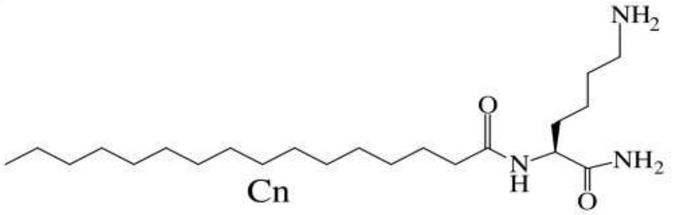

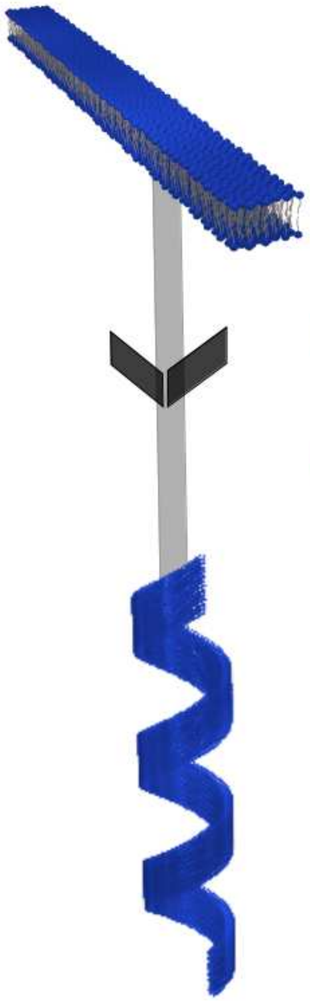

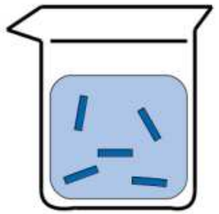

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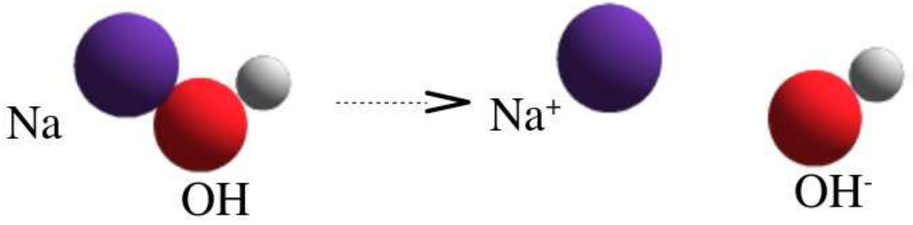

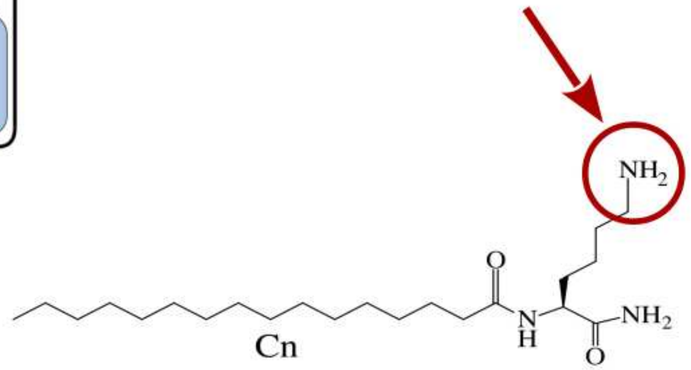

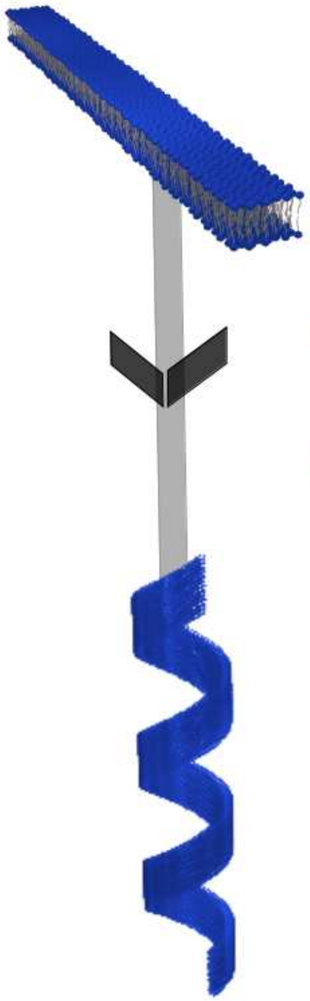

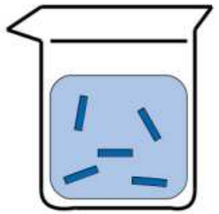

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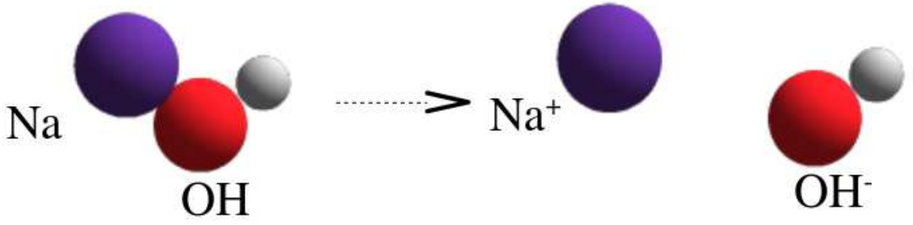

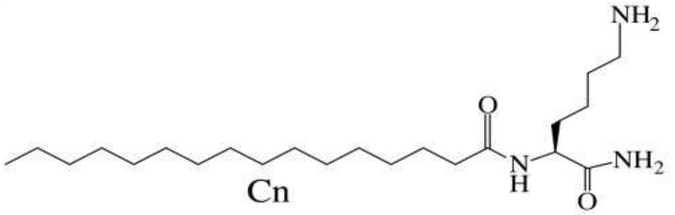

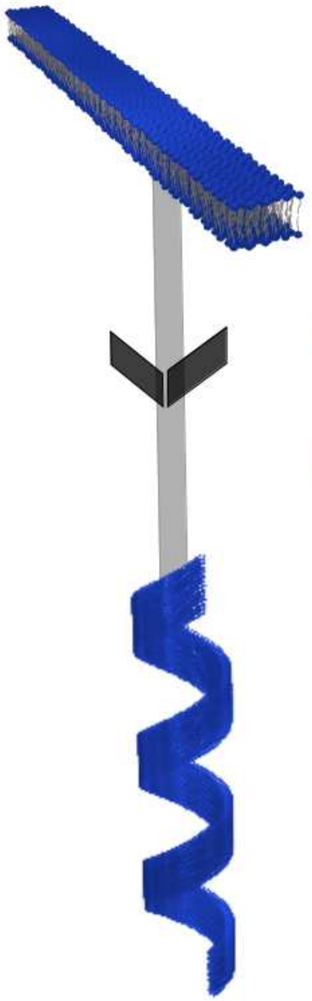

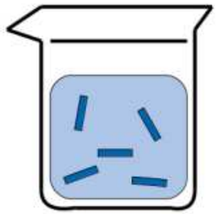

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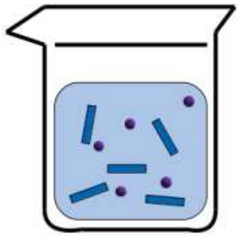
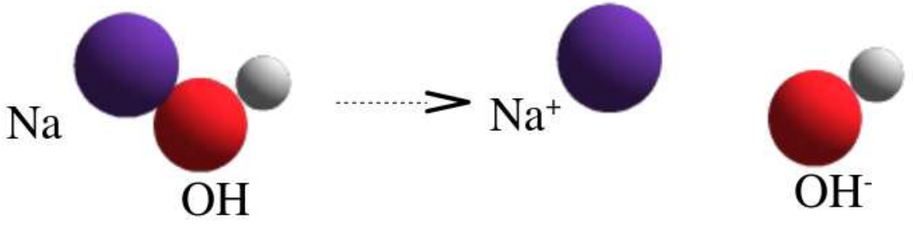
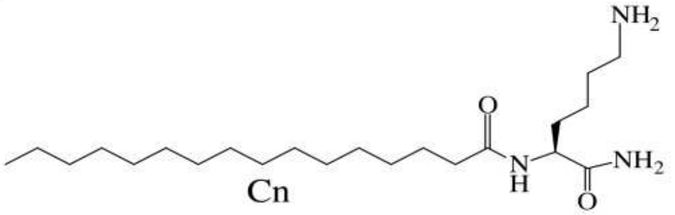
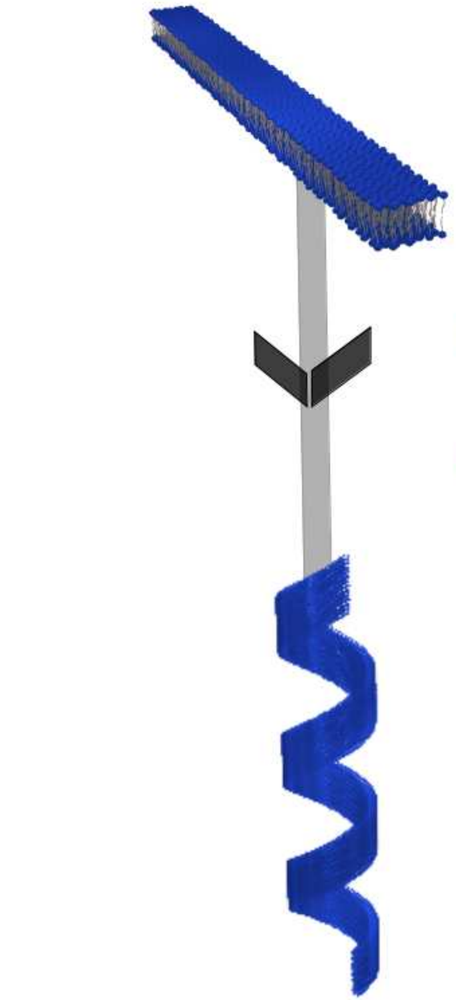
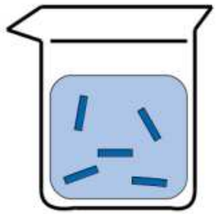


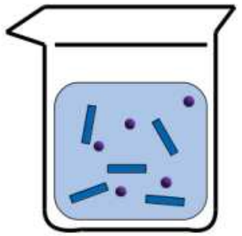


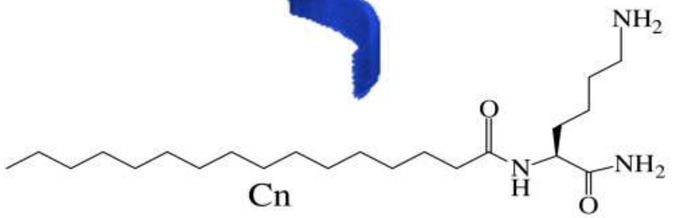


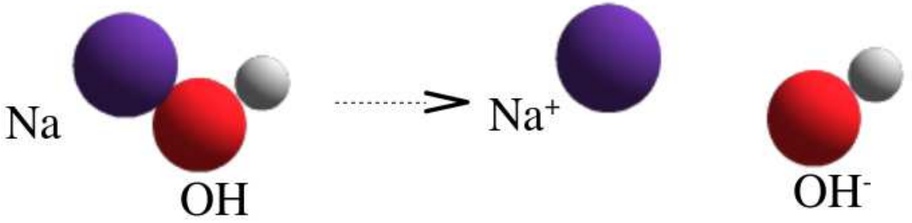


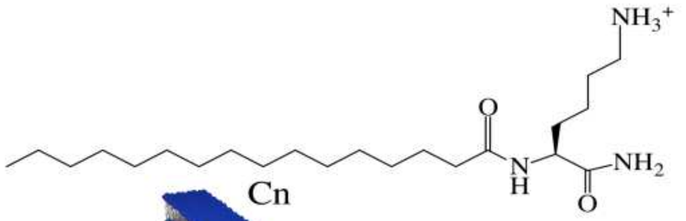


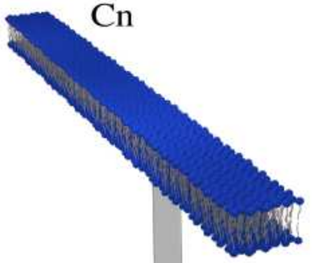
Decrease Charge (increase pH)

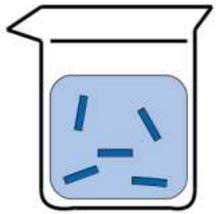












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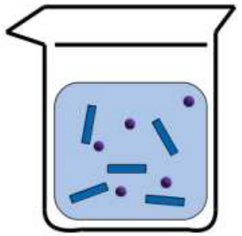

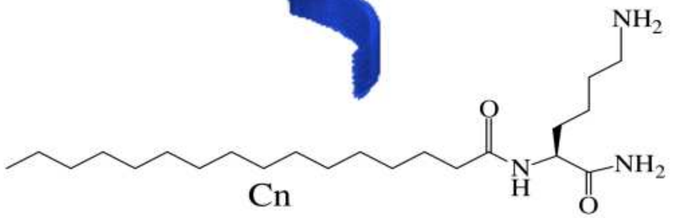

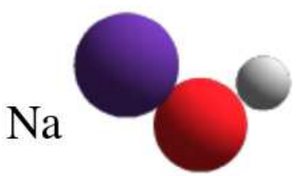

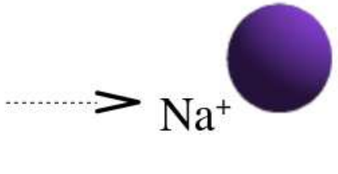


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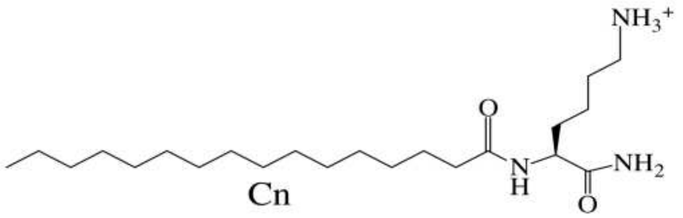
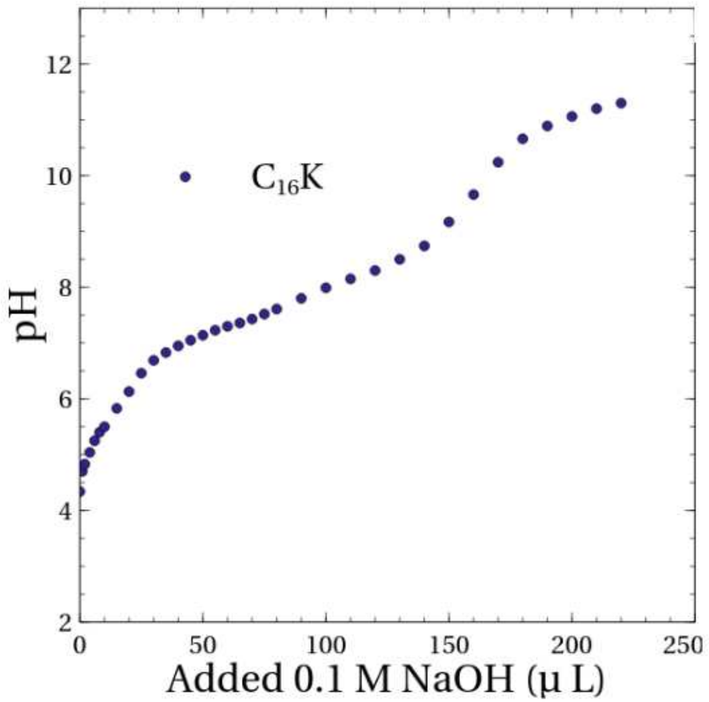
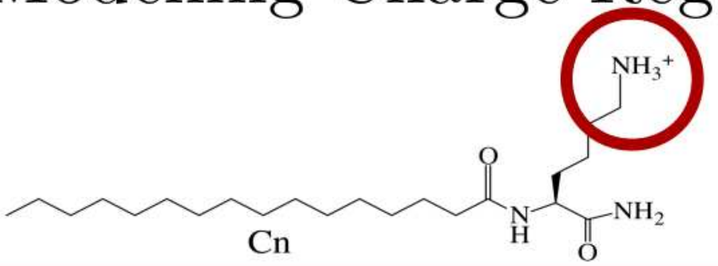
Modelling Charge Regulation: Titration Curves



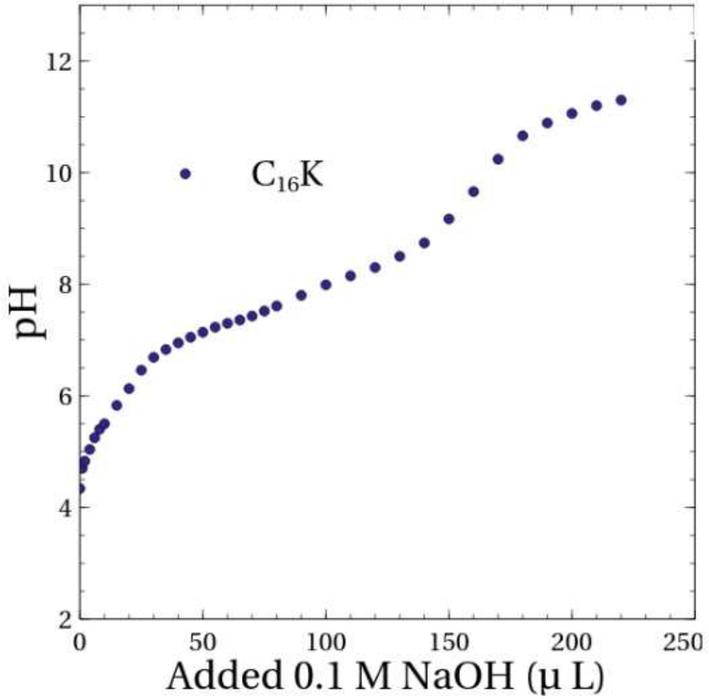


Titration Curve for $C_{16}K$

Modelling Charge Regulation: Titration Curves



$$NH_3^+ + OH^- \overset{K_a}{\rightleftharpoons} NH_2 + H_2O$$



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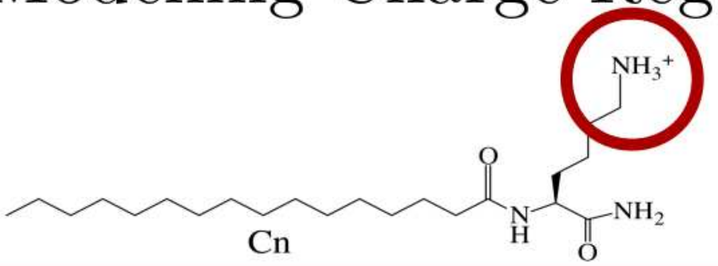

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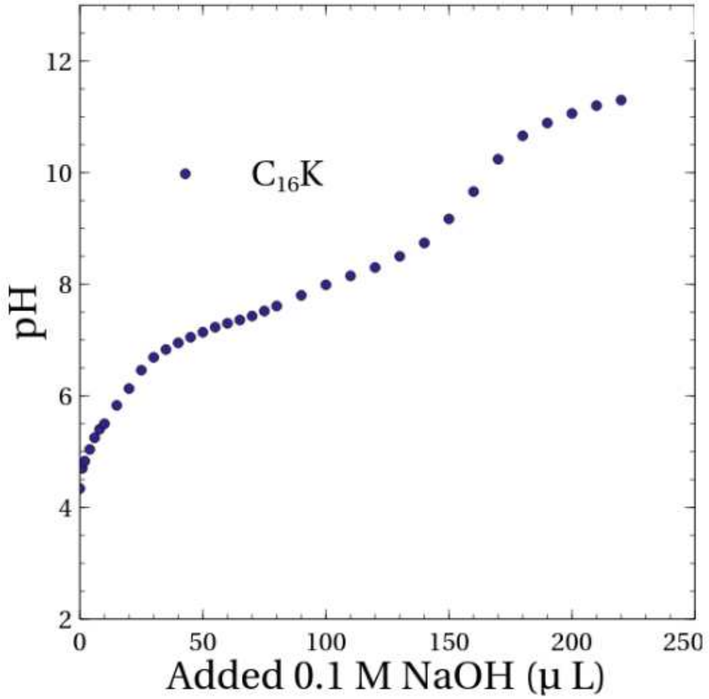

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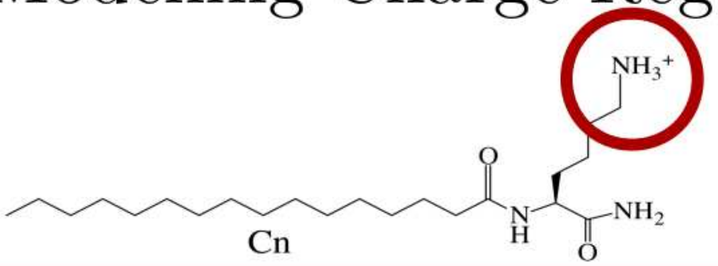

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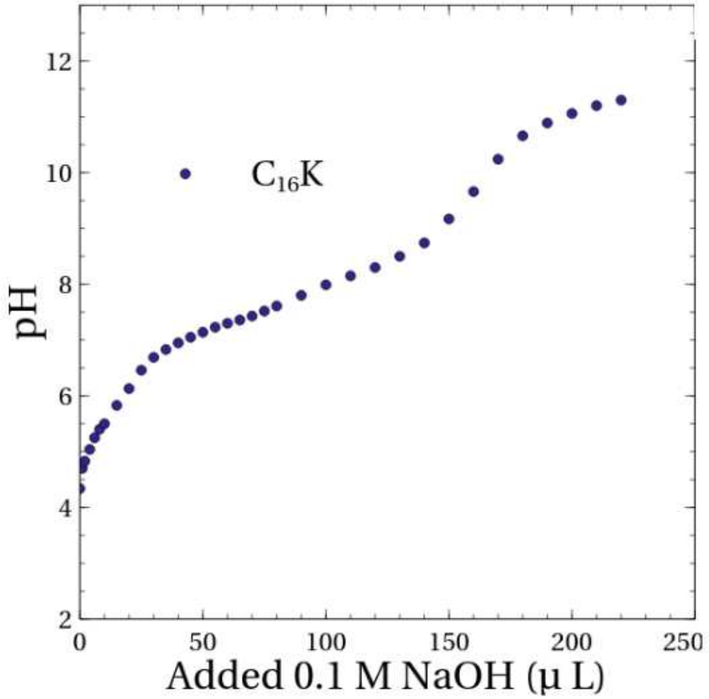

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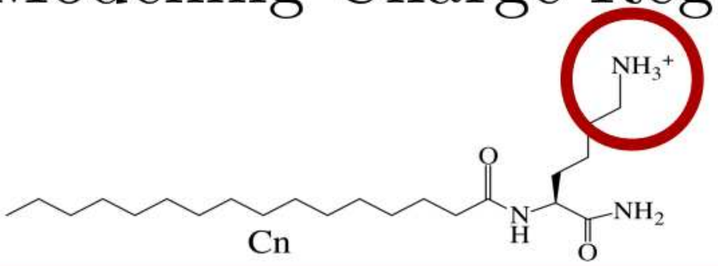

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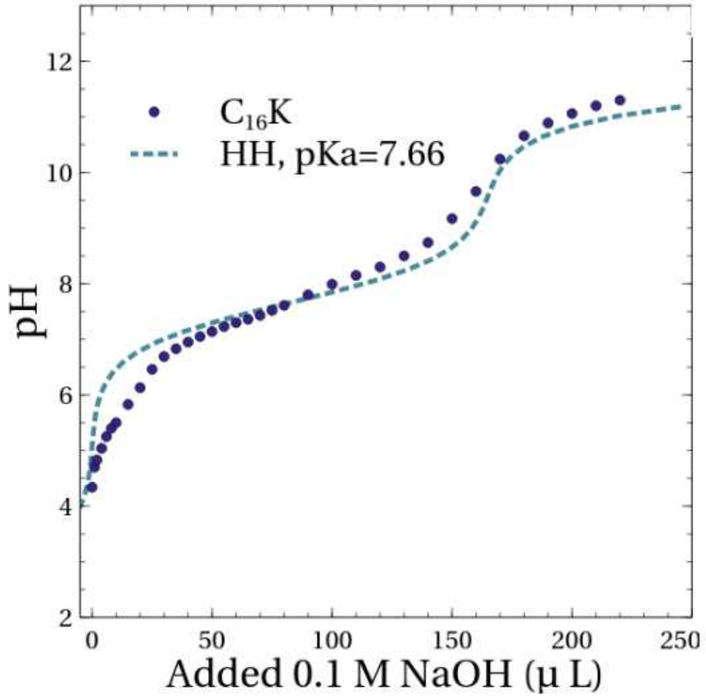

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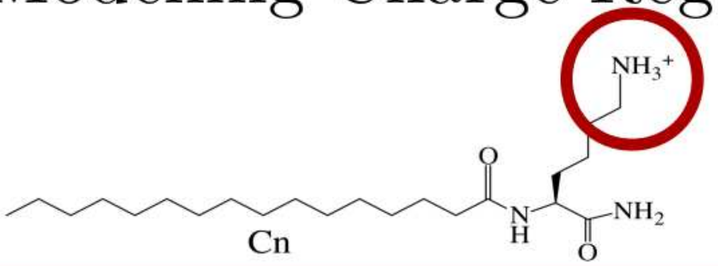

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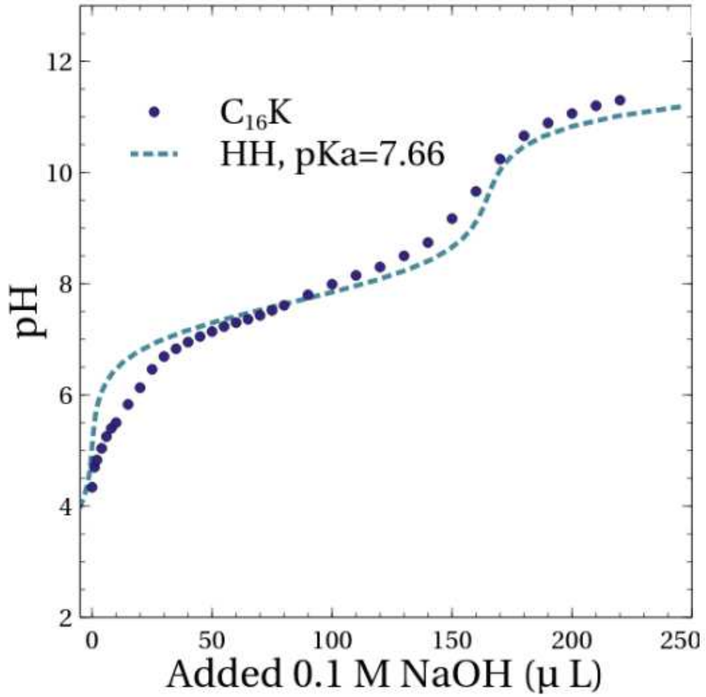

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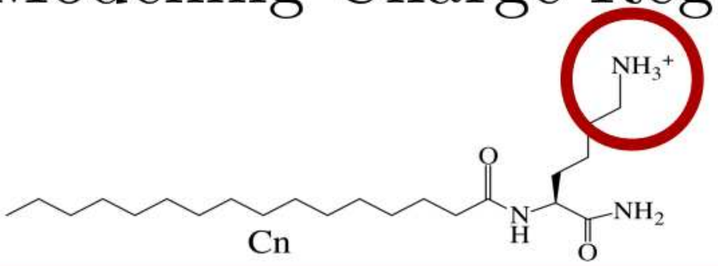

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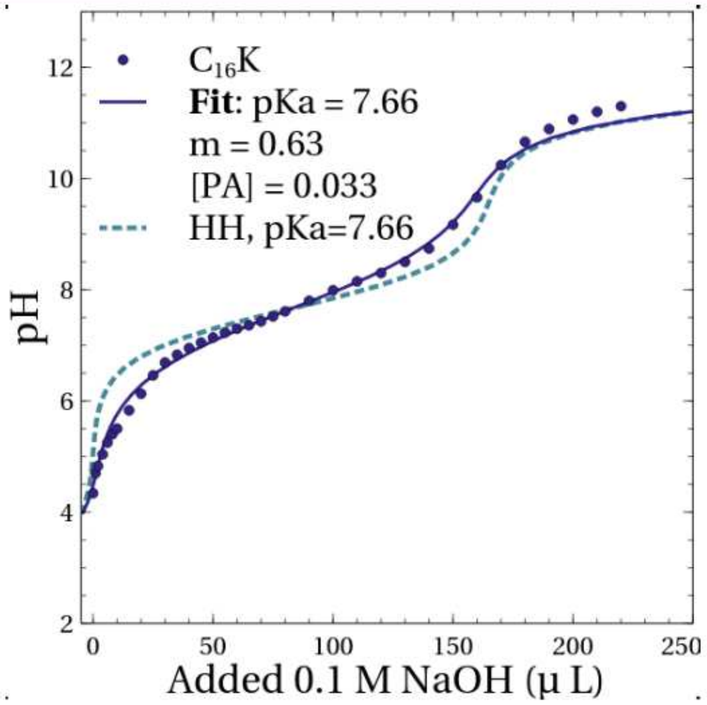

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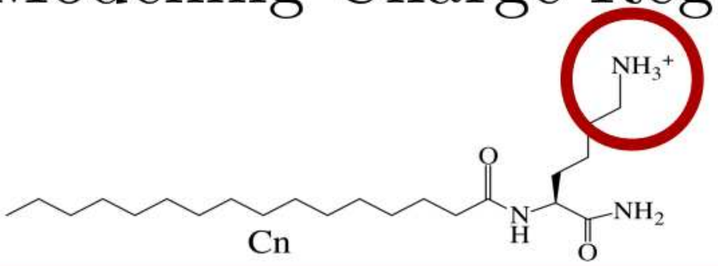

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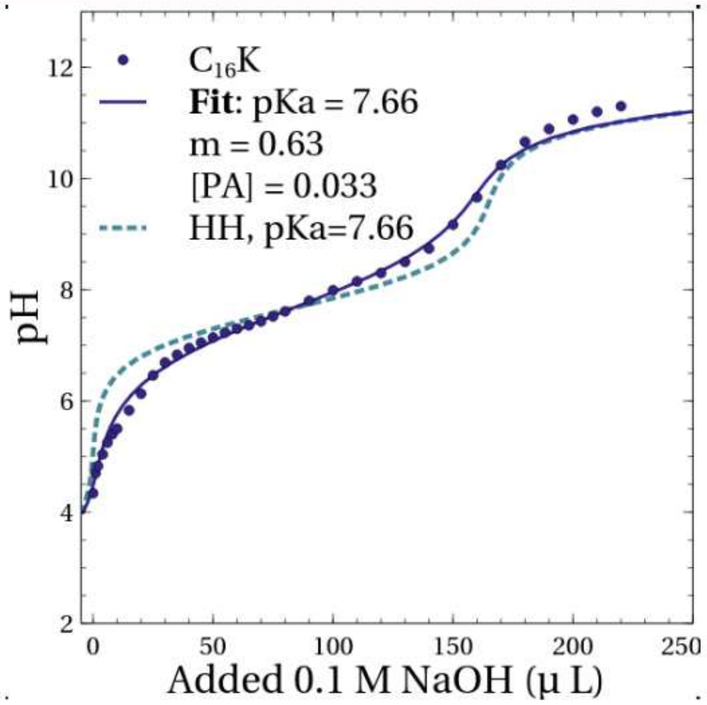

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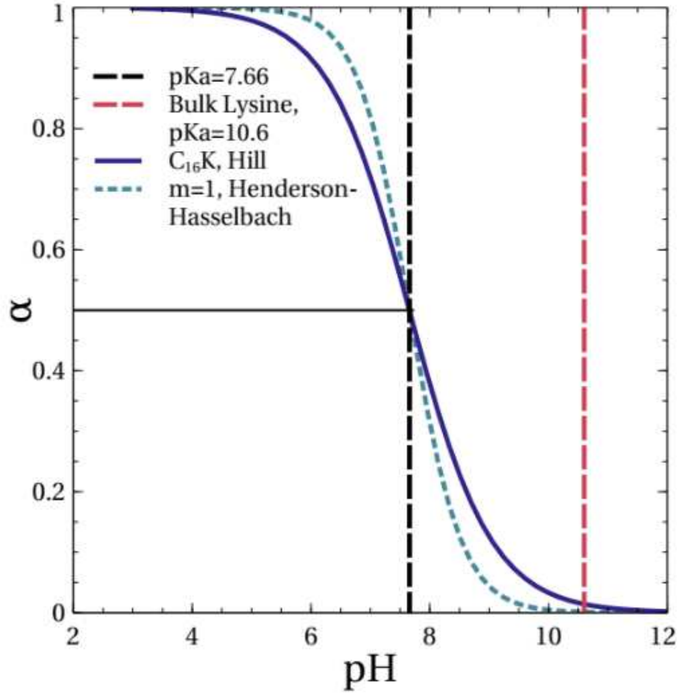

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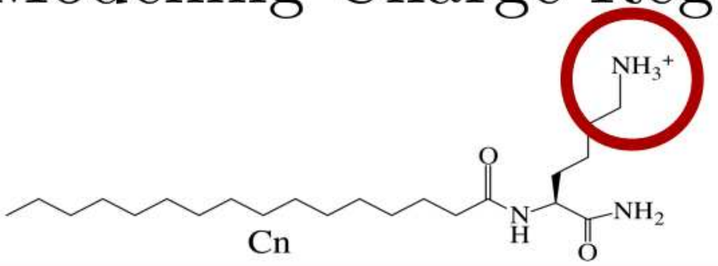

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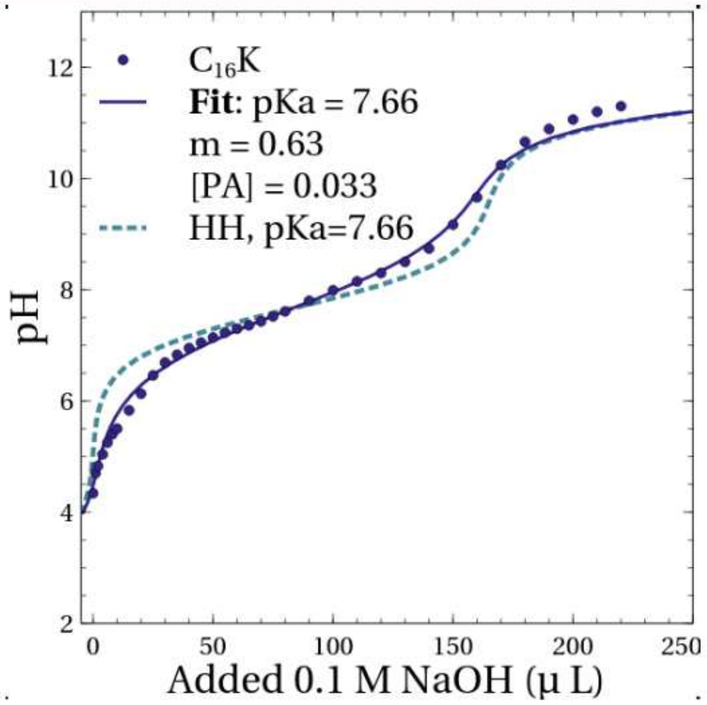

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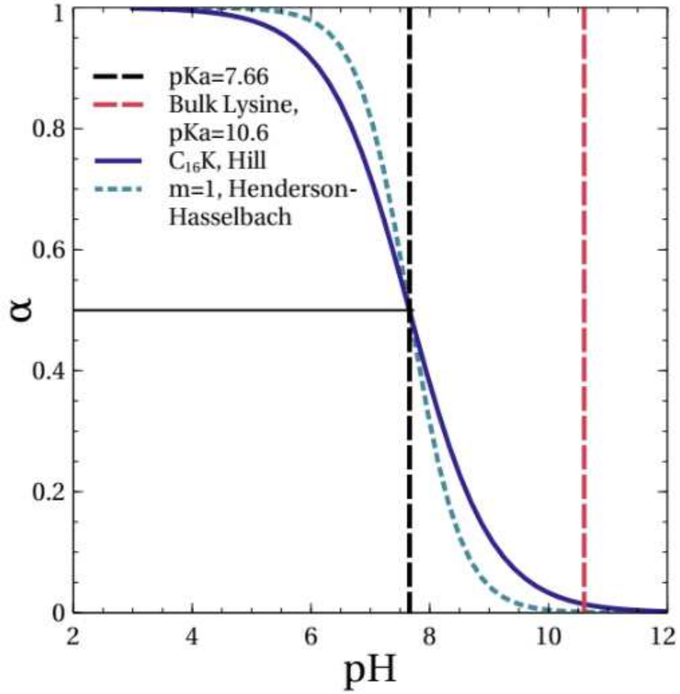

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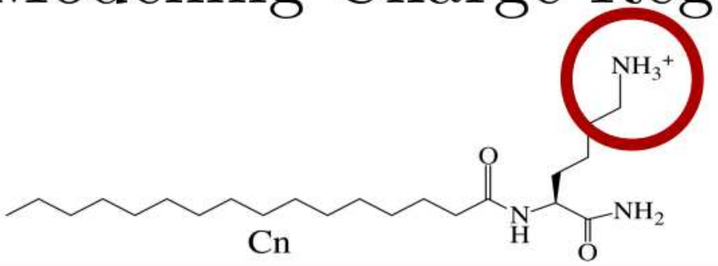

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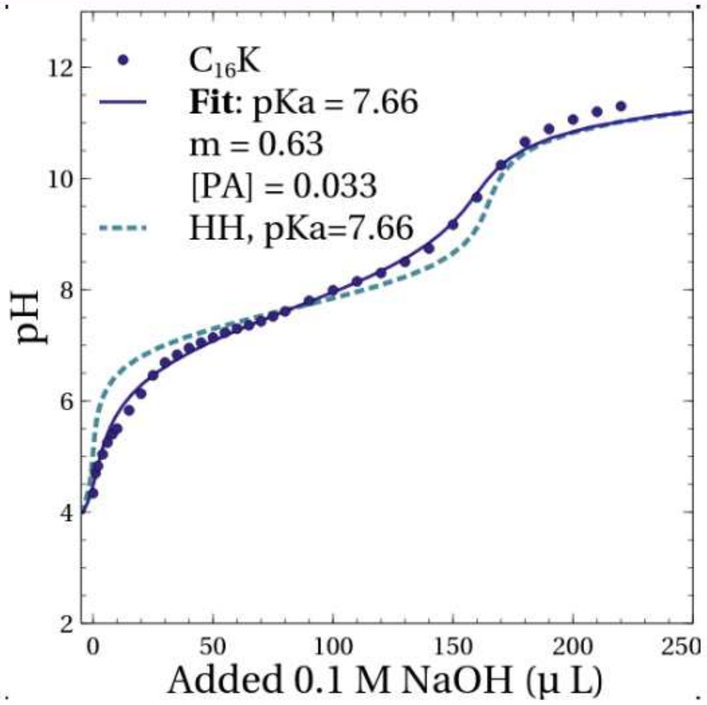

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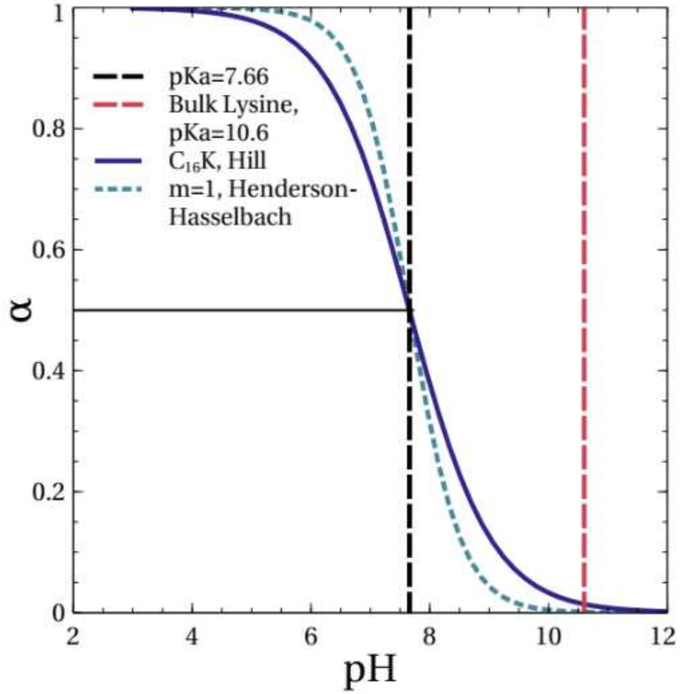

Models for Titration (Henderson-Hasselbach, Hill, Electrostatic)

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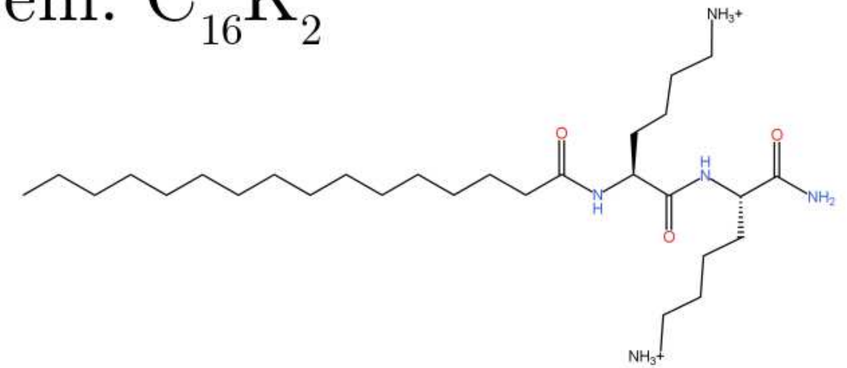
Similar System: $C_{16}K_2$



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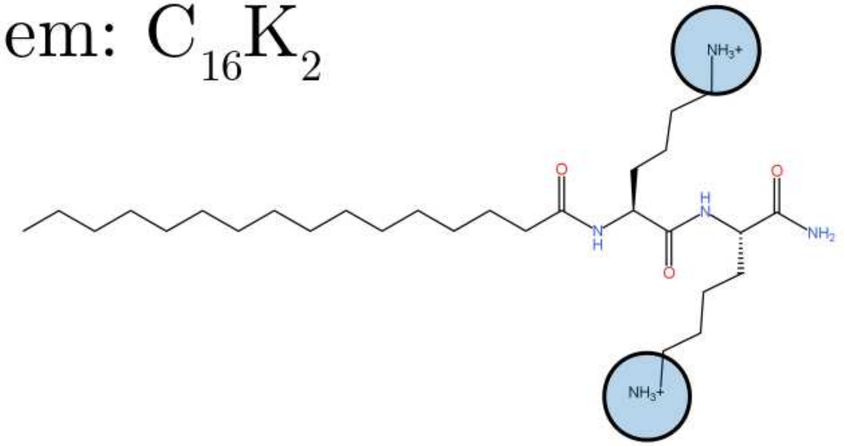

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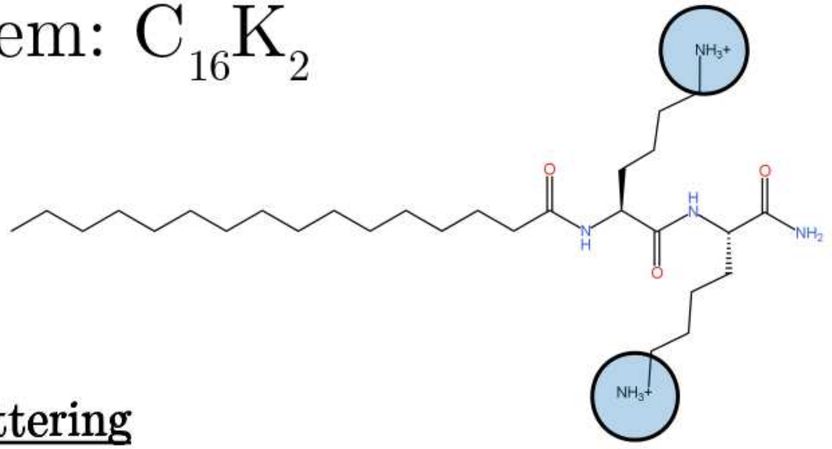
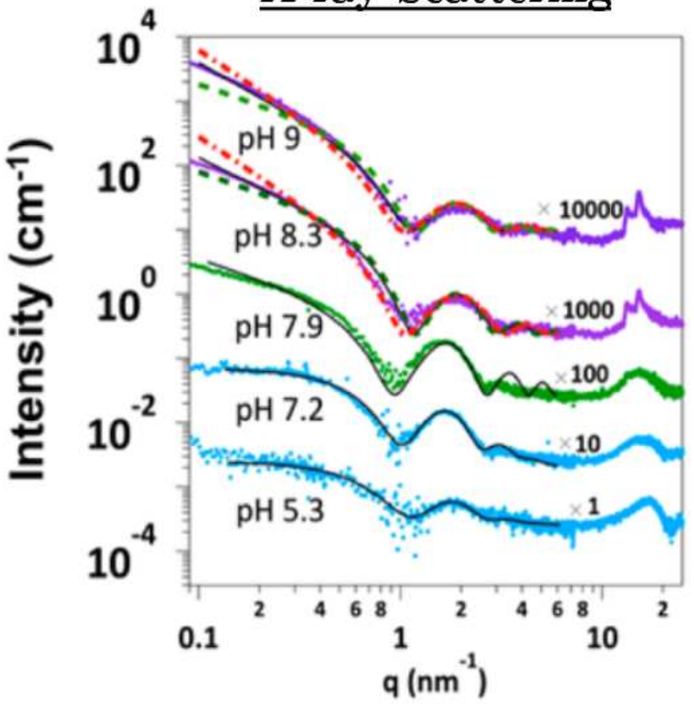
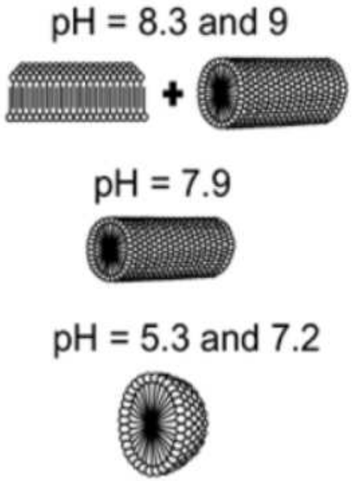


X-ray Scattering





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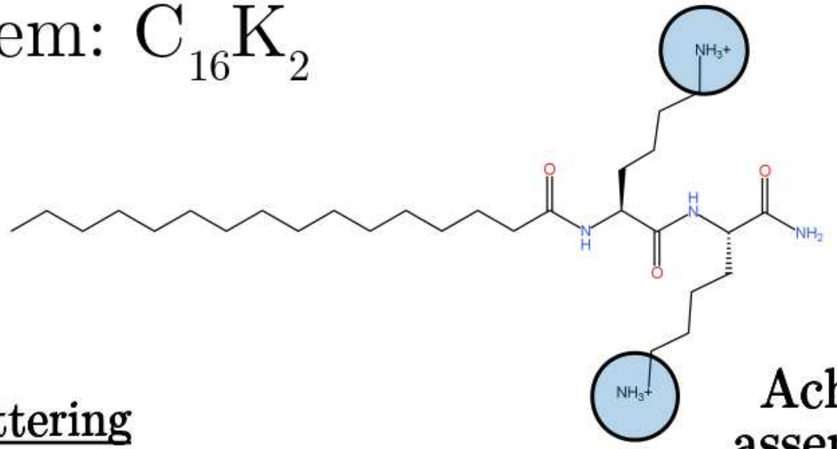

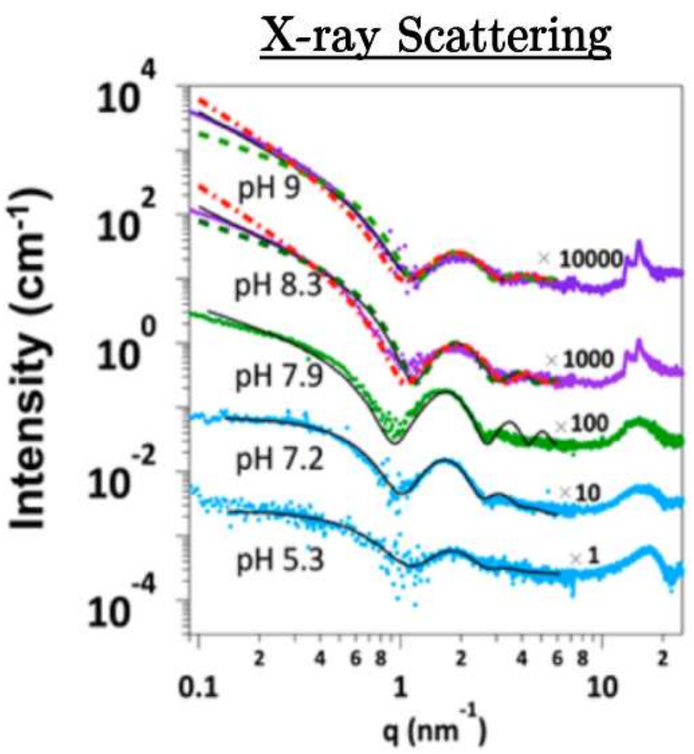

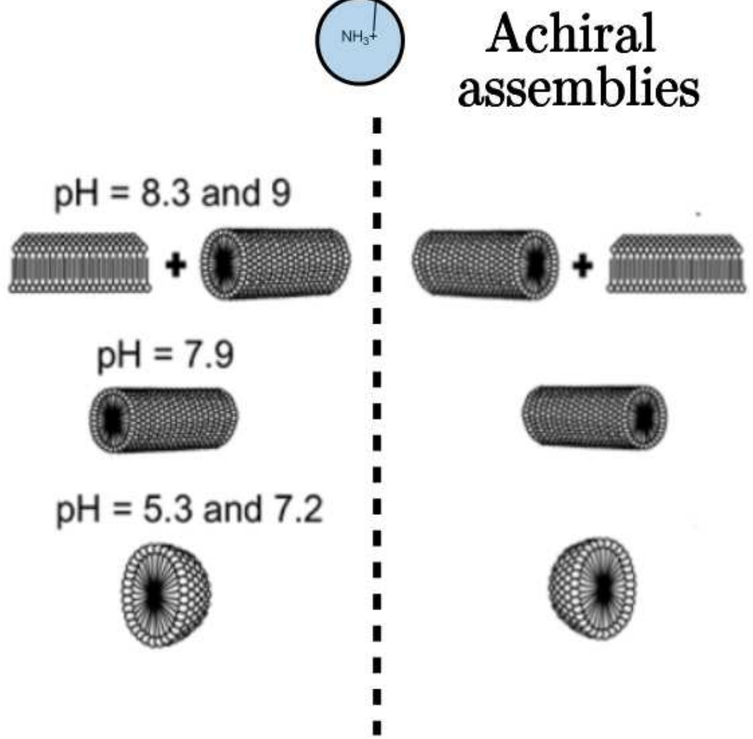

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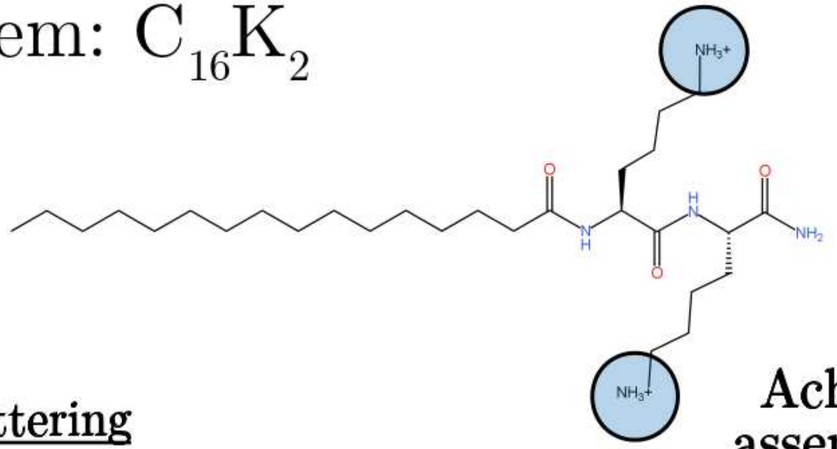
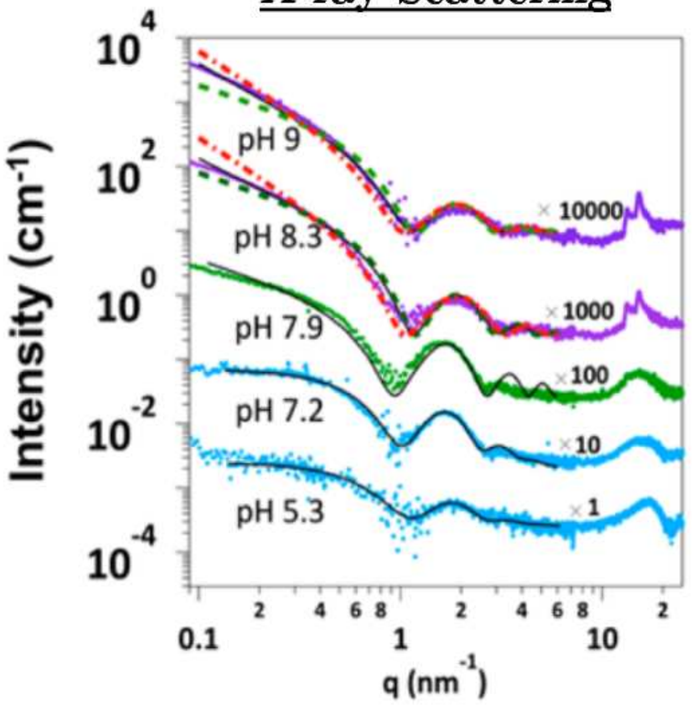
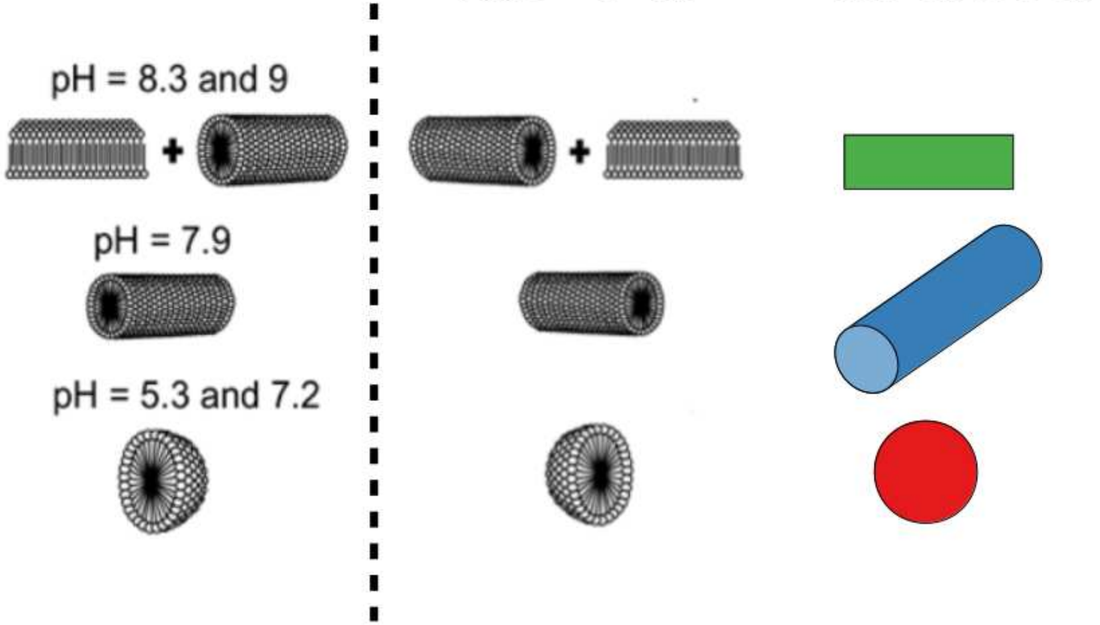
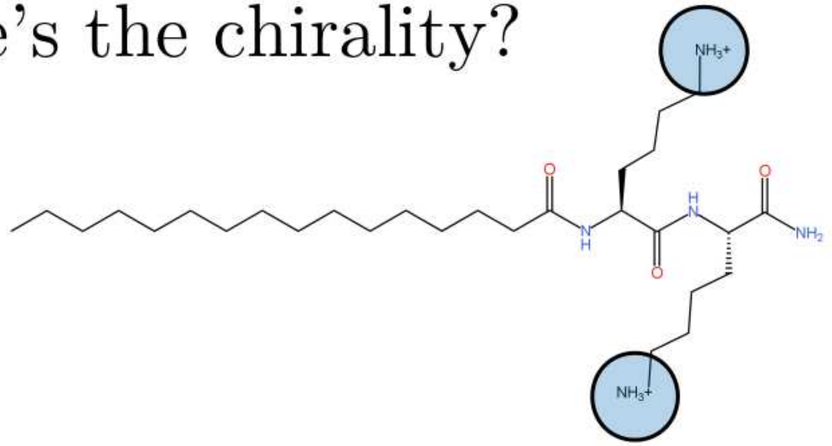


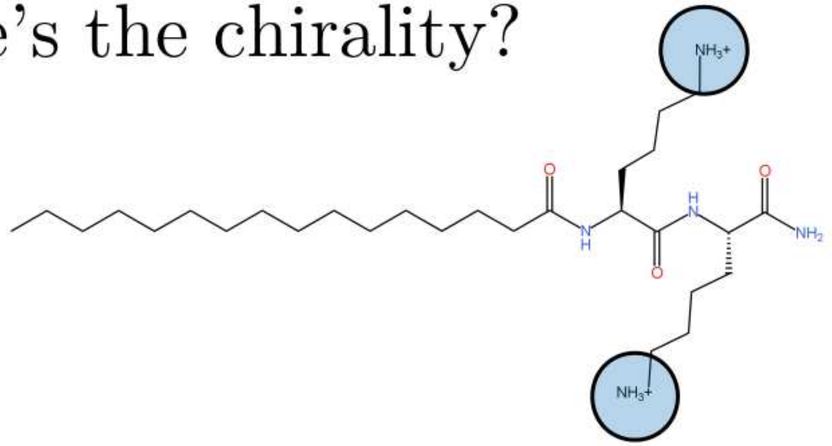


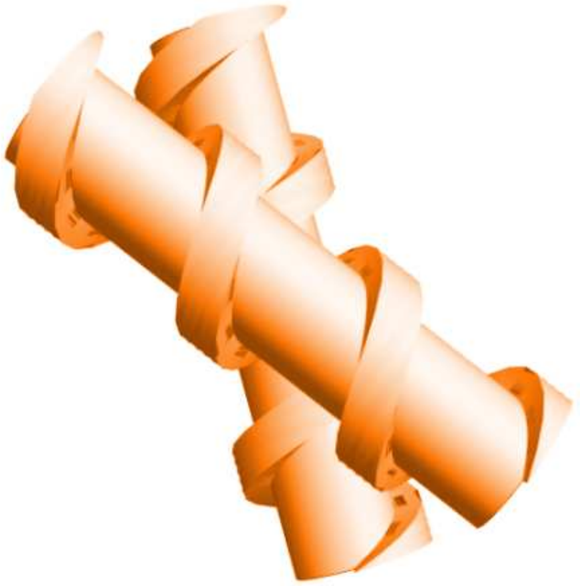


$C_{16}K_2$: where's the chirality?



$C_{16}K_2$: where's the chirality?





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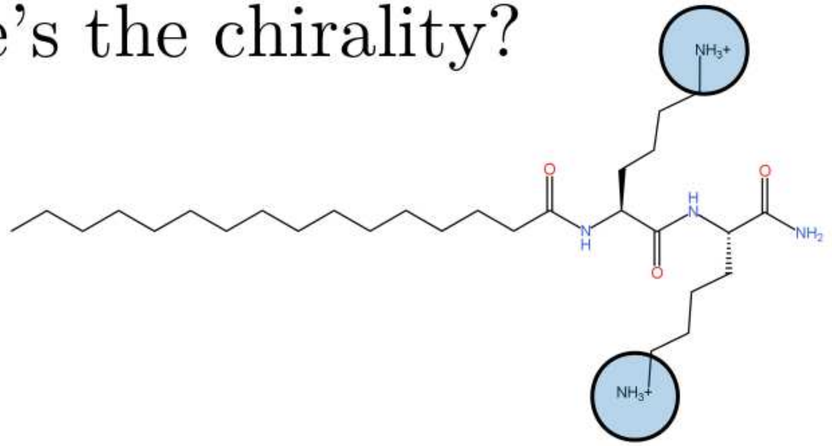

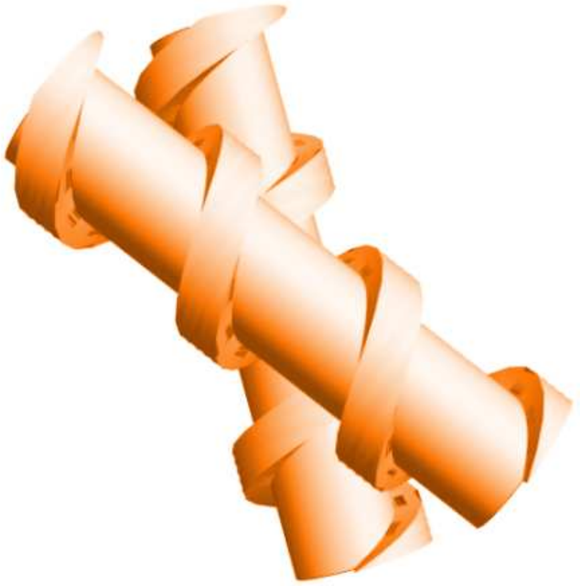

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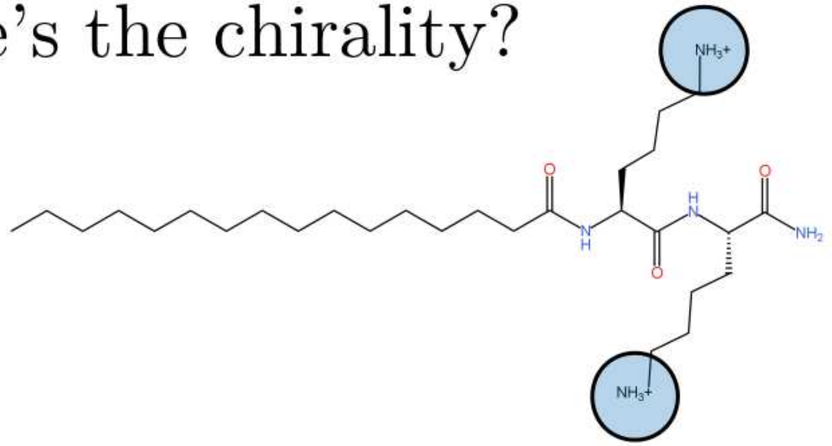

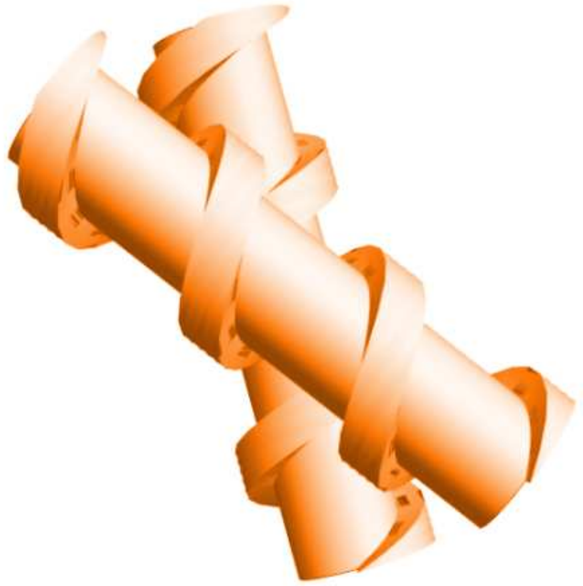

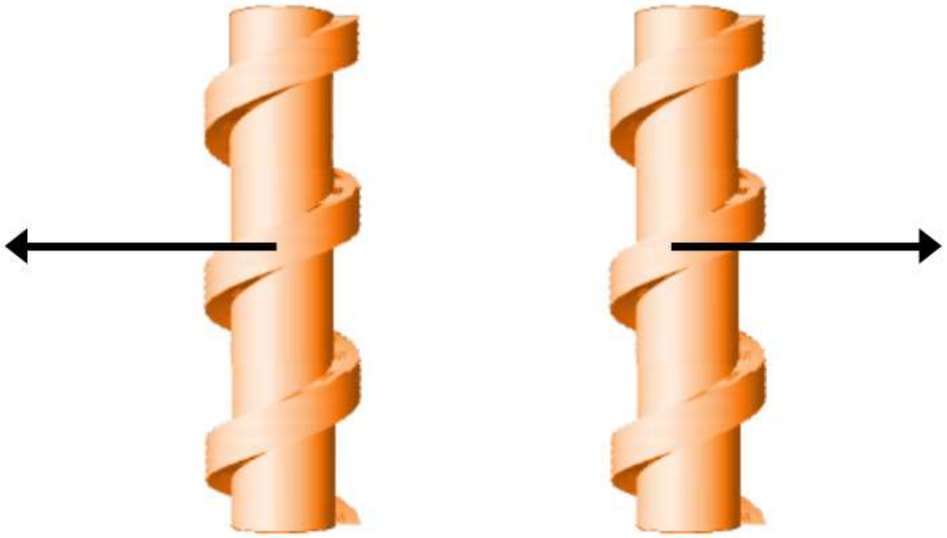

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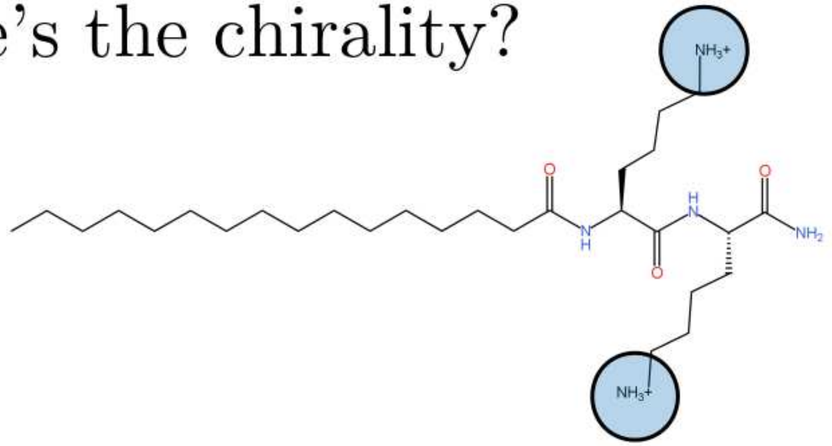
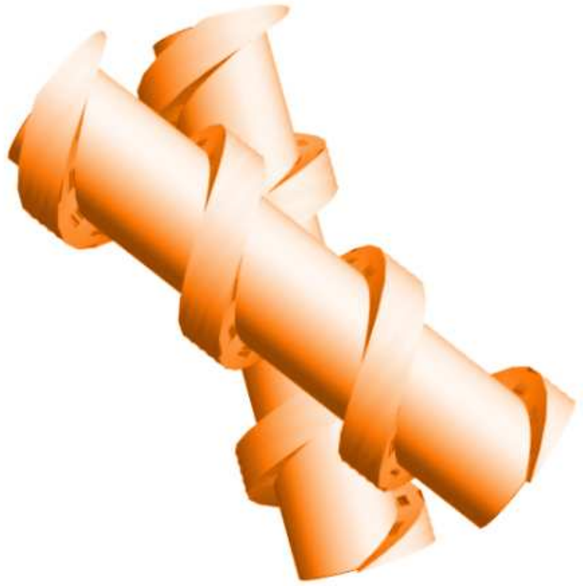
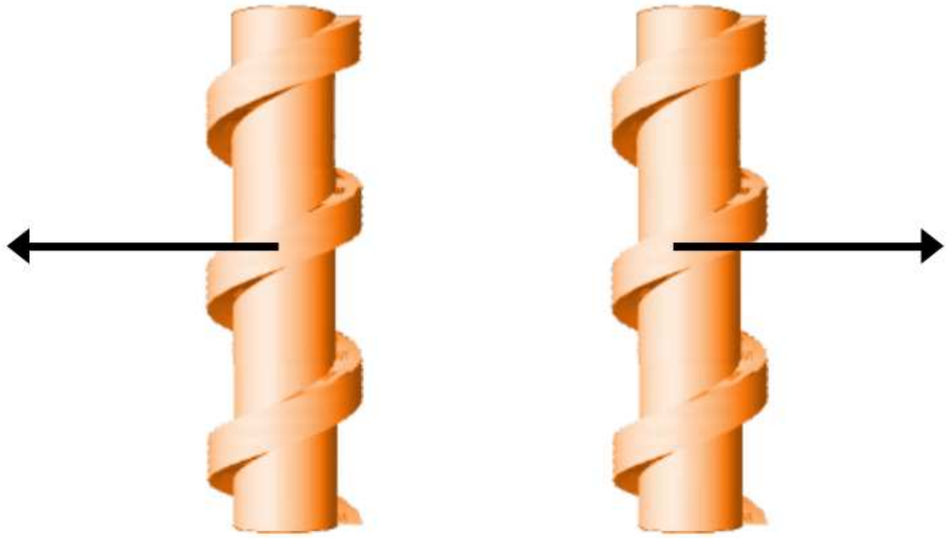
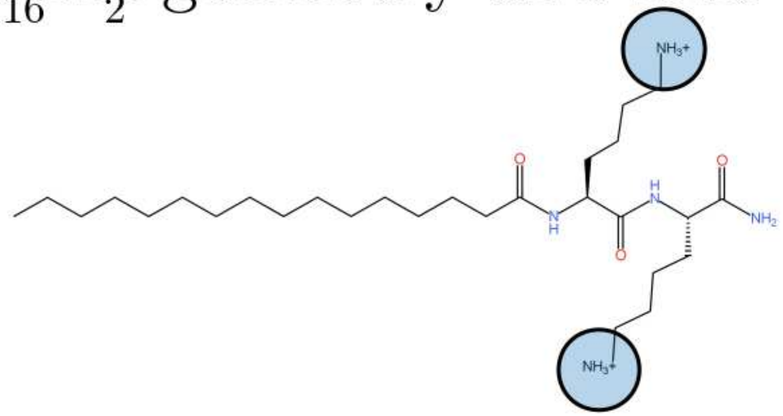




$$\longrightarrow \propto F_{electric} \gg F_{chiral}$$



$C_{16}K_2$: geometry and ions



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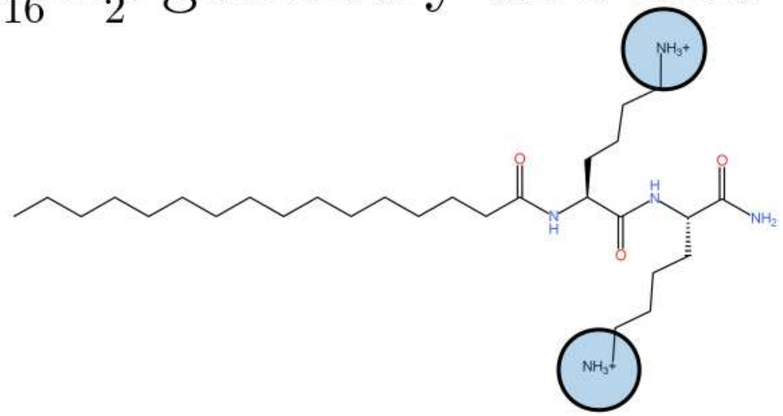
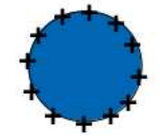
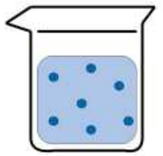
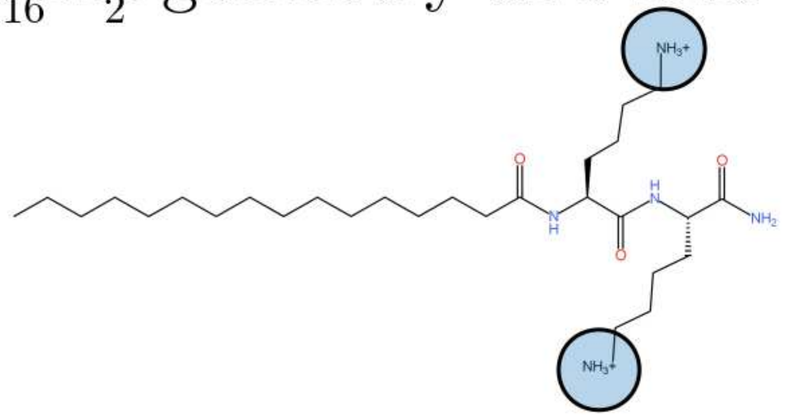


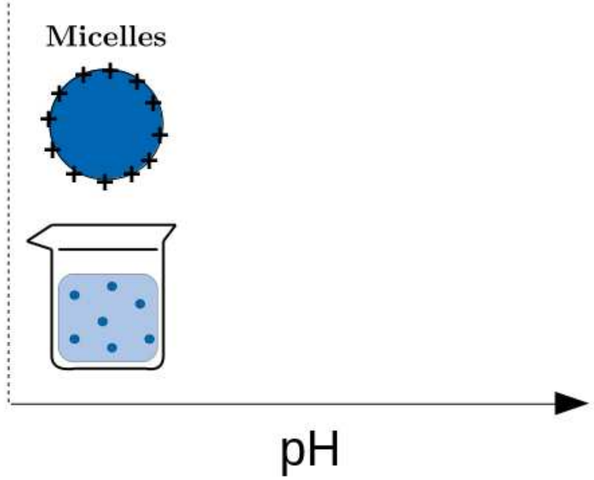
Micelles





$C_{16}K_2$: geometry and ions





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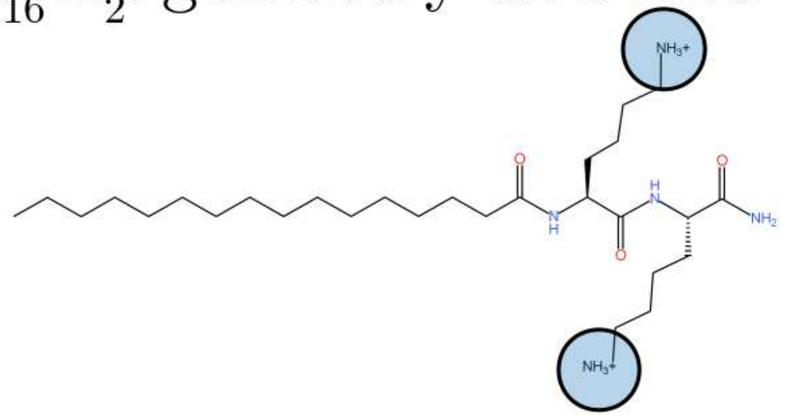

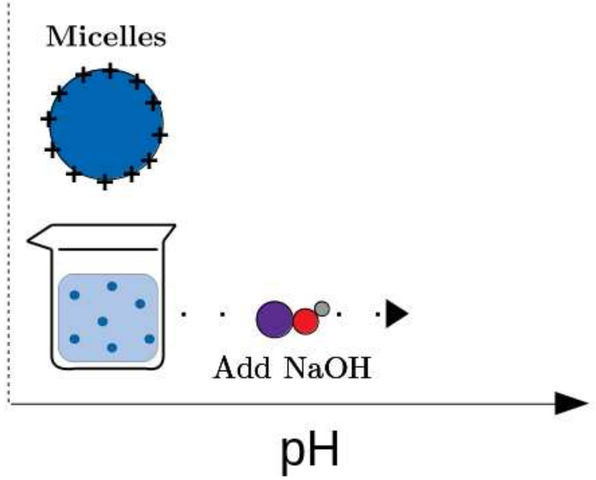

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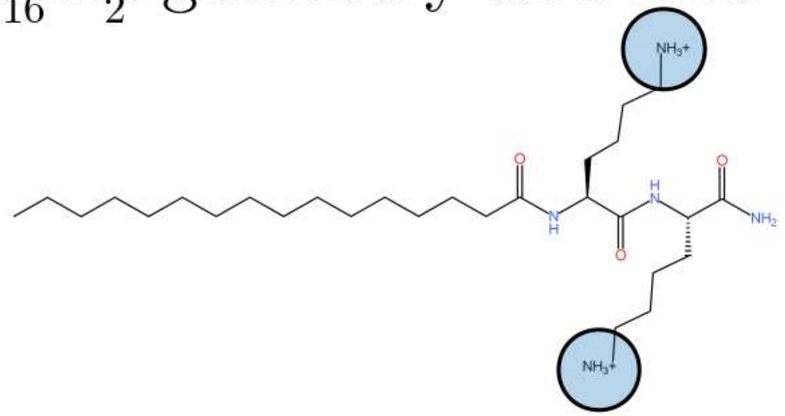
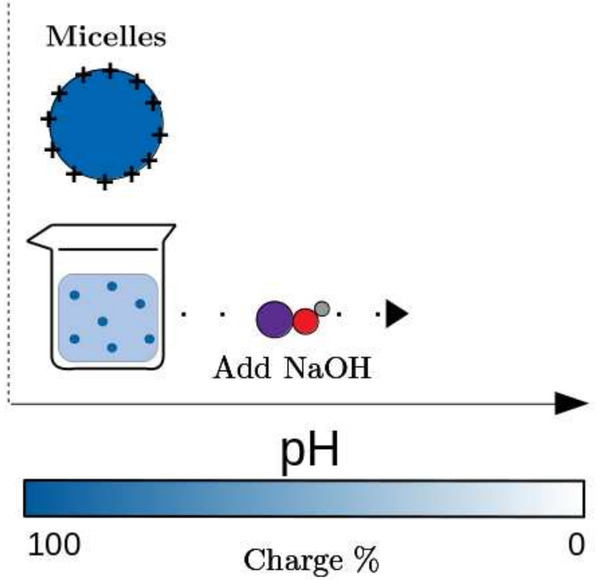
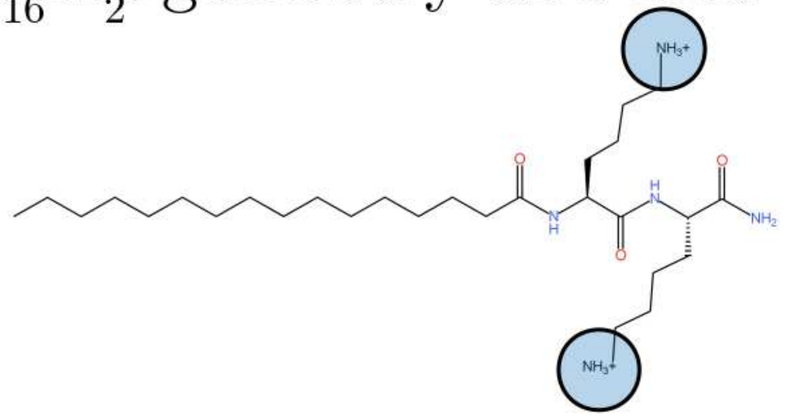
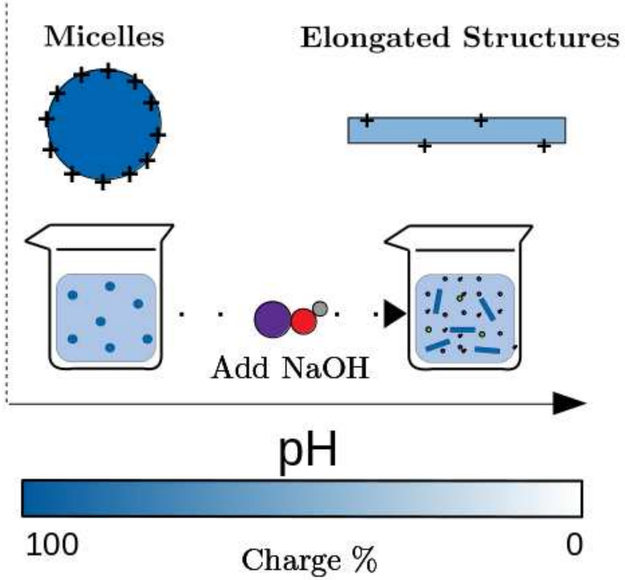


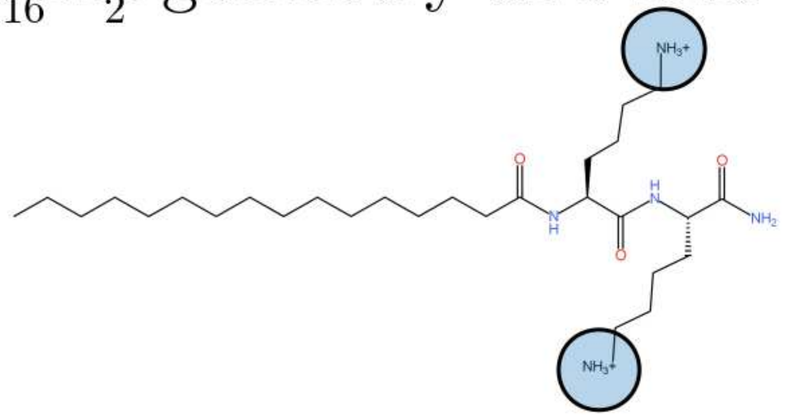


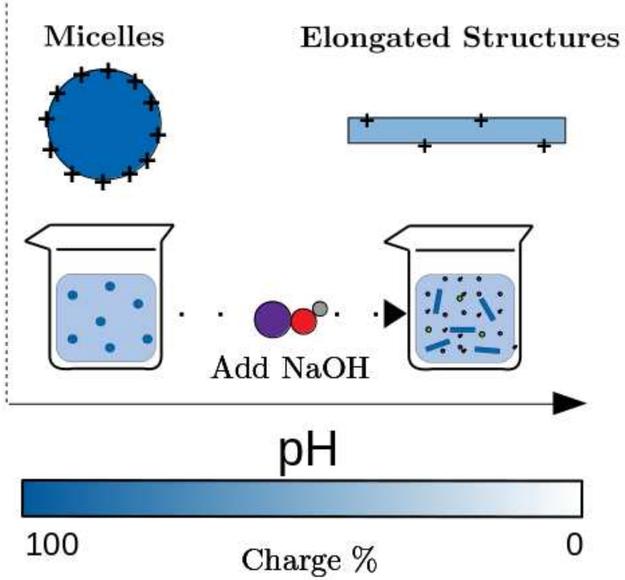
$C_{16}K_2$: geometry and ions

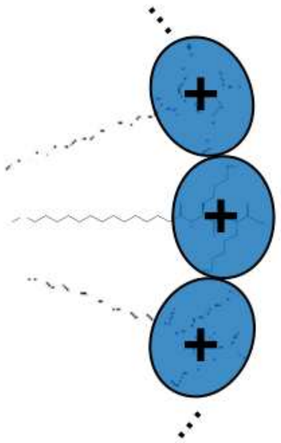




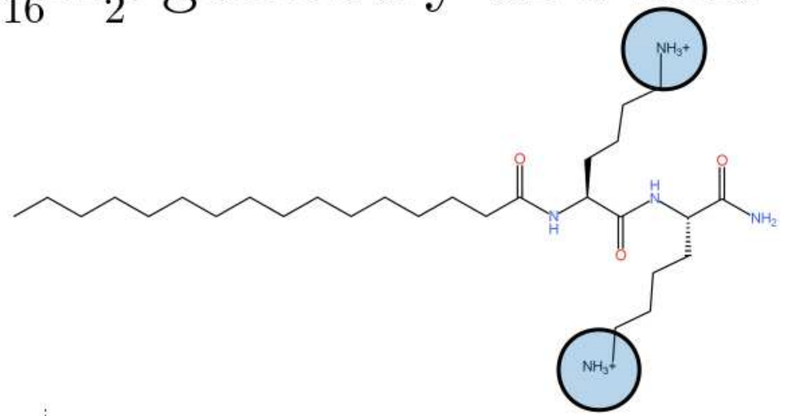
$C_{16}K_2$: geometry and ions

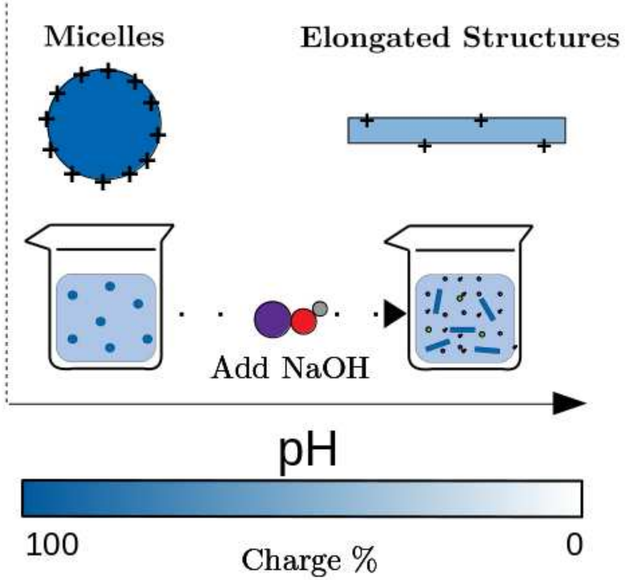


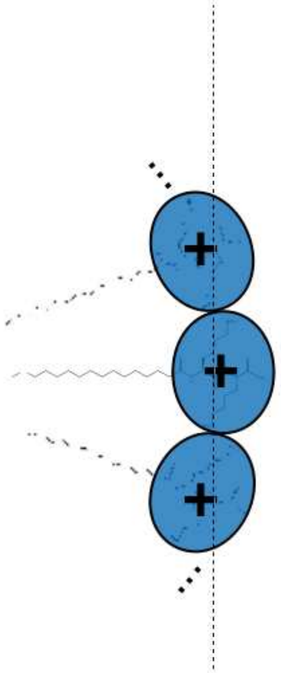




$C_{16}K_2$: geometry and ions







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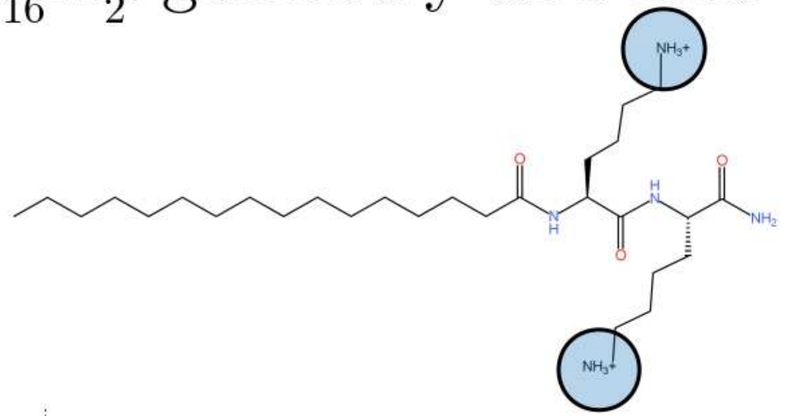

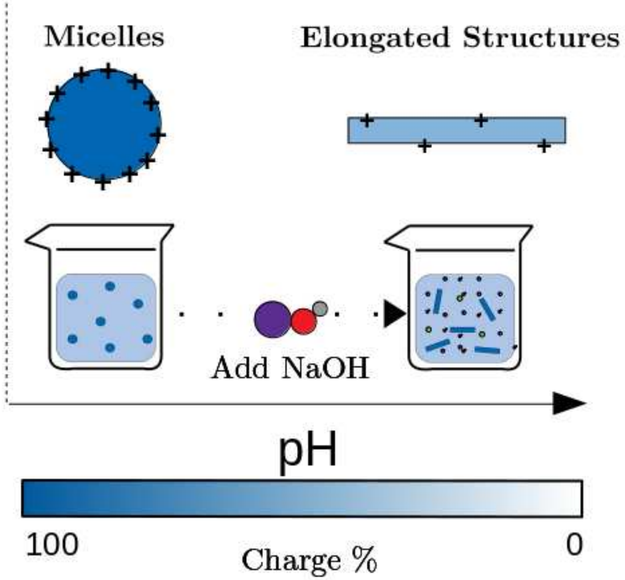

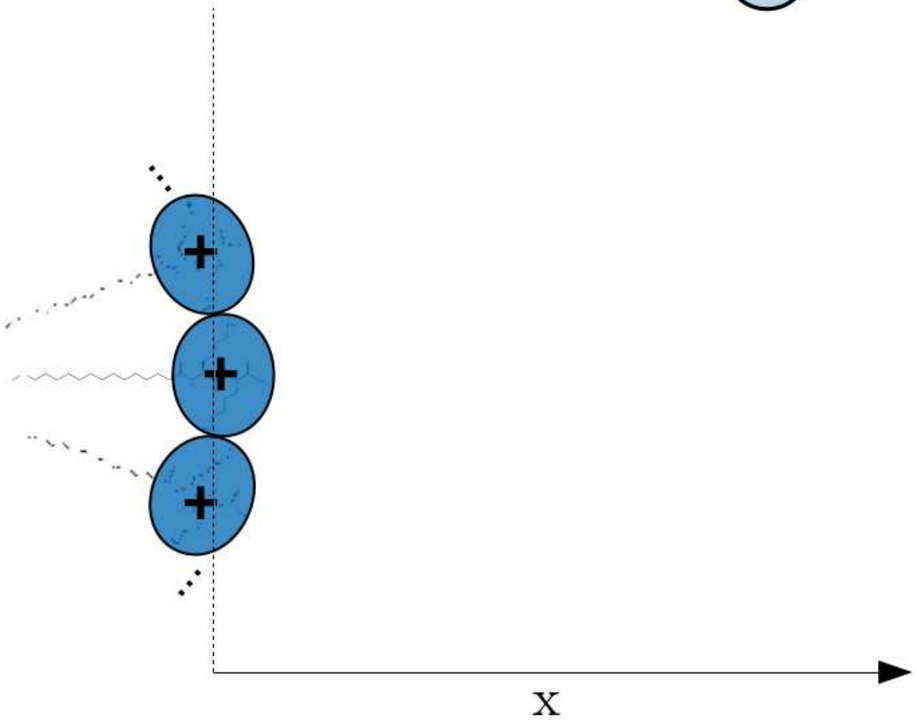

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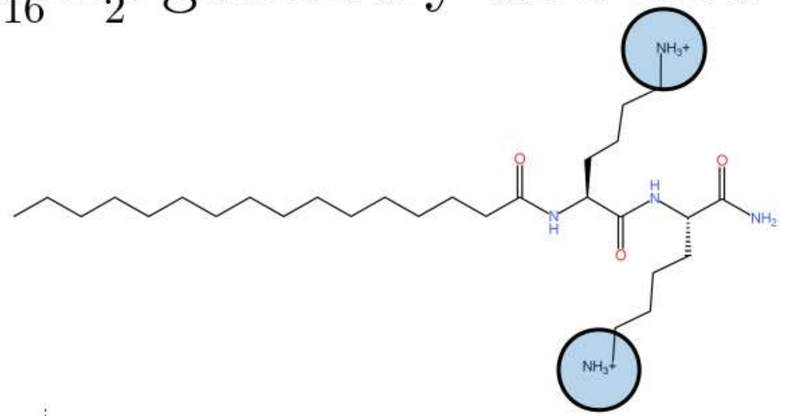
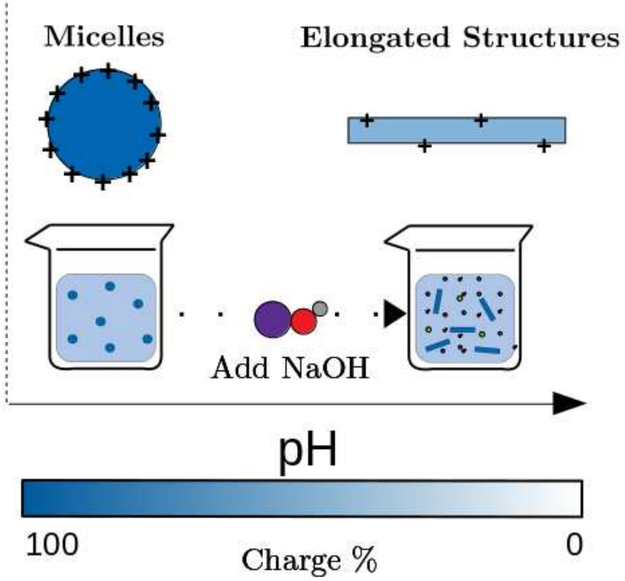
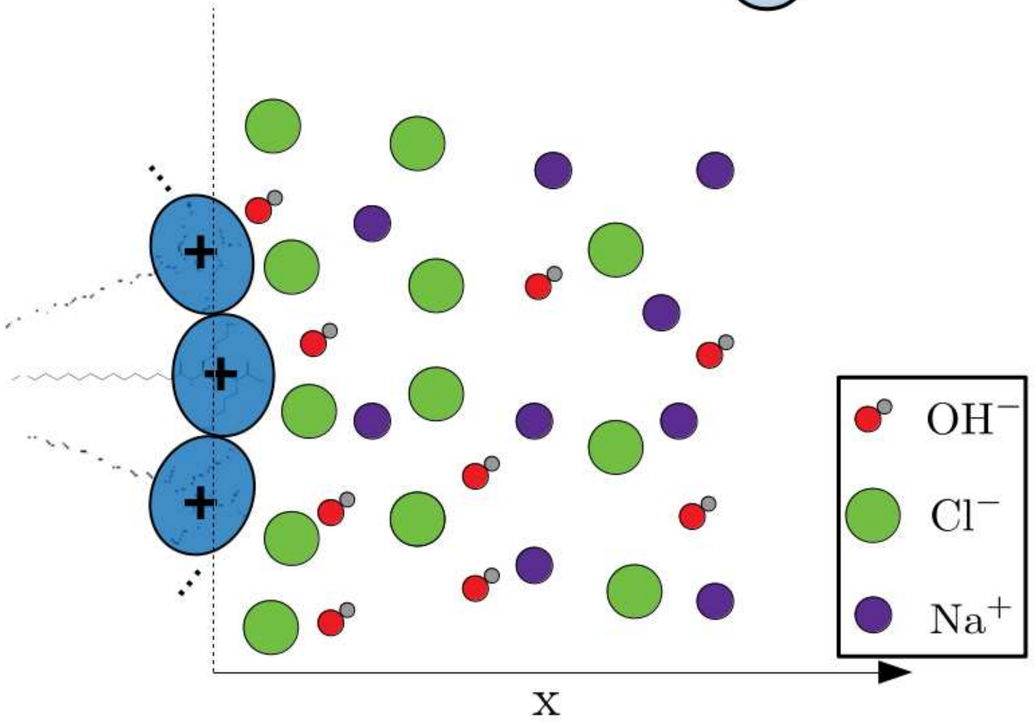
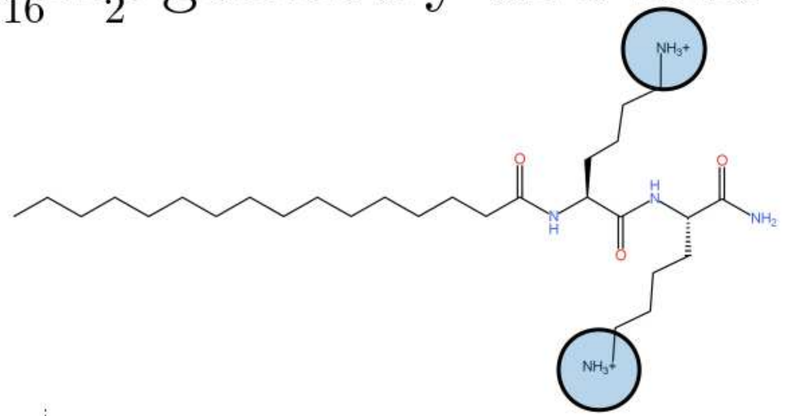
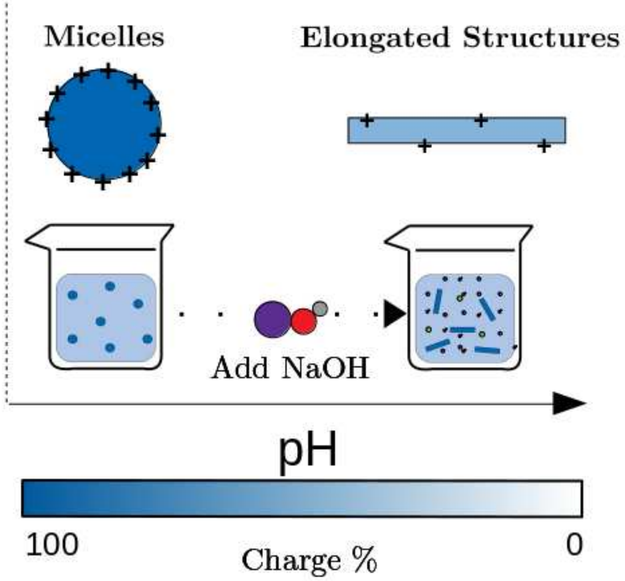


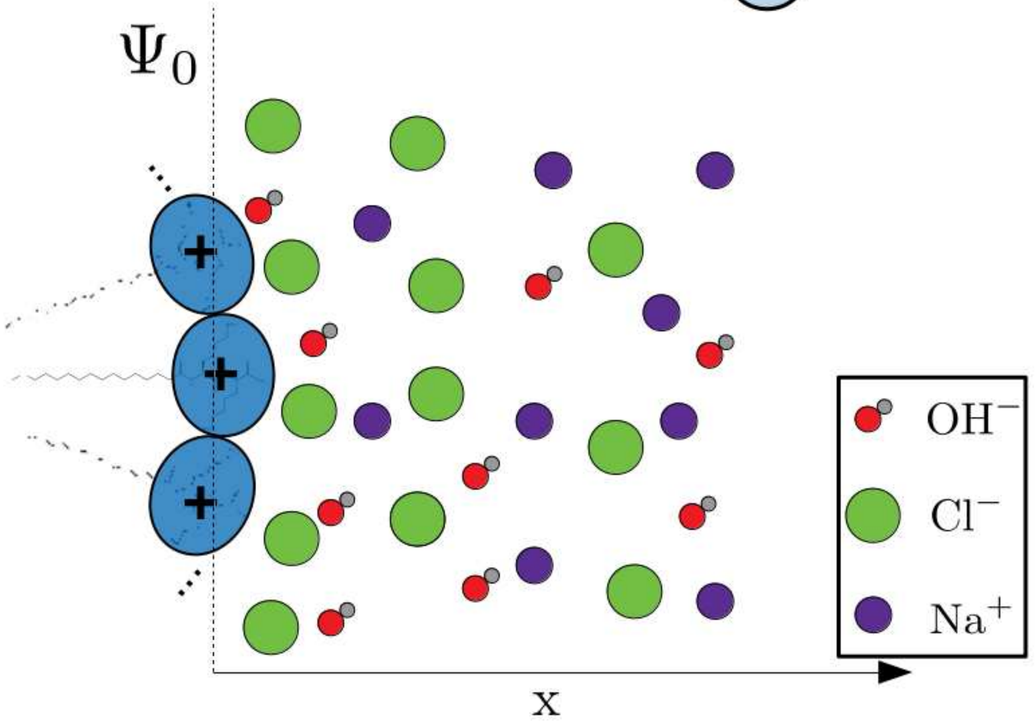




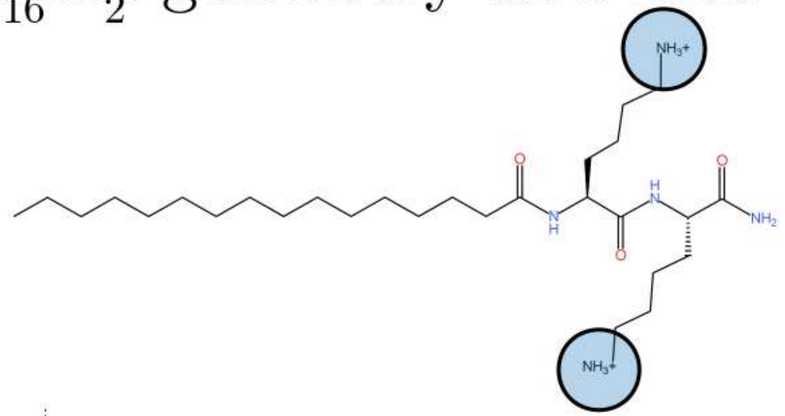
$C_{16}K_2$: geometry and ions

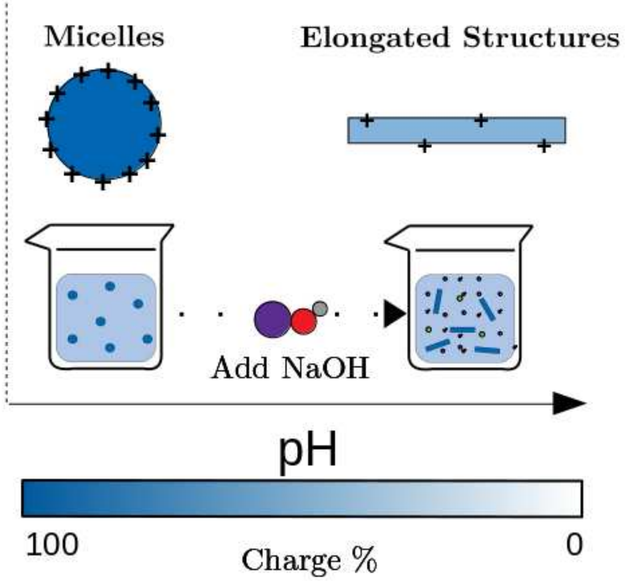


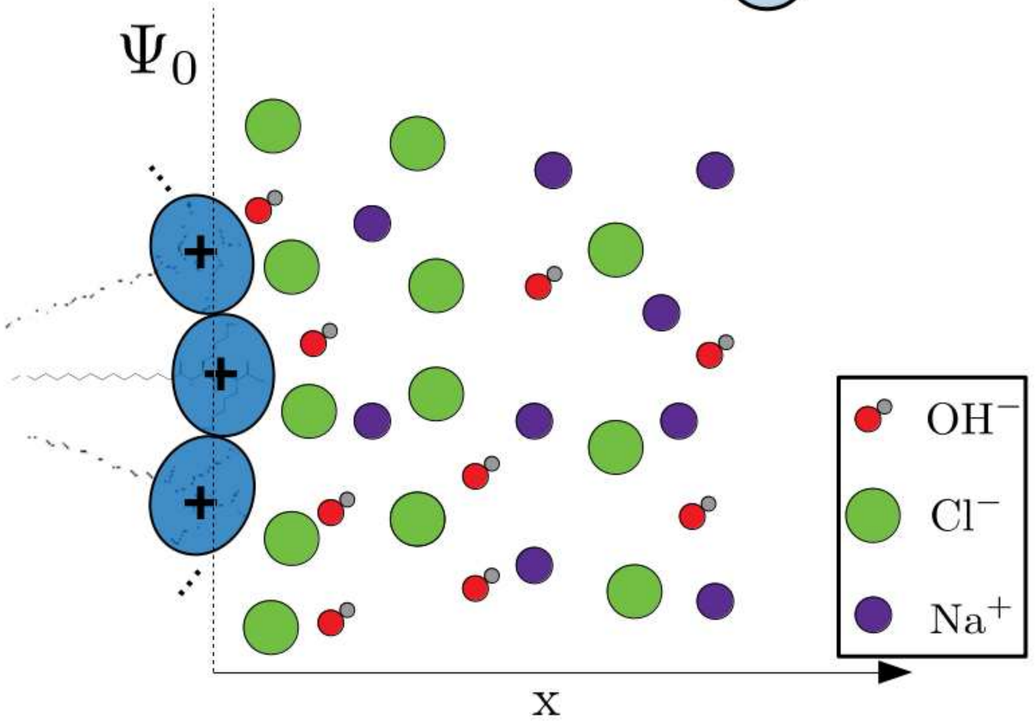


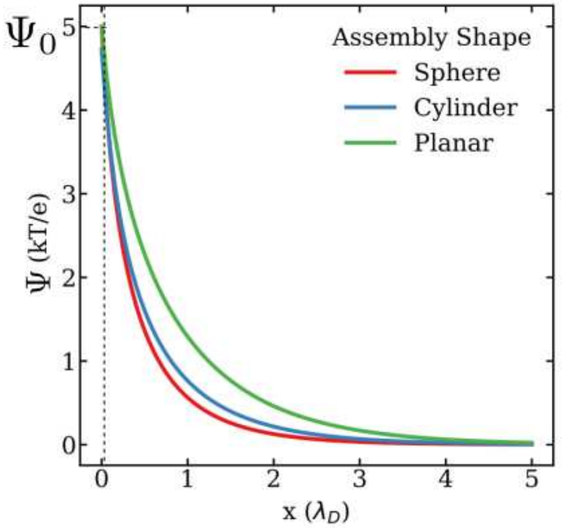


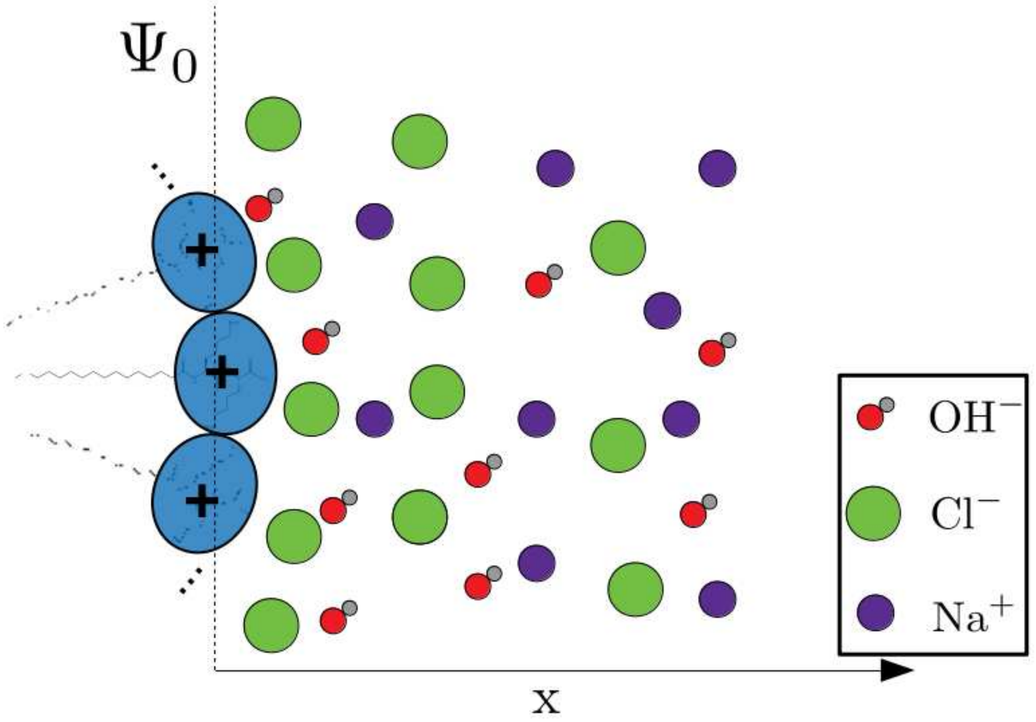
$C_{16}K_2$: geometry and ions



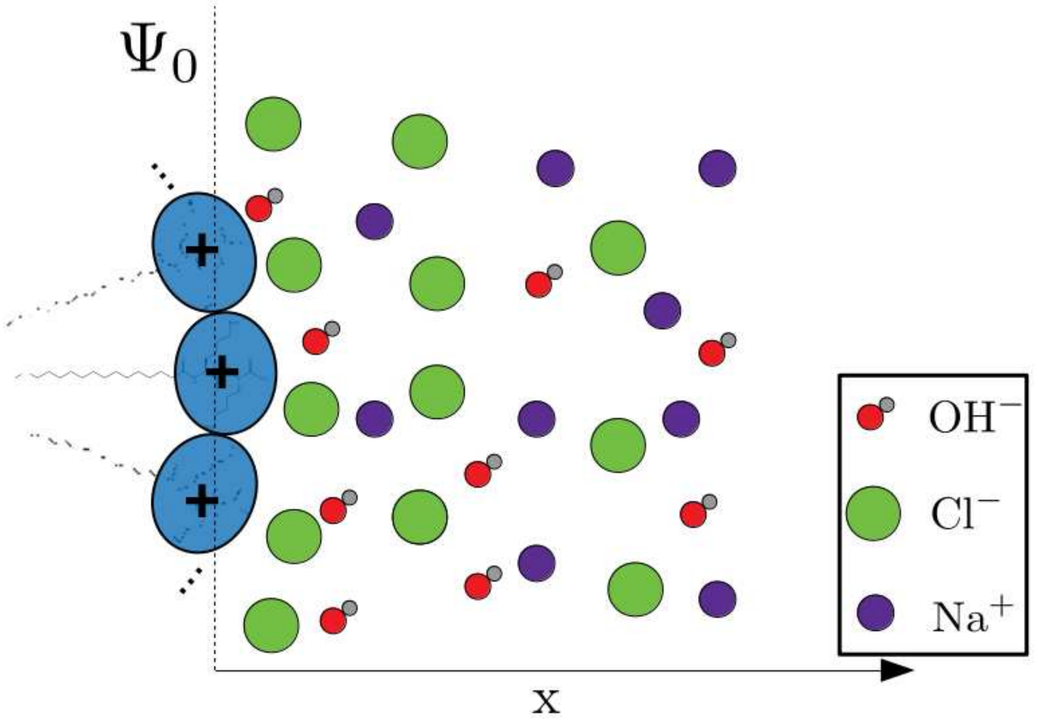






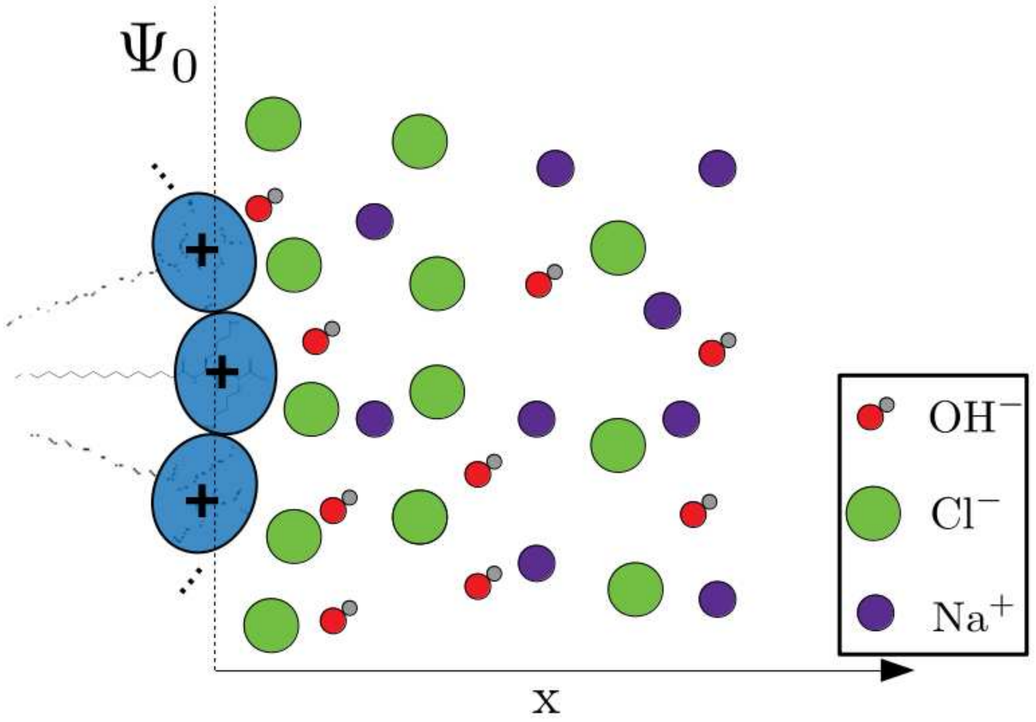

Ψ_0
OH^-
Cl^-
Na^+
x

Poisson-Boltzmann (PB)



Poisson-Boltzmann (PB)

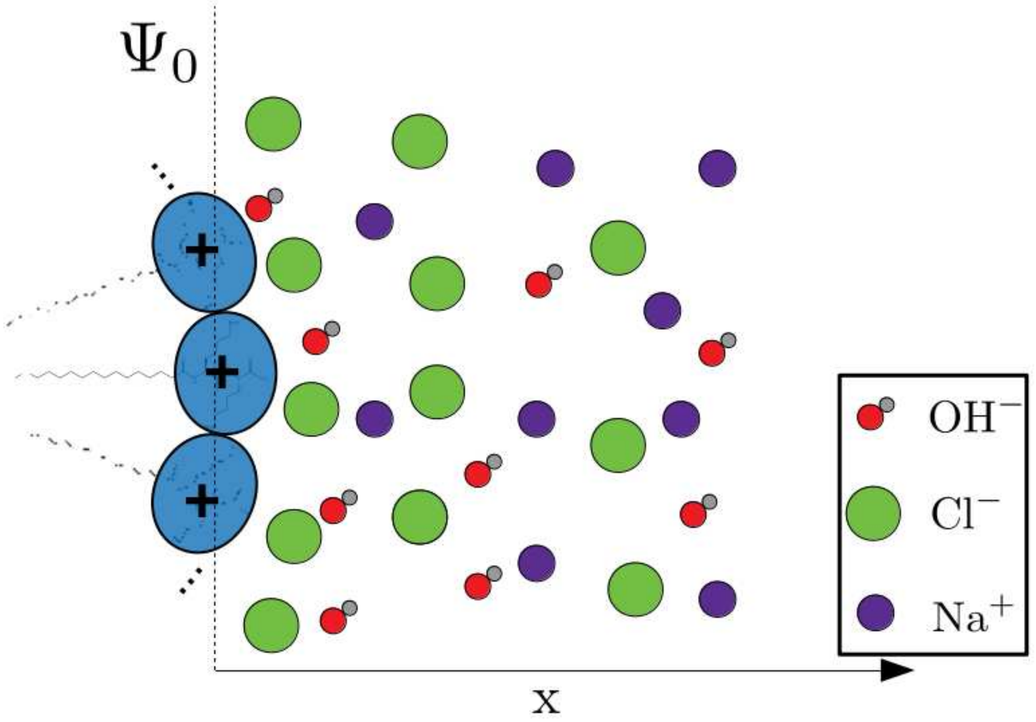
$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$



Poisson-Boltzmann (PB)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$

$$\rho_{\pm}(x) = \rho_{\pm,bulk} \mathrm{e}^{-e\beta\psi}$$



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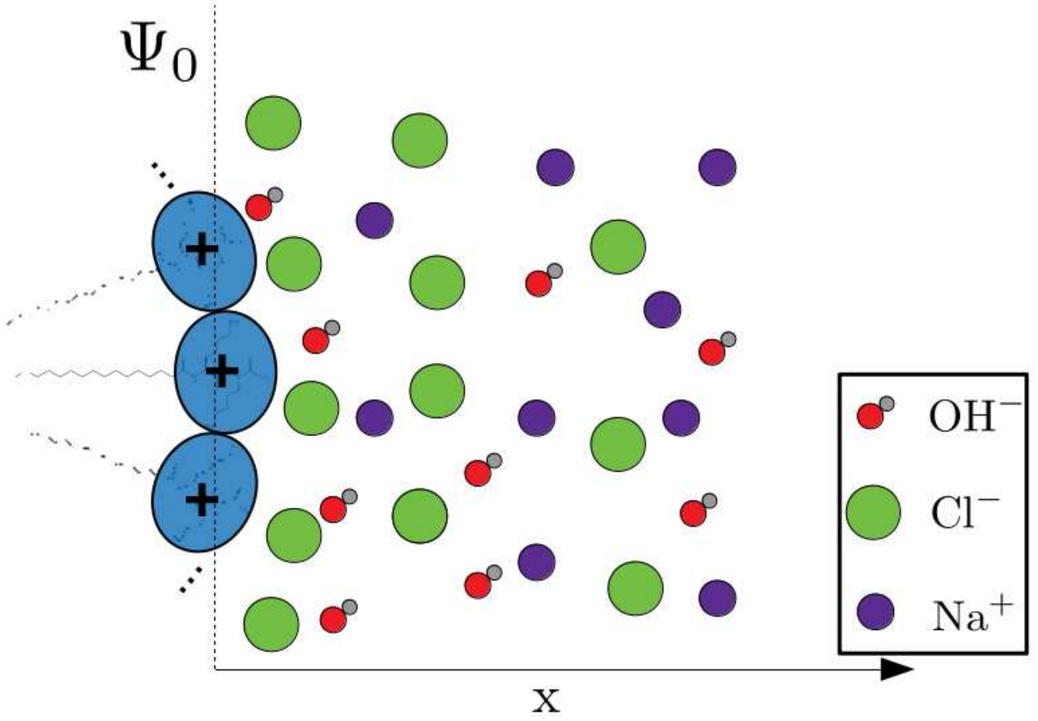
$$\frac{d^2\Psi}{dx^2} = \sinh\Psi \qquad \left(\Psi = \frac{e\psi}{k_B T},\ x = \kappa x\right)$$



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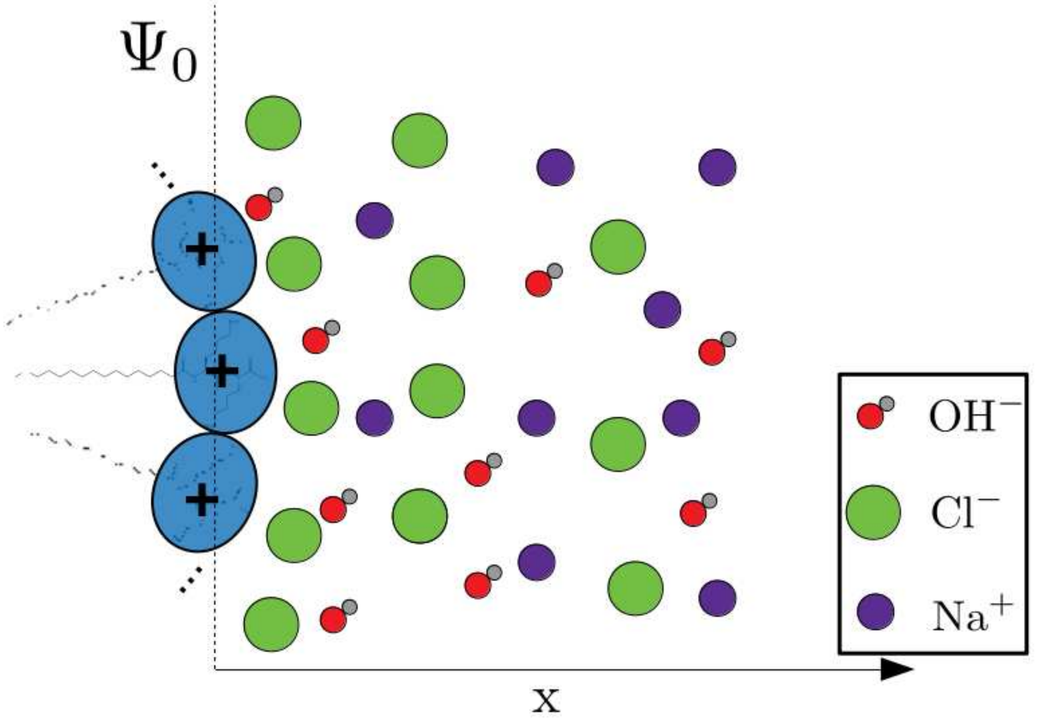

Charge Regulation

Poisson-Boltzmann (PB)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$

$$\rho_{\pm}(x) = \rho_{\pm,bulk} \mathrm{e}^{-e\beta\psi}$$

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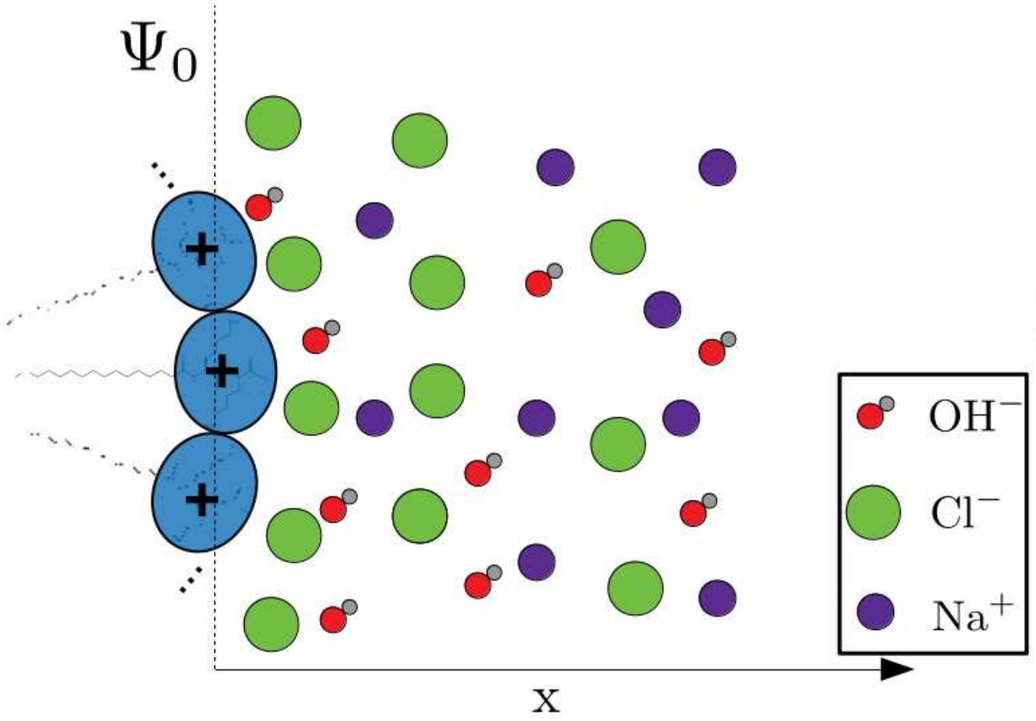


Charge Regulation

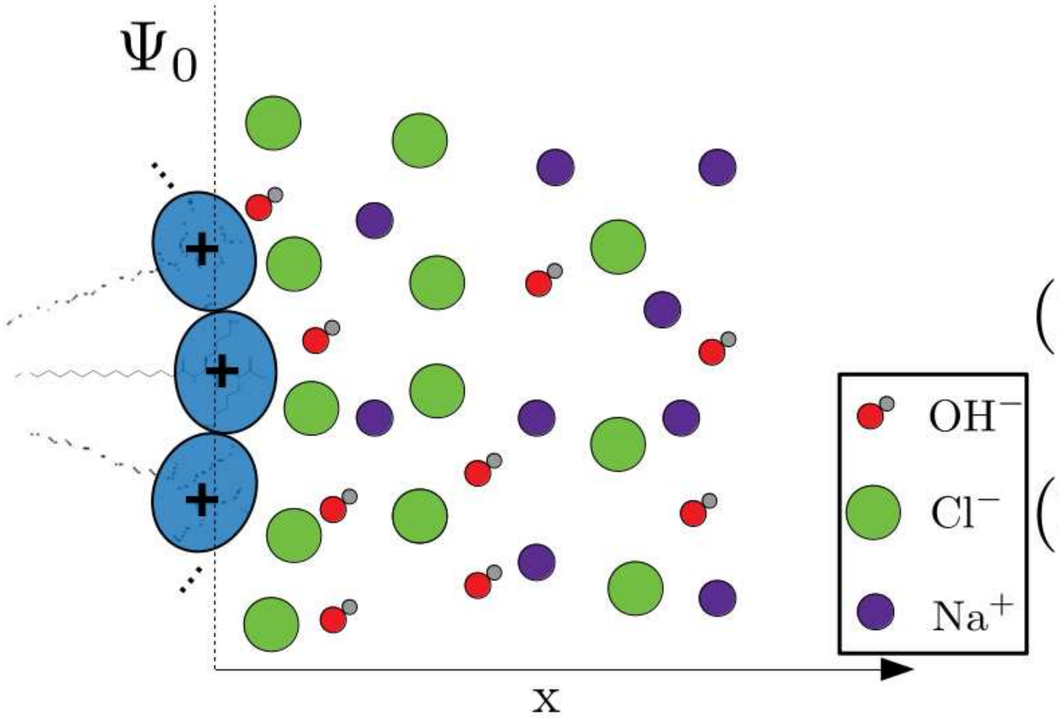
$$(1)\quad \alpha = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{pKa}} \mathrm{e}^{-\Psi_0}}$$

Poisson-Boltzmann (PB)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$

$$\rho_{\pm}(x) = \rho_{\pm,bulk}\mathrm{e}^{-e\beta\psi}$$

$$\frac{d^2\Psi}{dx^2} = \sinh\Psi \qquad \left(\Psi = \frac{e\psi}{k_BT},\ x = \kappa x\right)$$



Charge Regulation

$$(1)\quad \alpha = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{pKa}}\mathrm{e}^{-\Psi_0}}$$

$$(2)\quad \left.\frac{d\Psi}{dx}\right|_{x=x_0} = \frac{4\pi l_B\alpha}{S}$$

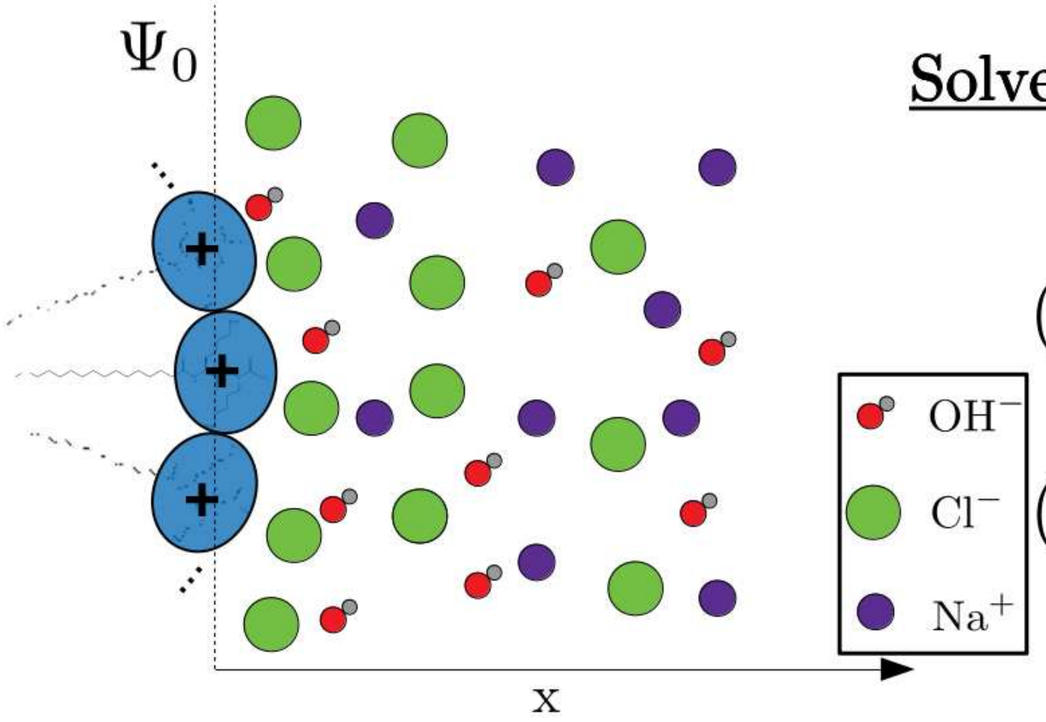
$$l_B = \frac{e^2\beta}{4\pi\epsilon_0\epsilon_w} \qquad S \equiv \text{area per site}$$

Poisson-Boltzmann (PB)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$

$$\rho_{\pm}(x) = \rho_{\pm,bulk} \mathrm{e}^{-e\beta\psi}$$

$$\frac{d^2\Psi}{dx^2} = \sinh\Psi \qquad \left(\Psi = \frac{e\psi}{k_B T},\ x = \kappa x\right)$$



Solve self-consistently for α and Ψ_0

Charge Regulation

$$(1)\quad \alpha = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{pKa}} \mathrm{e}^{-\Psi_0}}$$

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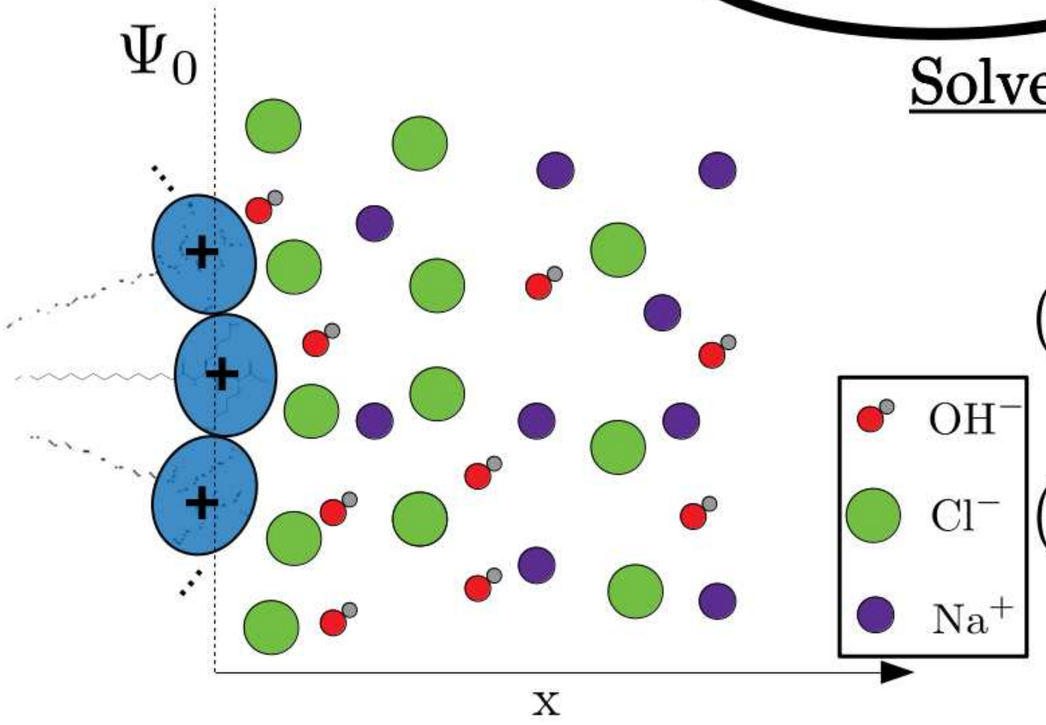
$$l_B = \frac{e^2\beta}{4\pi\epsilon_0\epsilon_w} \qquad S \equiv \text{area per site}$$

Poisson-Boltzmann (PB)

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi\rho(x)}{\epsilon}$$

$$\rho_{\pm}(x) = \rho_{\pm,bulk} e^{-e\beta\psi}$$

$$\frac{d^2\Psi}{dx^2} = \sinh\Psi \qquad \left(\Psi = \frac{e\psi}{k_B T},\ x = \kappa x\right)$$



Solve self-consistently for α and Ψ_0

Charge Regulation

$$(1)\quad \alpha = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{pKa}} e^{-\Psi_0}}$$

$$(2)\quad \left.\frac{d\Psi}{dx}\right|_{x=x_0} = \frac{4\pi l_B \alpha}{S}$$

$$l_B = \frac{e^2\beta}{4\pi\epsilon_0\epsilon_w} \qquad S \equiv \text{area per site}$$

Electrostatic Model of Titration

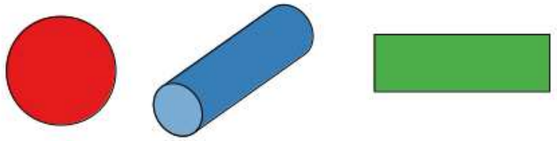
Input

$$\mathrm{pK}_a = 10.5$$

SAXS strucutural information (e.g. R, N_{lys})

[NaCl]

$$\Psi = \Psi_{\mathrm{sphere}},\ \Psi_{\mathrm{cyl}},\ \text{or}\ \Psi_{\mathrm{planar}}$$



Electrostatic Model of Titration

Input

$pK_a = 10.5$

SAXS strucutural information (e.g. R, N_{lys})

[NaCl]

$\Psi = \Psi_{\text{sphere}}$, Ψ_{cyl}, or Ψ_{planar}

Nonlinear PB Self Consistent Solution

Electrostatic Model of Titration

Input

$pK_a = 10.5$

SAXS strucutural information (e.g. R, N_{lys})

[NaCl]

$\Psi = \Psi_{\text{sphere}}$, Ψ_{cyl}, or Ψ_{planar}

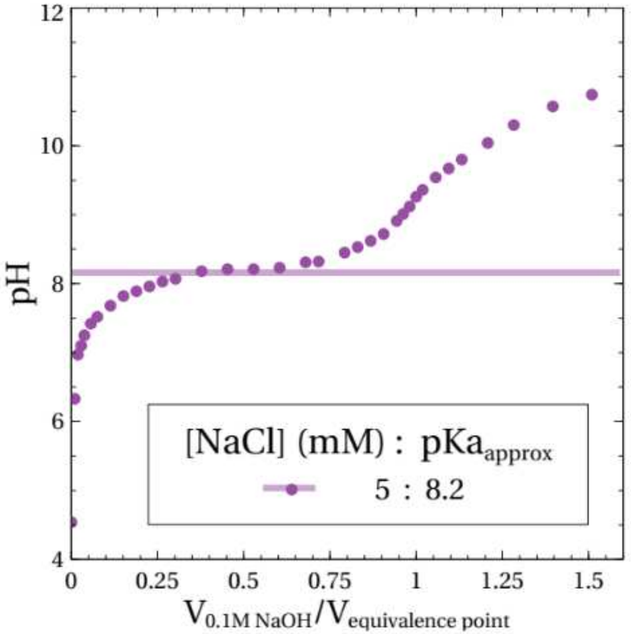
Nonlinear PB Self Consistent Solution

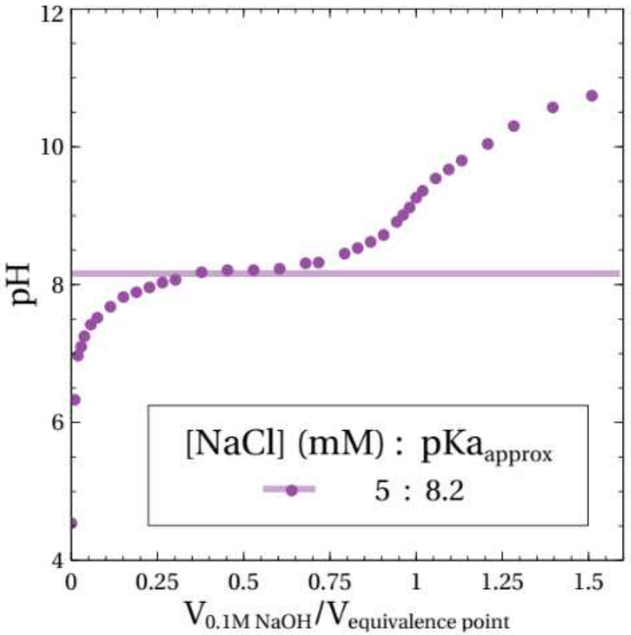
Output

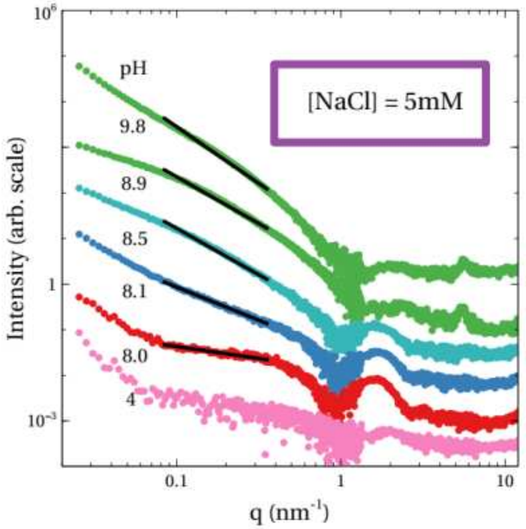
α

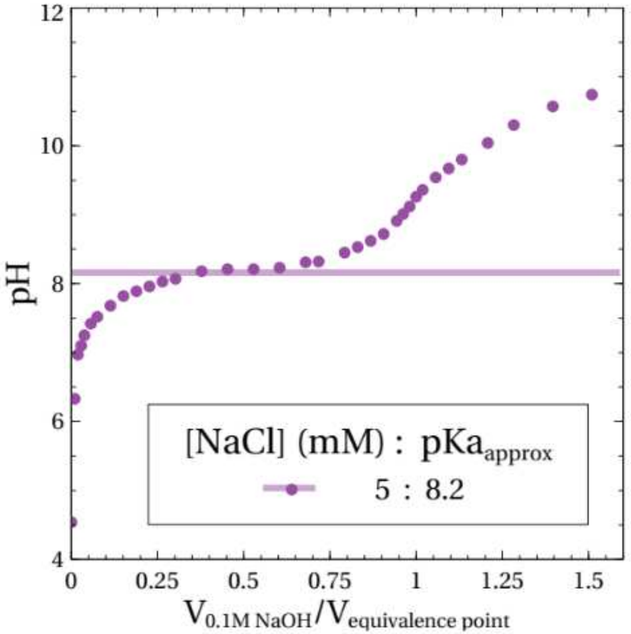
Ψ_0

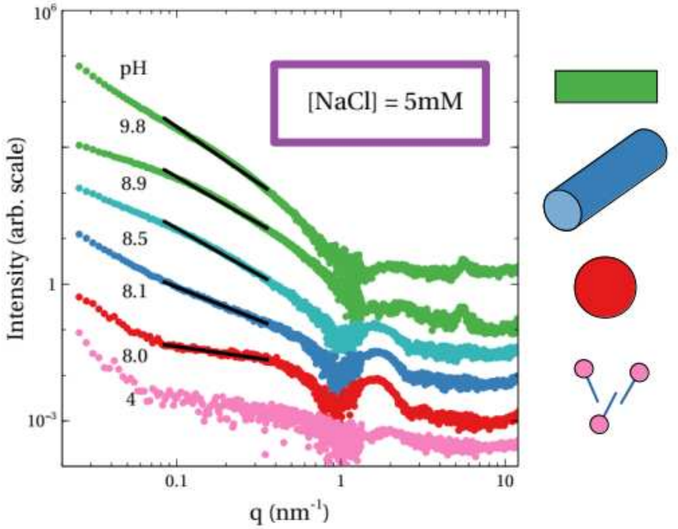
Then back-calculate titration curves

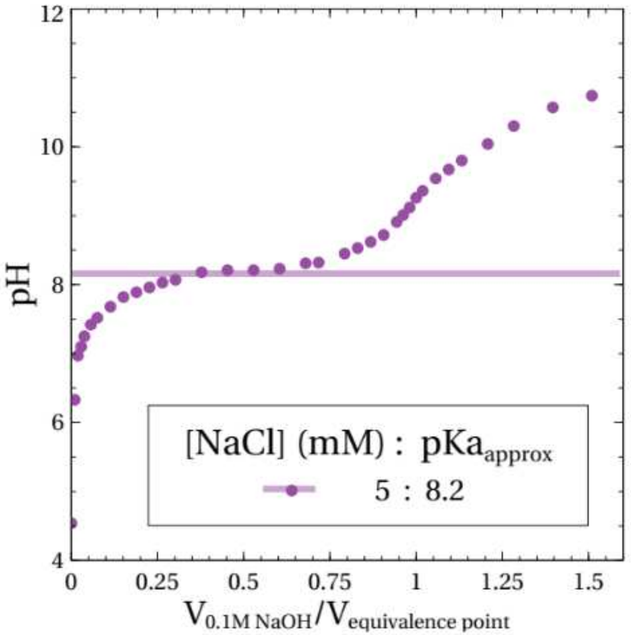

12
10
8
6
4
pH
0
0.25
0.5
0.75
1
1.25
1.5
$V_{0.1M\ NaOH}/V_{equivalence\ point}$
[NaCl] (mM) : pKa_{approx}
5 : 8.2

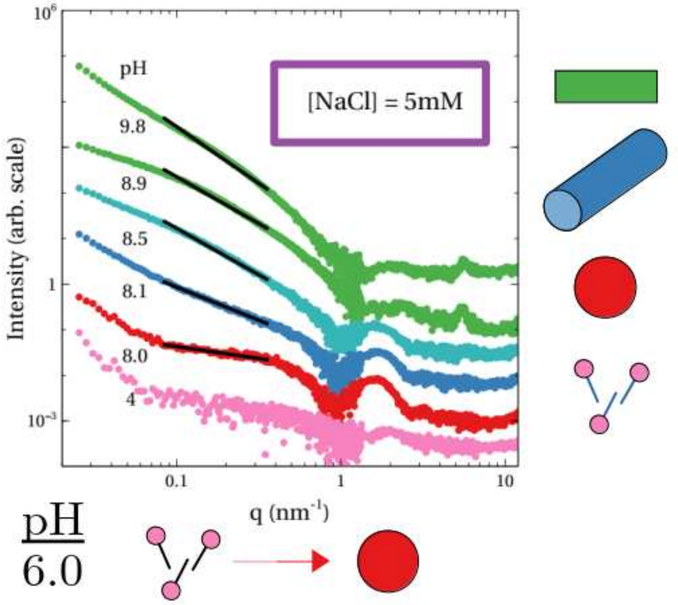

pH
$V_{0.1M\ NaOH}/V_{equivalence\ point}$
[NaCl] (mM) : pKa_{approx}
5 : 8.2

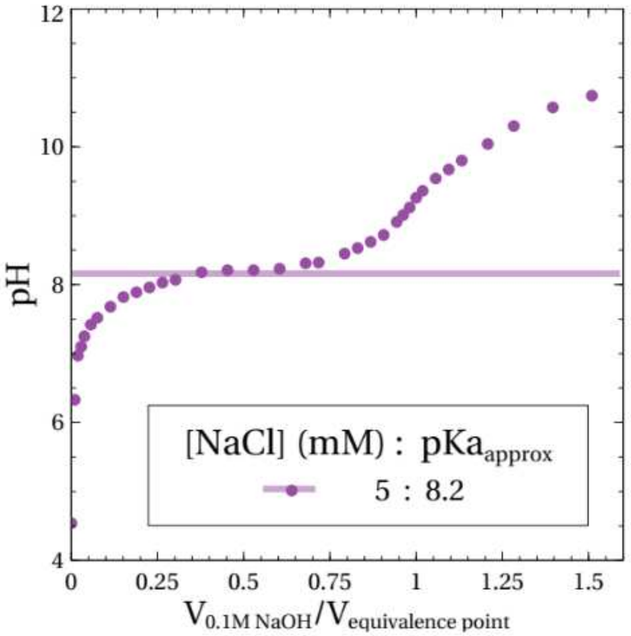

Intensity (arb. scale)
q (nm^{-1})
pH
9.8
8.9
8.5
8.1
8.0
4
[NaCl] = 5mM

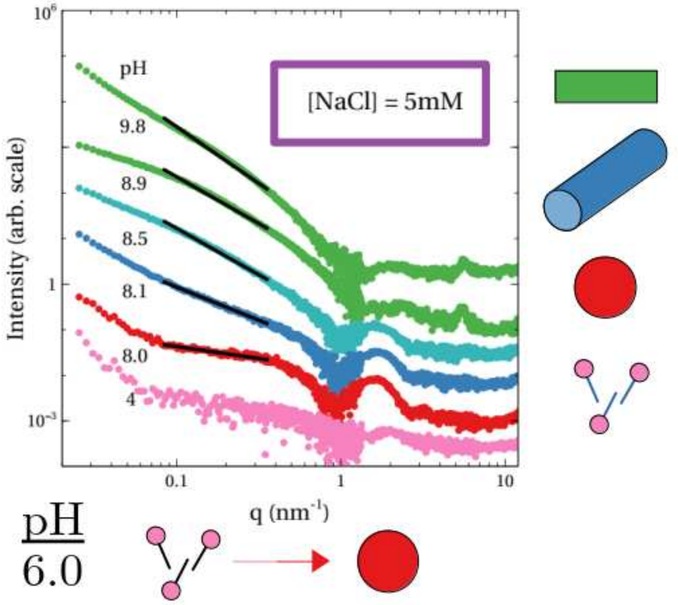

pH
$V_{0.1M\ NaOH}/V_{equivalence\ point}$
[NaCl] (mM) : pKa_{approx}
5 : 8.2

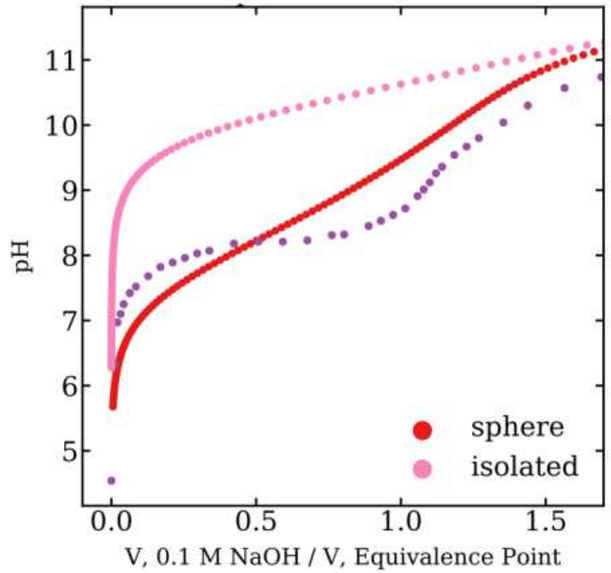

Intensity (arb. scale)
q (nm^{-1})
pH
9.8
8.9
8.5
8.1
8.0
4
[NaCl] = 5mM

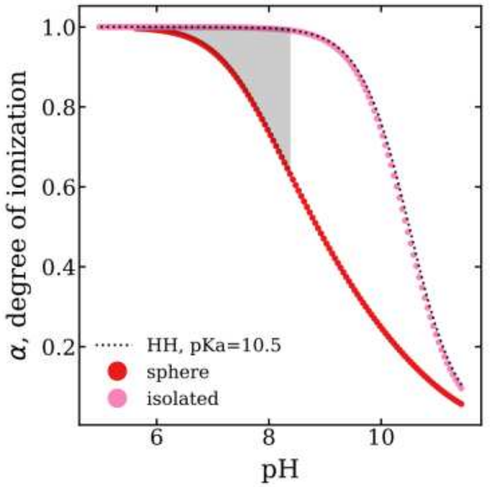

pH
$V_{0.1M\ NaOH}/V_{equivalence\ point}$
[NaCl] (mM) : pKa_{approx}
5 : 8.2


Intensity (arb. scale)
q (nm^{-1})
pH
9.8
8.9
8.5
8.1
8.0
4
[NaCl] = 5mM
pH
6.0



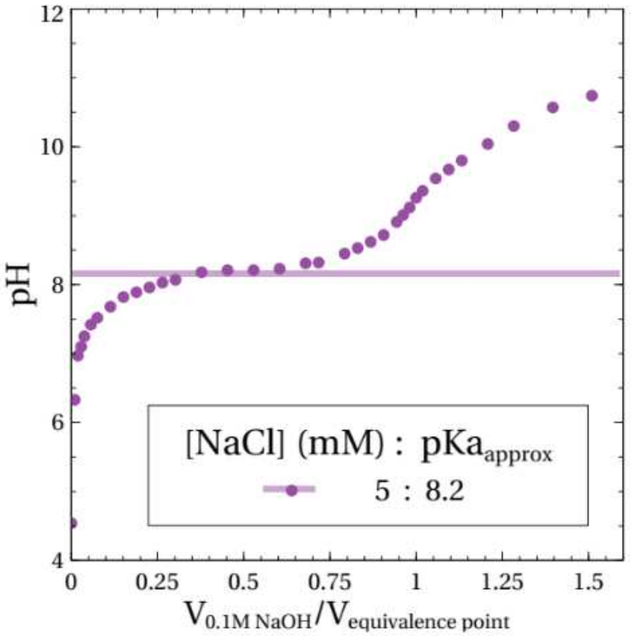


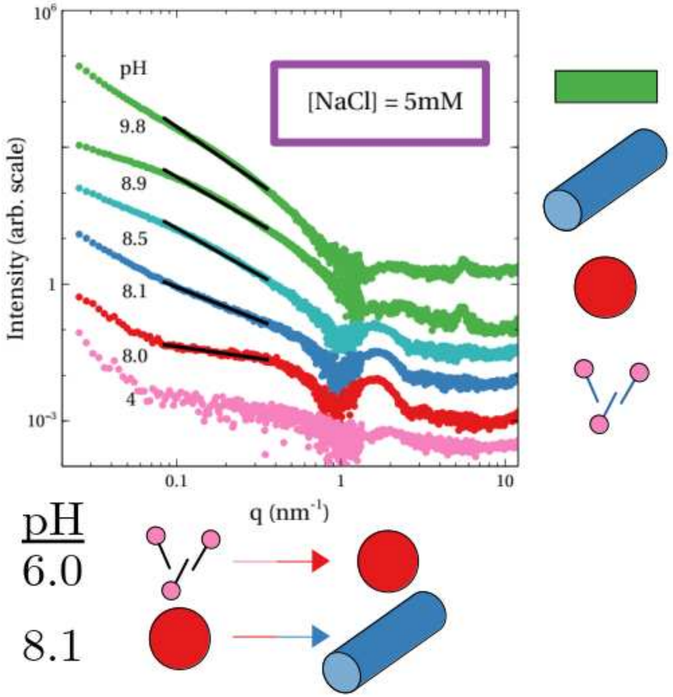


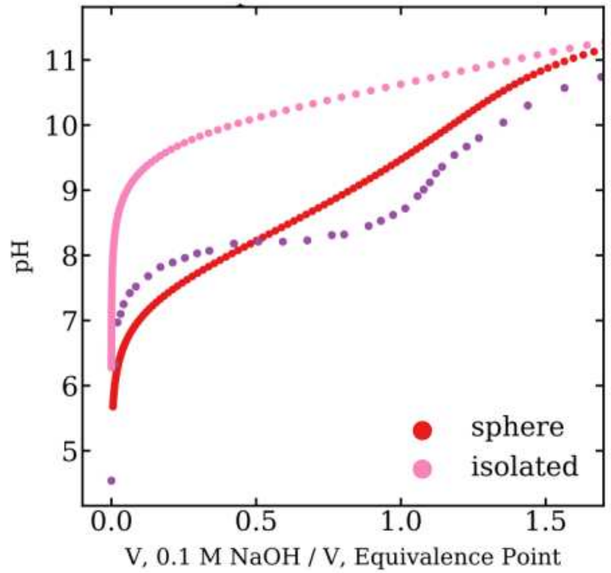


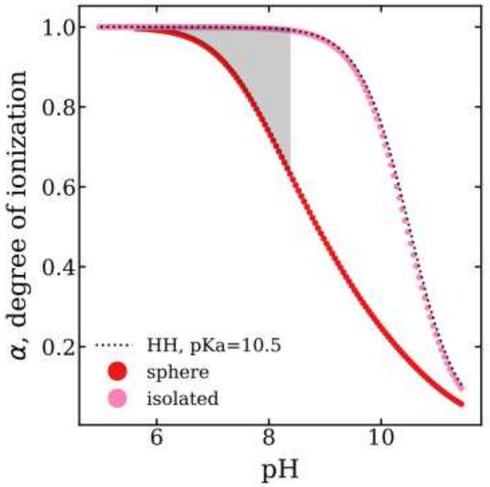
$$\mathbf{F}_{exp} = a\mathbf{F}_{isolated} + (1 - a)\mathbf{F}_{sphere}$$

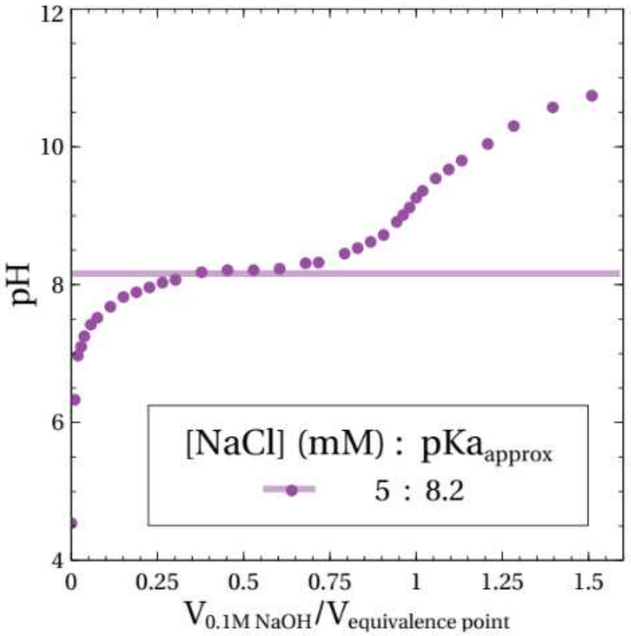
$$0 \leq a \leq 1$$

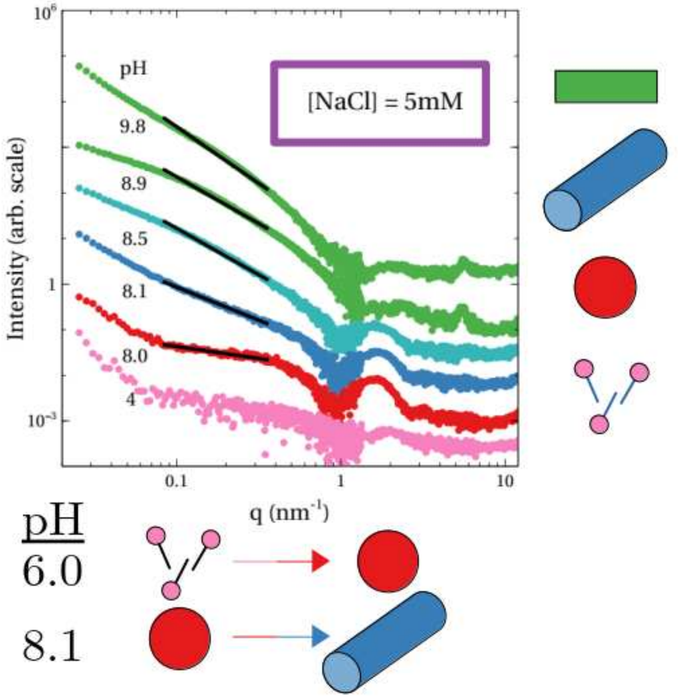

pH
[NaCl] (mM) : pKa$_{approx}$
5 : 8.2
$V_{0.1M\ NaOH}/V_{equivalence\ point}$

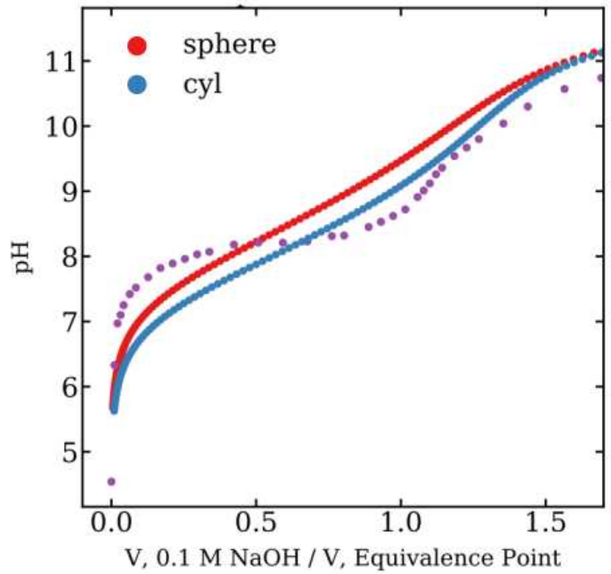

[NaCl] = 5mM
pH
9.8
8.9
8.5
8.1
8.0
4
Intensity (arb. scale)
q (nm^{-1})
pH
6.0
8.1

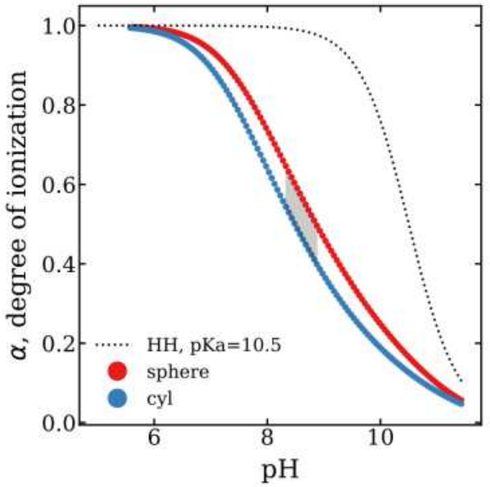

pH
sphere
isolated
V, 0.1 M NaOH / V, Equivalence Point


α, degree of ionization
HH, pKa=10.5
sphere
isolated
pH



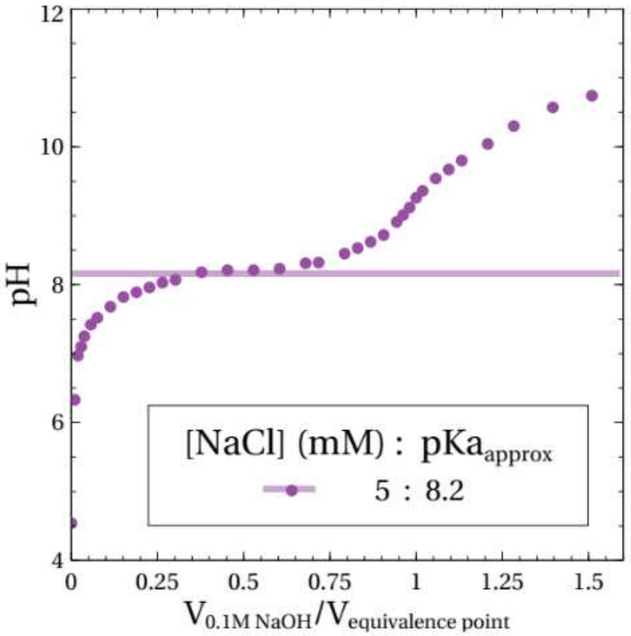


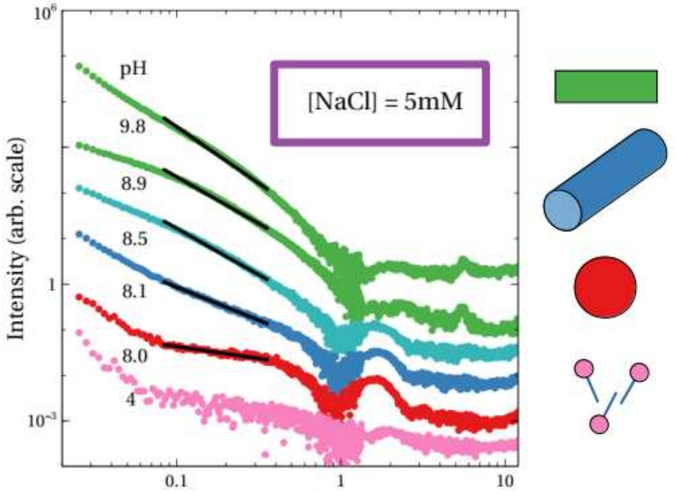


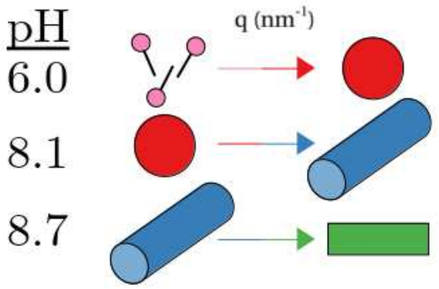


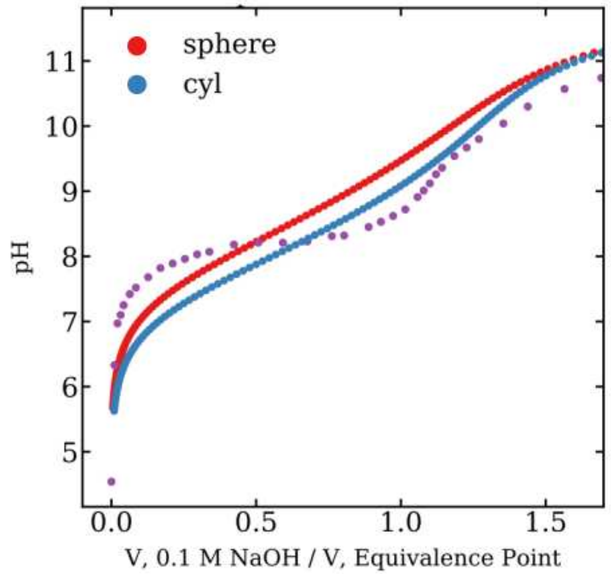
$$F_{exp} = bF_{sphere} + (1 - b)F_{cyl}$$

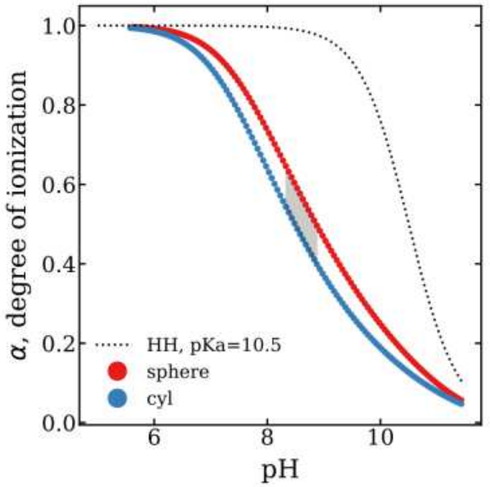
$$0 \le b \le 1$$

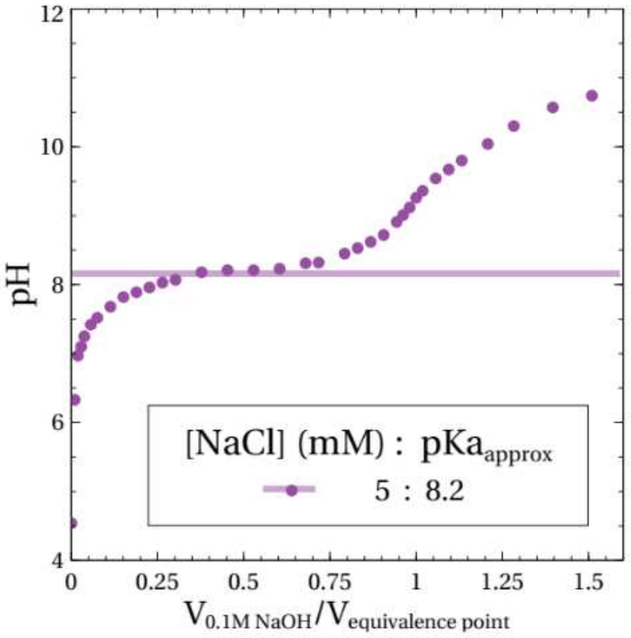

pH
[NaCl] (mM) : pKa$_{approx}$
5 : 8.2
V$_{0.1M\ NaOH}$/V$_{equivalence\ point}$

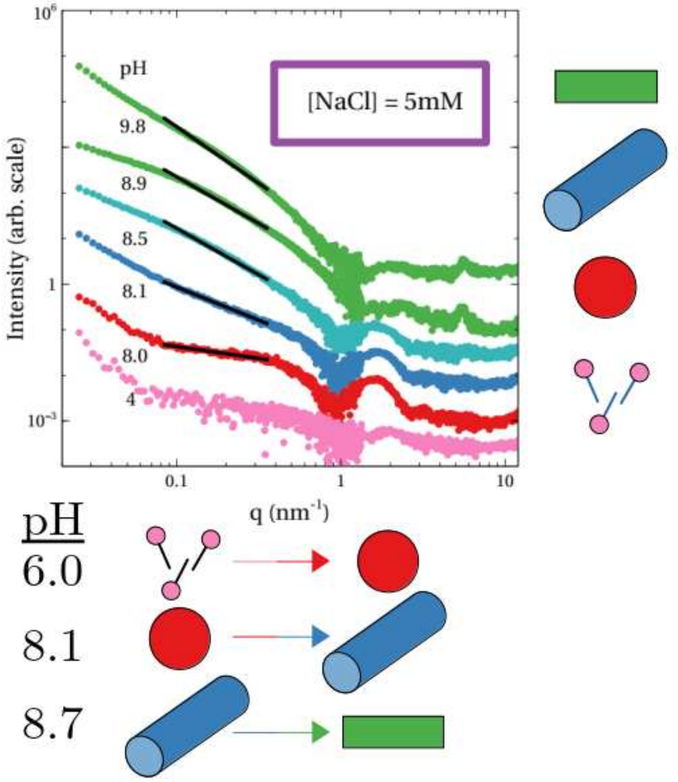

[NaCl] = 5mM
pH
9.8
8.9
8.5
8.1
8.0
4
Intensity (arb. scale)
q (nm^{-1})

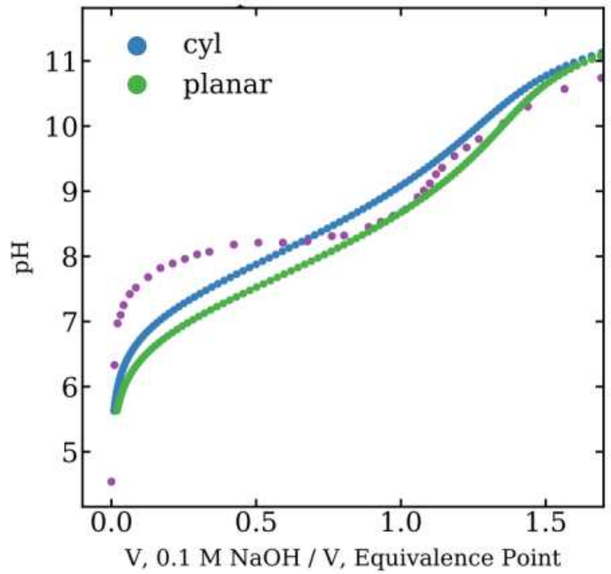

pH
6.0
8.1
8.7

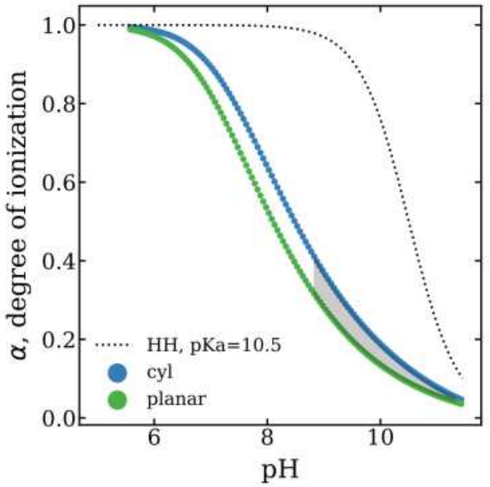

sphere
cyl
pH
V, 0.1 M NaOH / V, Equivalence Point


HH, pKa=10.5
sphere
cyl
α, degree of ionization
pH



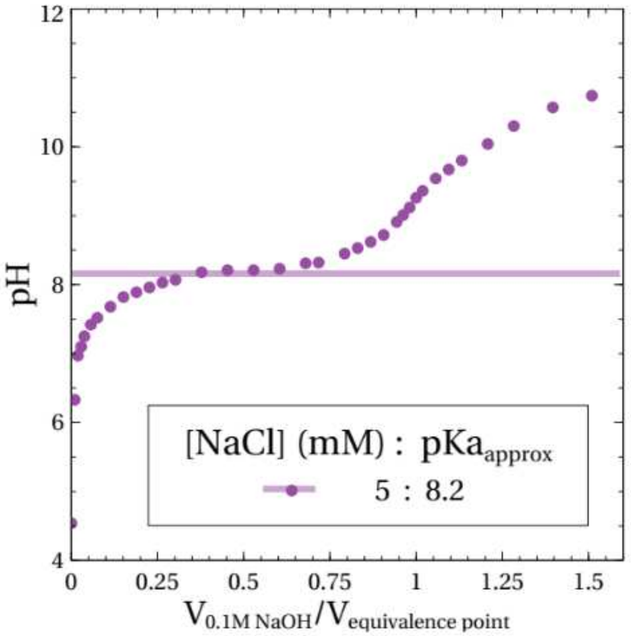


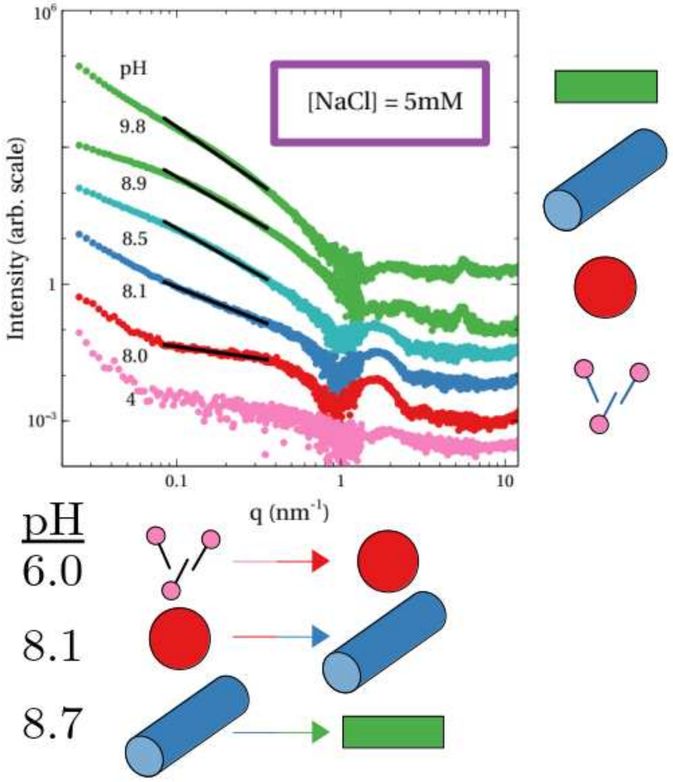




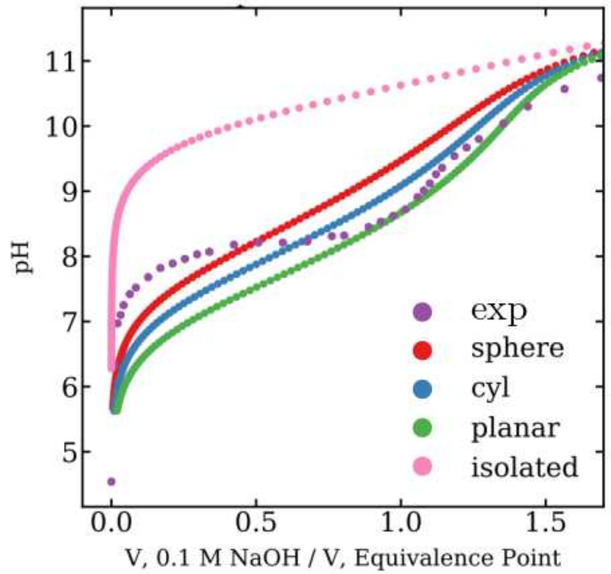
$$F_{exp} = cF_{cyl} + (1 - c)F_{planar}$$

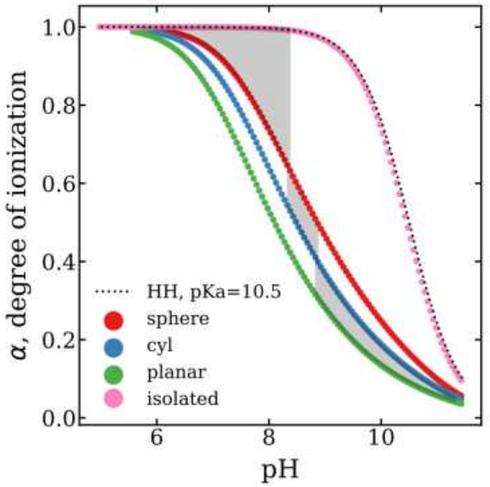
$$0 \leq c \leq 1$$

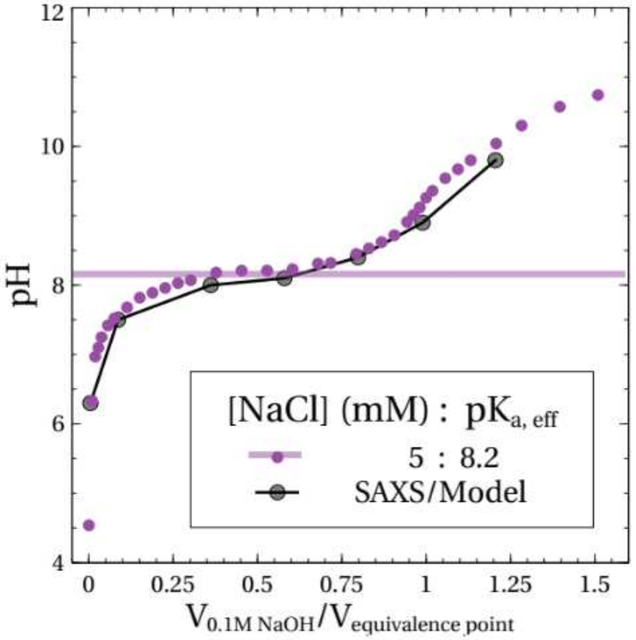

pH
[NaCl] (mM) : pKa$_{approx}$
5 : 8.2
V$_{0.1M\ NaOH}$/V$_{equivalence\ point}$

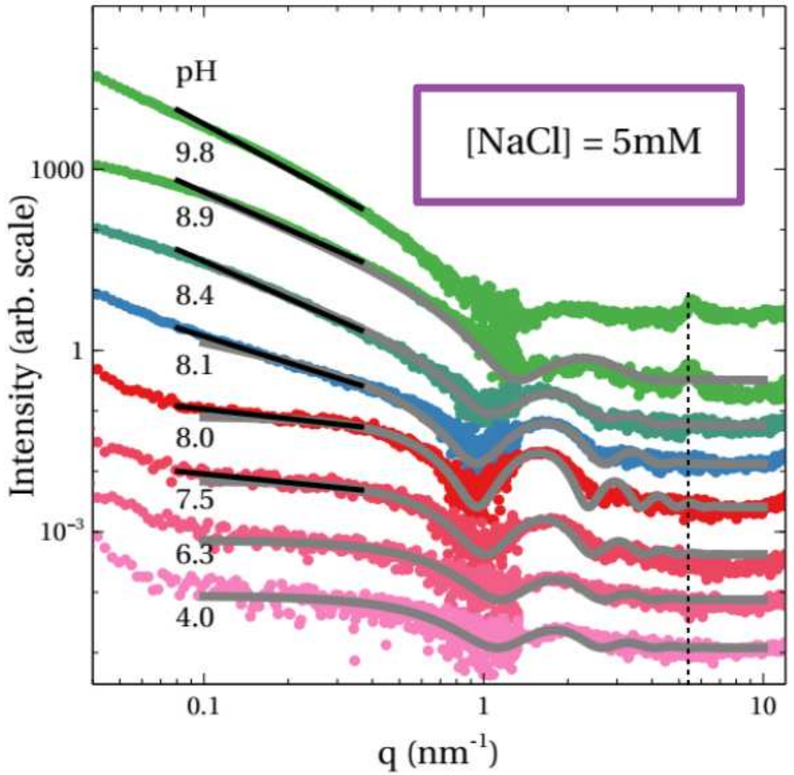

[NaCl] = 5mM
pH
9.8
8.9
8.5
8.1
8.0
4
Intensity (arb. scale)
q (nm^{-1})

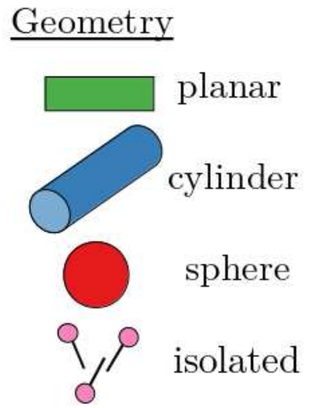
pH
6.0
8.1
8.7

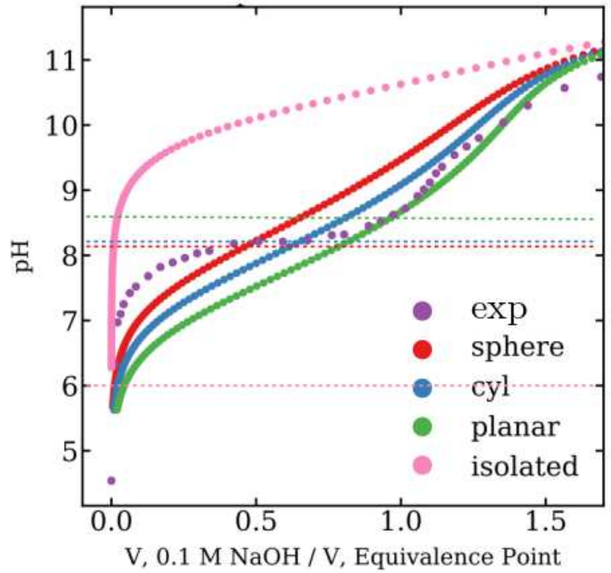

pH
exp
sphere
cyl
planar
isolated
V, 0.1 M NaOH / V, Equivalence Point

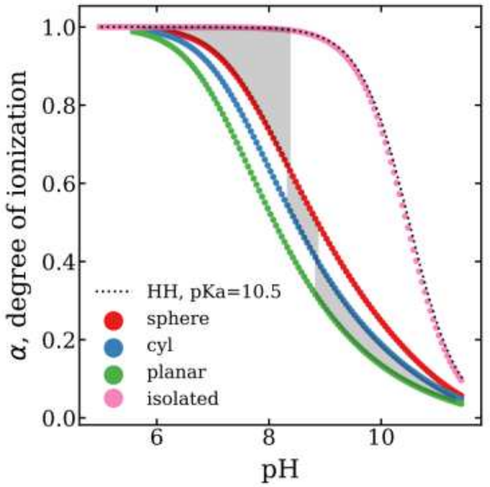

α, degree of ionization
HH, pKa=10.5
sphere
cyl
planar
isolated
pH











Reproduce titration curves and understand ionization behavior from nano-scale structure and the electrostatic interactions without additional parameters

Outline

I. Introduction to charged chiral amphiphile assemblies
    a) C_nK molecule

II. Chapter 1: Characterization of C_nK assemblies in different ionic environments, shape selection dictated by electrostatics

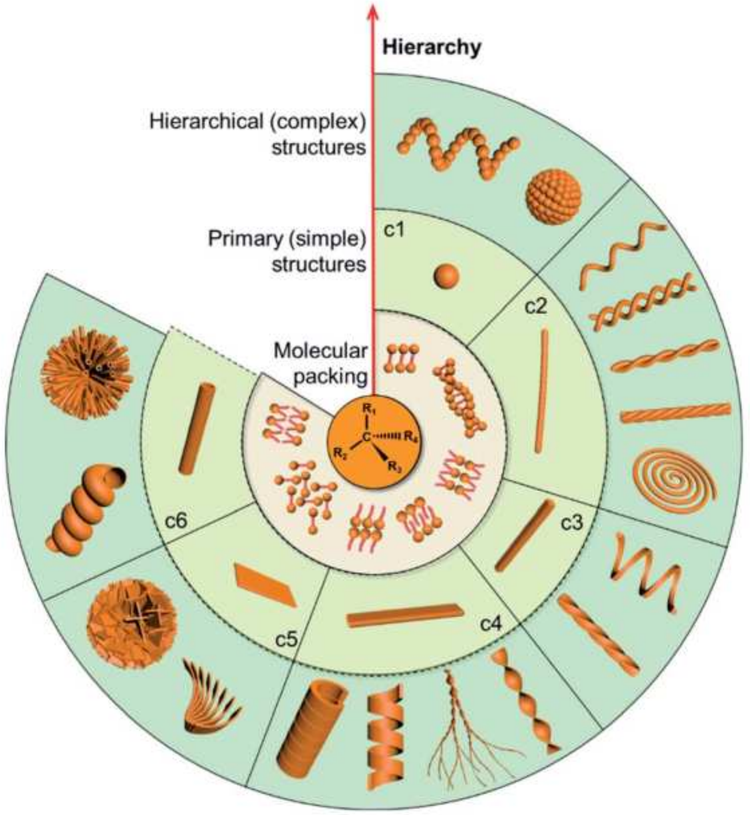
III. Chapter 2: Charge regulation in ionizable assemblies

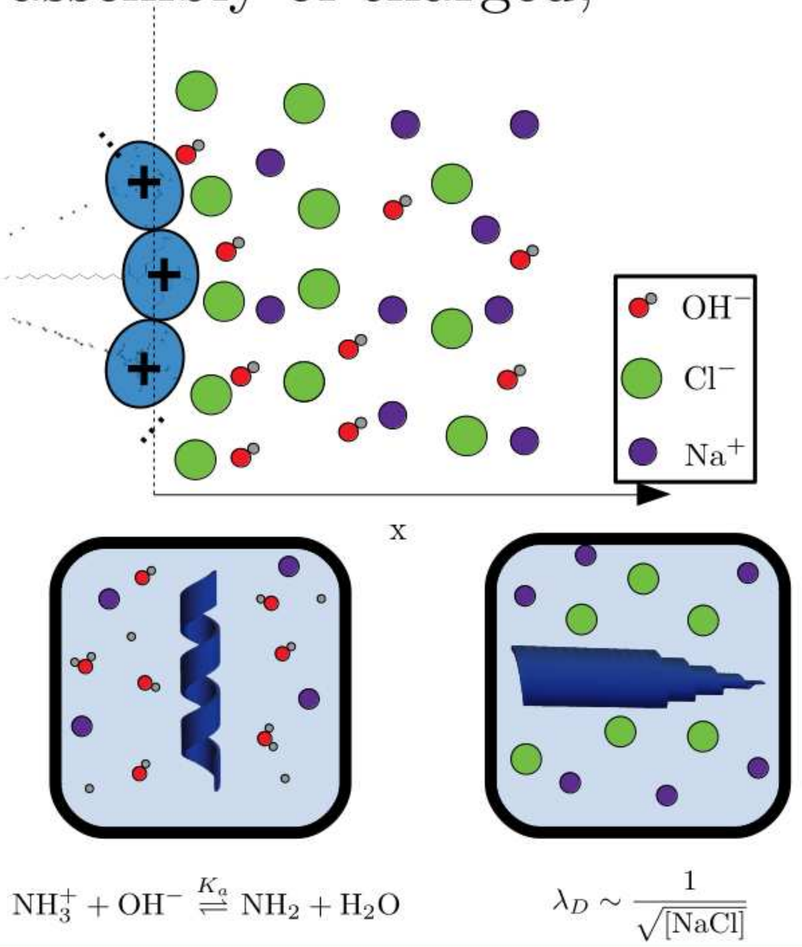
IV. Conclusion: summary, outlook, and acknowledgements

Northwestern

Future and Outlook

My dissertation sought to provide insight into using electrostatics for directing self-assembly of charged, chiral molecules





$$NH_3^+ + OH^- \overset{K_a}{\rightleftharpoons} NH_2 + H_2O$$

$$\lambda_D \sim \frac{1}{\sqrt{[NaCl]}}$$

Acknowledgements

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Bedzyk and Olvera de la Cruz
Research Groups

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Peptide synthesis was performed in the Peptide Synthesis Core Facility of the Simpson Querrey Institute at Northwestern University. (*Mark Karver*)

SQI SIMPSON QUERREY INSTITUTE
BIONANOTECHNOLOGY

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NUANCE
Northwestern University Atomic and Nanoscale Characterization Experimental Center

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DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline 5ID-D located at Sector 5 of the Advanced Photon Source (APS) and at the APS beamline 12 ID-C. (*Steven Weigand*, *Soenke Seifert*)

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My committee members:
Michael Bedzyk, Monica Olvera de la Cruz, John Marko,
Sumit Kewalramani, and Felipe Jimenez Angeles

Acknowledgements

Funding

Department of Energy (DOE),
Office of Basic Energy Sciences

CCTSM

Friends

A special thanks to my partner Kelsea, and to Aris, Mike, Danny, Nick, Roger, Carlos, Elise, David, and many other members of the Physics/Astronomy and Materials Science and Engineering Departments and those unaffiliated with academia

Family

Mom, Jimmy, Al, Tina, Kitty, Tommy, Herb, Erin, my cat Charlie and many more

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Thank you for your time

Questions?