Water in soft confinement of lipidic mesophase

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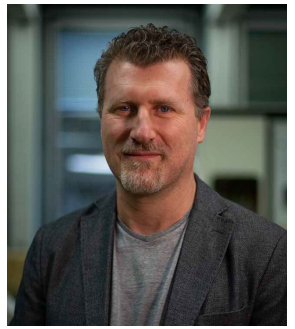

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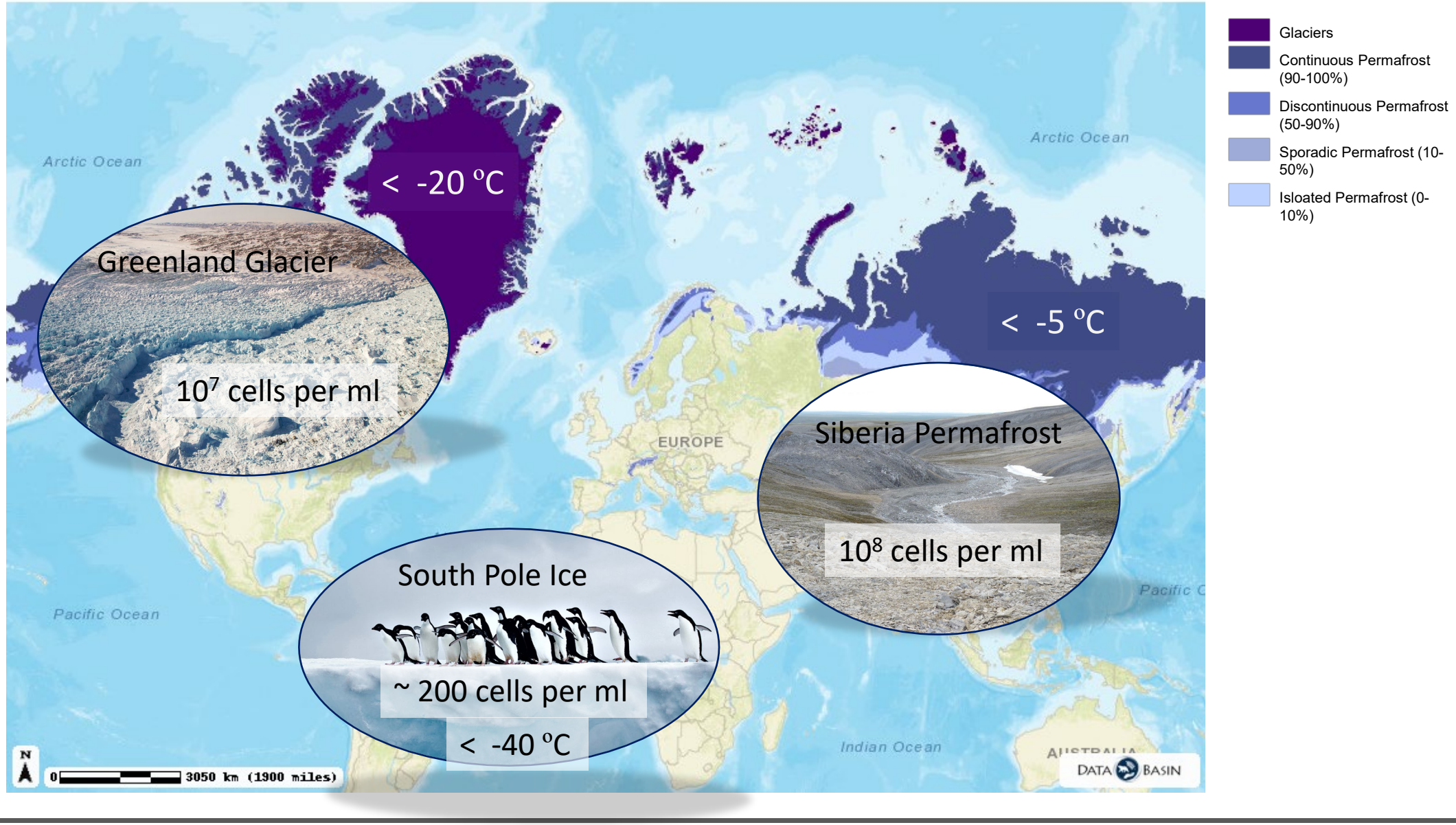
Dr. Fanni Juranyi
PSI

Map of Permafrost and Ground Ice

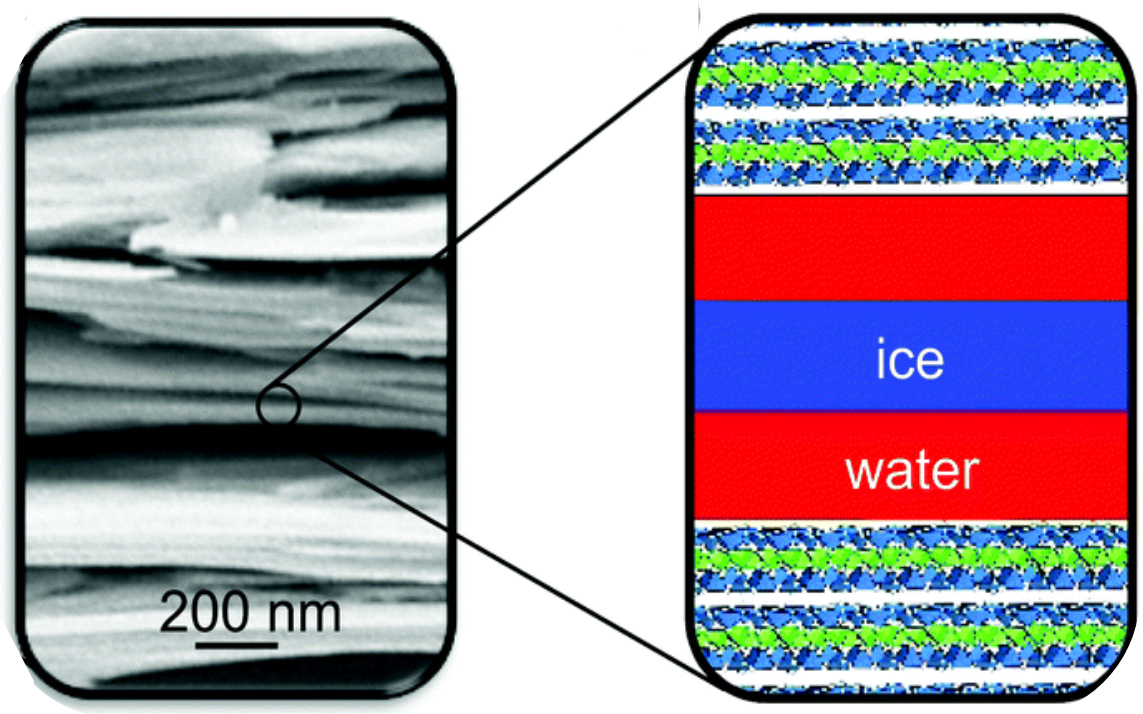


Life at subzero temperatures

Key: liquid water

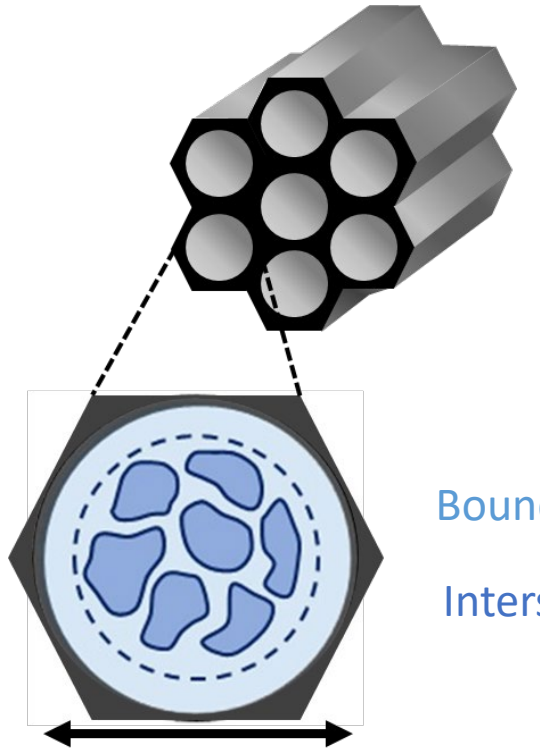
Maintain water in liquid state by hard, nano-sized confinement

Liquid water between clays



Li H. *et al*. *Phys. Chem. Chem. Phys.* 2019.

Mesoporous silica



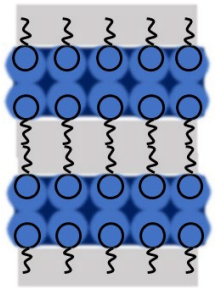
Bound liquid water

Interstitial liquid water

≤ 2.6 nm

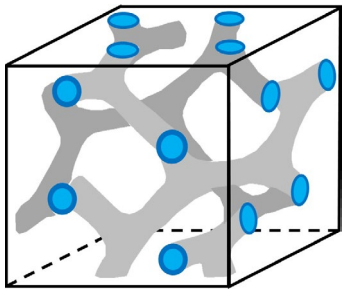
Langmuir, 2019.

Lipidic mesophase



$p = v/al = 1$

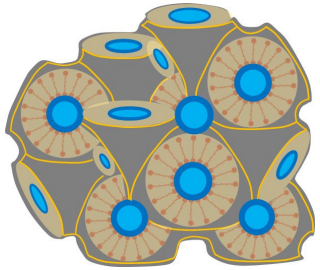
Lamellar (L_α)



Ia3d

Cubic phase

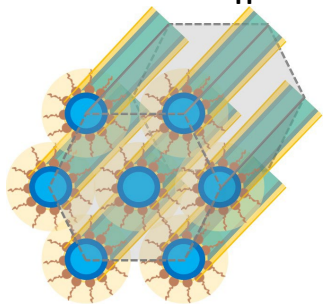
$v/al \geq 1$



Pn3m

Reverse hexagonal

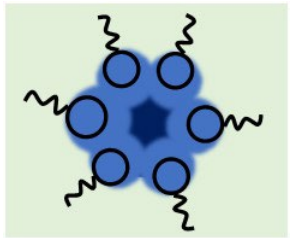
H_{II}

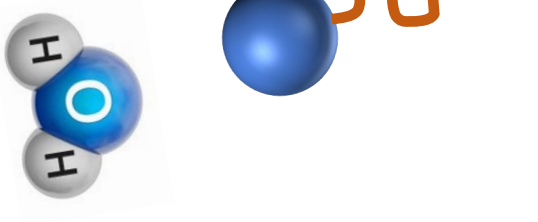


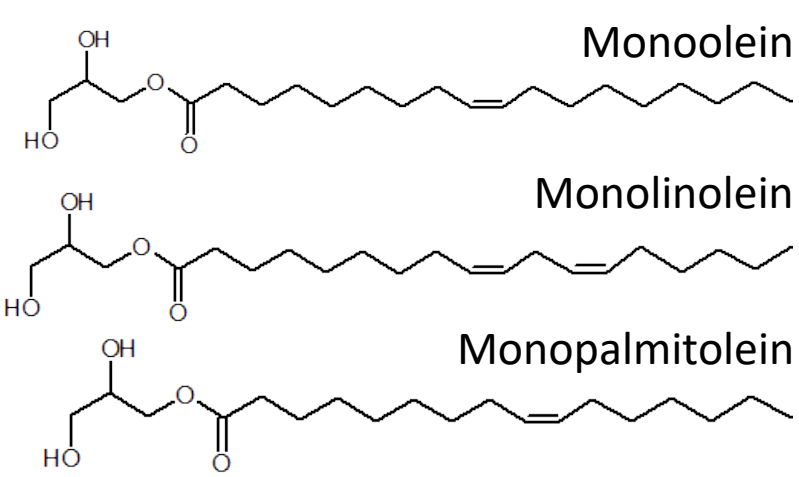
$v/al > 1$

Reverse micelle

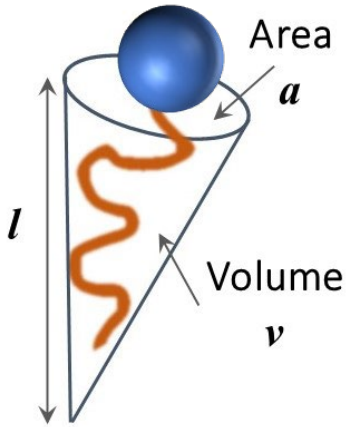
L_2





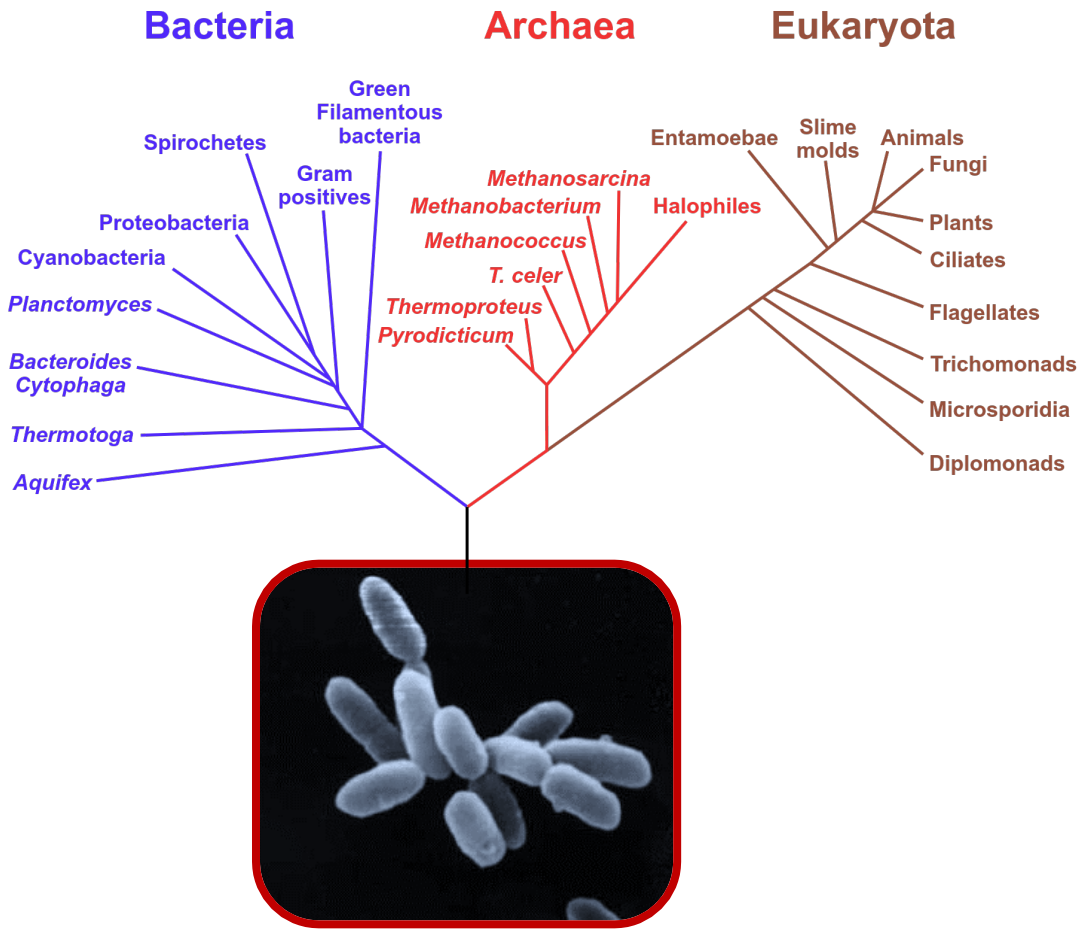


p = v/al



Increase packing parameter

Inspired by Archaea



The age of Archaea ~3.8 billion years vs. The age of the Earth ~4.54 billion years

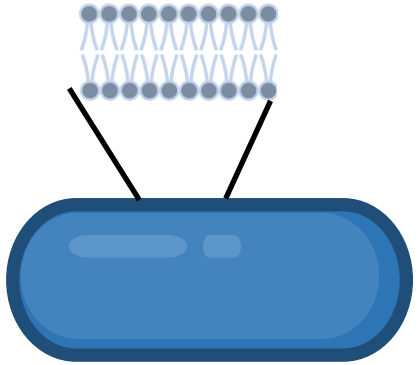
Archaea Habitats:

- Hot and cold environments;
- Acid or alkaline water;
- Highly saline conditions.

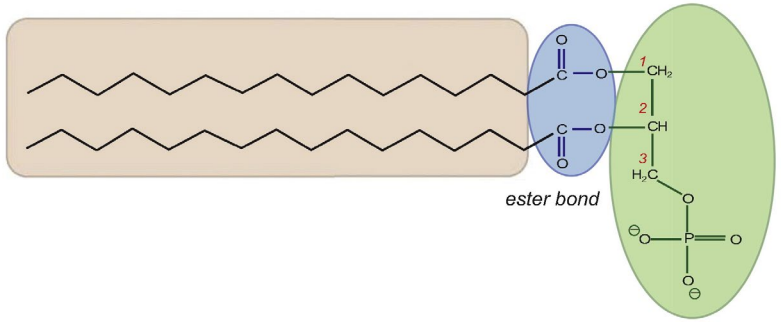
Hahn J, Haug P, *System Applied Microbiology*, 1986
Woese CR, Kandler O, Wheelis ML, *Proc. Natl. Acad. Sci. U.S.A*, 1990

https://www.britannica.com/science/archaea
https://sciworthy.com/microbes-from-extreme-environments

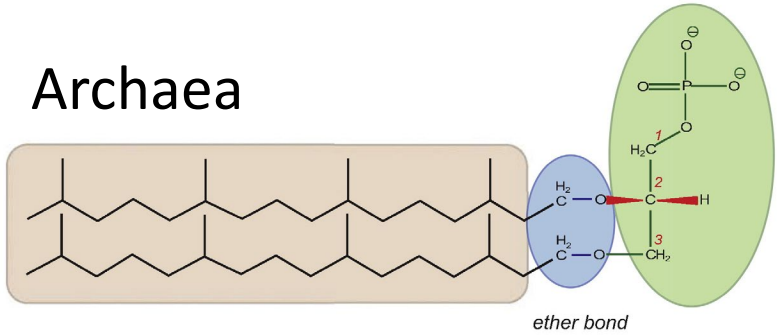
Inspired by Archaea



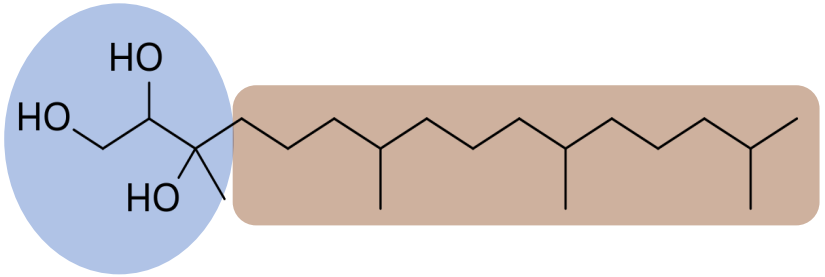
Bacteria and eukaryota



Archaea



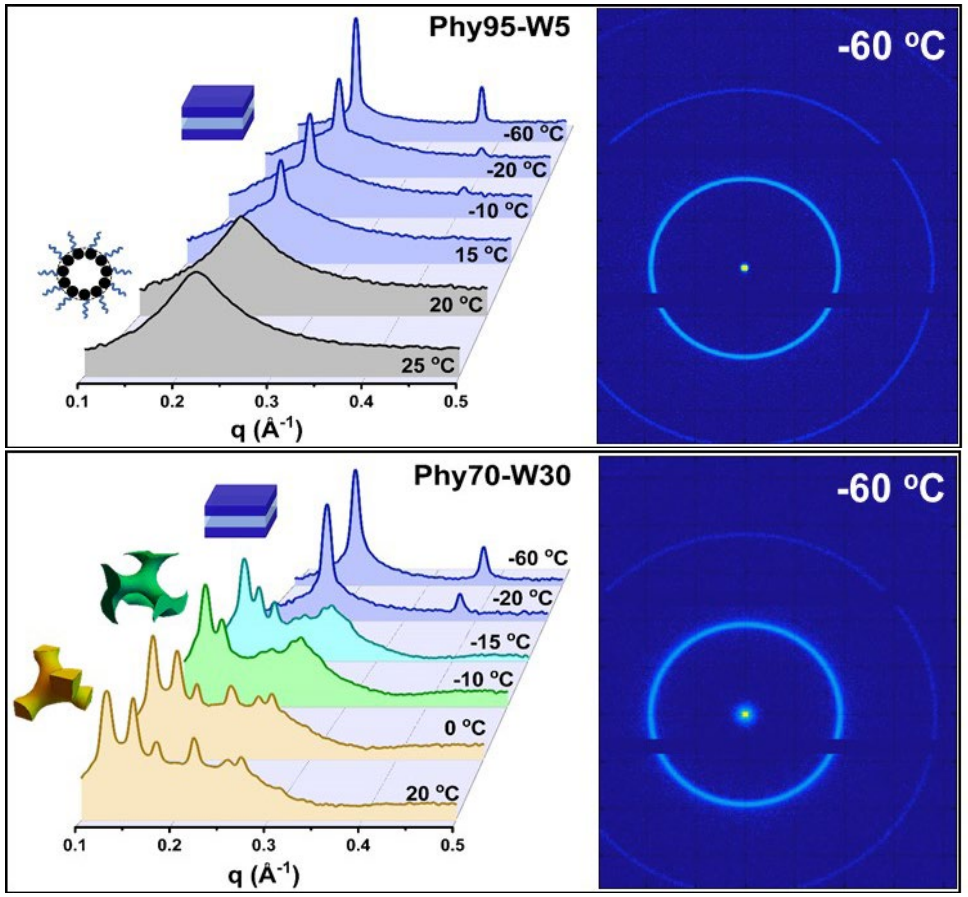
Phytantriol (Phy)



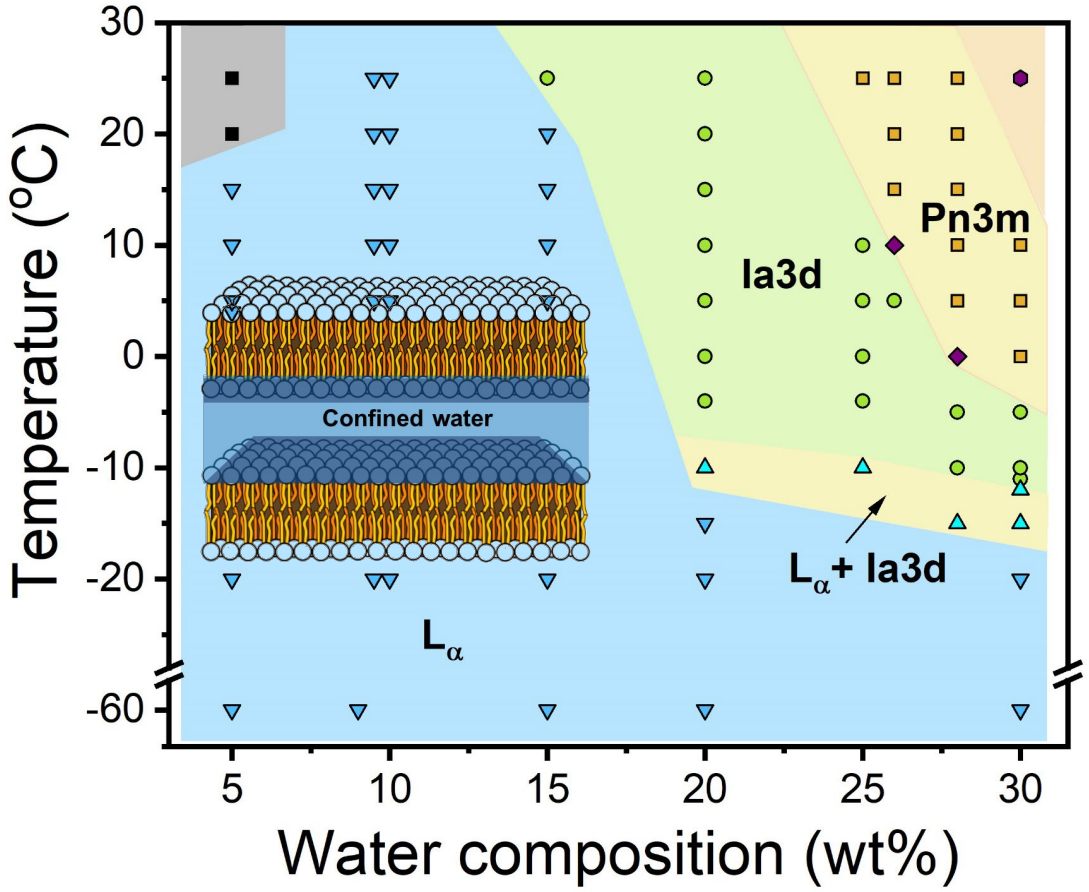
Caforio A. & Driessen A. J. *Biochimica et Biophysica Acta (BBA)-Molecular and Cell Biology of Lipids* 2017.

Lipidic mesophase structure

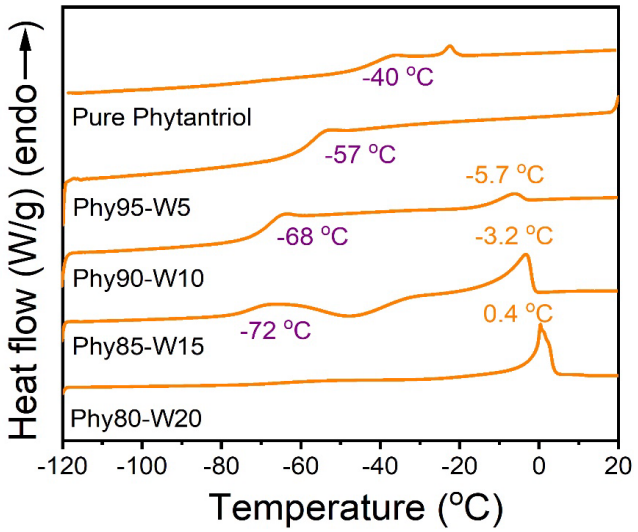
SAXS

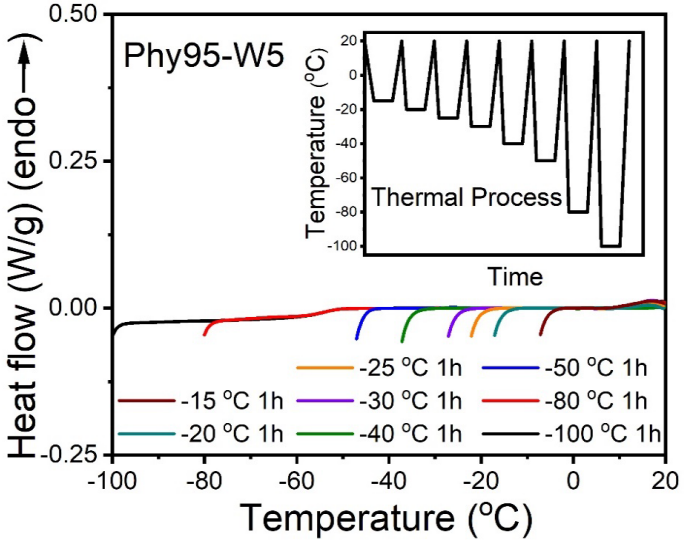


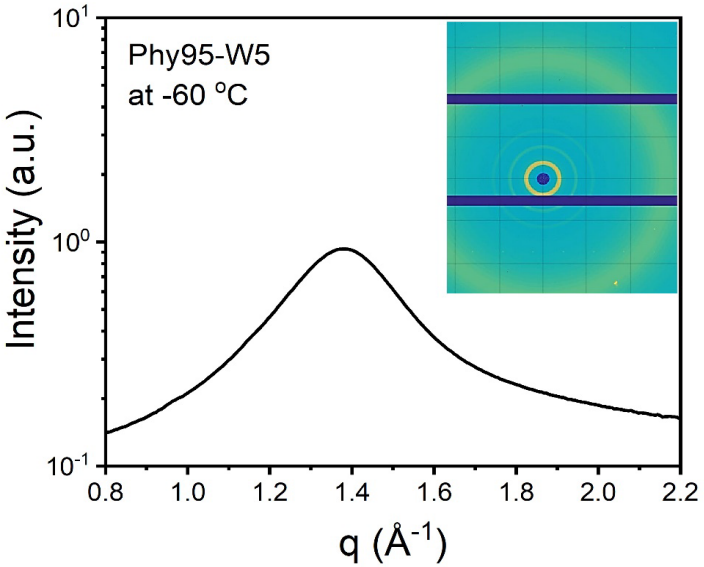
Phase diagram

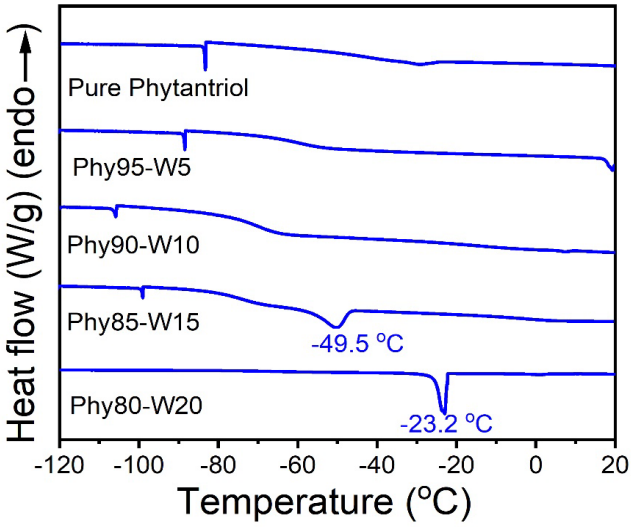


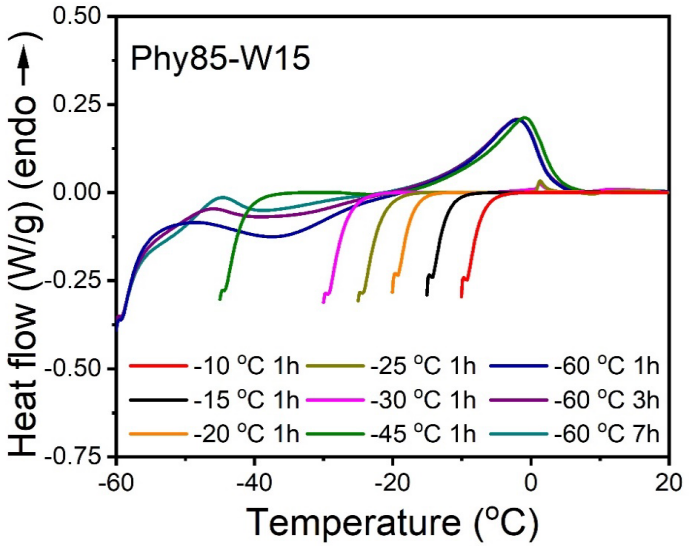
Water crystallization in lipidic mesophase

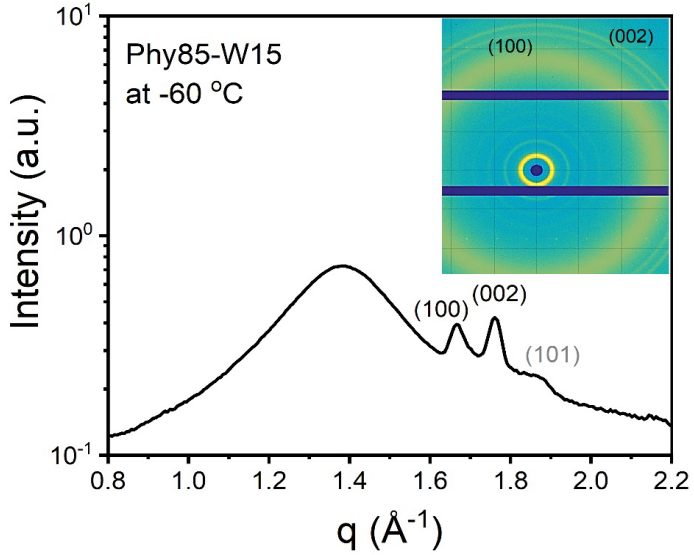




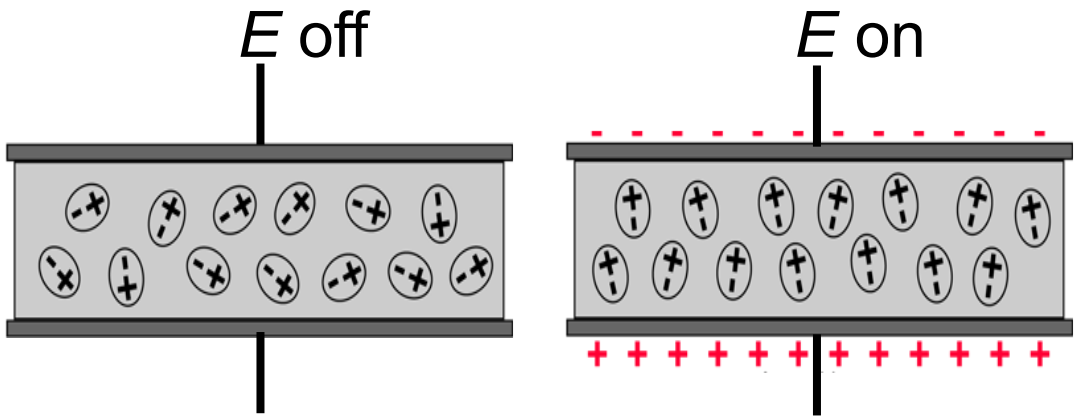








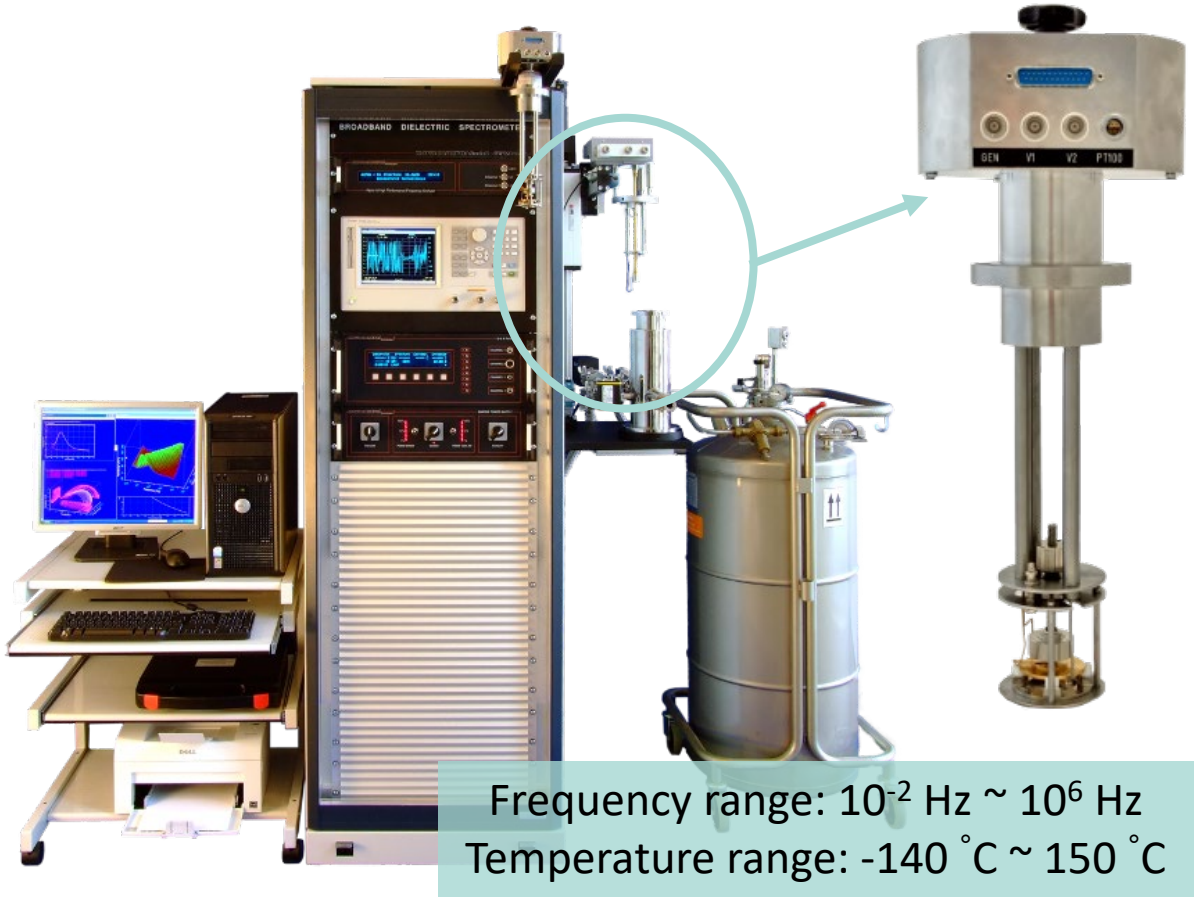
Broadband dielectric spectroscopy



Dielectric properties:

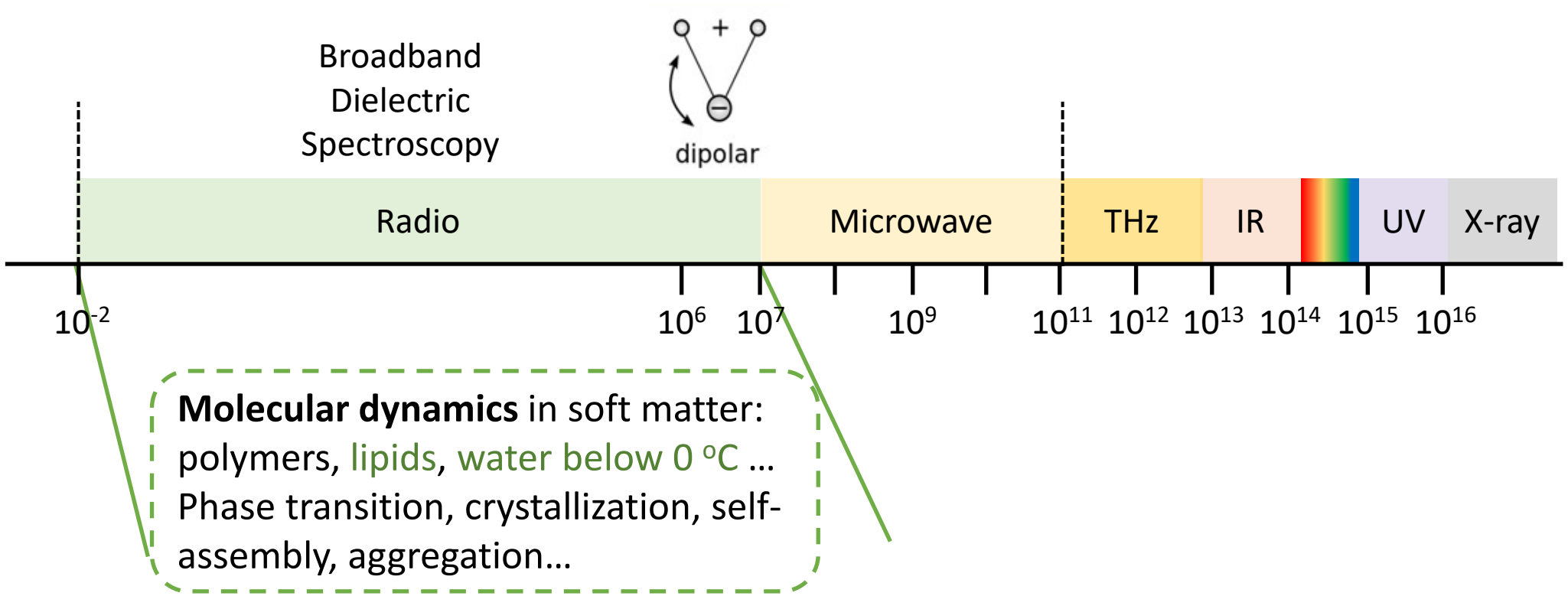
- Complex dielectric permittivity
$$\varepsilon^* = \varepsilon' - i\varepsilon''$$
- Complex conductivity
$$\sigma^* = \sigma' + i\sigma''$$
- Complex electric modulus
$$M^* = M' + iM''$$

as a function of frequency and temperature

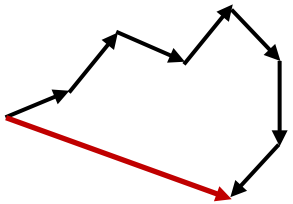


Frequency range: 10^{-2} Hz ~ 10^{6} Hz
Temperature range: -140 ˚C ~ 150 ˚C

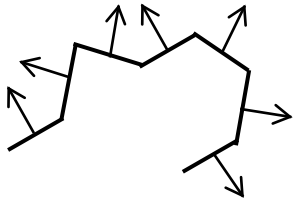
Electromagnetic spectrum



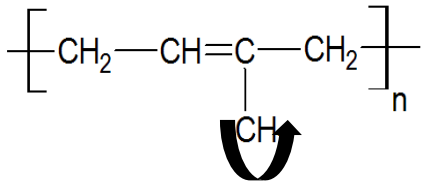
Chain dynamics



Segmental dynamics

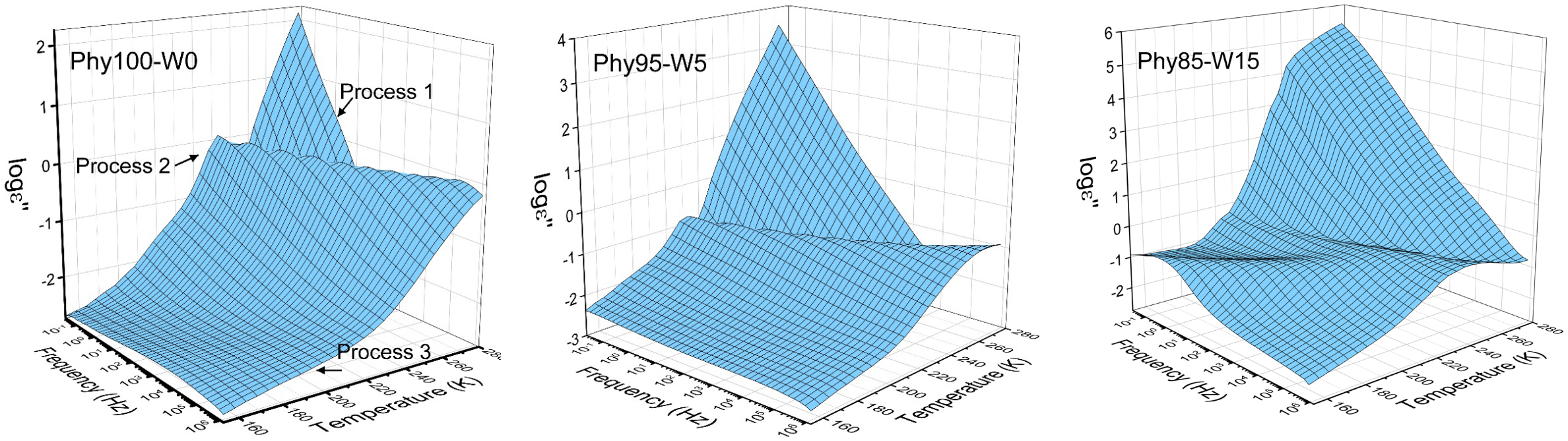


Local dynamics

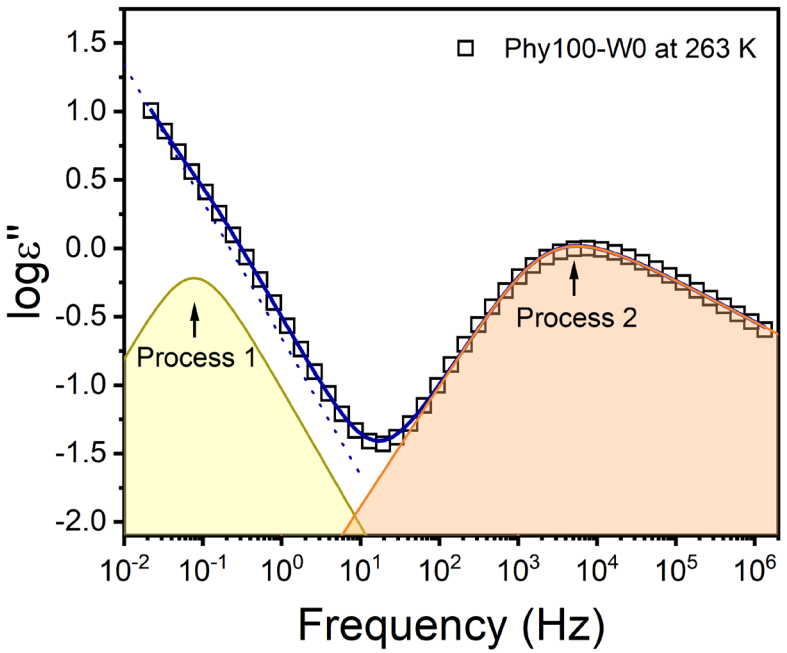


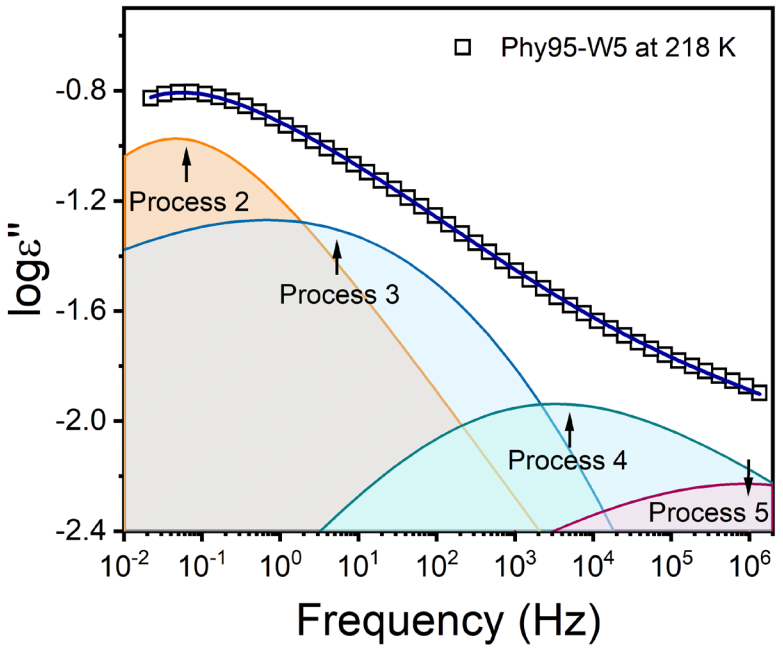
Water and lipid dynamics in lipidic mesophase

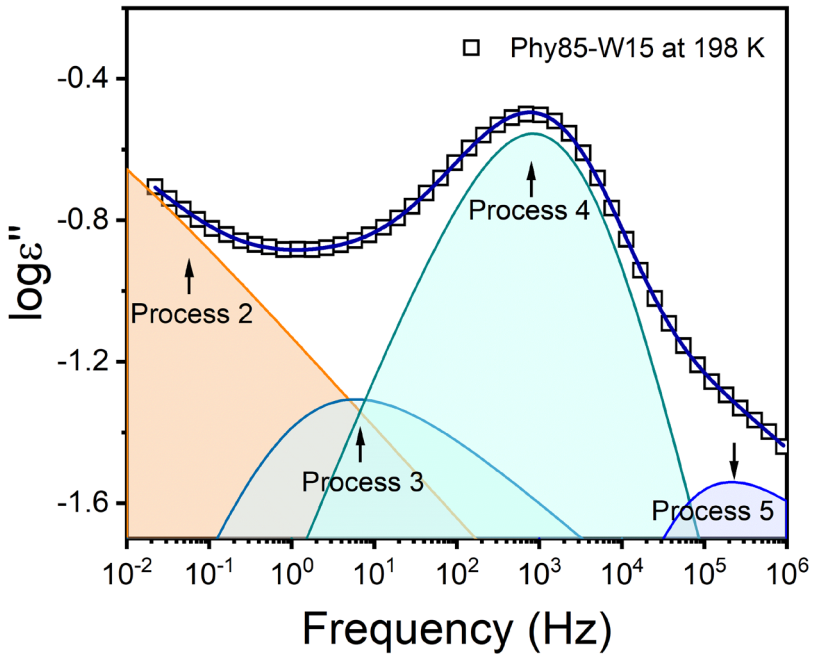
Broadband dielectric spectra



Water and lipid dynamics in lipidic mesophase





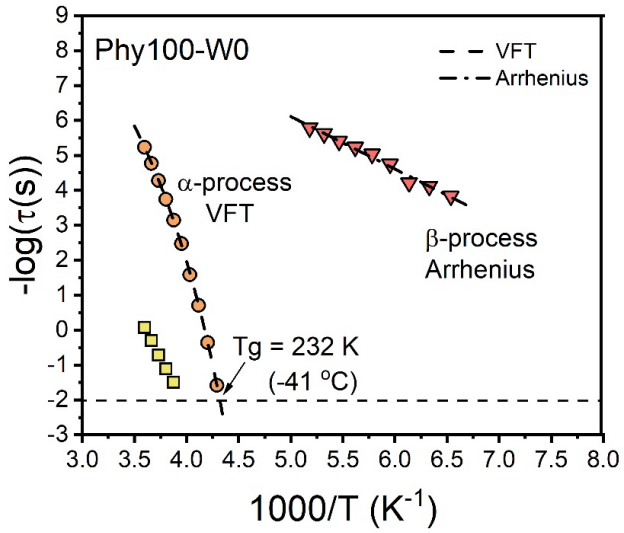


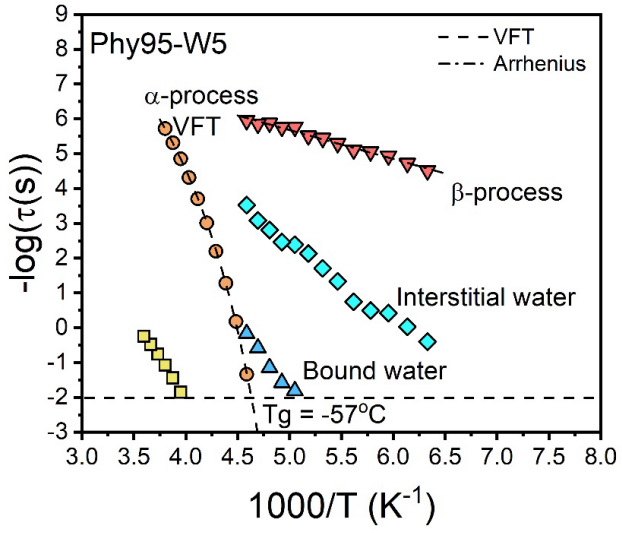
Havriliak and Negami (HN) Equation:

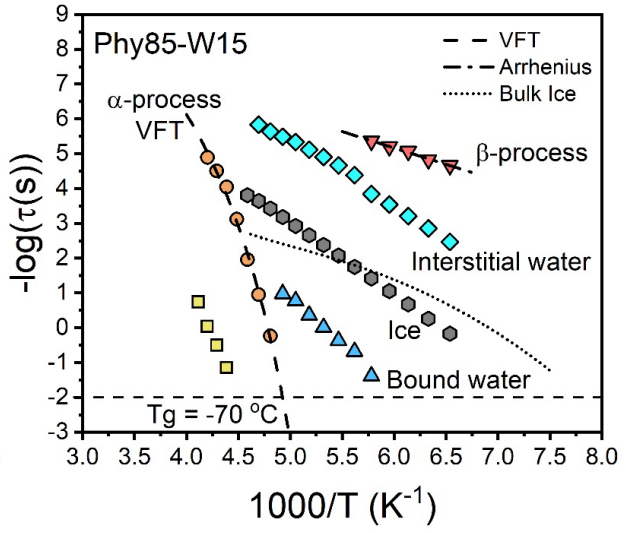
$$\varepsilon^*_{HN}(\omega,T) = \varepsilon_\infty(T) + \frac{\Delta\varepsilon(T)}{\left[1+\left(i\omega\cdot\tau_{HN}(T)\right)^m\right]^n} + \frac{\sigma_0(T)}{i\varepsilon_f\omega}$$

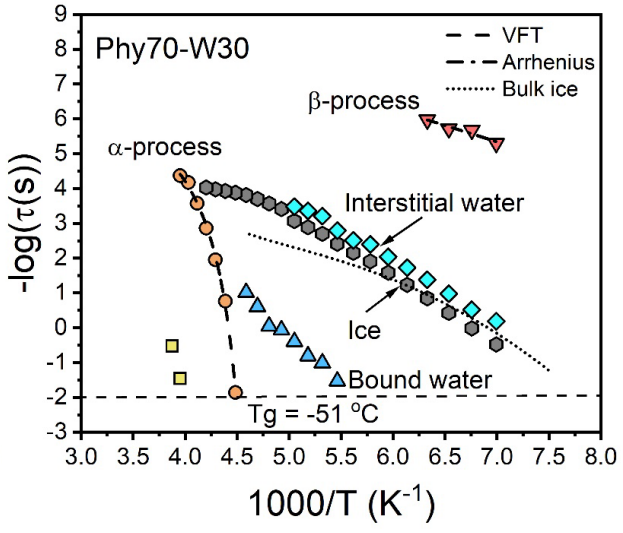
Water and lipid dynamics in lipidic mesophase

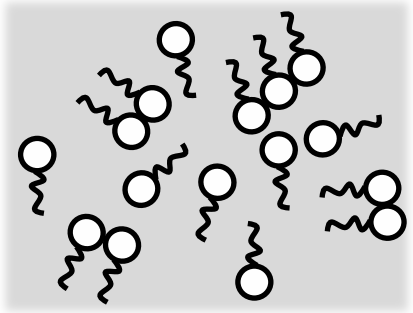
Relaxation time vs. temperature

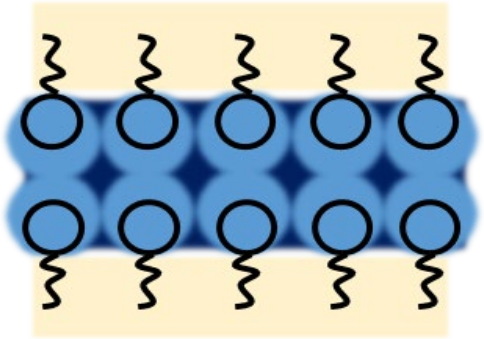


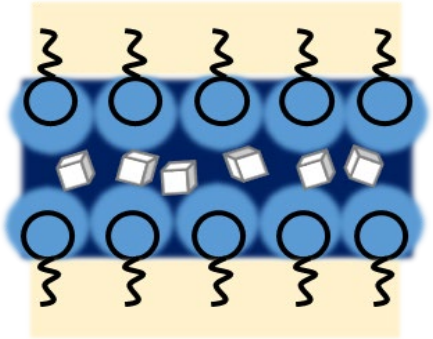


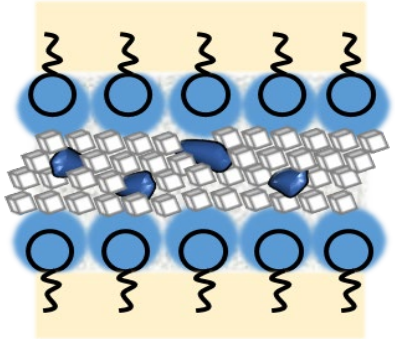




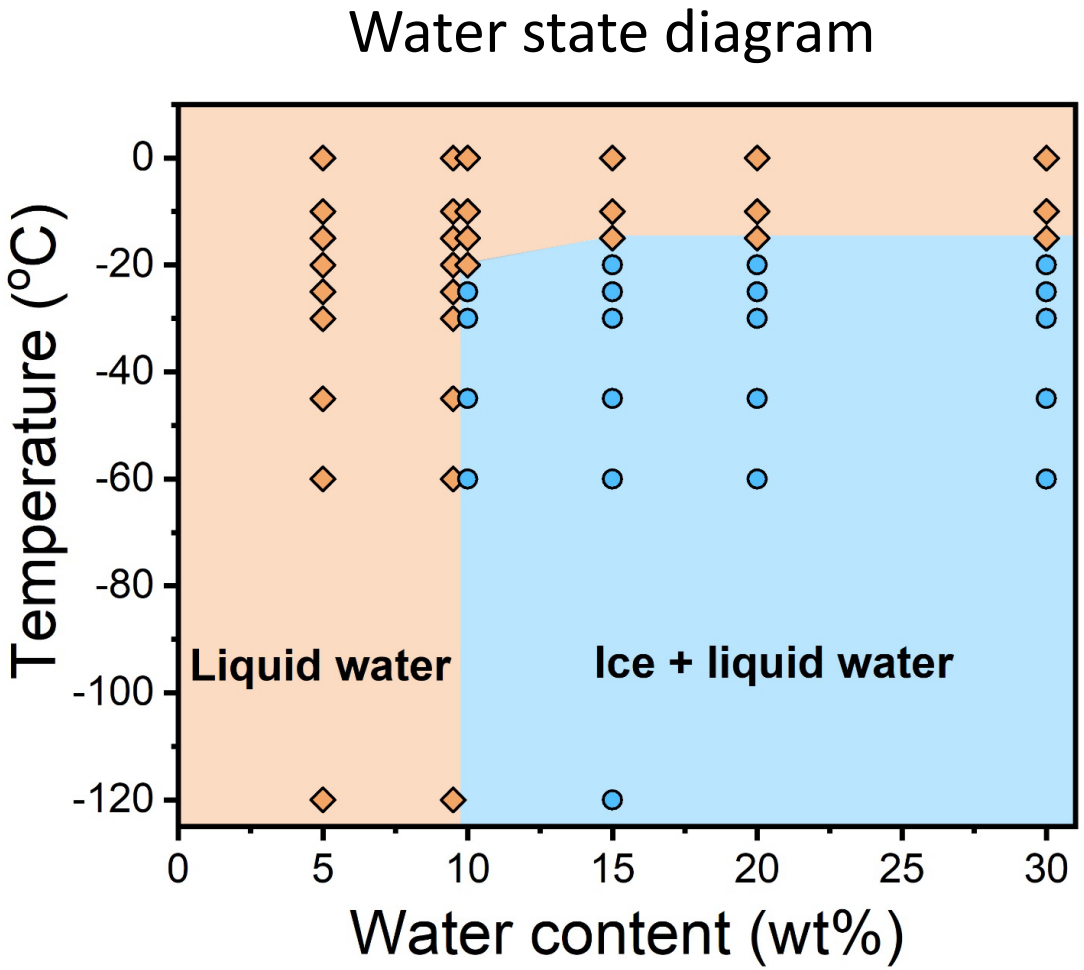


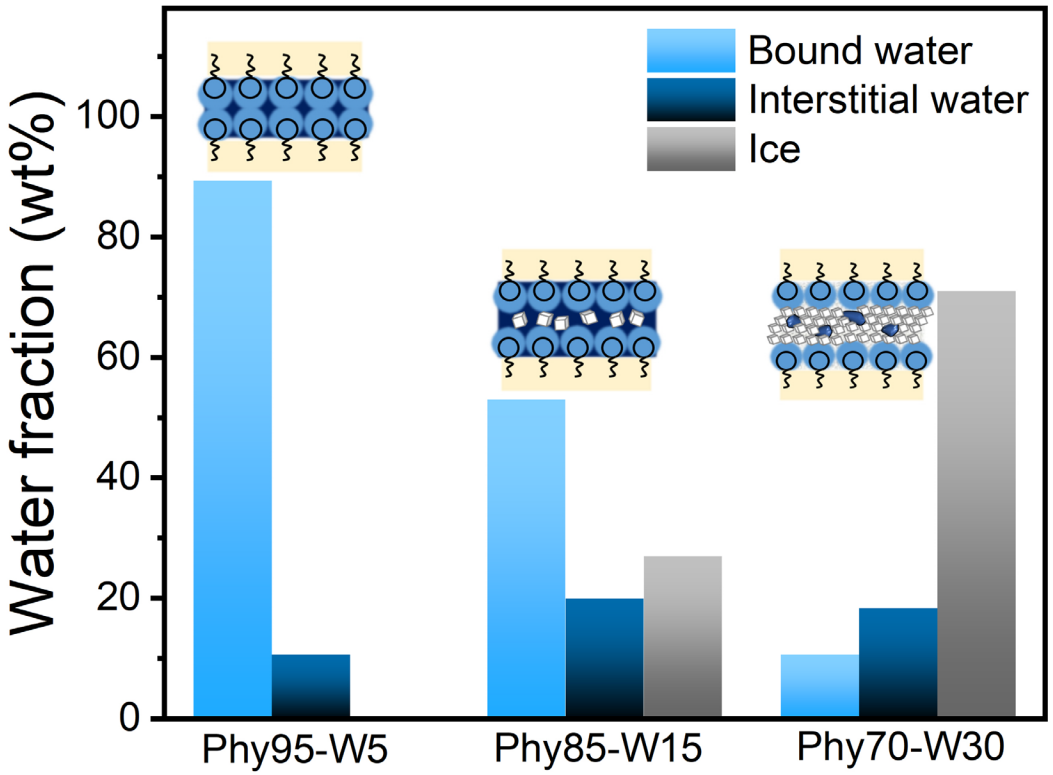






Water in lipidic mesophase





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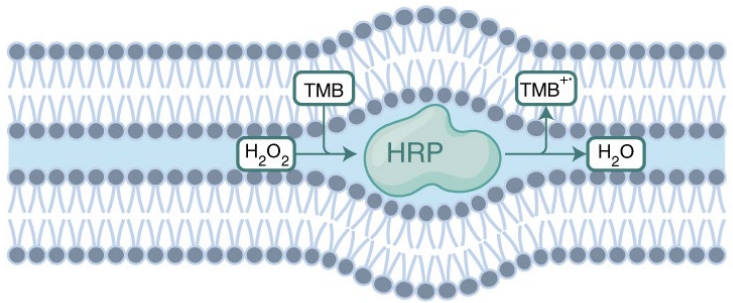
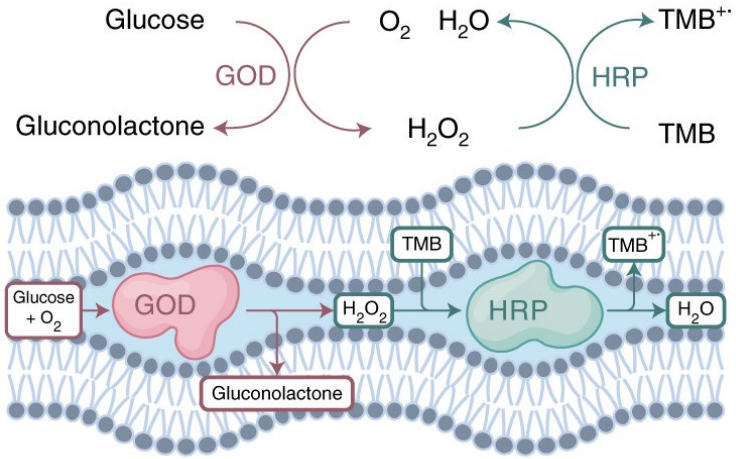
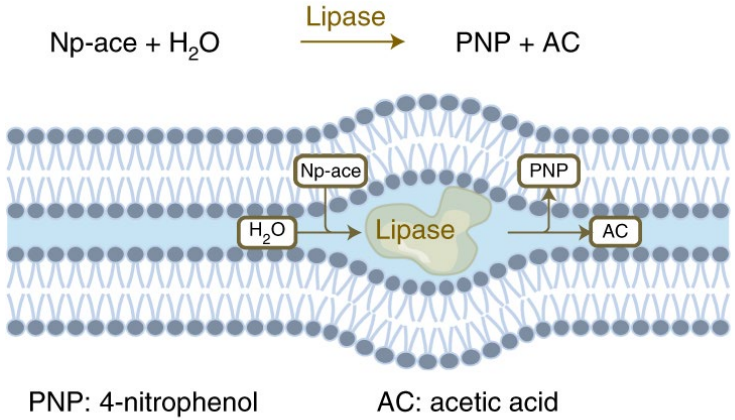
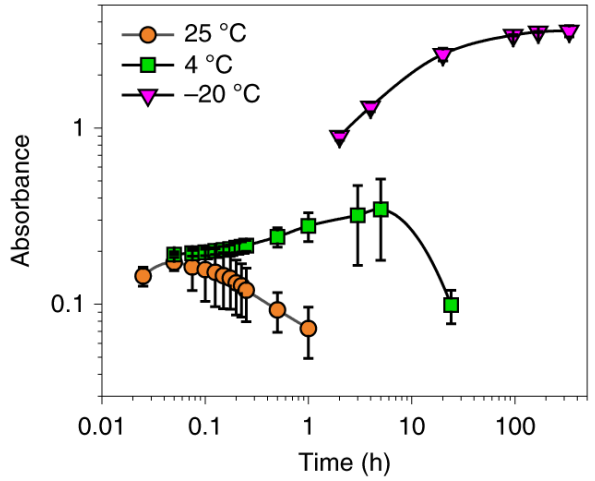
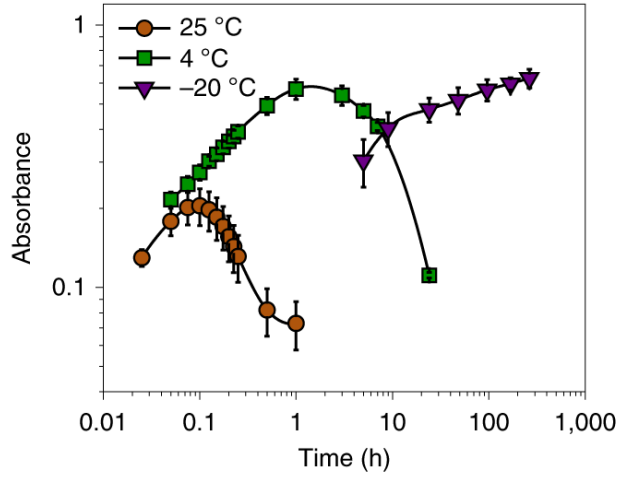
Cryo-enzymatic reactions in lipidic mesophase

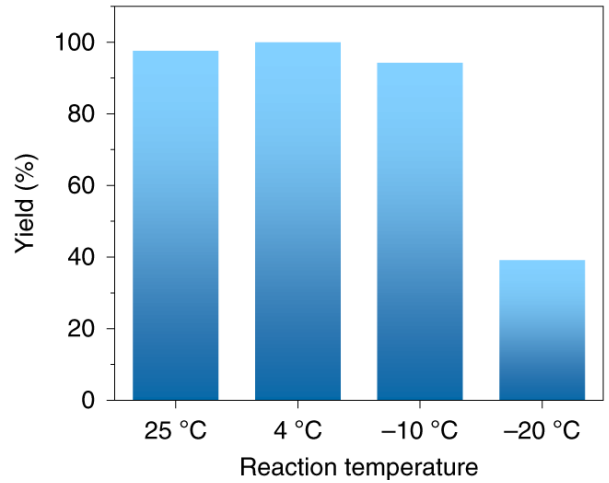












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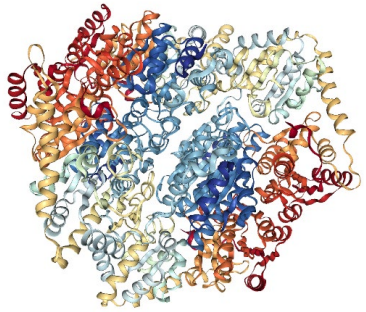
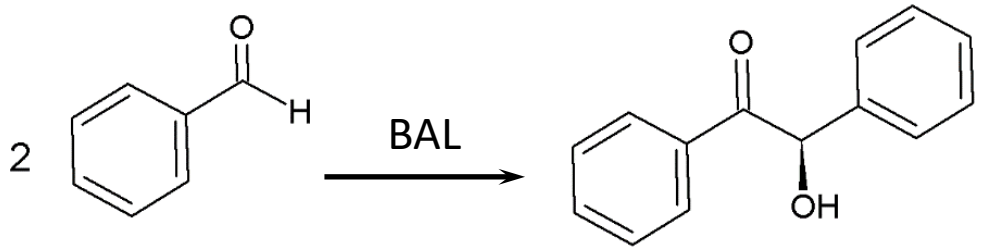
Enzyme conformation in lipidic mesophase (LMP)

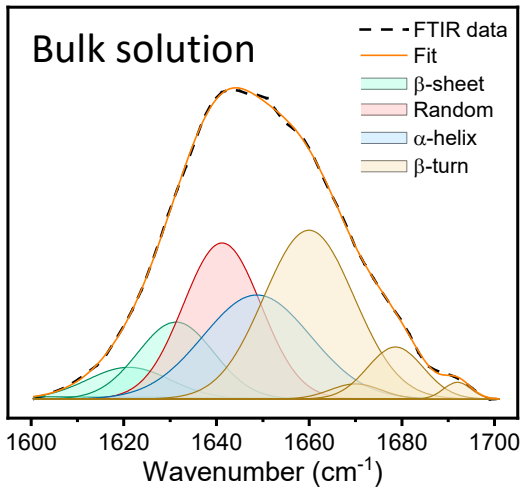
Benzaldehyde Lyase (BAL)
Provided by Prof. Donald Hilvert group

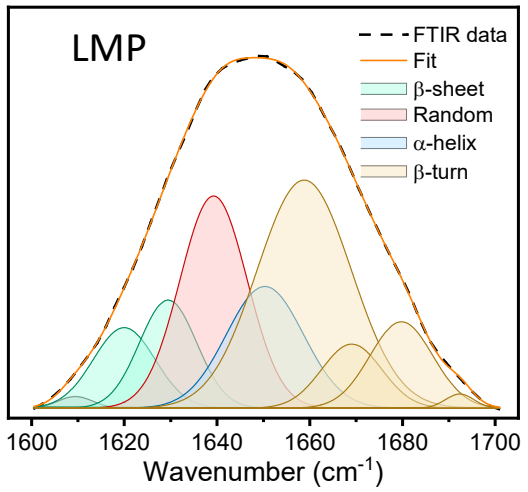


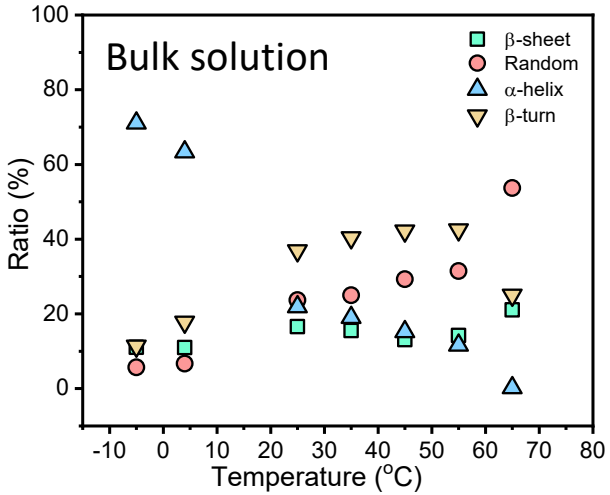


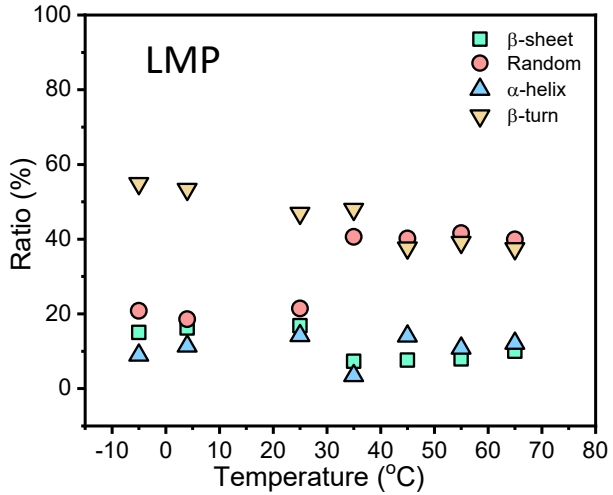
2-naphthaldehyde (NA) (R)-benzoin

FTIR



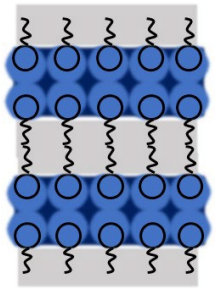






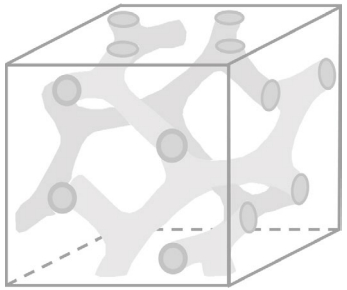
Chemical Communications 57 (46), 5650-5653, 2021

Lipidic mesophase



$p = v/al = 1$

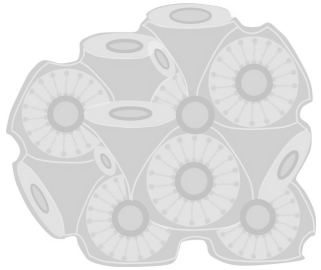
Lamellar (L_α)



Cubic phase

$v/al \geq 1$

Ia3d

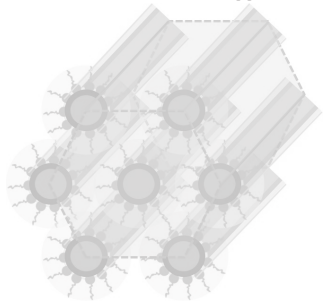


Pn3m

Reverse hexagonal

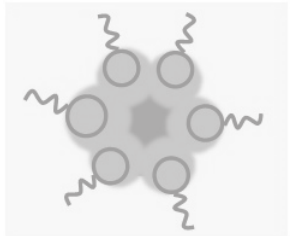
H_{II}

$v/al > 1$

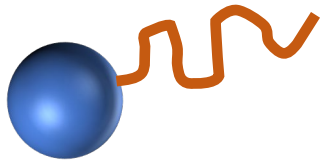


Reverse micelle

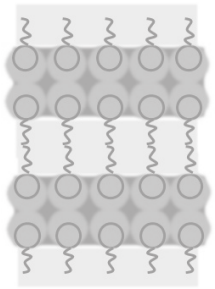
L_2



Increase packing parameter

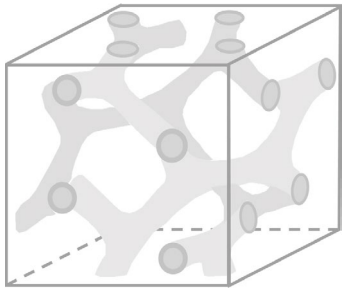


Lipidic mesophase



$p = v/al = 1$

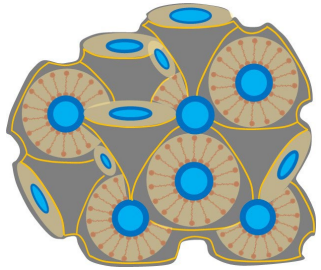
Lamellar (L_α)



Ia3d

Cubic phase

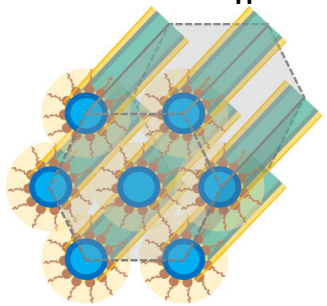
$v/al \geq 1$



Pn3m

Reverse hexagonal

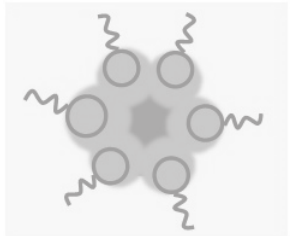
H_{II}



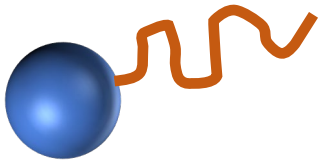
$v/al > 1$

Reverse micelle

L_2

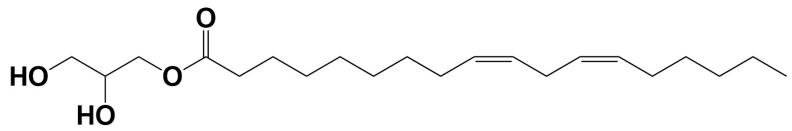


Increase packing parameter



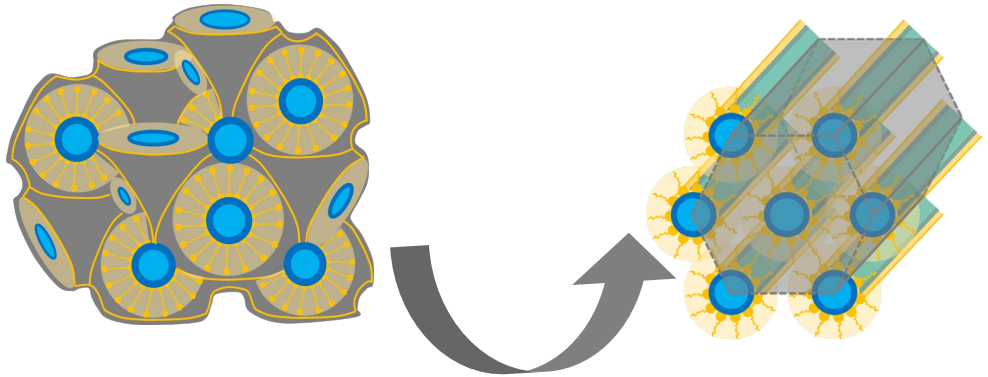
Lipidic mesophase phase transition

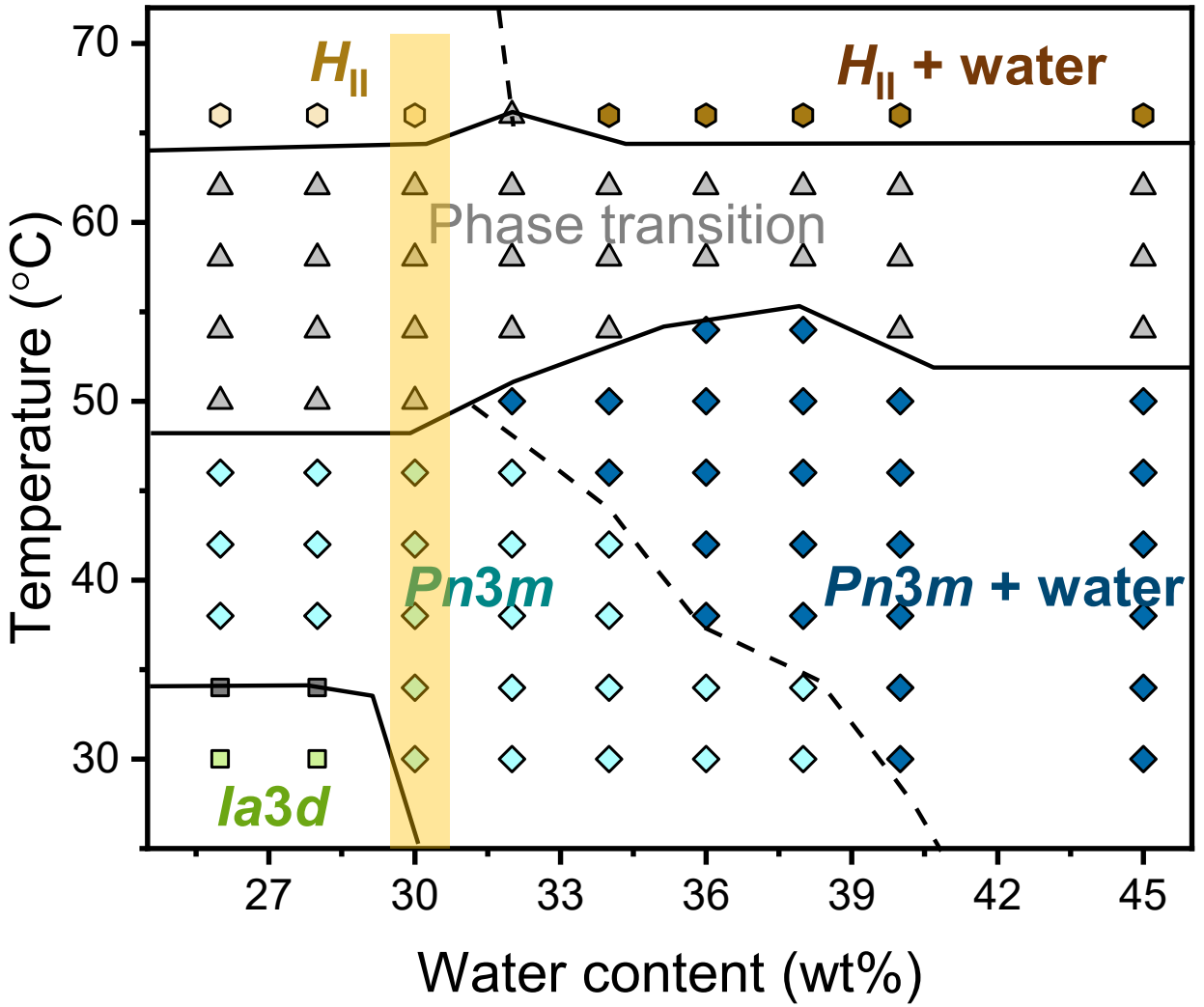
Dimodan (monolinolein)



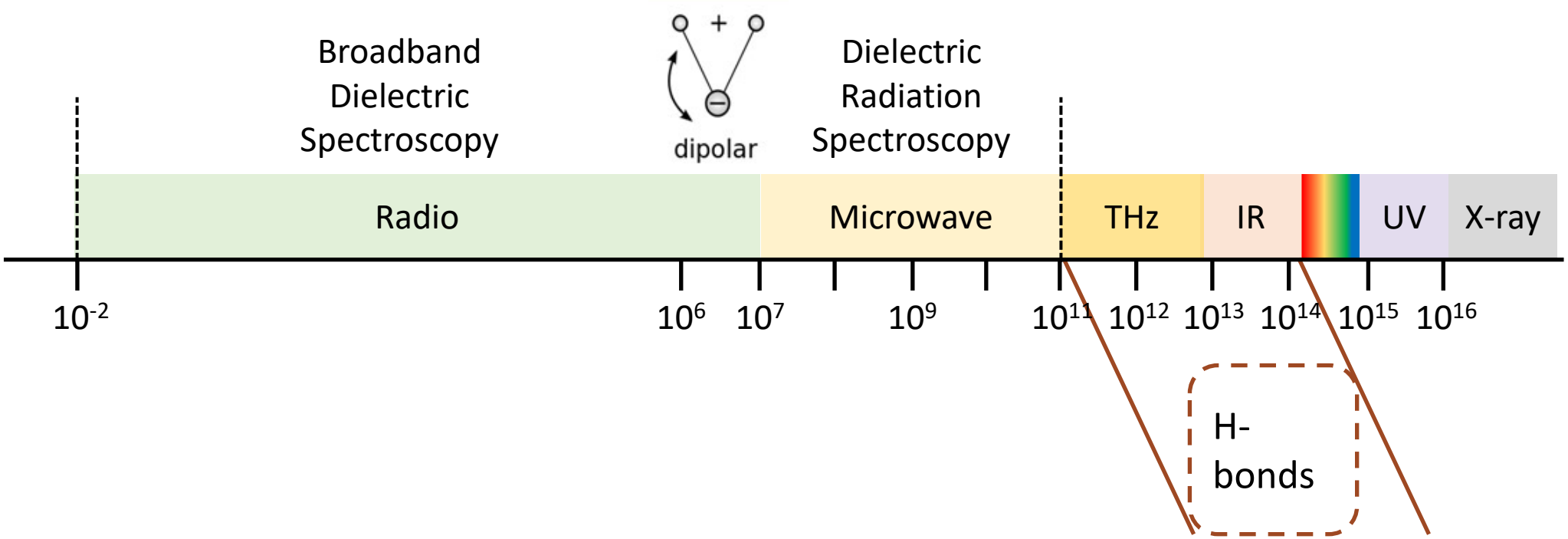
Pn3m

H_{II}



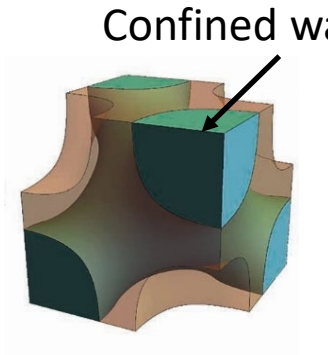


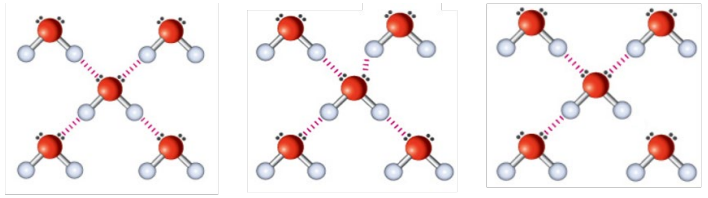
Electromagnetic spectrum

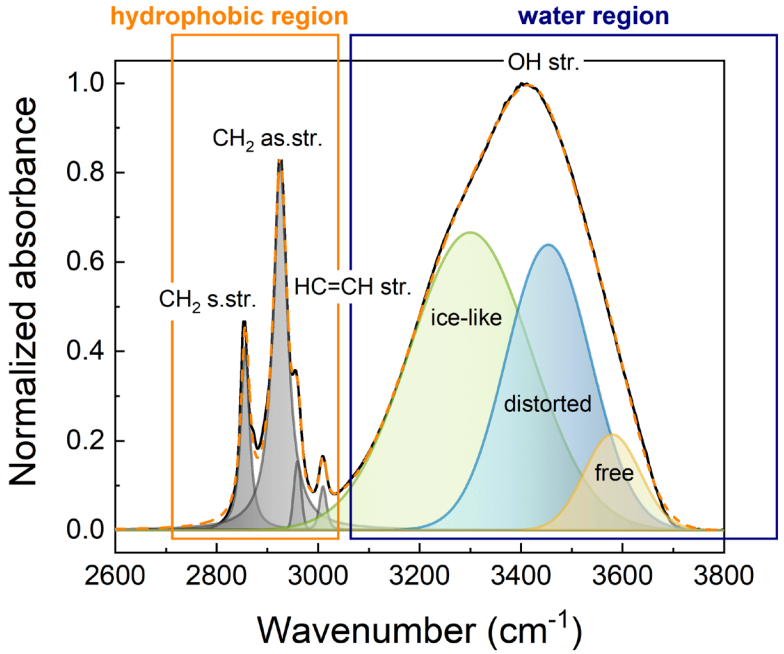


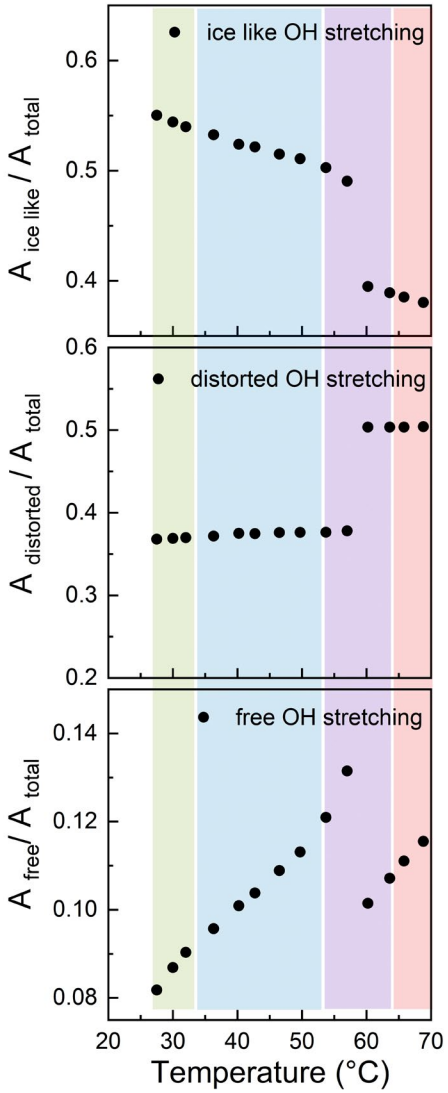
Hydrogen-bond network of confined water

Collaboration with Dr. Sara Catalini, LENS, Italy

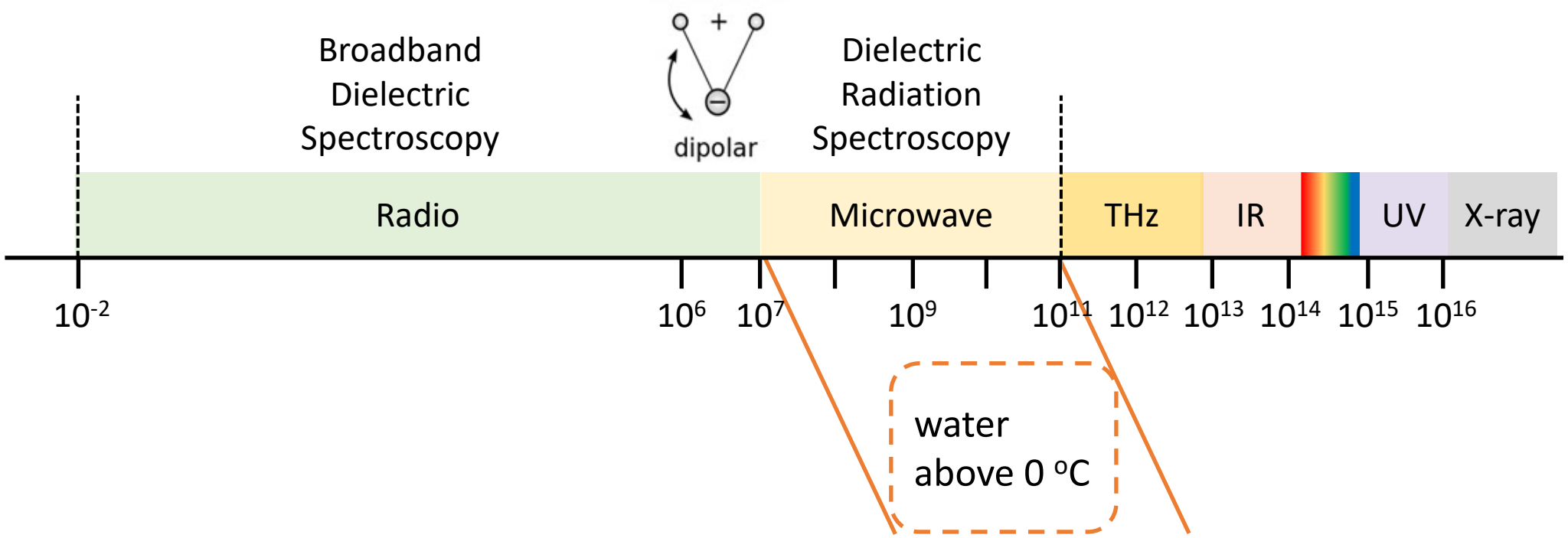








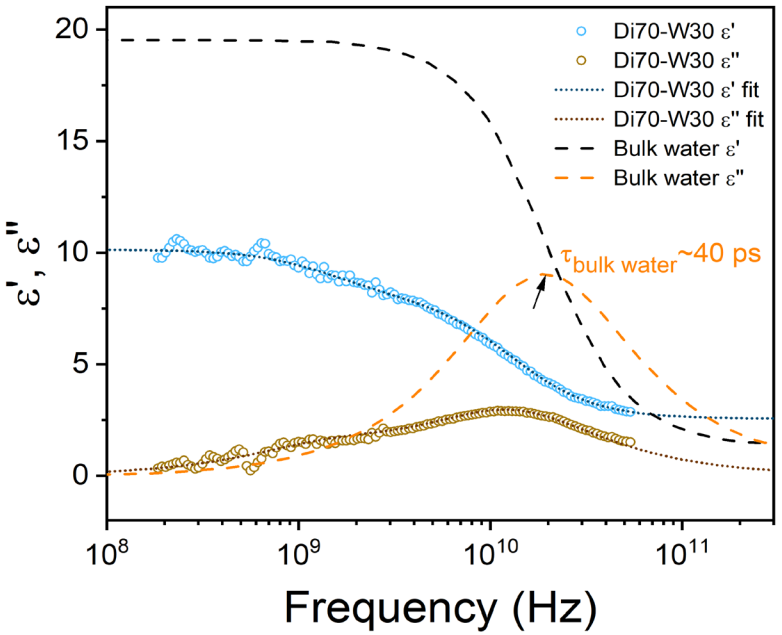
Electromagnetic spectrum

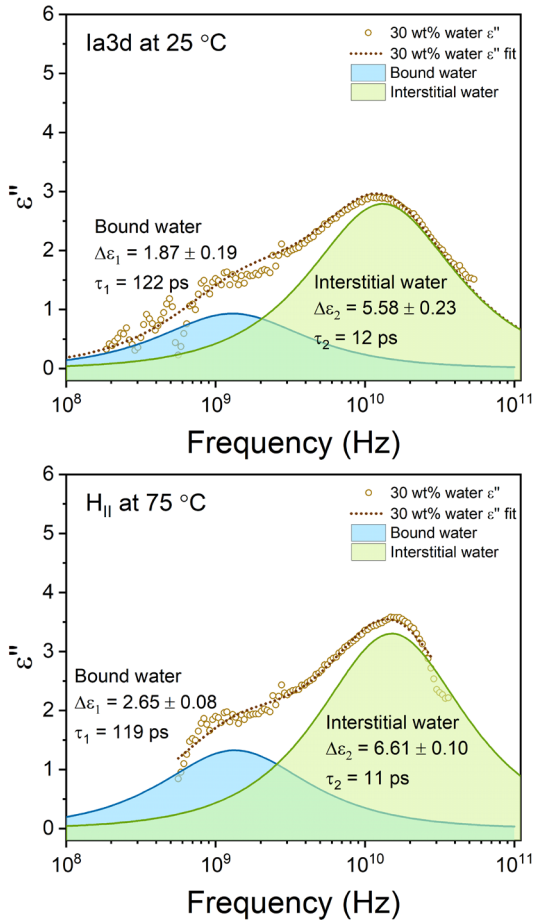


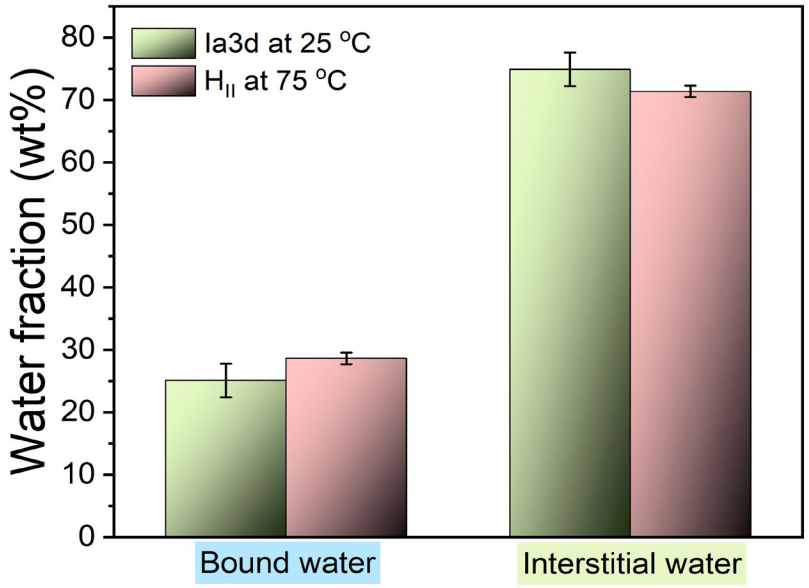
Water dynamics during phase transition

Collaboration with Dr. Johannes Hunger
MPIP, Germany

Dielectric radiation spectroscopy (high frequency BDS)



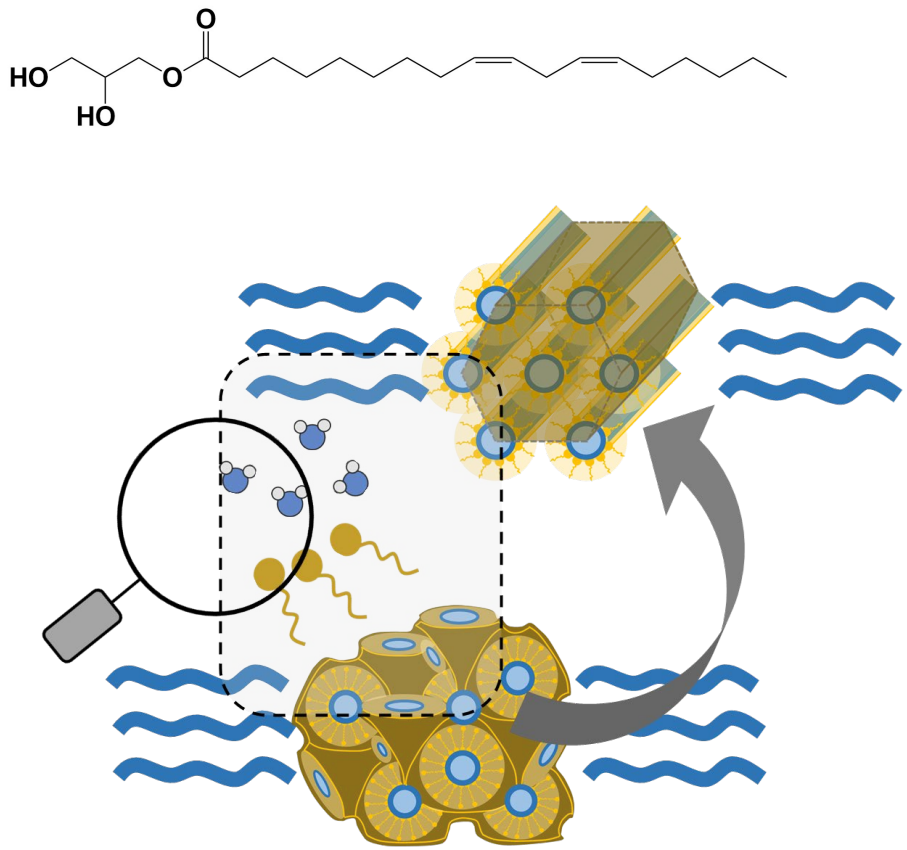


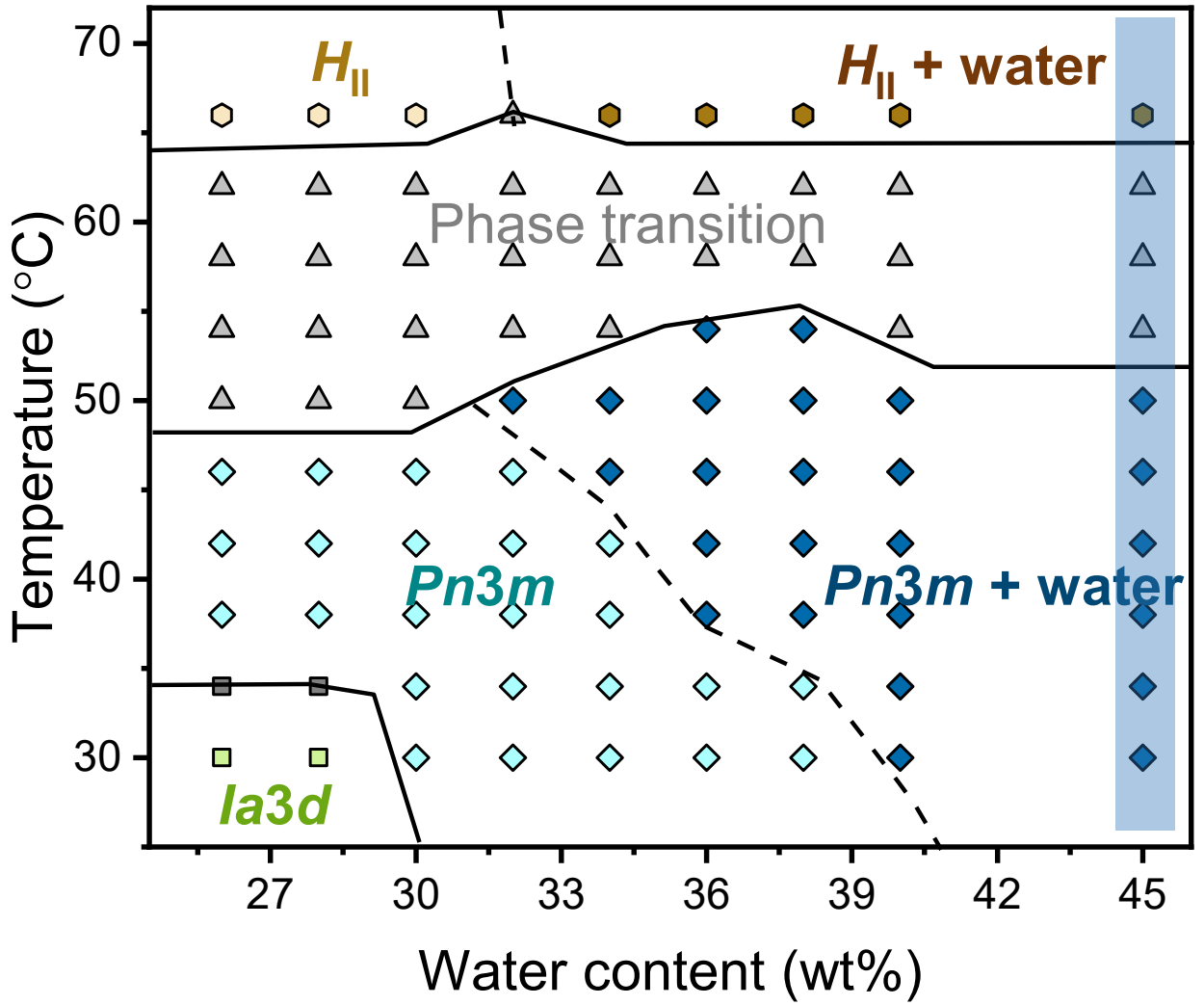


Angew. Chem. Int. Ed., *133*(48), 25478-25484, 2021

Lipidic mesophase phase transition with **excess water**

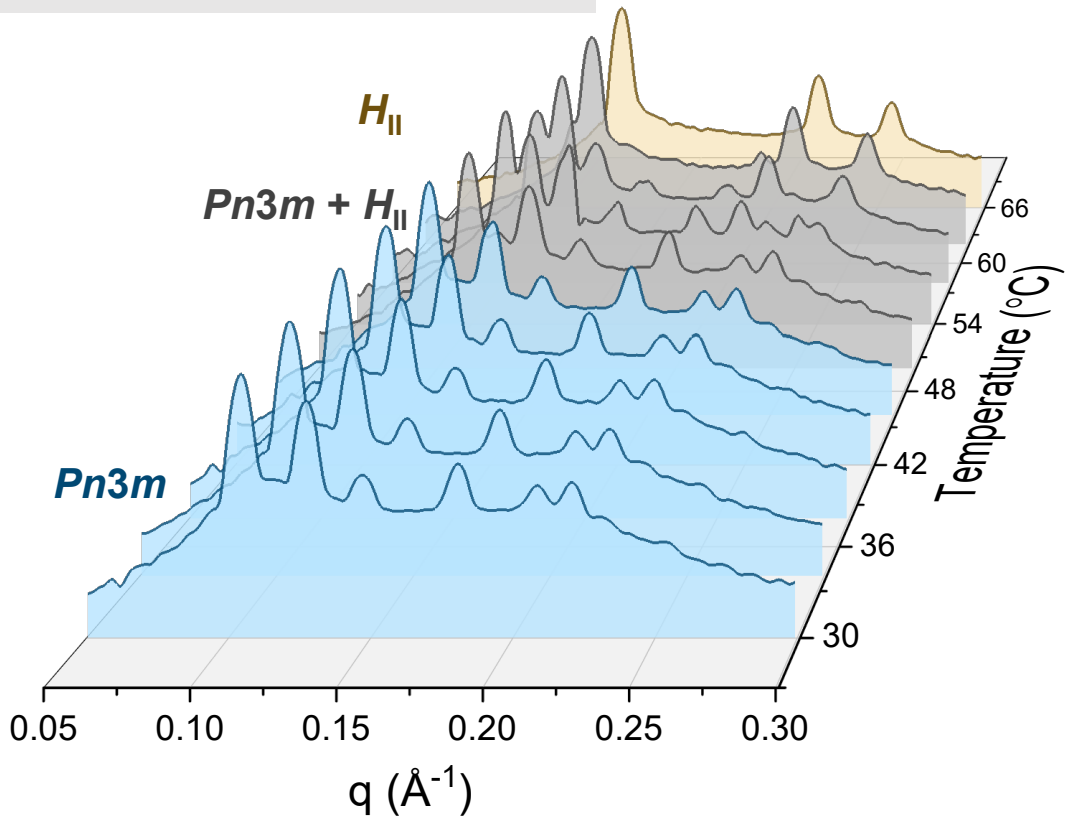
Dimodan (monolinolein)



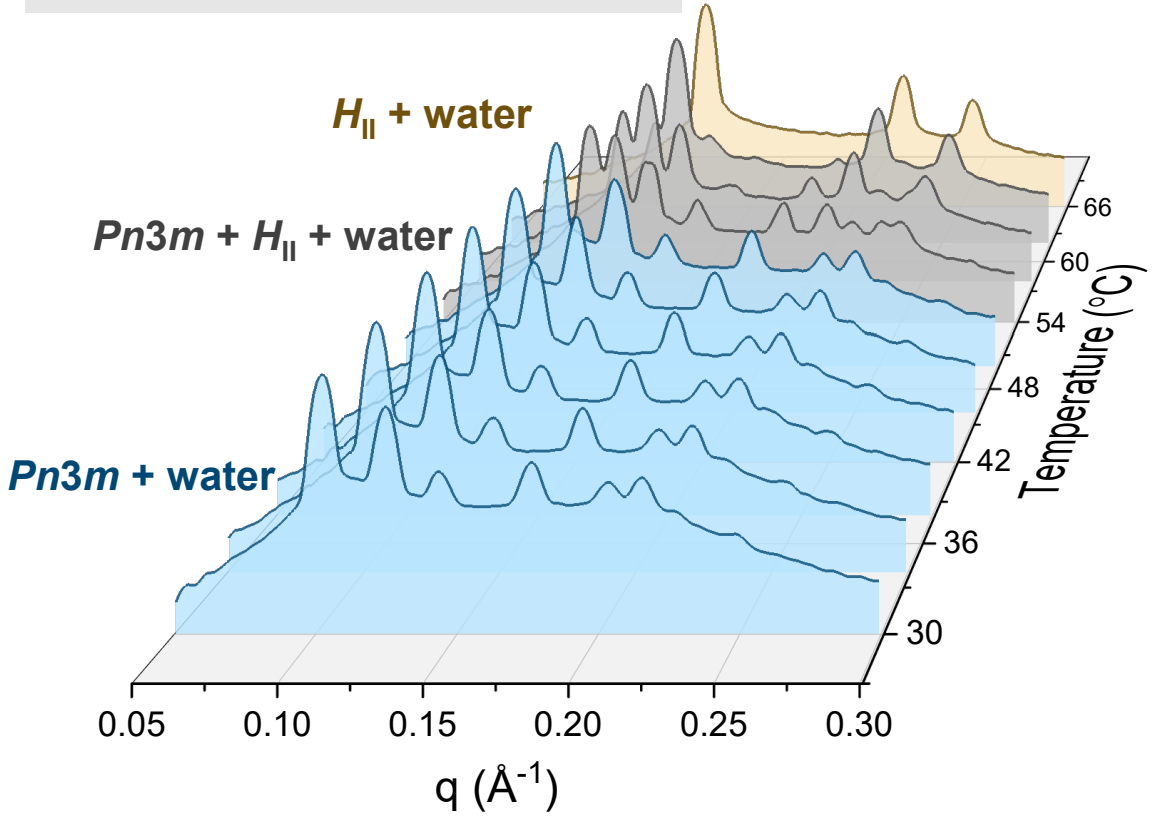


Lipidic mesophase phase transition with **excess water**

30 wt% water (no excess water)

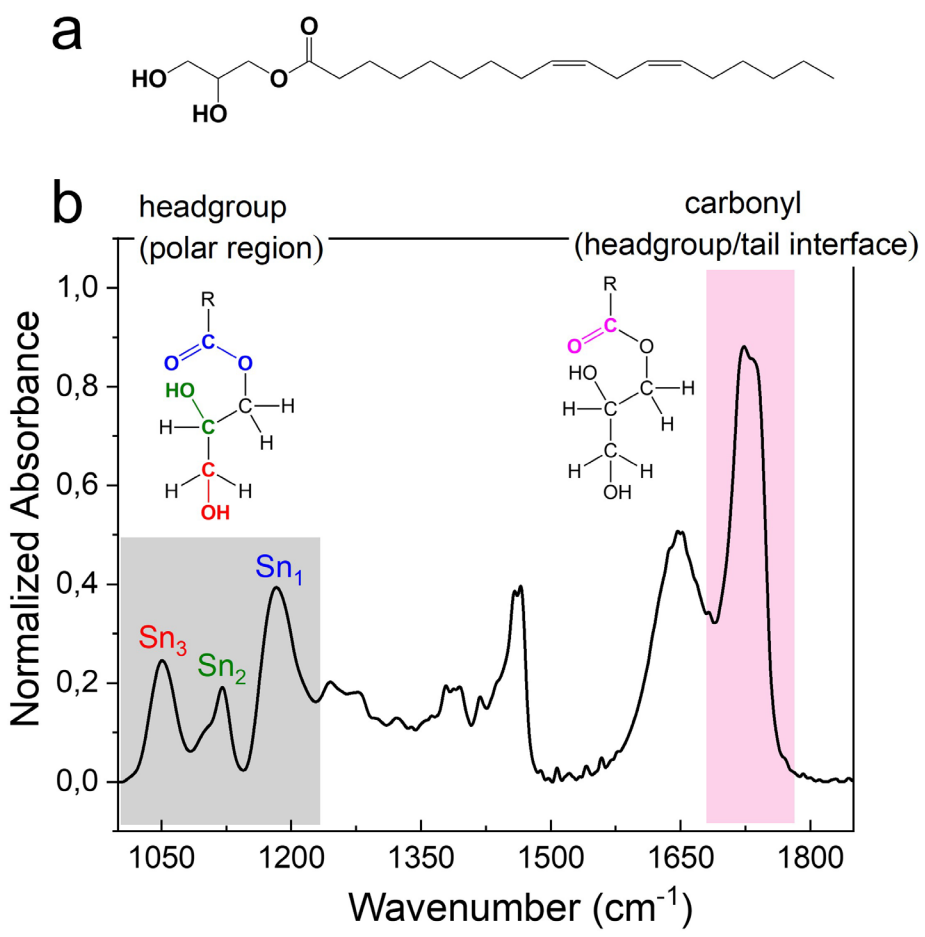


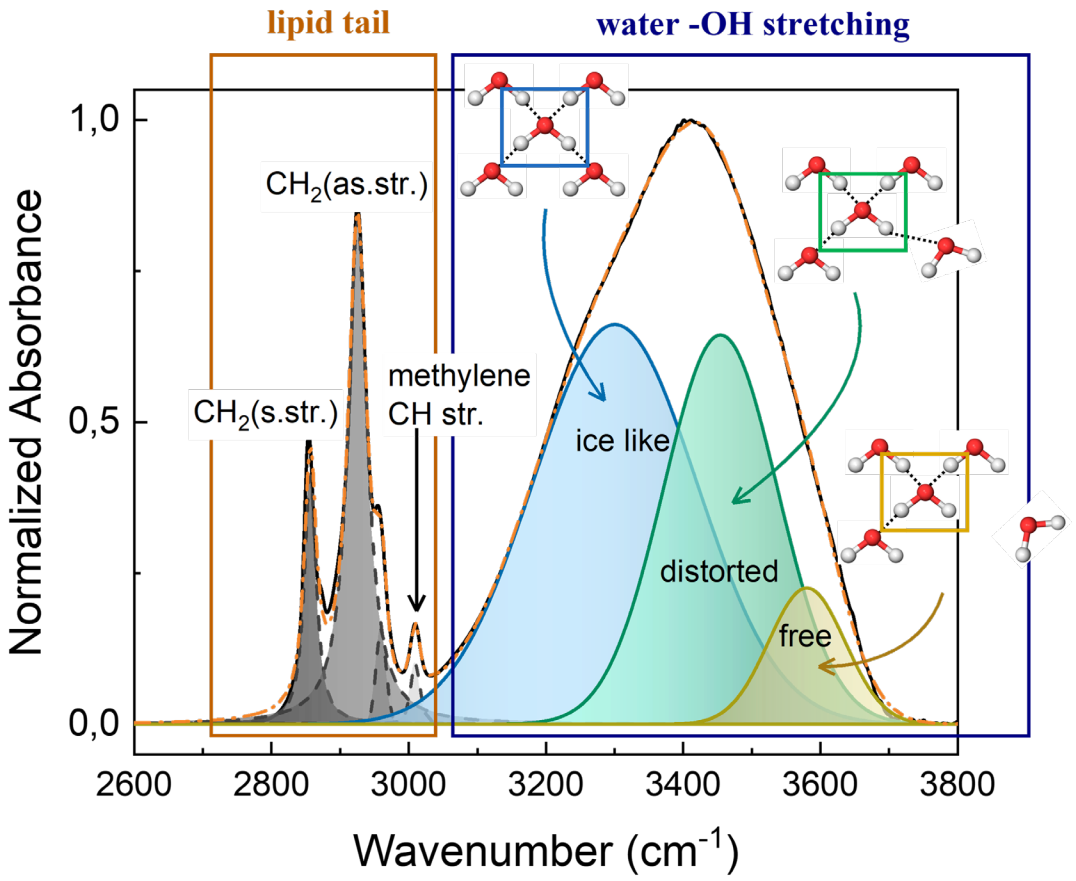
45 wt% water (excess water)



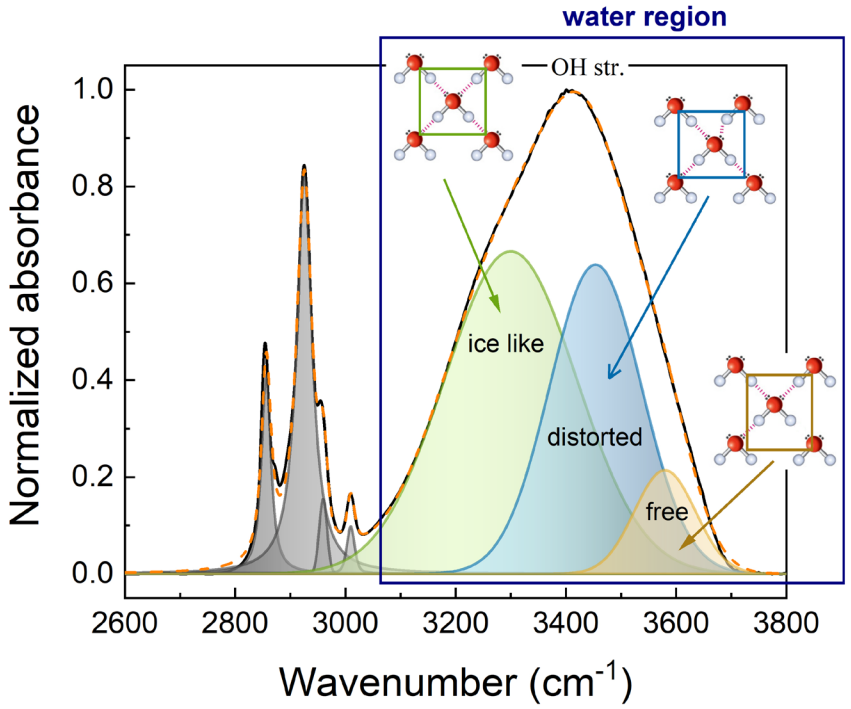
Lipidic mesophase phase transition with **excess water**

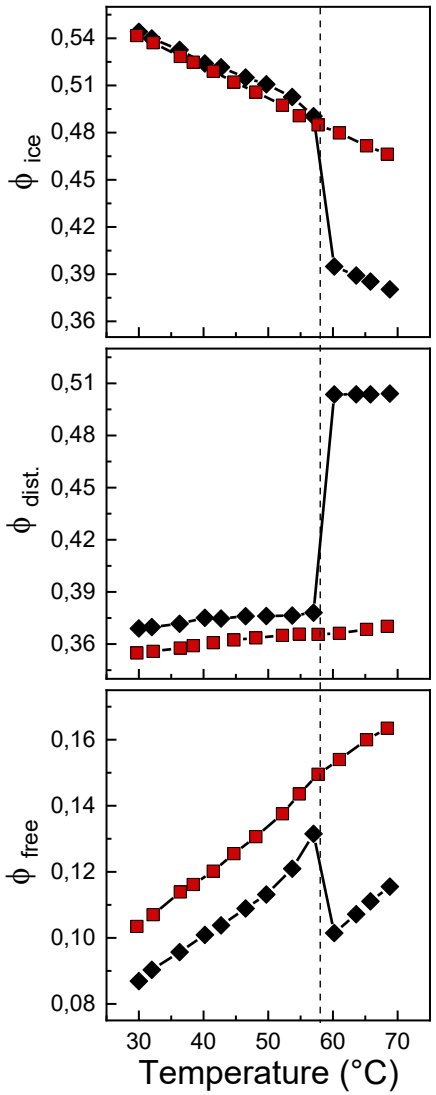
FTIR analysis





Lipidic mesophase phase transition with **excess water**



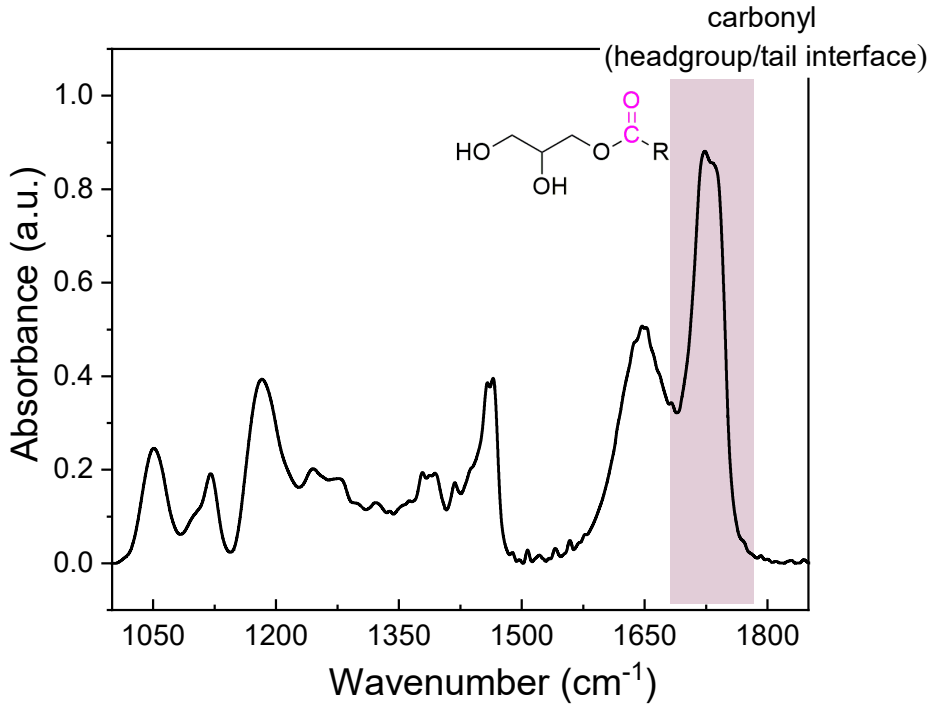


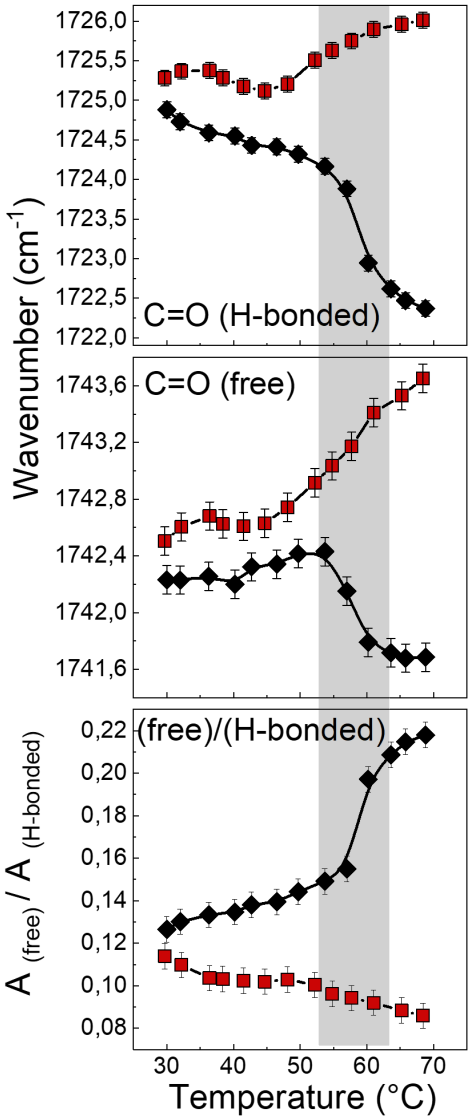
30 wt% water

45 wt% water

Faraday Discuss., 249, 469-484, 2024

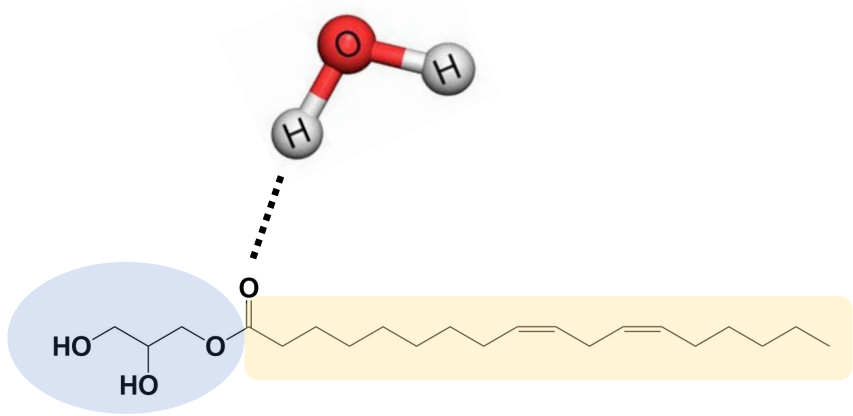
Lipidic mesophase phase transition with **excess water**





30 wt% water

45 wt% water



Faraday Discuss., 249, 469-484, 2024

Summary

- In hard confinement, below 2.6 nm in diameter water was unable to form stable crystals.
- Water confined in the lamellar phase remained in the liquid state down to −120 °C when the water content was below 9.5 wt%.
- In both hard and soft confinement, we detected two dynamically different fractions of water: bound water and interstitial water.
- The hydrogen bond network depends strongly on the geometry of the mesophase.
- Excess water forms new hydrogen bonds with the lipids at the interface between the headgroup and tail.

Open PhD position

Thank you !