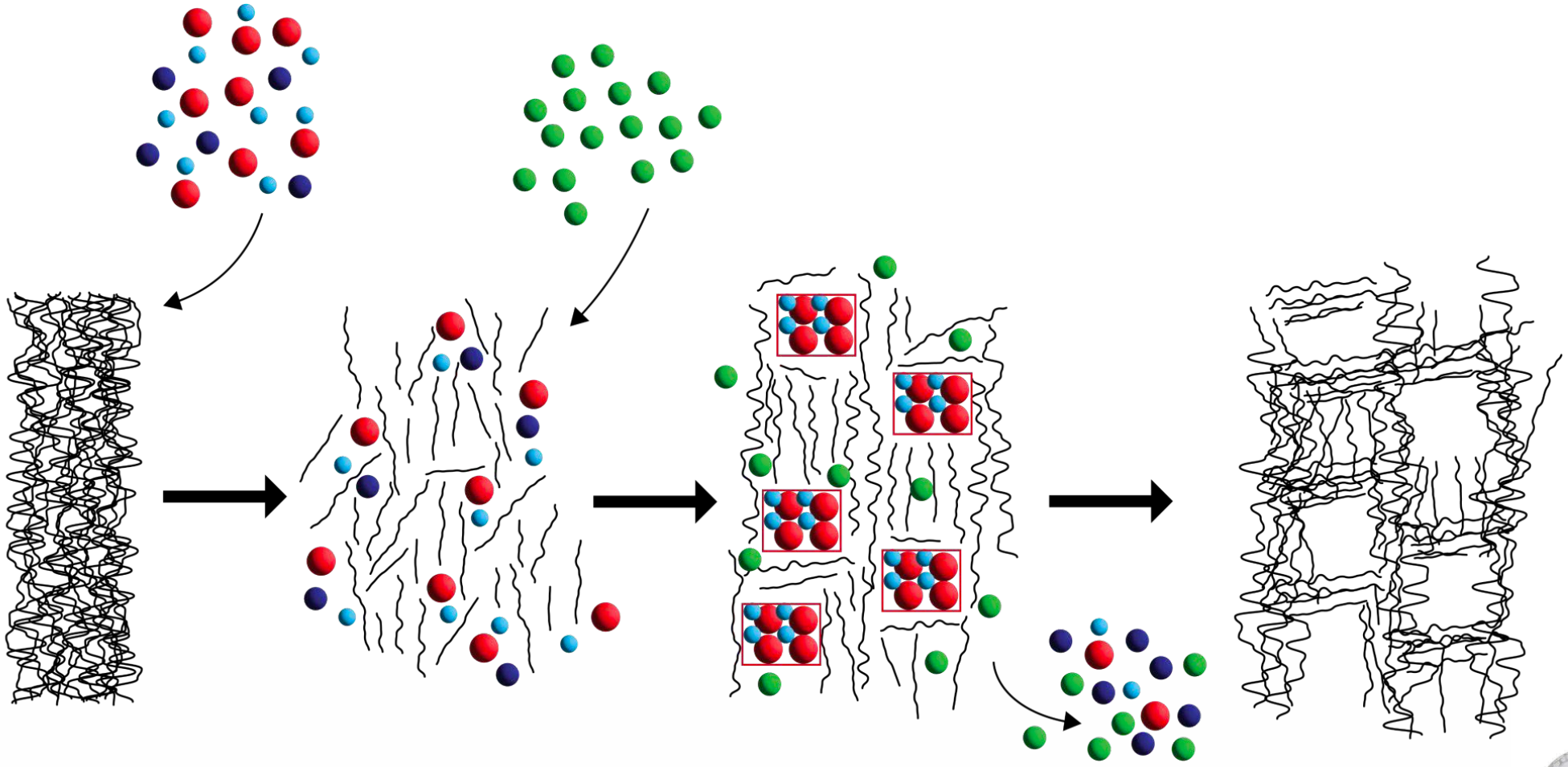
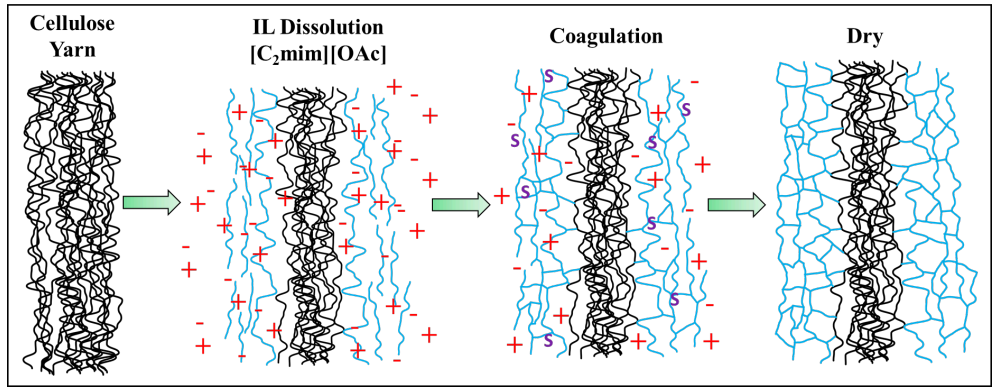
Impact of coagulant solvent polarity on porous morphology evolution in cellulose xero gels

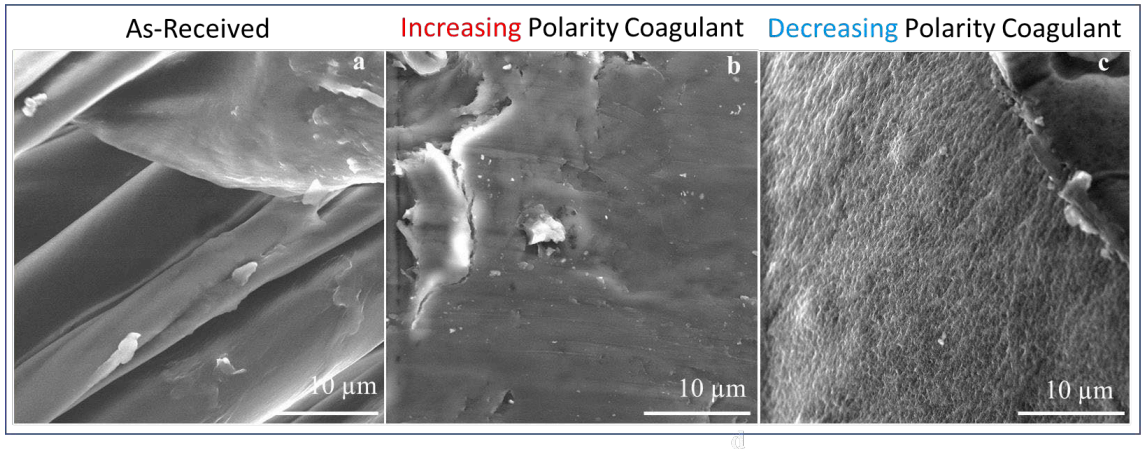


TAPPI NANO DIVISION

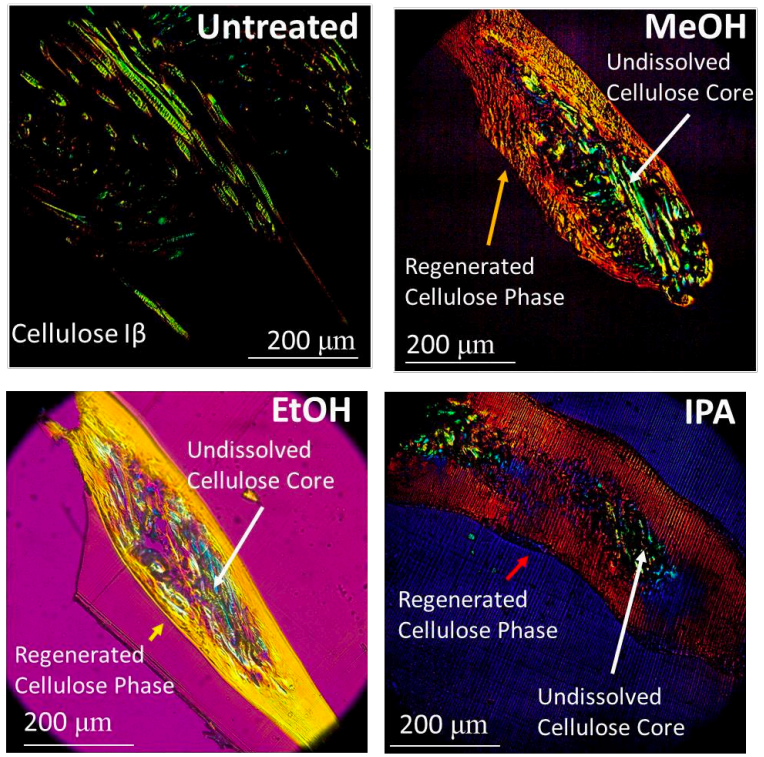
Xerogels From Cellulose



Different rinse solvents
result in different surface topology

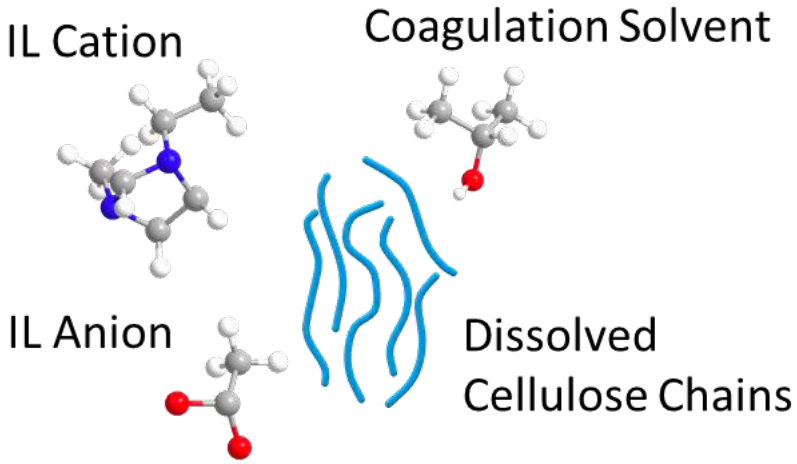


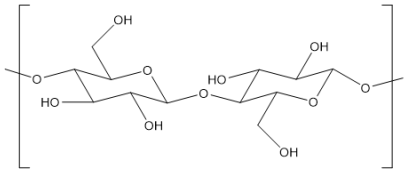
Longitudinal microtome slices



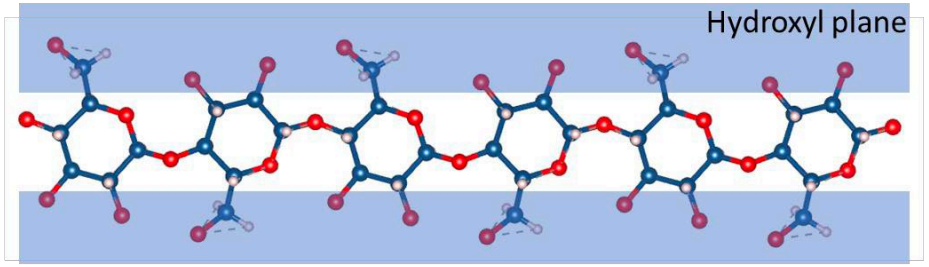
Take home: The crystalline phase is Impacted

Actors in the dance

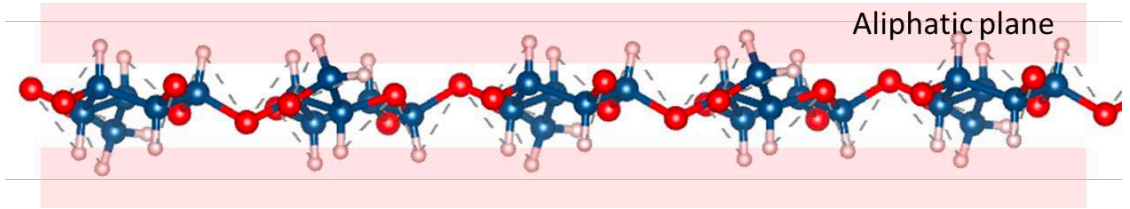




Hydrophilic orientation



Hydrophobic orientation



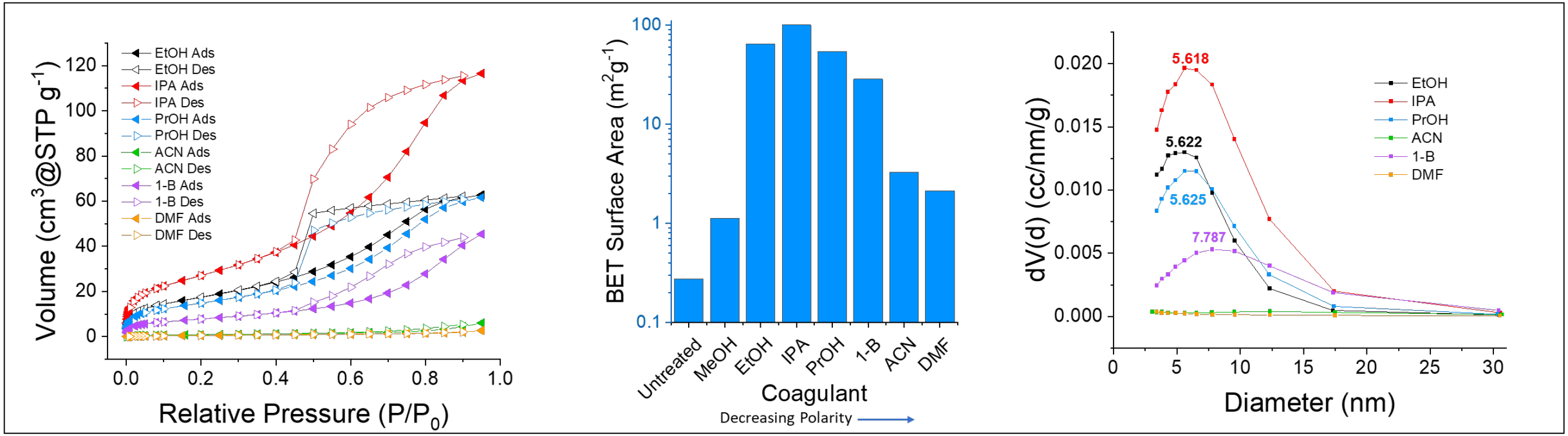
Multibody interactions…

Could use some theoretician help…(Fred?)

About 70% of cellulose is hydrophobic by volume

Cotton does not have lignin (thank goodness)

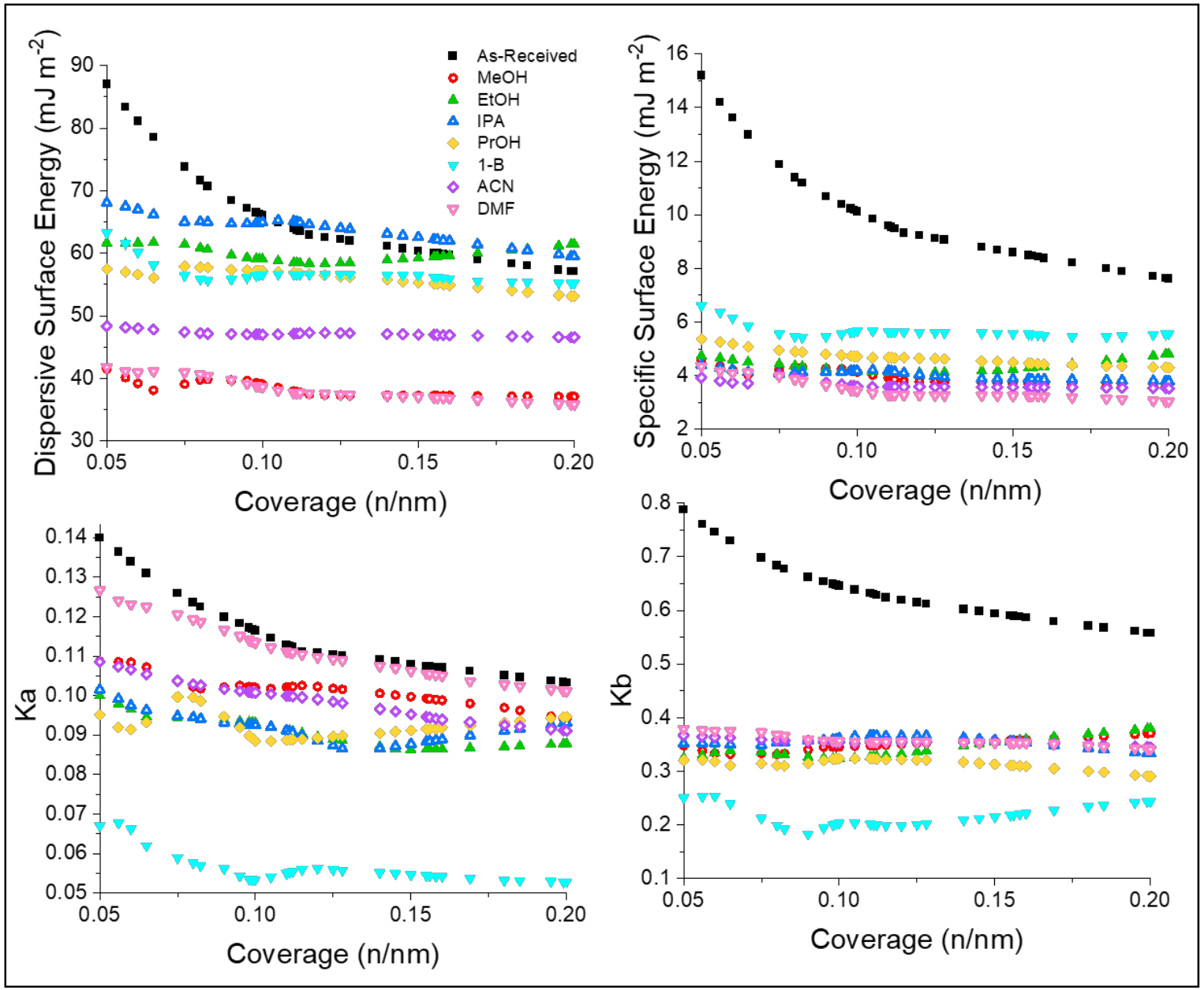
Solvent Polarity impact porosity



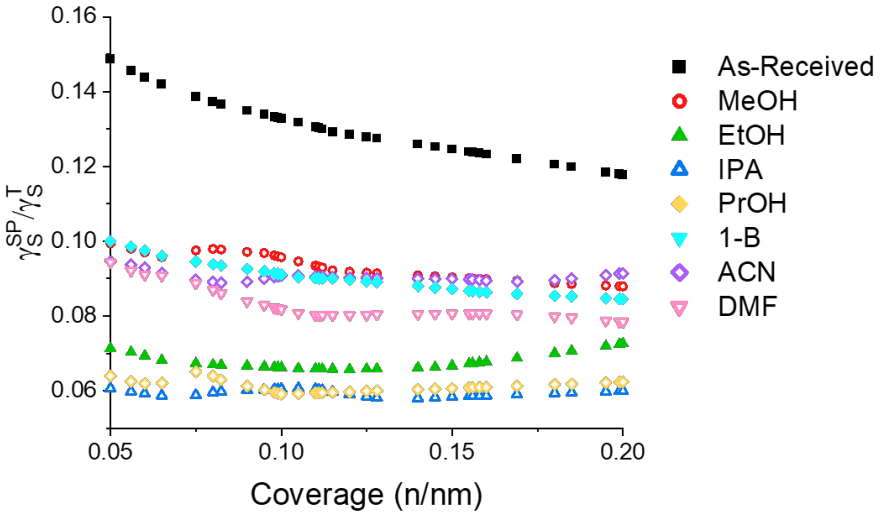
Solvent Polarity shows some impact on how the cellulose comes back together

Purely from a surface area point of view and porosity and pore diameter distribution

iGC surface energy



hydrophilicity



Specific surface free energy = $\gamma SSP = 2\ \gamma S{+}\gamma S{-}$

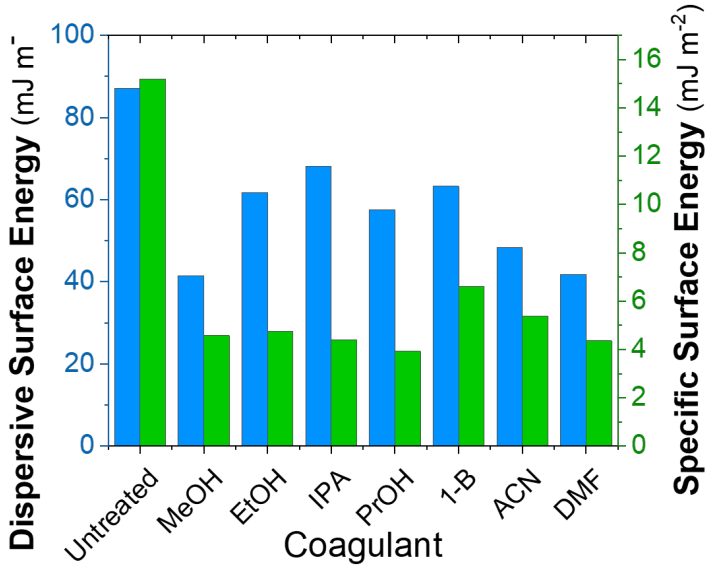
$\gamma s+$ = Lewis acid surface free energy (dichloromethane -CH2Cl2)

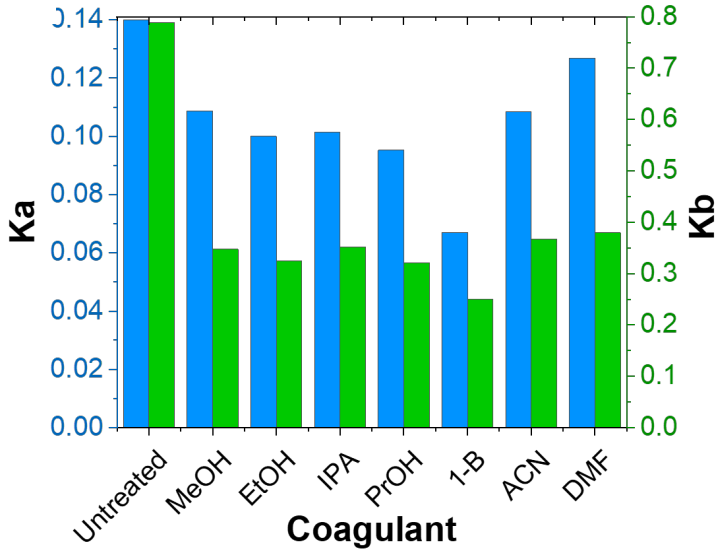
$\gamma s-$ = Lewis base surface free energy (ethyl acetate -C4H8O2)

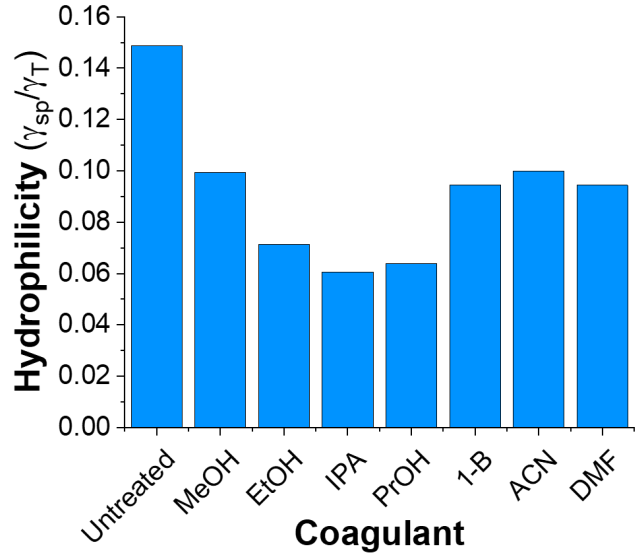
Total surface energy = $\gamma ST = \gamma SD + \gamma sSP$

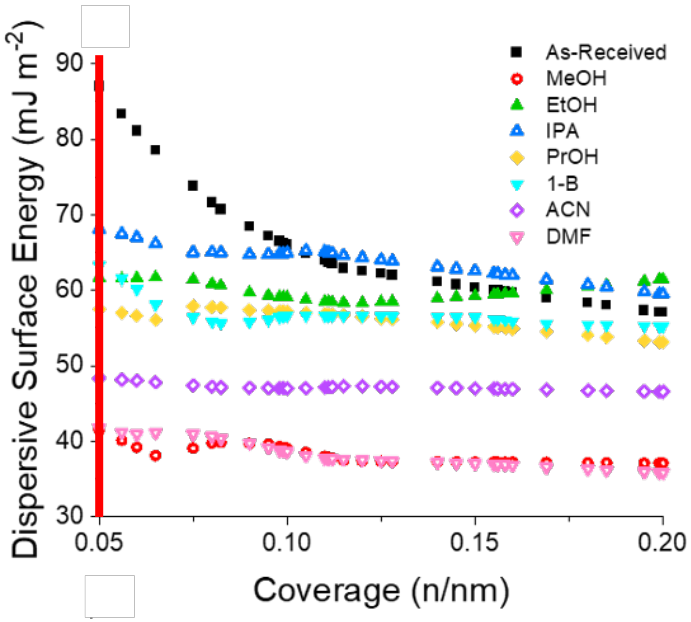
hydrophilicity = $\boldsymbol{\gamma sSP/\gamma s}$

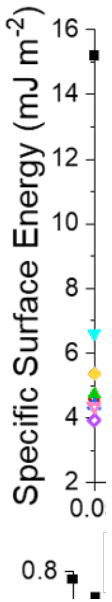
Take a look at 5% fractional surface coverage

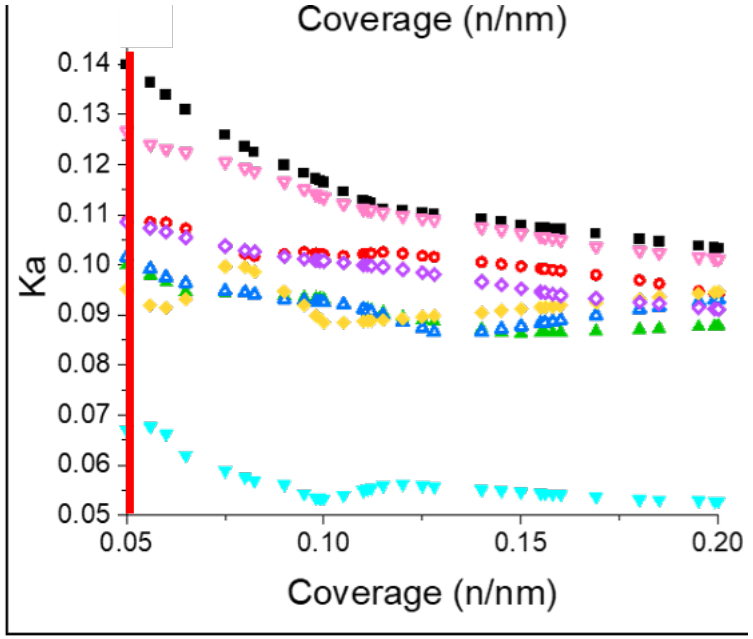


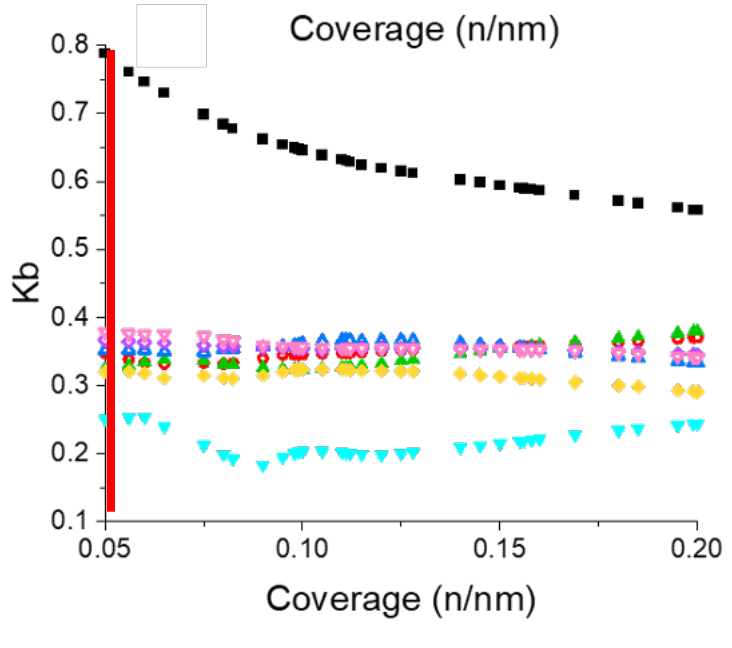










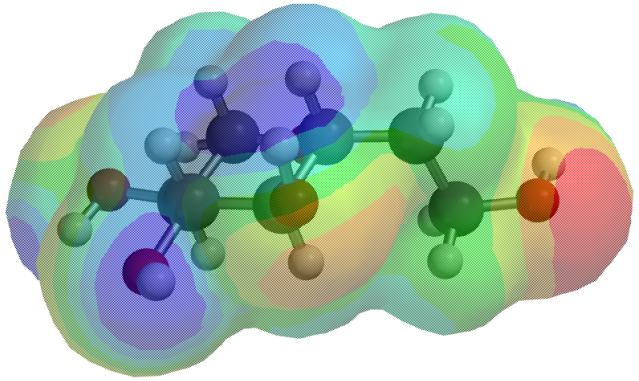


Ka and Kb

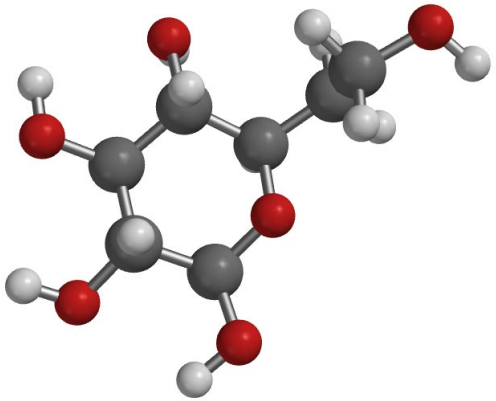
Ka is the Lewis acid constant: How well an atom can accept a free pair of electrons. Electron acceptor

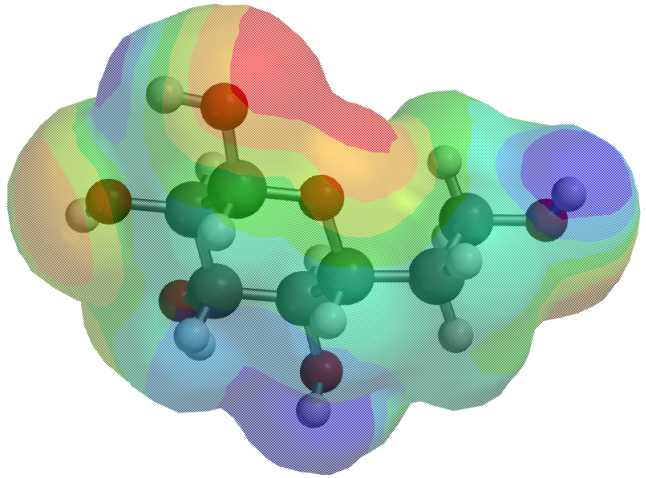
Kb is the Lewis base constant: How well an atom can donate a free pair of electrons: Electron donator

Glucose repeat unit



More hydrophobic or surface

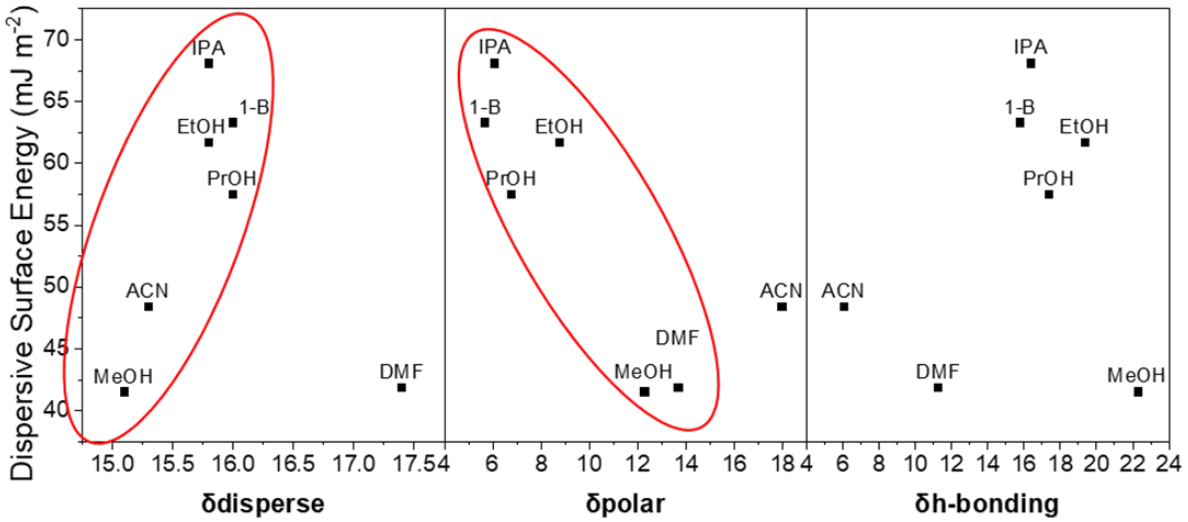


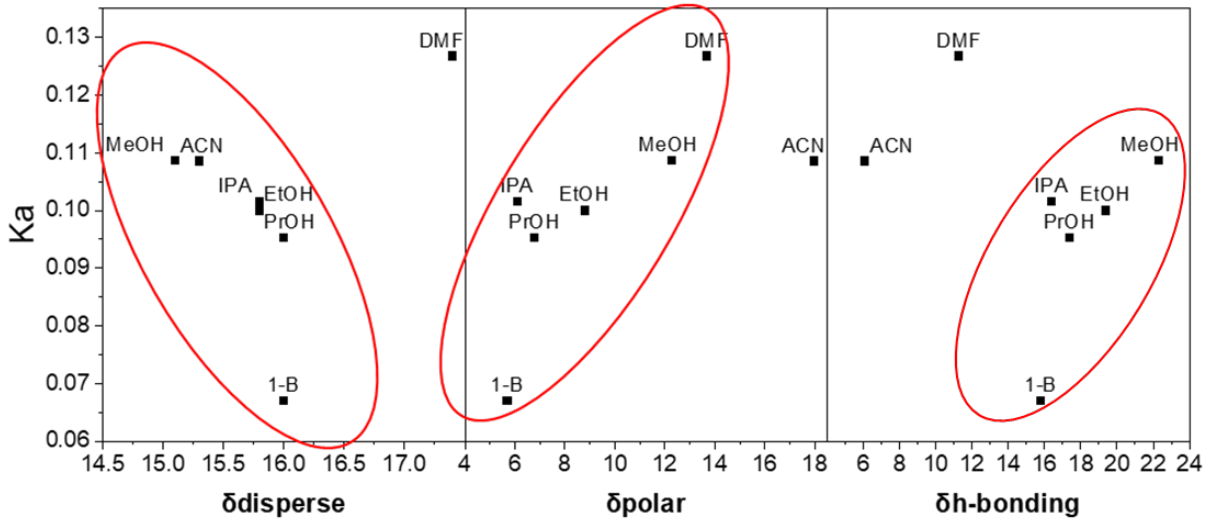


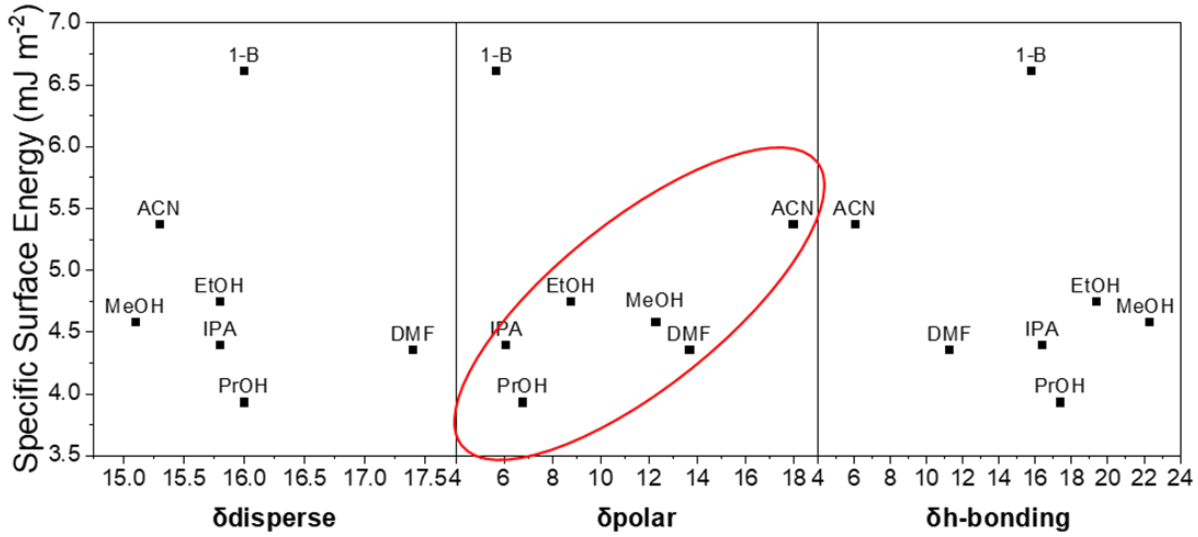
More hydrophilic surface

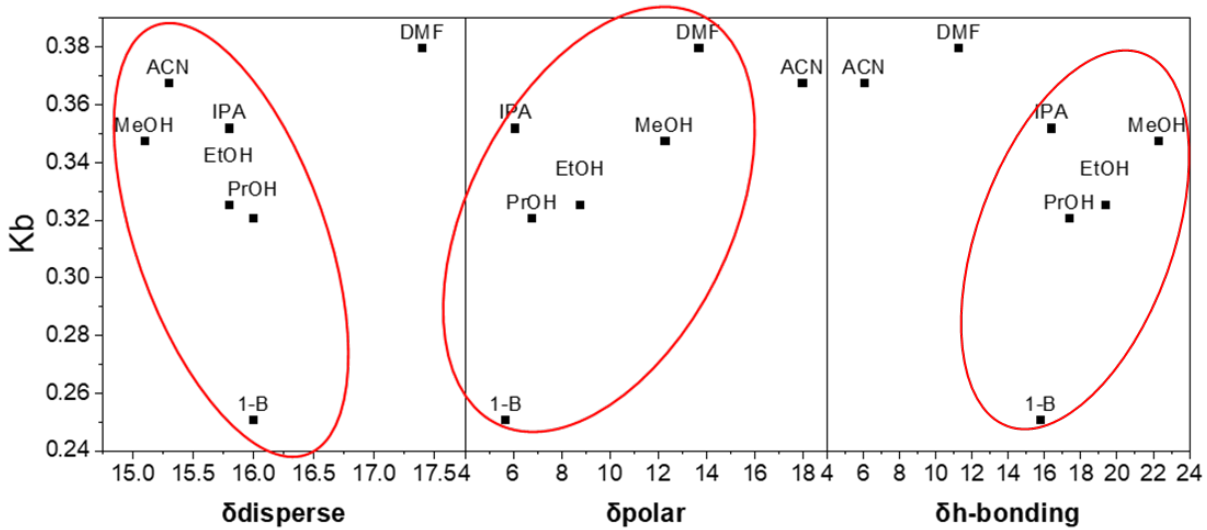
Need some solid state NMR to confirm the actual morphology…. (Coming soon, hopefully….)

iGC vs Hansen solubility parameters



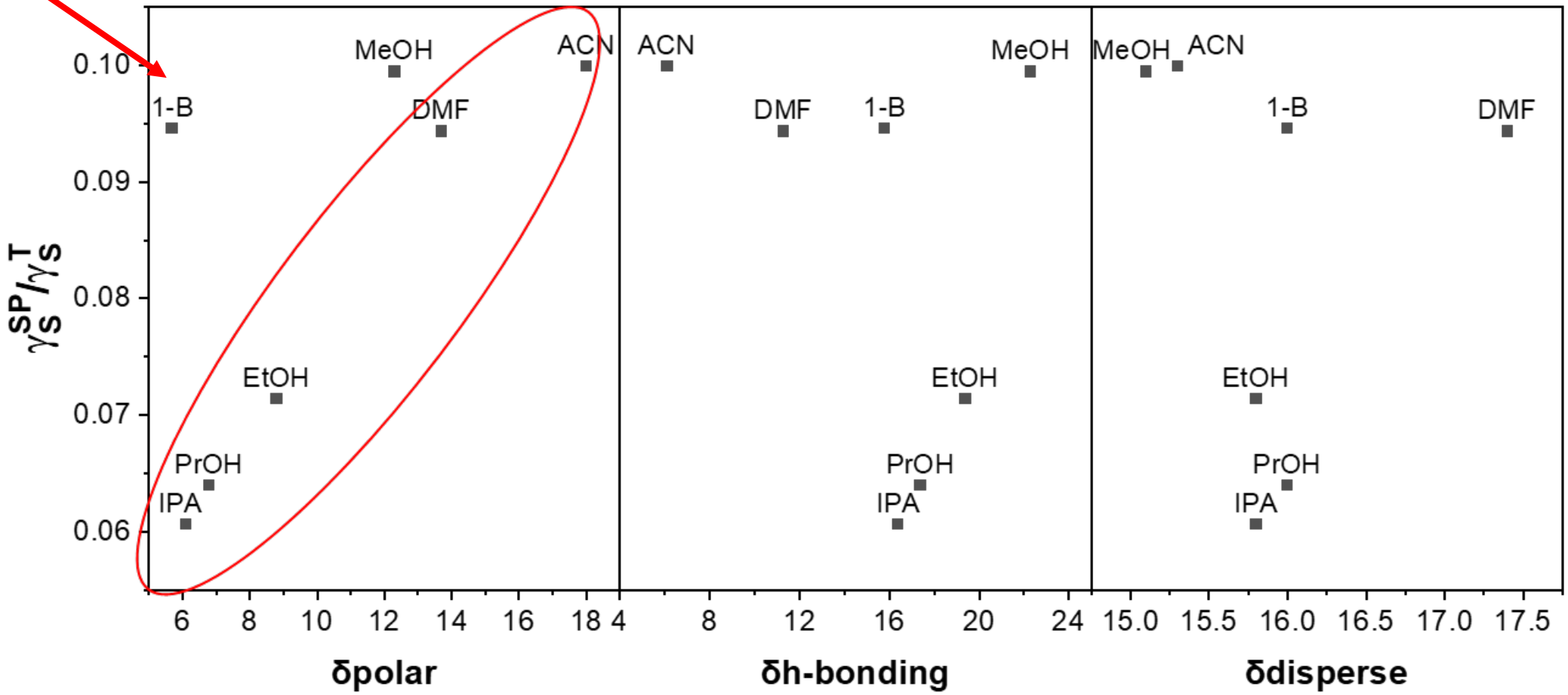




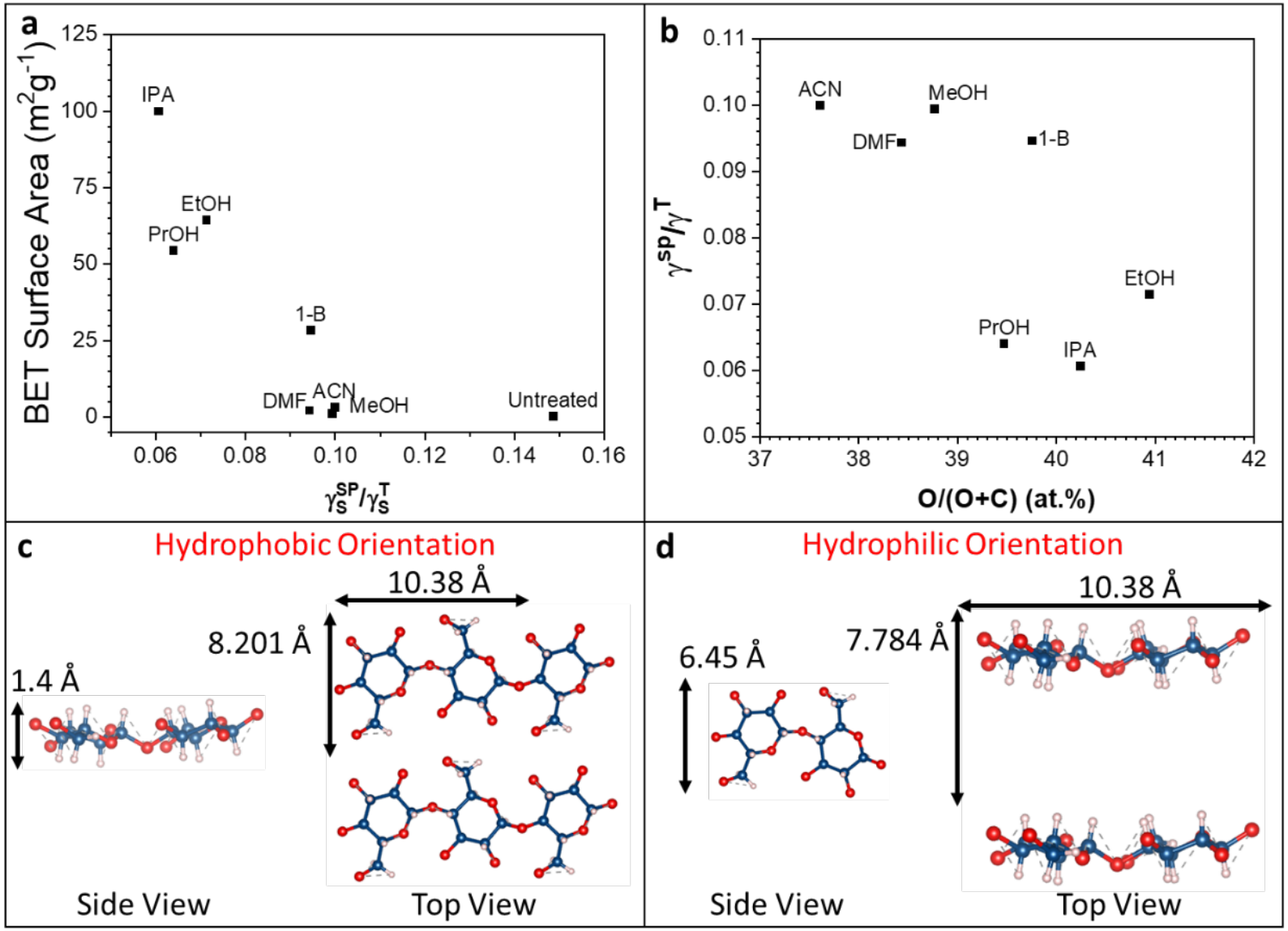


There is some trend…..

This one….



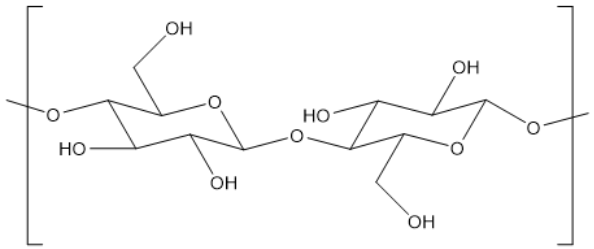
BET surface area and XPS versus hydrophilicity



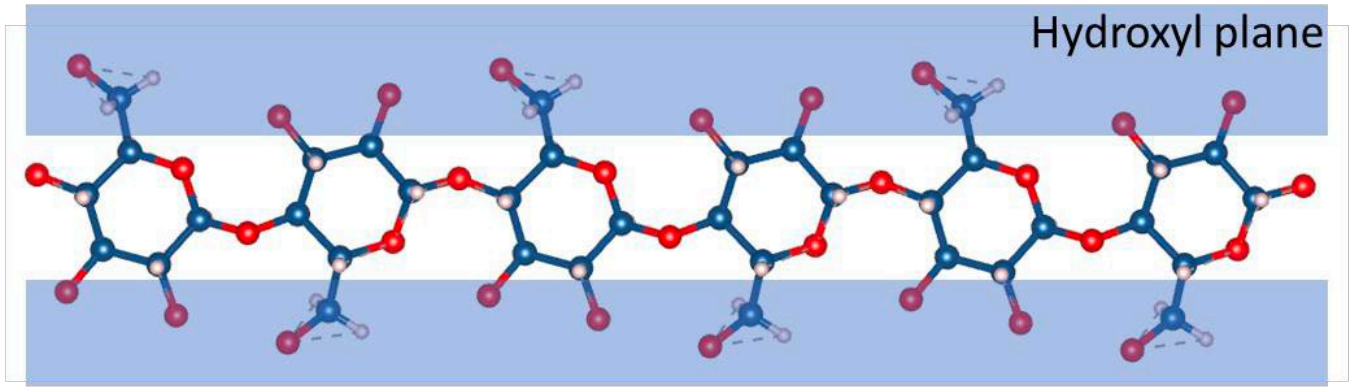
There is a trend in BET surface area with surface hydrophilicity

The carbon/oxygen ration from xps shows a general ROUGH trend with hydrophilicity

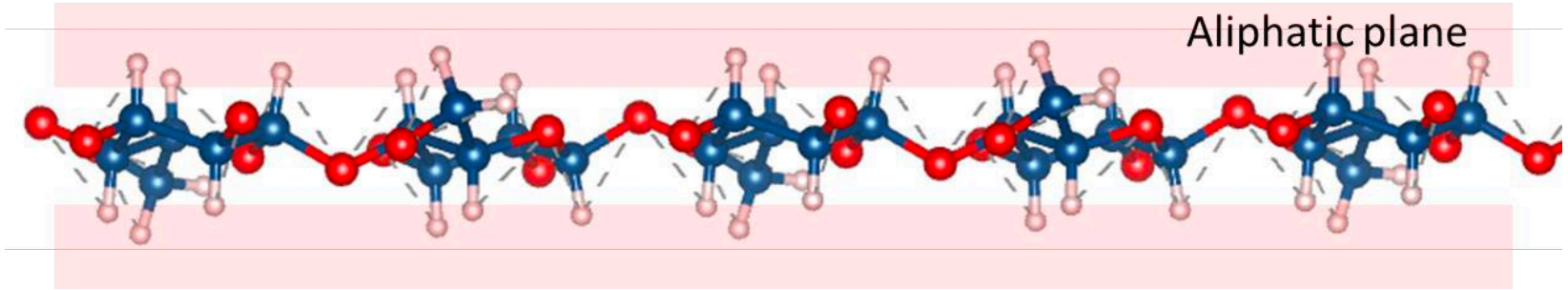
A lot less mobility in polymer chain

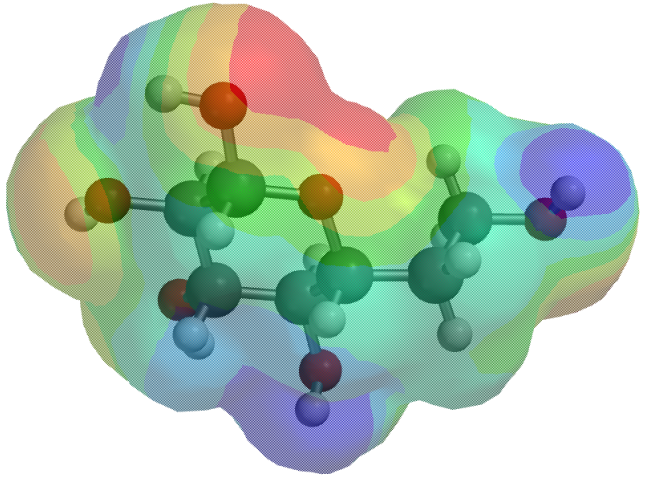


Hydrophilic orientation

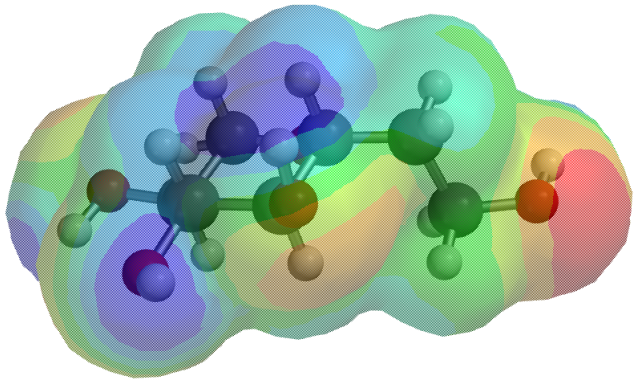


Hydrophobic orientation





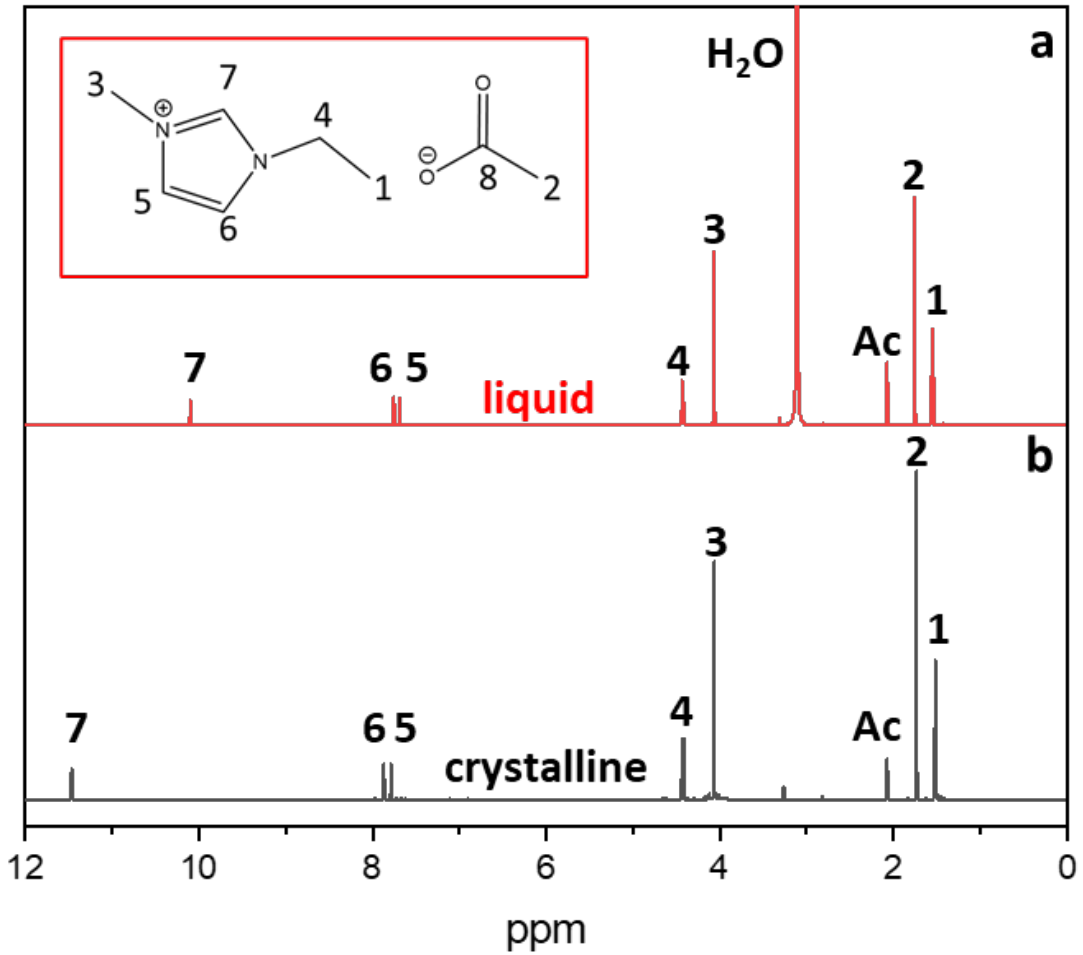
More hydrophilic surface



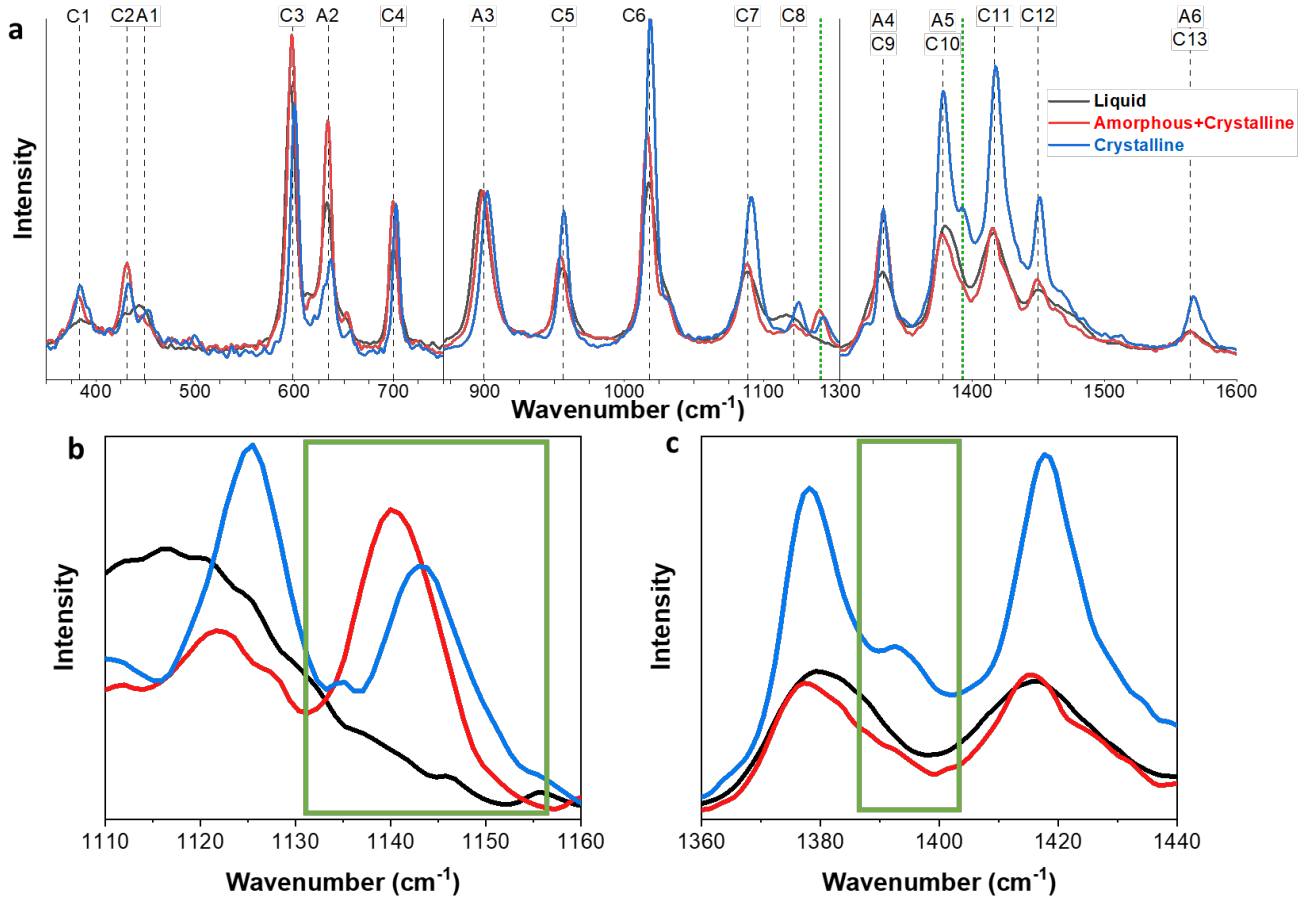
More hydrophobic or surface

From the Ionic liquid's perspective

Solution NMR

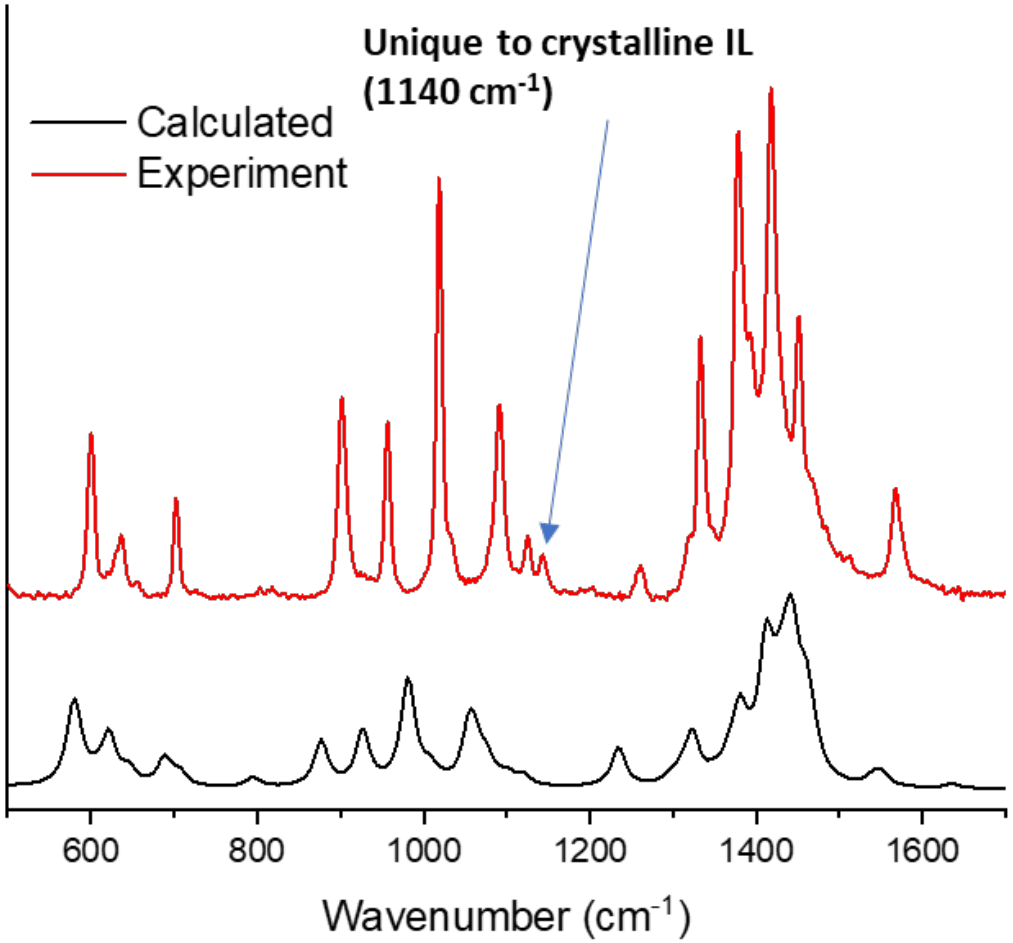


Raman

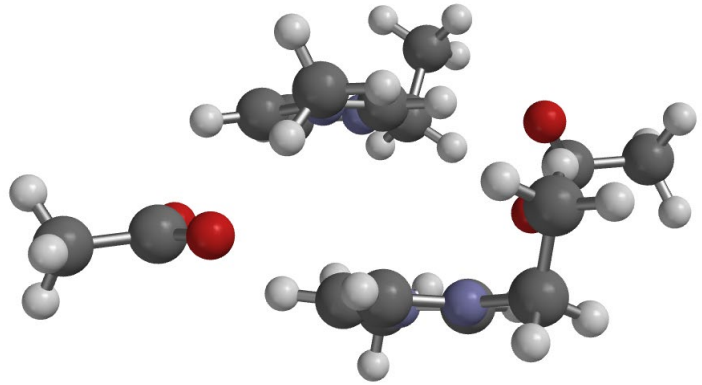


DFT predicted vs experiment

Single ion pair



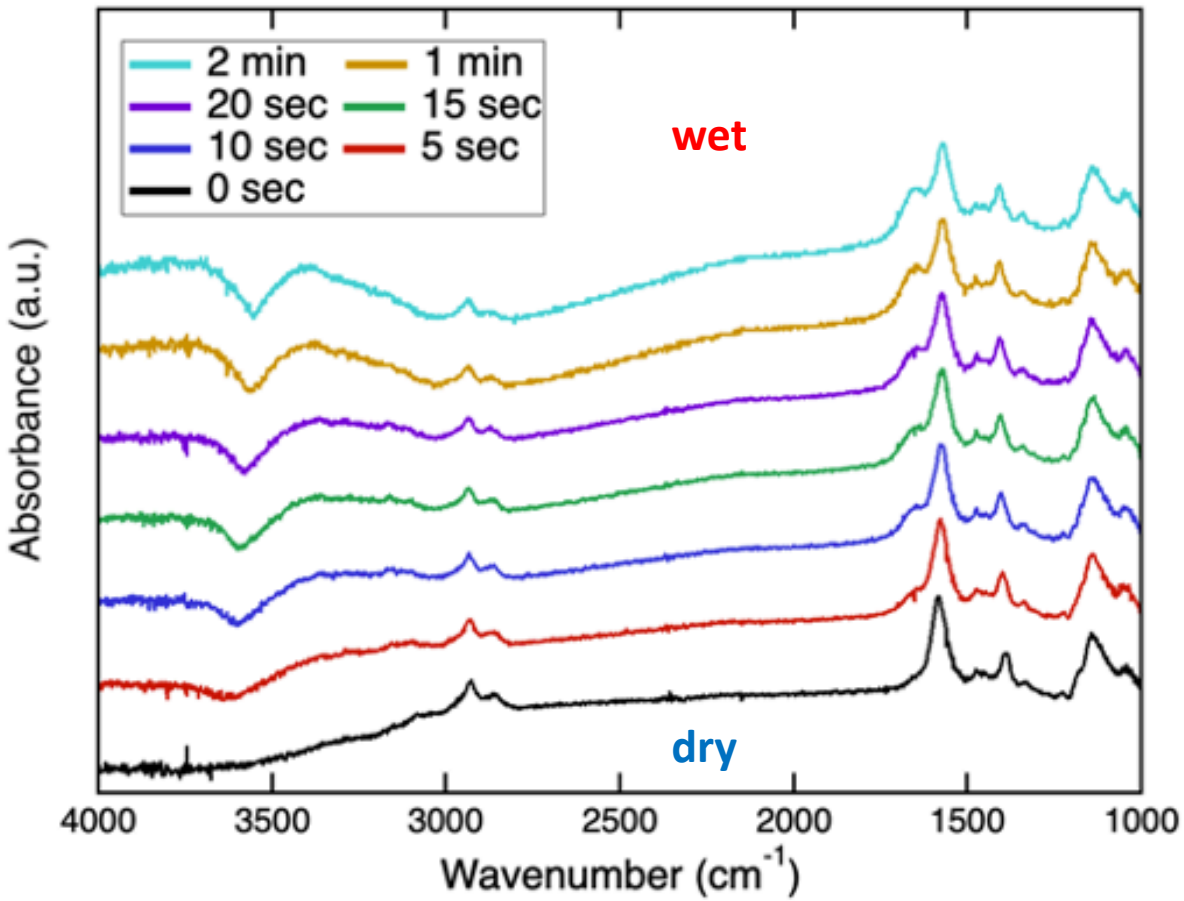
Possible arrangement by DFT

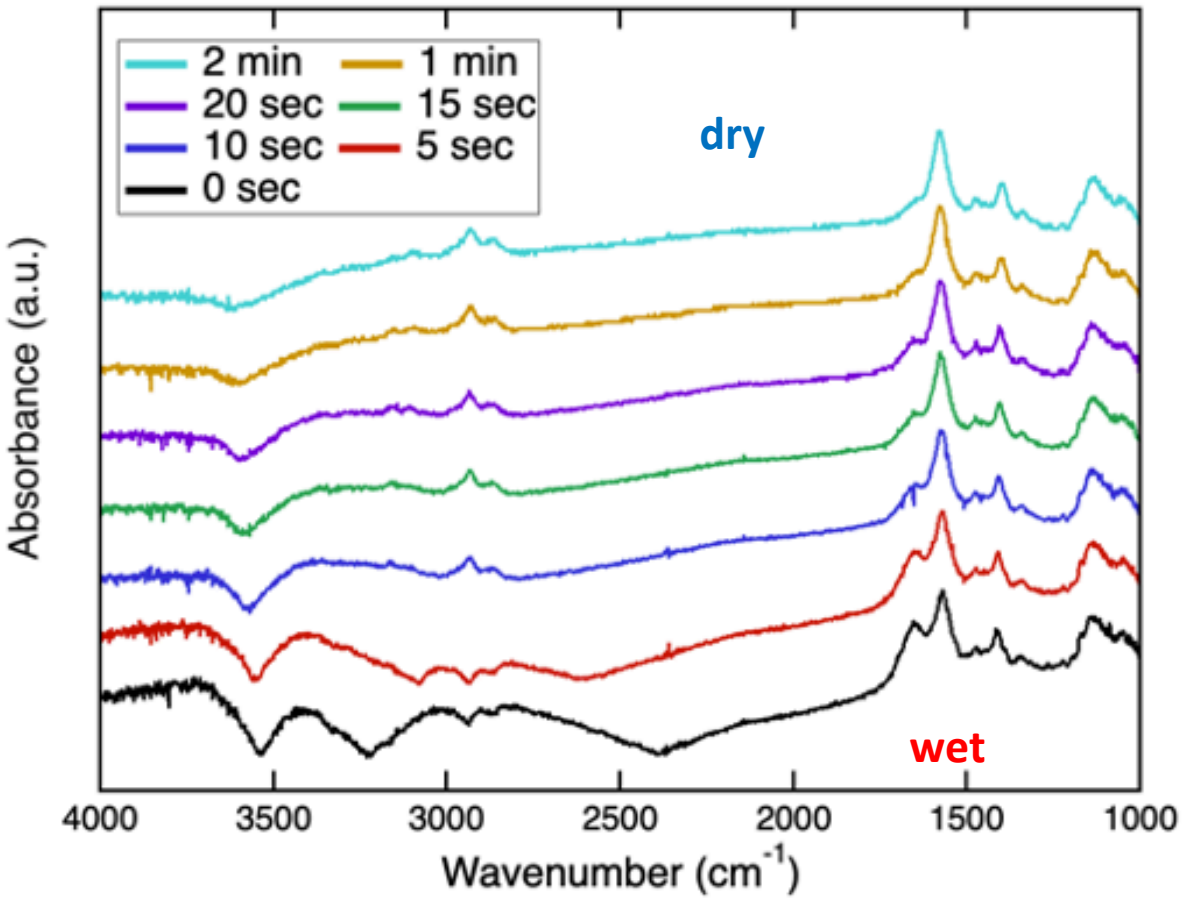


Minimized geometry

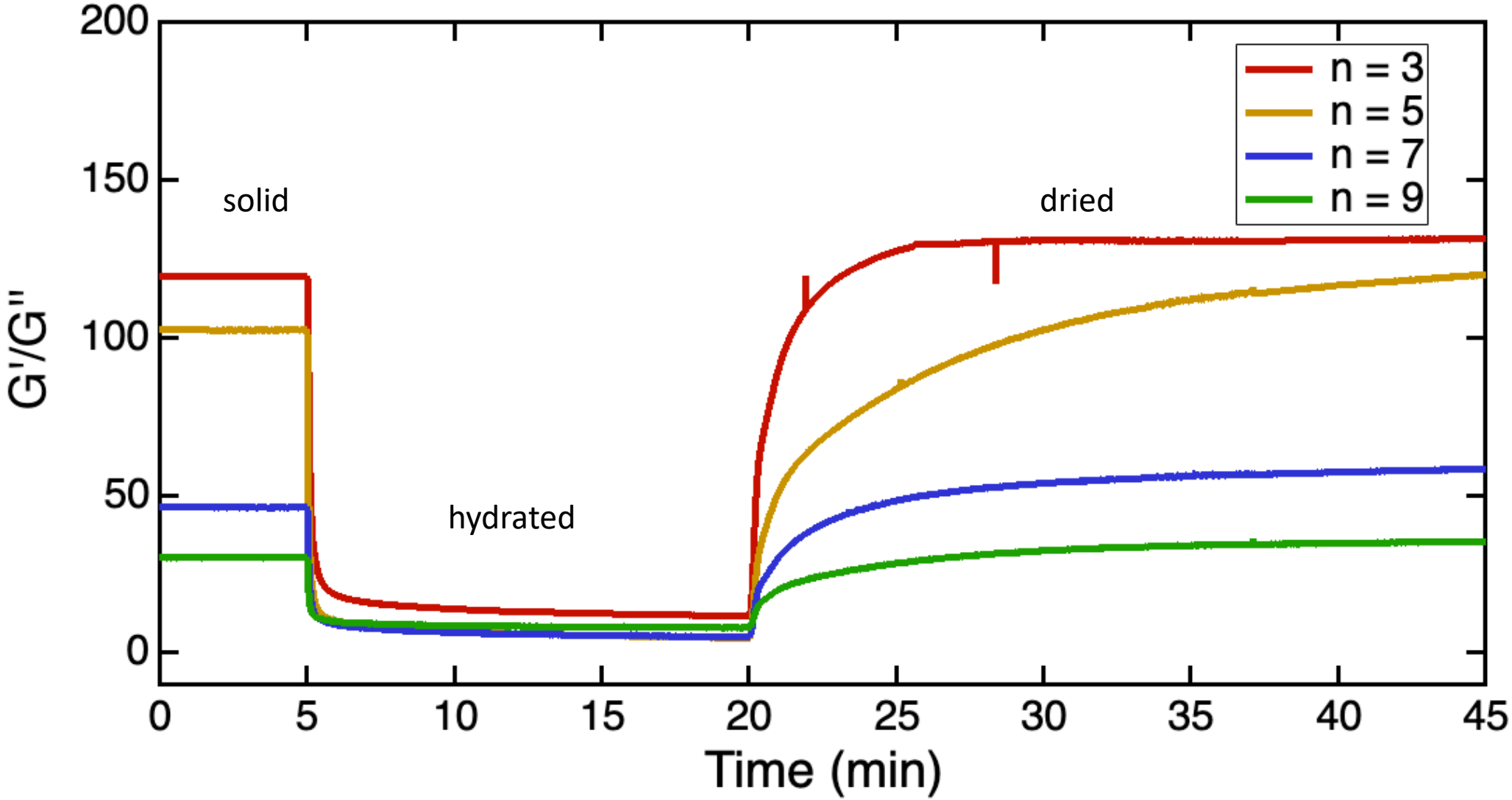
DFT in vacuum B3LYP 631G*

Absorption and desorbance of water



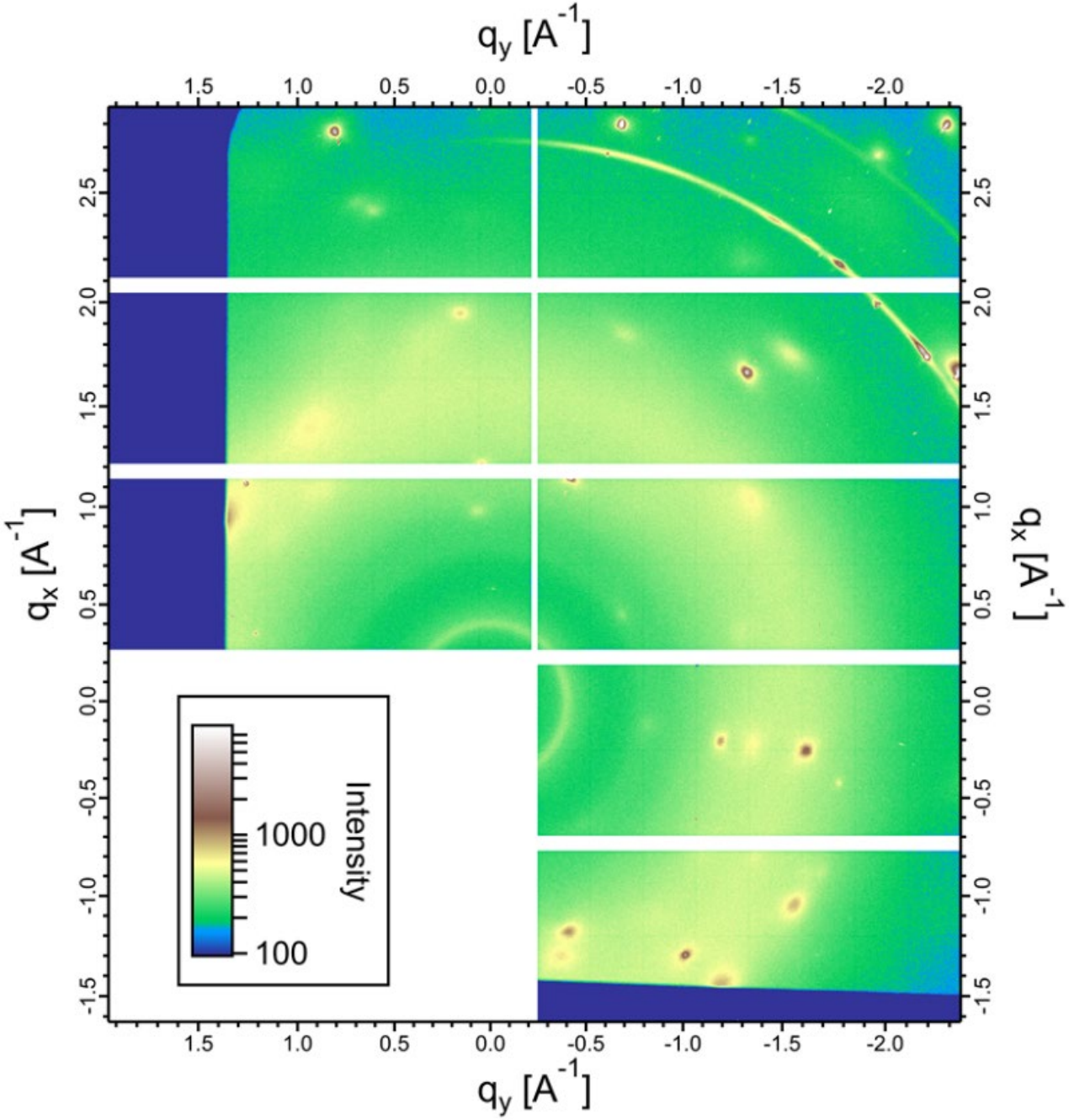


QCM results for hydration and dehydration



For Fun

Not a single crystal…….



Hypothesis of process