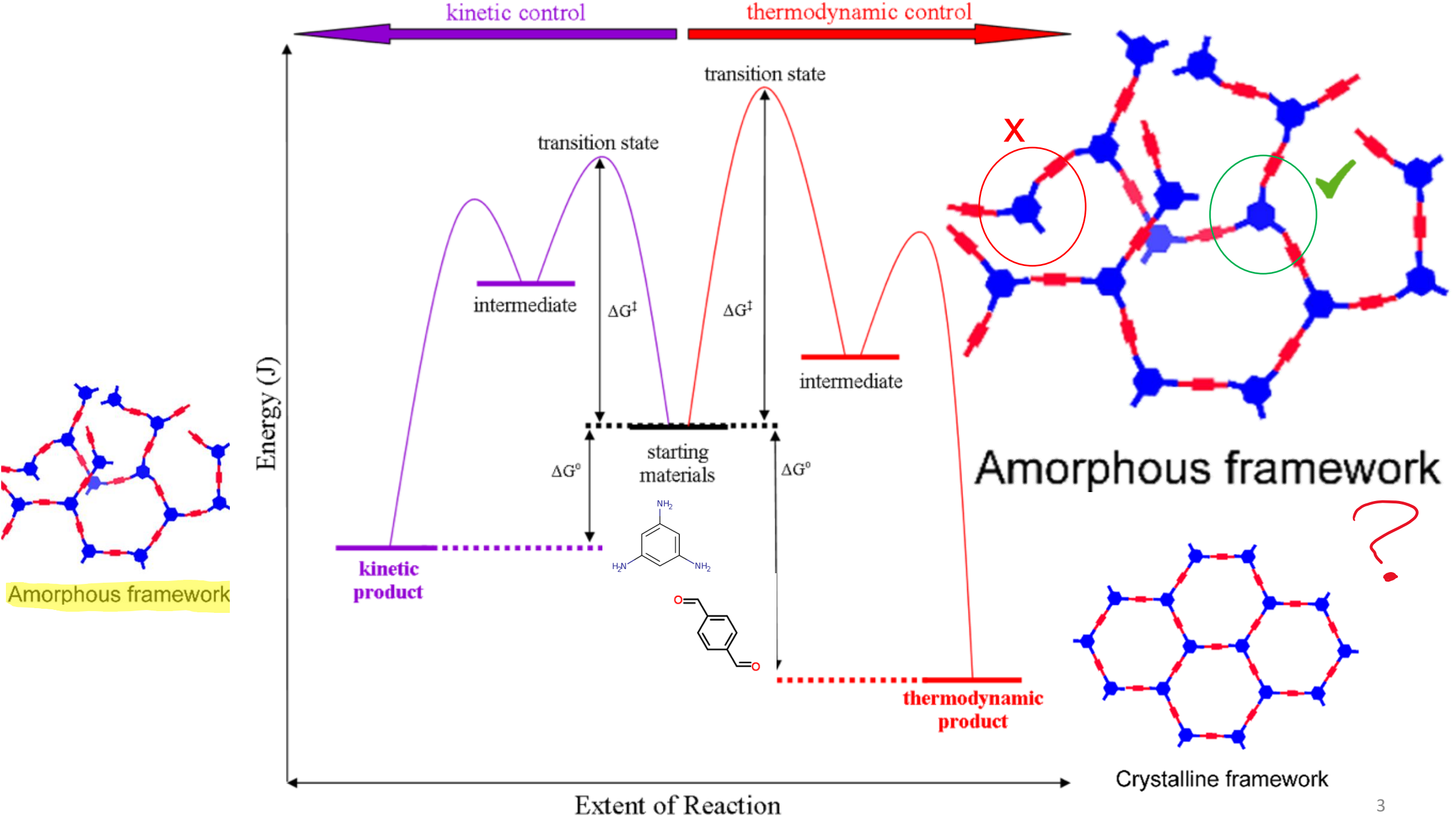


Shaping Imine-Based COFs: From Dynamic Gels to Functional 3D Architectures

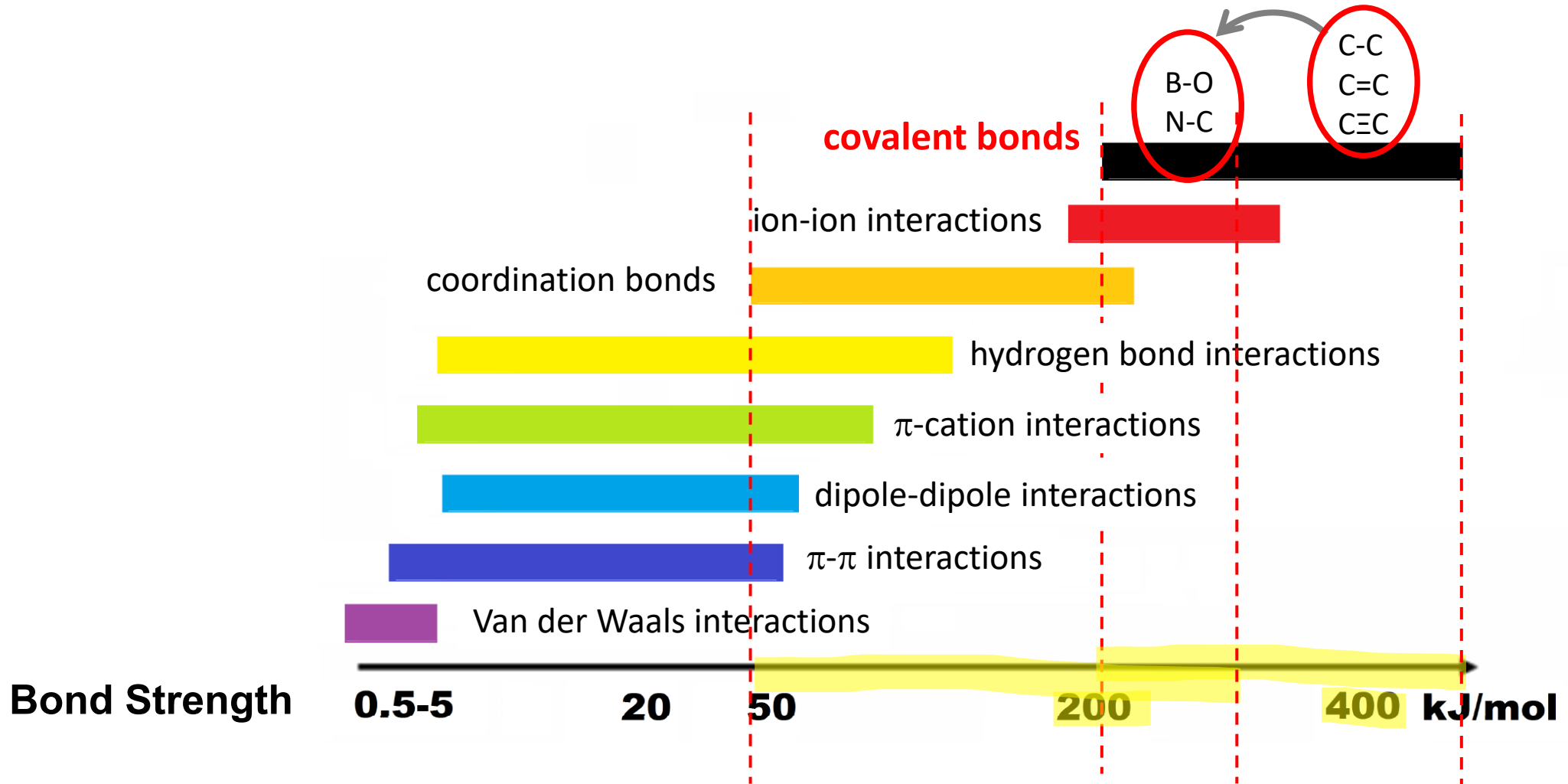
Félix Zamora / Universidad Autónoma de Madrid



1. The challenge: COFs are powerful
but hard to shape



Dynamic Covalent Bonds





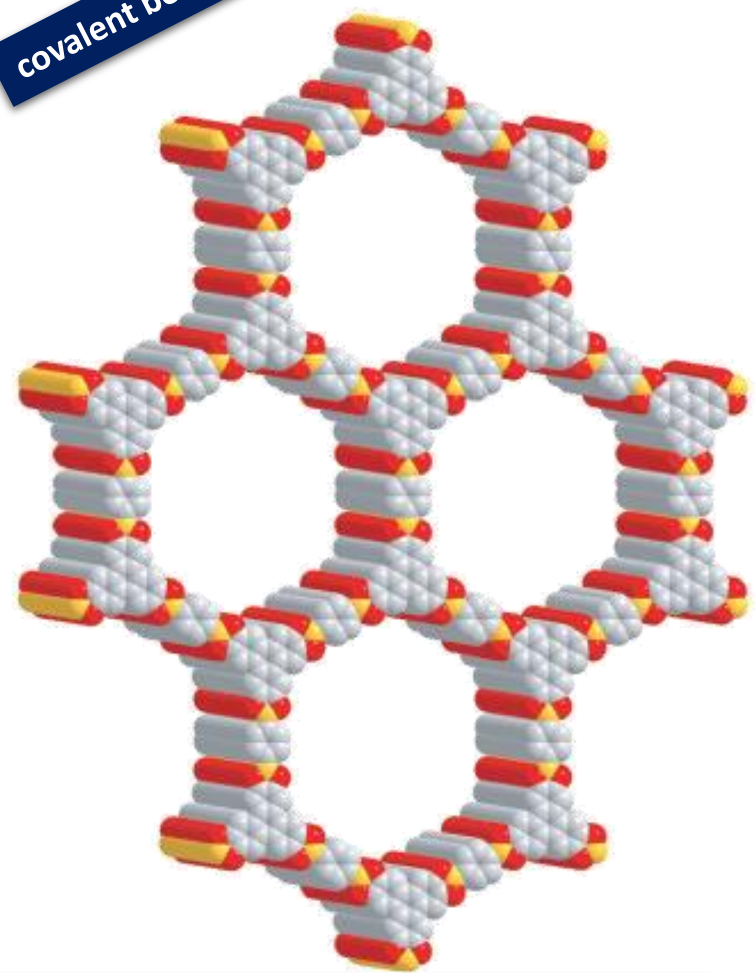
O. Yaghi



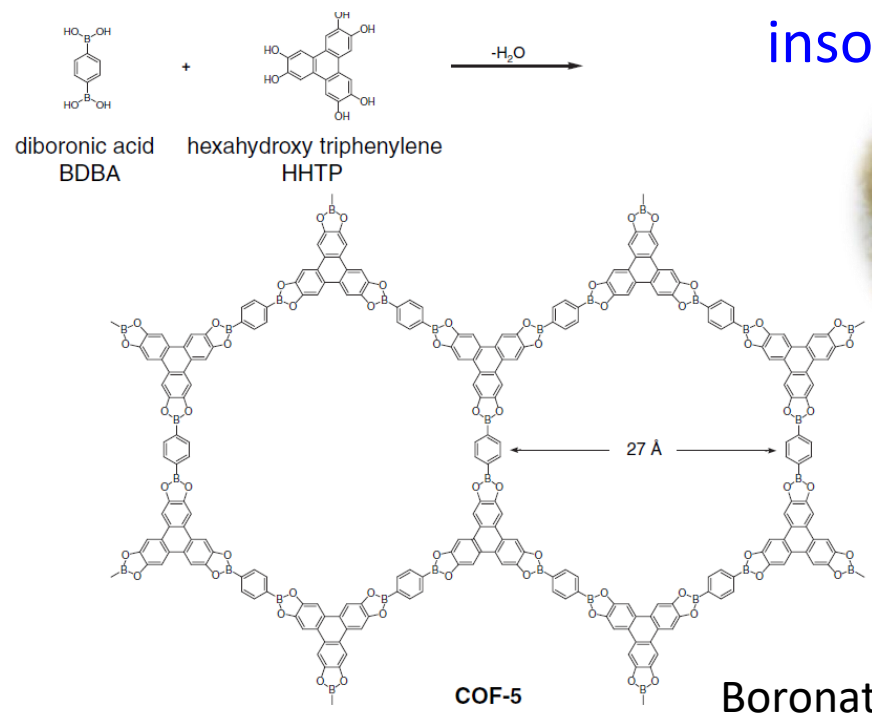
Solvothermal conditions

covalent bonds

Layered material



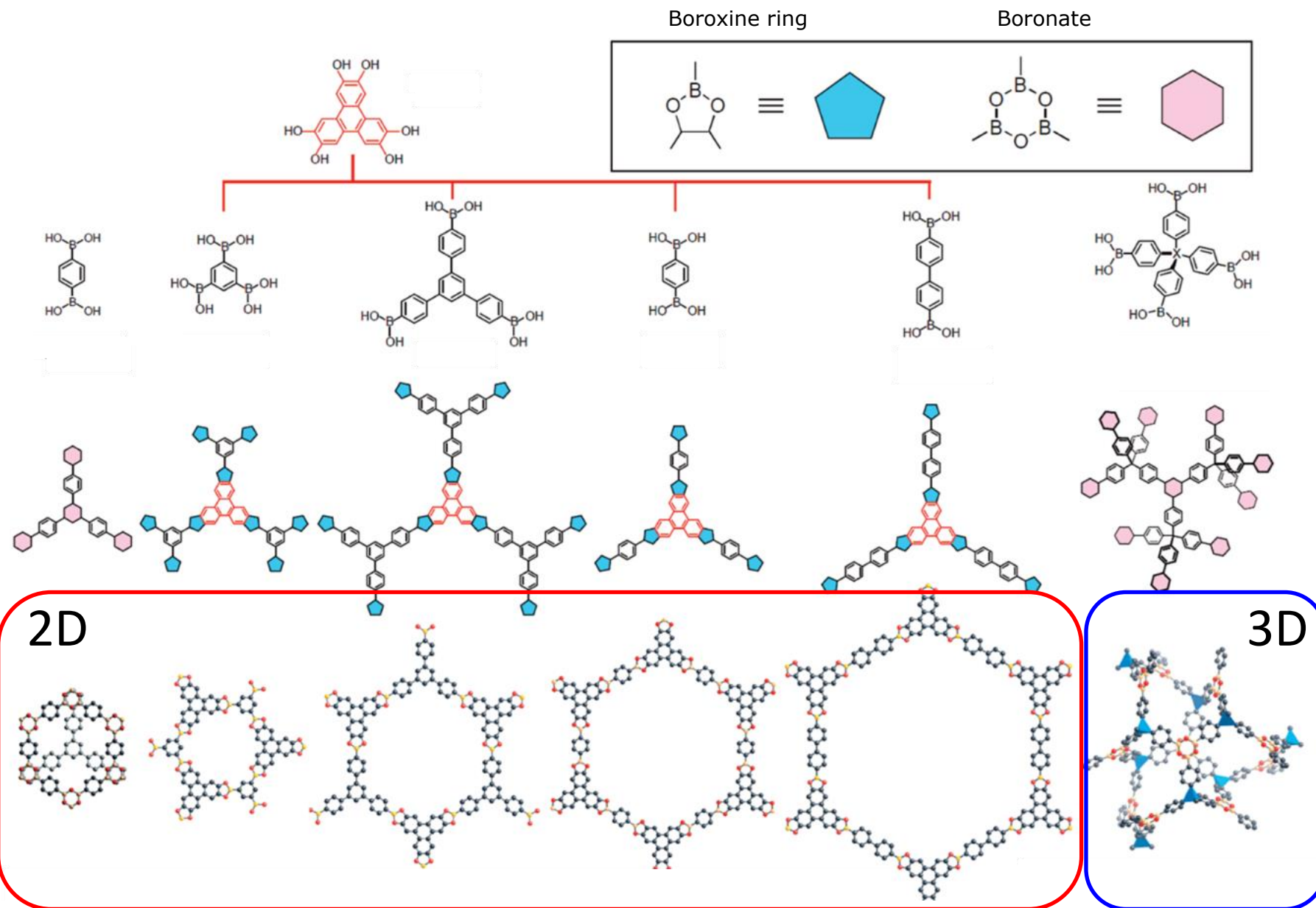
Permanent Porosity / Low Density



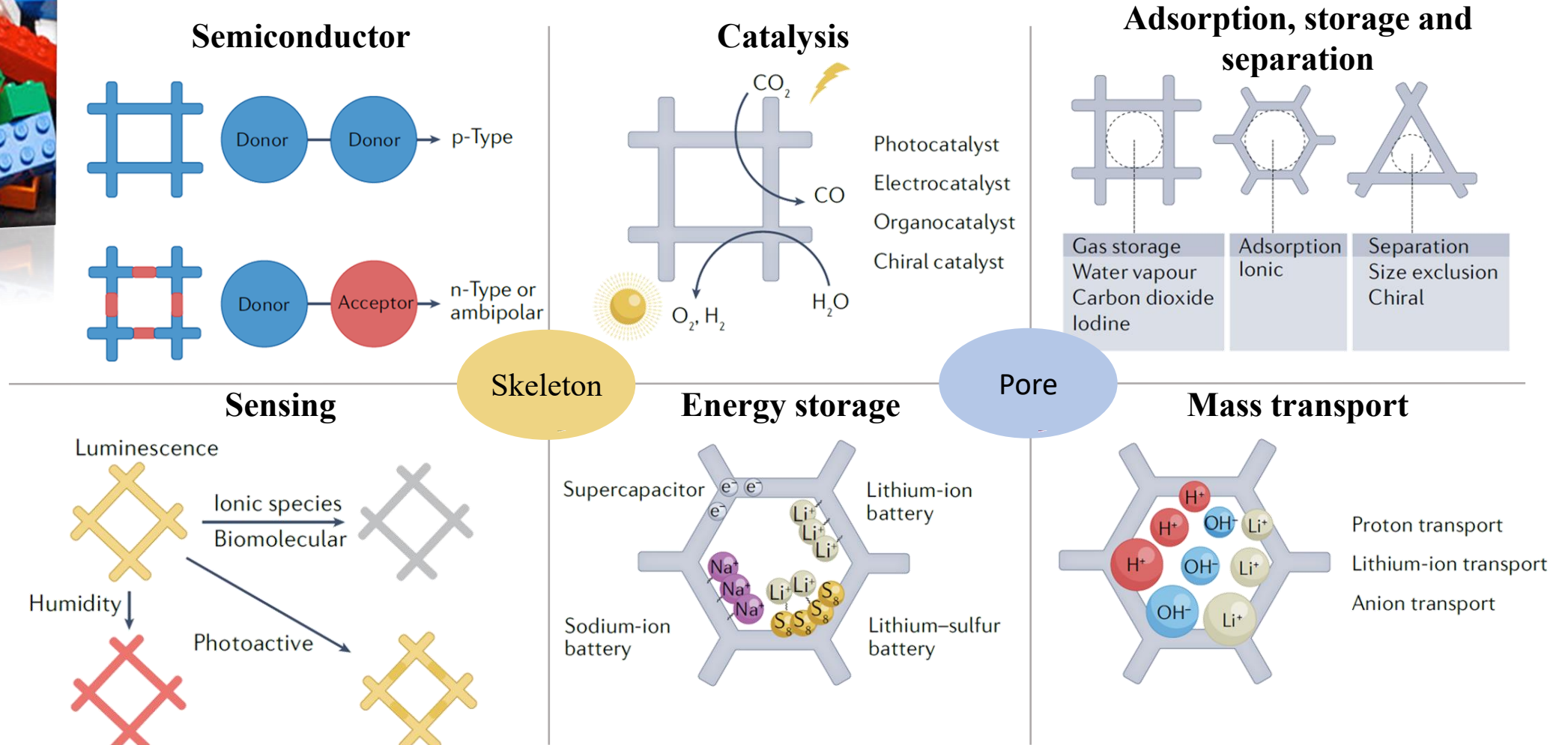
insoluble powders



Covalent Organic Frameworks: Boron-based COFs

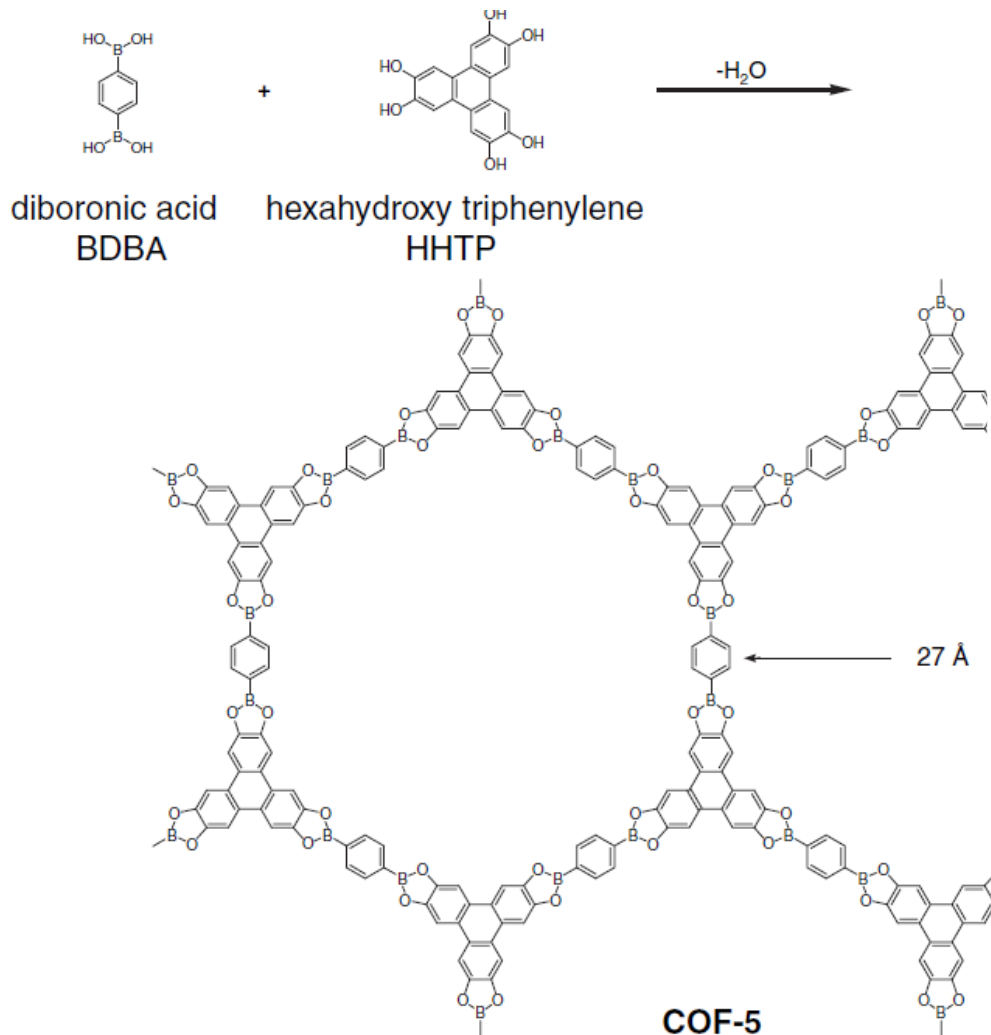


COFs Design Properties & Applications



Nat Rev Methods Primers. **2023**, 3, 1

Covalent Organic Frameworks: Material Design Evolution

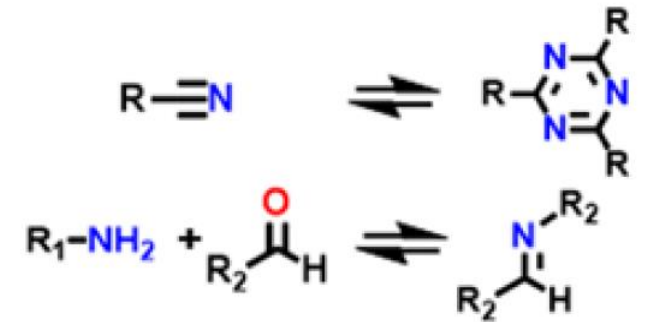
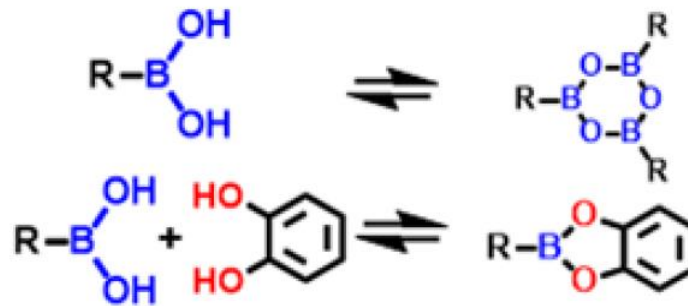


Applications: Robust Materials

Boroxine and Boronate-ester COFs
Thermally robust: 400-500 °C
Low Chemical Stability: Hydrolysis

Boron-containing

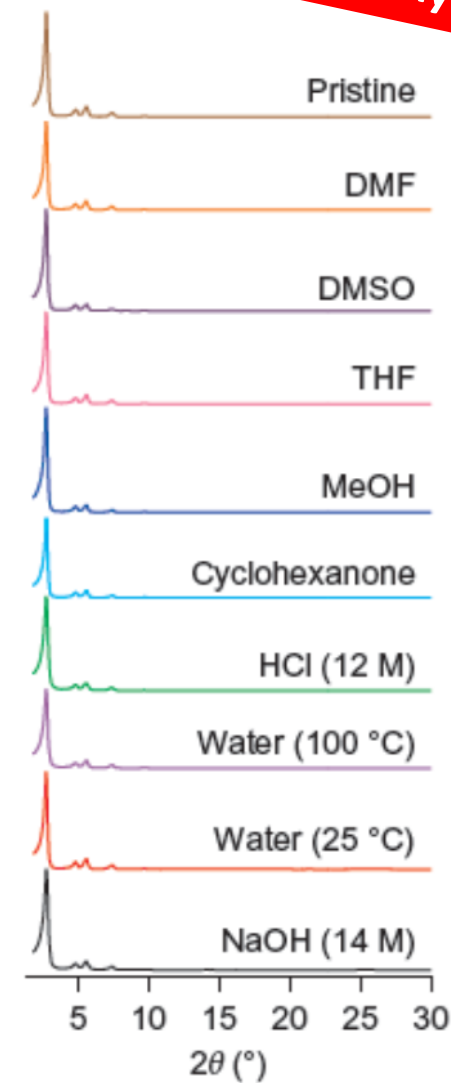
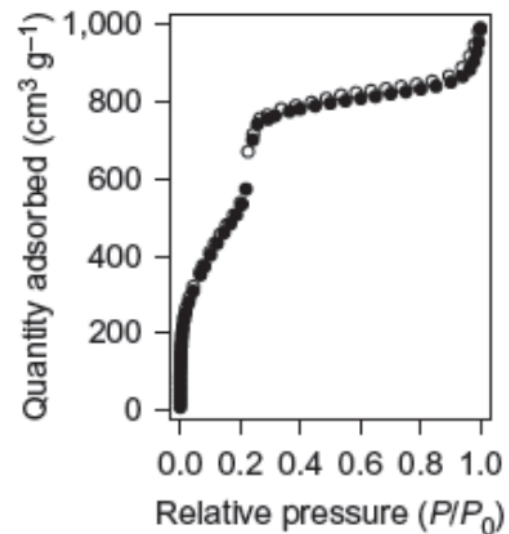
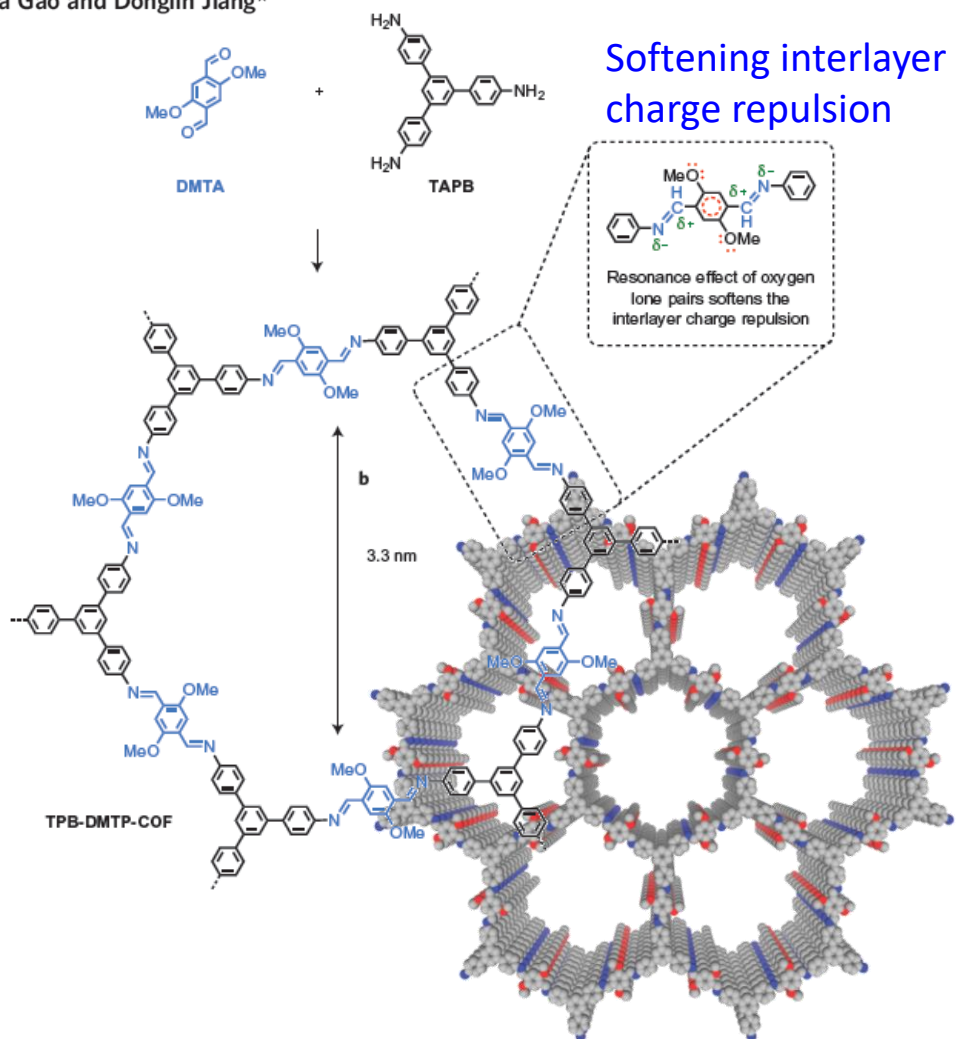
Nitrogen-containing



Chemically Robust Imine Based COFs

Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts

Hong Xu, Jia Gao and Donglin Jiang*



Covalent Organic Frameworks



Structural Material Design

Properties

Thermal stability

Chemical stability

High Surface Area

Tuneable Pore Sizes & Shapes

Crystallinity

Robust Materials



RT-COF-1Ac

Processability

Production methods

controlling the shaping and sizing of COFs

Applications

Semiconductors

Luminescence & sensing

Catalysis

Adsorption, storage & separation

Energy storage

Mass transport

The Objective: Shaping without losing crystallinity/porosity

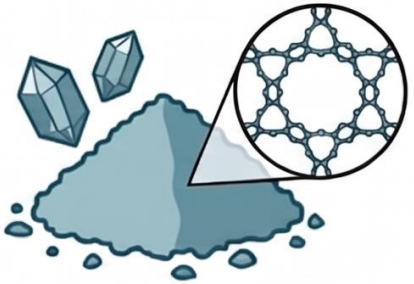
Our strategy: Dynamic imine chemistry + controlled nanoaggregation

TODAY ROADMAP

THE EVOLUTION OF COF MATERIALS: FROM POWDER TO FUNCTIONAL ARCHITECTURES

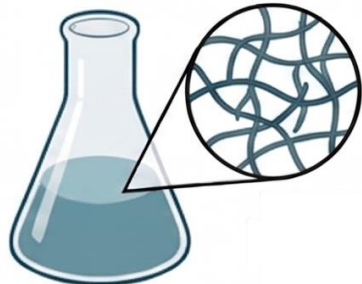
KEY CONCEPT: CONTROLLED NANOAGGREGATION

POWDER COFs



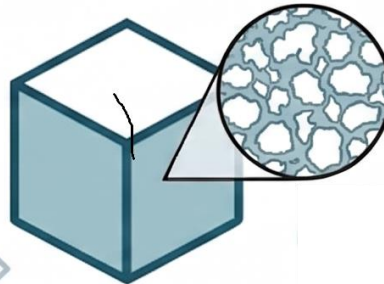
High-crystallinity
Crystalline Organic Frameworks
Limited processability

COF GELS



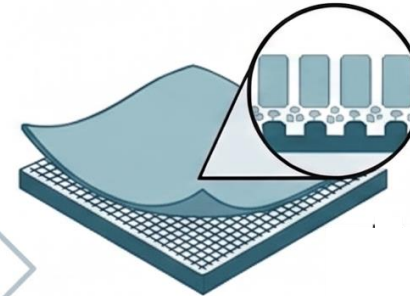
Controlled
Nanoaggregation
Cross-linking &
Solvent Trap

COF AEROGELS



Supercritical
drying/Freeze drying
High Porosity &
Surface Area
Extremely low density

COF MEMBRANES



Continuous films
& coatings
Molecular Sieving
Selective Separation

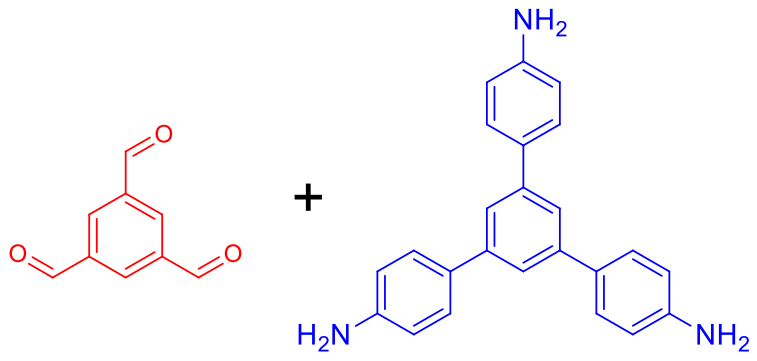
3D-PRINTED OBJECTS



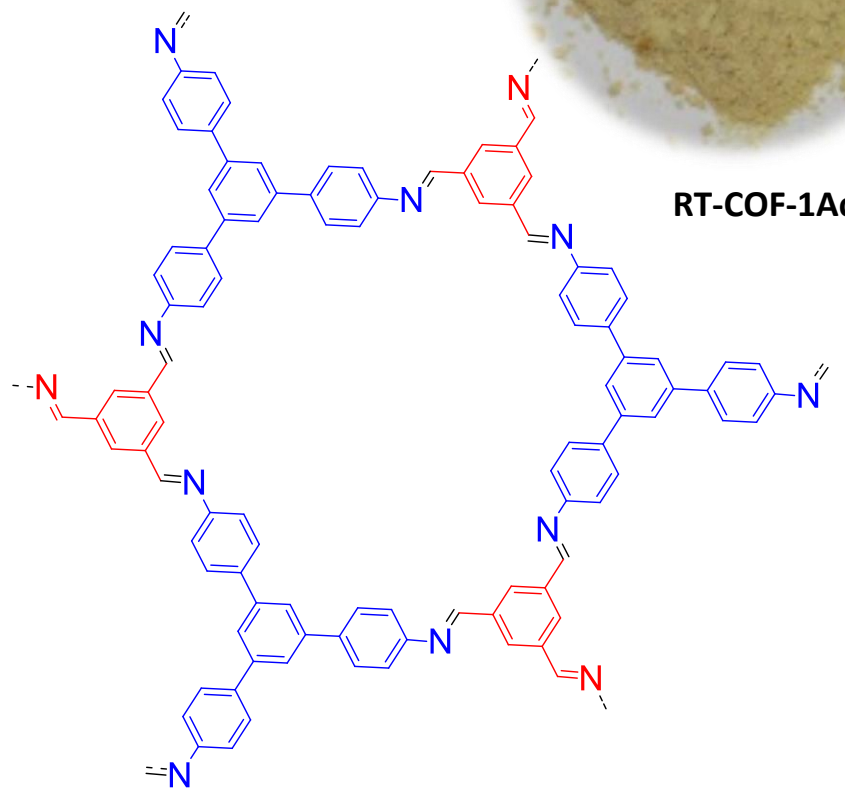
Additive
Manufacturing
Programmable
Architectures

2. Dynamic imine chemistry as a route to processability

Hampering COF Processability

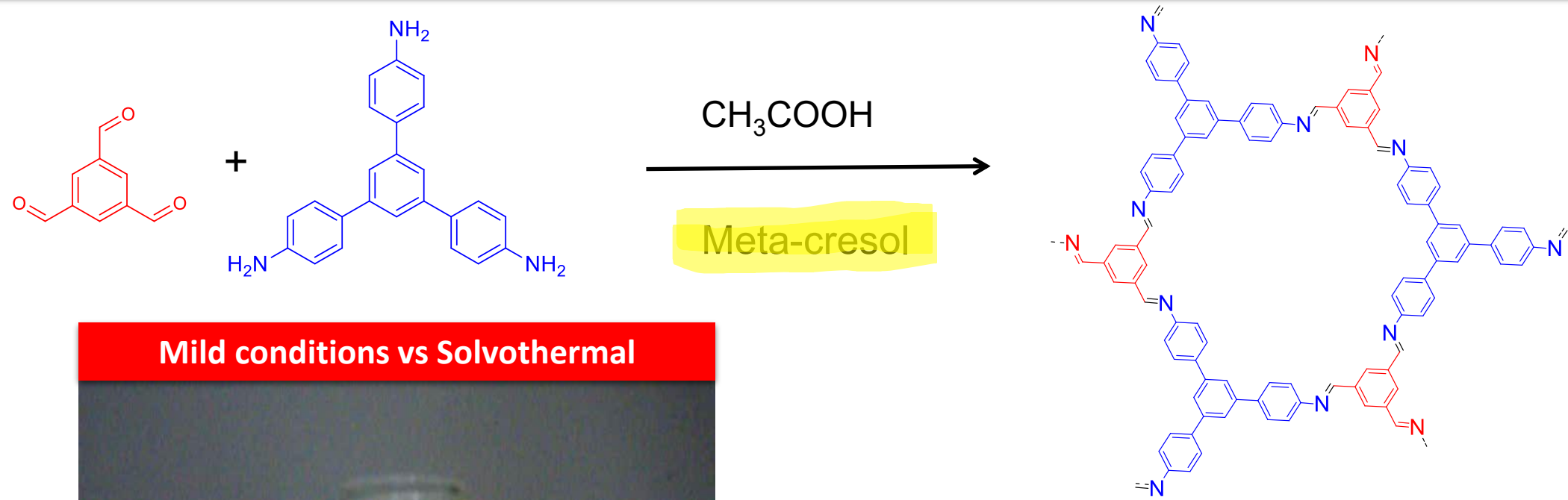


Dioxane/Mesitilene
cat. CH₃COOH
solvoth, 12 h



RT-COF-1Ac

Imine COF Formation at Room Temperature



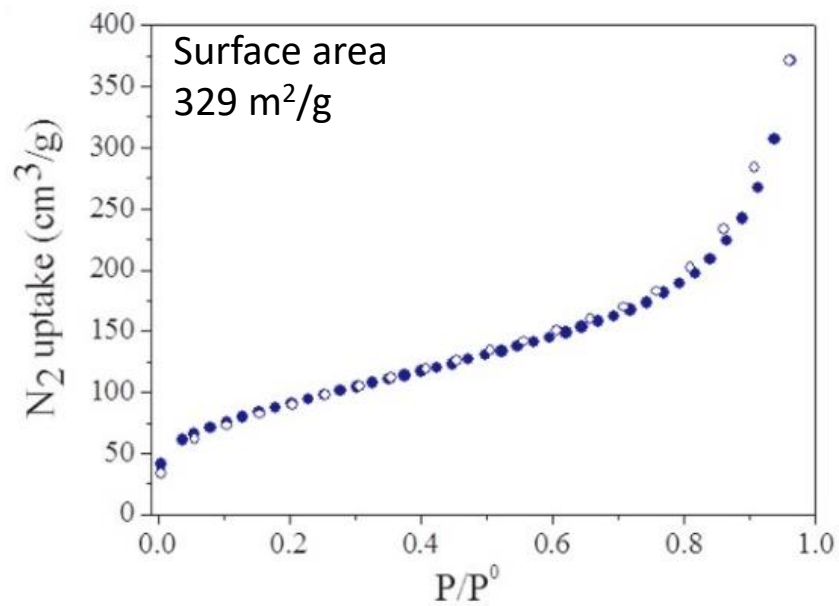
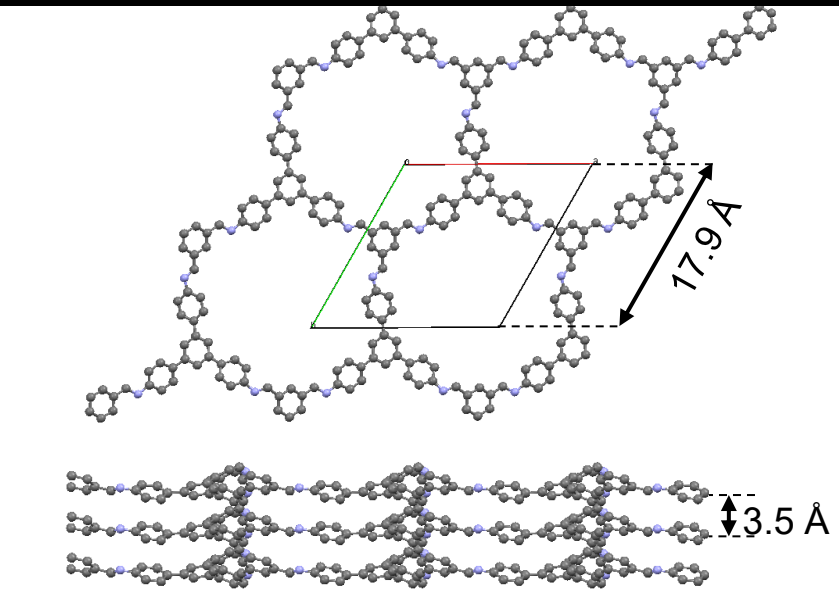
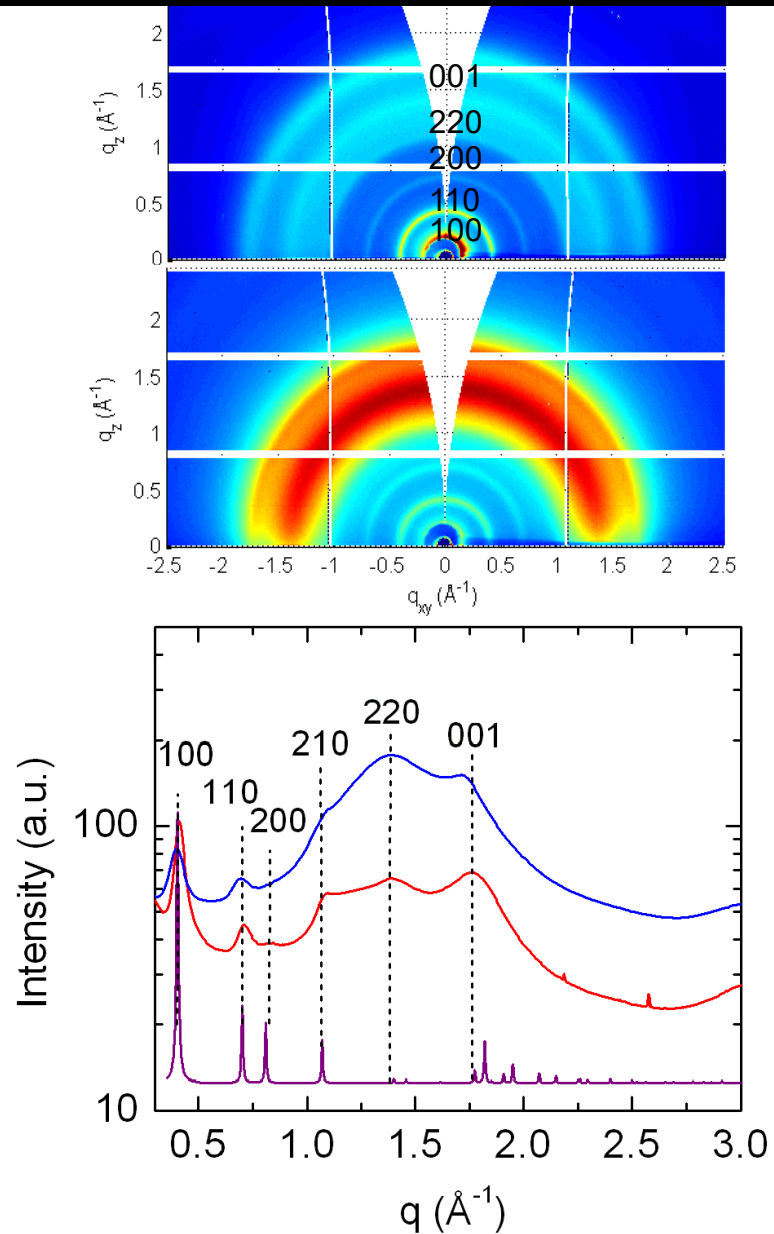
Mild conditions vs Solvothermal



Very unusual gel based on 2D flakes

IR and NMR (in solid) spectra confirm imine formation

GIXRD measurements & isotherm



First reported COF gel

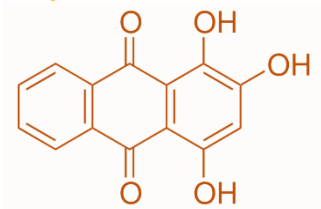
Gels: “Dynamic imine chemistry enables COF gelation under mild conditions”

First COF,
at R.T.!

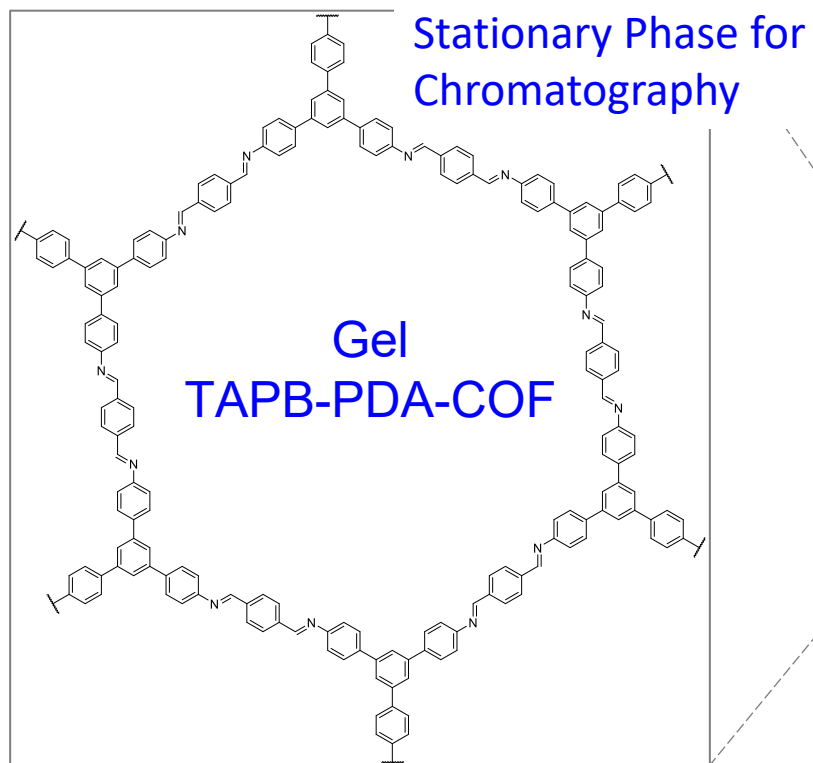
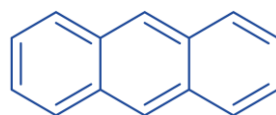


Uses of imine-based COF gels: Stationary Phase

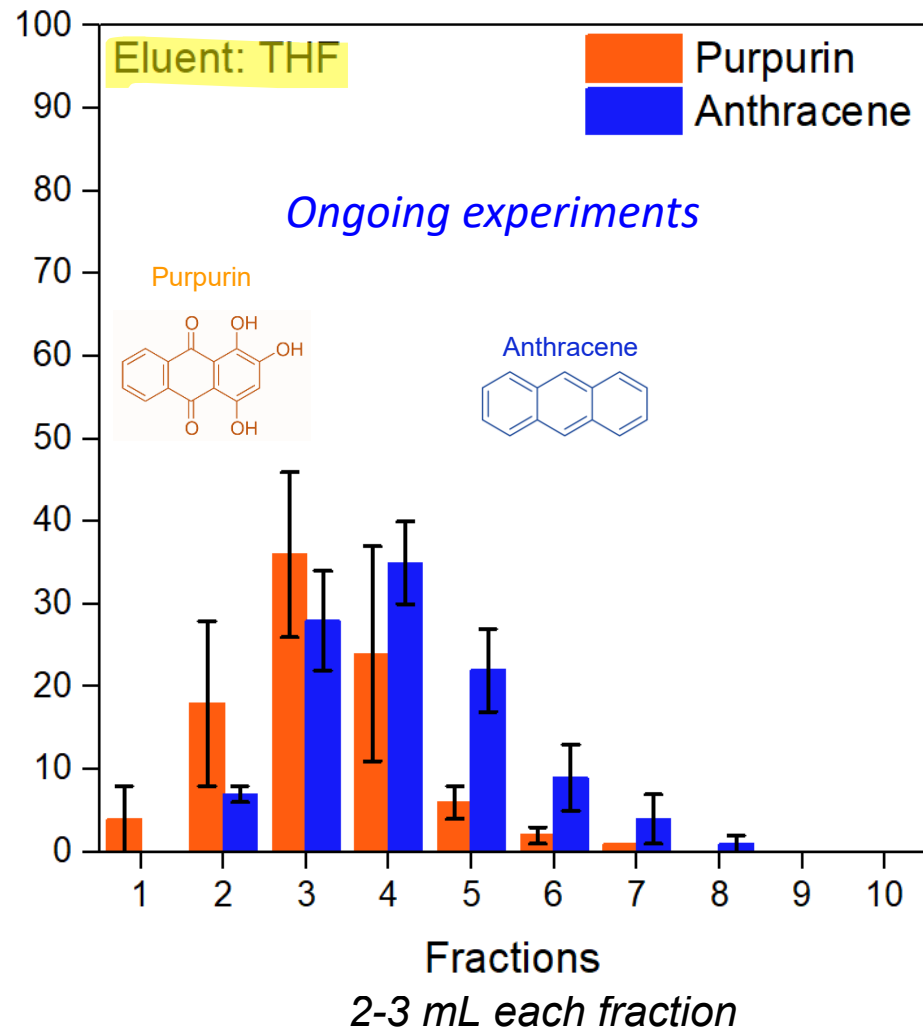
Purpurin



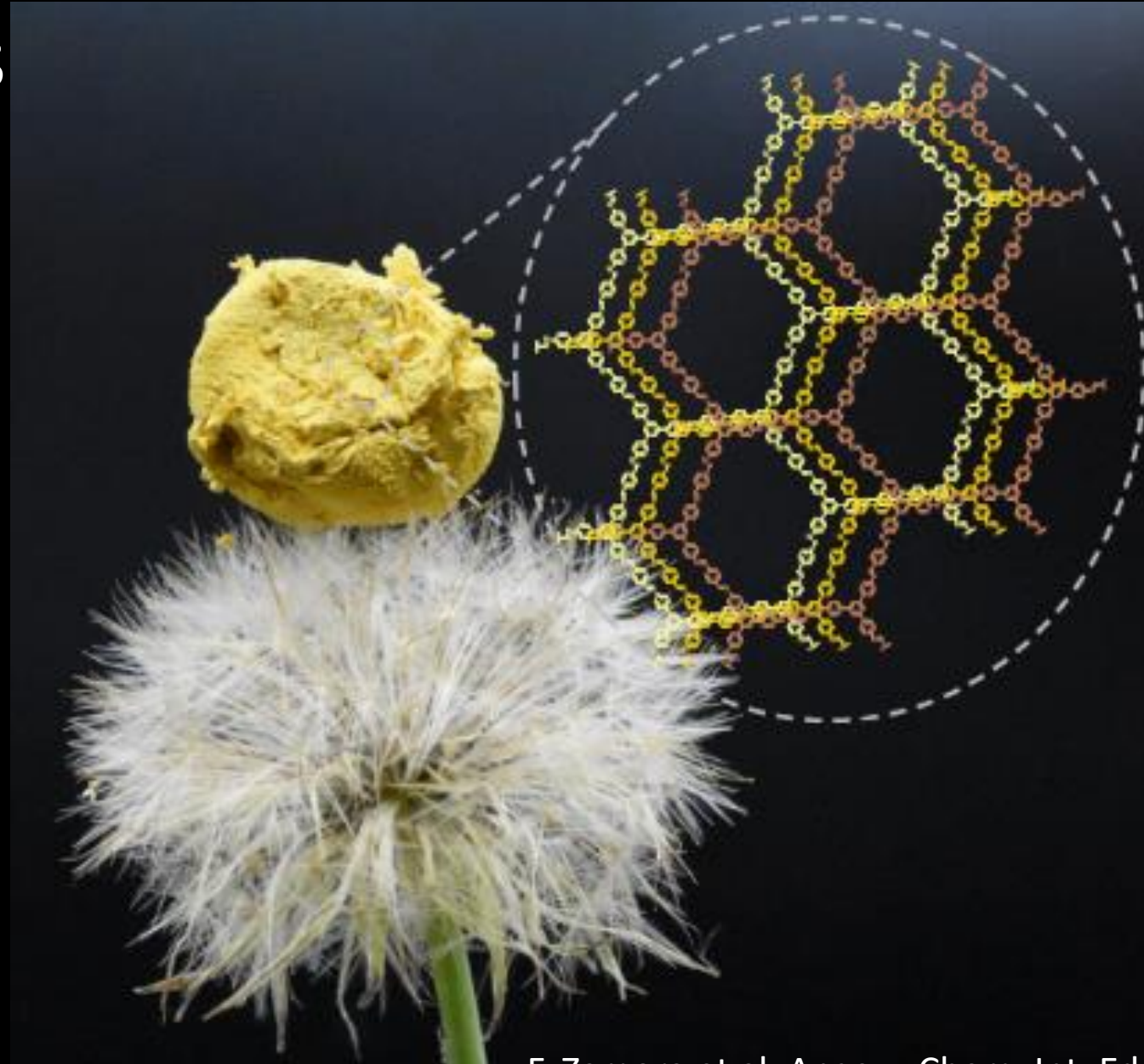
Anthracene



250 μL of 10^{-3} M Anthracene & Purpurin in THF



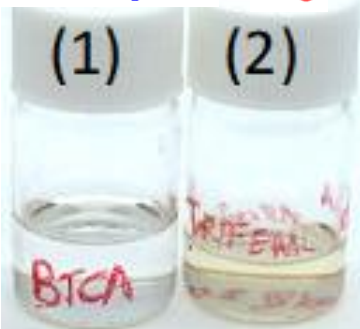
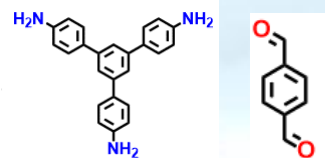
3. COF gels and aerogels: porous monoliths from molecular frameworks



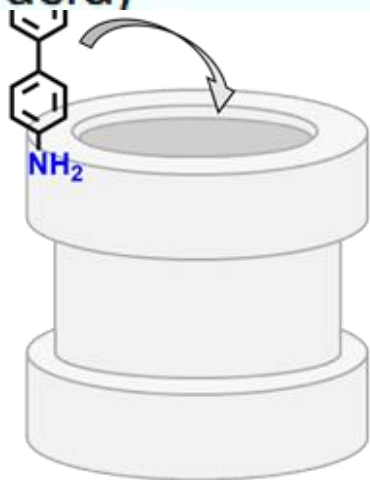
How to make a COF Aerogel



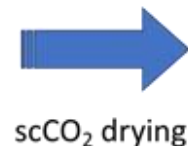
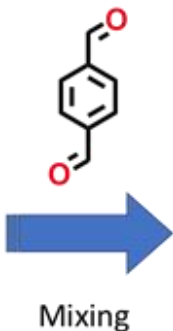
Jesus A. Martín



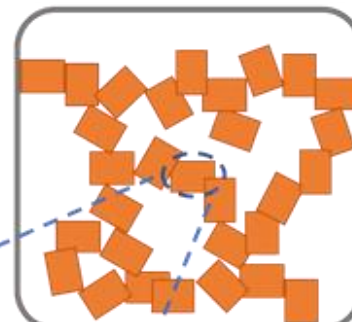
(Acetic acid)



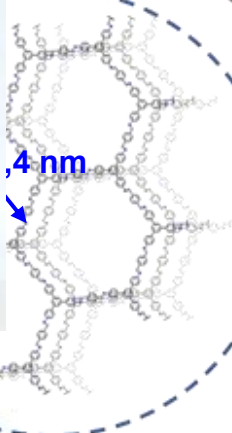
HAcO as solvent of reaction



Monolith of COF-aerogel



Hierarchical aerogel



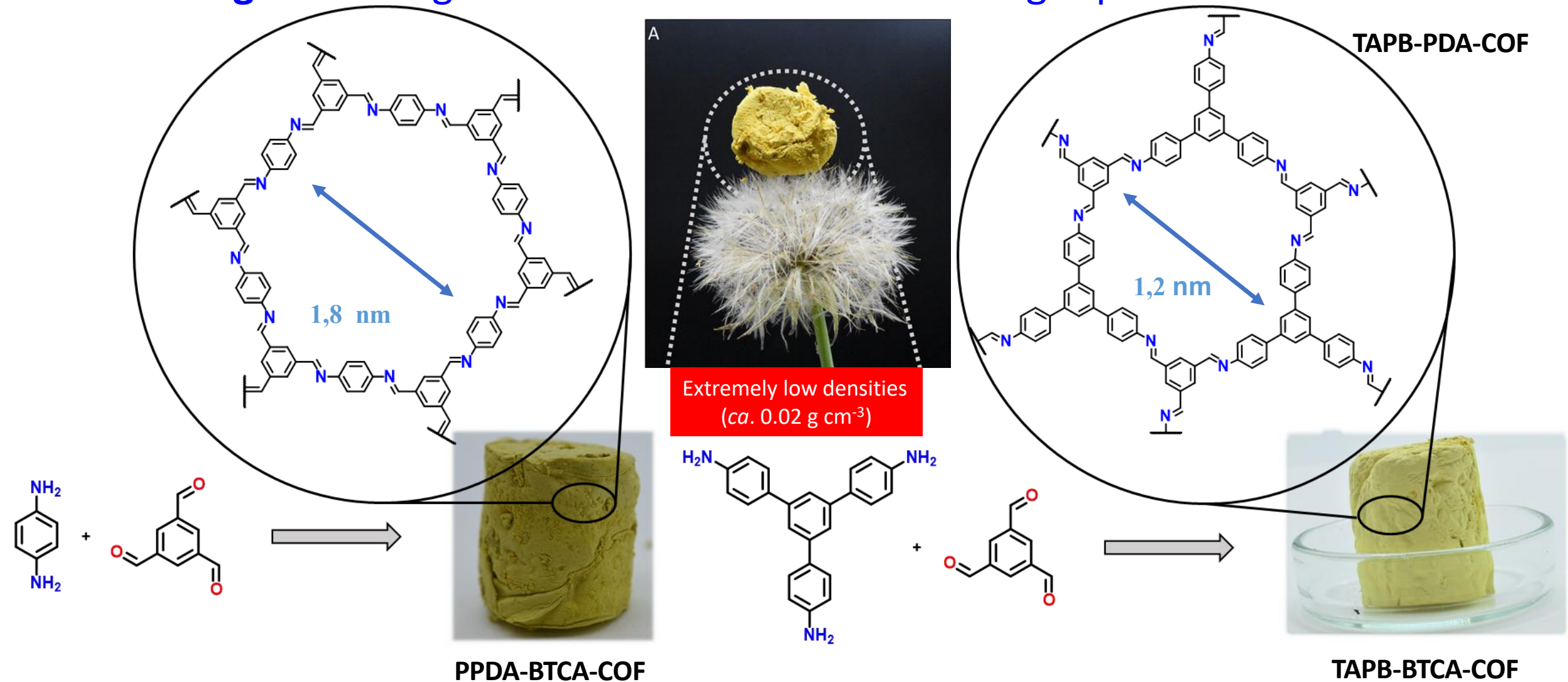
COF-nanoparticles mediated by solvent



Prof. D. Maspoch

COF Aerogels

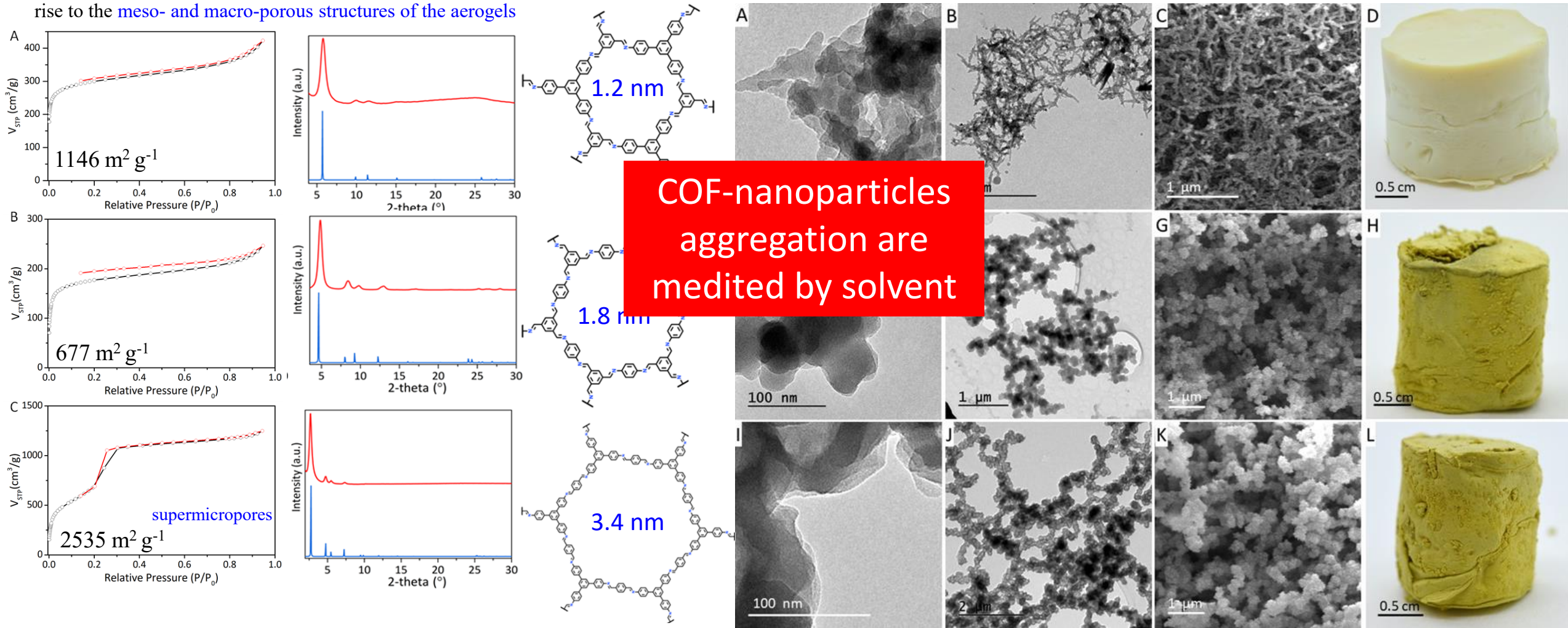
Aerogels: "COF gels can be converted into ultralight porous monoliths"



COF Aerogels

disordered porosity to stable interparticle aggregates that give rise to the meso- and macro-porous structures of the aerogels

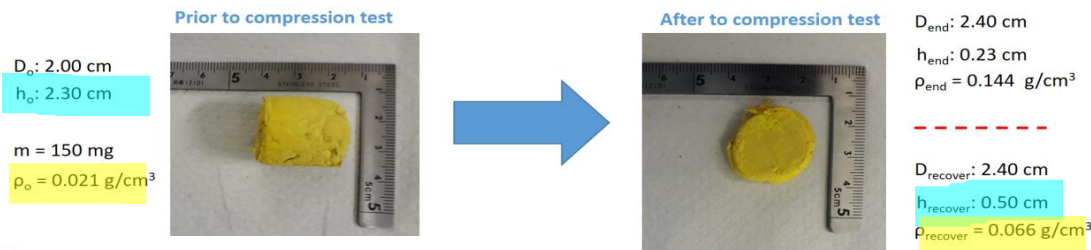
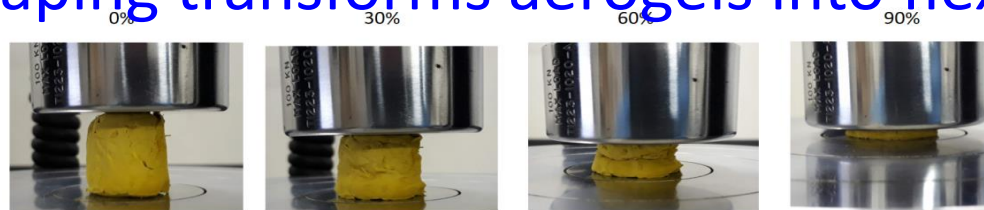
COF nanolayers connected to form 3D aerogel structure



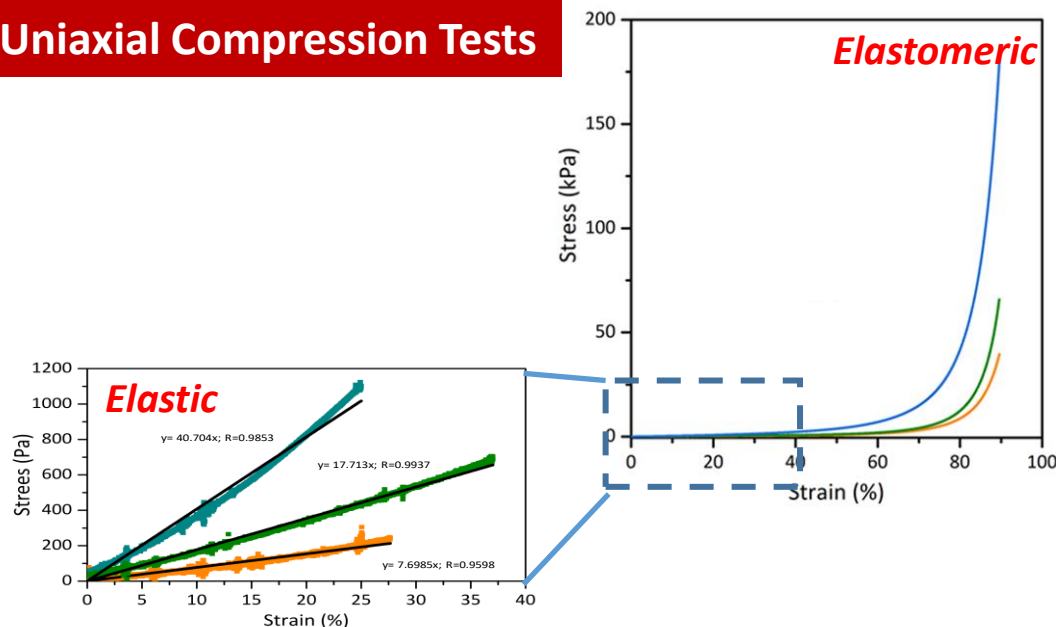
4. From aerogels to membranes: shaping without losing function

Mechanical Properties of COF Aerogels

Membranes: Pressure-induced shaping transforms aerogels into flexible membranes



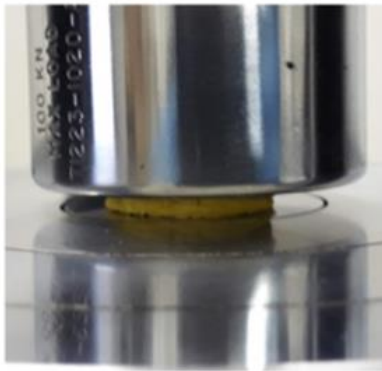
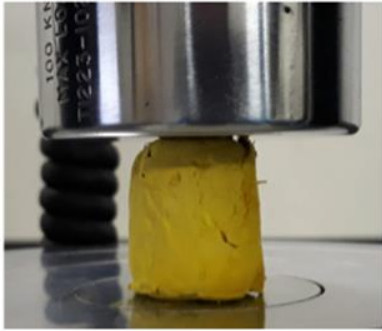
Uniaxial Compression Tests



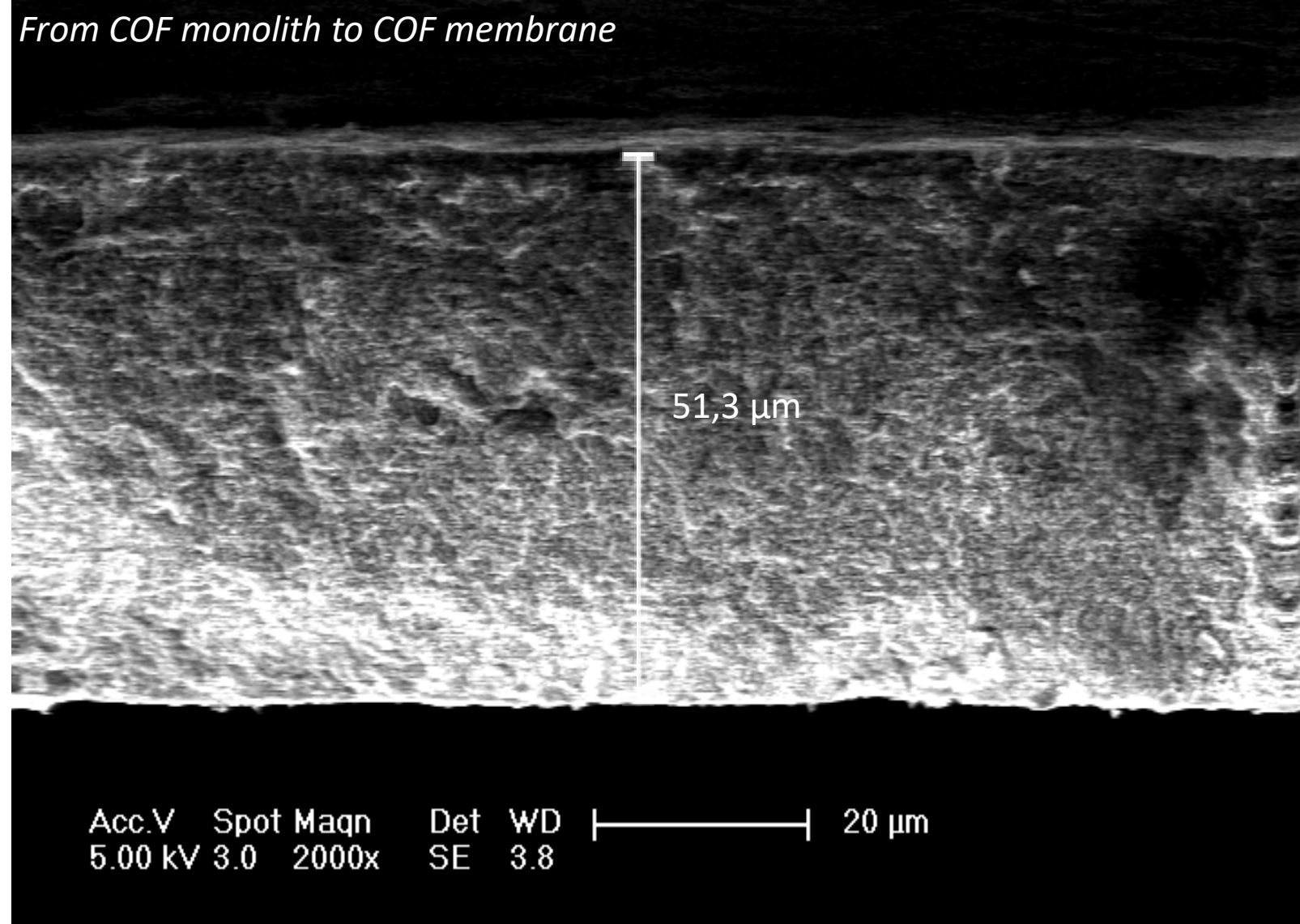
Sample	E (Pa)	$E_{specific}$ (Pa m ³ Kg ⁻¹)
TAPB-BTCA-AGCOF	4070.4	208.64
PPDA-BTCA-AGCOF	1771.3	85.33
TAPB-PDA-AGCOF	769.85	44.48

Membrane Formation under Pressure from COF Aerogels

From COF monolith to COF membrane



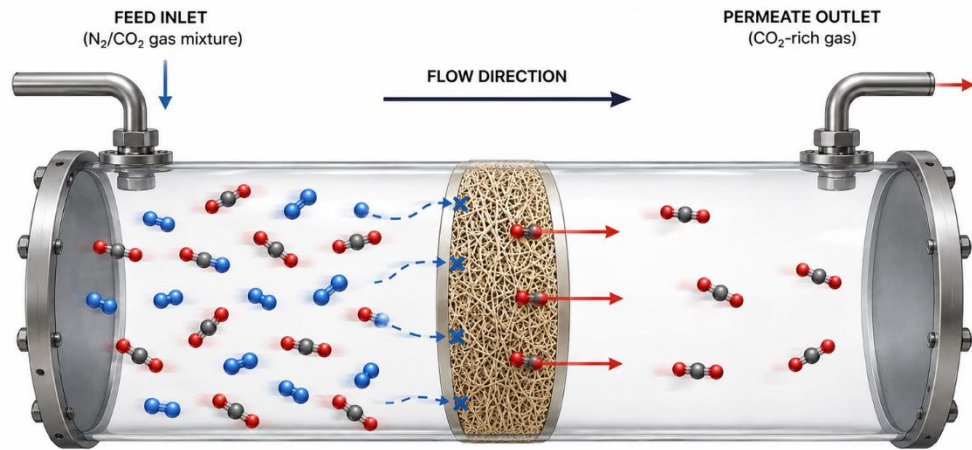
120 MPa



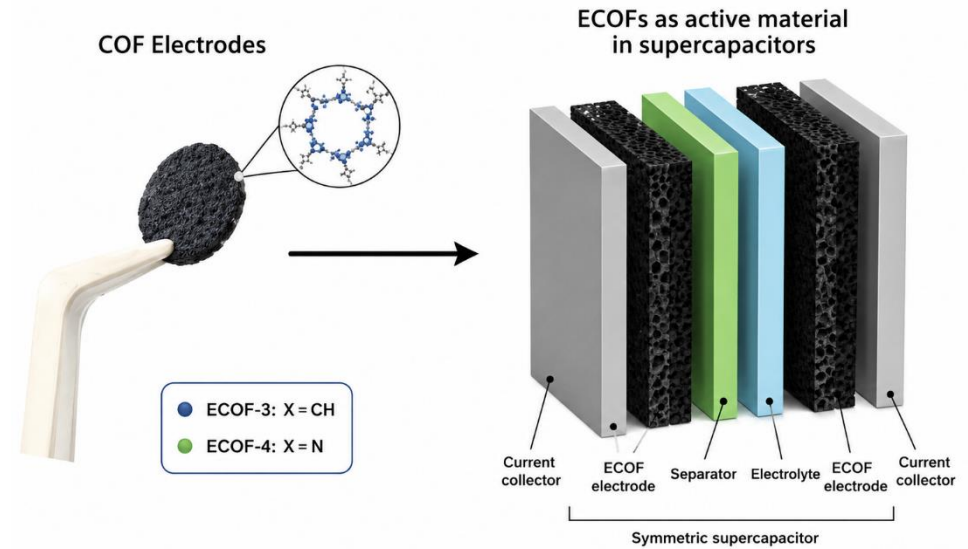
Flexible COF membranes: Crystallinity and Hierarchical Porosity

Properties & Applications of COF Aerogels

Gas mixture separation



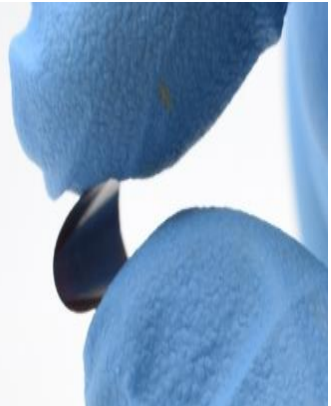
Supercapacitors



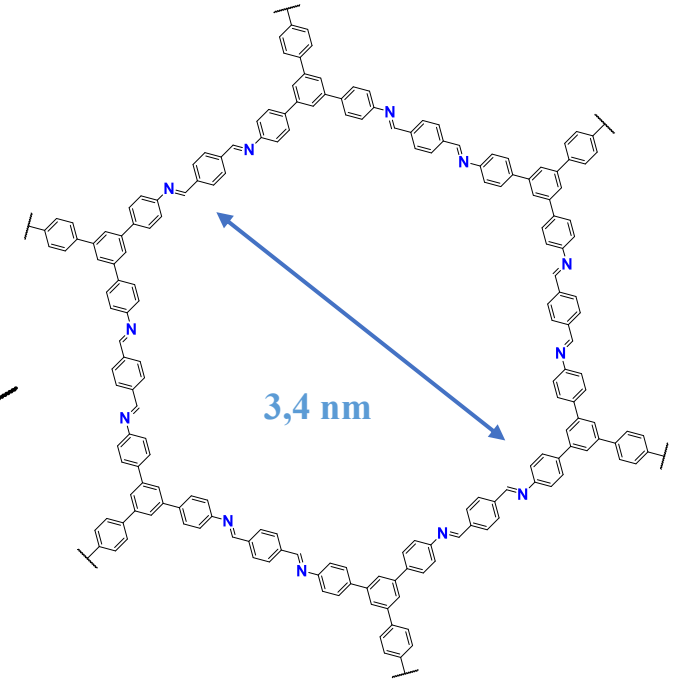
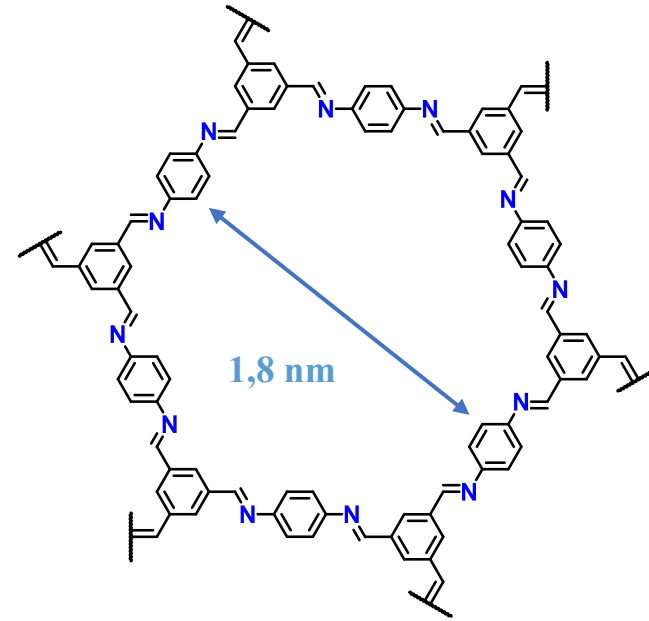
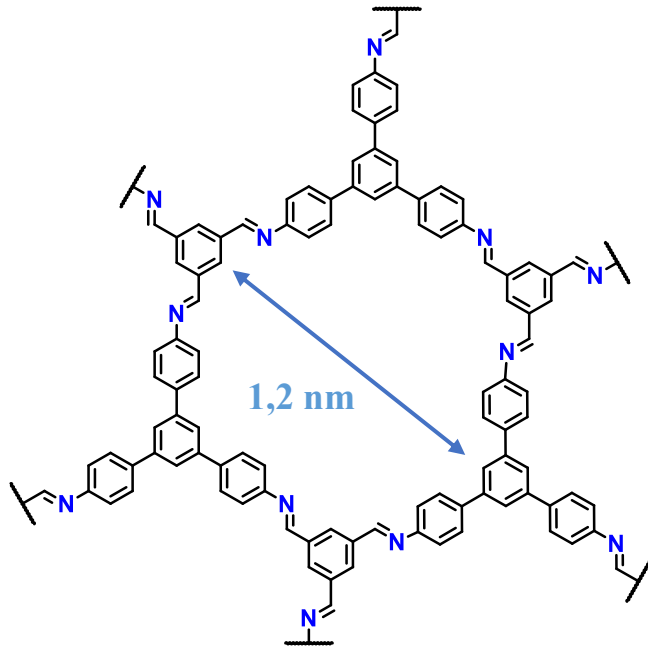
Gas Separation using COF membranes



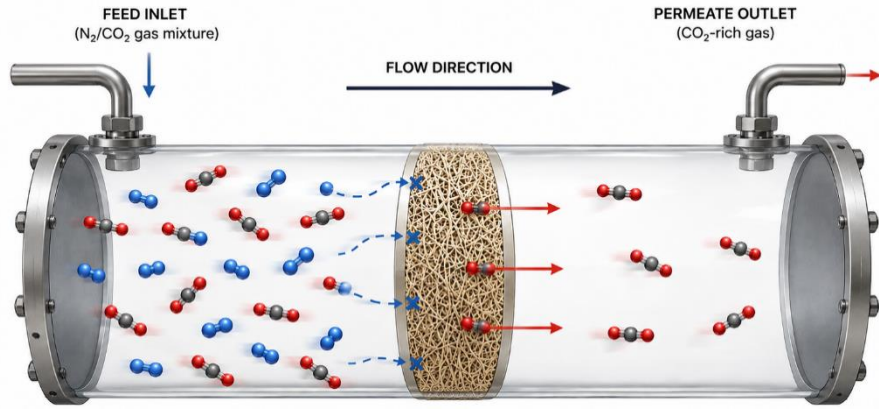
Prof. Dan Zhao



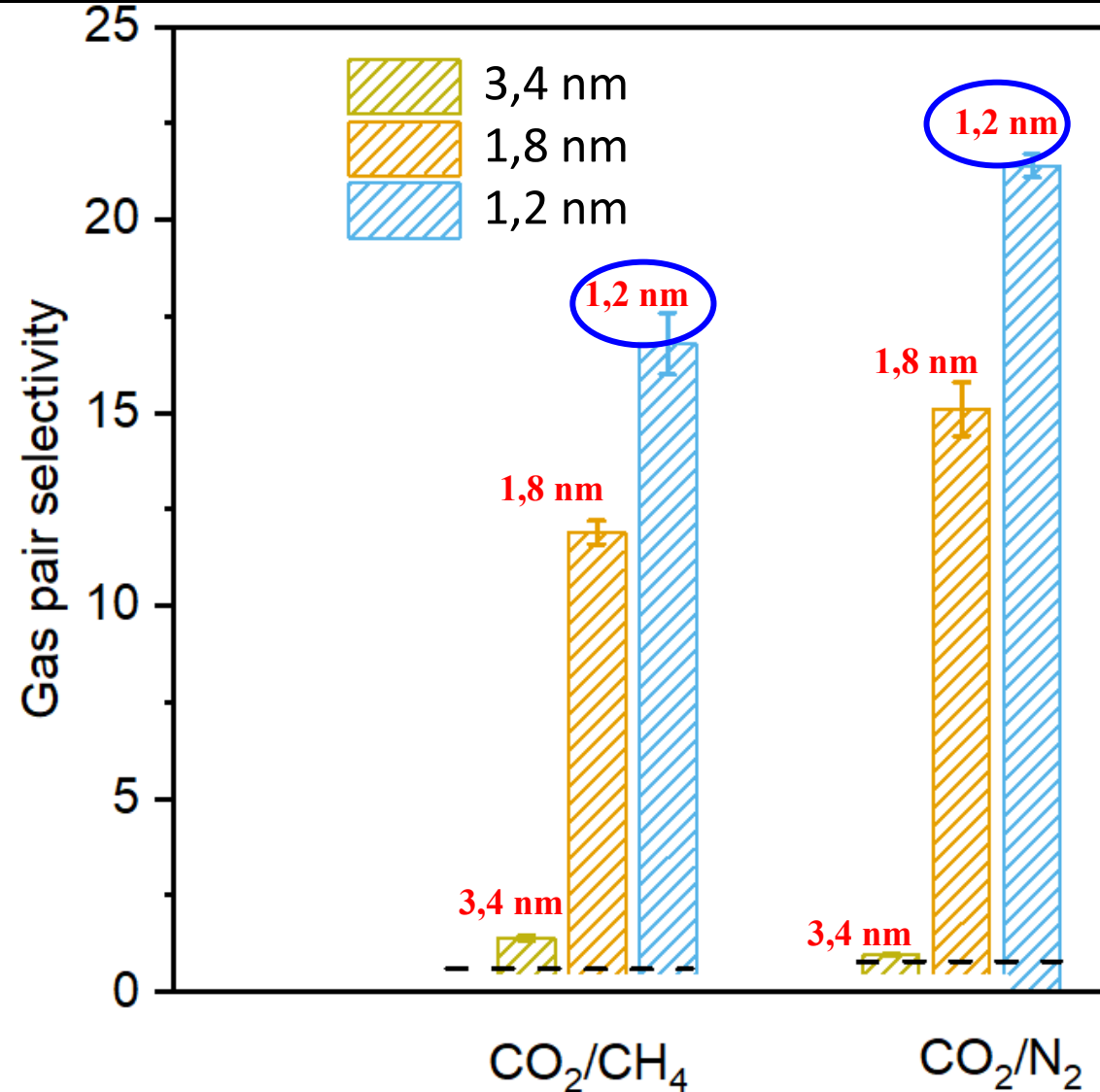
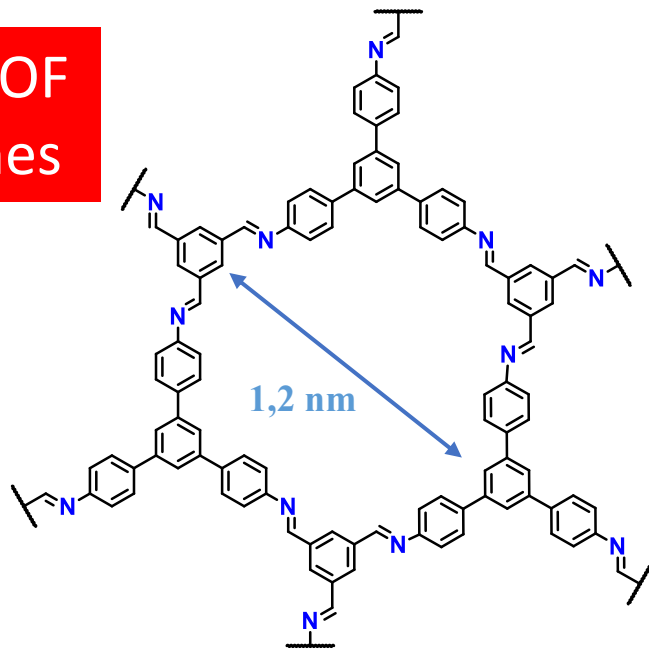
Flexible COF membranes



Gas Separation using COF membranes



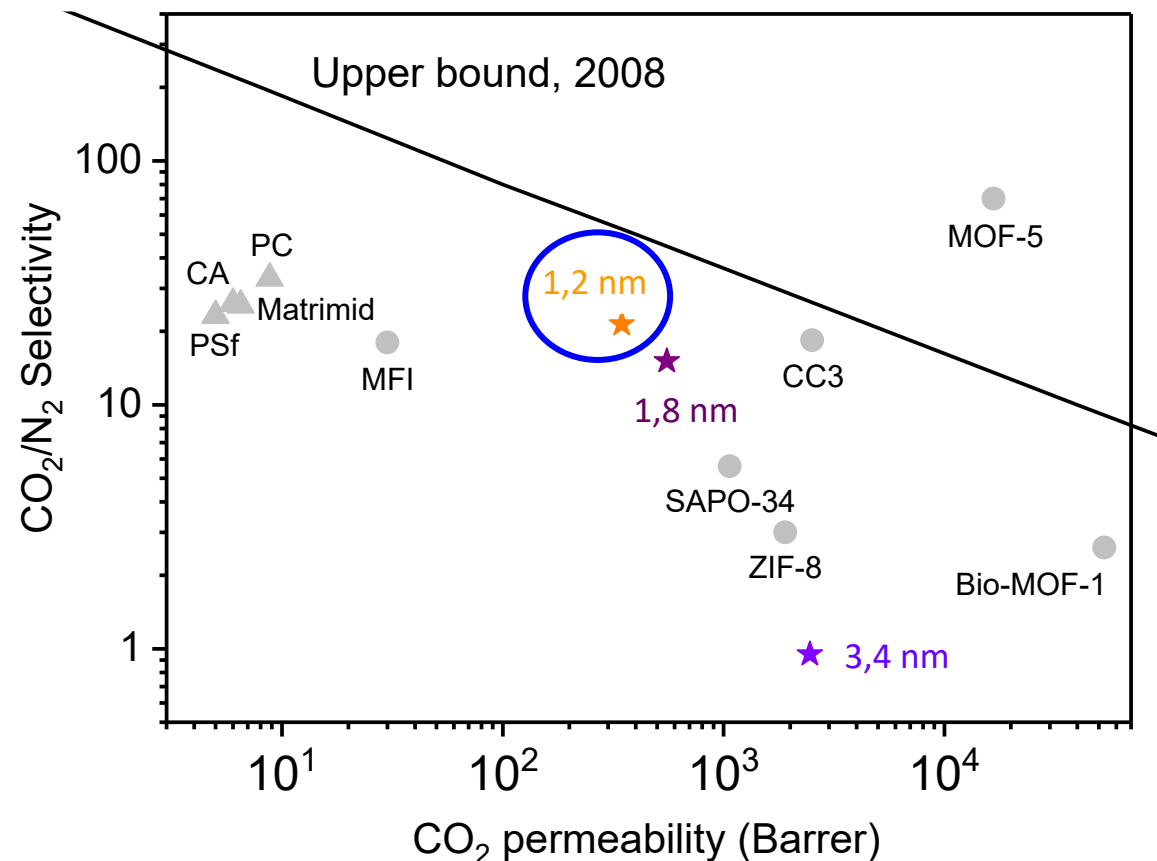
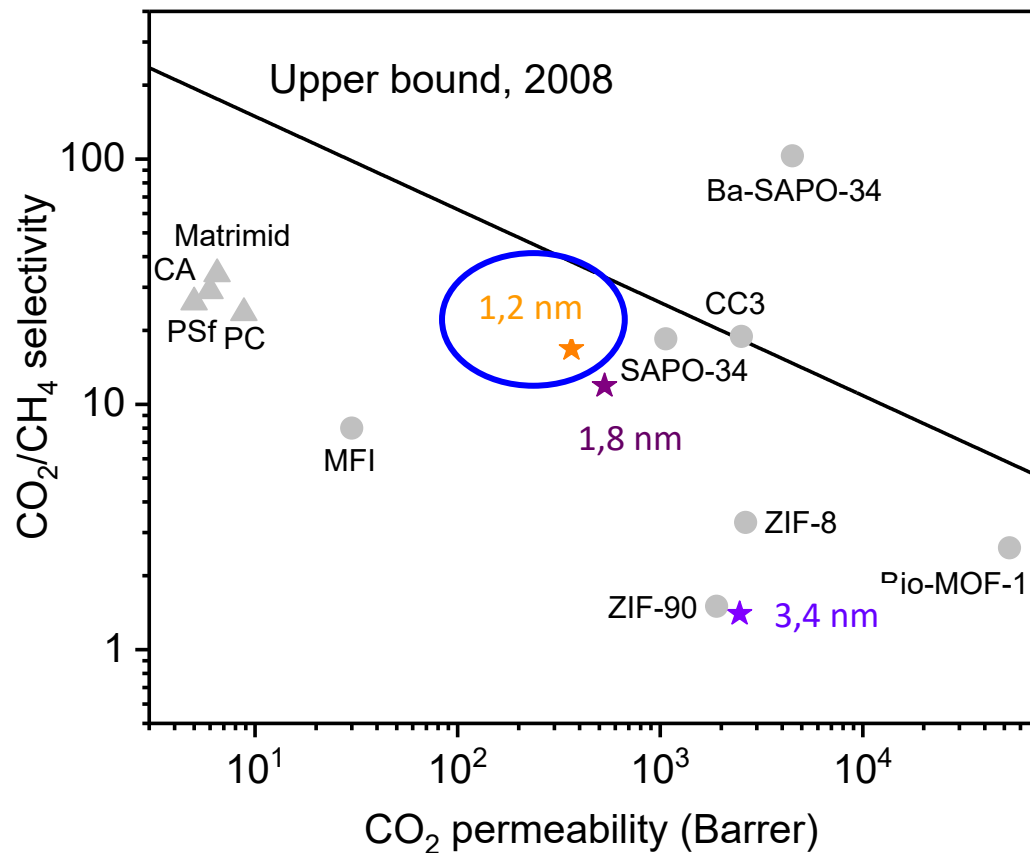
Flexible COF membranes



The mixed gas pair selectivity is higher compared to the ideal gas pair selectivity owing to the sorption and diffusion competition between the gas mixtures.

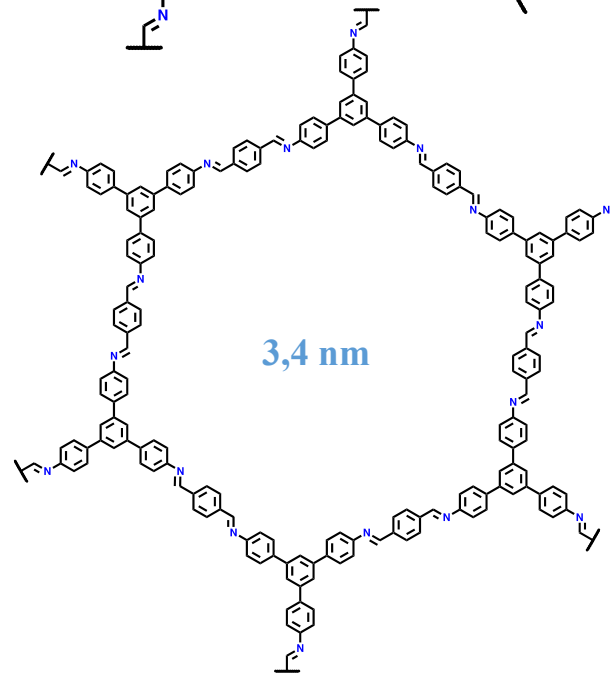
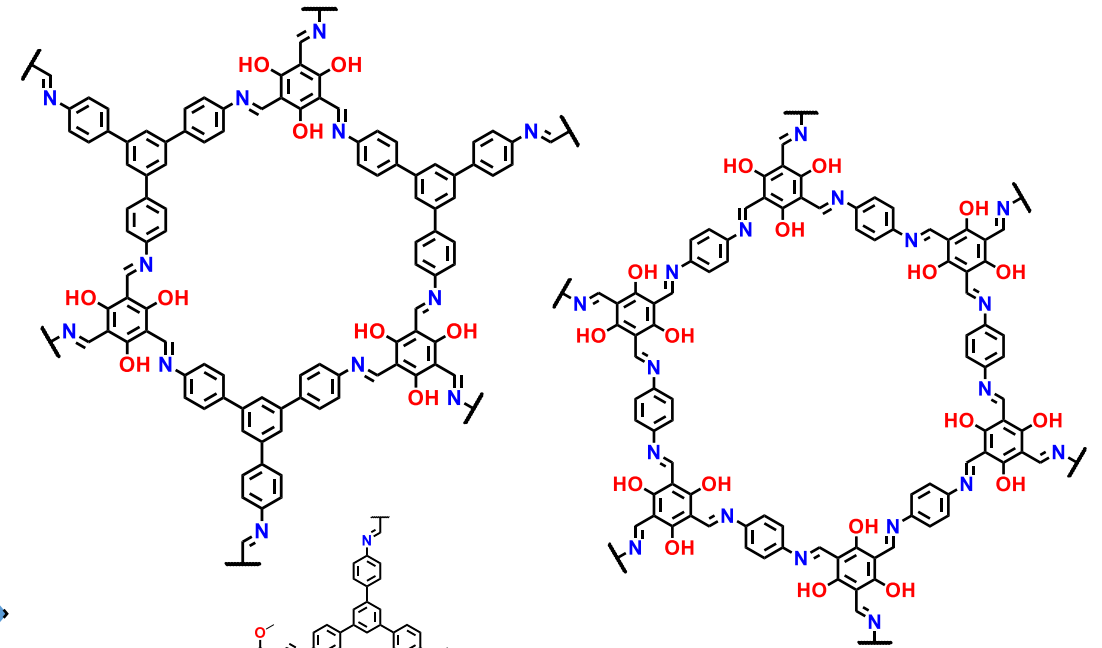
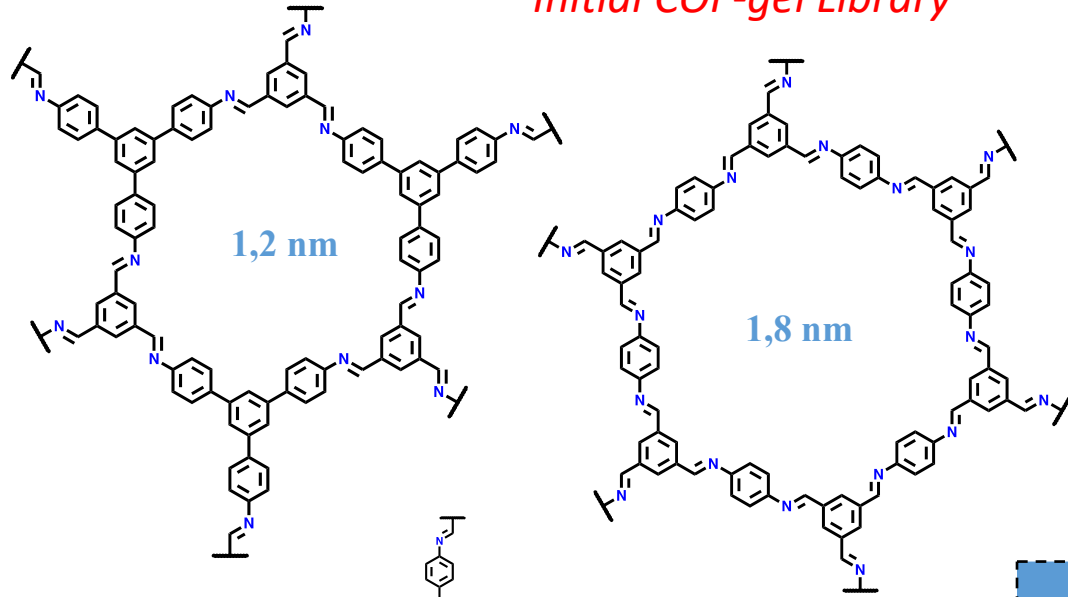
COF membranes Performances for Gas Separation

COF membranes show **much higher CO₂ permeability compared with commercial membranes** and the **separation performance of our membranes is close to the 2008 upper bound limits**

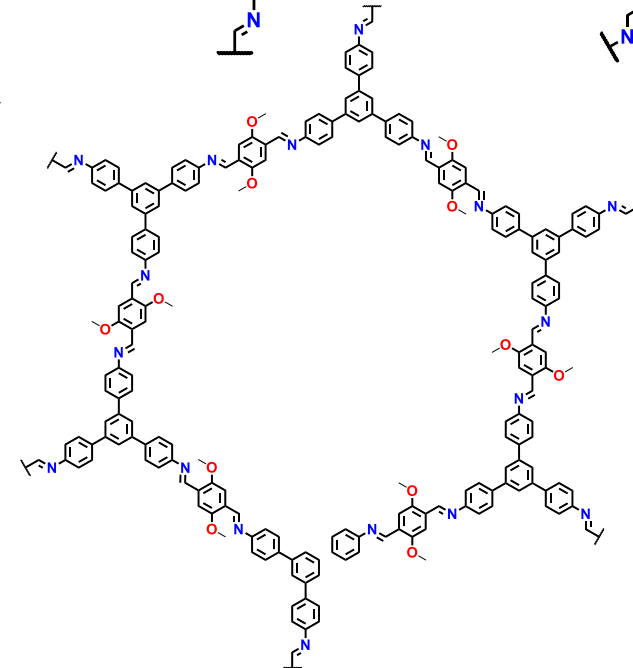


Imine-based COFs: Gel to Gel to Aerogel synthesis

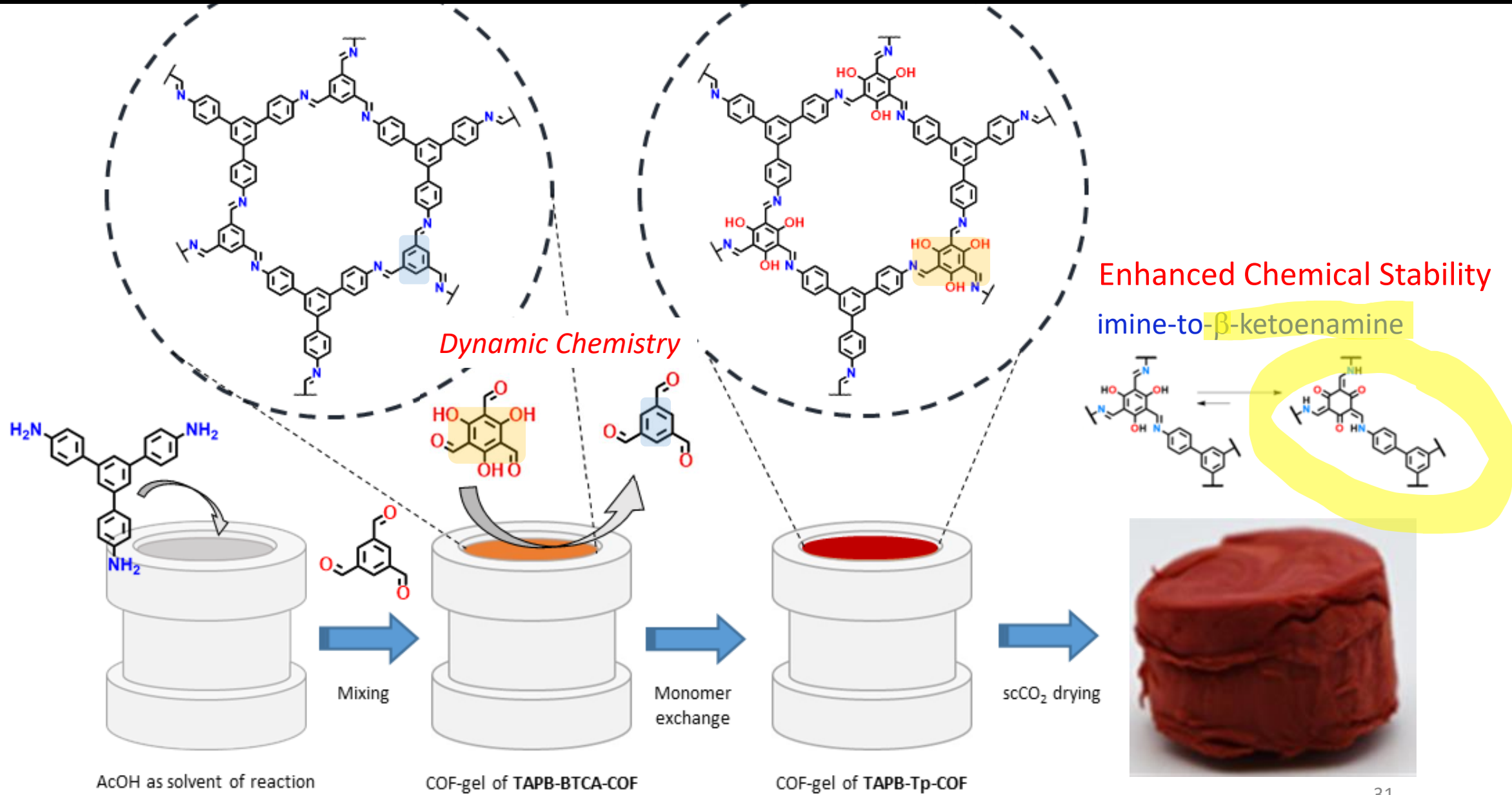
Initial COF-gel Library



Dynamic Bonds



Imine-based COFs: Gel to Gel to Aerogel synthesis



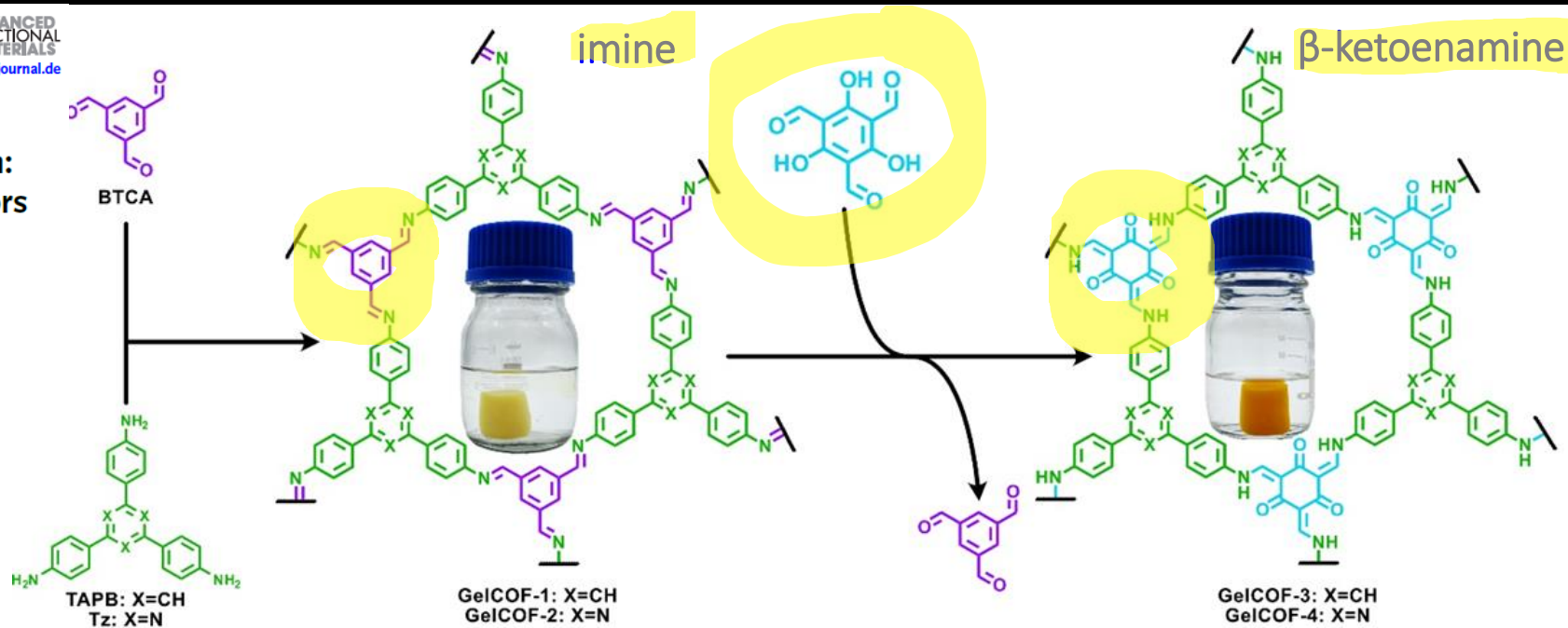
β -Ketoenamine-Linked COFs via Gel-to-Gel Monomer Exchange Reaction

RESEARCH ARTICLE

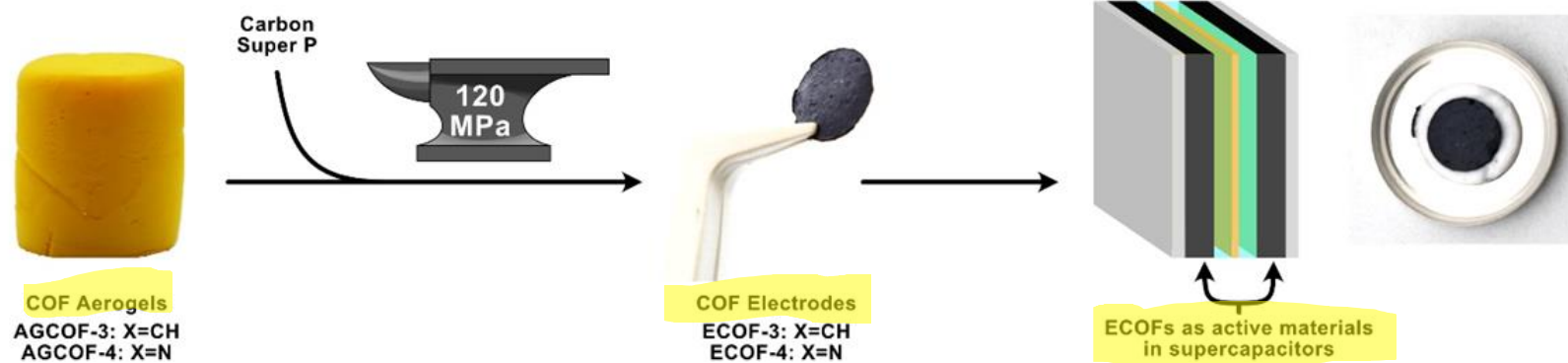
ADVANCED
FUNCTIONAL
MATERIALS
www.afm-journal.de

β -Ketoenamine-Linked Covalent Organic Frameworks Synthesized via Gel-to-Gel Monomer Exchange Reaction: From Aerogel Monoliths to Electrodes for Supercapacitors

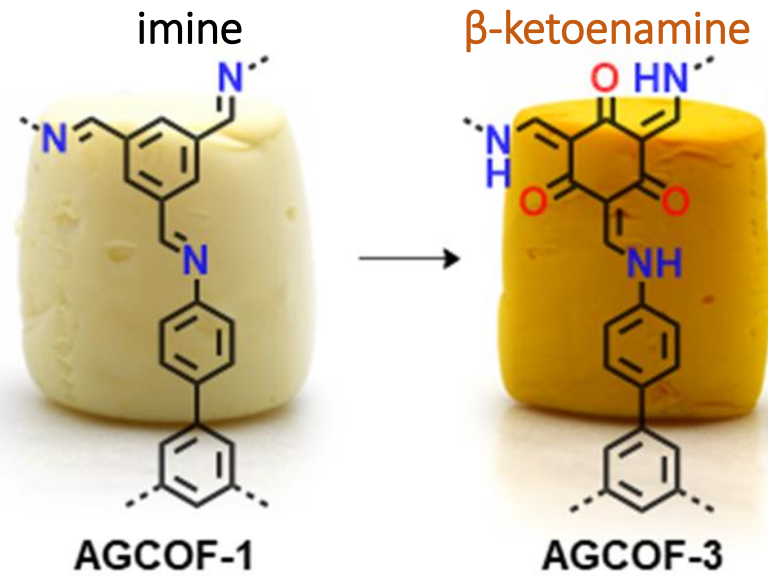
Jesús Á. Martín-Illán, Laura Sierra, Ana Guillem-Navajas, José Antonio Suárez, Sergio Royuela, David Rodríguez-San-Miguel, Daniel Maspoch, Pilar Ocón, and Félix Zamora*



Enhanced Chemical Stability



Carbon@COF Aerogels: Electrochemical Characterization



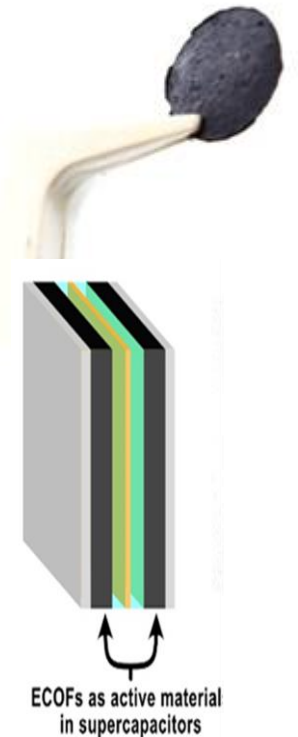
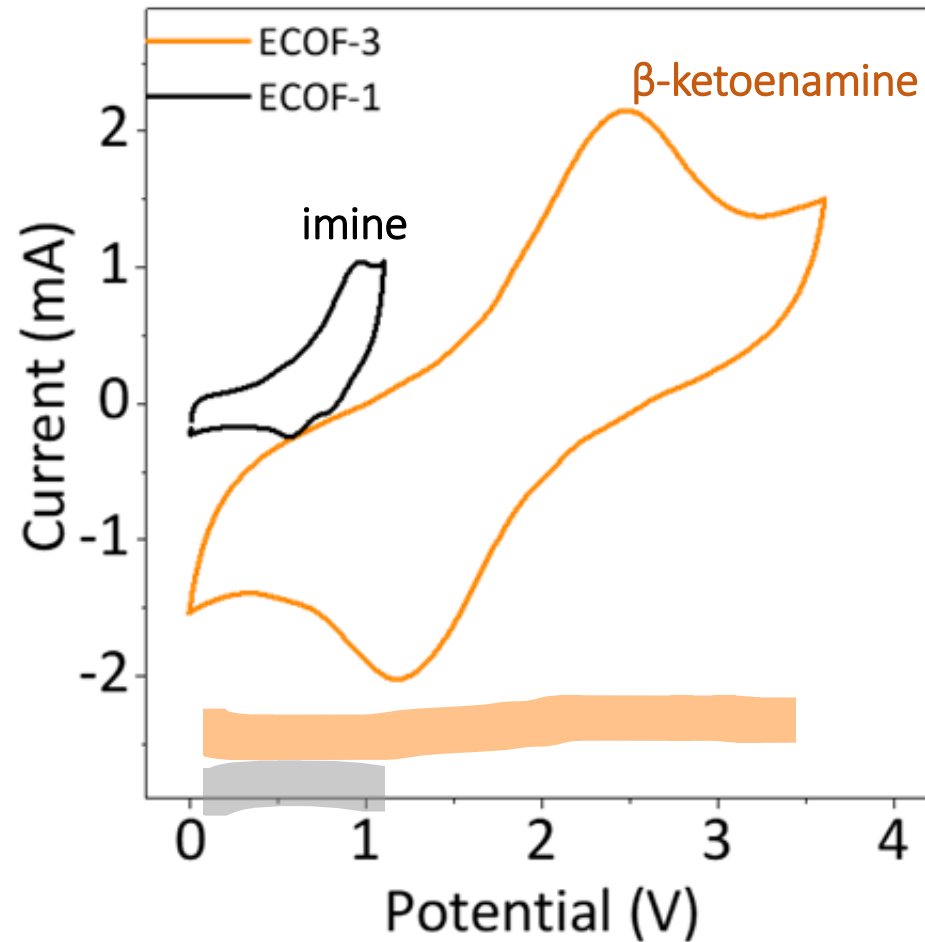
Enhanced Chemical Stability

Capacitance Values (without TFA)

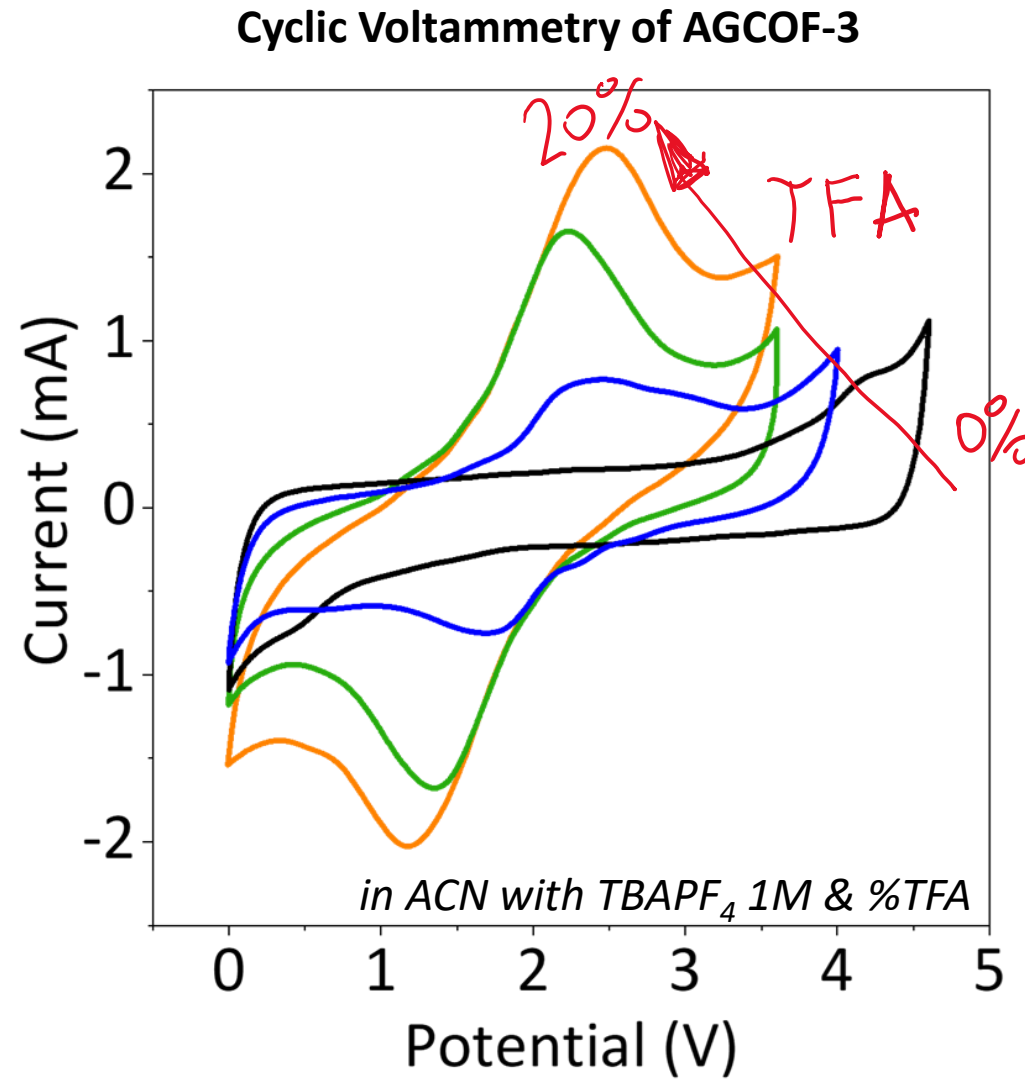
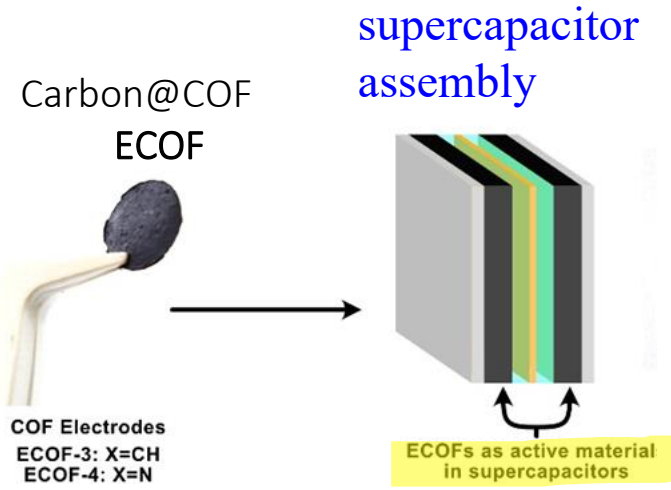
22 mF cm⁻² ECOF-3 (β -ketoenamine)

3.6 mF cm⁻² ECOF-1 (imine)

Cyclic Voltammetry of ECOF-3 and ECOF-1
using 20 % of TFA with a 50 mV s⁻¹ scan rate



Carbon@COF Aerogels: Electrochemical Characterization



in ACN with TBAPF₄ 1M & %TFA

Capacitance Values (20% TFA):

- 82 mF cm⁻² ECOF-3
- 88 mF cm⁻² ECOF-4

Excellent stability at a high current density rate (2.0 mA cm⁻²) over 10,000 charge-discharge cycles

Capacitance Values (without TFA)

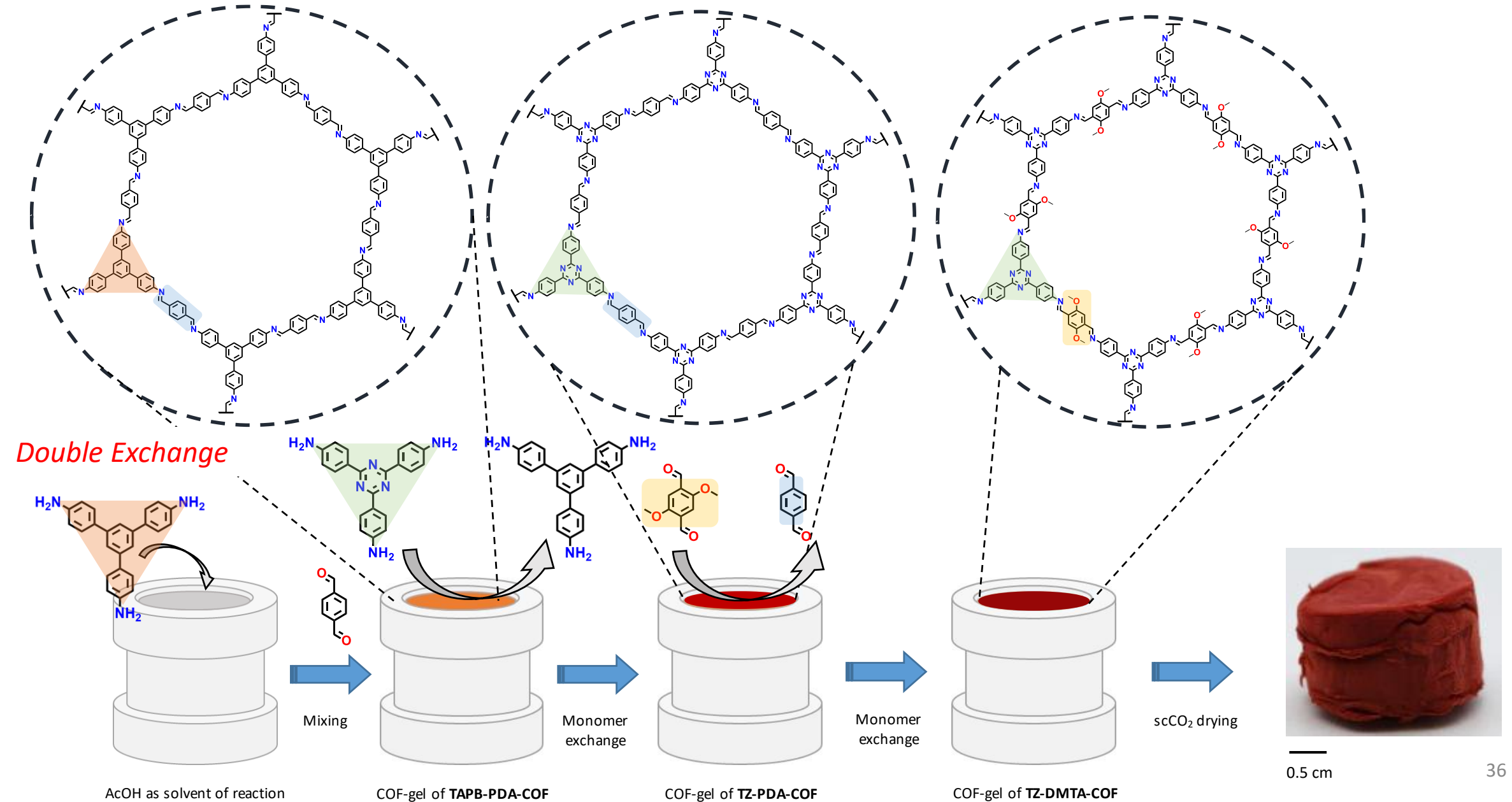
- 22 mF cm⁻² ECOF-3
- 18 mF cm⁻² ECOF-4

Carbon@COF Aerogels: Supercapacitors

Comparative electrochemical performance of different COF based supercapacitors

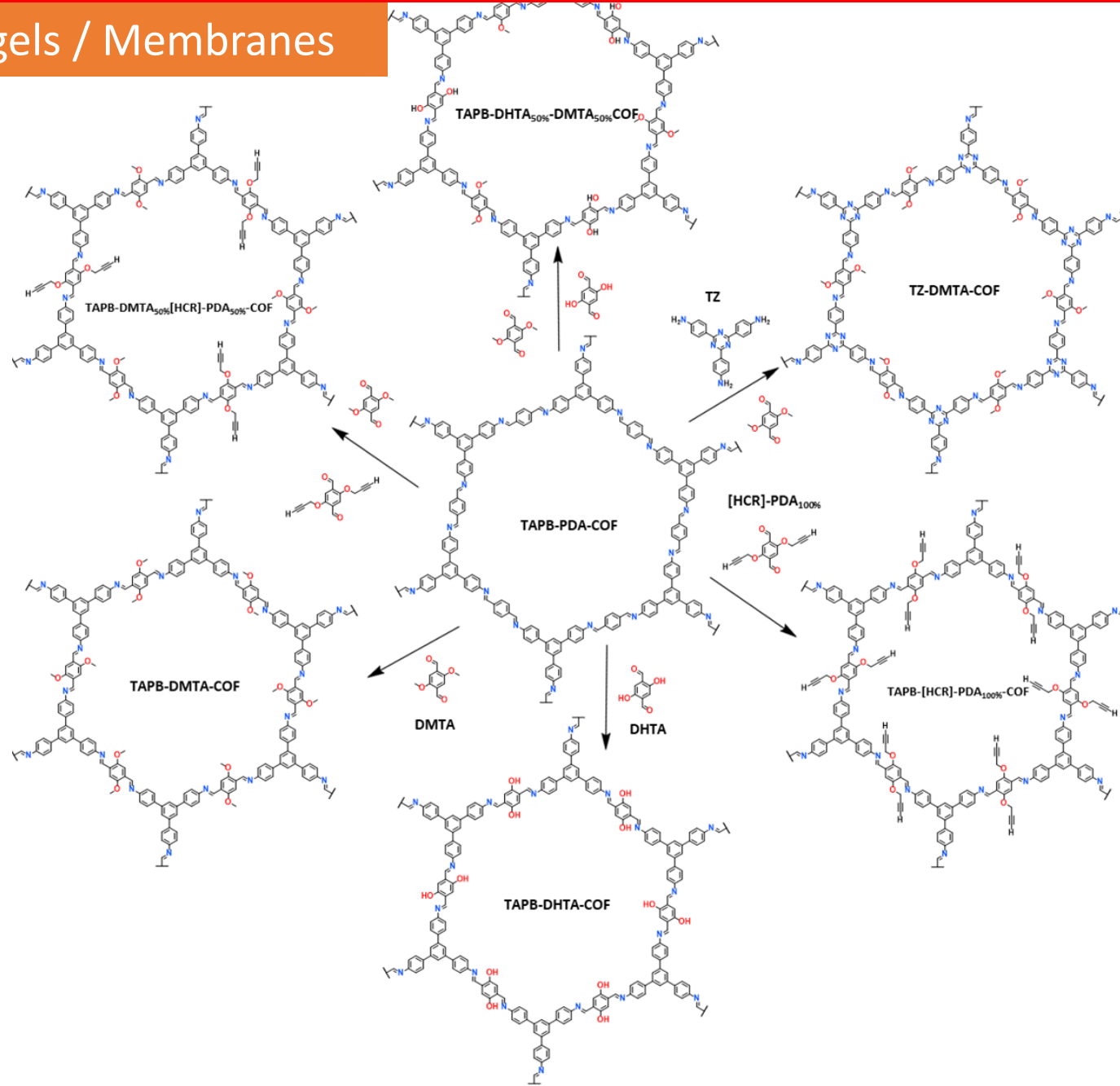
Active material	Electrolyte	Capacitance (mF cm ⁻²)	Energy (μW h cm ⁻²)	Power (μWcm ⁻²)
Dq ₁ Da ₁ Tp COF (Anthraquinone)	PVA-H ₂ SO ₄ gel electrolyte	8.5 (0.39 mA cm ⁻²)	0.3	960
Dq ₁ Tp COF (Anthracene)	PVA-H ₂ SO ₄ gel electrolyte	12 (0.39 mA cm ⁻²)	0.4	980
TpOMe-DAQ COF	PVA-H ₂ SO ₄ gel electrolyte	84 (0.25 mA cm ⁻²)	2.9	61.8
TpPa-(OH) ₂ COF	1 M phosphate buffer	98 (1.3 mA cm ⁻²)	19.4	No data found
ECOF-3	TBABF ₄ 1 M in ACN + 20% TFA	82 (2.0 mA cm ⁻²)	148	7100
ECOF-4	TBABF ₄ 1 M in ACN + 20% TFA	88 (2.0 mA cm ⁻²)	158	7100

Imine-based COFs: Gel to Gel to Aerogel synthesis



Claim : Dynamic Gel to Gel to Aerogel Exchanges – New Synthetic Platform

Gels / Shapping Aerogels / Membranes





5. 3D printing: toward designed COF objects

3D Printing COFs

A new methodology enabling the 3D printing of pure COF monoliths

ADVANCED FUNCTIONAL MATERIALS

Research Article | [Open Access](#) |  

3D Printing of Covalent Organic Frameworks: A Microfluidic-Based System to Manufacture Binder-Free Macroscopic Monoliths

Sergio Royuela, Semih Sevim, Guillermo Hernanz, David Rodríguez-San-Miguel, Peter Fischer, Carlos Franco, Salvador Pané, Josep Puigmartí-Luis ✉, Félix Zamora ✉

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Prof. Josep Puigmartí

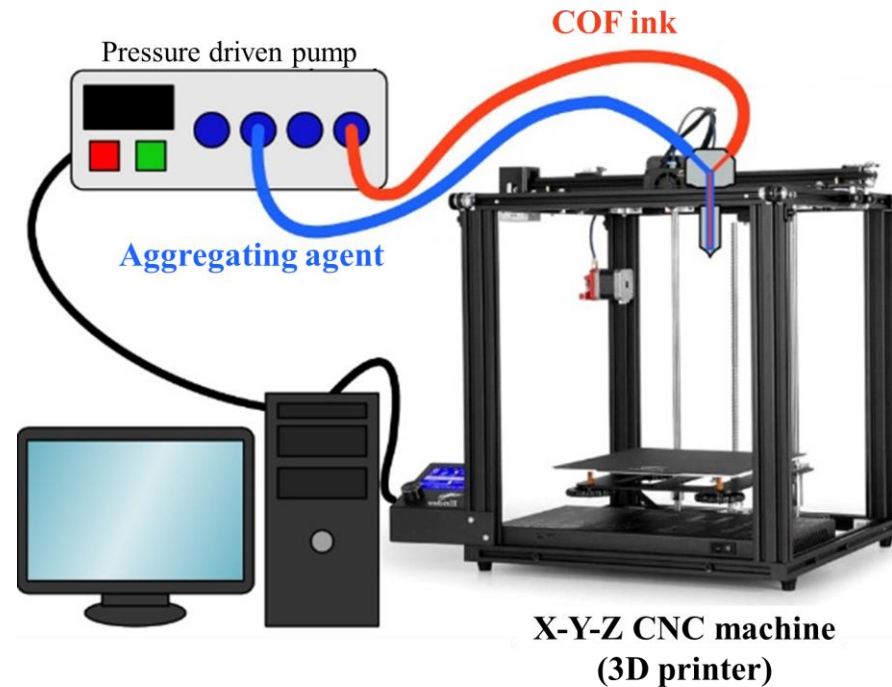


Dr. Sergio Royuela

1 - Ink preparation

2 - 3D printer development

3 - 3D printing



Biomimetic Synthesis of Sub-20 nm Covalent Organic Frameworks in Water

Carlos Franco,¹ David Rodríguez-San-Miguel,¹ Alessandro Sorrenti, Semih Sevim, Ramon Pons, Ana E. Platero-Prats, Marko Pavlovic, Istvan Szilágyi, M. Luisa Ruiz Gonzalez, José M. González-Calbet, Davide Bochicchio, Luca Pesce, Giovanni M. Pavan, Inhar Imaz, Mary Cano-Sarabia, Daniel Maspoch, Salvador Pané, Andrew J. de Mello, Felix Zamora,* and Josep Puigmartí-Luis*

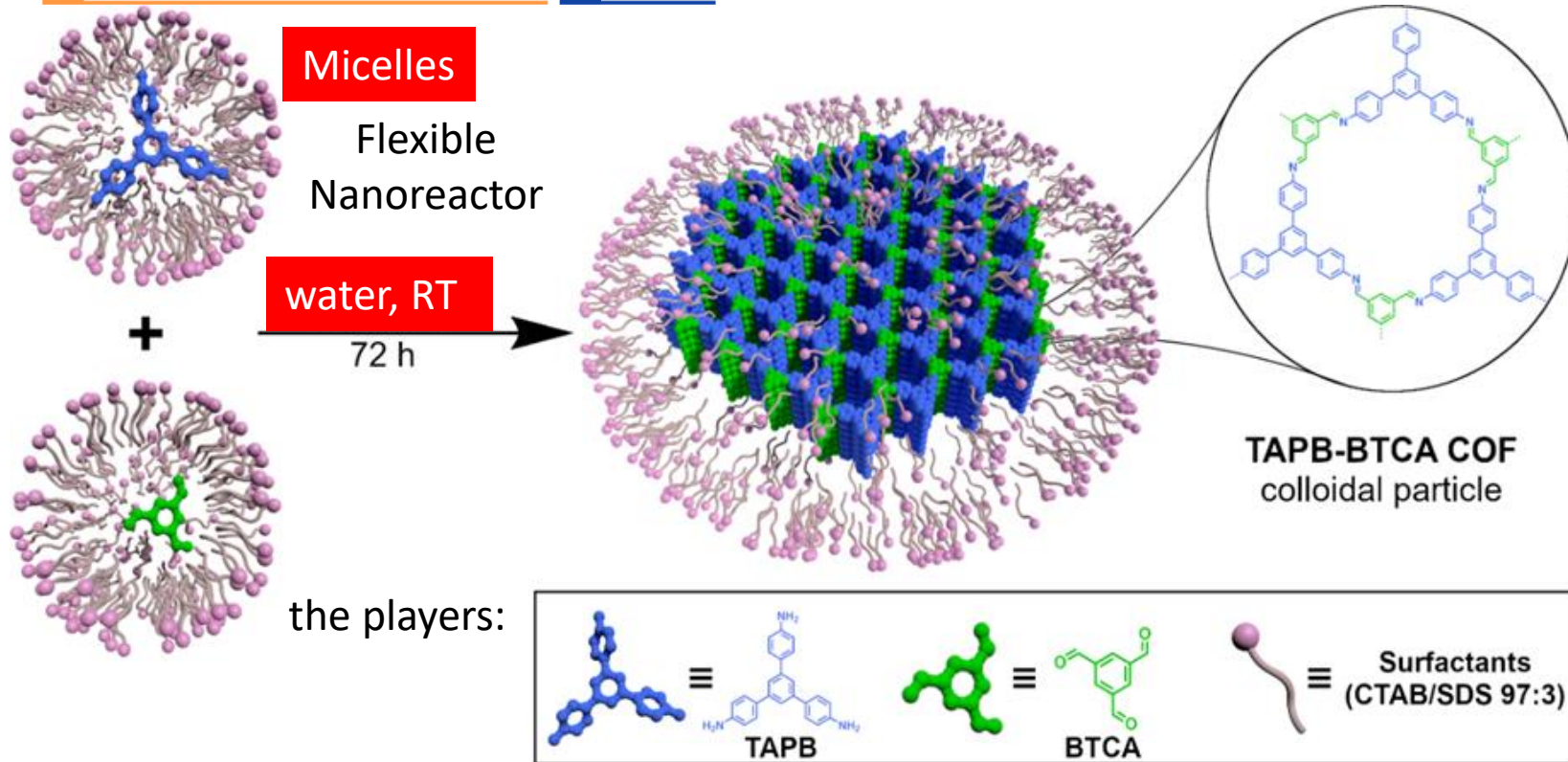
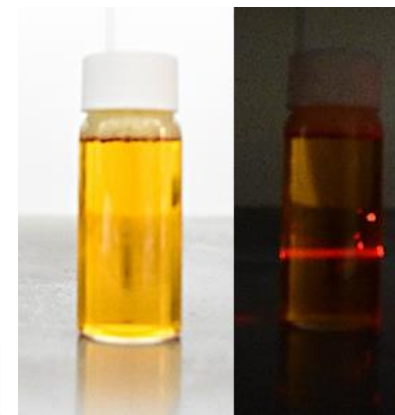
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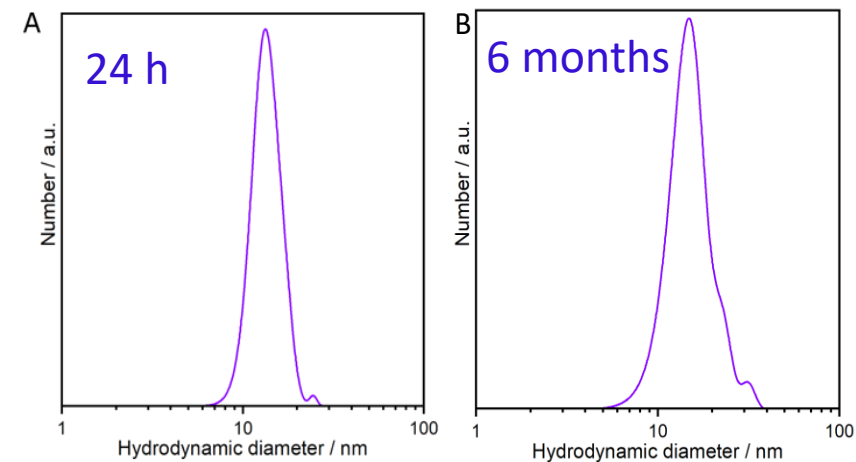
Dr. David Rodríguez



Prof. Josep Puigmartí



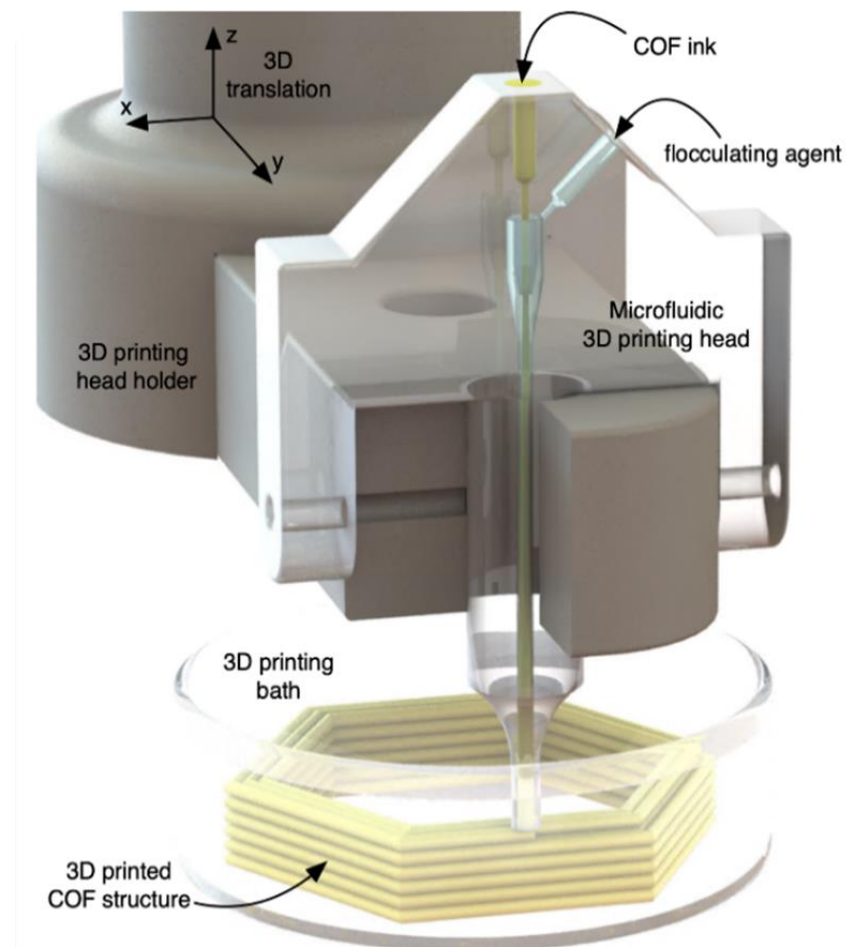
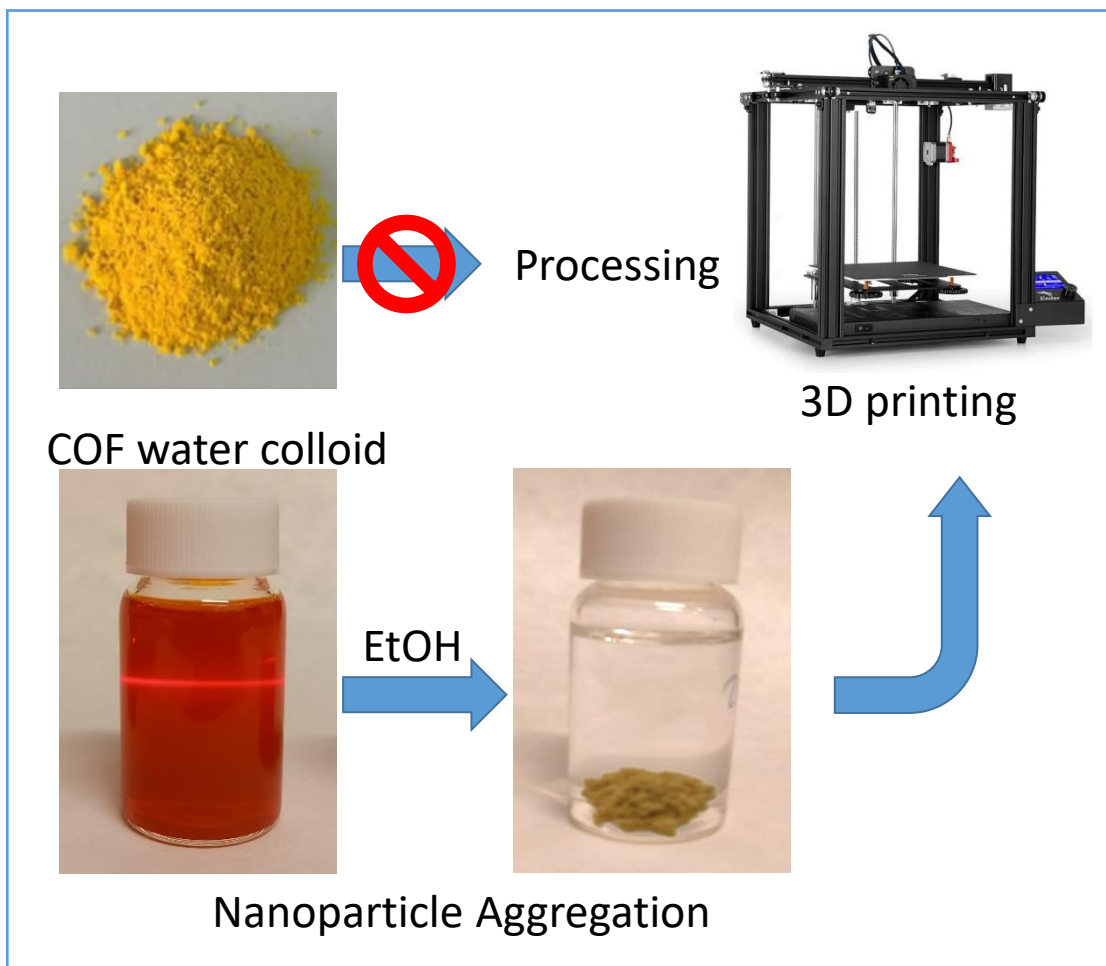
DLS



cationic hexadecyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulfate (SDS) surfactants

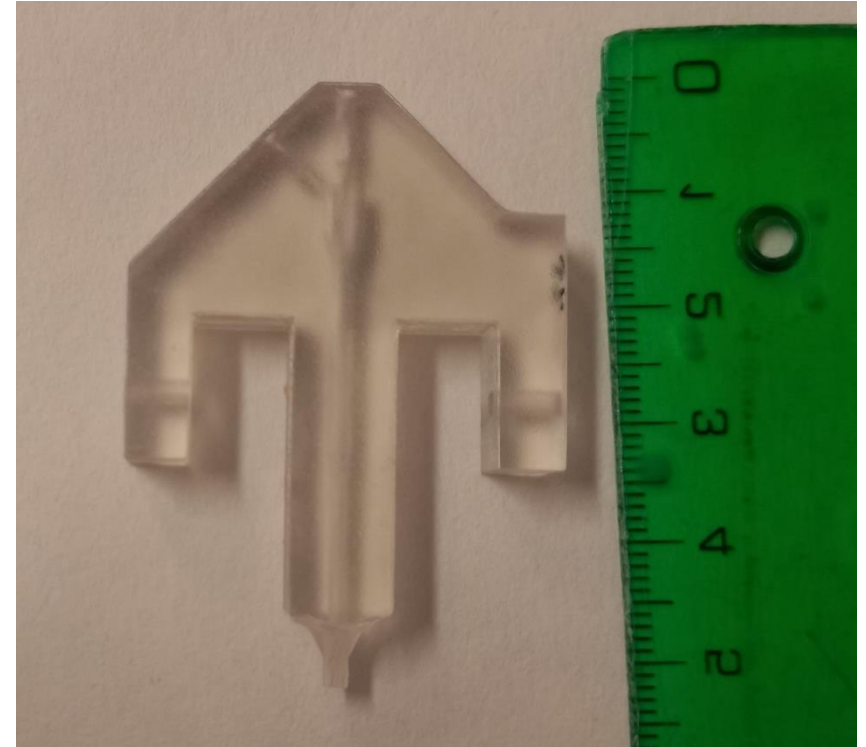
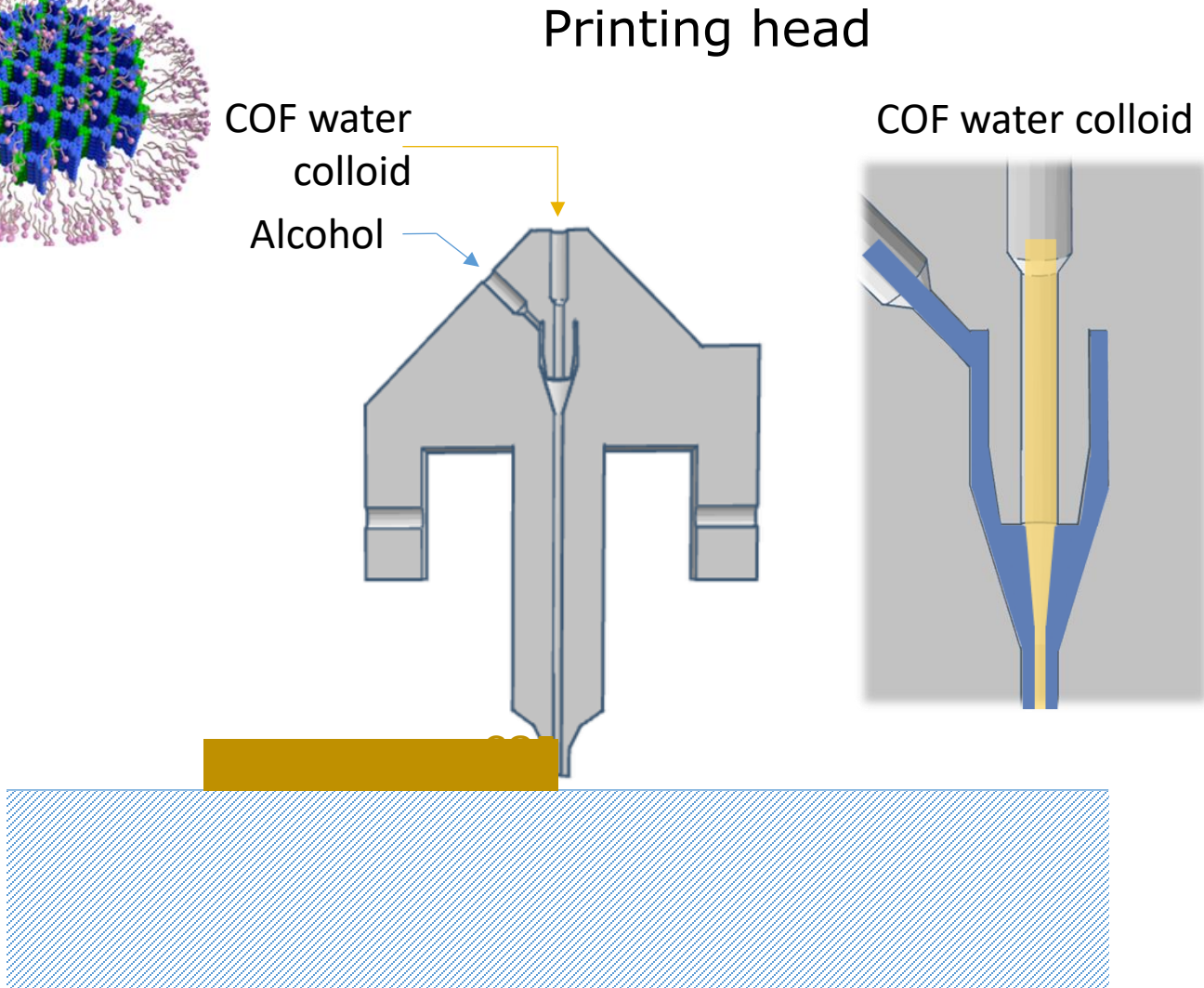
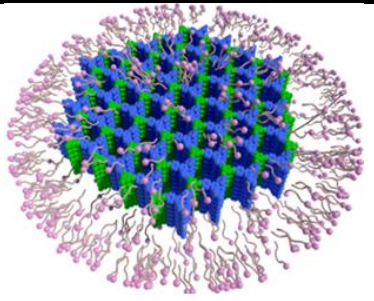
3D Printing of COFs

3D printing: “Colloidal control enables direct printing of pure COF architectures”



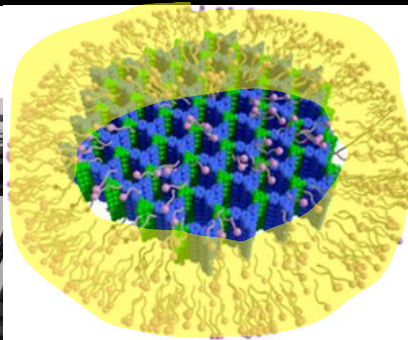
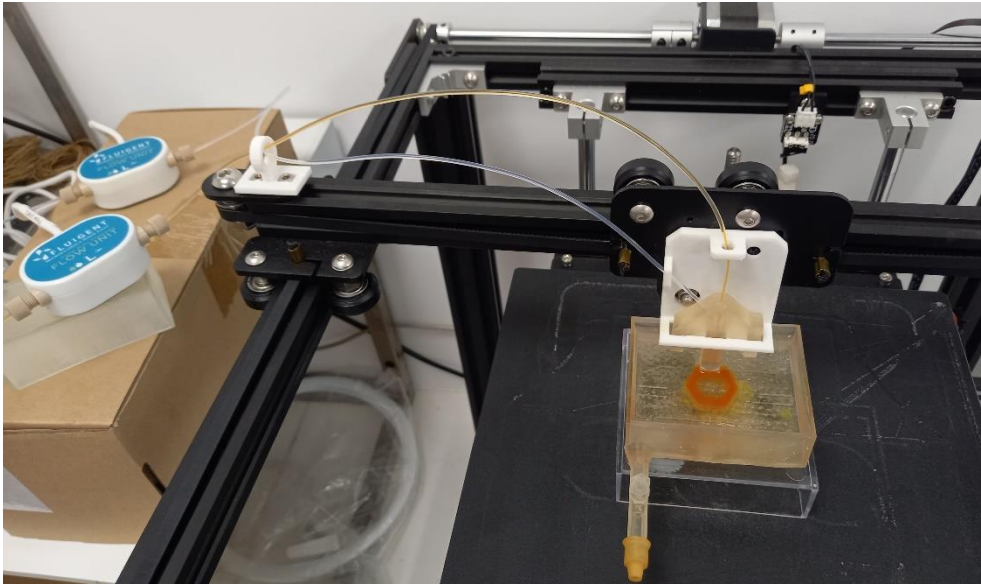
3D Printing of COFs

2 - 3D printer development

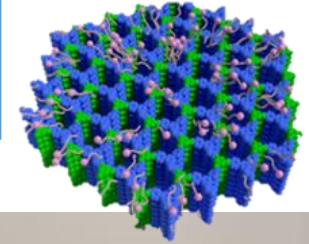


3D Printing of COFs

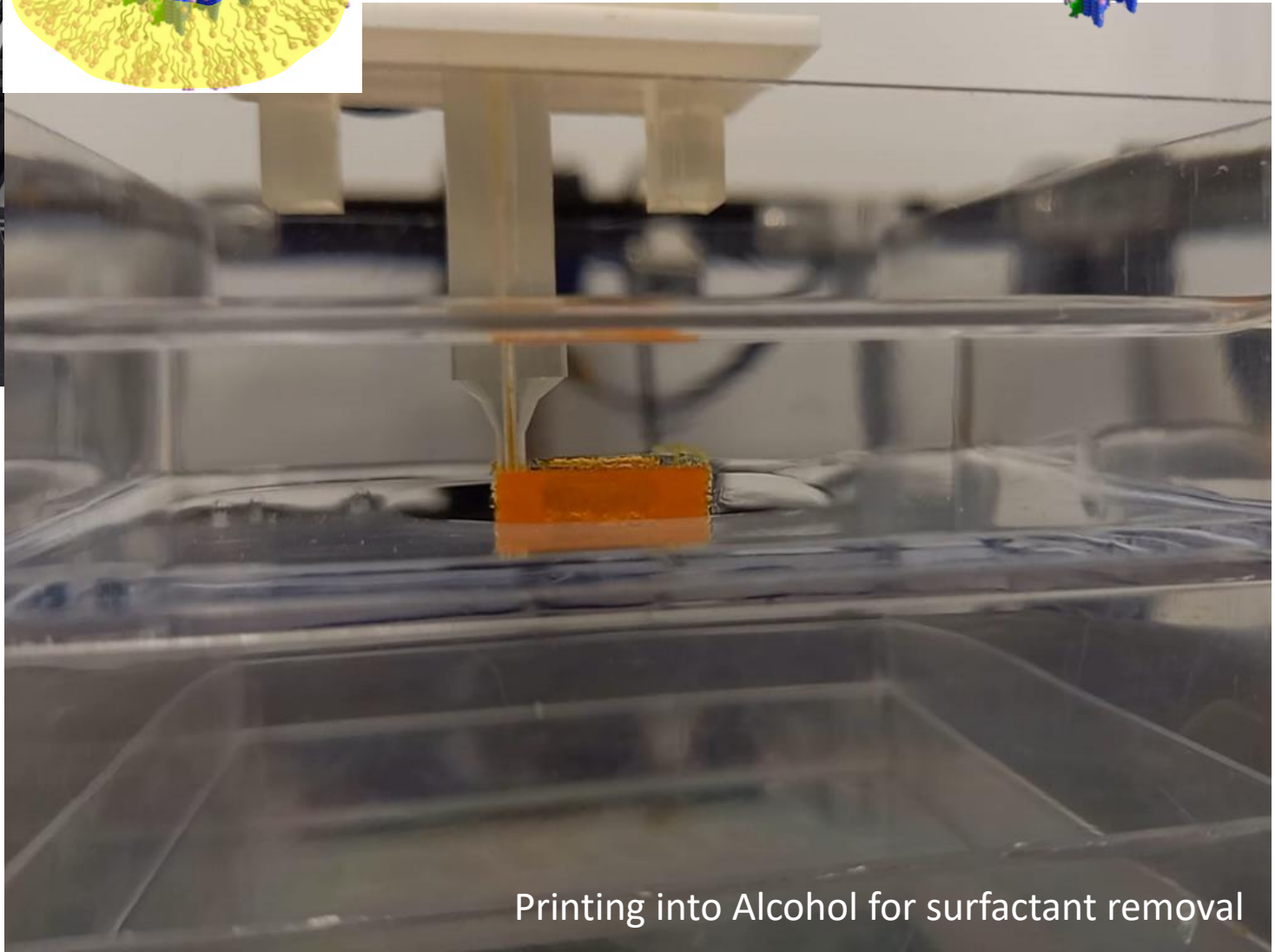
2 - 3D printer development



Printing into alcohol for direct surfactant removal



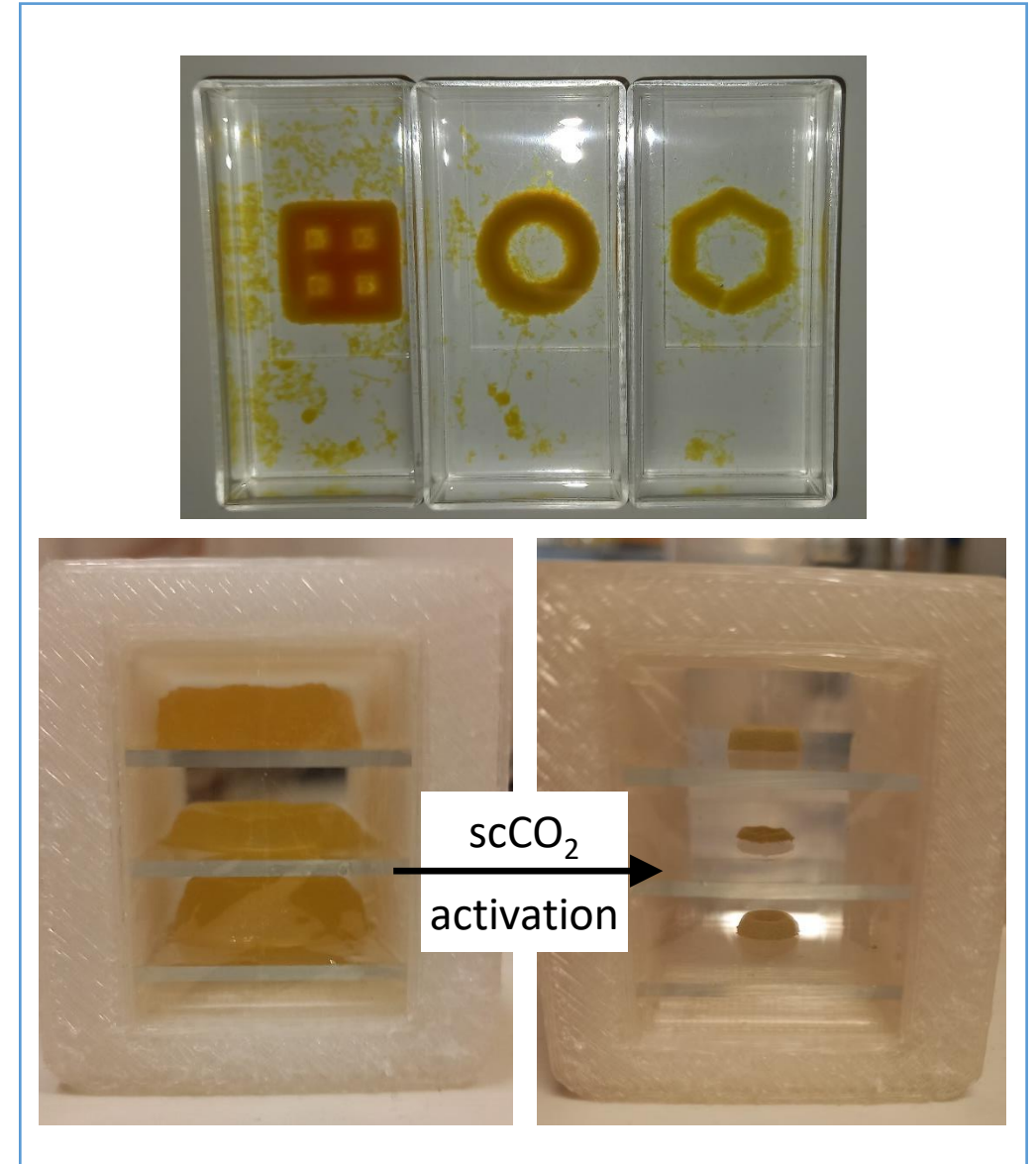
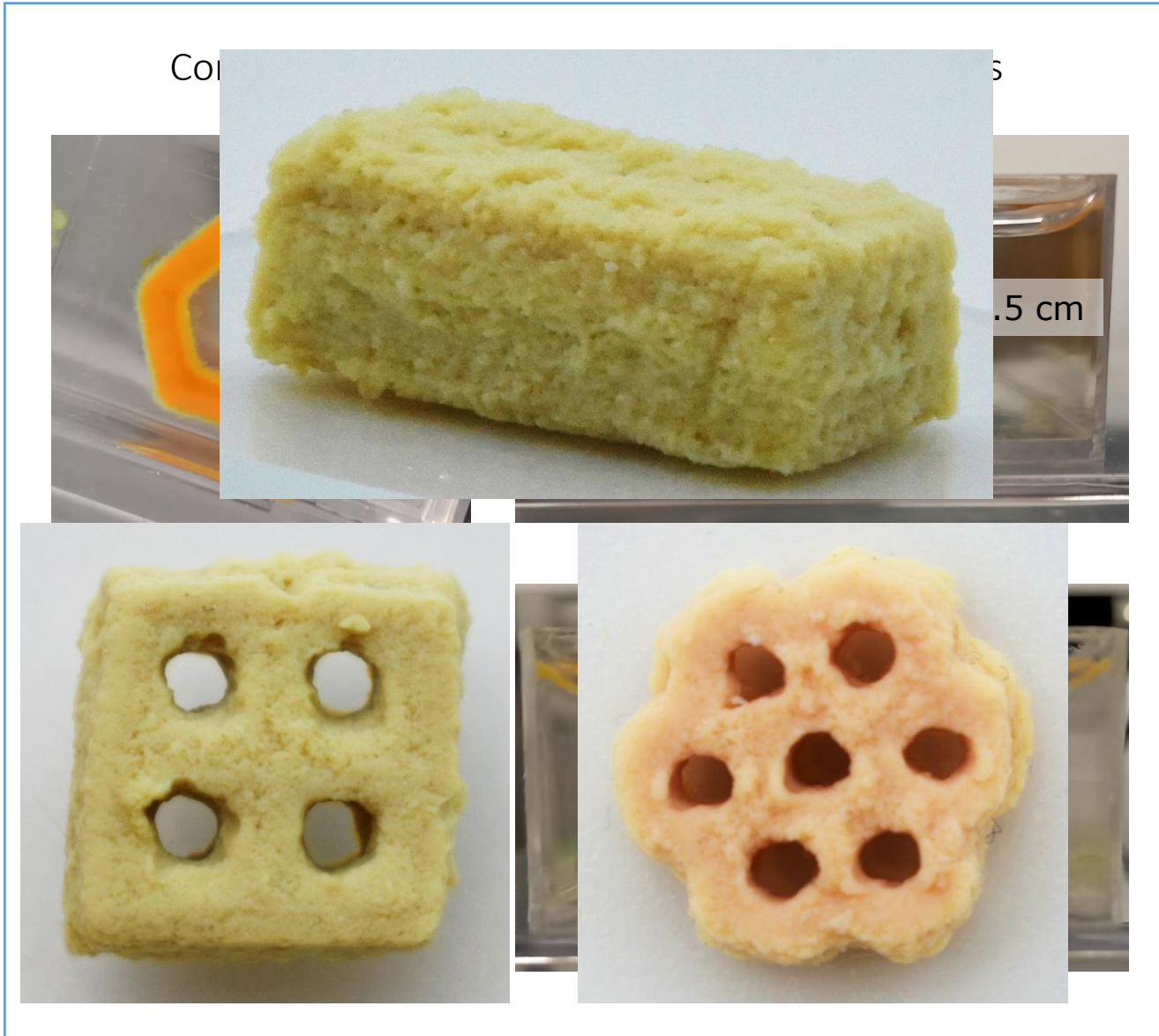
3 - 3D printing



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Printing into Alcohol for surfactant removal

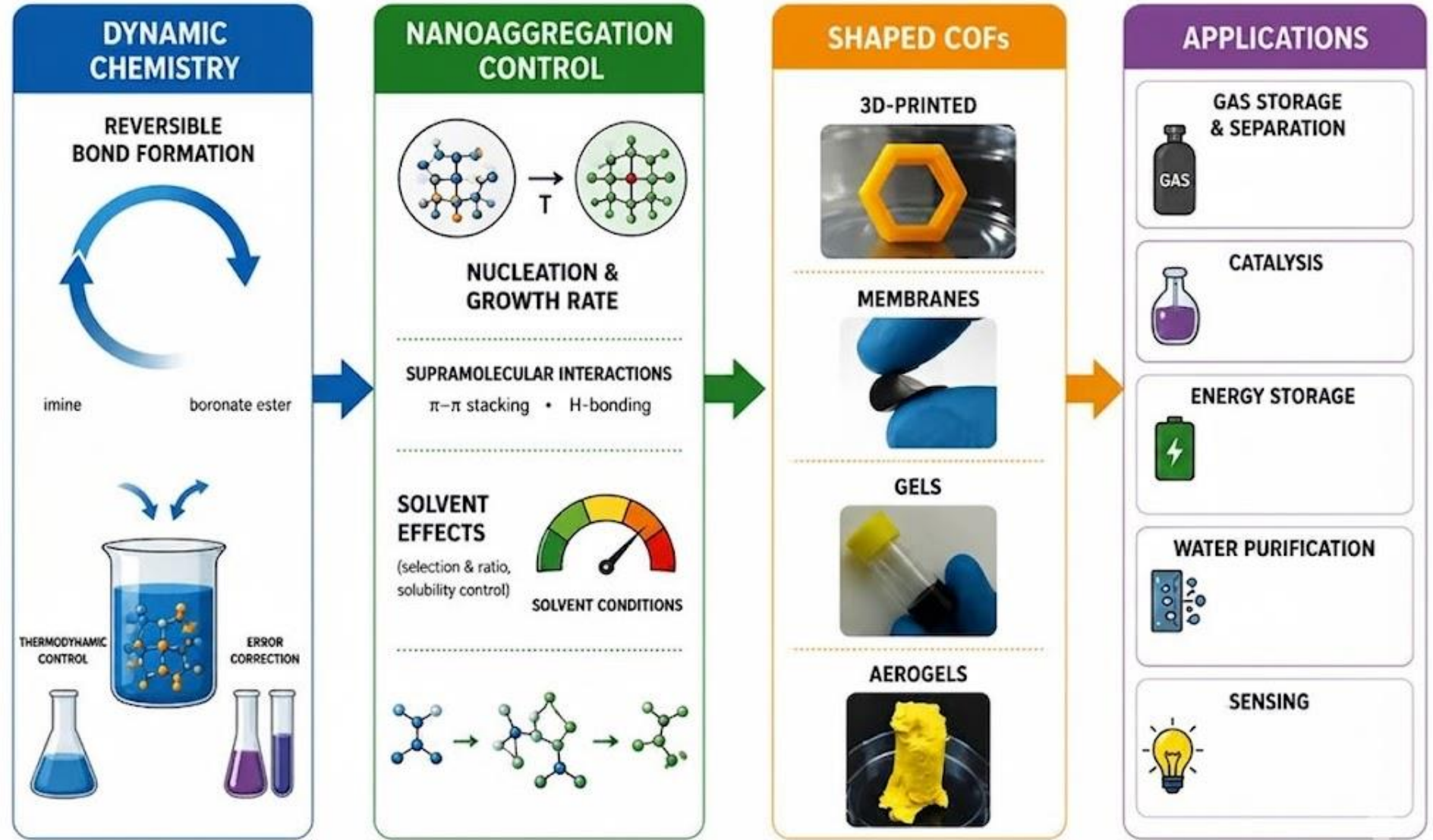
3D Printing of COFs



5. Outlook: processability is a design rule for functional COFs

Take-home message: FROM DYNAMIC CHEMISTRY TO SHAPED COFs AND APPLICATIONS

Processability is not a secondary property of COFs, is a design principle



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Iñigo

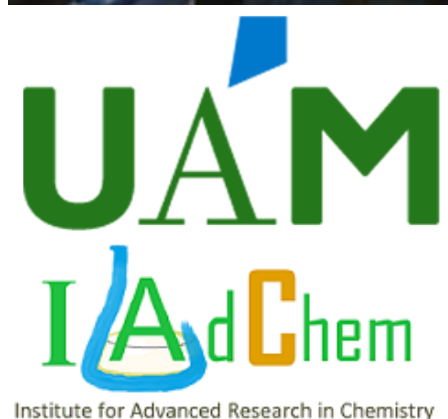
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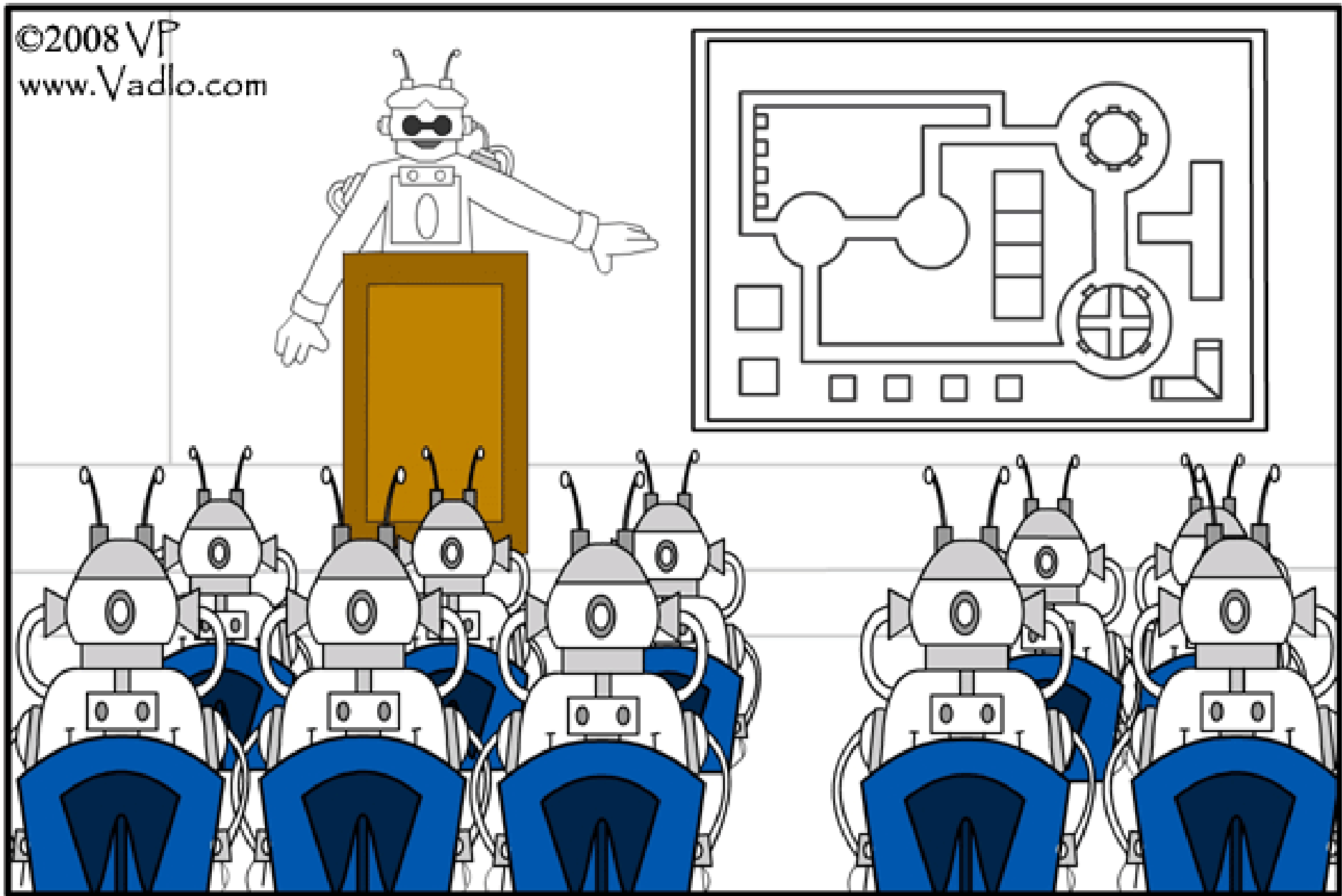
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Thanks for your kind attention !!



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