

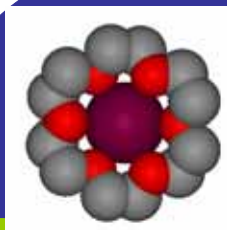
Hybrid biomimetic membranes: past present and beyond...

Mihail Barboiu

Adaptative Supramolecular Nanosystems Group

**Institut Européen des Membranes
Montpellier, France**

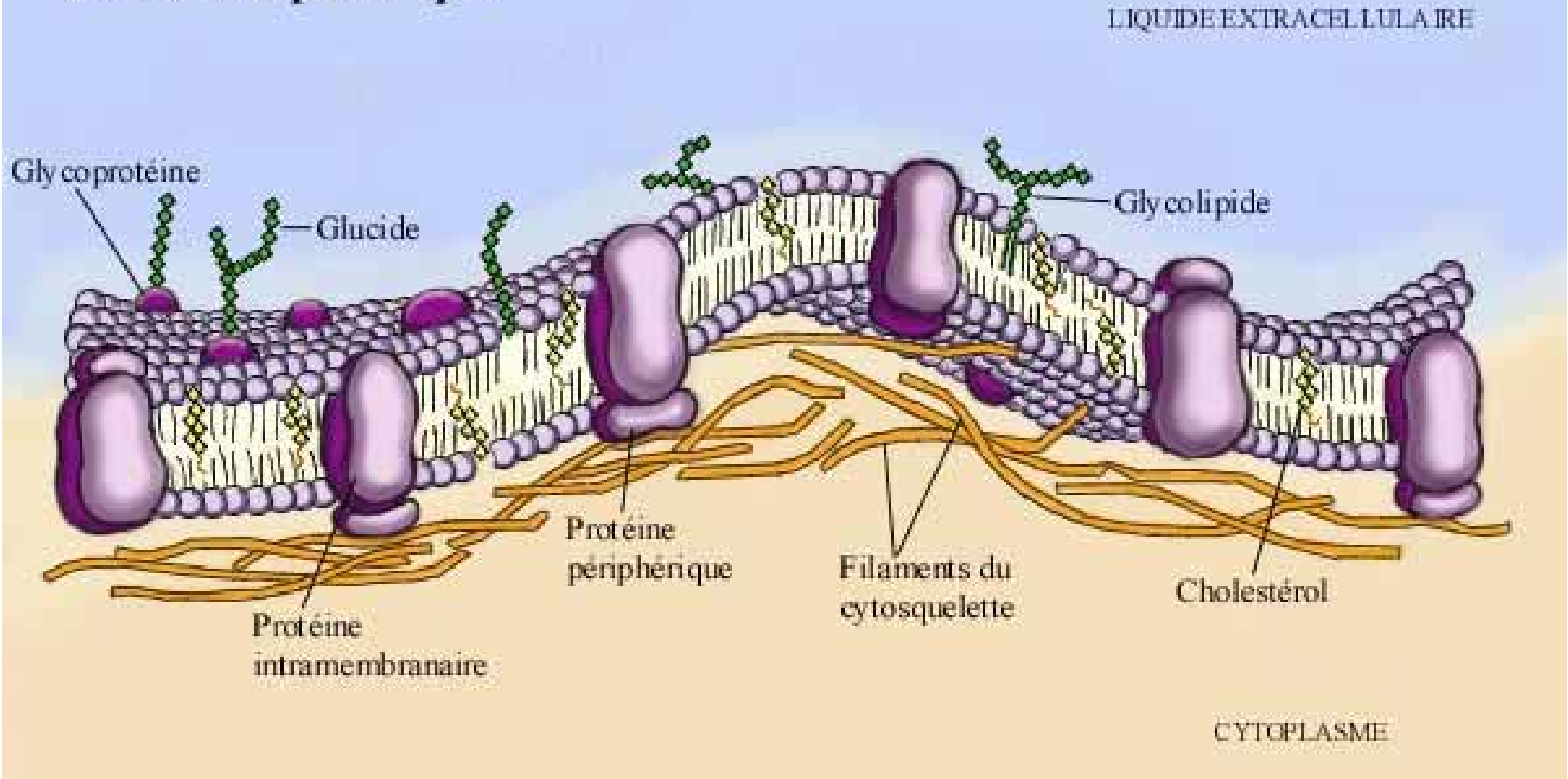
Informed molecular components
Molecular recognition

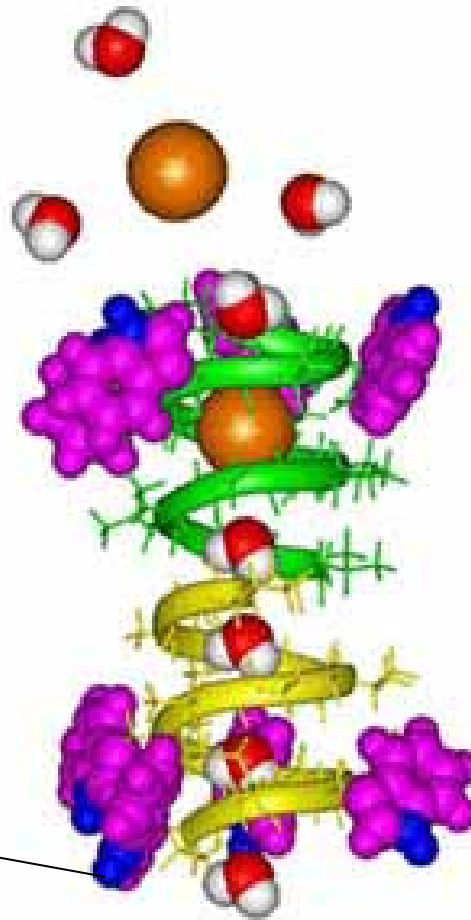


Supramolecular self-assembly
Self-organization

Supramolecular function
Transport

Membrane plasmique





Evolutionary

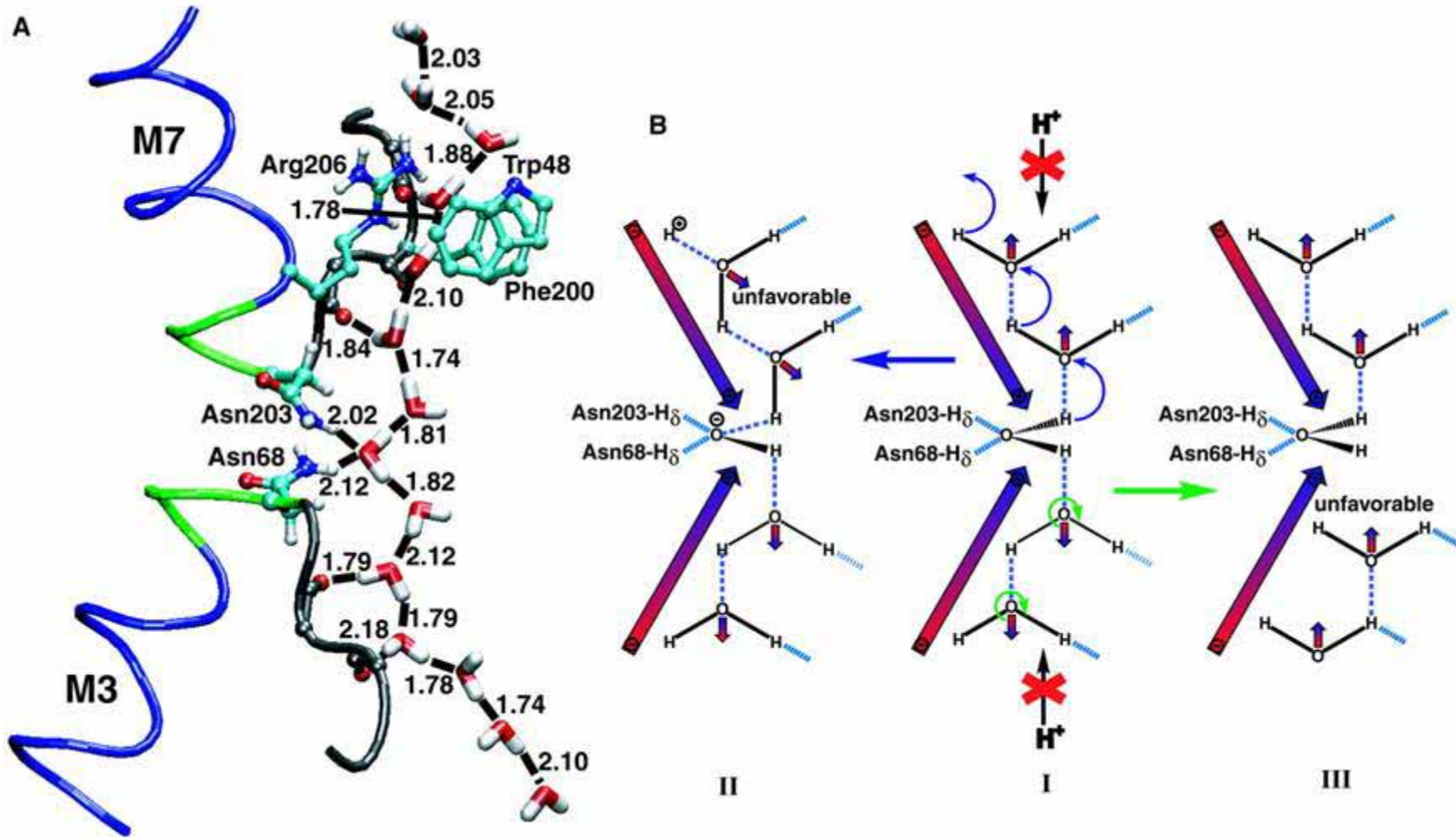
Adaptative

Dynamic

Collective

Water versus proton permeability of AQP1

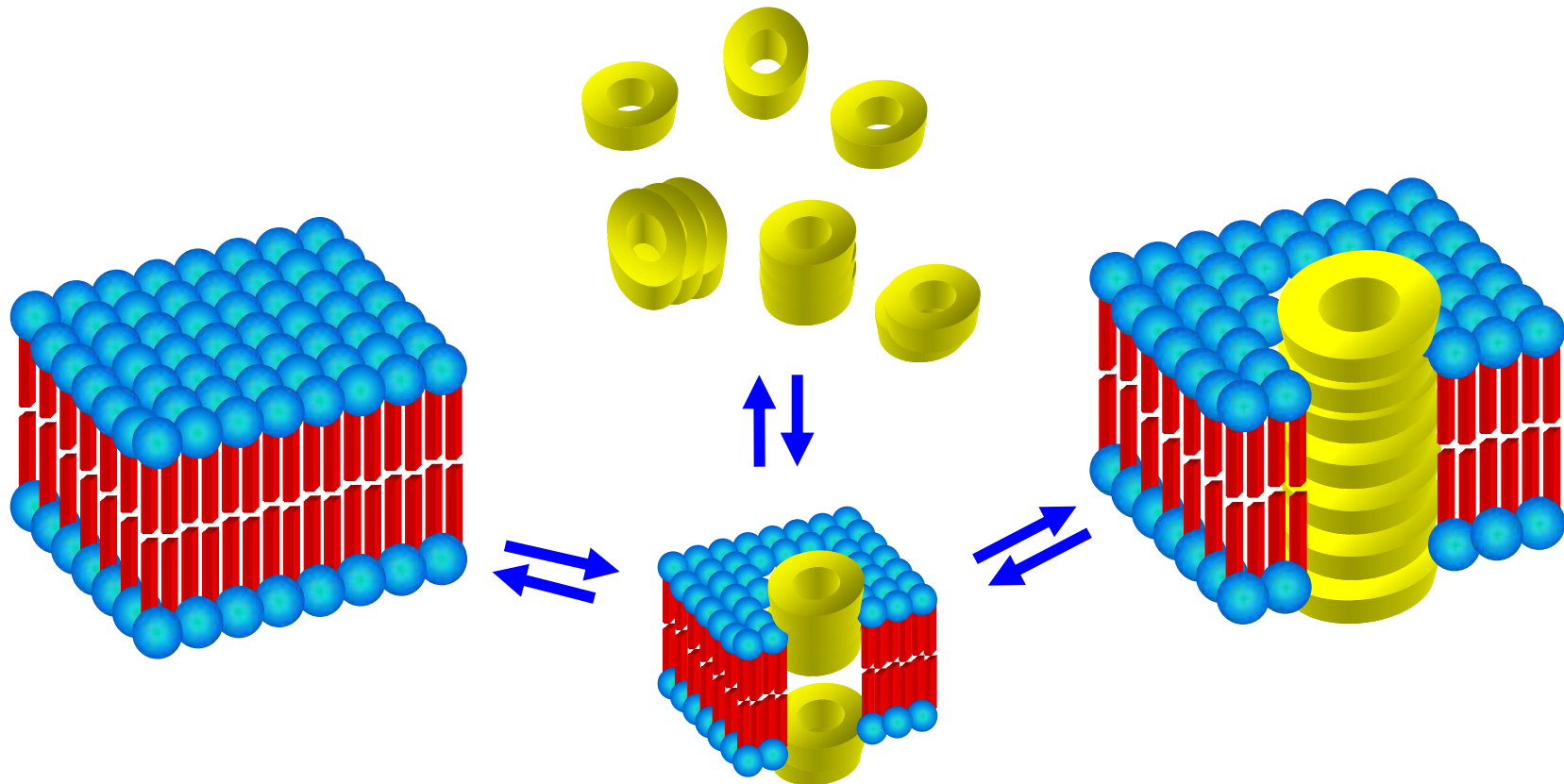
Proton release can only be half-propagated to the central water and results in an unfavourable relative water orientation on the other half-terminus



E. Tajkhorshid et al., Science 296, 525 -530 (2002)

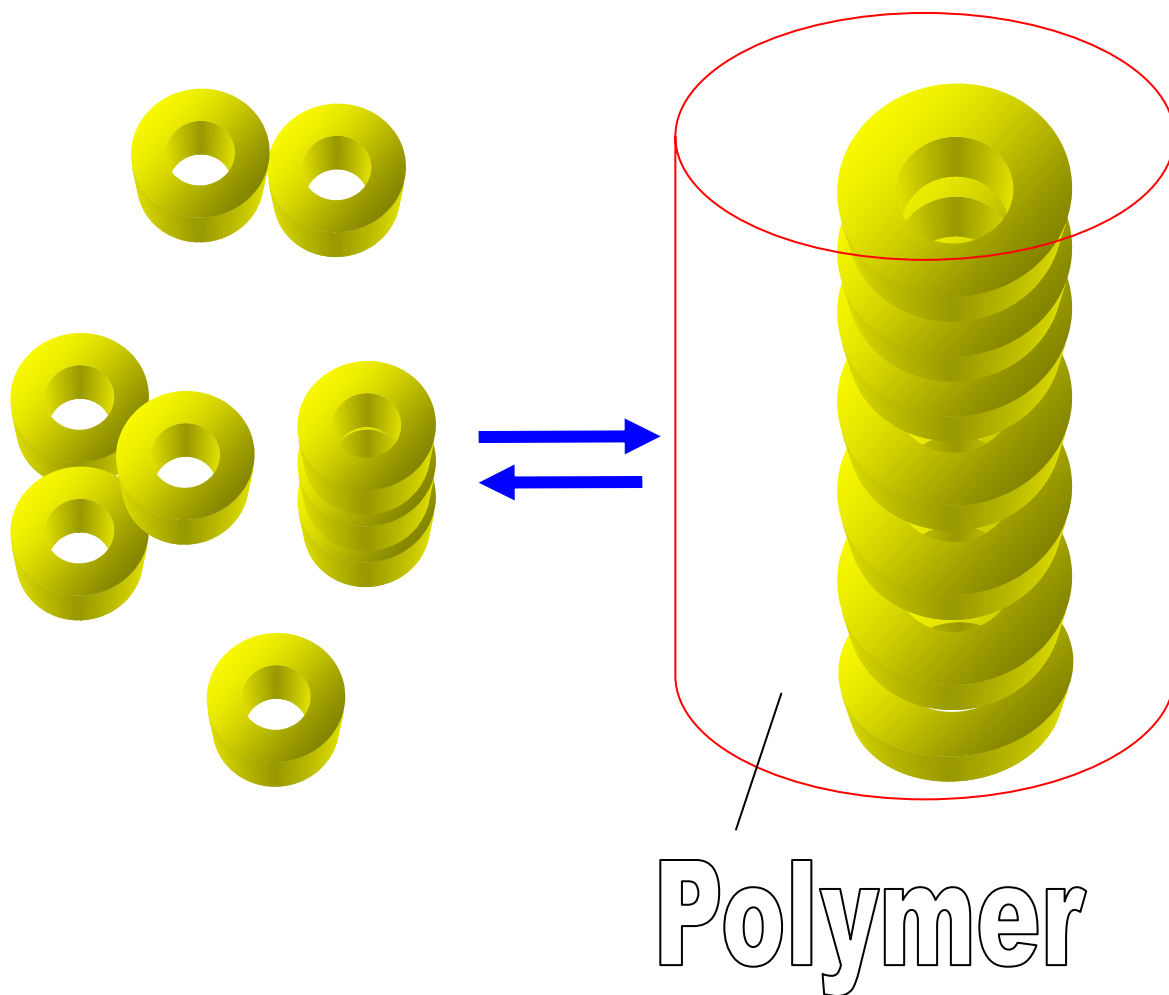
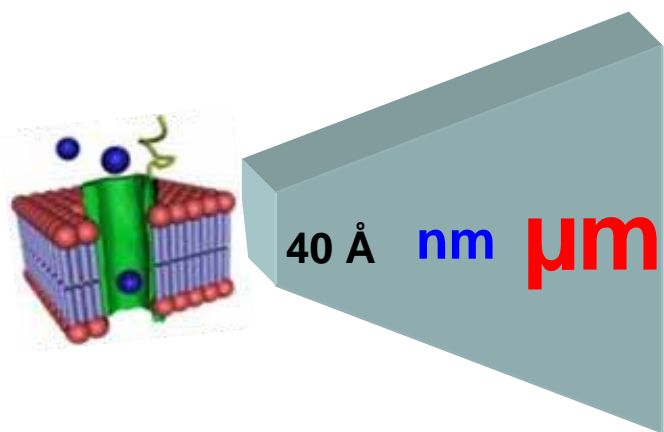
Going to functional transport pathways...by self-assembly

Despite the thermodynamic stability of the assemblies resulted from simple molecular components they are in dynamic equilibrium between monomer and supramolecular oligomers and only few examples clearly showed single-channel activity in lipid bilayers (40 Å)



Going to functional supramolecular devices....by self-assembly

"Supracombimat"
exploring the
chemical
diversity by:
selection,
amplification,
fixation
in polymers

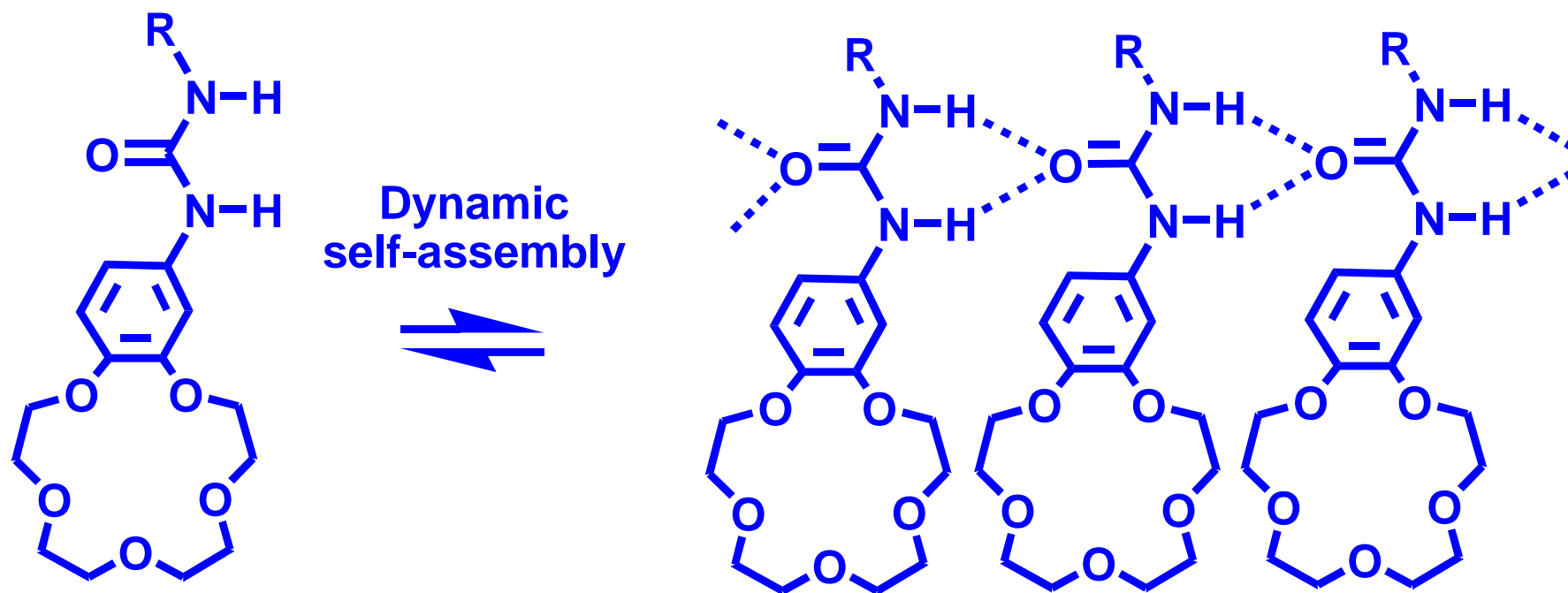


Self-organized membranes



1, R= -C₆H₅, 2, R= -C₅H₁₁, 3, R= -C₁₈H₃₇,
4, R= -C₃H₇, 5, R= -C₃H₇SiO(Et)₃,

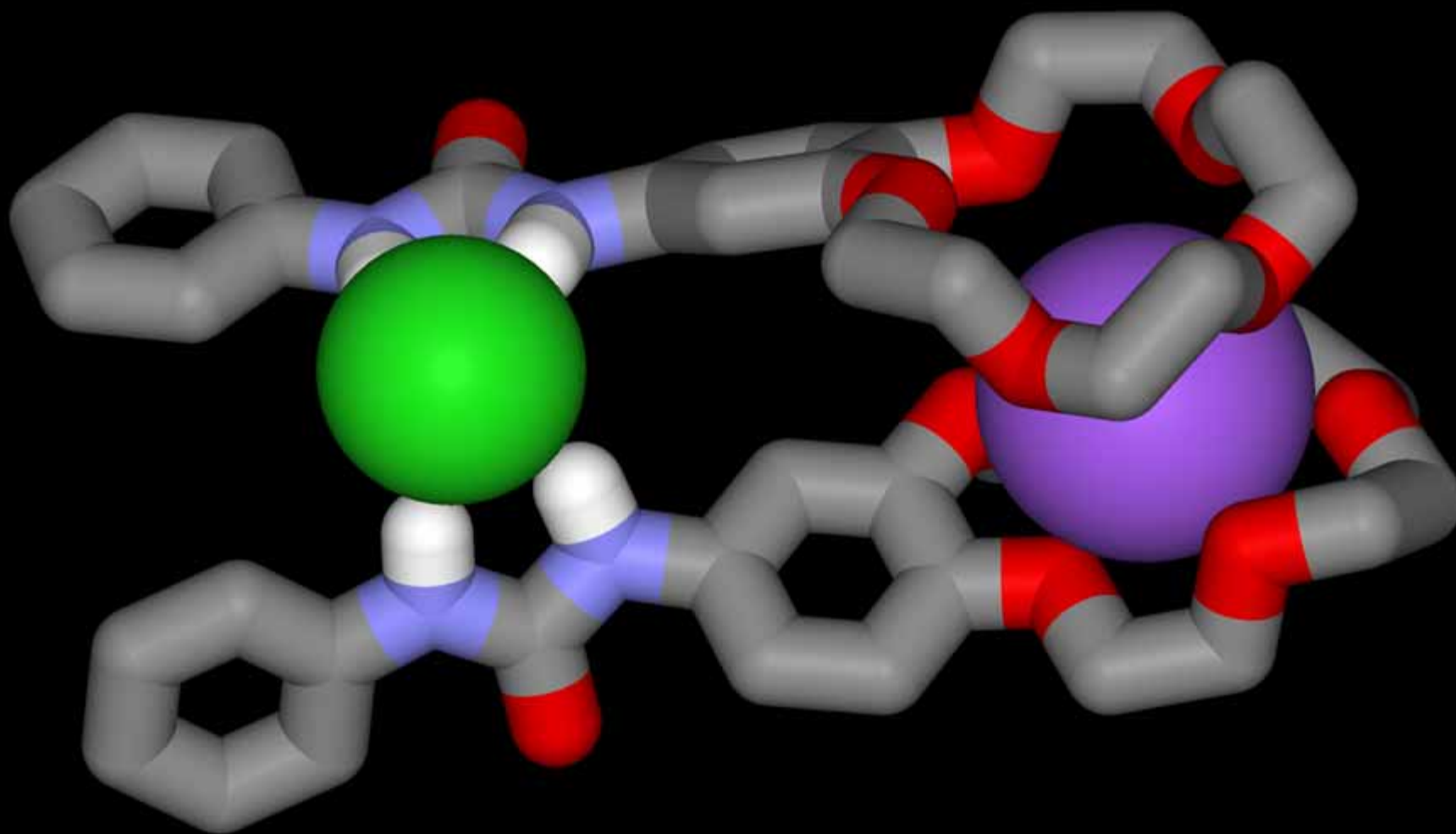
Self-organized membranes



Molecular recognition of the carrier monomers

Channel-forming polyassociated superstructures

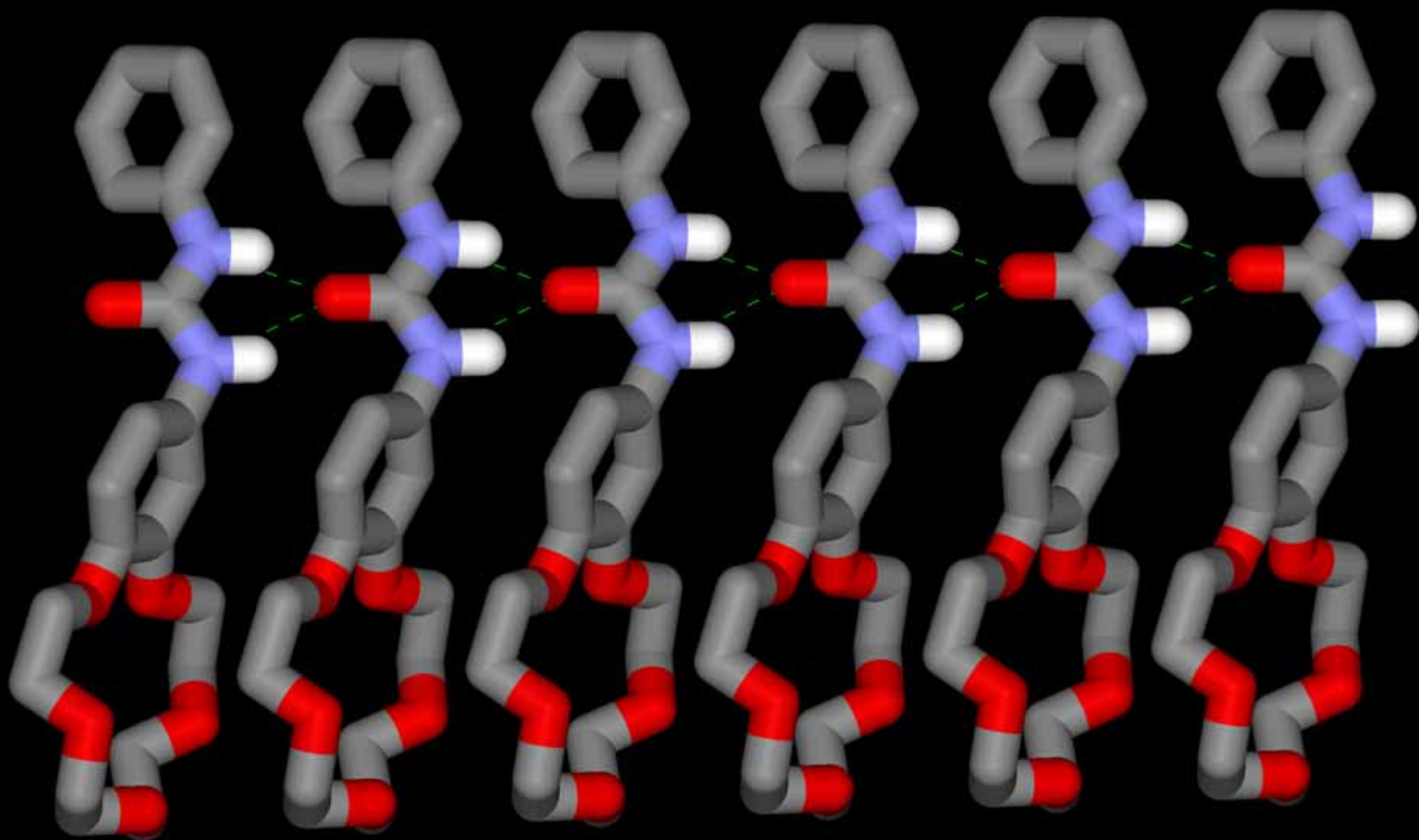
Heteroditopic receptors-dimers



Org. Lett. **5**, 3073 (2003).

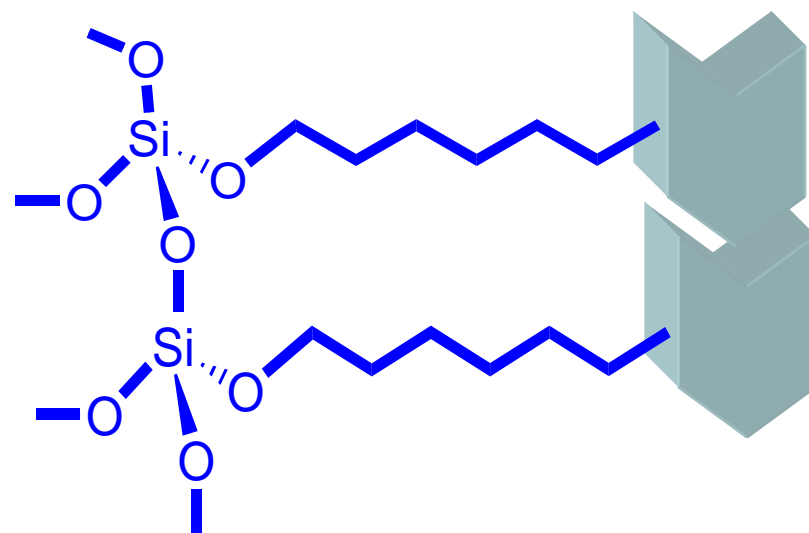
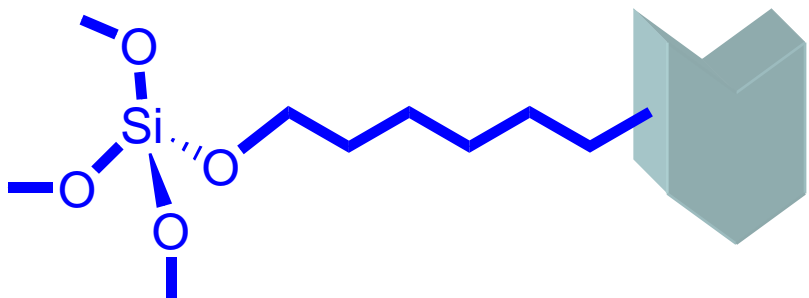
Crystal structure of the 15C5*NaCl complex

Self assembled receptors

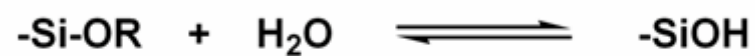


Crystal structure of the B15C5 receptor

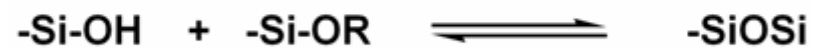
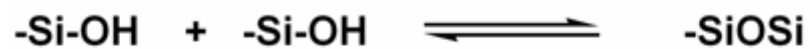
Hybrid supramolecular heteropolysiloxanes by sol-gel



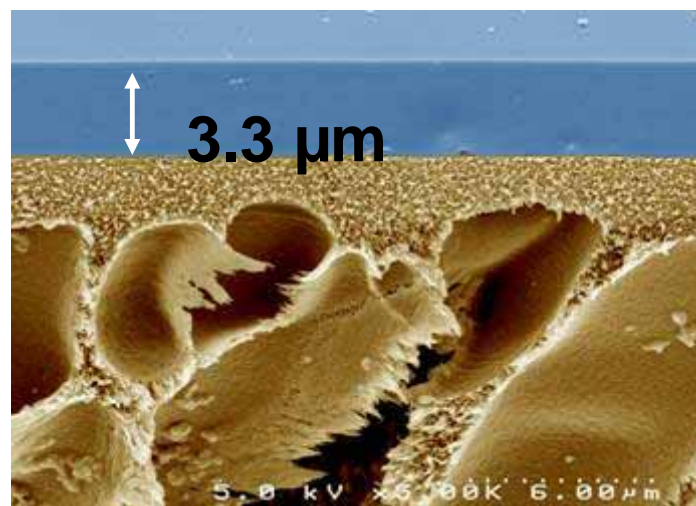
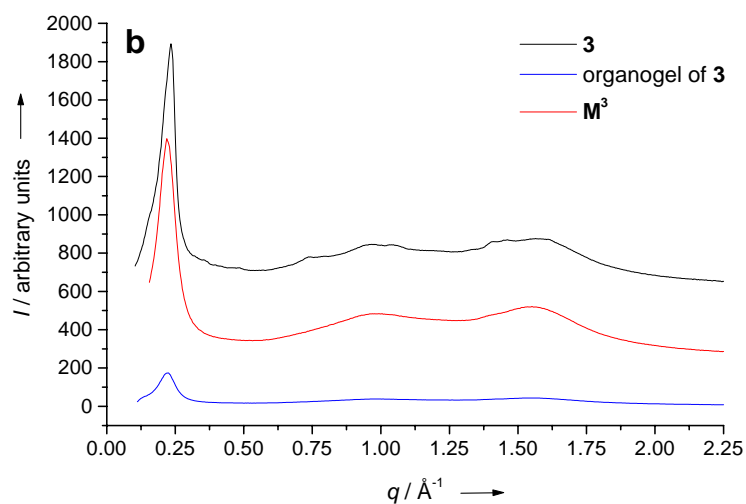
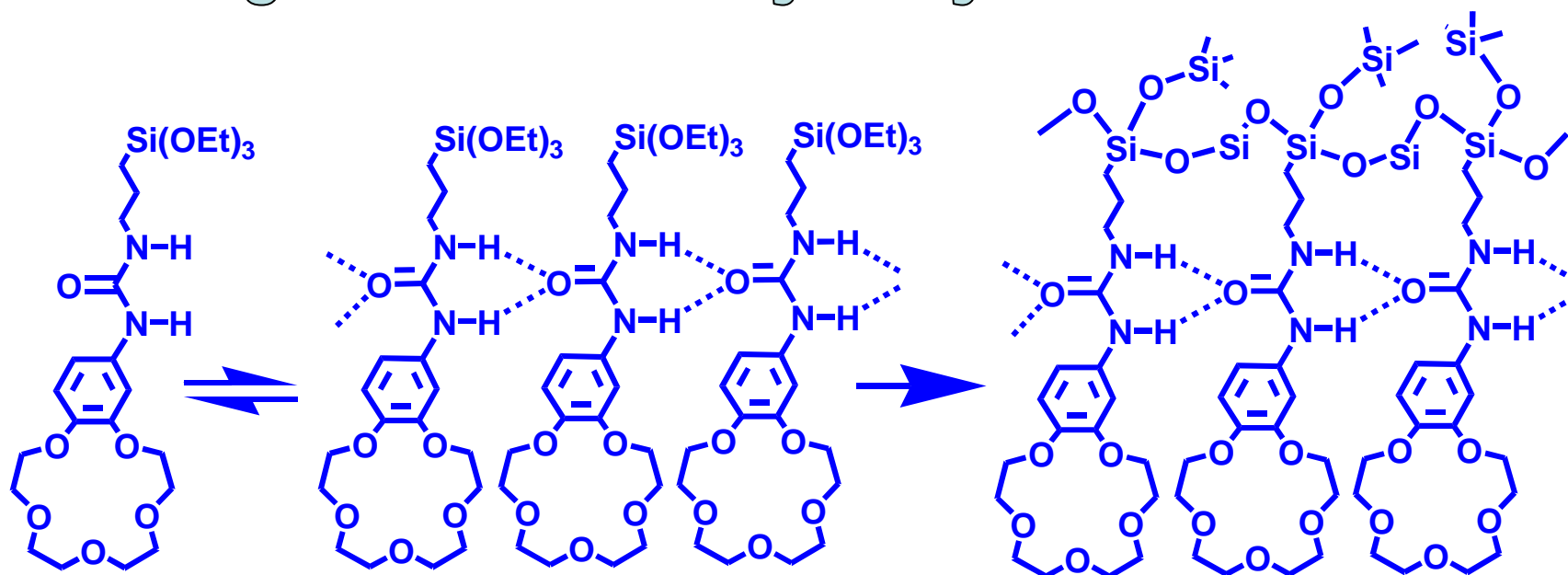
Hydrolysis: slow, H⁺



Condensation: fast, OH⁻



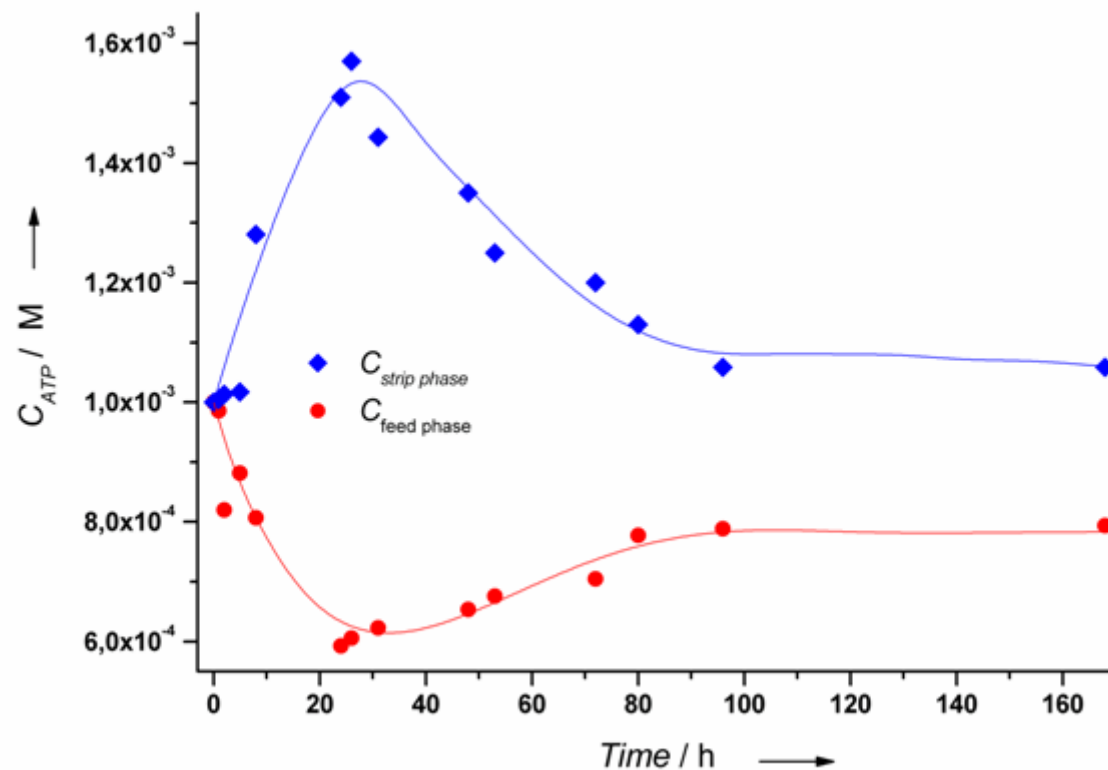
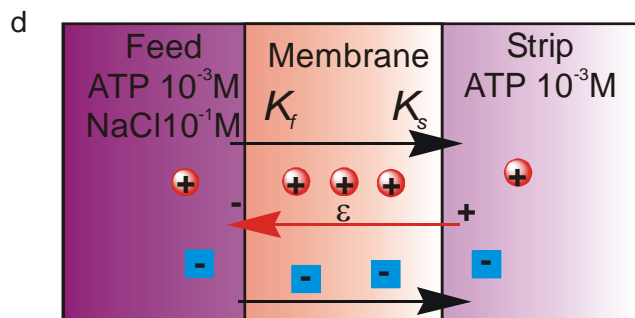
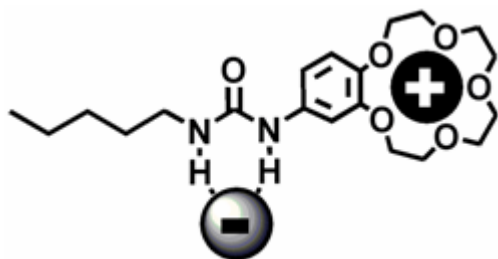
Self-organized thin-layer hybrid membranes



J. Am Chem.Soc., 2004, 126, 3545-3550.

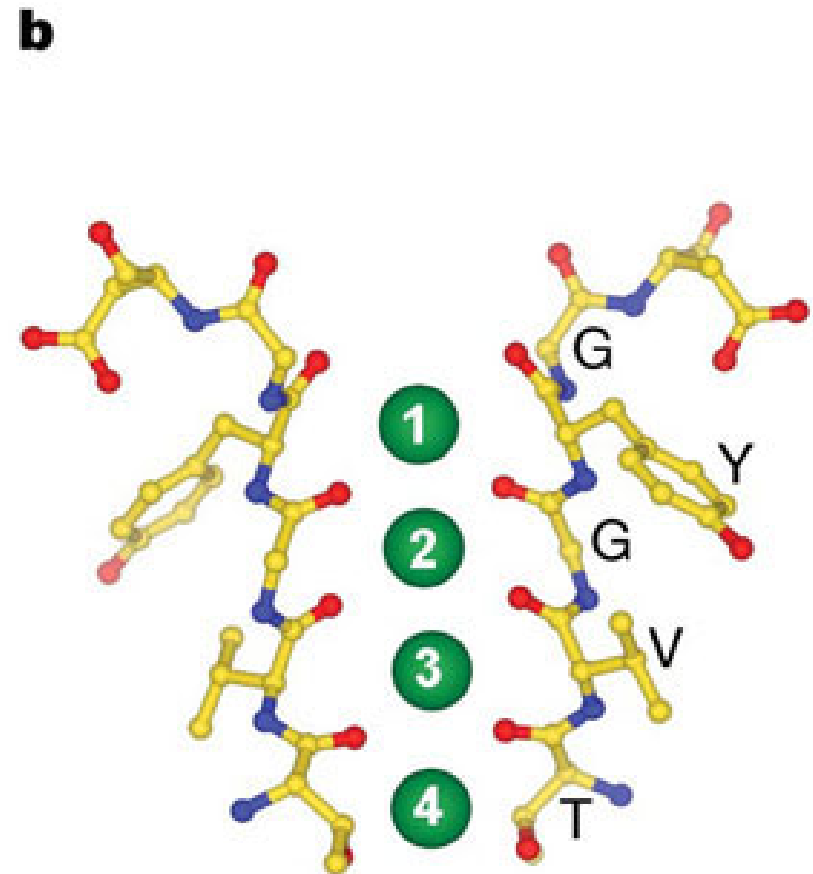
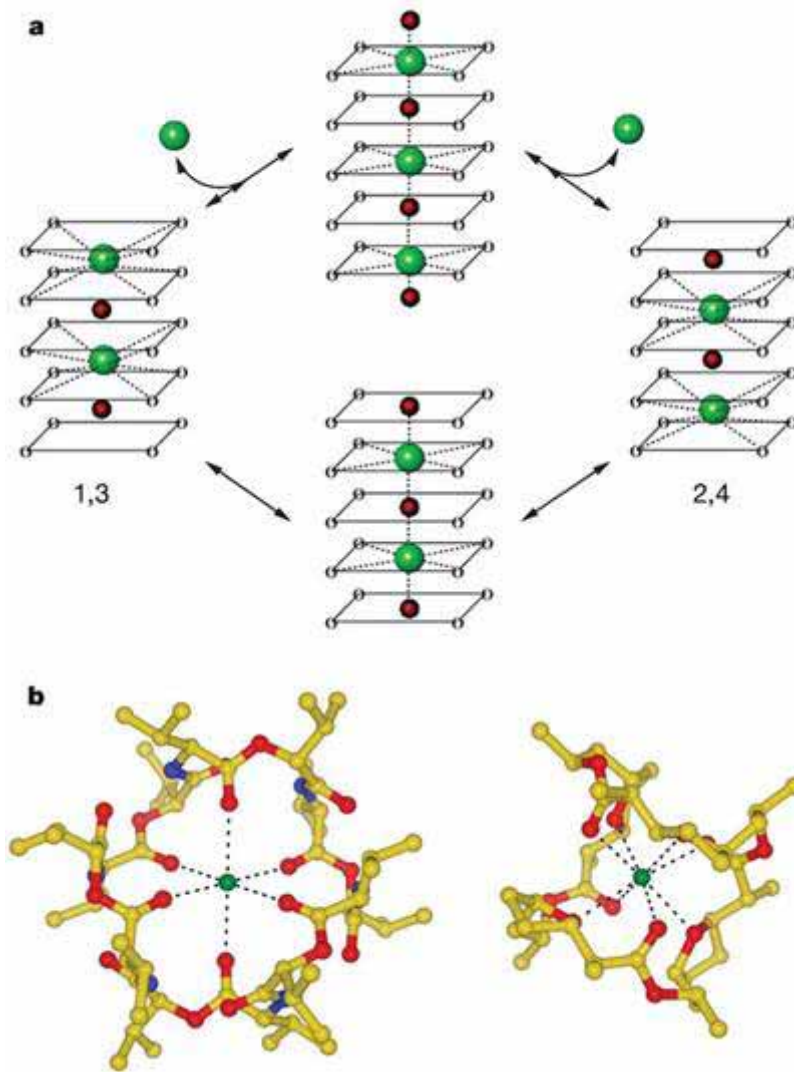
Self-organized membranes

ATP ion-pump fuelled by Na^+ concentration gradient

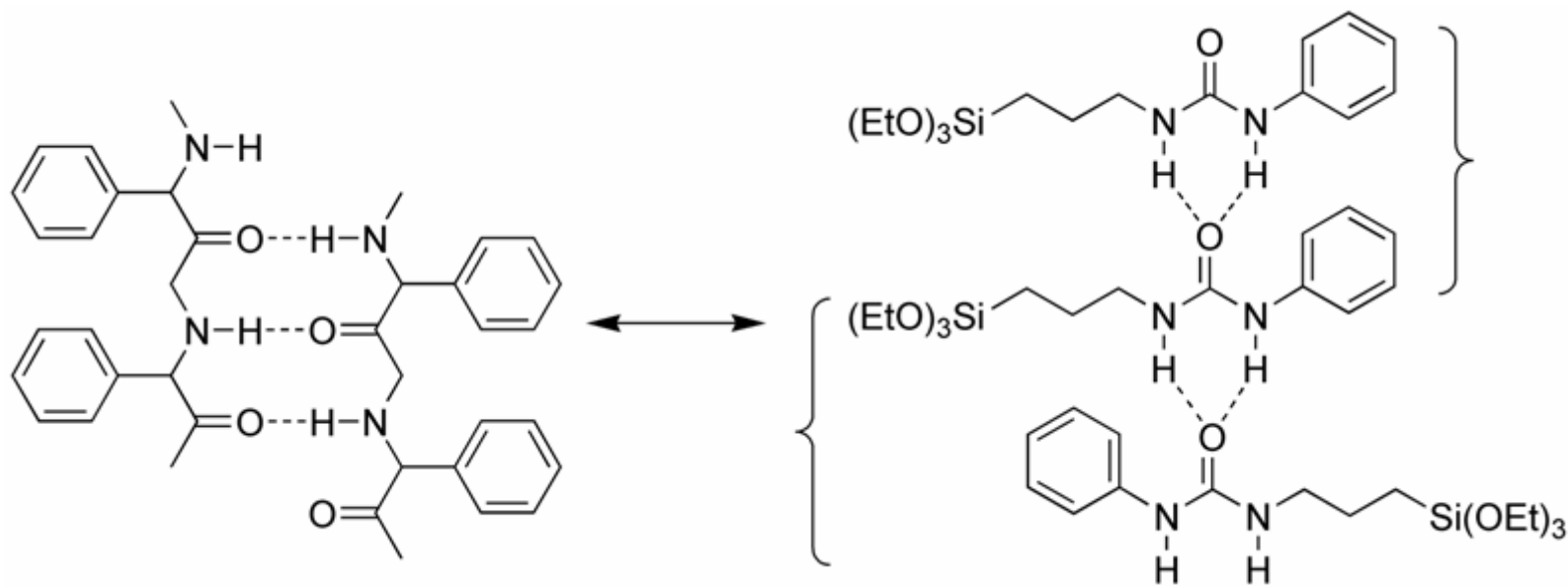
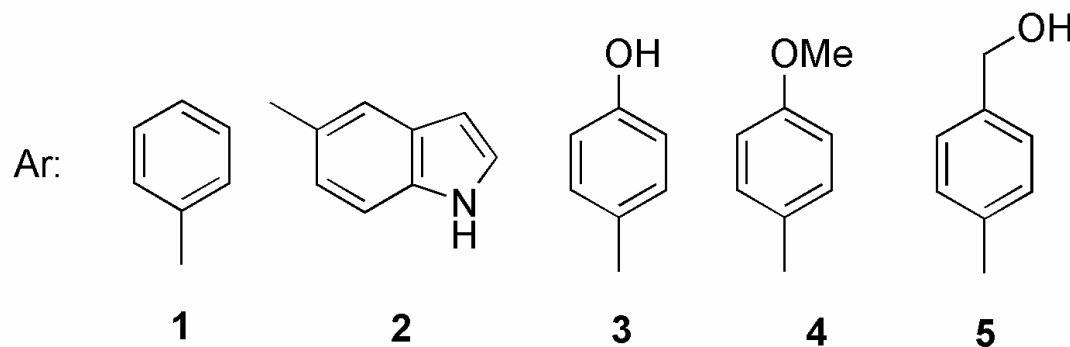
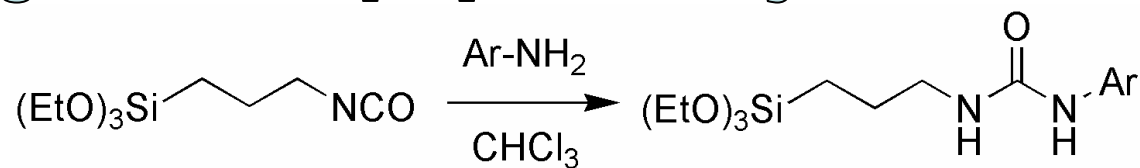


J. Am. Chem. Soc., 2004, 126, 3545

KSCa Transport Channel: functional devices

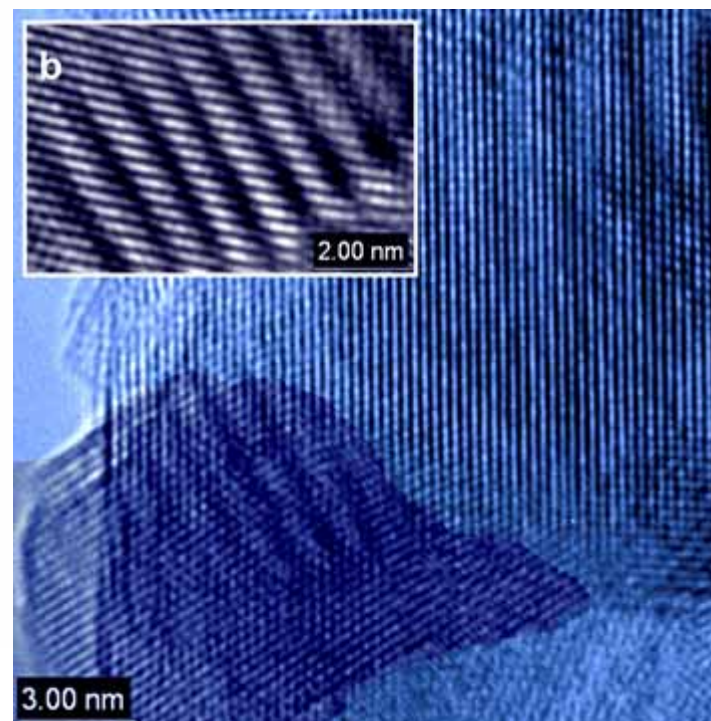
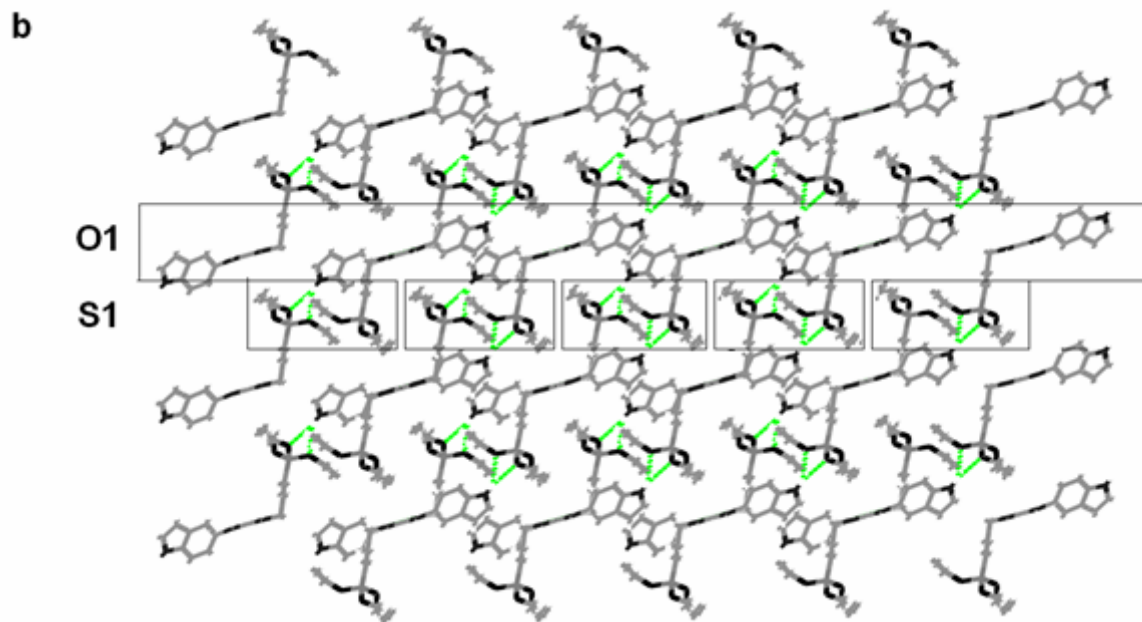
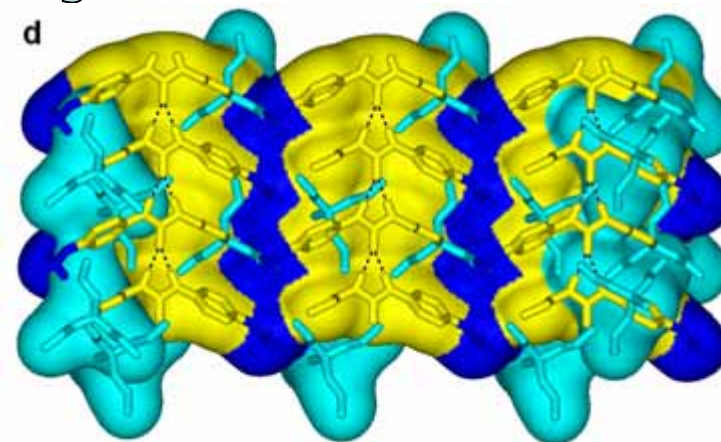
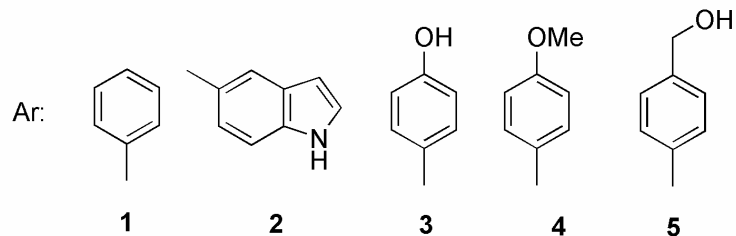
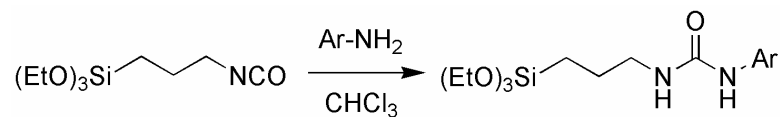


Self-organized "peptoid" hybrid membranes



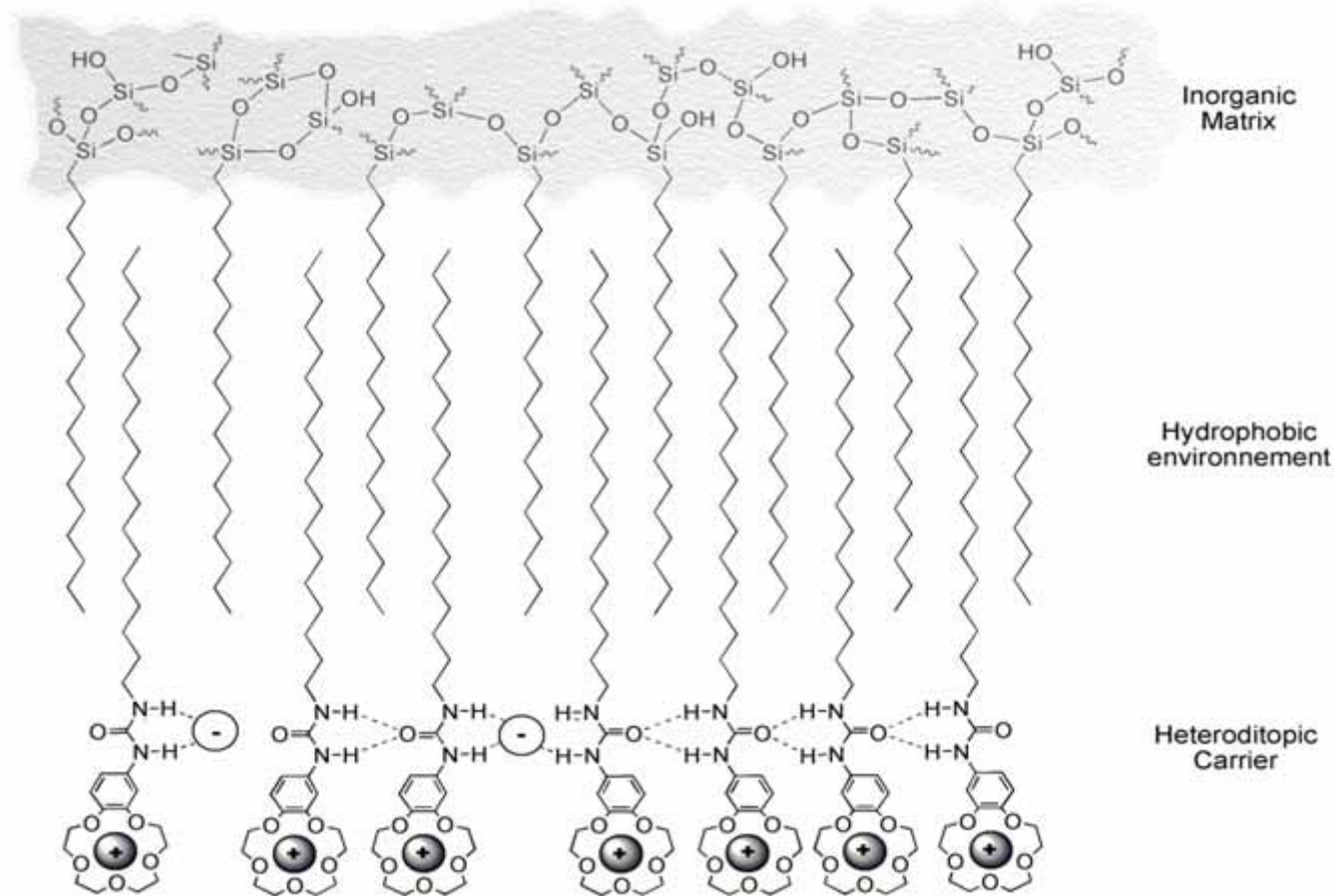
Chem. Eur.J. **2008**, *14*, 1776-1783.

Self-organized "peptoid" hybrid membranes



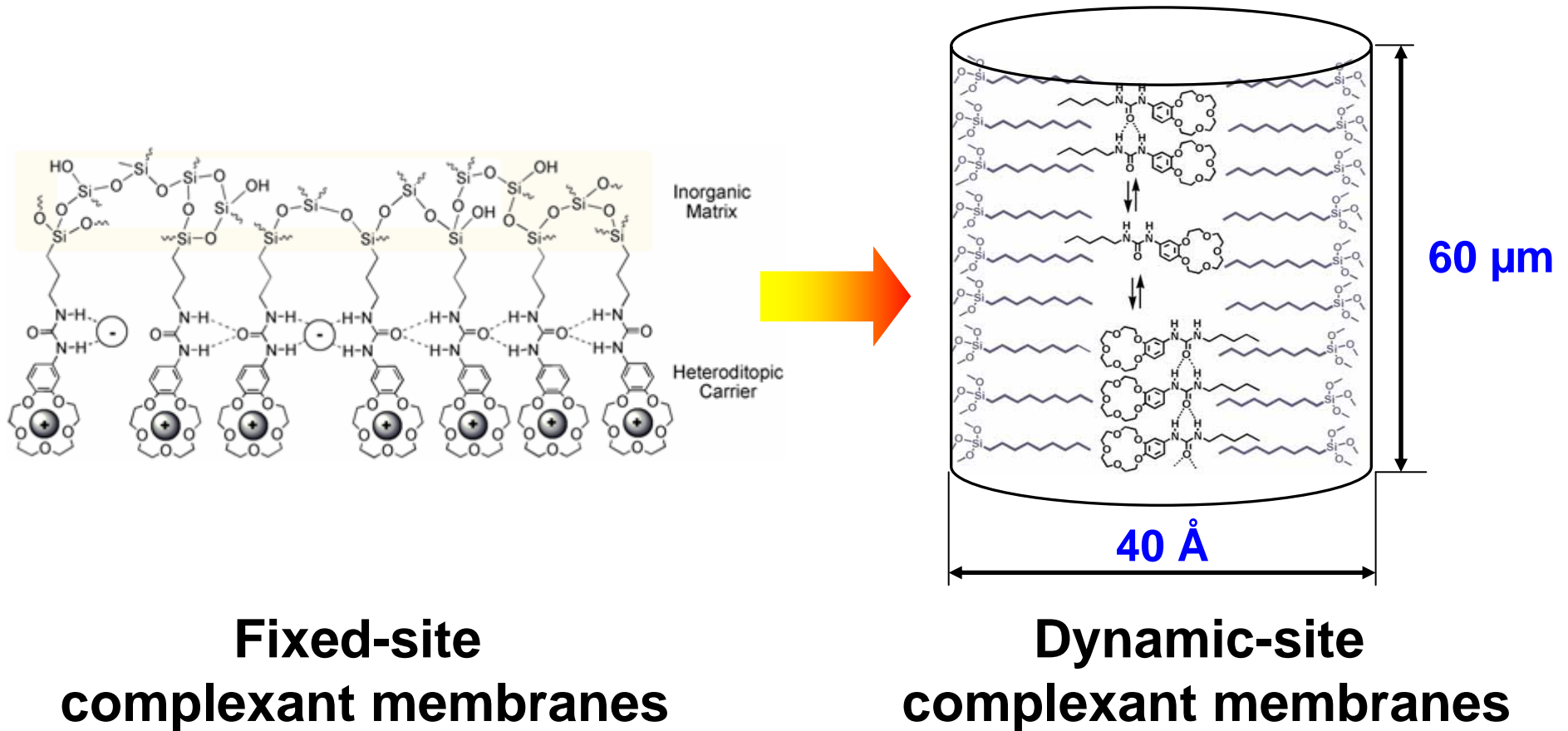
Chem. Eur.J. **2008**, *14*, 1776-1783.

Dynamic Supramolecular Membranes

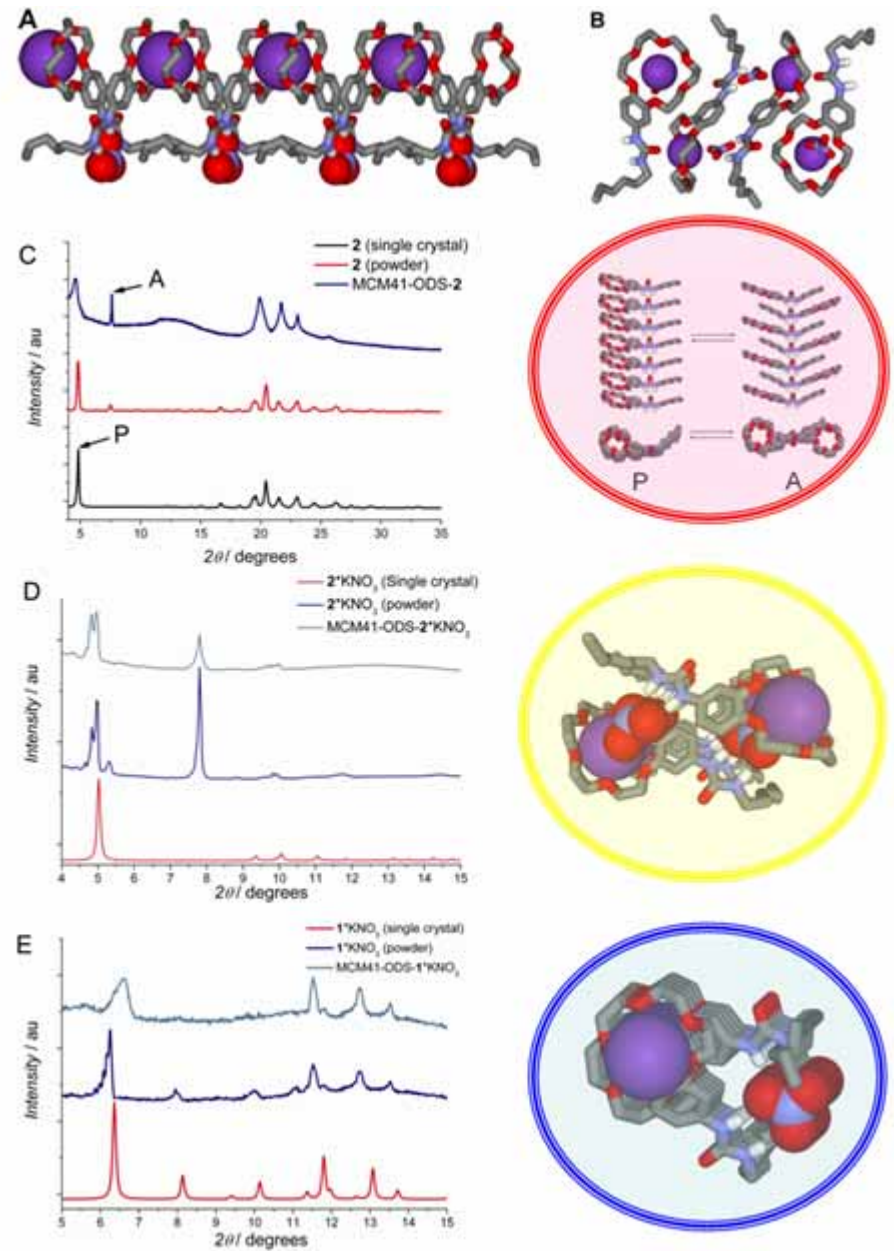
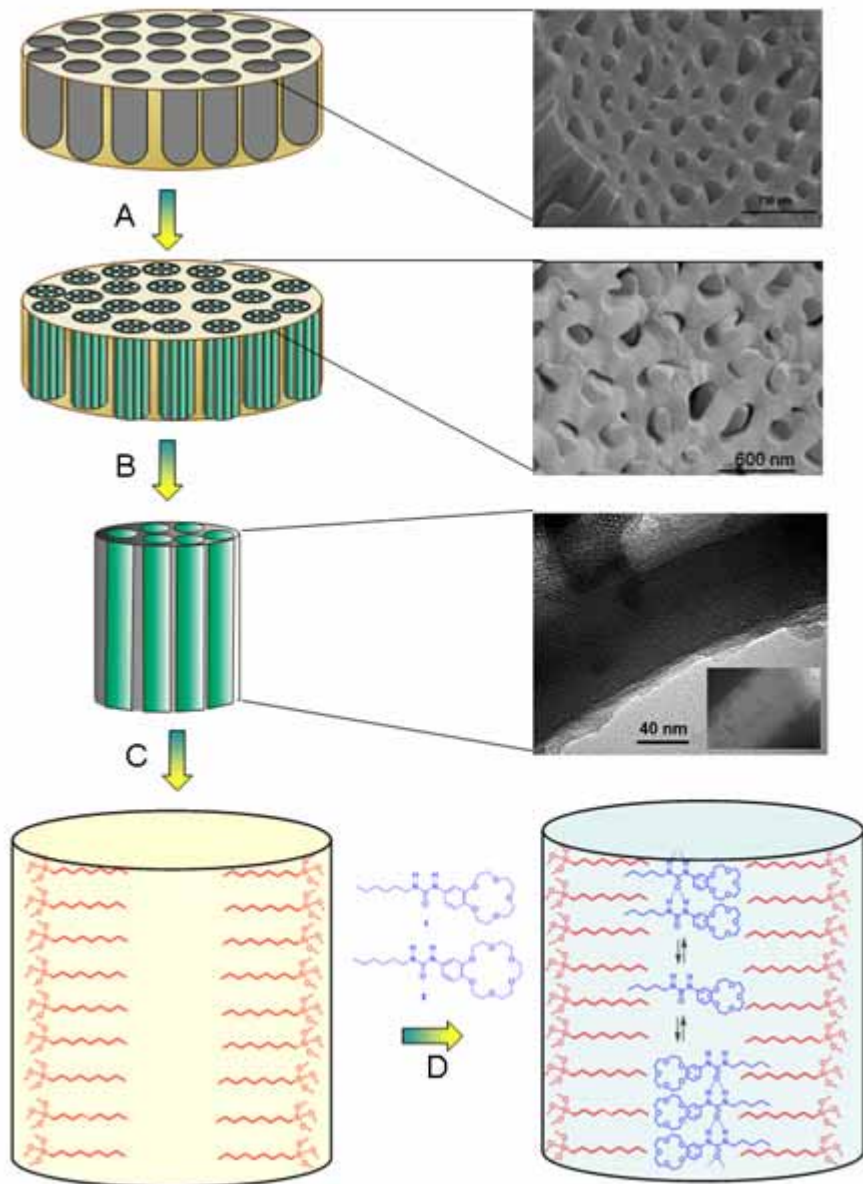


Dynamic hydrophobic transcription of self-organization in mesostructured membranes

Fluid Mosaic Model in Mesopores

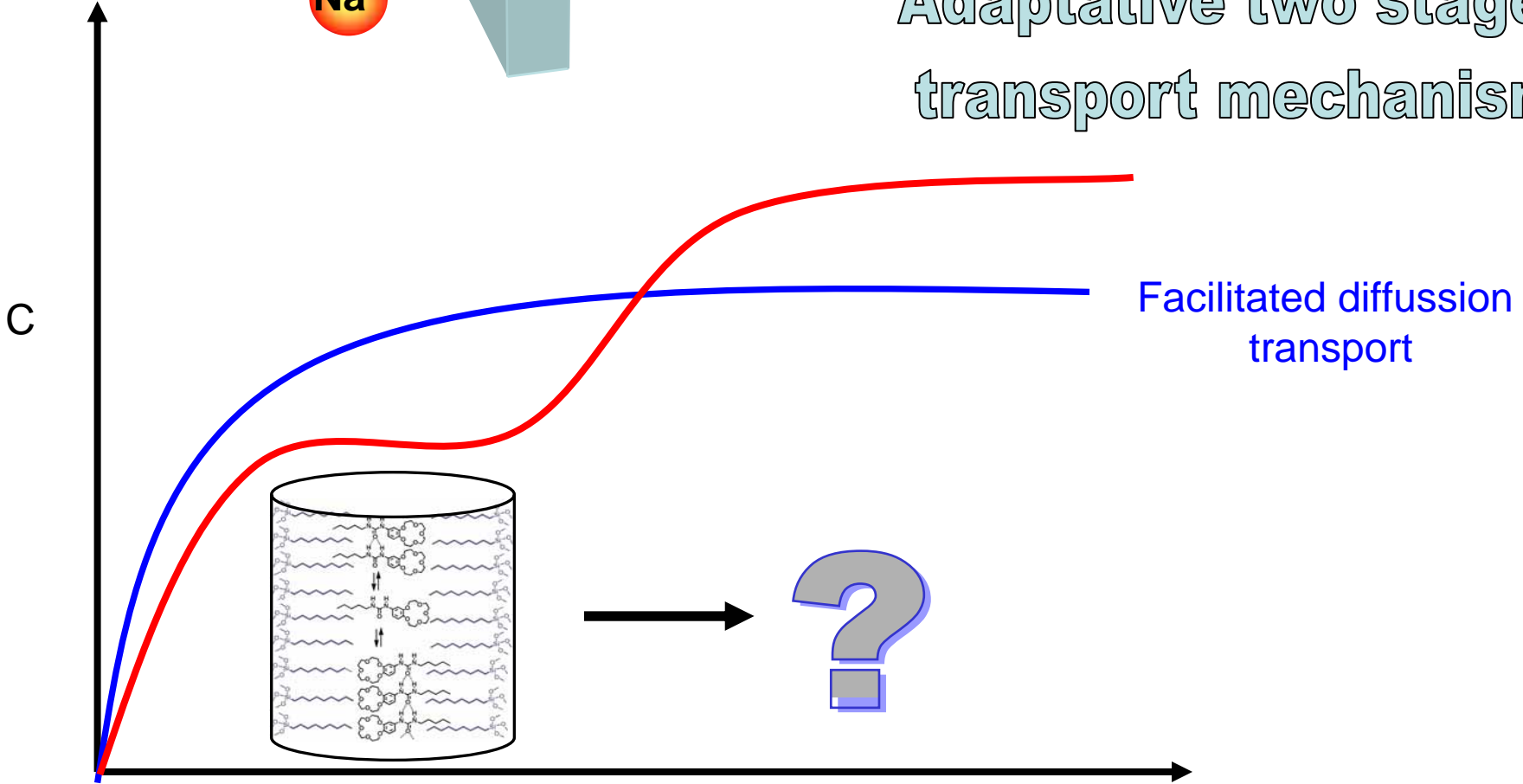


Dynamic adaptative membranes





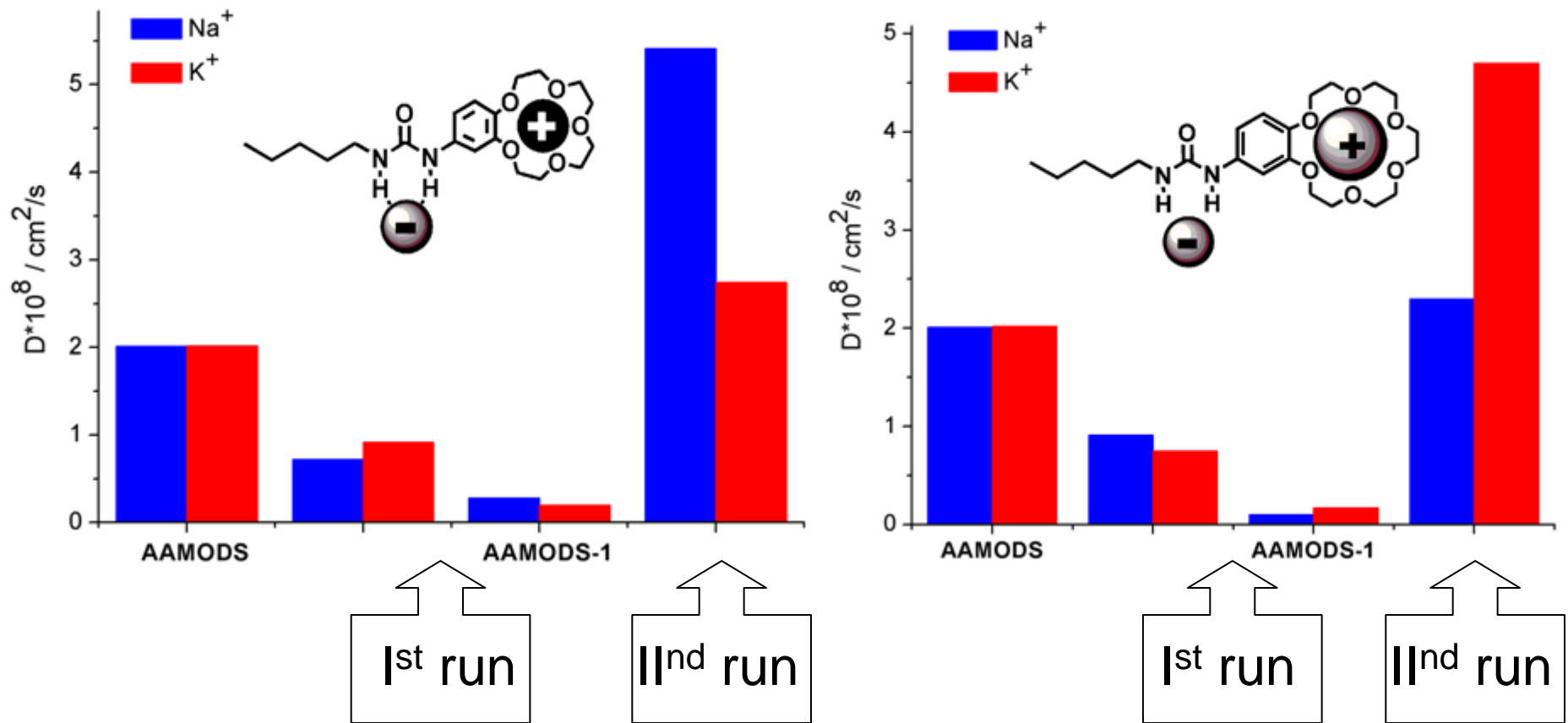
Adaptative two stages transport mechanism

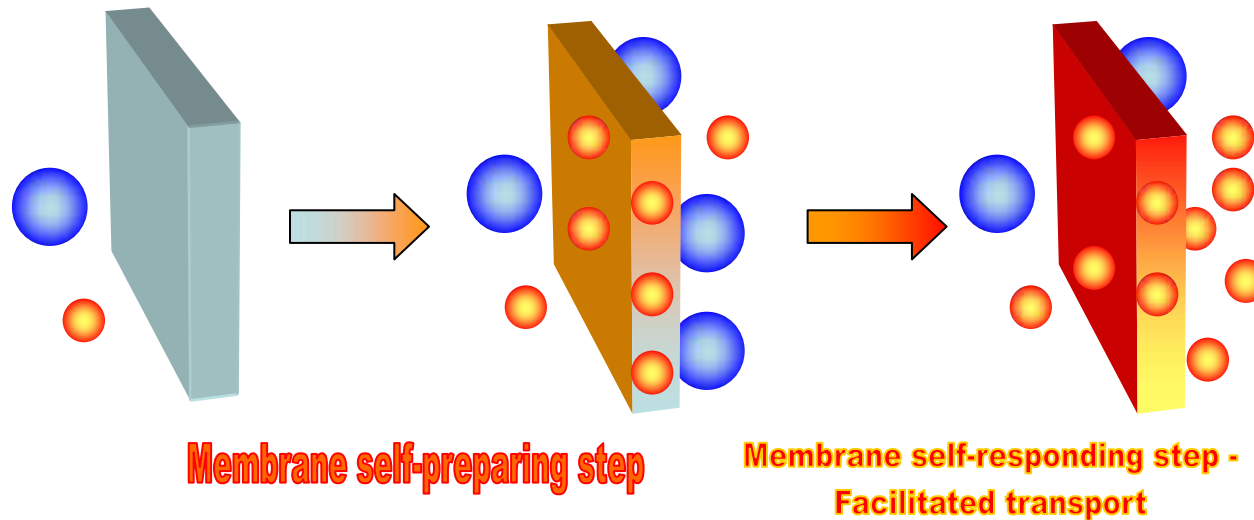


Time

A. Cazacu, manuscript submitted

Adaptative self-organization in the mesopores

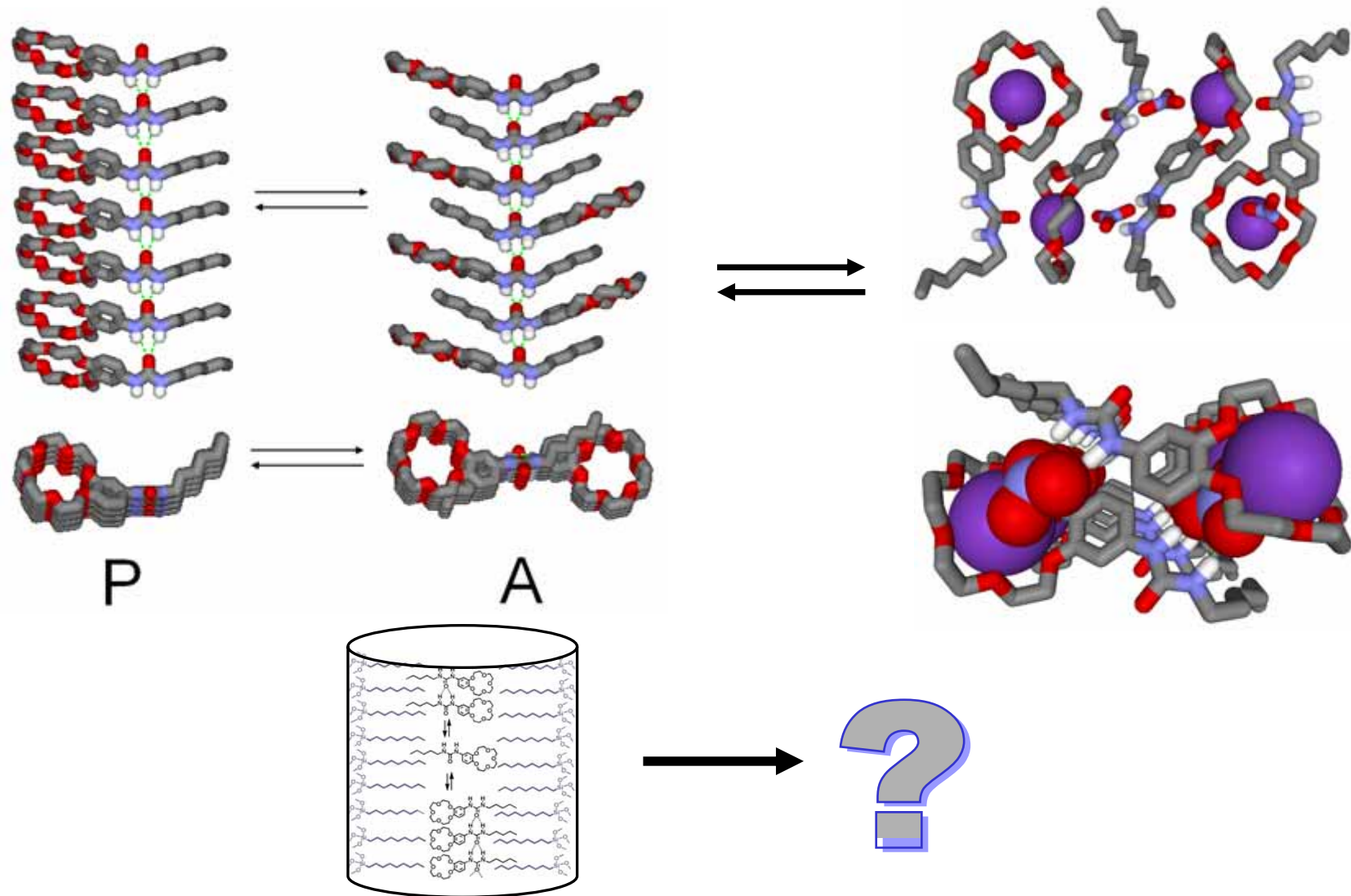




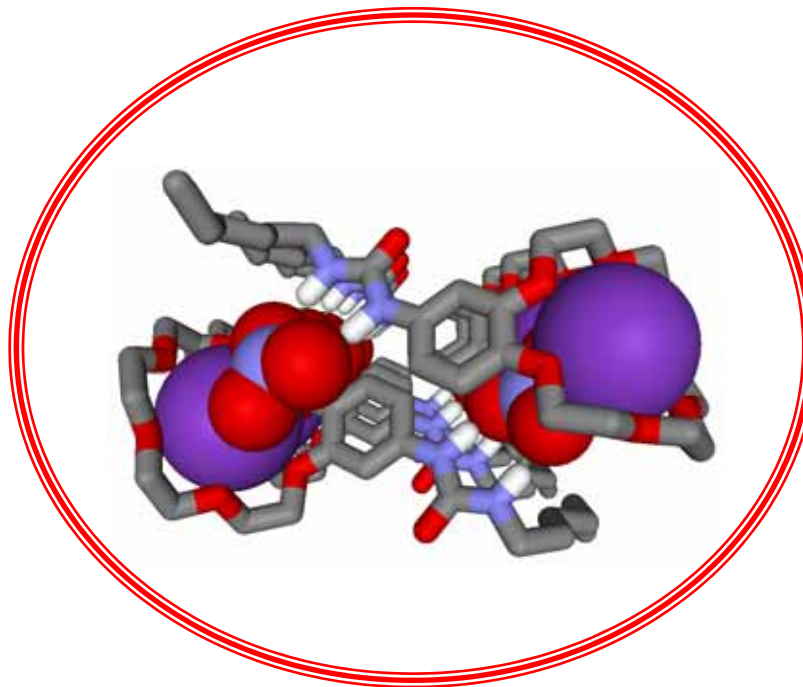
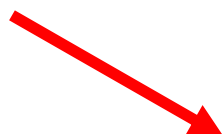
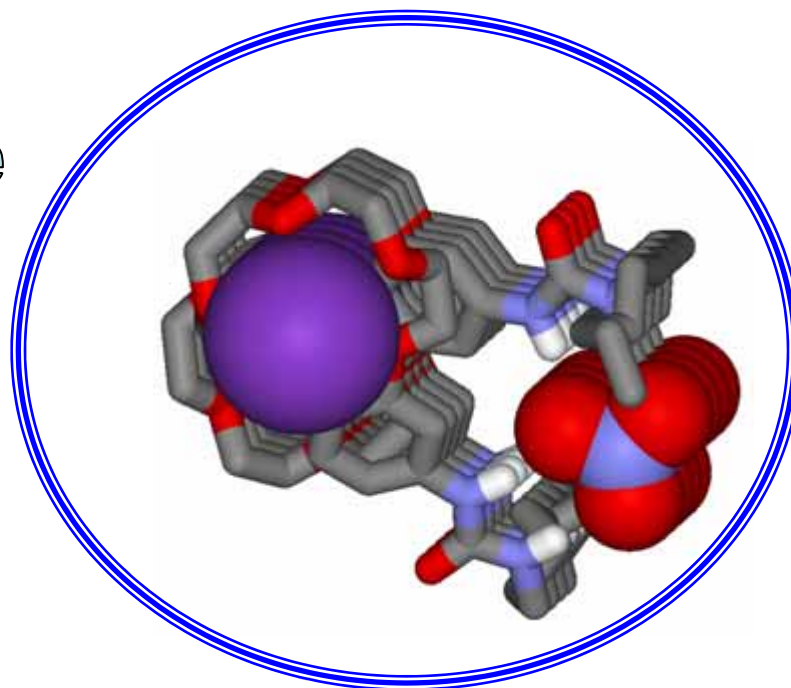
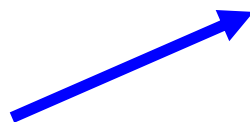
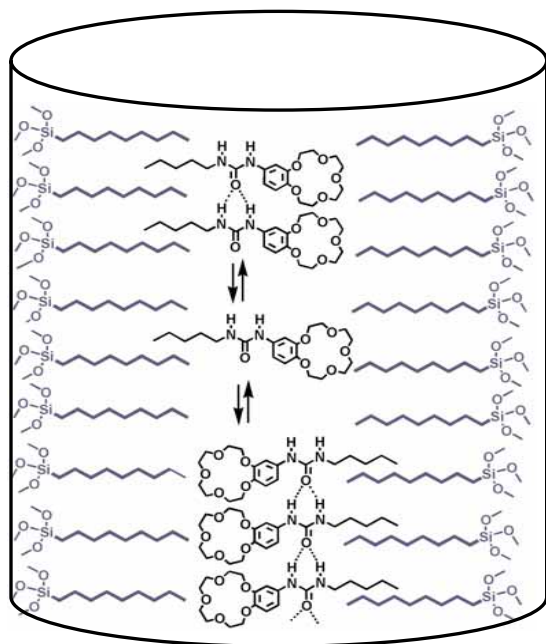
In the first step, the membrane is functioning like a “*sponge*”, with the selective complexation of the fittest cation and with the membrane reorganization; it is the so-called “**membrane self-preparing step**”.

Then, a selective transport of the specific cation (Na^+ for 15C5 and K^+ for 18C6) occurs in the second stage, much faster; it is the so-called “**membrane self-responding step - facilitated transport- SRS-FT**”.

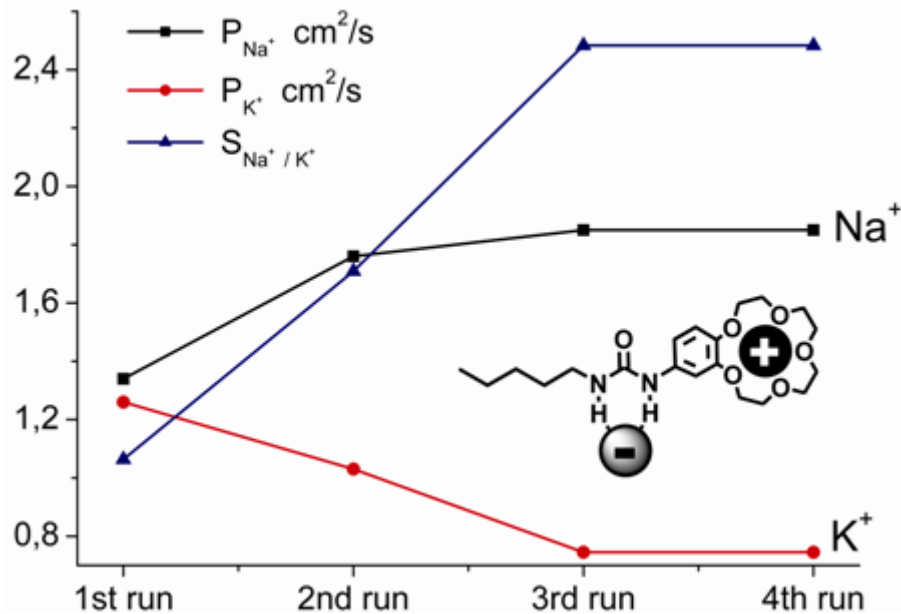
Adaptative self-organization in the mesopores



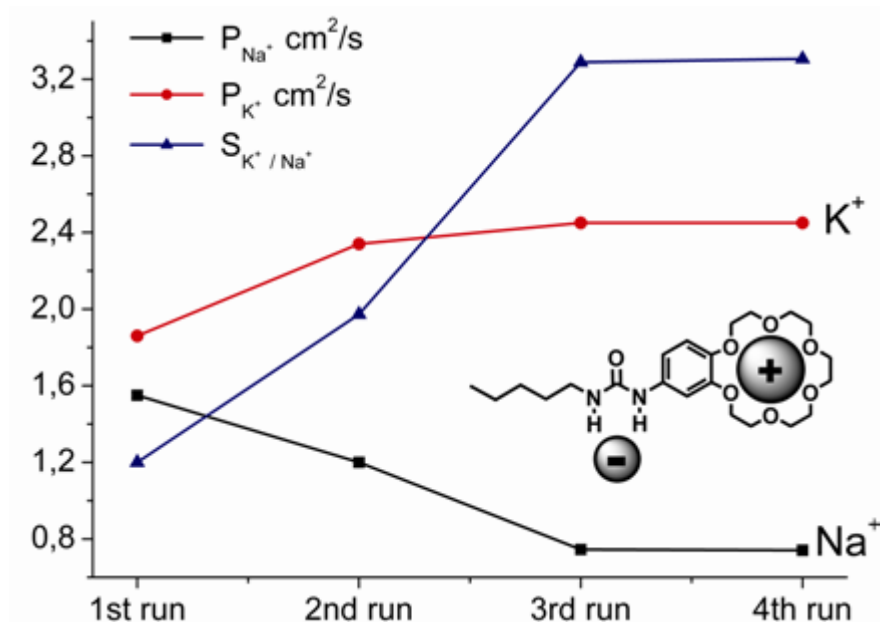
Adaptative self-organization in the presence of the solute



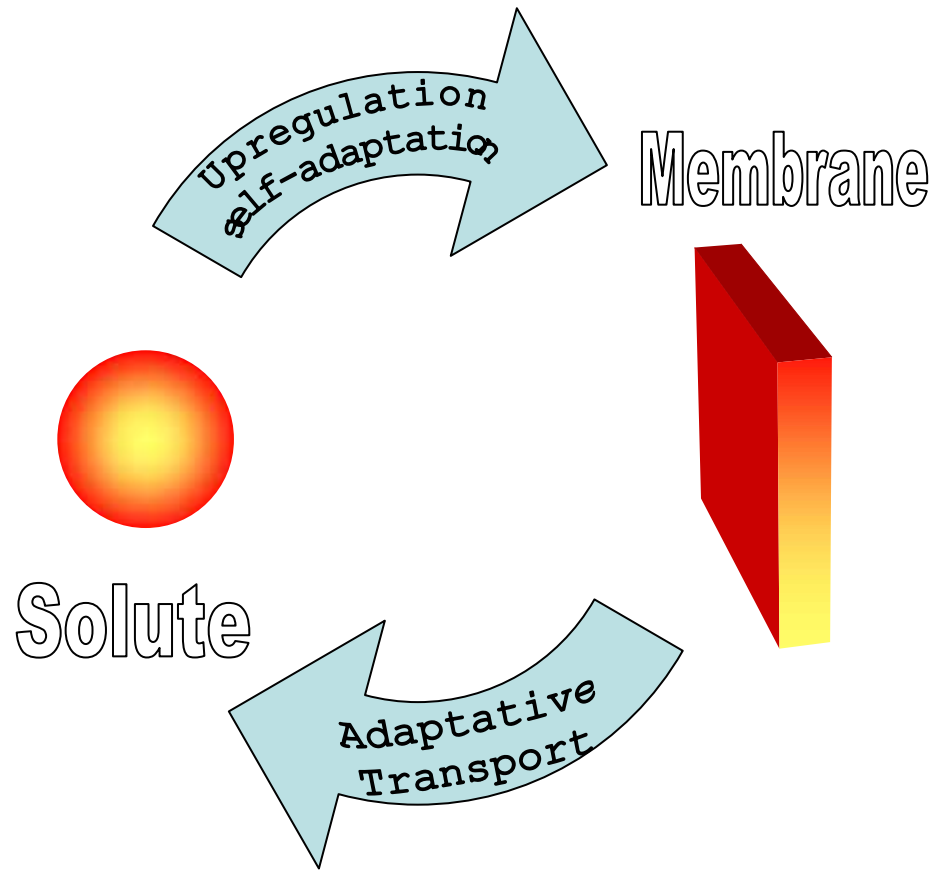
Ion-conditioned membranes



Selectivity and Permeability
are both increasing



The membrane is
dynamically self-instructed!

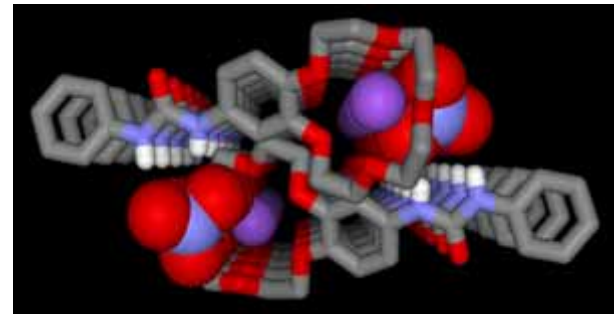


Dynamic-site complexant membranes

This concept embodies a constitutional self-reorganization (self-adaptation) of the membrane configuration producing an adaptative response in the presence of its solute.

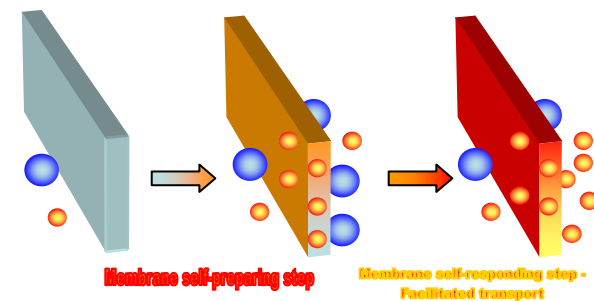
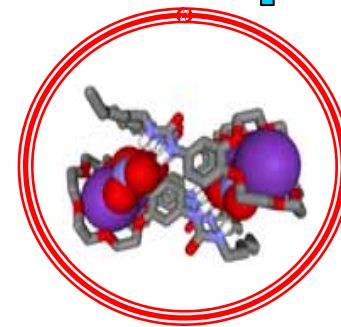
Supramolecular control of ionic conduction pathways

The present results show the first evidence for the possible hybrid transport carrier vs. channel mechanisms by solid self-organized membranes.



Constitutional control of ionic conduction pathways

A first example of dynamic “constitutional” membranes where a solute induces the upregulation of (prepare itself) its own selective membrane





Institut Européen des Membranes, Montpellier
Adaptative Supramolecular Nanosystems Group

