



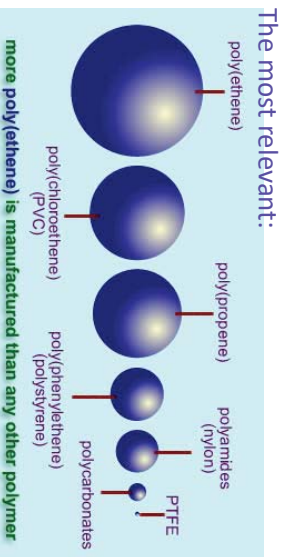
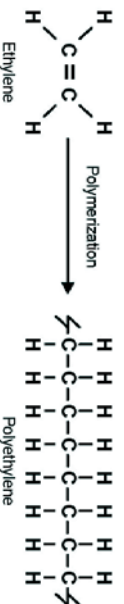
Design and Processability of Imine-based Covalent Organic Frameworks (COFs)

Félix Zamora / Química Inorgánica

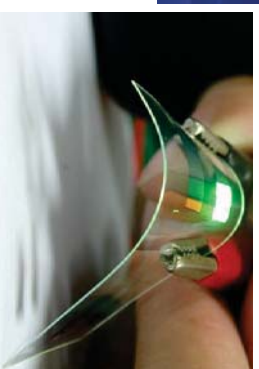


Félix Zamora
Dpto. Química Inorgánica
Universidad Autónoma de Madrid
E-mail: felix.zamora@uam.es
<http://www.nanomater.es>

Covalent Organic Synthetic Polymers

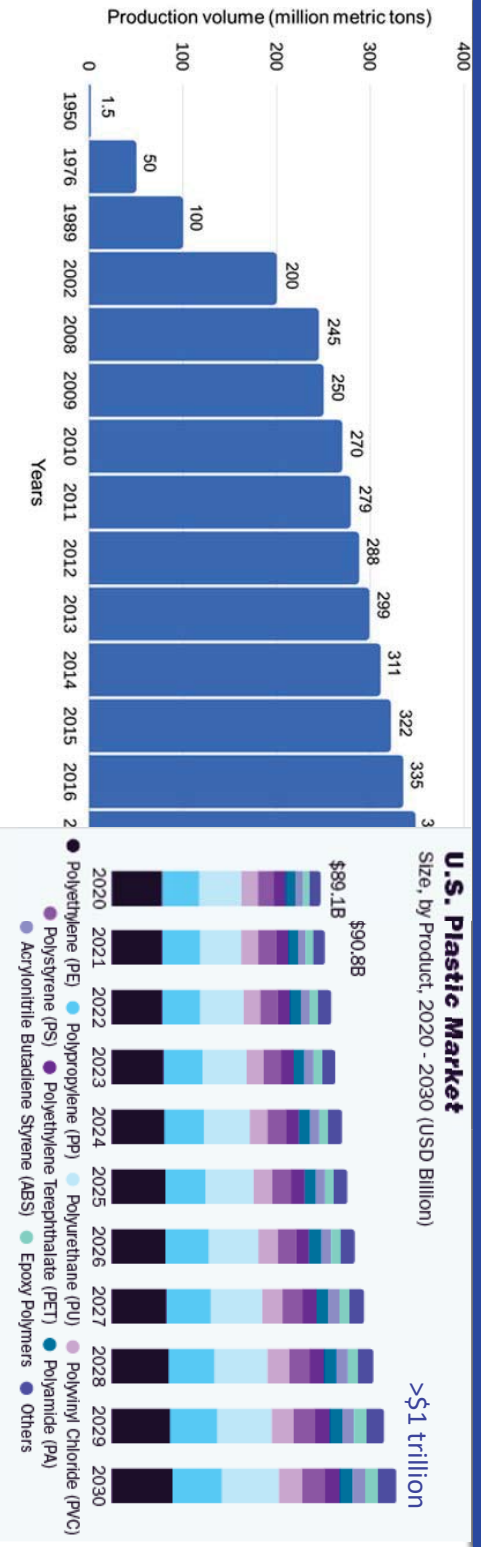


Industrial synthesis
Processability
Properties



Covalent Organic Synthetic Polymers

- The most chemical products industrially fabricated > 300 mil. Tons/year // \$3 trillion/year
- The most relevant 20th century materials

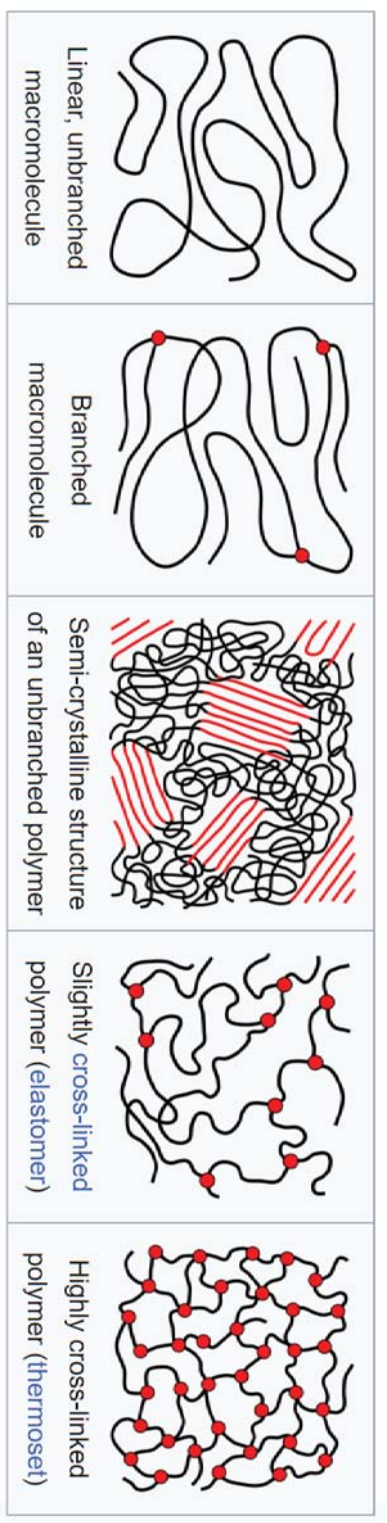


3

Covalent Organic Synthetic Polymers



Amorphous Architectures: Hampering Structural Design



4

On the Possibility of Making 2D and 3D Organic Networks

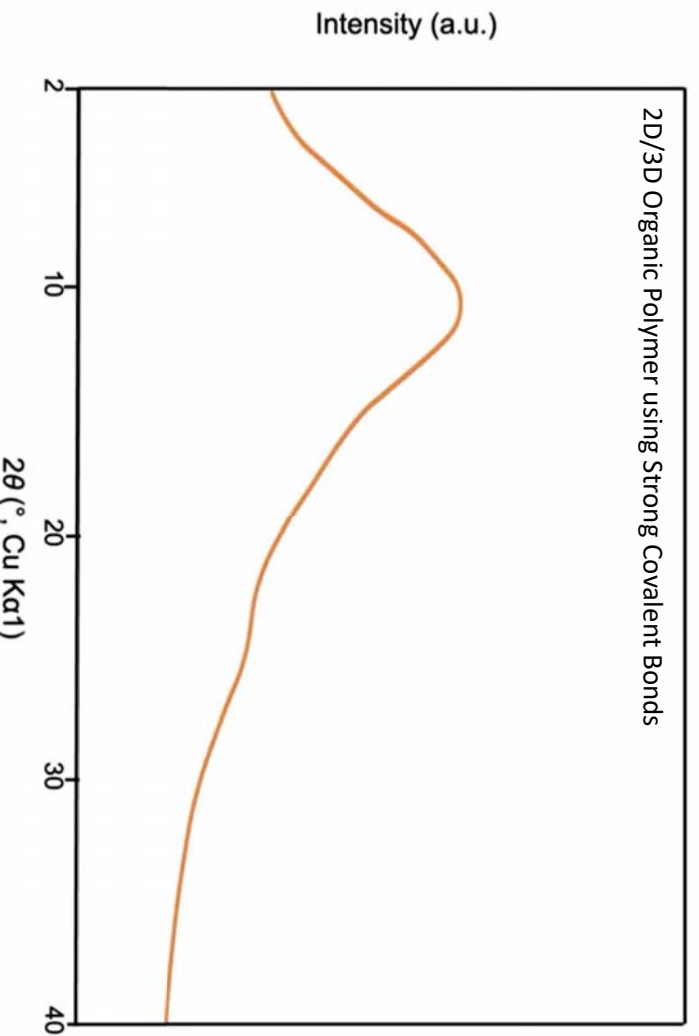
*“Organic chemists are masterful at exercising control in zero dimension. One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders... **But in two or three dimensions, it is a synthetic wasteland.** The methodology for exercising control so that one can make unstable but persistent extended structures on demand is nearly absent. Or to put it in a positive way—this is a certain growth point of the chemistry of the future.”*



R. Hoffmann, *Scientific American*, Feb 1993, 65–73.

5

Powder X-Ray Diffraction (PXRD) of an Amorphous Solid

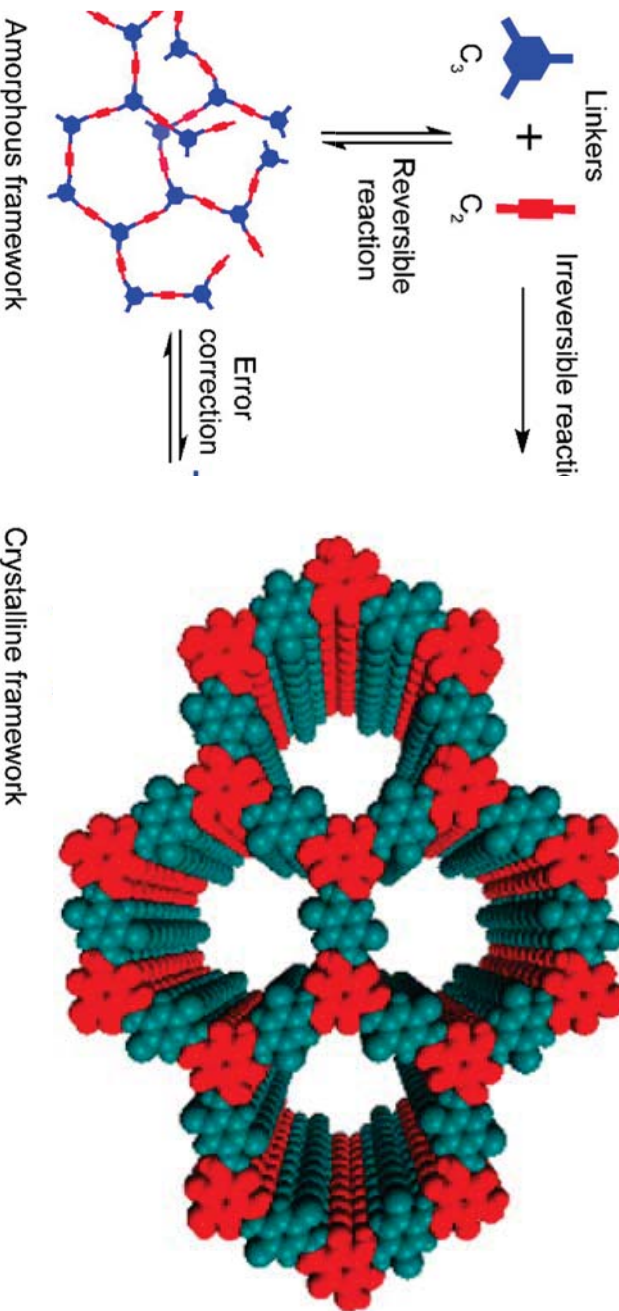


6

Covalent Organic Frameworks: Formation / Reversibility

Dynamic Covalent Bonds: Reversibility

Error correction: Experimental Conditions

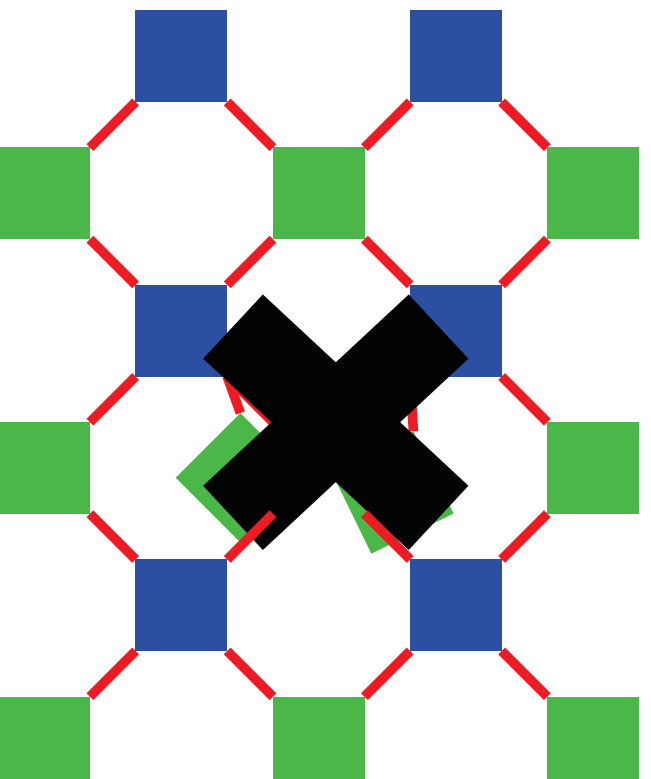


R. Banerjee et al. J. Am. Chem. Soc. 2019, 141, 1807–1822

Covalent Organic Frameworks: Formation / Reversibility

Dynamic Covalent Bonds: Reversibility

Error correction: Experimental Conditions





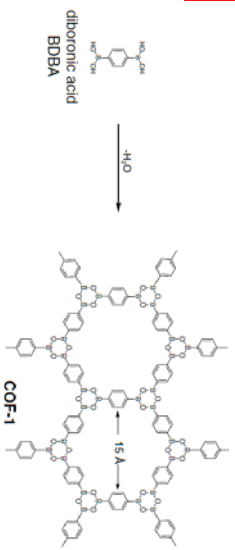
O. Yaghi



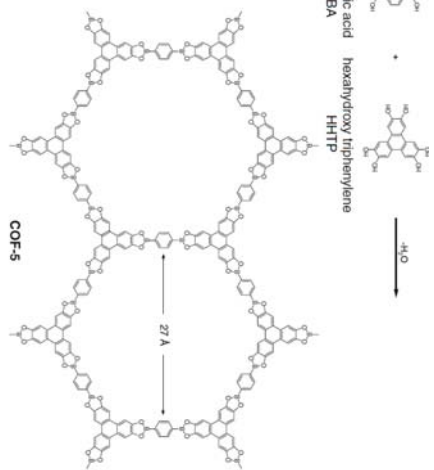
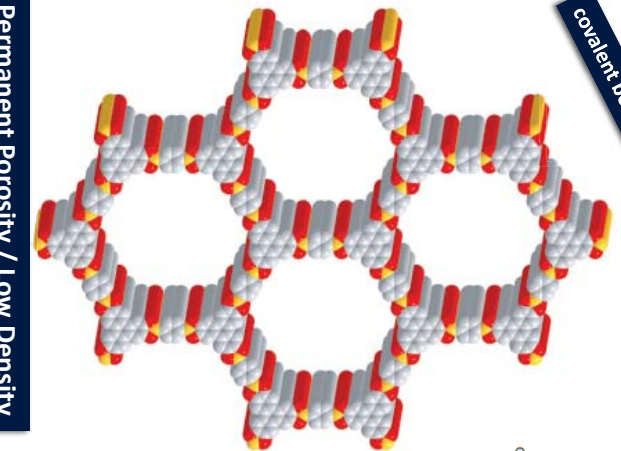
Solvothermal conditions

Layered material

covalent bonds



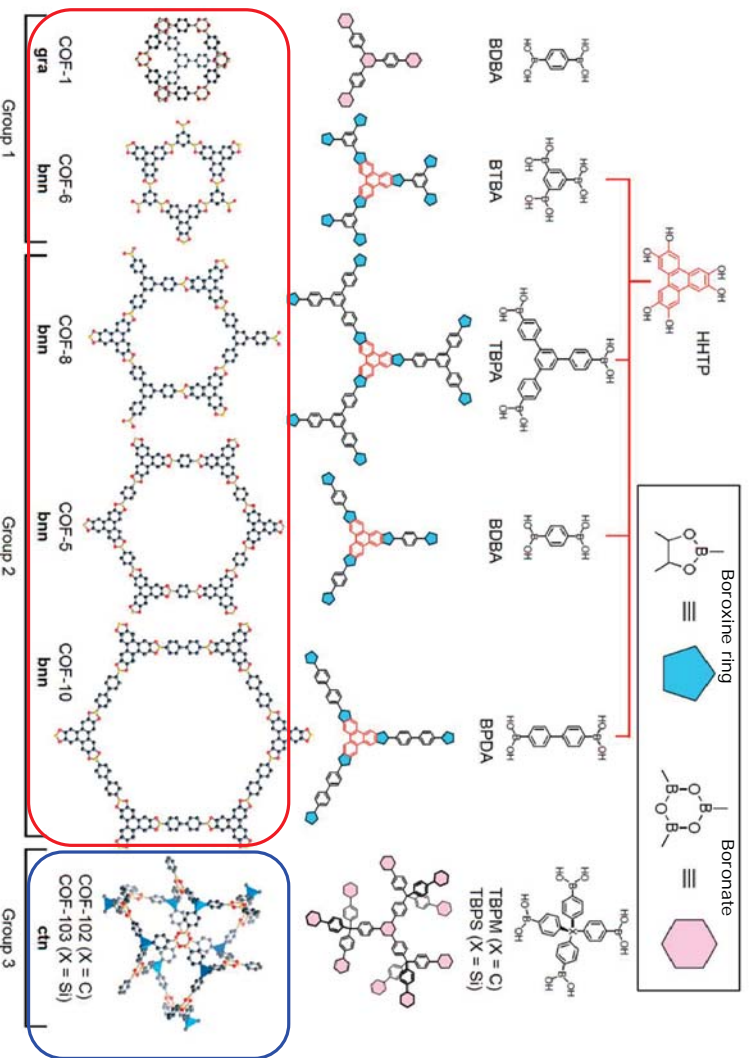
Boroxine

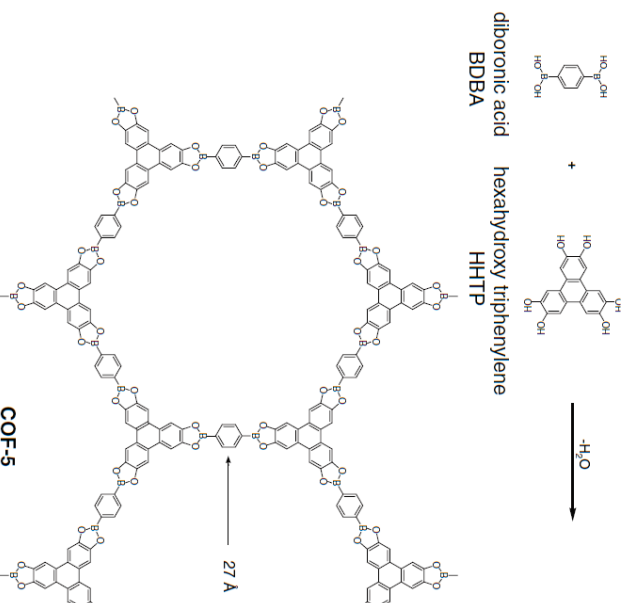


Boronato-ester

Permanent Porosity / Low Density

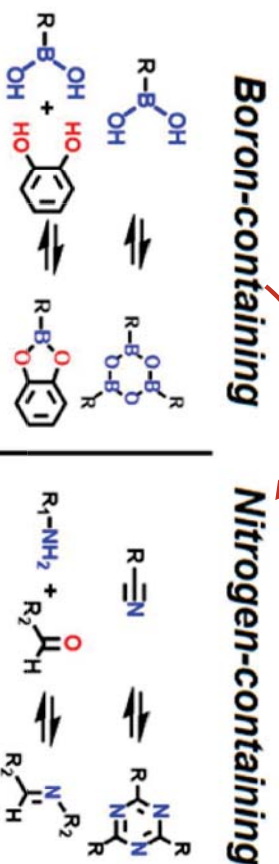
Covalent Organic Frameworks: Boron-based COFs





Applications: Robust Materials

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

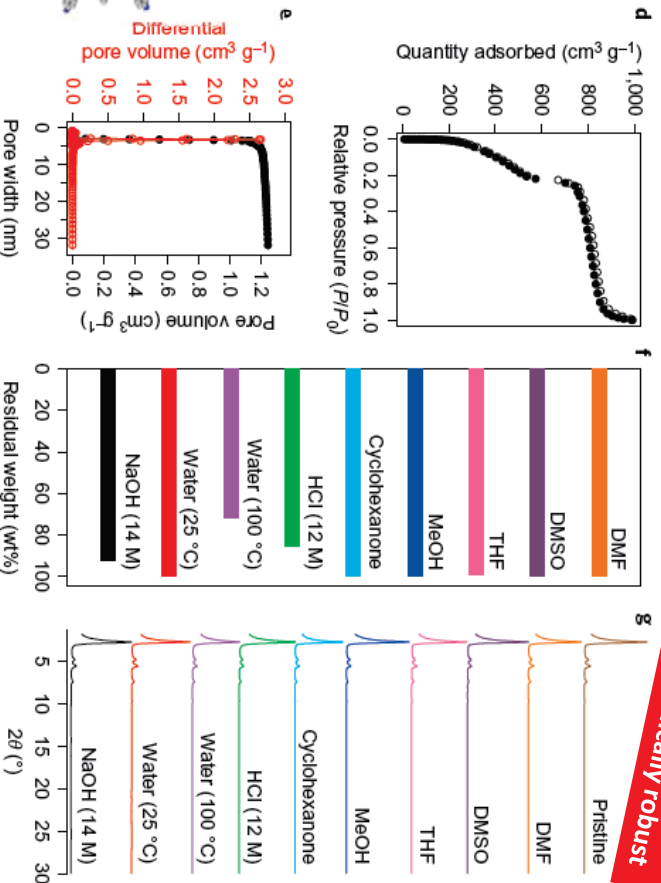
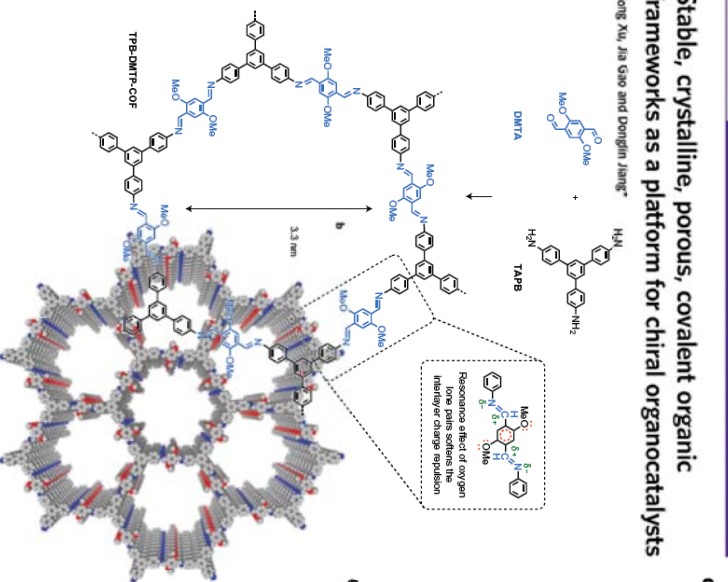


11

Schiff-base chemistry or dynamic imine chemistry

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

Hong Xu, Jia Gao and Dongjin Jiang*

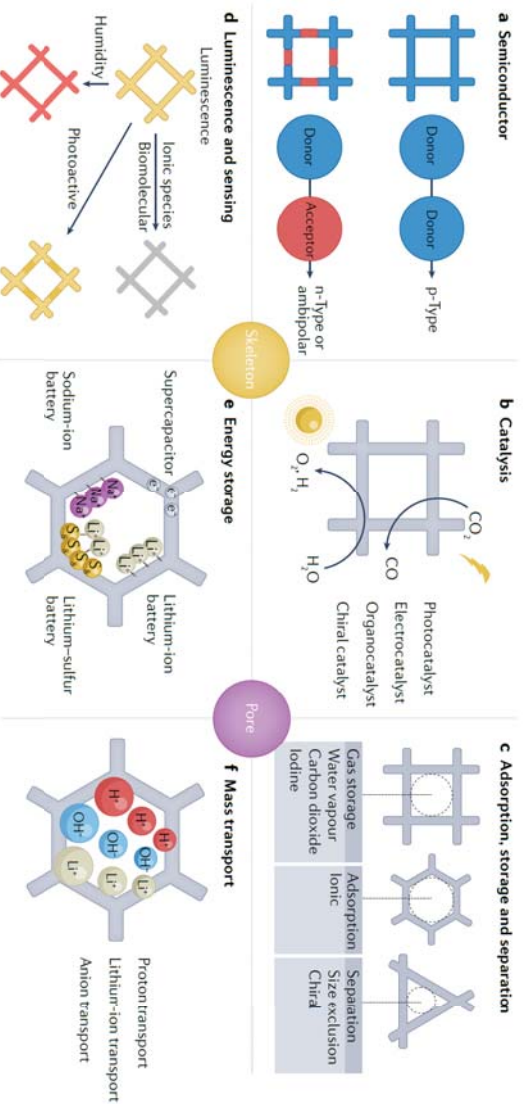


12

Covalent organic frameworks

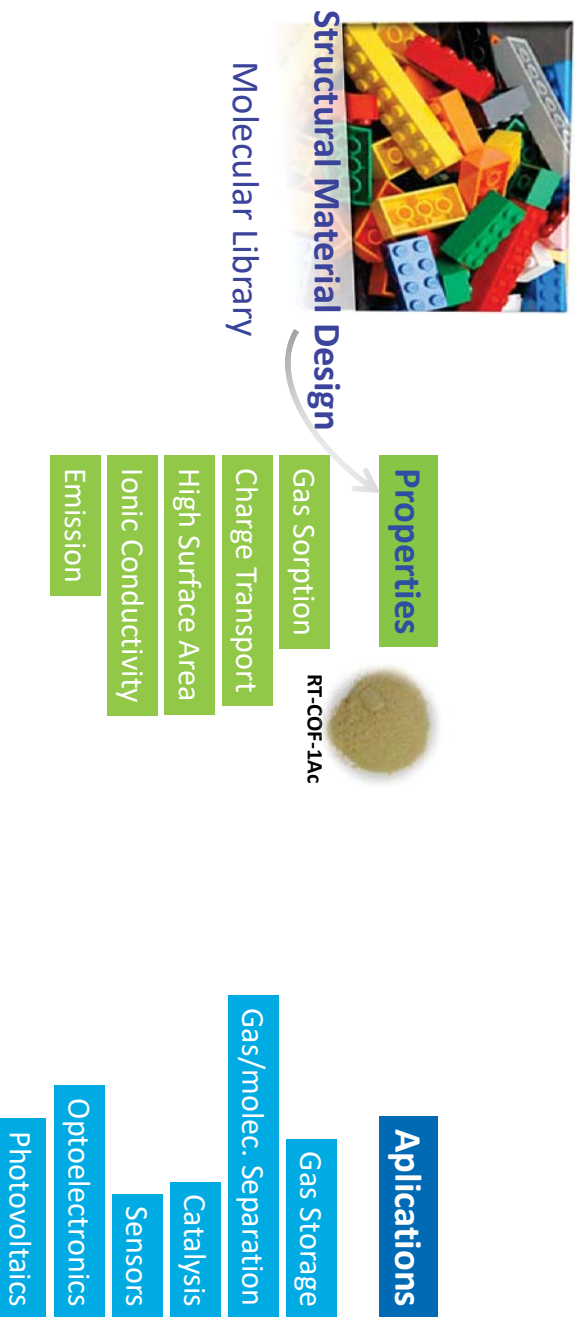
Ke Tian Tan¹, Samrat Chakrabarti^{2,3}, Zhiyong Wang^{2,4}, Fukang Wen², David Rodriguez-San-Miguel⁵, Jie Feng^{6*}, Ning Huang⁶, Wei Wang⁷, Felix Zamora⁸, Xinliang Feng⁹, Arne Thomas⁹, & Donglin Jiang¹⁰✉

Applications



13

Covalent Organic Frameworks: Design for Properties & Application



14

Chemical design of COFs



15

Journal of
Materials Chemistry A



PAPER



Prof. José L. Segura



Cite this: *J. Mater. Chem. A* 2017, 5,
17973

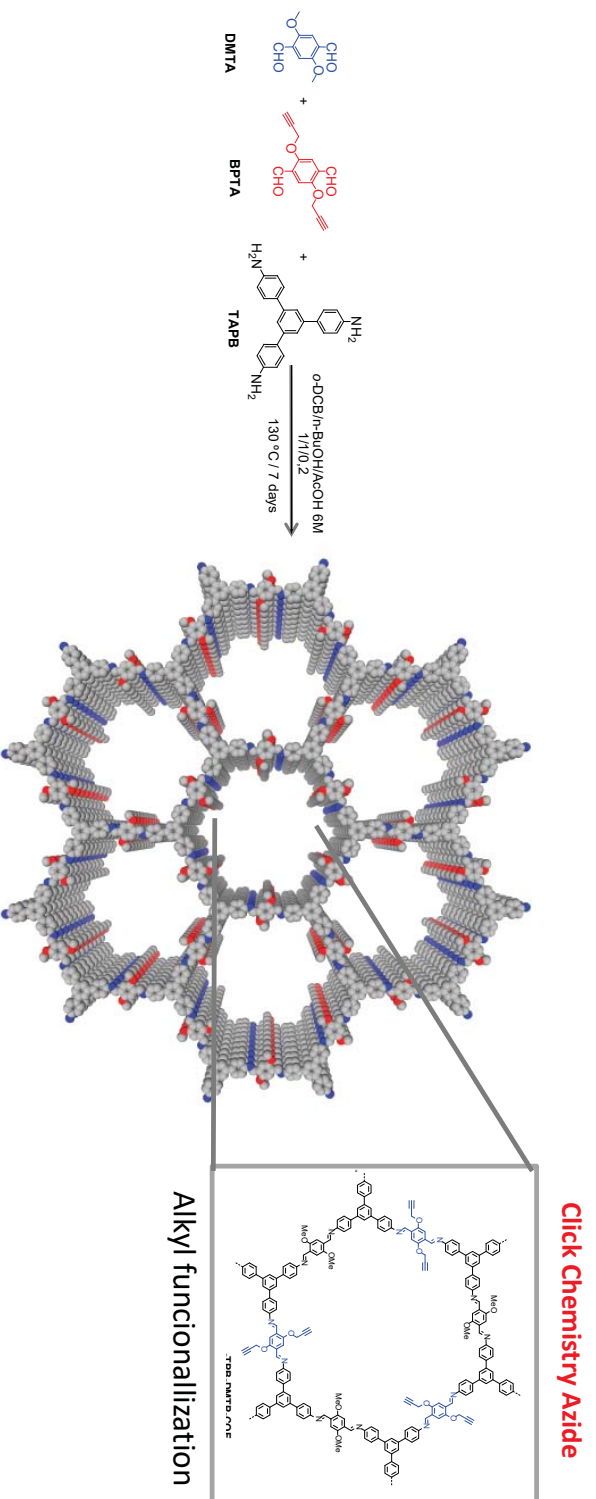
Thiol grafted imine-based covalent organic frameworks for water remediation through selective removal of Hg(II)[†]

Laura Meri-Bofi,^a Sergio Royuela,^{1b} Félix Zamora,^{1b} M. Luisa Ruiz-González,^c
José L. Segura,^{*a} Riansares Muñoz-Olivas^{*d} and María José Mancheno^{1b}^{*a}

Idea for COF design: Cavities decorated with thiol groups

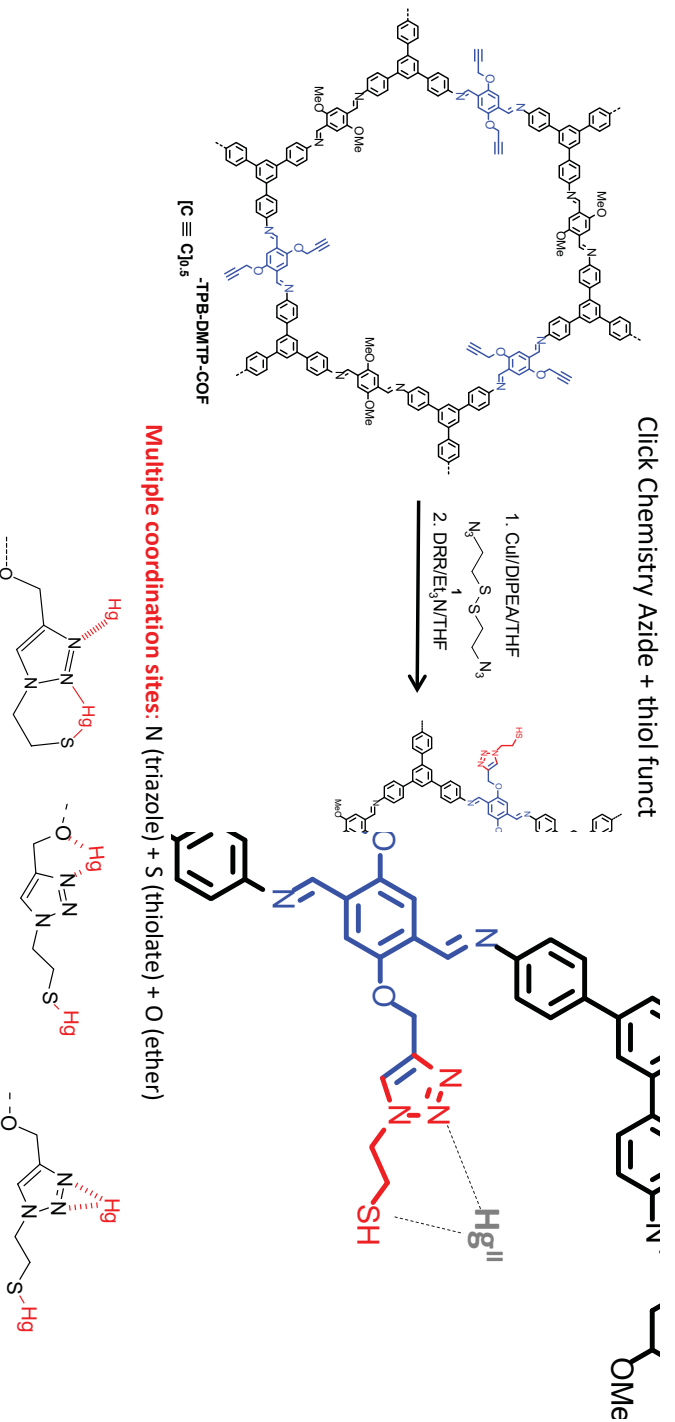
16

COF Post-synthesis: Click Chemistry Azide-Alkyne



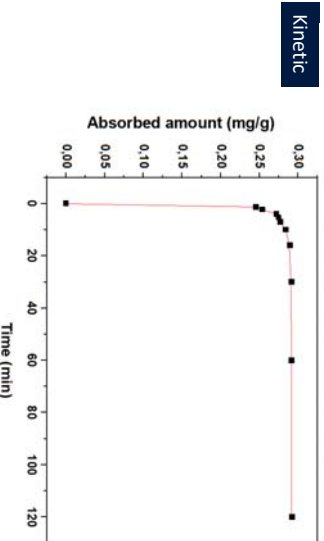
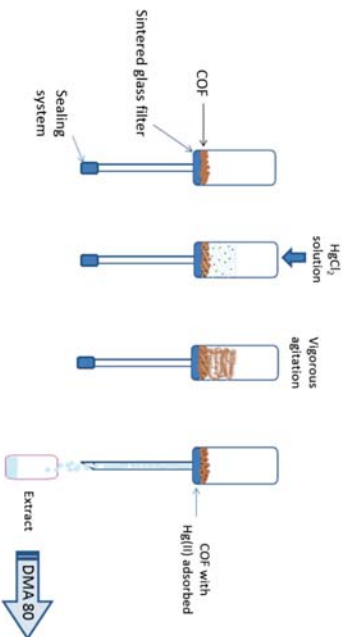
H. Xu, J. Gao, D. Jiang. *Nat. Chem.* **2015**, 7, 905

Thiol Grafted Imine-Based Covalent Framework for Water Remediation Through Selective Removal of Hg(II)

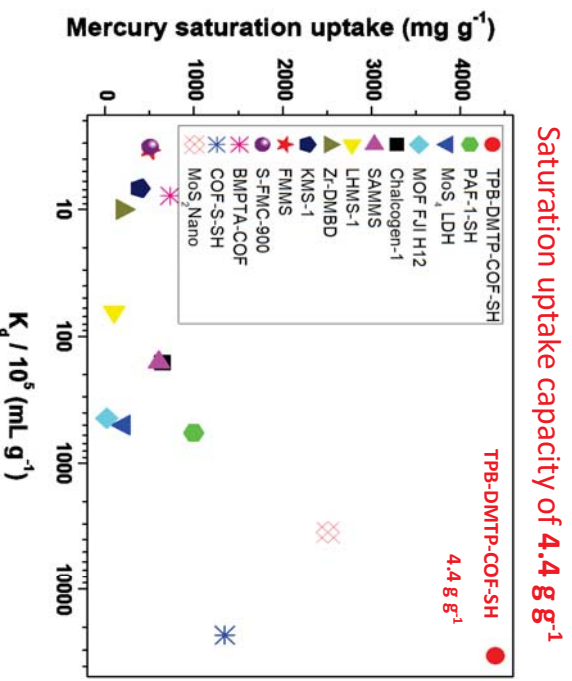


M. J. Mancheño *et al.* *J. Mater. Chem. A*, **5**, 17973-17981 (2017)¹⁸

Mercury Adsorption from water: Kinetic & Capacity

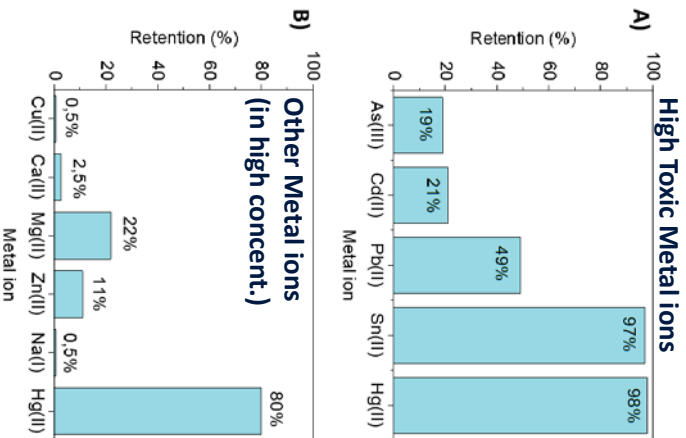


In just 10 min 99.98 % of removal efficiency (2.5 min for 2 mg⁻¹ V/m^{cor})

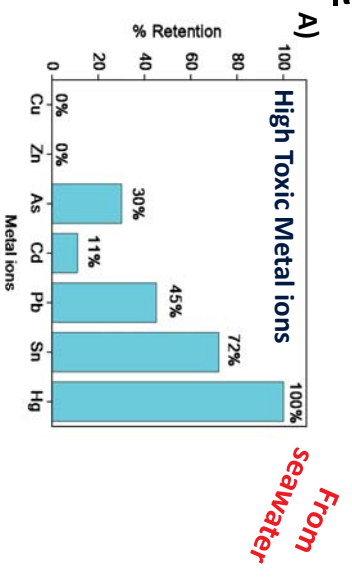


J. Mater. Chem. A., 5, 17973-17981 (2017)

Selectivity Test

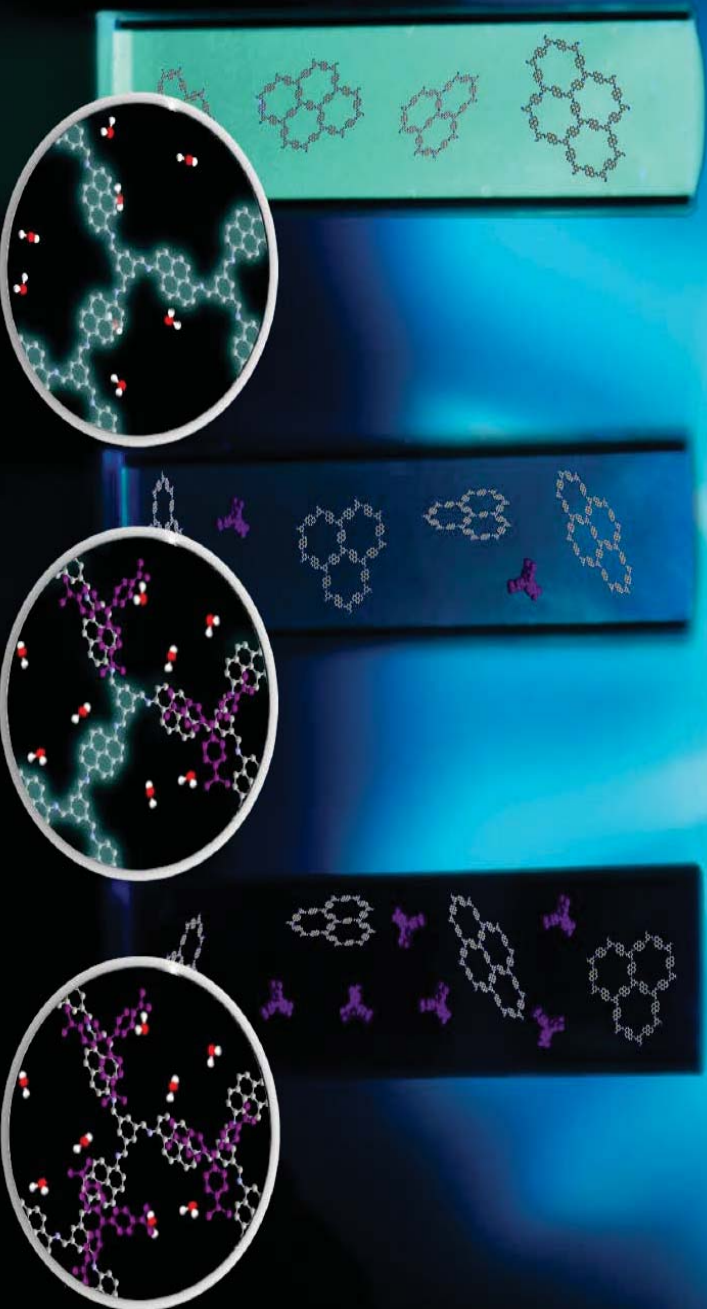


ATPB-DMTP-COF-SH in the presence of ions: A) As(III), Cd(II), Pb(II), Sn(II), Hg(II) (equimolar concentration, 1 mg L⁻¹). B) Cu(II), Ca(II), Mg(II), Zn(II), Na(I) (100 mg L⁻¹), Hg(II) (1 mg L⁻¹).



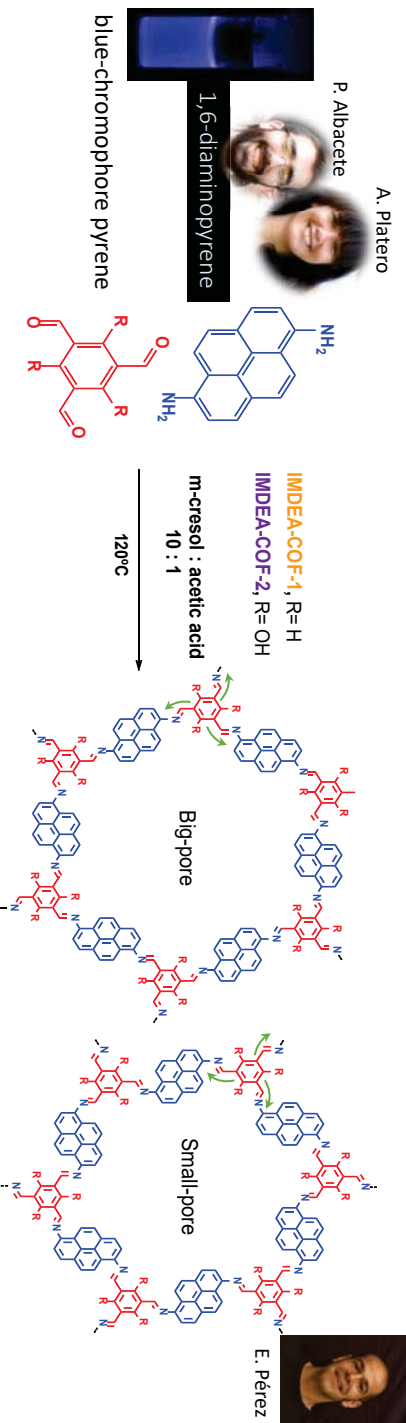
TPB-DMTP-COF-SH in seawater in the presence of ions: A) Cu(II), Zn(II), As(III), Cd(II), Pb(II), Sn(II) Hg(II) (equimolar concentration, 1 mg L⁻¹). B) Zn(II), As(III), Cd(II), Pb(II), Sn(II) (equimolar concentration, 100 mg L⁻¹) vs Hg(II) (1 mg L⁻¹).

Designing Fluorescence imine-COFs



21

Layer-Stacking-Driven Fluorescence in a Two-Dimensional Imine-Linked COF

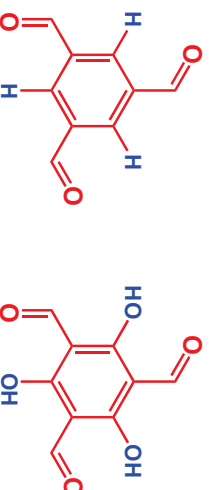


Idea for COF design: Use a Fluorescent Building Block avoiding π - π stacking between the layers COF structure

Aimed at causing a staggered stacking

R= H, OH

1,3,5-Benzenetricarbaldehyde
2,4,6-Triformylphloroglucinol

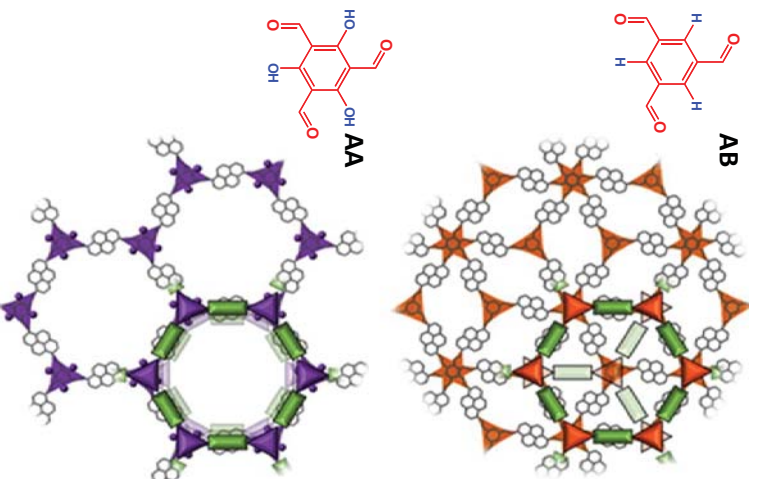


Theoretical Studies: Preferential Stacking

Calculated Cohesive Energy values for the two pore-isomer in either eclipsed (AA) or staggered (AB) conformations.

COF	Pore	Stacking	L_p , Å	E_c , kcal mol ⁻¹
IMDEA-1	Small	AA	3.543	-41.05
IMDEA-1	Small	AB	3.482	-38.28
IMDEA-1	Big	AA	3.760	-42.89
IMDEA-1	Big	AB	3.749	-39.66
IMDEA-2	Small	AA	3.570	-40.36 ^a / -38.742 ^b
IMDEA-2	Small	AB	3.637	-14.53 ^a / -16.37 ^b
IMDEA-2	Big	AA	3.780	-48.20 ^a / -46.81 ^b
IMDEA-2	Big	AB	3.638	-20.99 ^a / -19.83 ^b

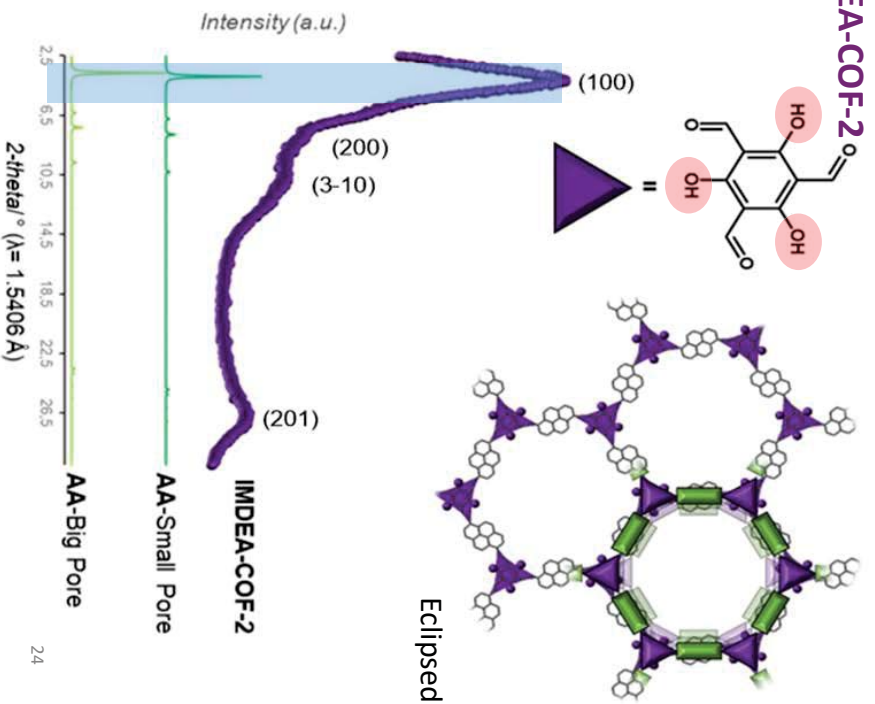
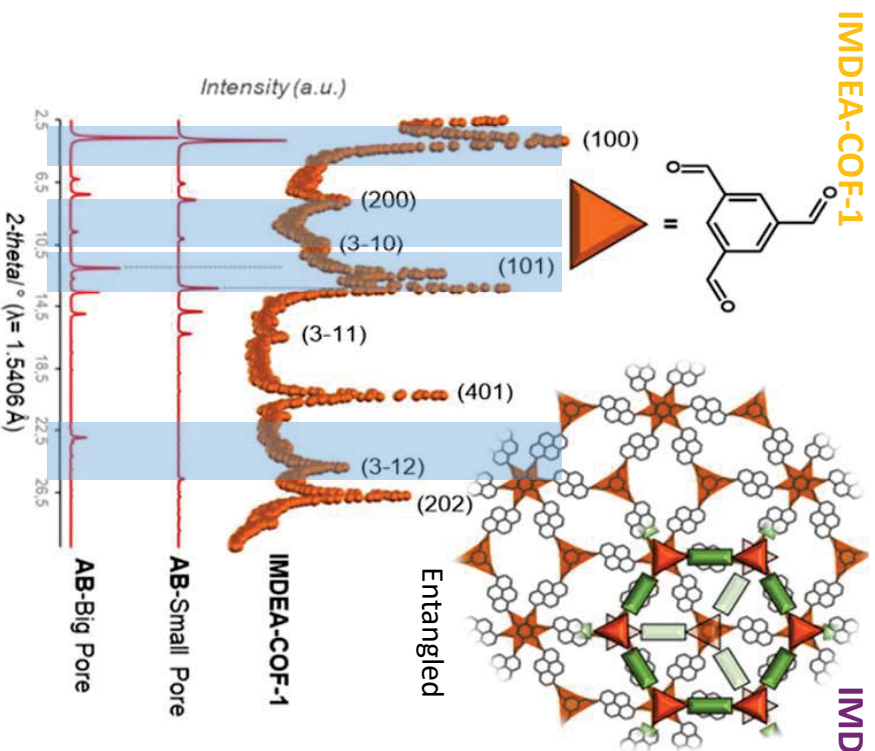
^aEnol-imine form. ^bKeto-enamine form.



In layered systems due to aggregation-caused quenching driven by $\pi-\pi$ interactions

J. Am. Chem. Soc. 2018, 140, 12922

23



24

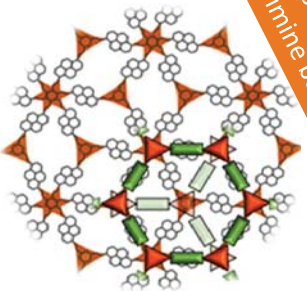
In Summary: Layer-packing-driven fluorescence in solid-state



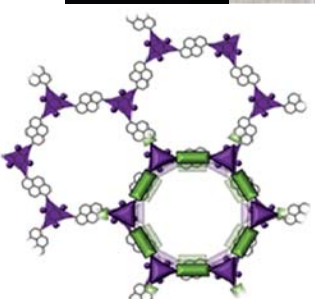
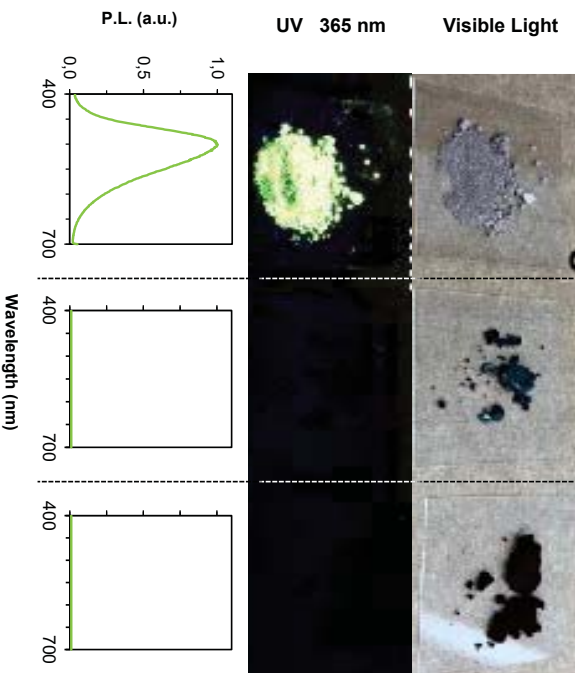
Prof. K.P. Loh

Dr. Li Xing

First sample of solid-state emissive imine-based-COF



green color emission at 501 nm
blue-chromophore pyrene



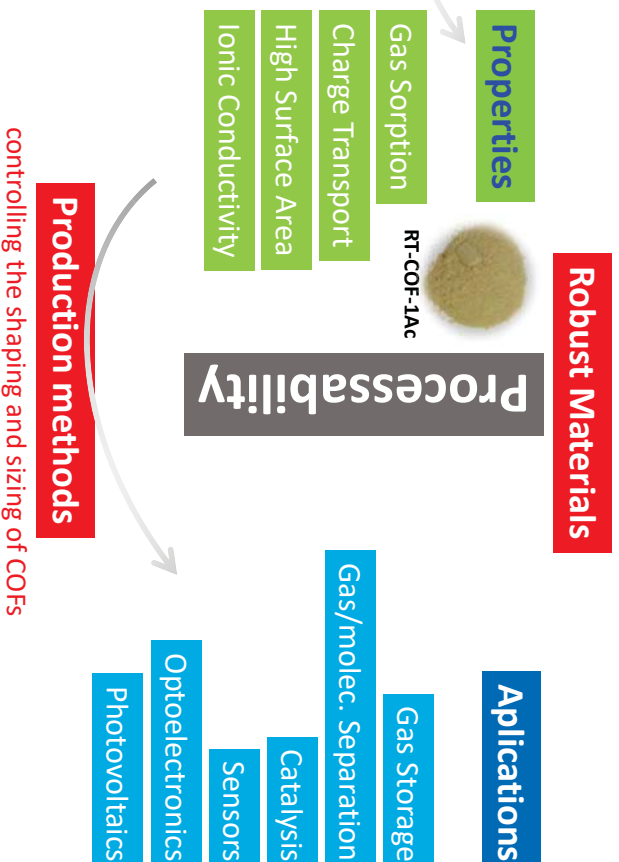
AA Layer-packing
quench fluorescence

J. Am. Chem. Soc. 2018, 140, 12922

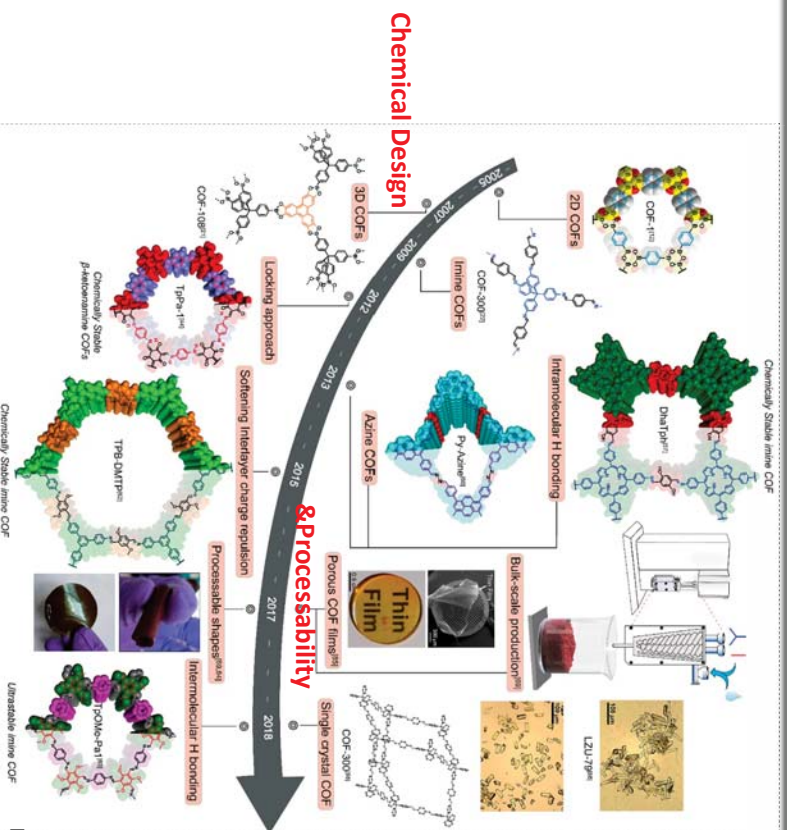
Covalent Organic Frameworks



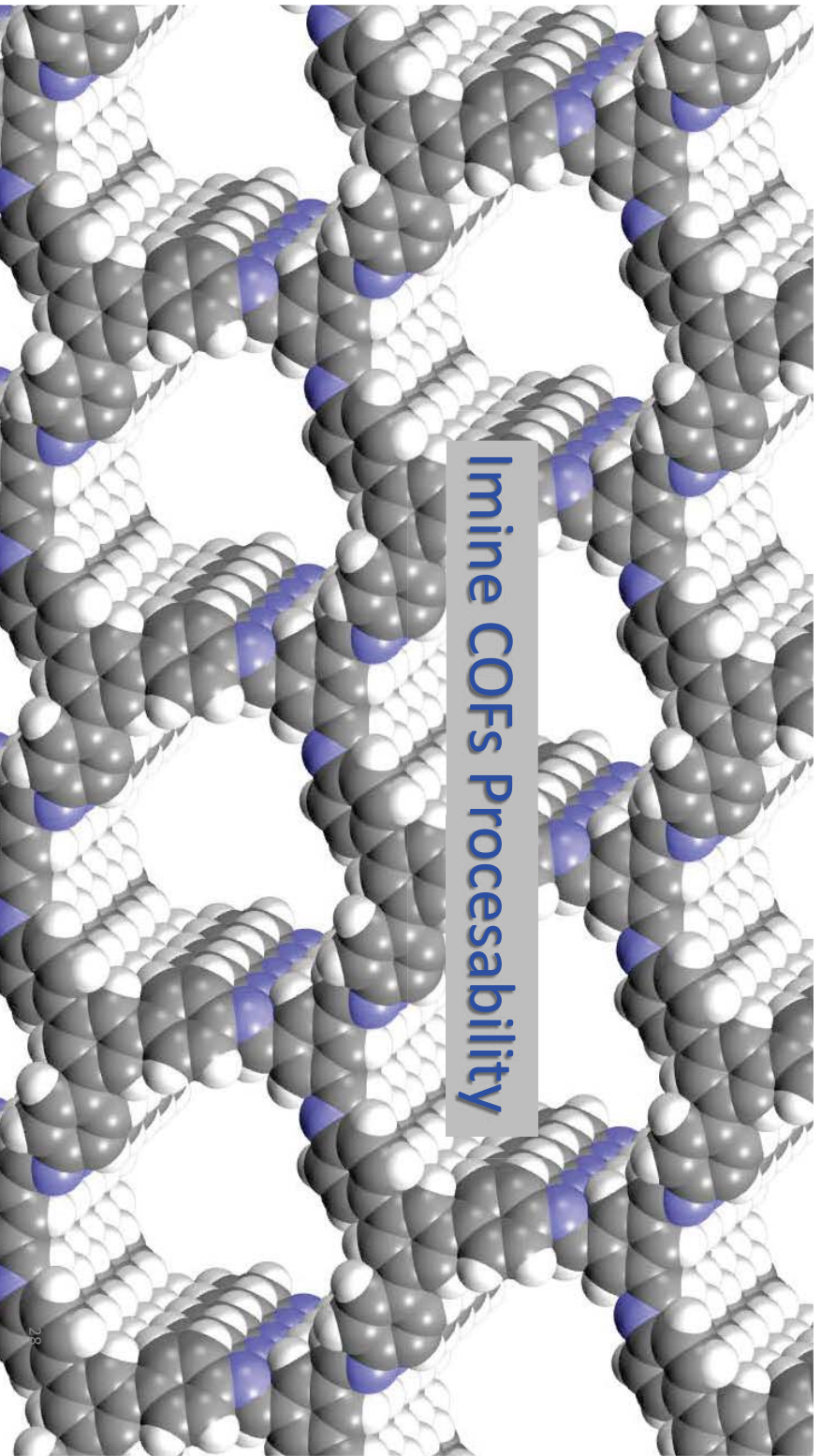
Structural Material Design



Timeline of COFs Developing



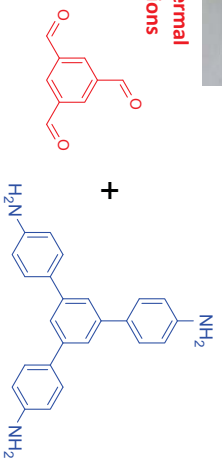
Banerjee et al. *J. Am. Chem. Soc.* (2019) 141, 1807²⁷



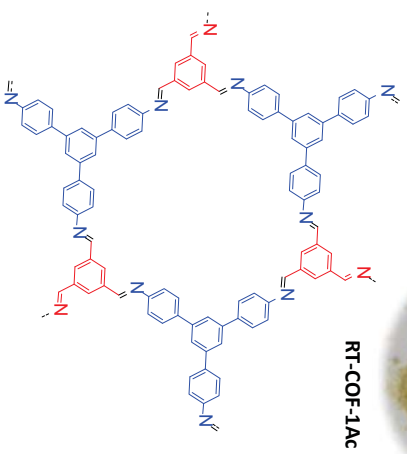
Imine COFs Processability



Solvothermal conditions



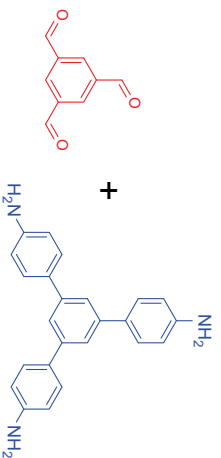
Dioxane/Mesitilene
cat. CH_3COOH



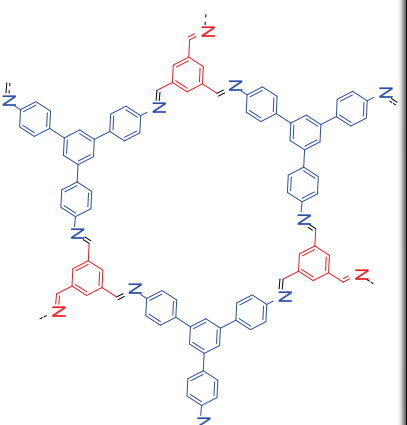
Hampering COF Processability

29

Imine COF Formation at Room Temperature

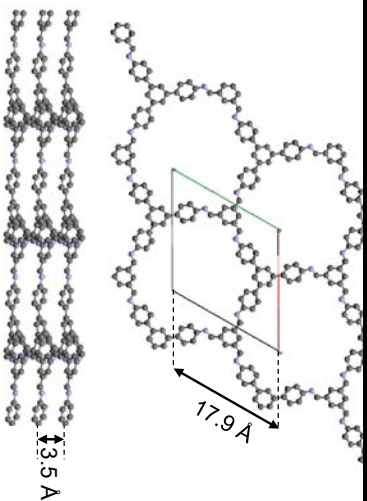
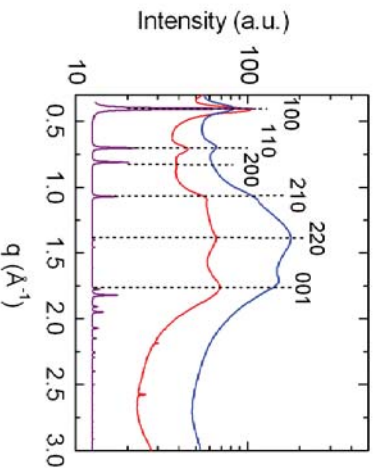
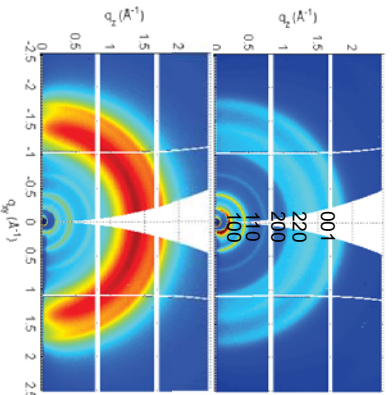


CH_3COOH
Meta-cresol

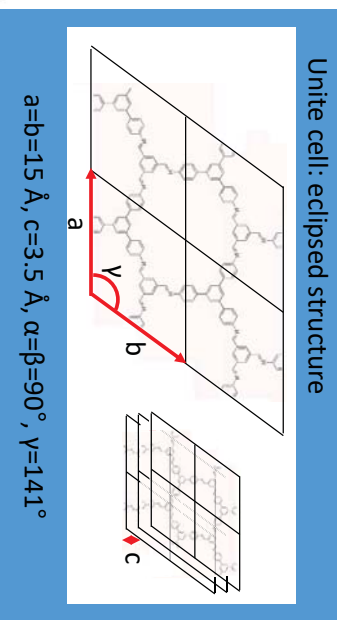


From 2005 !!

Very unusual gel based on 2D flakes

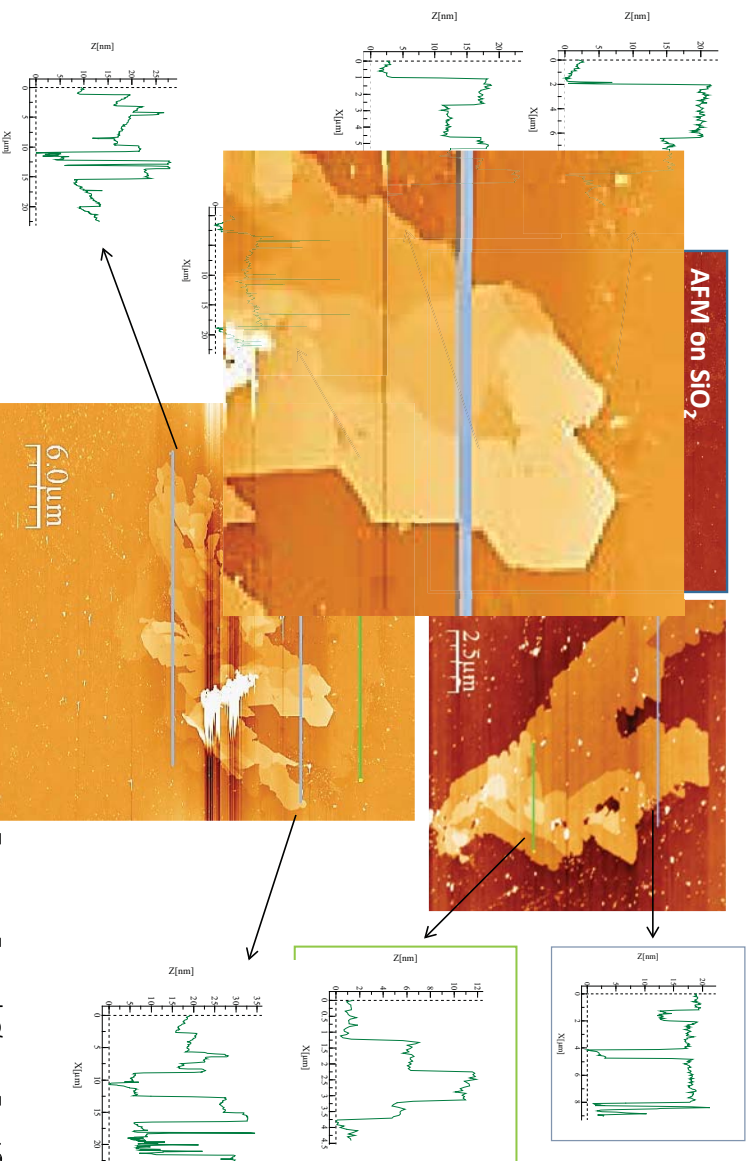


Fabiola Lisio



Zamora, F. et al *Chem-Eur J* 2015, 21, 10666-10670.

Nanolayer isolation: Atomic Force Microscopy

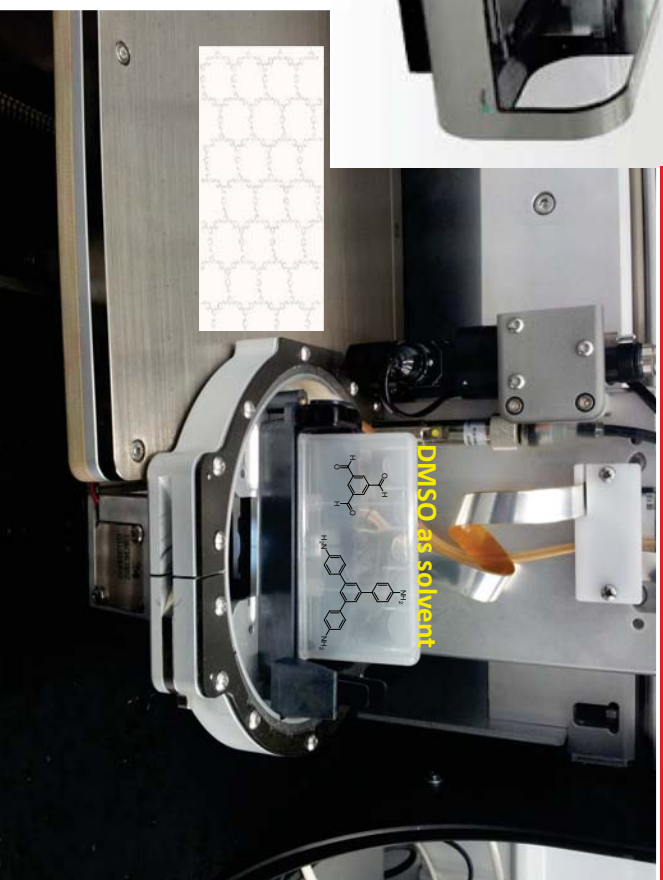


Zamora, F. et al *Chem-Eur J* 2015, 21, 10666.

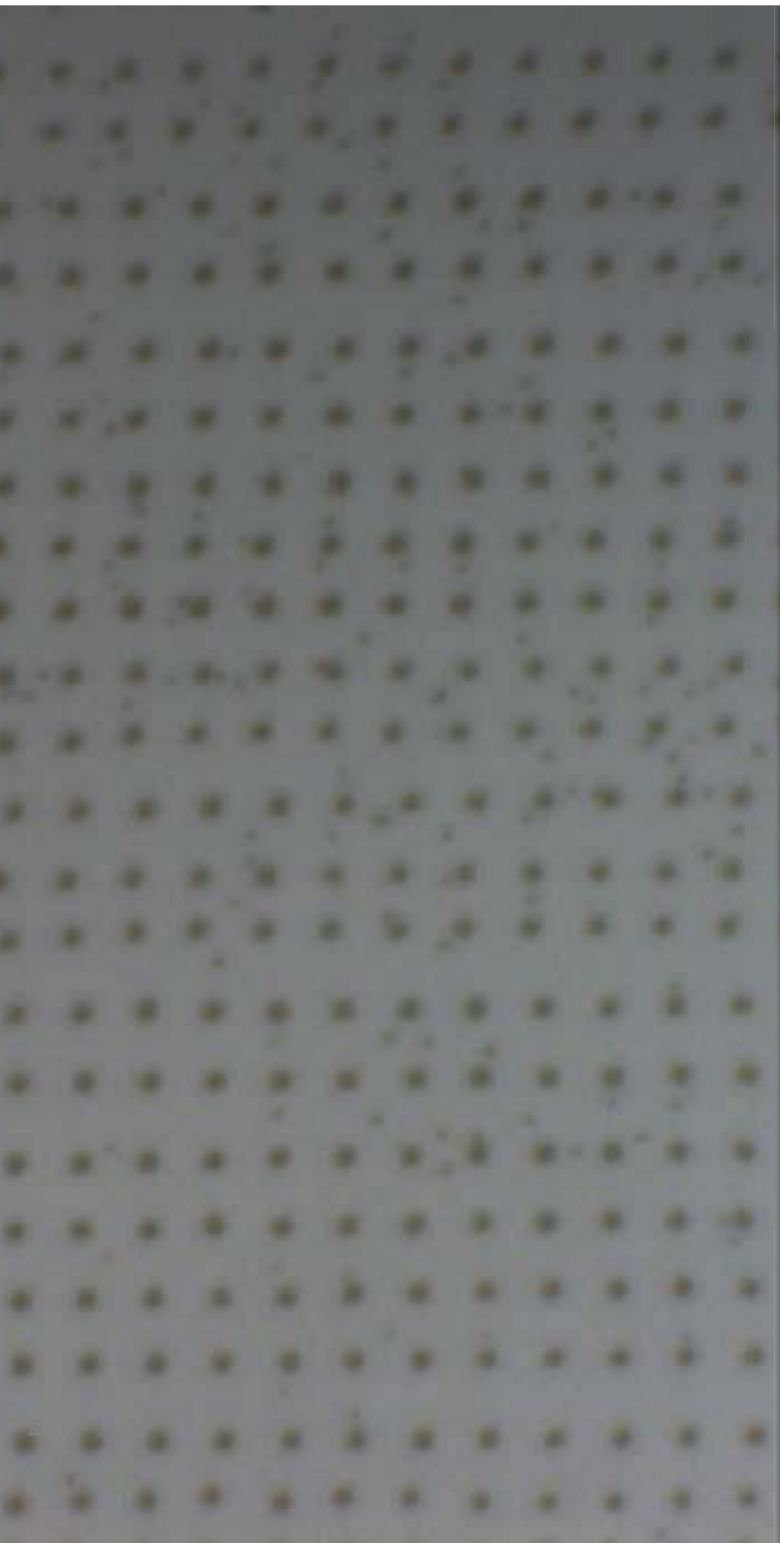
COF-Processability: Ink-jet Printing



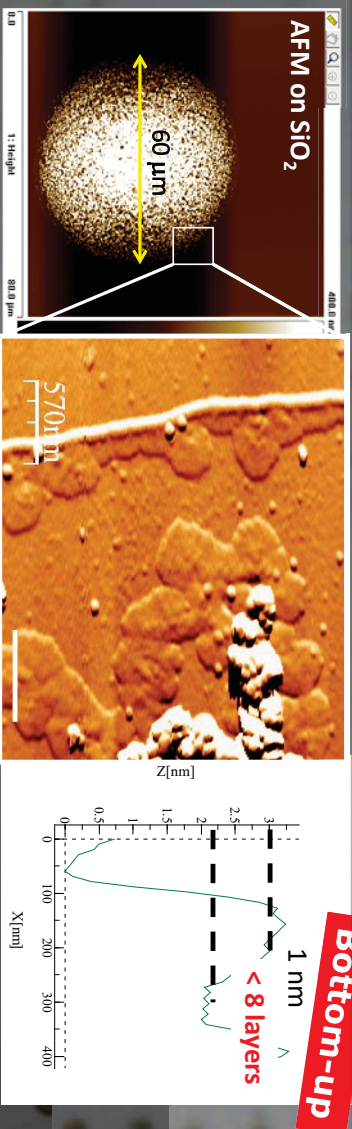
Fuji Dimatrix materials ink-jet printer DMP-2800



COF-Processability: Ink-jet Printing



COF-Processability: Ink-jet Printing

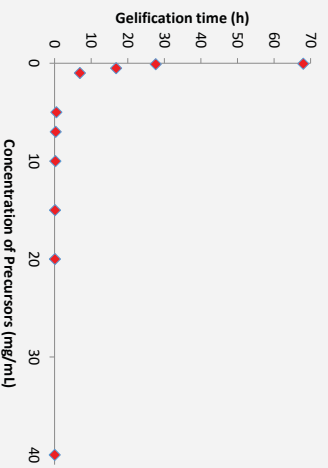


Control of the material deposition

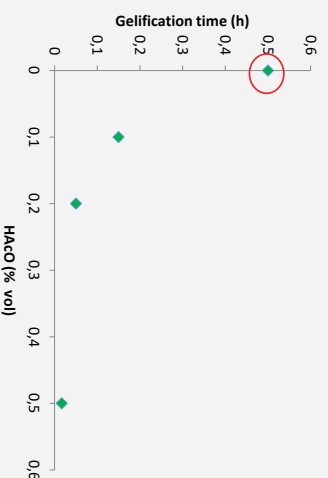
F. Zamora et al. Chem. Eur. J. 2015, 21, 10666 – 10670

Jell-O-Legos

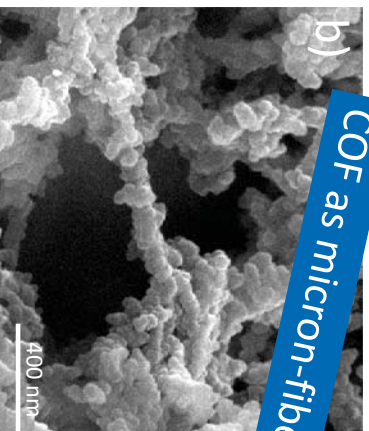
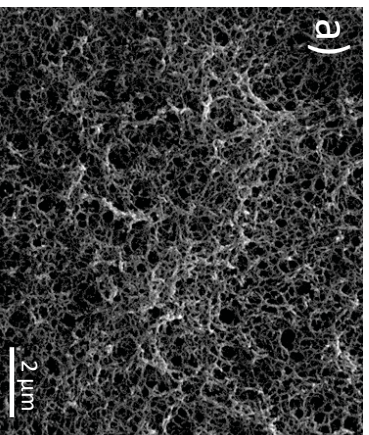
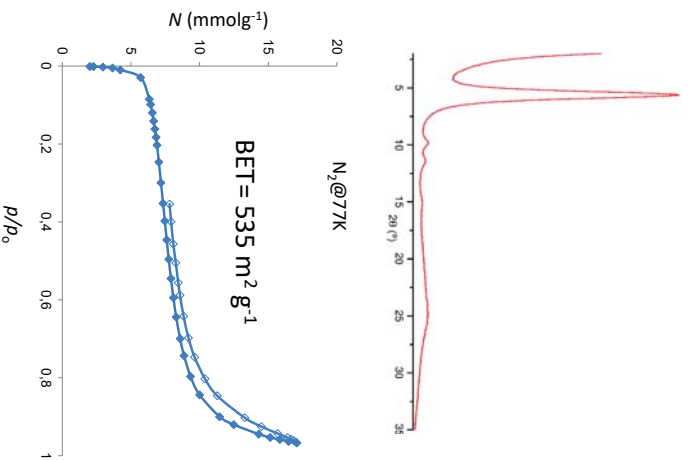
Gelification vs concentration of precursors



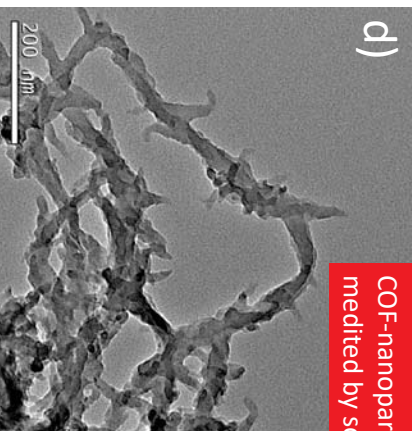
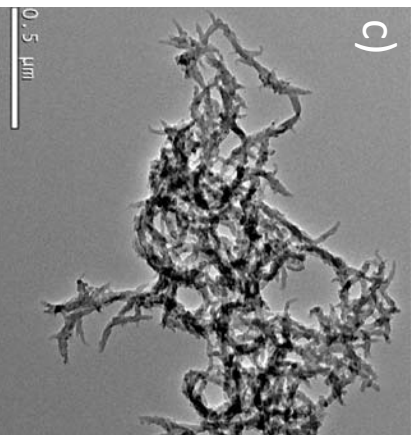
Gelification vs concentration of HAcO



COF-1 fibrillar micro-structures



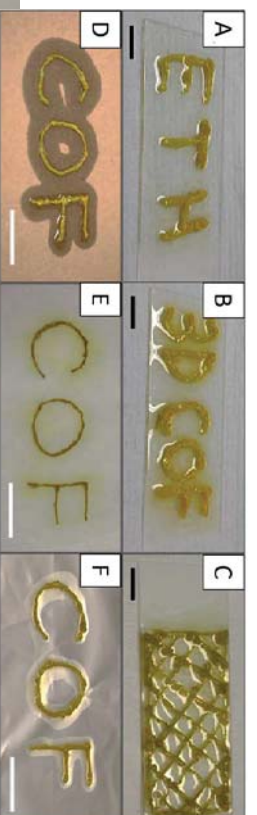
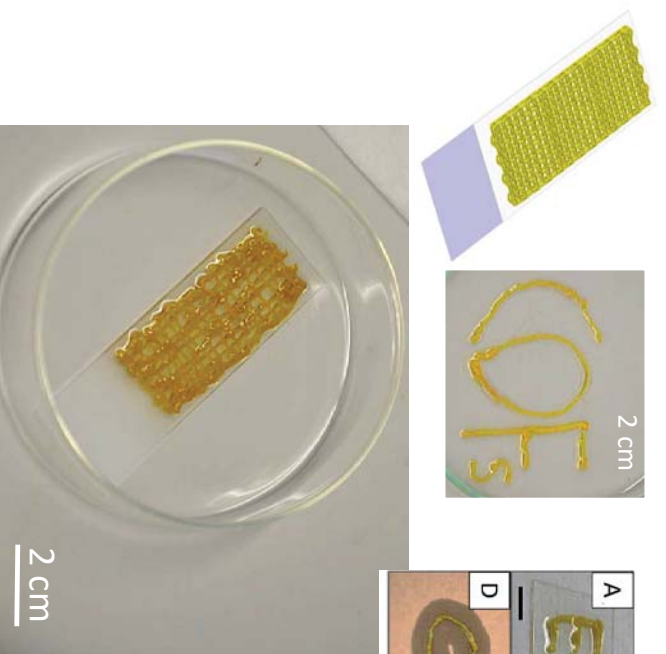
COF as micron-fibers



COF-nanoparticles mediated by solvent

ChemCommun. 2016,52, 9212-9215

COF-1 fibrillar micro-structures mechanical stable for direct 3D drawing of objects on a surface



Result: continuous 3D drawing

ChemCommun. 2016,52, 9212-9215

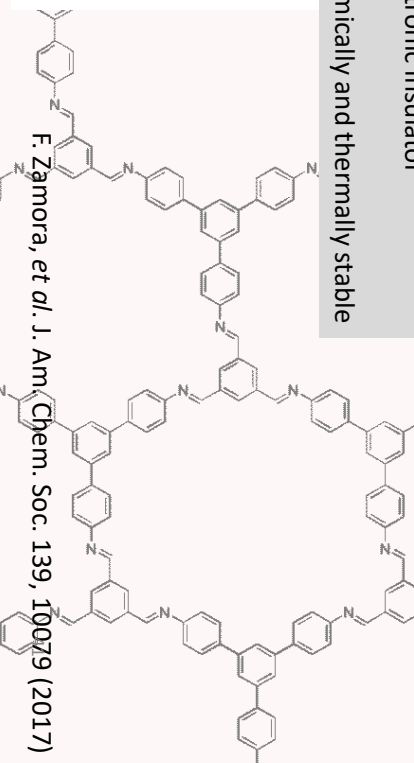
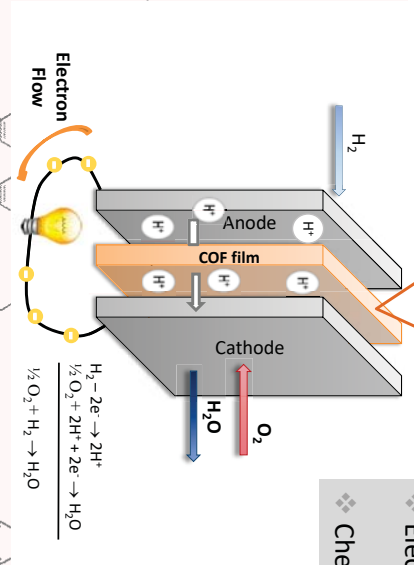
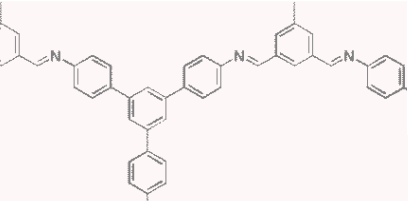
Ionic Conductivity and Potential Application for Fuel Cell of a Modified Imine-Based Covalent Organic Framework

Carmen Montoro,[†] David Rodríguez-San-Miguel,[†] Eduardo Polo,[†] Ricardo Escudero-Cid,[‡] Maria Luisa Ruiz-González,[†] Jorge A. R. Navarro,[§] Pilar Ocón,^{‡,*} and Félix Zamora^{*,†,||,¶}



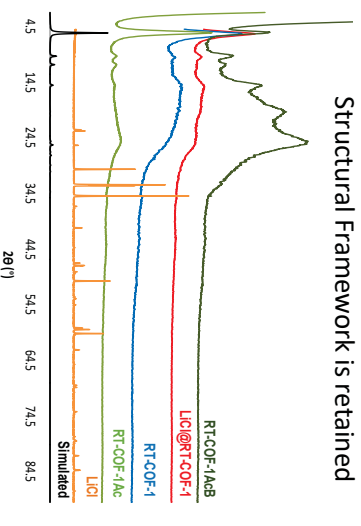
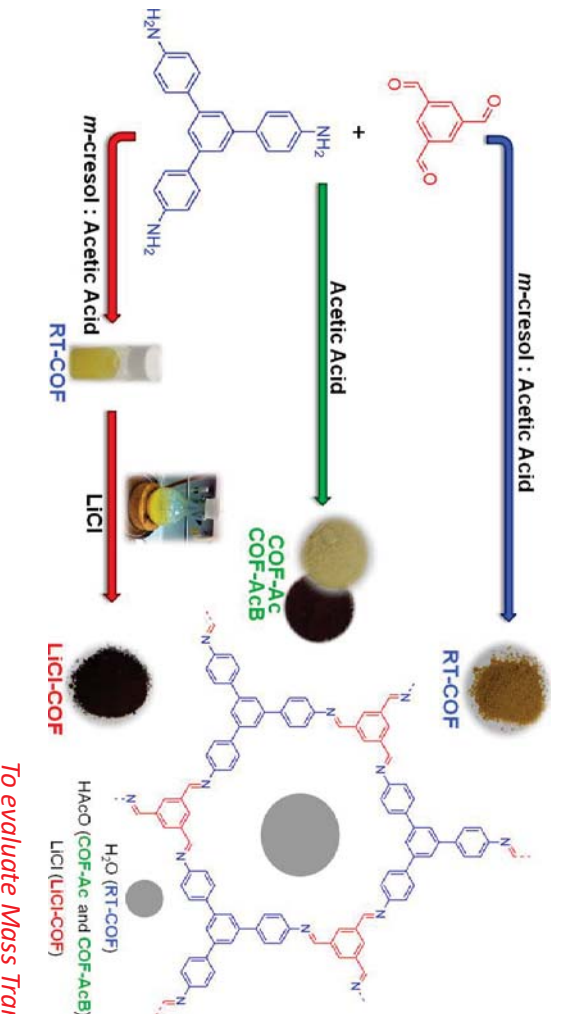
Dr. C. Montoro Prof. P. Ocón Prof. J. Rodríguez

- Imine-Based COFs:**
- ❖ Proton conductivity
 - ❖ Electronic insulator
 - ❖ Chemically and thermally stable



Functionalized COFs for ionic conductivity

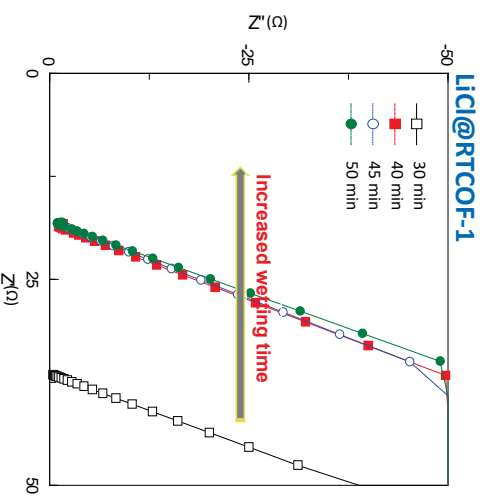
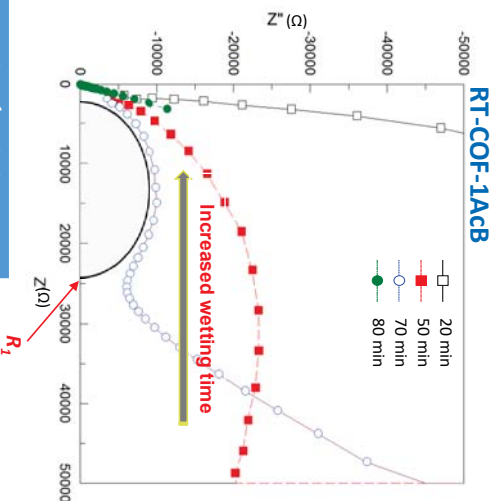
Evaluation of ion mobilities into an imine-COF framework



To evaluate Mass Transport

Ionic Conductivity Measurements

Impedance Spectroscopy:
Nyquist plots at 100 % RH and 313 K



σ , S cm ⁻¹ at 313 K	
22% RH	100% RH
RT-COF-1	1.83×10^{-5}
RT-COF-1Ac	1.07×10^{-4}
RT-COF-1AcB	5.25×10^{-4}
LiCl@RT-COF-1	6.45×10^{-3}

$$\sigma = \frac{l}{R_1 \cdot A}$$

l : film thickness

R_1 : electrolyte resistance

A : electrode area

the highest ionic conductivity value reported so far for both COFs and MOFs under similar operative conditions, but still far from Nafion[®] (6.04×10^{-2} S cm⁻¹ at 51% RH)

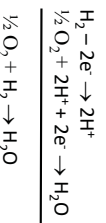
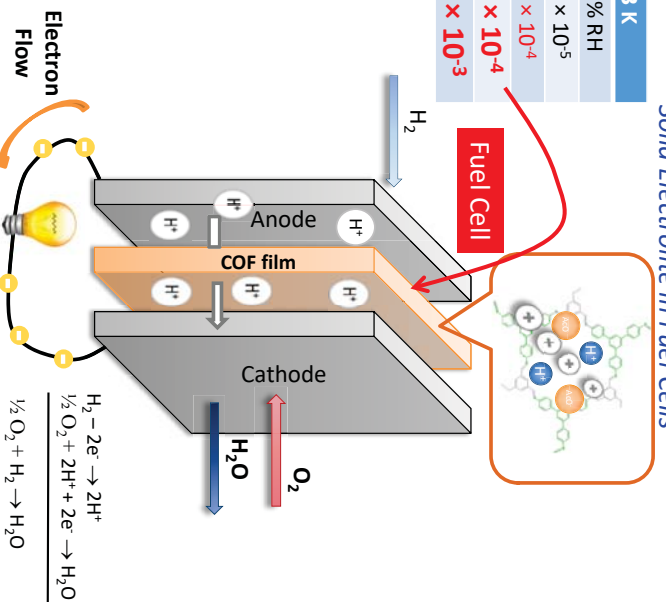
43

Performances as Proton Exchange Membranes

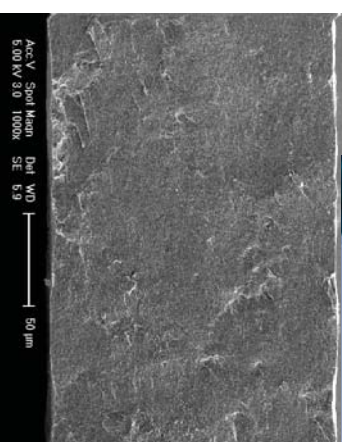
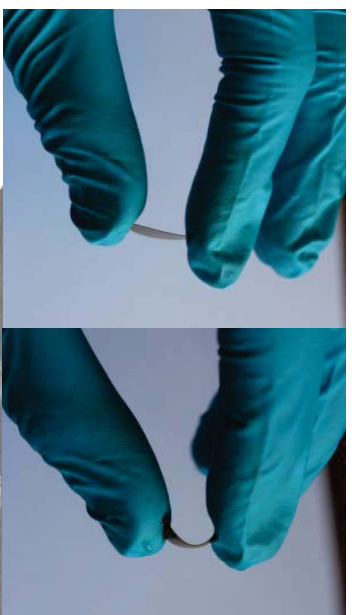
Solid Electrolyte in Fuel Cells

σ , S cm ⁻¹ at 313 K	
22% RH	100% RH
RT-COF-1	1.83×10^{-5}
RT-COF-1Ac	1.07×10^{-4}
RT-COF-1AcB	5.25×10^{-4}
LiCl@RT-COF-1	6.45×10^{-3}

Fuel Cell



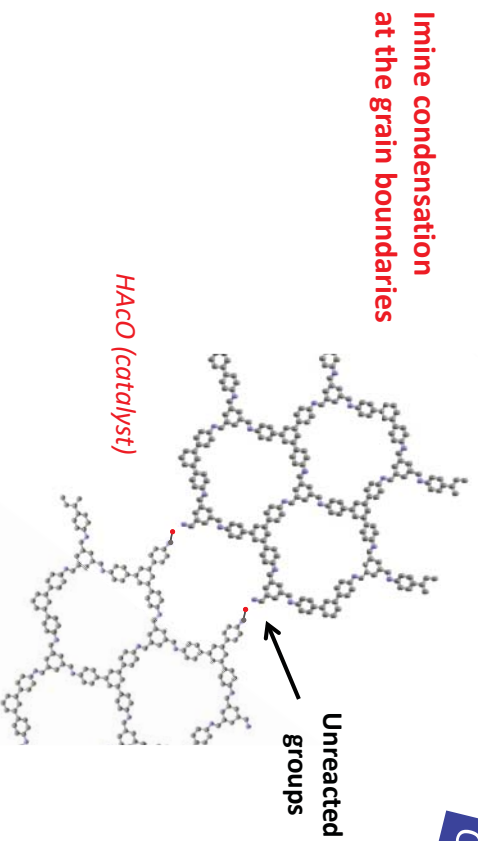
RT-COF-1Ac : Membrane Formation under Pressure



F. Zamora, *et al.* J. Am. Chem. Soc. 139, 10079 (2017)

Function of acetic acid as catalyst under the pressure

Imine condensation reaction at the material grain boundaries of the COF-polyimine layers giving rise to the formation of larger aggregates.



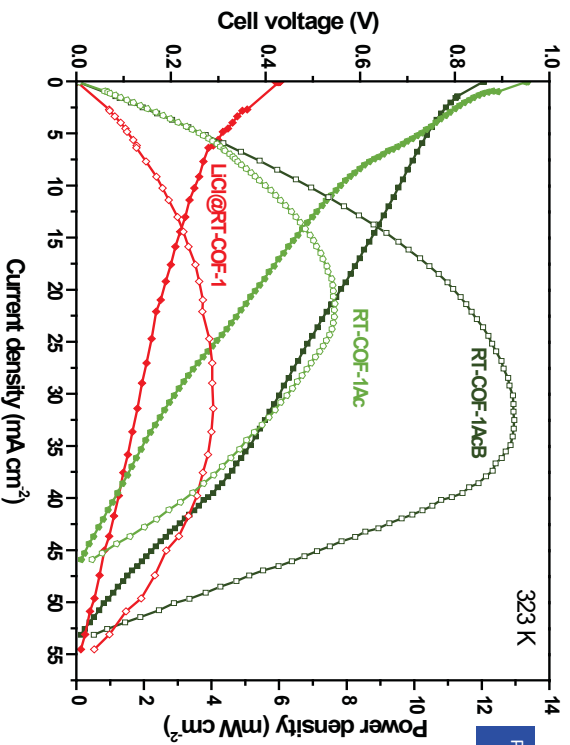
Our Hypothesis

Film: nanoparticle aggregation
mediated by either solvent or
new imine bonds

F. Zamora, *et al.* J. Am. Chem. Soc. 139, 10079 (2017)

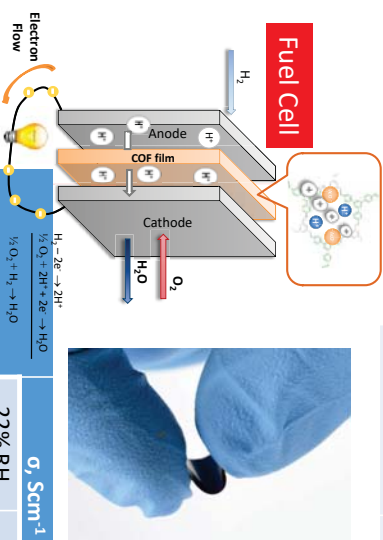
Fuel-cell measurements

Polarization and power density curves



Processability as Film vs Pellets

Material	Power Density, mW cm ⁻²	Current Density, mA cm ⁻²
RT-COF-1AC	7.64	45.9
RT-COF-1ACB	13	53.1
LiCl@RT-COF-1	4.1	54.5

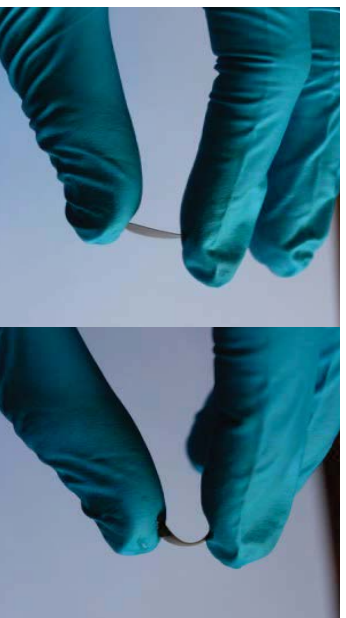


Material	o, Scm ⁻¹ at 313 K
RT-COF-1	22% RH
RT-COF-1AC	$< 1 \times 10^{-10}$
RT-COF-1ACB	$< 1 \times 10^{-10}$
LiCl@RT-COF-1	$< 1 \times 10^{-9}$

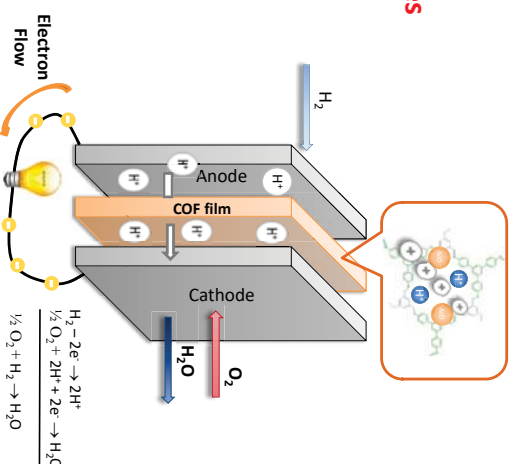
F. Zamora, *et al.* J. Am. Chem. Soc. 139, 10079 (2017)

Better Performances as Proton Exchange Membranes

Result: COF shapping - membranes



Excellent Mechanical Properties Enhance Performances



COF Aerogels

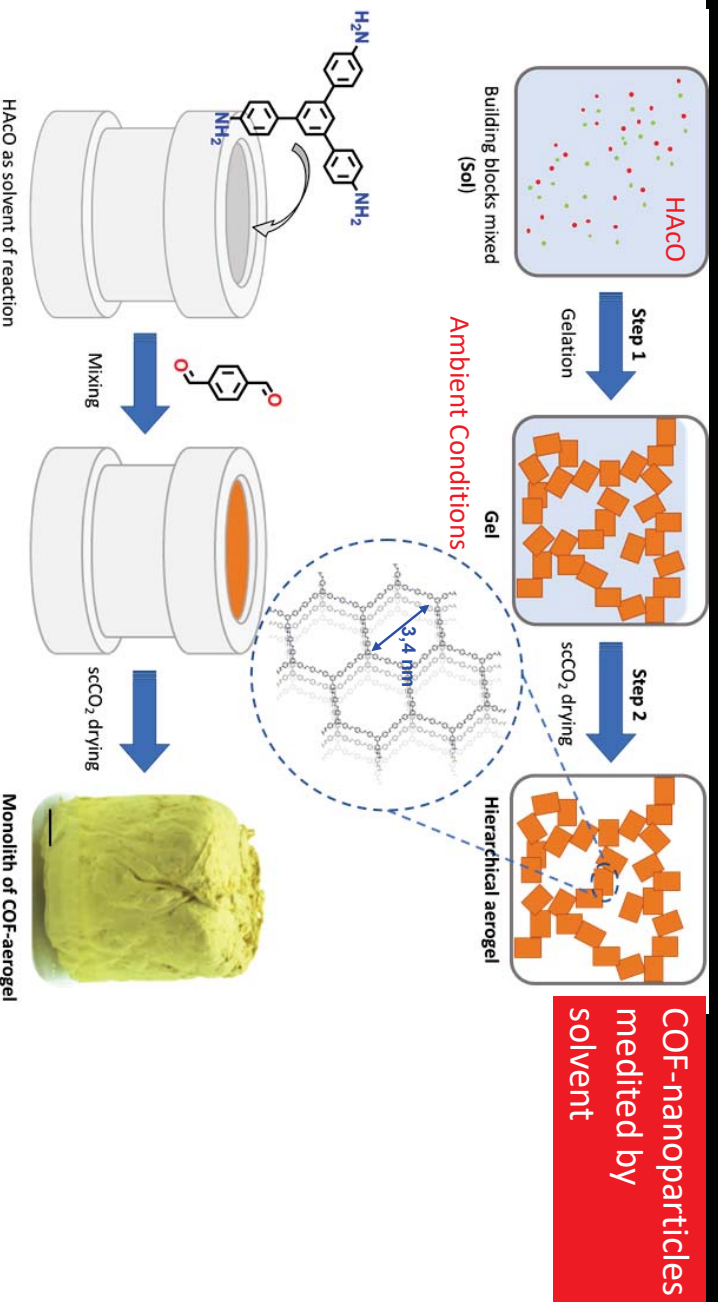


F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977⁴⁹

How to make a COF Aerogel

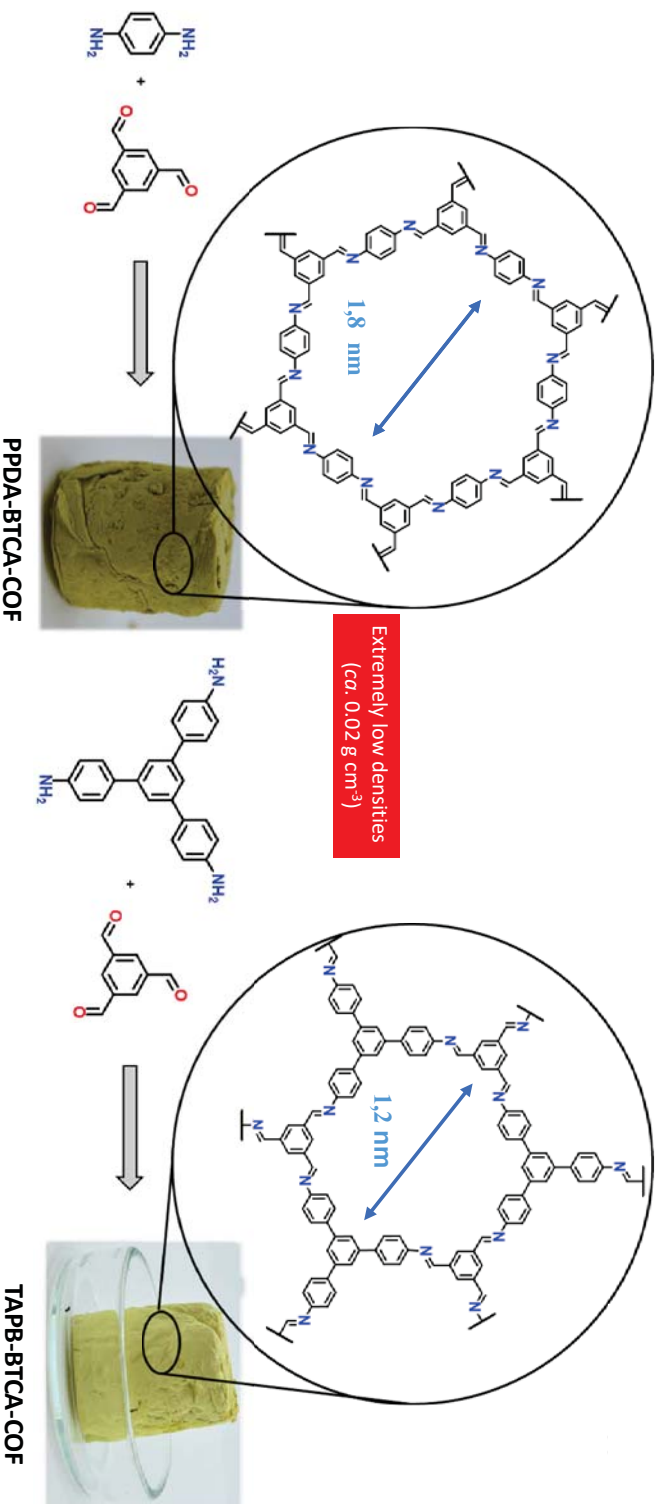


Jesus A. Martín



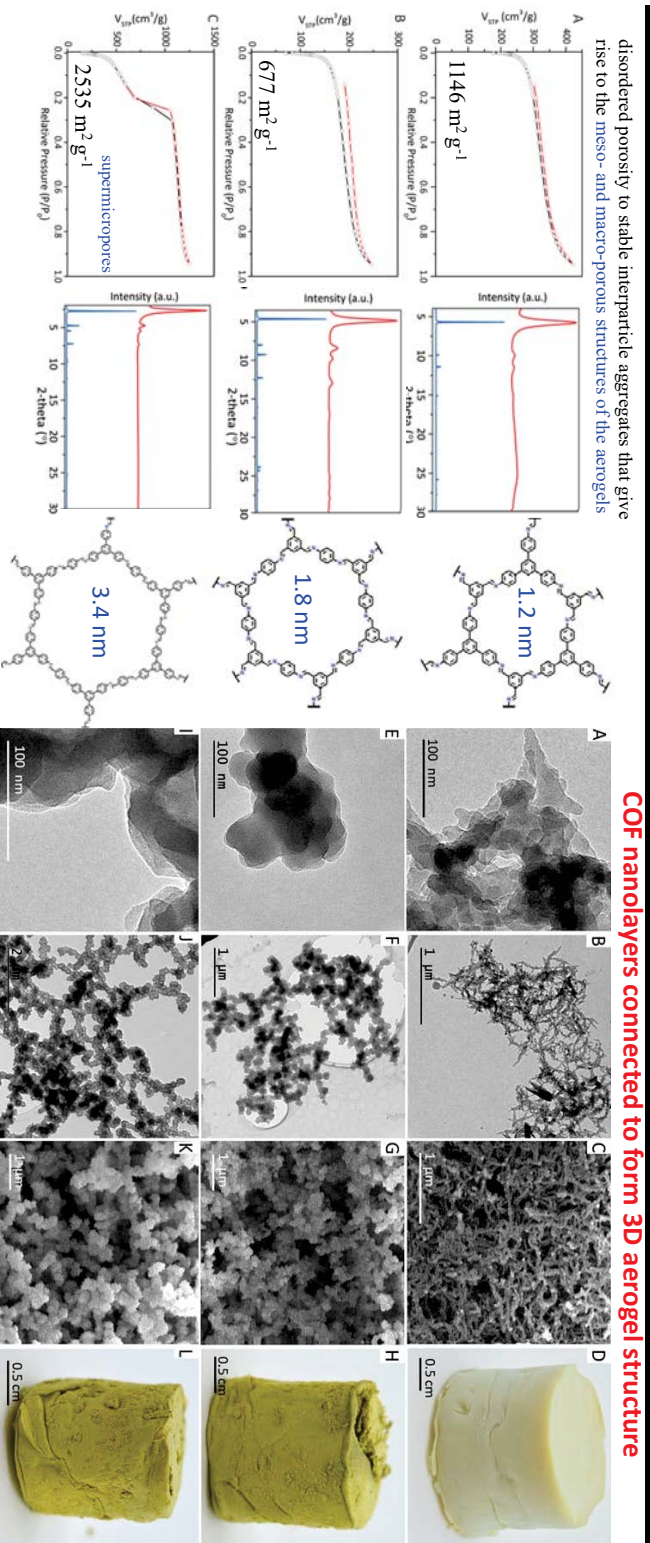
F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977⁵⁰

COF Aerogels



F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977

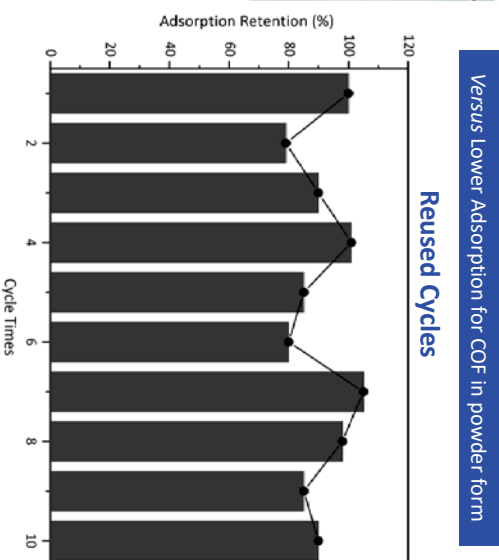
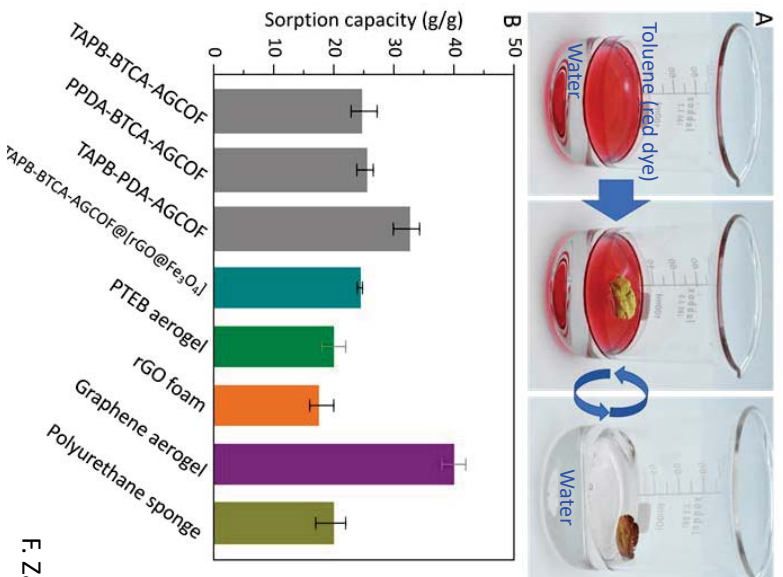
COF Aerogels



F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977

Adsorption Properties of COF Aerogels

Prof-of-Concept

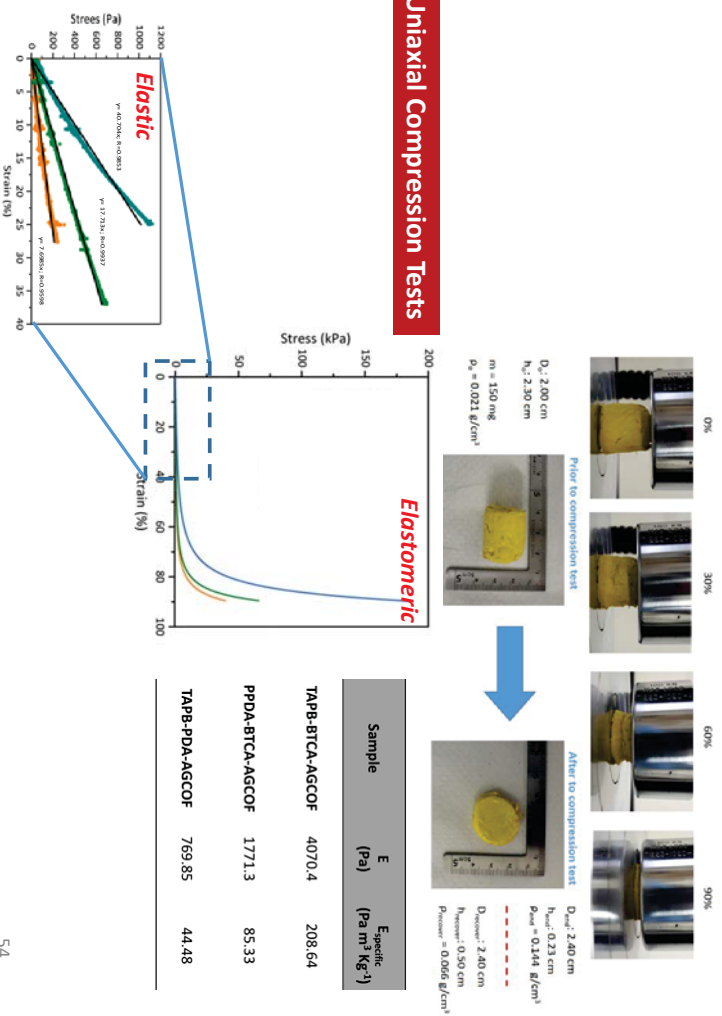
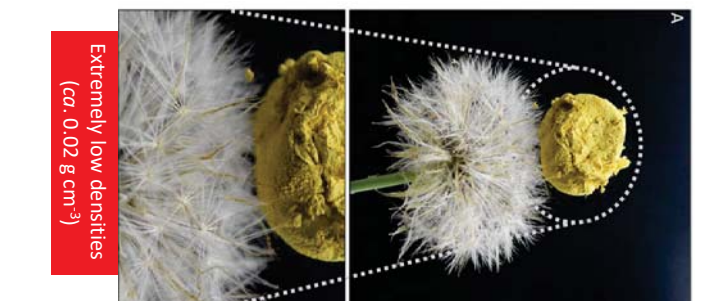


Versus Lower Adsorption for COF in powder form

Reused Cycles

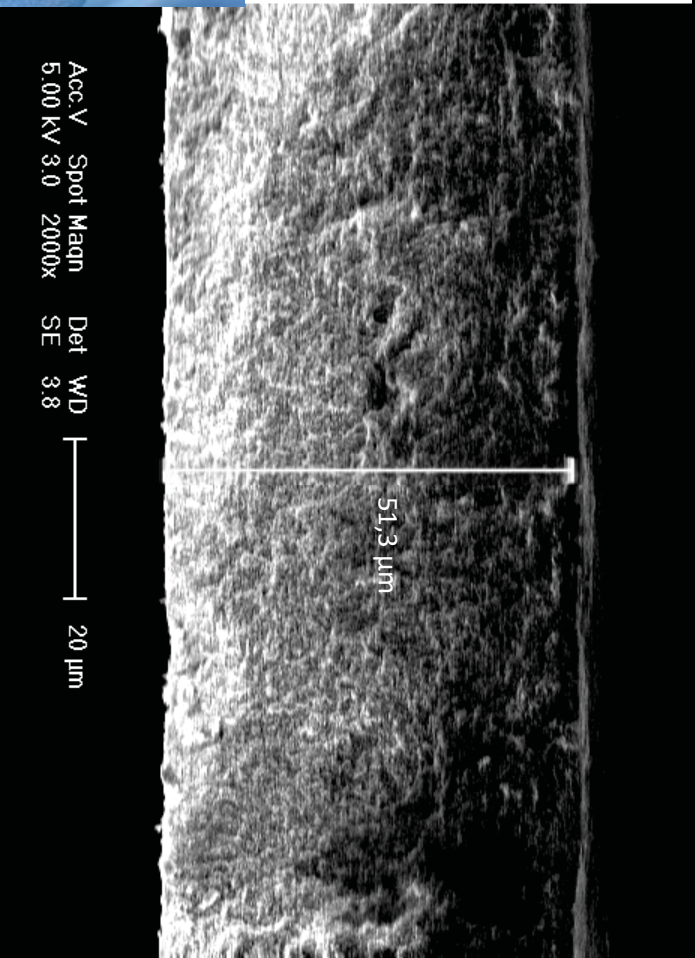
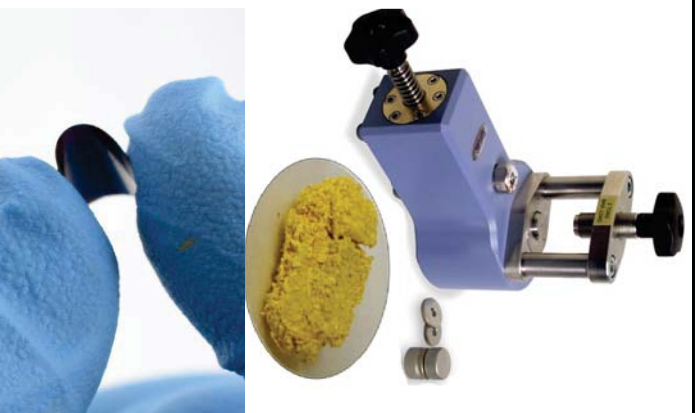
F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977⁵³

Mechanical Properties of COF Aerogels



F. Zamora et al. *Angew. Chem. Int. Ed.* 2021, 60, 13969–13977⁵⁴

Membrane Formation under Pressure from COF Aerogels

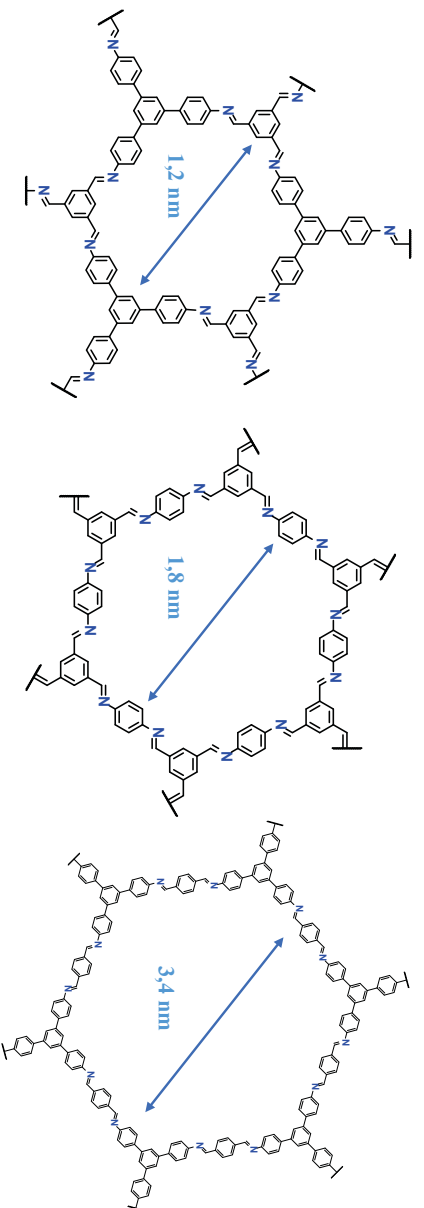
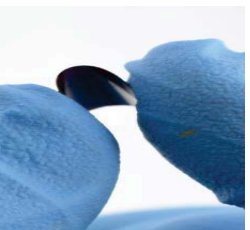


F. Zamora et al. Adv. Sci. 2022, 2104643

Gas Separation using COF membranes

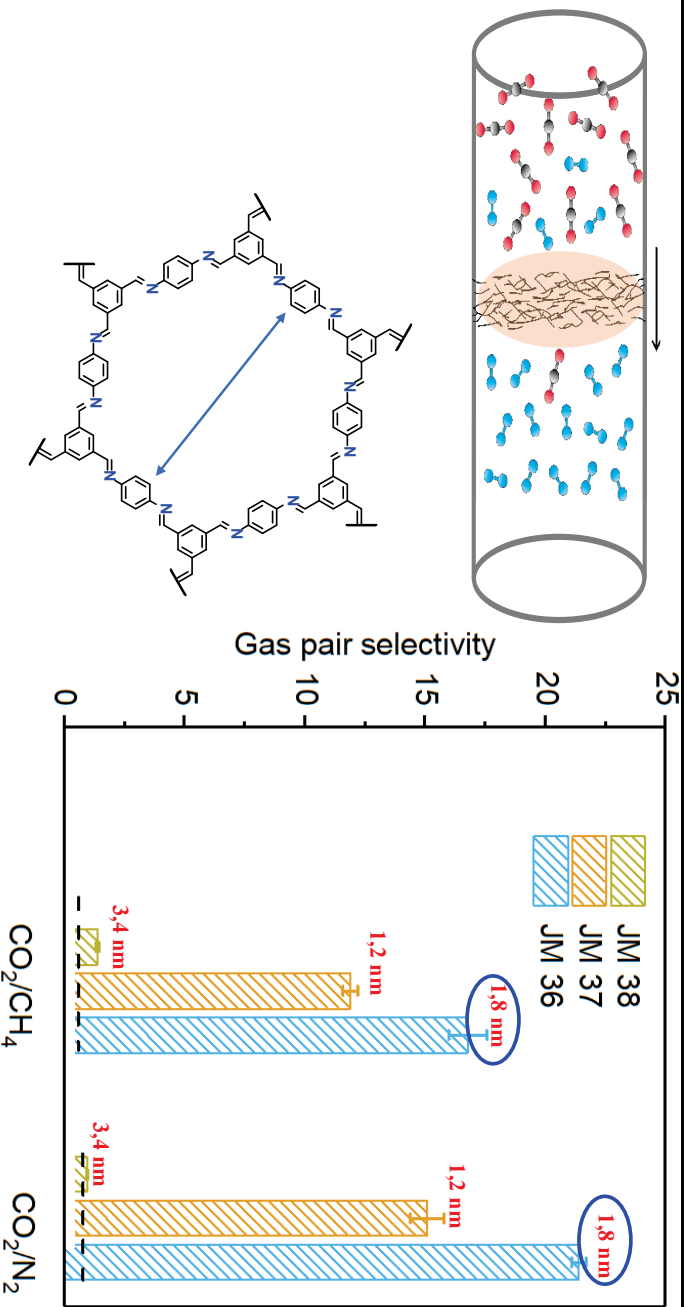


Prof. Dan Zhao



F. Zamora et al. Adv. Sci. 2022, 2104643

Gas Separation using COF membranes



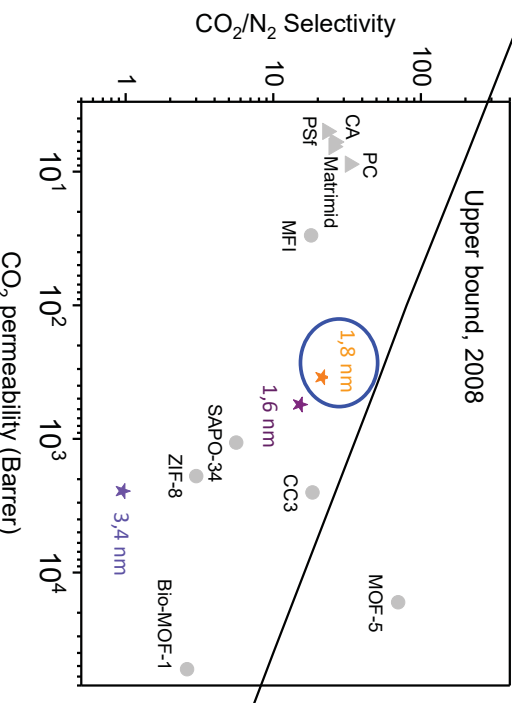
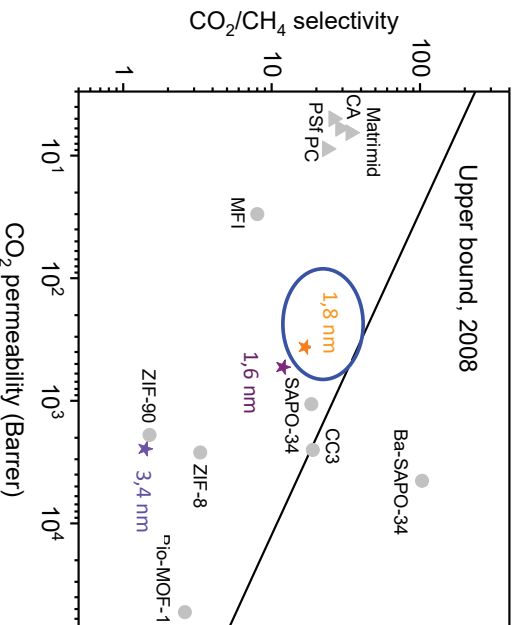
The mixed gas pair selectivity is higher compared to the ideal gas pair selectivity owing to the sorption and diffusion competition between the gas mixtures.

F. Zamora et al. Adv. Sci. 2022, 2104643

COF membranes Performances for Gas Separation

We plotted the separation performance of pure COF membranes and compared them with other membranes on the **Robeson upper bound plots**.

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

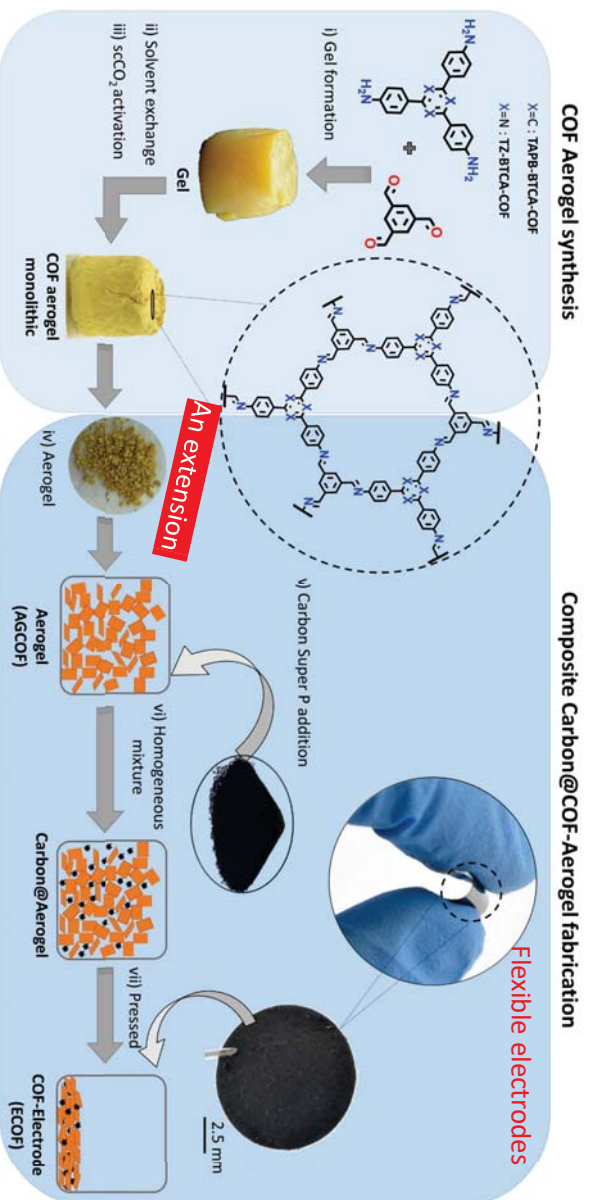


F. Zamora et al. Adv. Sci. 2022, 2104643



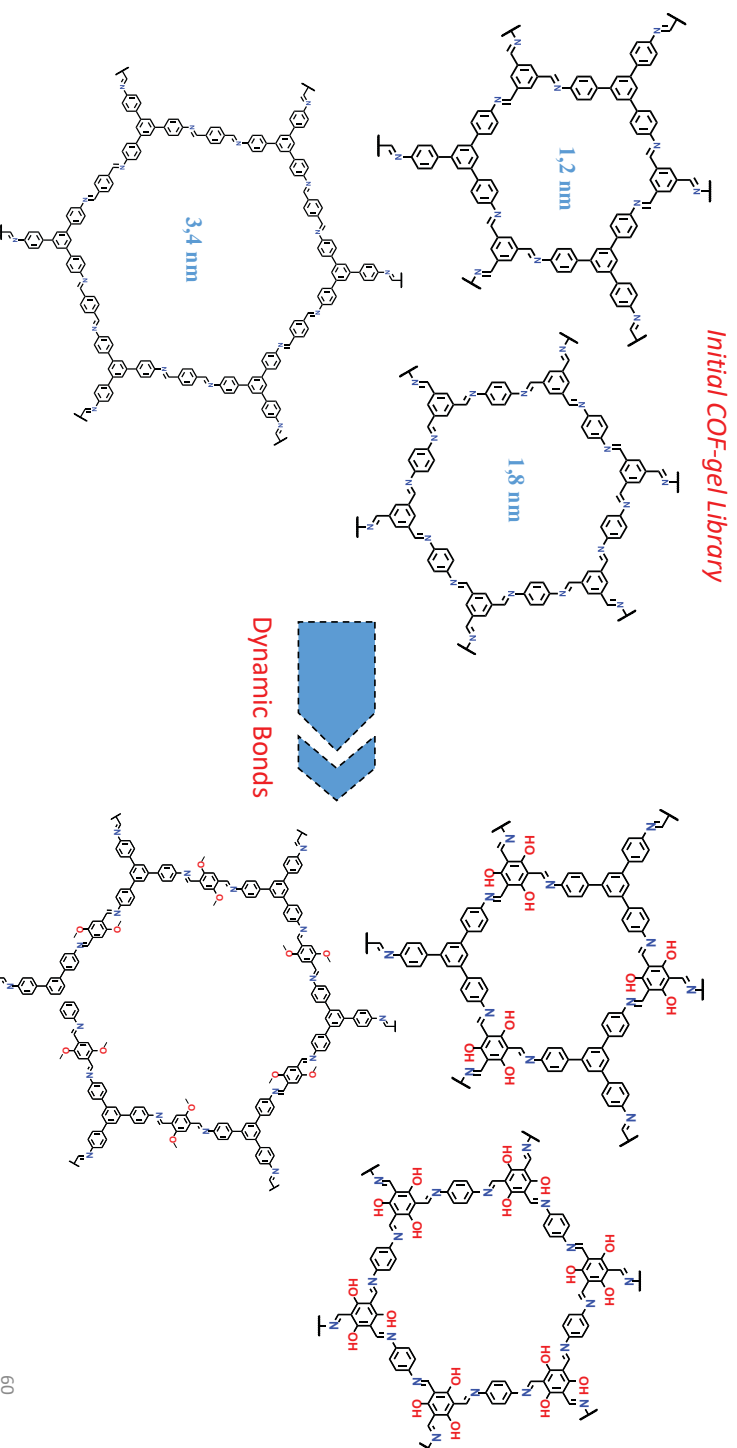
Electrochemical Double-Layer Capacitor based on Carbon@ Covalent Organic Framework Aerogels

Jesús A. Martín-Illán[†], Laura Sierra[†], Pilar Ocón,^{*} and Félix Zamora^{*}



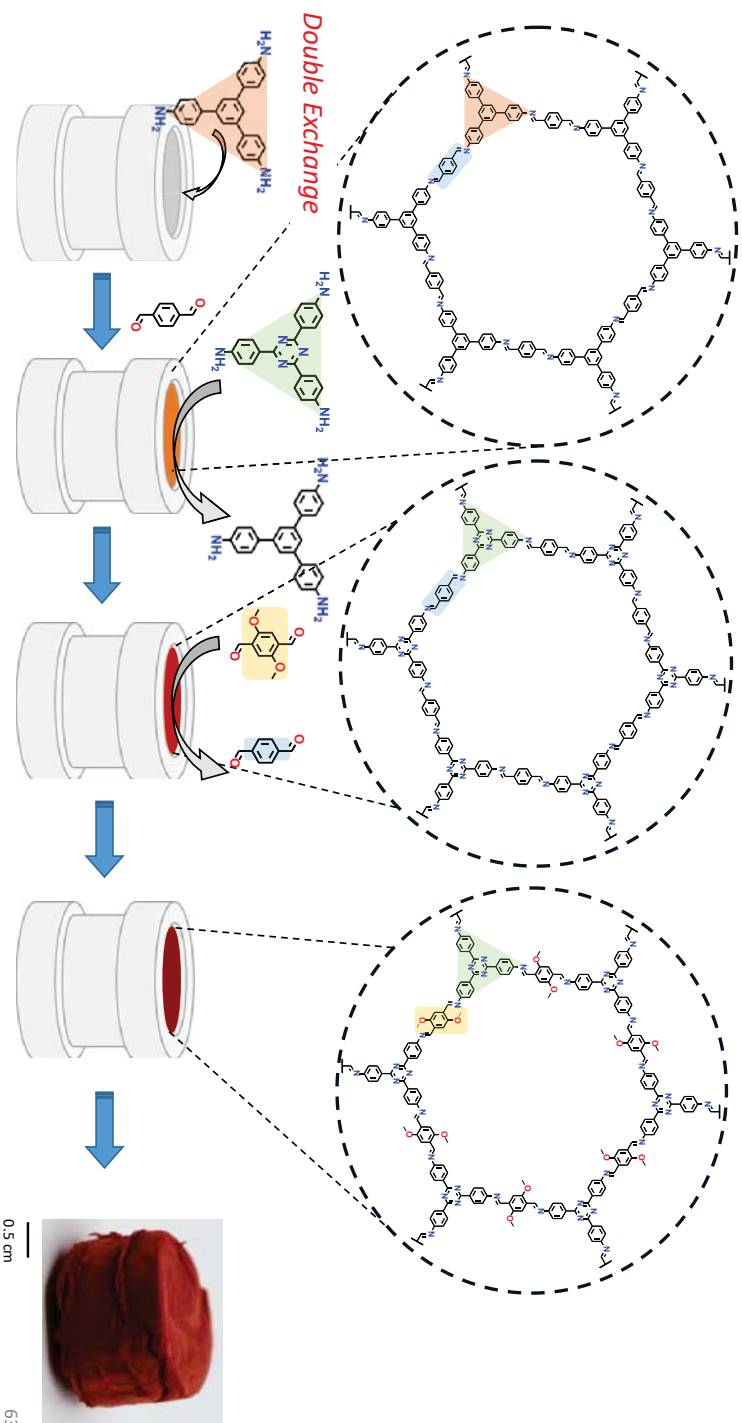
59

Imine-based COFs: Gel to Aerogel synthesis

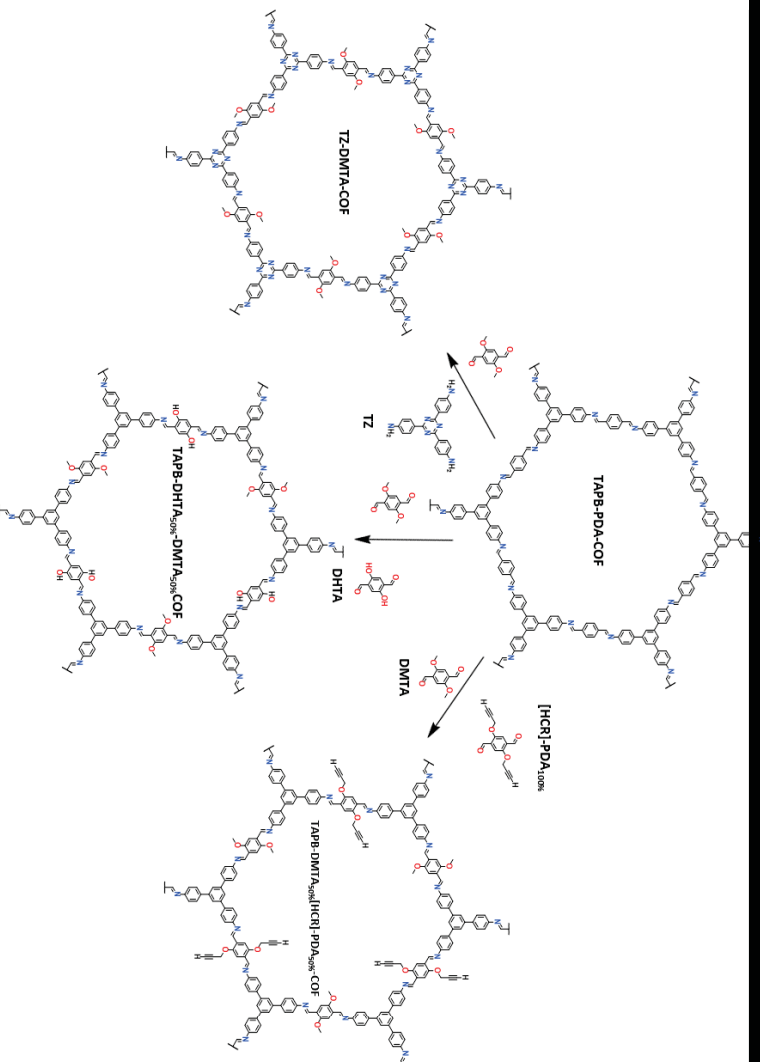


60

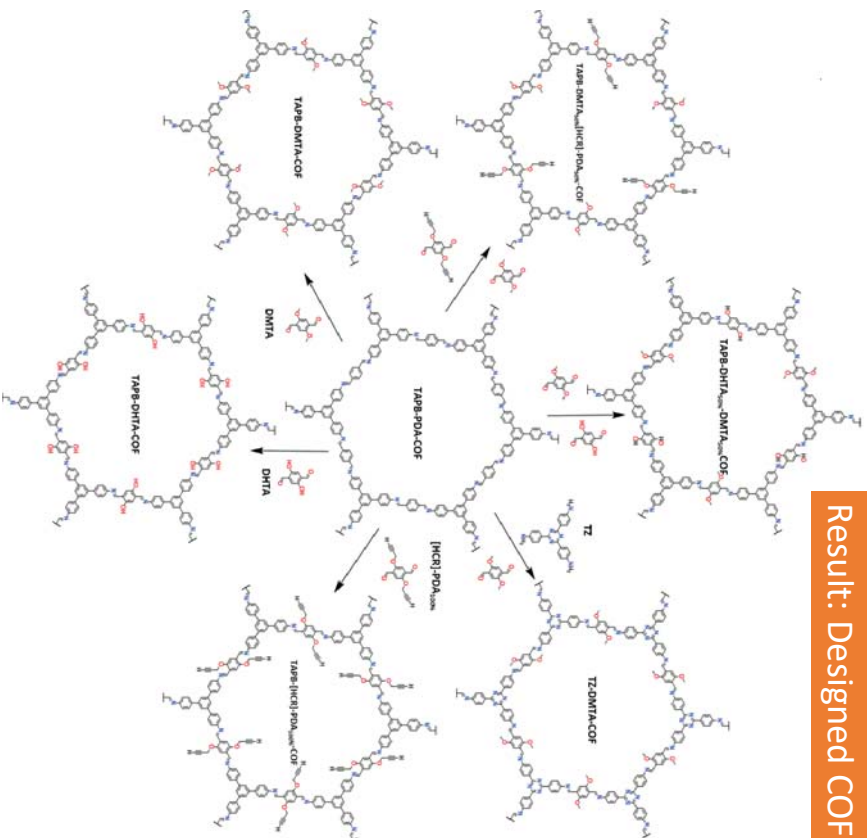
Imine-based COFs: Gel to Gel to Aerogel synthesis



Imine-based COFs: Gel to Gel to Aerogel synthesis

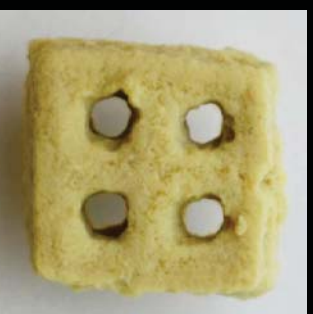


Result: Designed COF membranes & aerogels



65

3D Printing COFs



66

3D Printing of COFs: Antecedents

GO@COF Composite

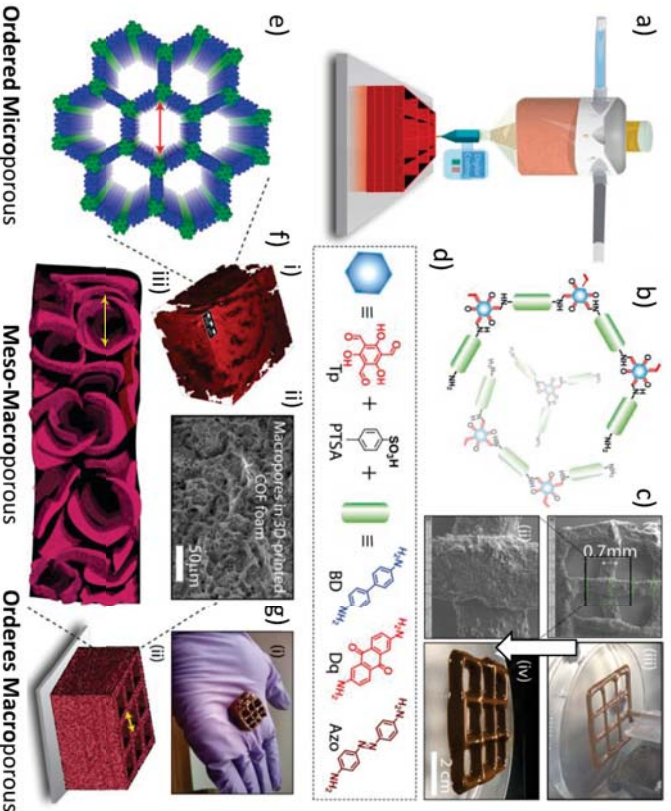


Fig. 10. A) Illustration of the cof-go foam synthesis and 3d printing process: a hydrogel is created when graphene oxide, water, and cof precursors are combined, this hydrogel is employed in 3d printing. b) schematic depiction of the cof's incomplete frameworks, at this point, we anticipate that the 3d printing ink will begin to form oligomers or incomplete framework structures c) (i-ii) the sem image of a cof-go foam grid that was 3d printed at a millimeter scale with a print resolution of ~ 0.7 mm and pore size of ~1.5 mm. c) (iii, iv) The digital images of a COF-GO foam grid that was 3D manufactured at a centimeter scale. d) The ingredients used to create COF-GO foam. e) The TpbD COF space-filled model. X-ray microtomography of TpbD foam created via 3D printing. It exhibits the macropores in the matrix of the COF-GO foam, the macropores in the matrix of the CCF-GO foam, the TpbD foam monolith, and the macropores in the matrix of the graphical representation of the macroporous foam. g) A graphic representation of the nine-pore COF-GO foam grid and 1 a digital photograph of a 2.3 × 2.3 cm self-supported nine-pore COF-GO foam grid that was 3D printed. Adapted from reference 91 with permission of the copyright holders.

V. Singh, H.R. Byon, *Water. Mater. Adv.* 2 (2021) 3188–3212

67

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Article

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-Prius, Marko Pavlovic, Ihtvan Sraljagić, M. Luisa Ruiz Gonzalez, José M. González-Calbet, Davide Rodighiero, Luca Pesce, Giovanni M. Pavan, Inbar Imaz, Mary Cano-Sardina, Daniel Maspooh, Salvador Pané, Andrew J. de Mello, Felix Zamora,* and Josep Puigmarç-Laus*

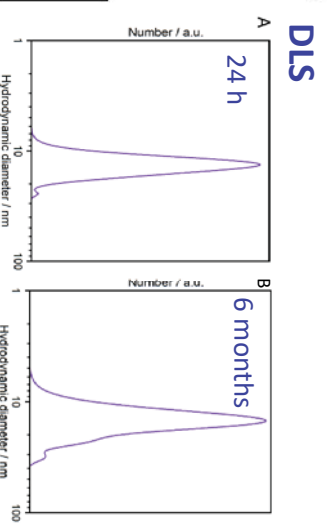
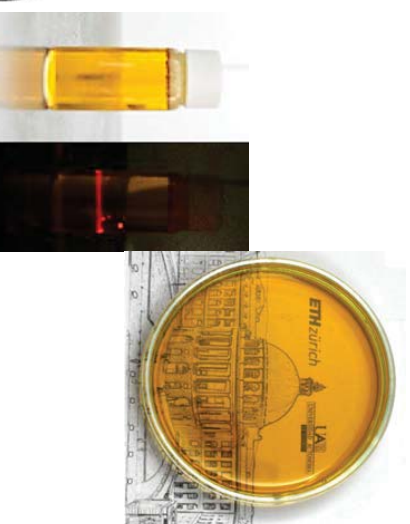
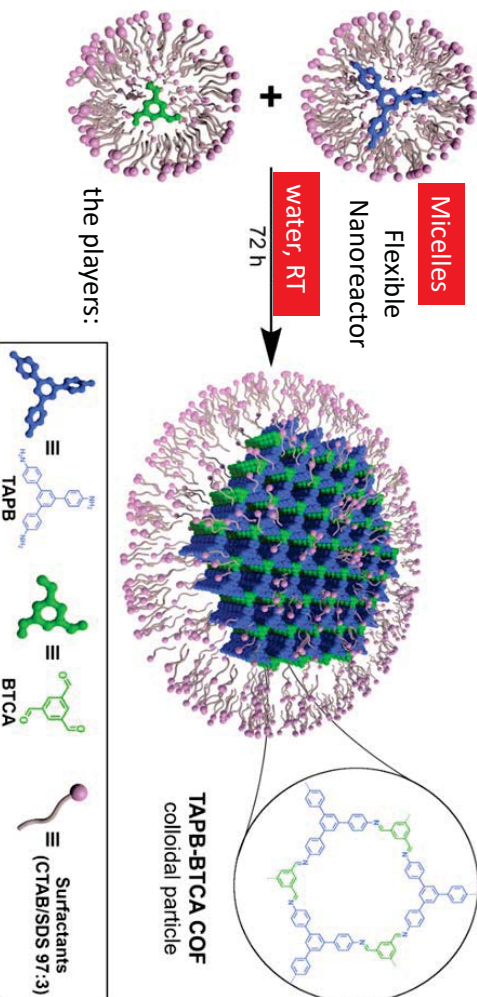
Chem. Mater. 2020, 32, 3540–3547

Read Online



Dr. David Rodríguez

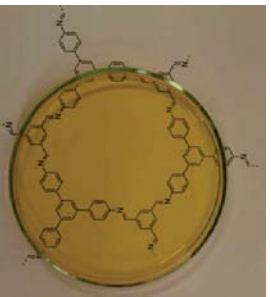
Prof. Josep Puig-Martí



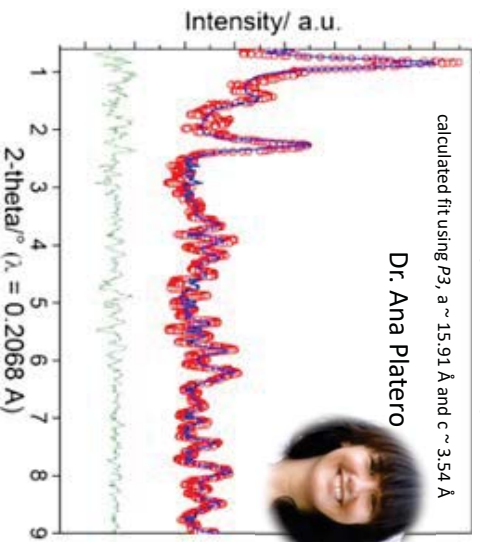
EP18179325.8 / WO2019243602

68

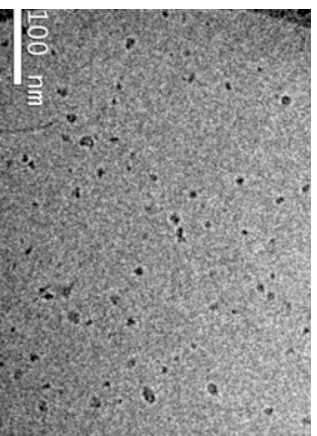
Characterization of TAPB-BTCA COF colloidal sub-20nm particles



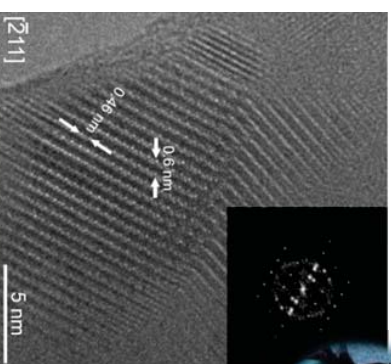
Synchrotron X-ray diffraction pattern



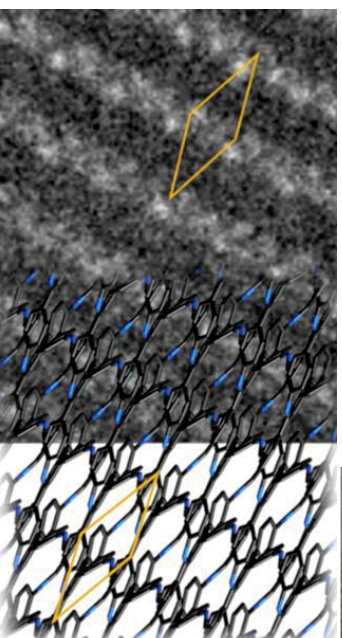
Cryo-TEM



Dr. Luisa Ruiz
HRTEM



schematic structural model of TAPB-BTCA COF along the $[-211]$ projection

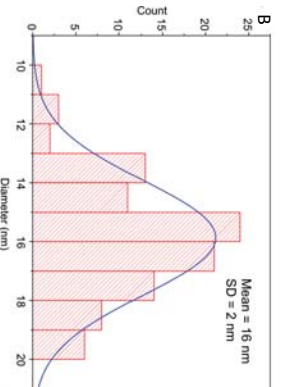
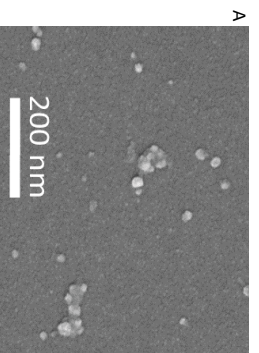


69

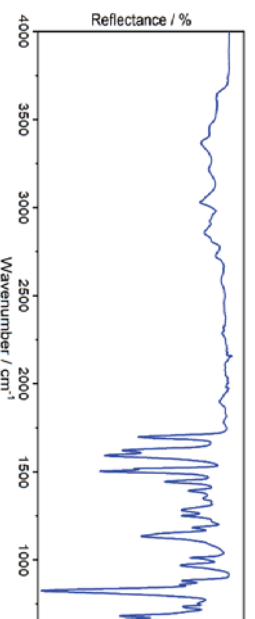
Characterization of TAPB-BTCA COF sub-20nm particles

Particles are isolated by centrifugation

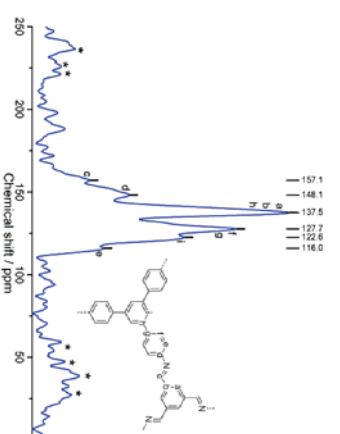
SEM



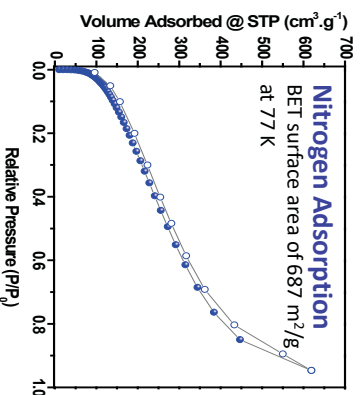
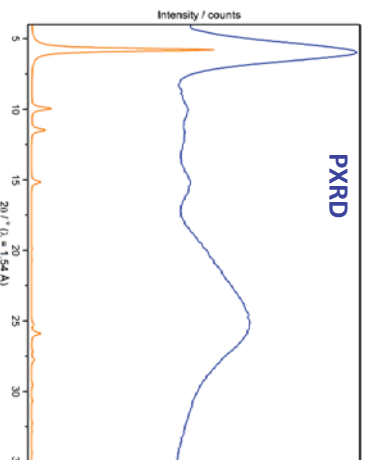
ATR-FT-IR



¹³C CP-MAS NMR spectrum

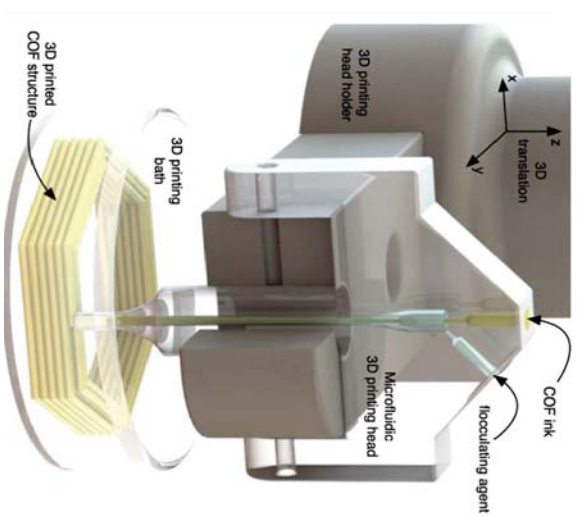
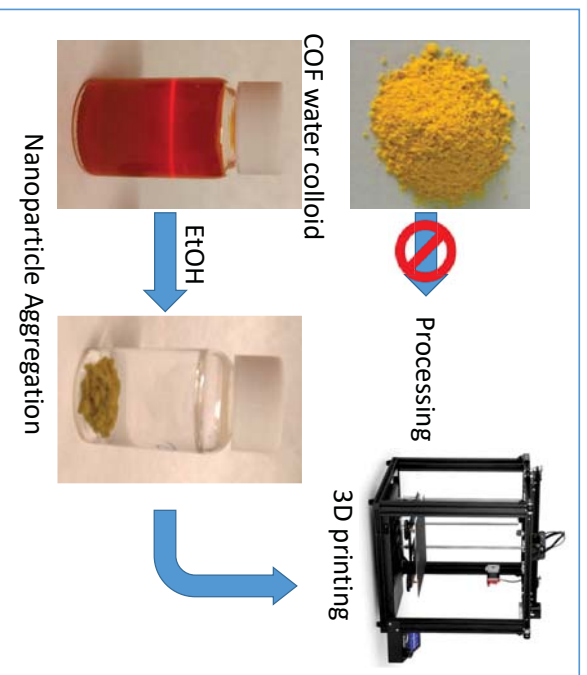


PXRD

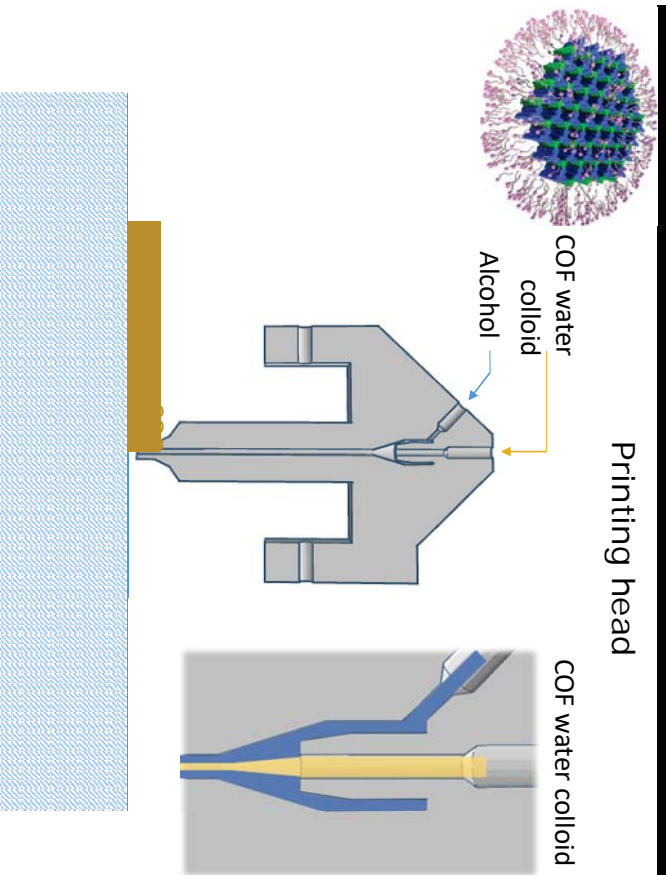


EP18179325.8 / WO2019243602

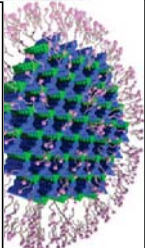
3D Printing of COFs



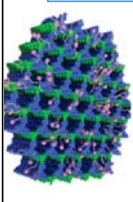
3D Printing of COFs



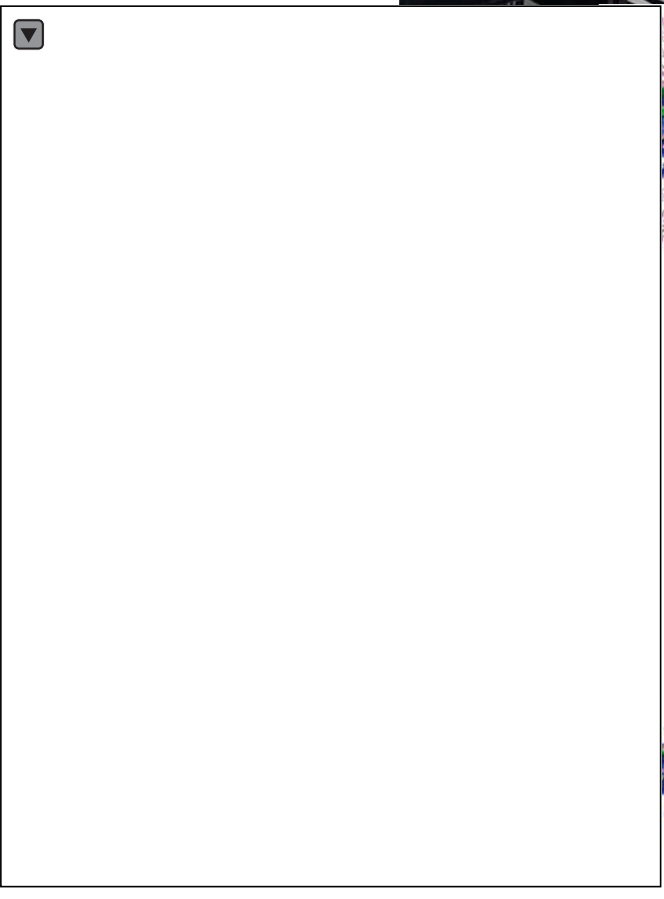
3D Printing of COFs



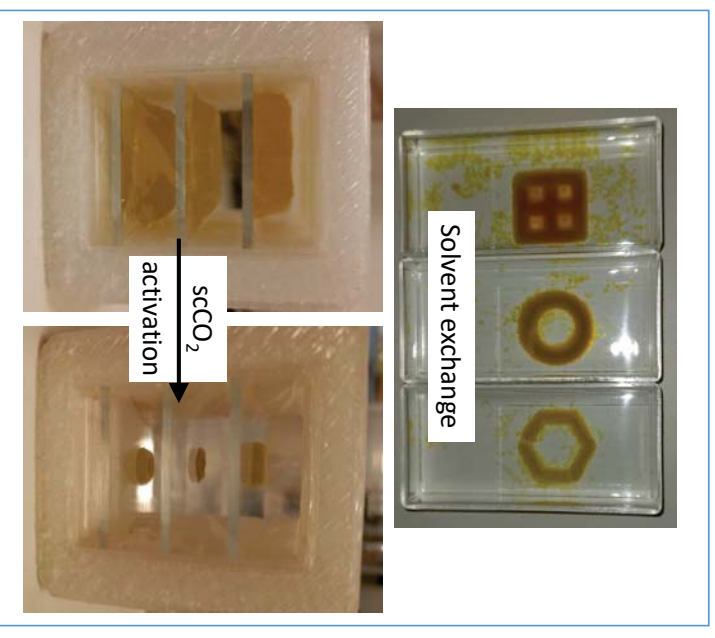
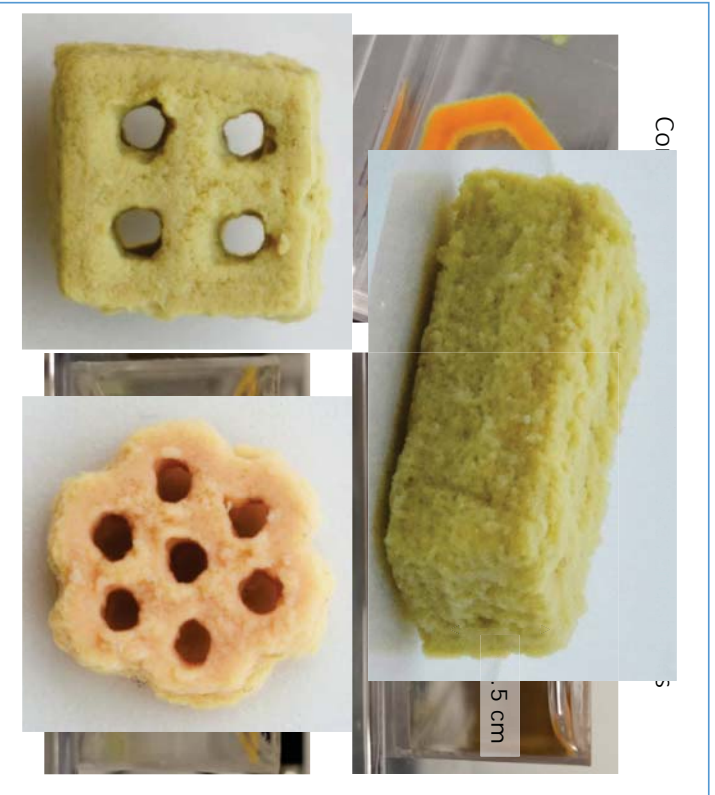
Printing into alcohol for direct
surfactant removal



Dr. Sergio Royuela

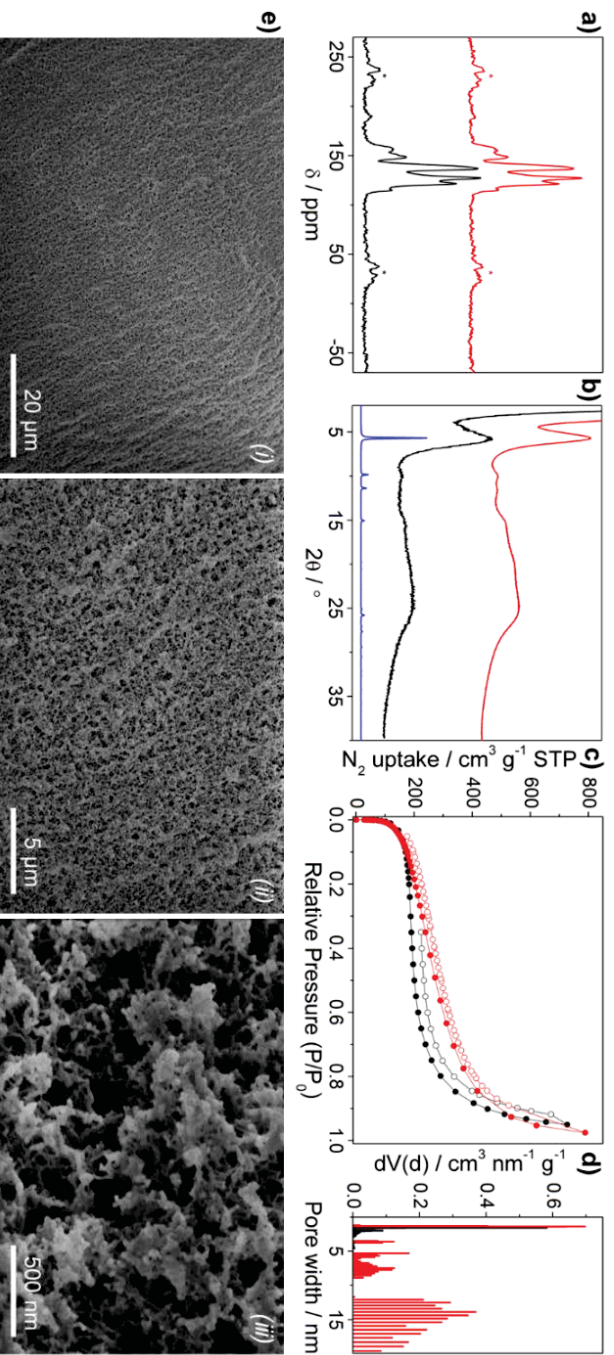


3D Printing of COFs



3D Printing of COFs

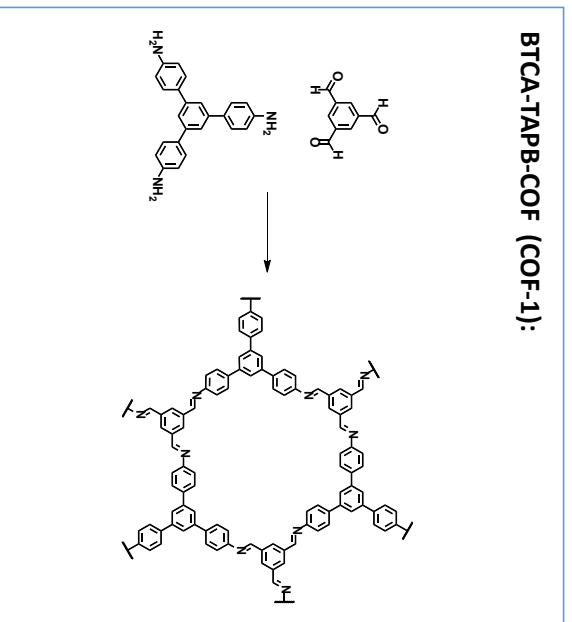
BET Surface Area: 483 m²/g
Pore volume: 0.918 cm³/g



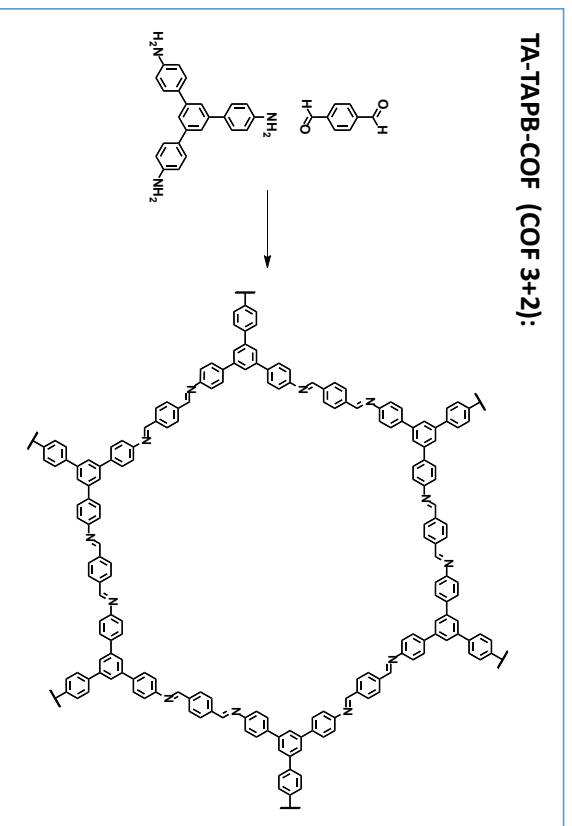
EP18179325.8 / WO2019243602

3D Printing of COFs

BTCA-TAPB-COF (COF-1):



TA-TAPB-COF (COF 3+2):



EP18179325.8 / WO2019243602

In Summary: Variety of Morphologies Enlarge Potential Applications of imine-COFs

Key of Processability : Nanoprocessability

RT-COF-1Ac

gel

nanolayers

film

spheres

super-structures

micelles

nanolayers

aerogels

O=C1C(=O)C(=O)N1

Take Home Message

Structural Design

Properties

- Gas Sorption
- Charge Transport
- High Surface Area
- Ionic Conductivity

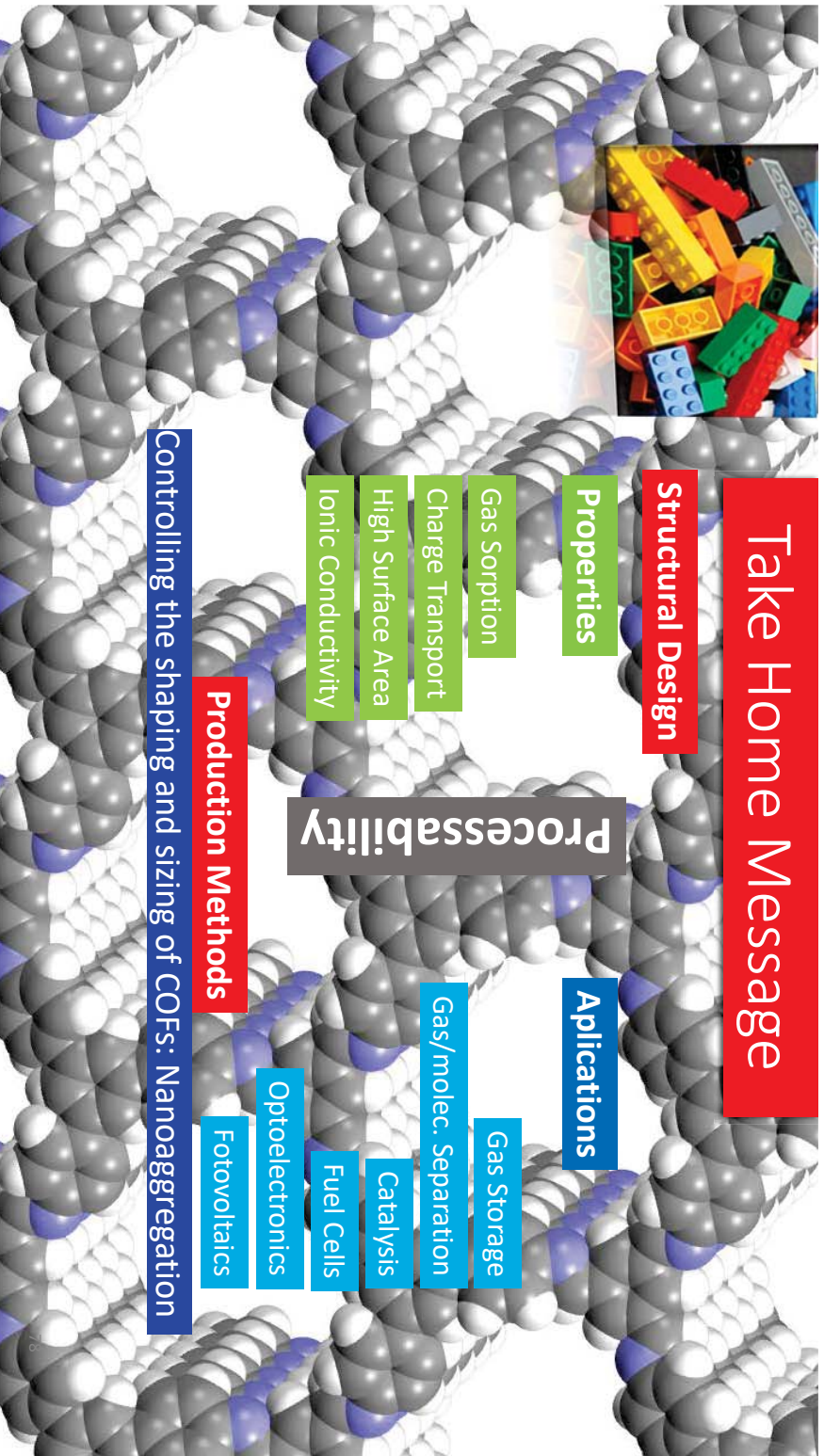
Processability

Production Methods

Controlling the shaping and sizing of COFs: Nanoaggregation

Applications

- Gas Storage
- Gas/molec. Separation
- Catalysis
- Fuel Cells
- Optoelectronics
- Fotovoltaics



Thanks:



nano Materials Lab



Institute for Advanced Research in Chemistry
IAdChem

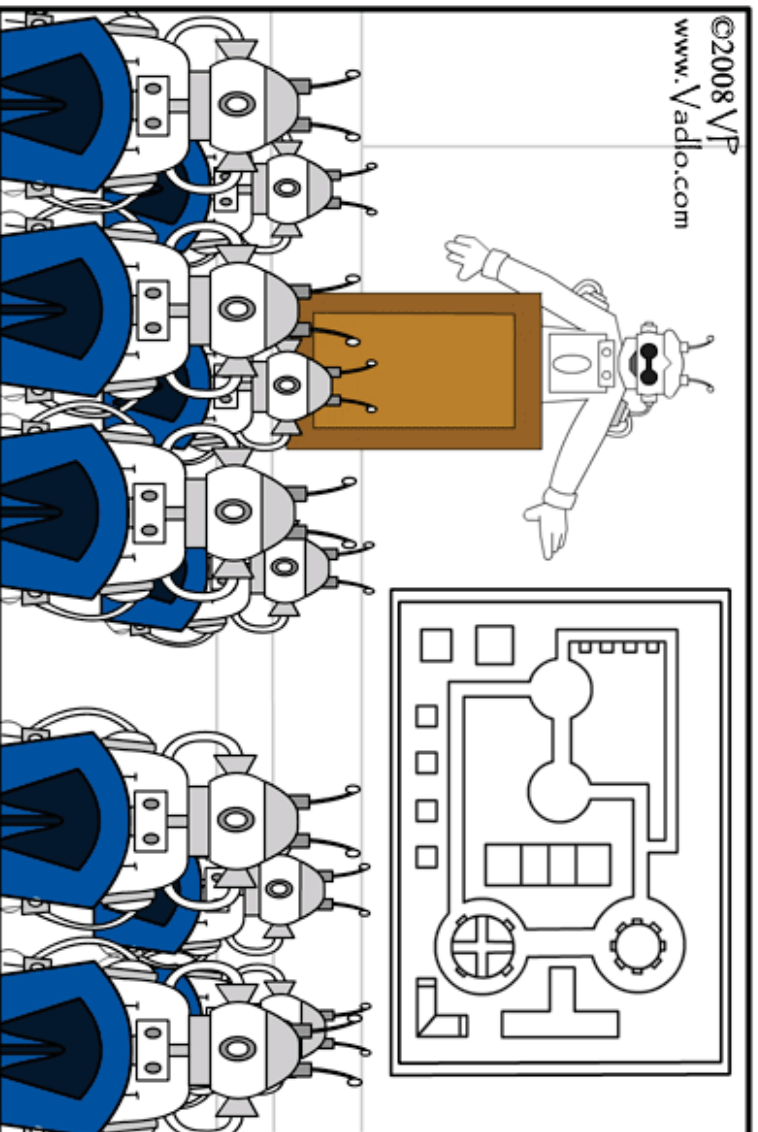
Nanomaterials Group
Dpto. Química Inorgánica
Universidad Autónoma de Madrid
E-mail: felix.zamora@uam.es
<http://www.nanomater.es>





Thanks for your kind attention !!

ROBOT SEMINARS



As we have just five minutes left, I will take only 3 million questions.

83

If you want to review this talk :



From imine-based covalent frameworks design to their processability and applications

Félix Zamora / Química Inorgánica UAM



<https://www.youtube.com/watch?v=9AVcvhVIDGU&t=1278s>

84