Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2 + 2] Cycloaddition

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FUNSOM
功能纳米与软物质研究院
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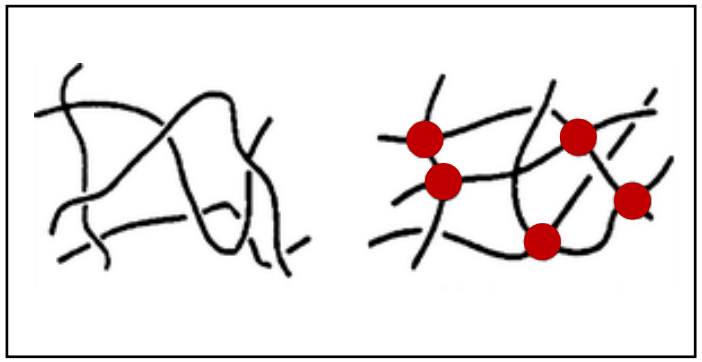
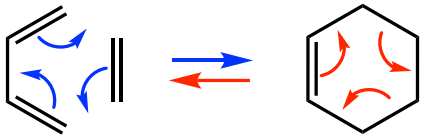
Cross-linking of polymers

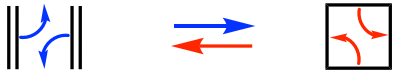


Reversible

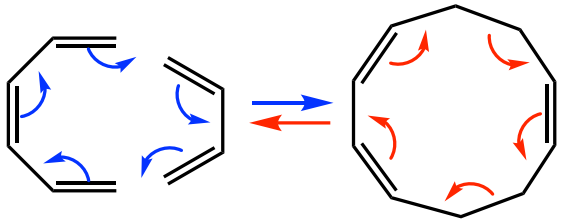
[4+2]



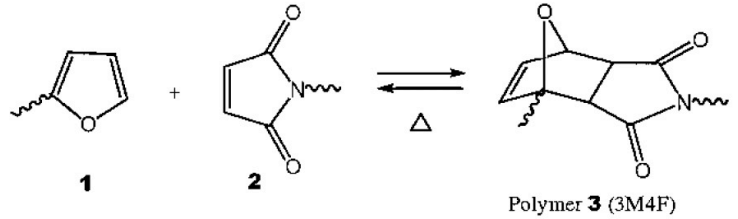
[2+2]



[6+4]



Self-healing plastics

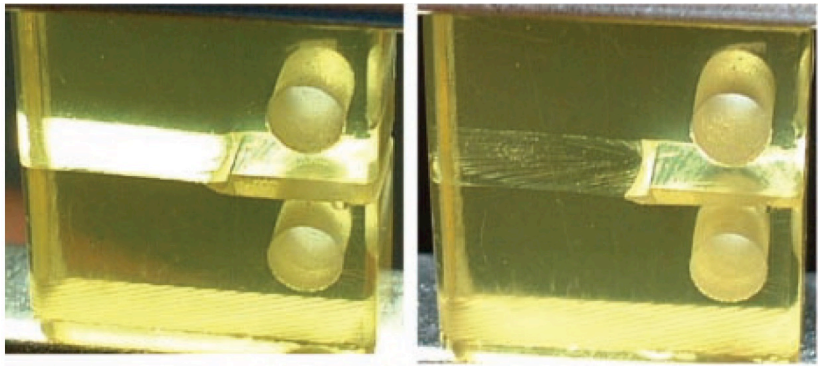


Reversible Diels-Alder reaction used for the crack healing mechanism

Formulation of adhesives

before

after heating



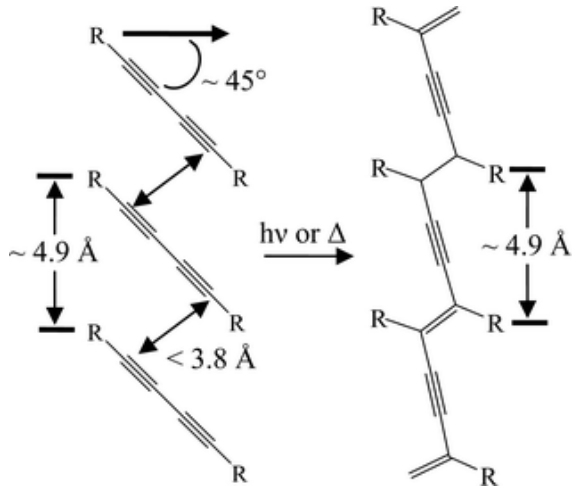
Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F., *Science* **2002,** *295*, 1698-1702

Cycloaddition reactions of olefin containing polymers are of particular interest because of their reversibility, which creates new opportunities for self-healing plastics and dynamic materials.

Cross-linking in ordered manner

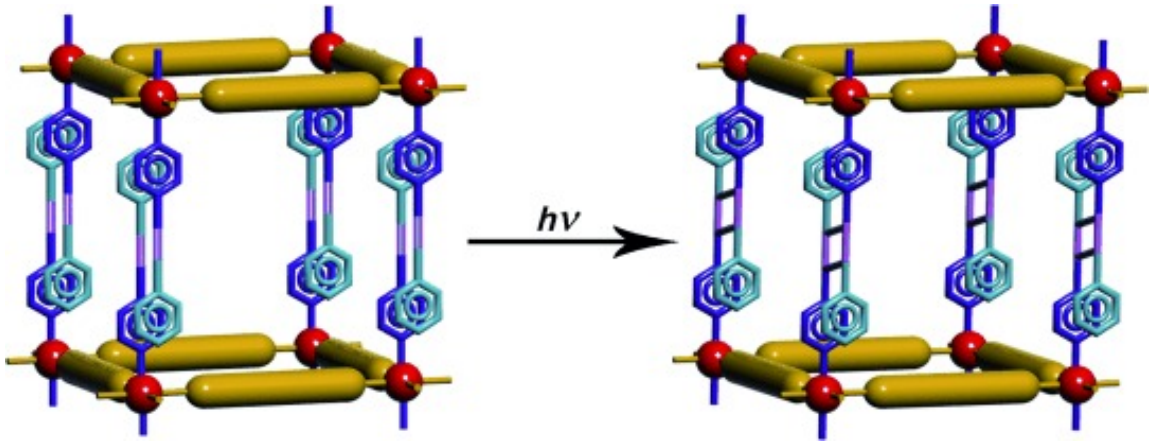
Topological reaction ≡ the order of the precursor defines the structure of the (crosslinked) product.

1,4-addition polymerization of diacetylenes



Signature **solid-state topological reaction** that can produce single crystals of poly(diacetylene) upon irradiation of monomer crystals

Coordination Polymers and Metal Organic Frameworks (MOFs)

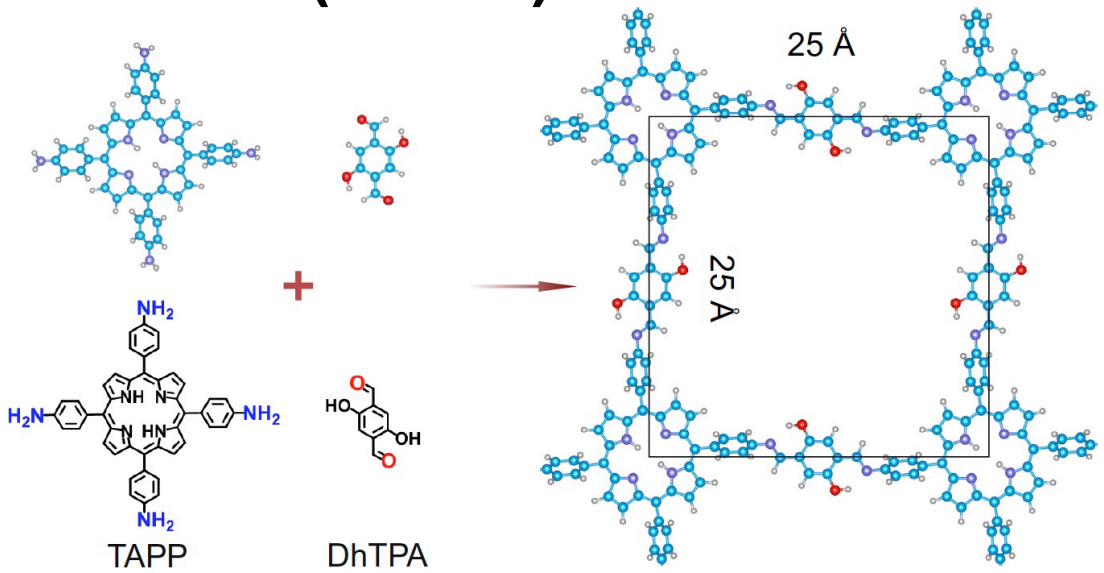


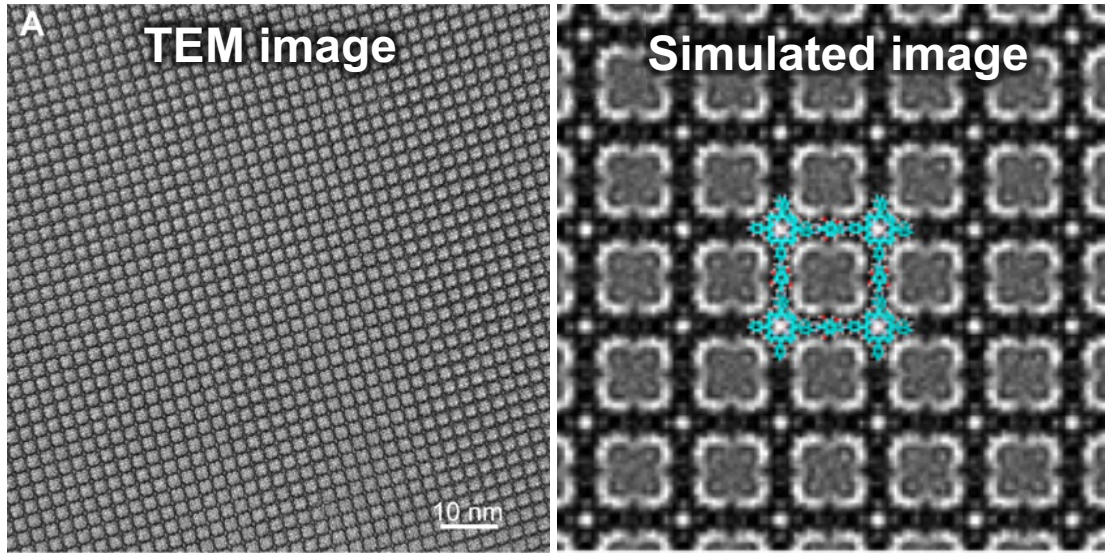
Polymerization in a single-crystal-to-single-crystal manner via [2 + 2] cycloaddition

1) Enkelmann, V.; Leyrer, R. J.; Schleier, G.; Wegner, G. *J. Mater. Sci.* **1980**, *15*, 168. **2)** Medishetty, R.; Koh, L. L.; Kole, G. K.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10949.

Covalent Organic Frameworks (COFs)

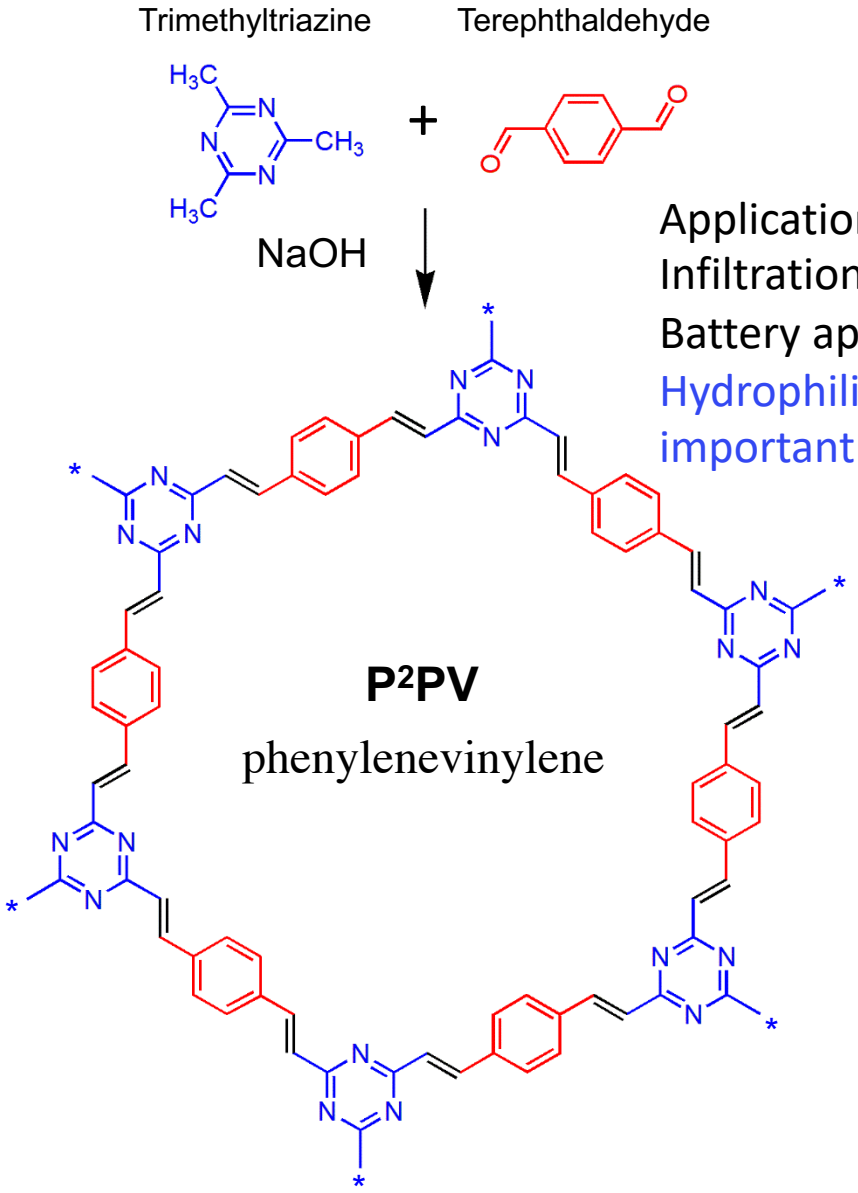
- Recent discovery of graphene has caused a surge of interest in the research and development of 2D materials
- Covalent organic frameworks (COFs) have been rapidly developed
- A class of **crystalline** **porous** **organic** polymers with predesigned skeletons, permanent porosity and highly ordered structures
- Potentials for a wide variety of applications, including energy conversion and storage, gas storage, separation, etc.





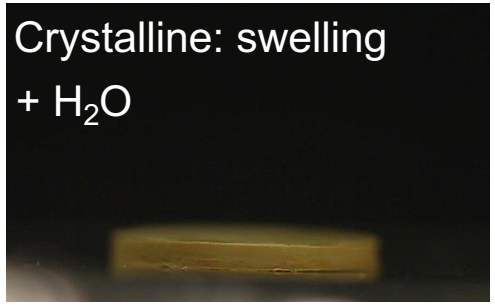
Qi, H.; Sahabudeen, H.; Liang, B.; Polozij, M.; Addicoat, M. A.; Gorelik, T. E.; Hambsch, M.; Mundszinger, M.; Park, S.; Lotsch, B. V.; Mannsfeld, S. C. B.; Zheng, Z.; Dong, R.; Heine, T.; Feng, X.; Kaiser, U., *Sci Adv* **2020,** *6*, eabb5976.

Two-dimensional sp^2 π–conjugated covalent organic frameworks

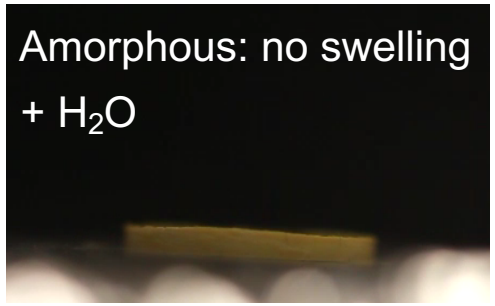


Applications:
Infiltration membranes
Battery applications
Hydrophilicity is important

COF sponge

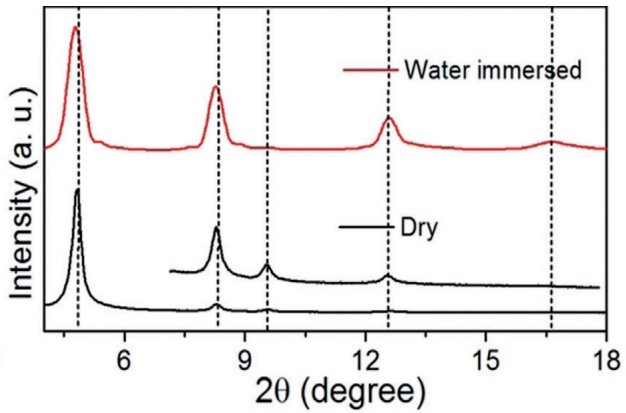


Hydrothermal method

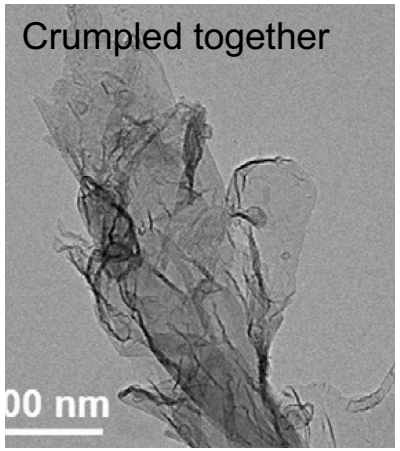


Made at RT

PXRD



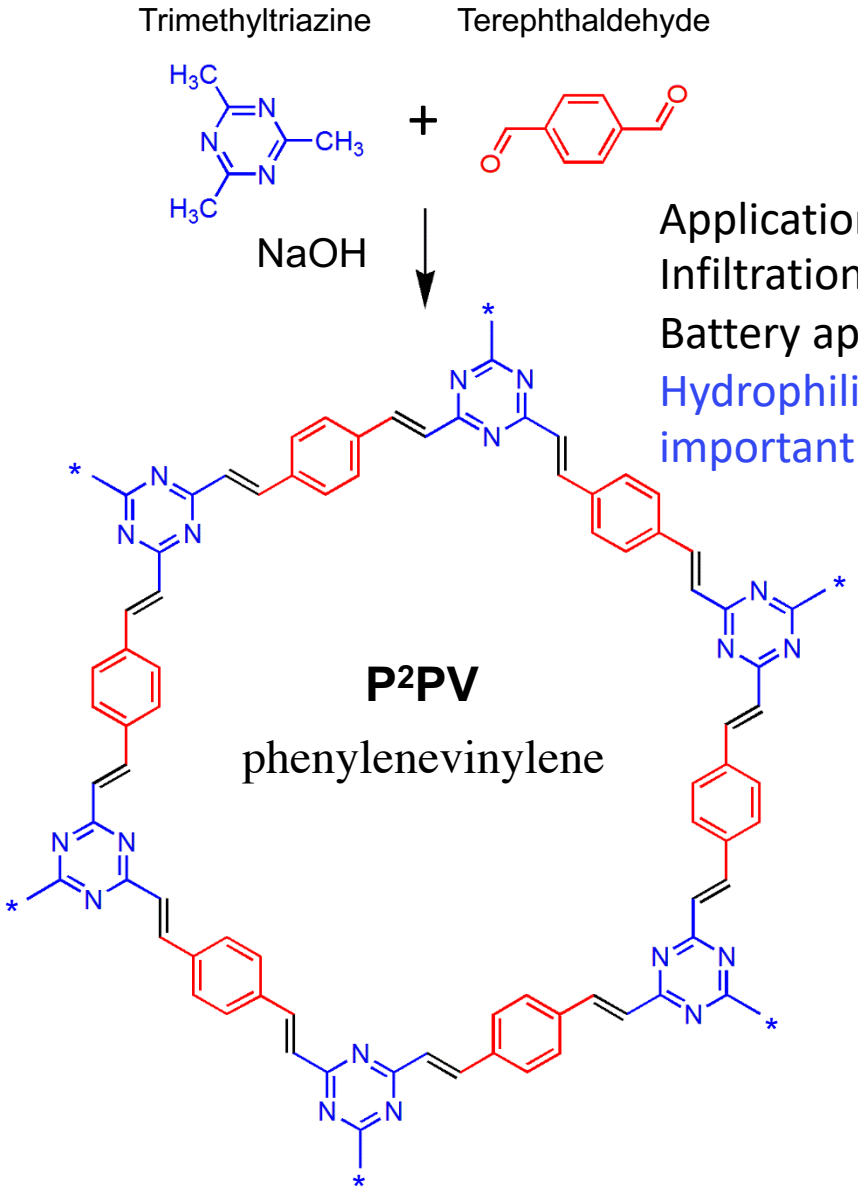
TEM: exfoliation



Solid state electrolyte

Jadhav, T.; **Fang, Y.**; Patterson, W.; Liu, C.-H.; Hamzehpoor, E.; Perepichka, D. F., *Angew. Chem., Int. Ed.* **2019,** *58*, 13753

Two-dimensional sp^2 π–conjugated covalent organic frameworks



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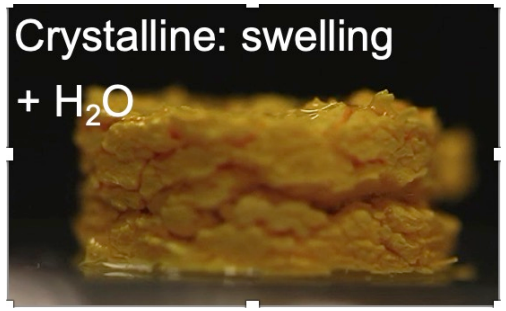

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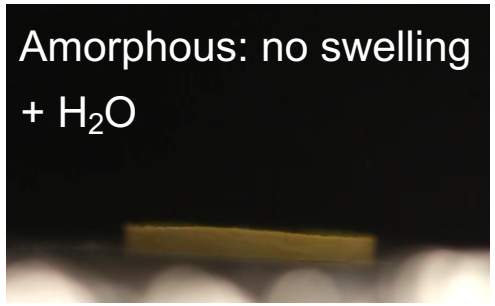

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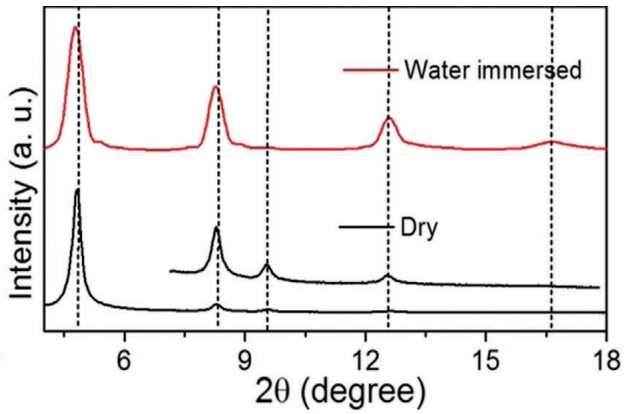

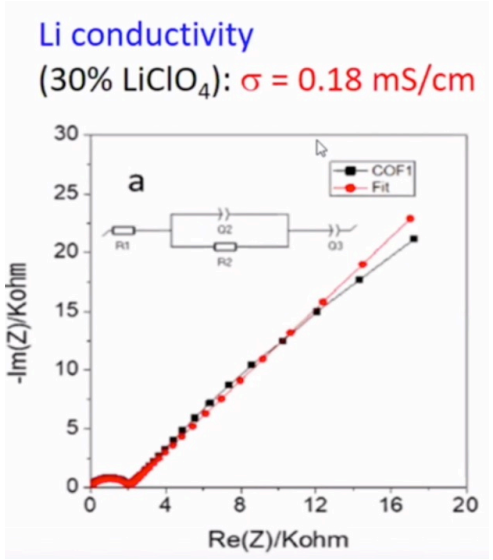

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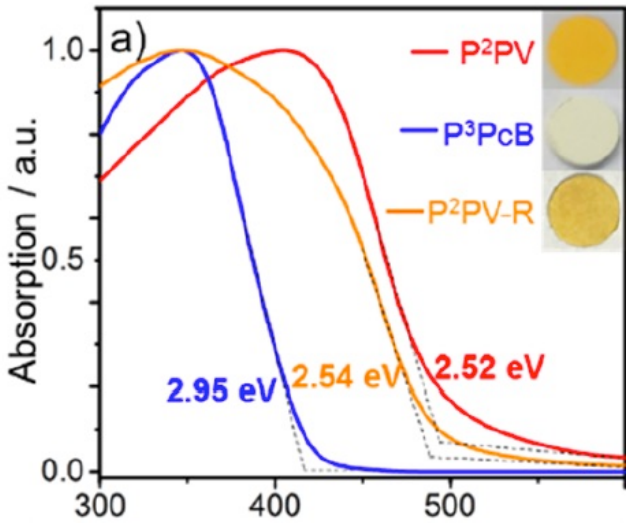
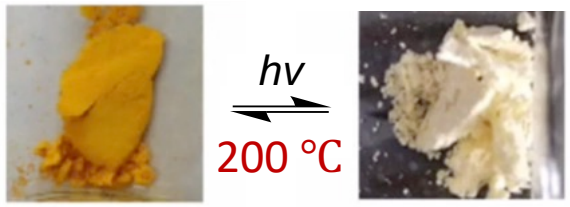
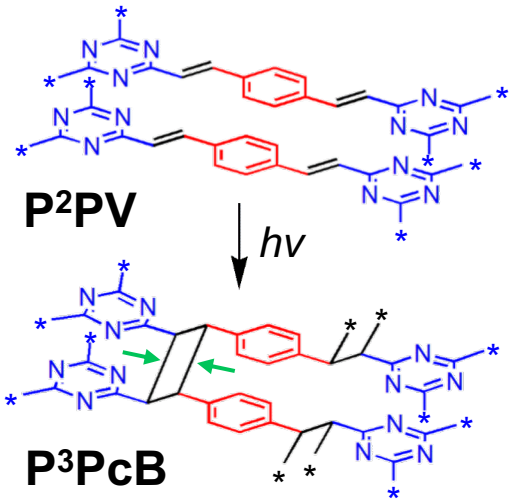
[2 + 2] photocycloaddition of 2D poly(arylene vinylene)

Diffuse reflectance spectra



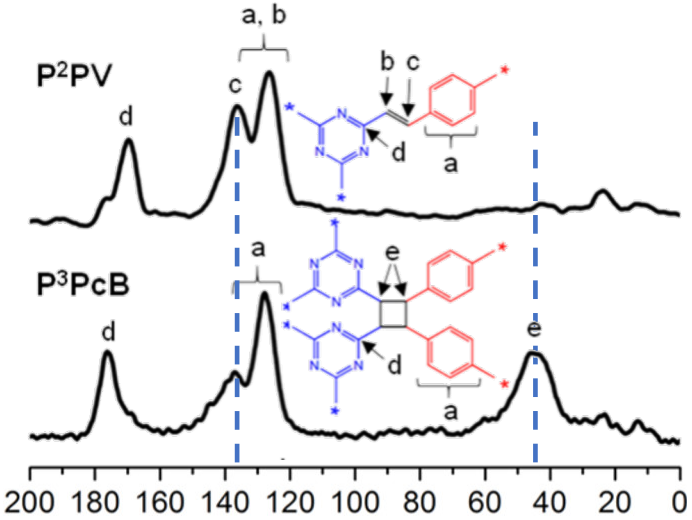
P²PV = SP^2 phenylenevinylene COF
P³PcB = SP^3 phenylene cyclobutylene COF





[2 + 2] cyclization of the adjacent vinylene bonds

Solid state carbon NMR

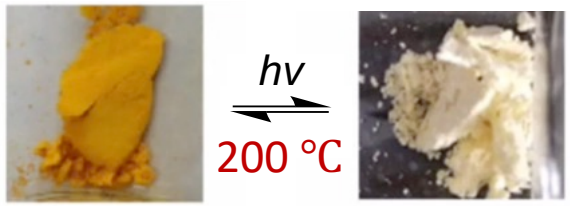


New peak at 44 ppm ≡ cyclobutane's carbons

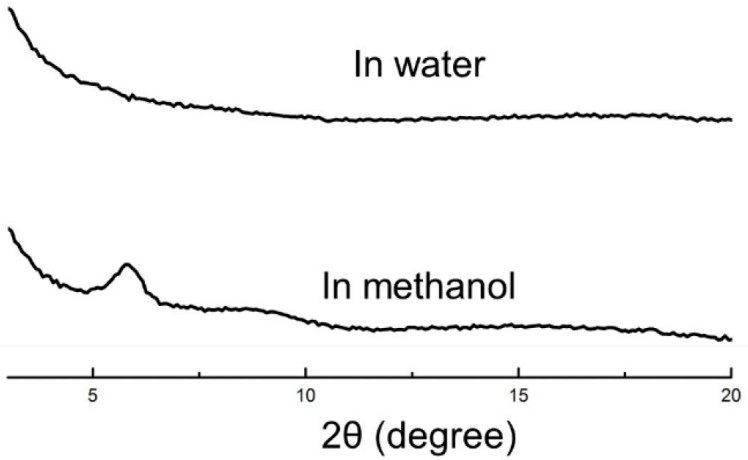
Jadhav, T.;‡ **Fang, Y.**;‡ Liu, C.-H.;‡ Dadvand, A.; Hamzehpoor, E.; Patterson, W.; Jonderian, A.; Stein, R. S.; Perepichka, D. F.,* *JACS.* **2020,** *142*, 8862

Solvent effect on the topological reaction

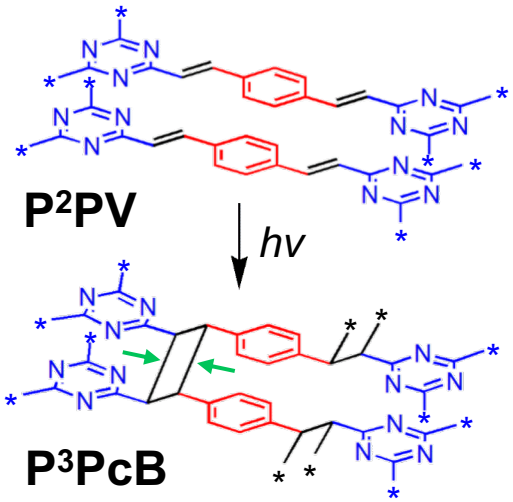
Acharjya, A.; Pachfule, P.; Roeser, J.; Schmitt, F.-J.; Thomas, A., *Angew. Chem., Int. Ed.* **2019,** *58*, 14865



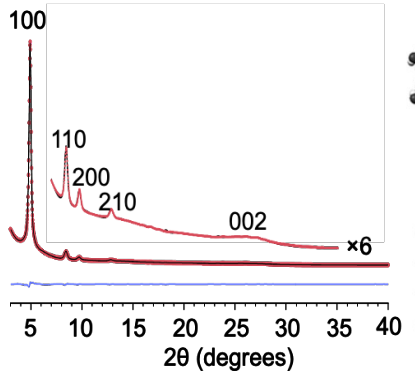
Protic solvents

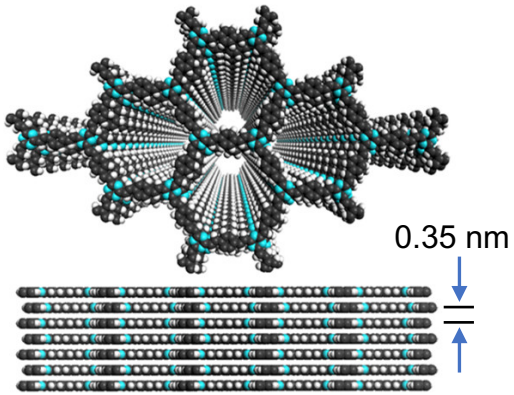


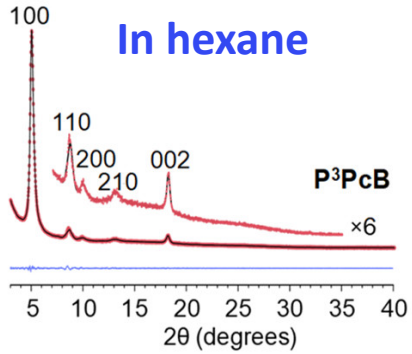
Amorphous products or low crystalline

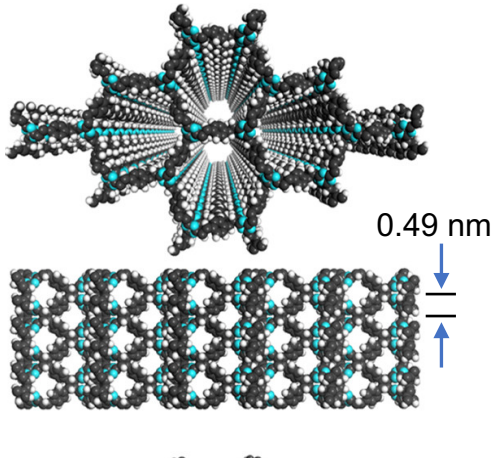


[2 + 2] cyclization of the adjacent vinylene bonds







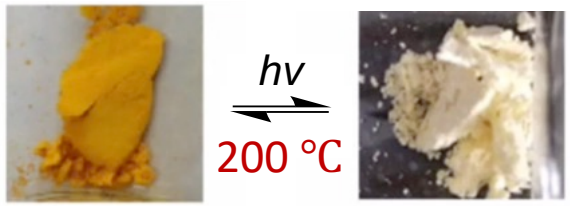


Jadhav, T.;‡ **Fang, Y.**;‡ Liu, C.-H.;‡ Dadvand, A.; Hamzehpoor, E.; Patterson, W.; Jonderian, A.; Stein, R. S.; Perepichka, D. F.,* *JACS.* **2020,** *142*, 8862

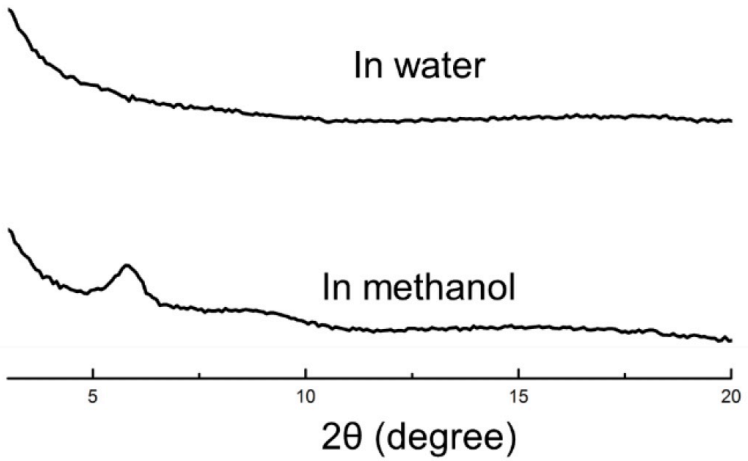
Crystalline to crystalline cycloreversion

Although [2 + 2] cyclization reactions are well established, the solid-state cleavage of the cyclobutane ring **preserving the crystallinity** is relatively rare

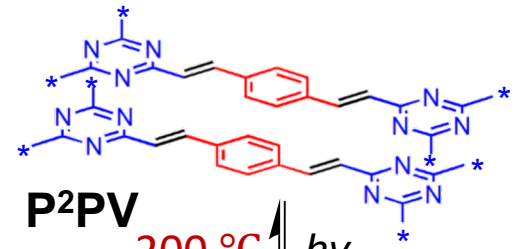
Acharjya, A.; Pachfule, P.; Roeser, J.; Schmitt, F.-J.; Thomas, A., *Angew. Chem., Int. Ed.* **2019,** *58*, 14865



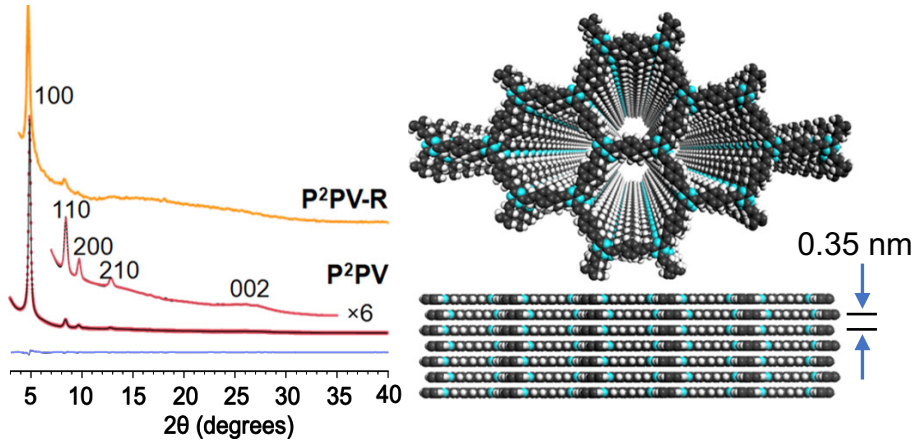
Protic solvents

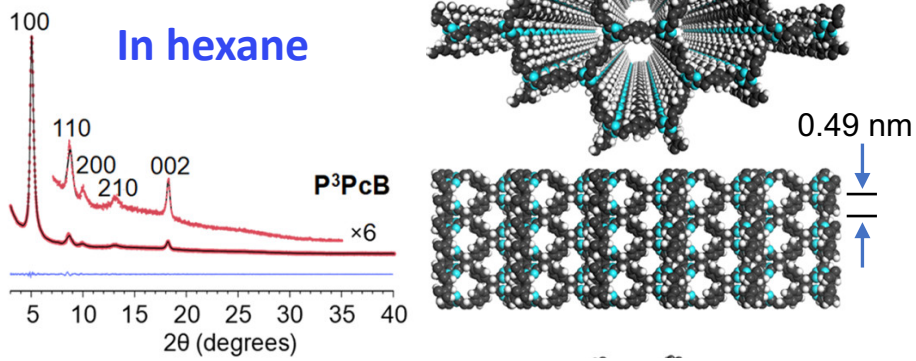


Amorphous products or low crystalline



[2 + 2] cyclization of the adjacent vinylene bonds





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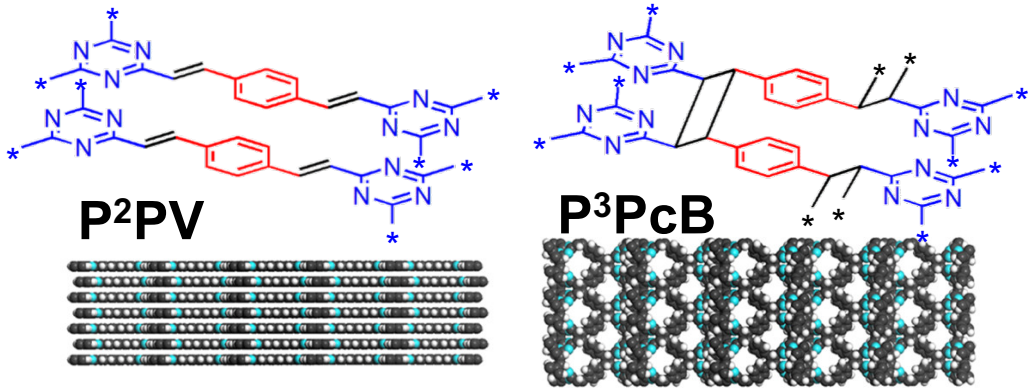
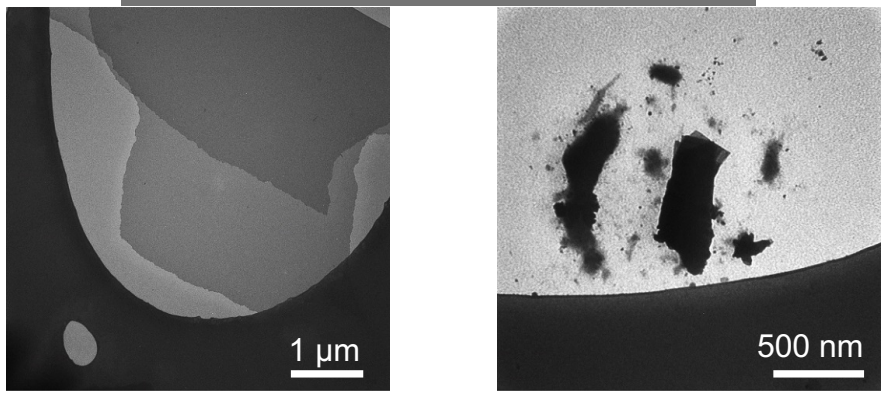
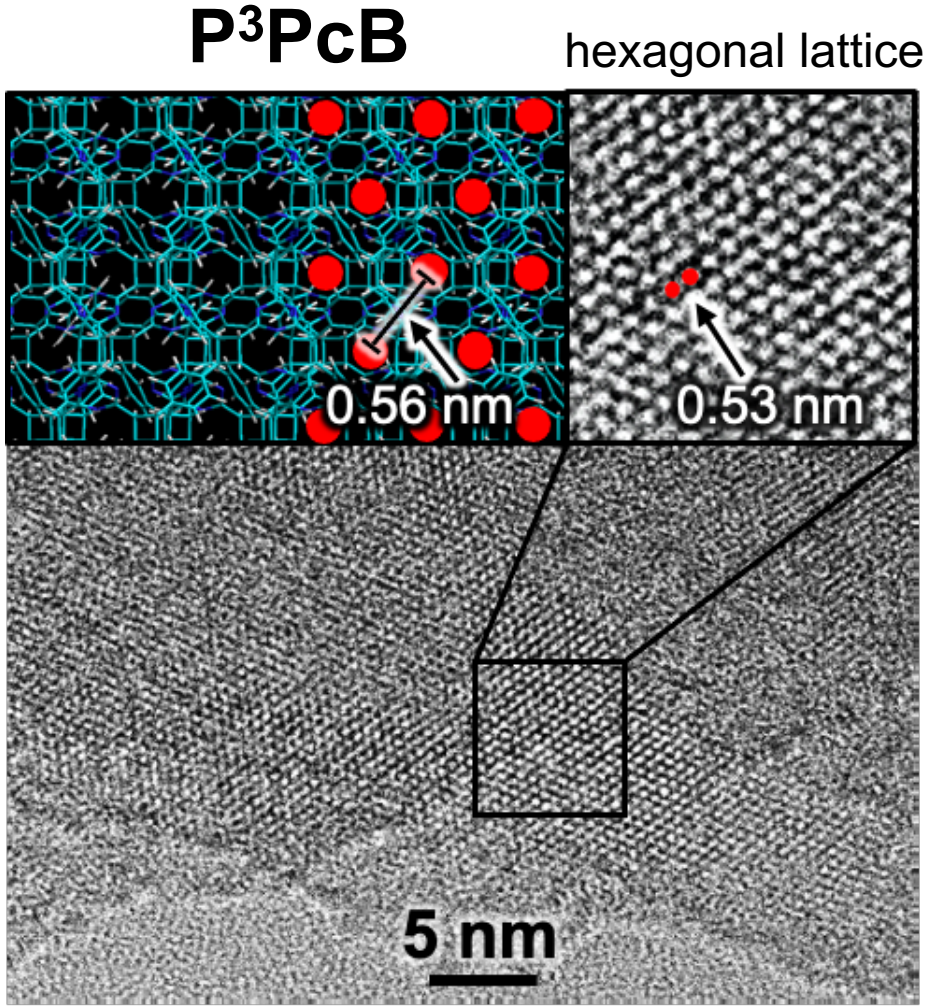
Concentrated H_2SO_4 exfoliation of COFs



Stirred in H_2SO_4 overnight



Another peace of evidence of this transformation between 2D and 3D



Crystalline 3D structure of this **crosslinked COF**

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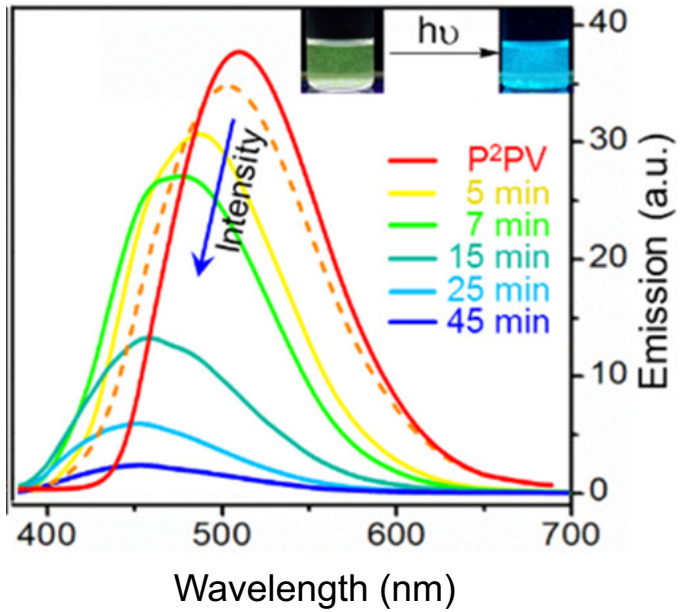
To prove its generality

Fluorescence

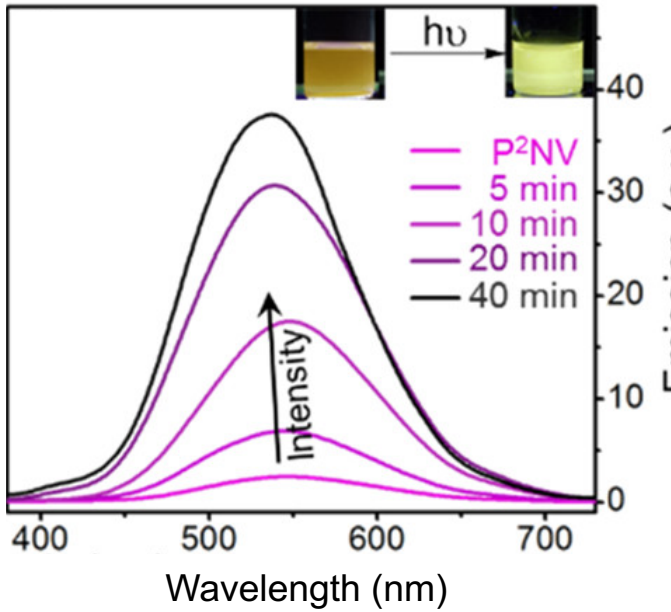
Trimethyltriazine + Terephthaldehyde → (NaOH) → SP^2 phenylene Vinylene **P^2PV** ⇌ (Δ / *hv*) → SP^3 phenylene cyclobutylene **P^3PcB**

- Photocyclization of the phenylene-linked P_2PV is accompanied by **quenching of the COF fluorescence** intensity
- The same transformation in the naphthalene-linked P_2NV leads to **enhanced fluorescence**

Quenching of fluorescence band



Fluorescence becomes more intense



Trimethyltriazine + Naphthalenedialdehyde → (NaOH) → SP^2 naphthalene Vinylene **P^2NV** ⇌ (Δ / *hv*) → SP^3 naphthalene cyclobutylene **P^3NcB**

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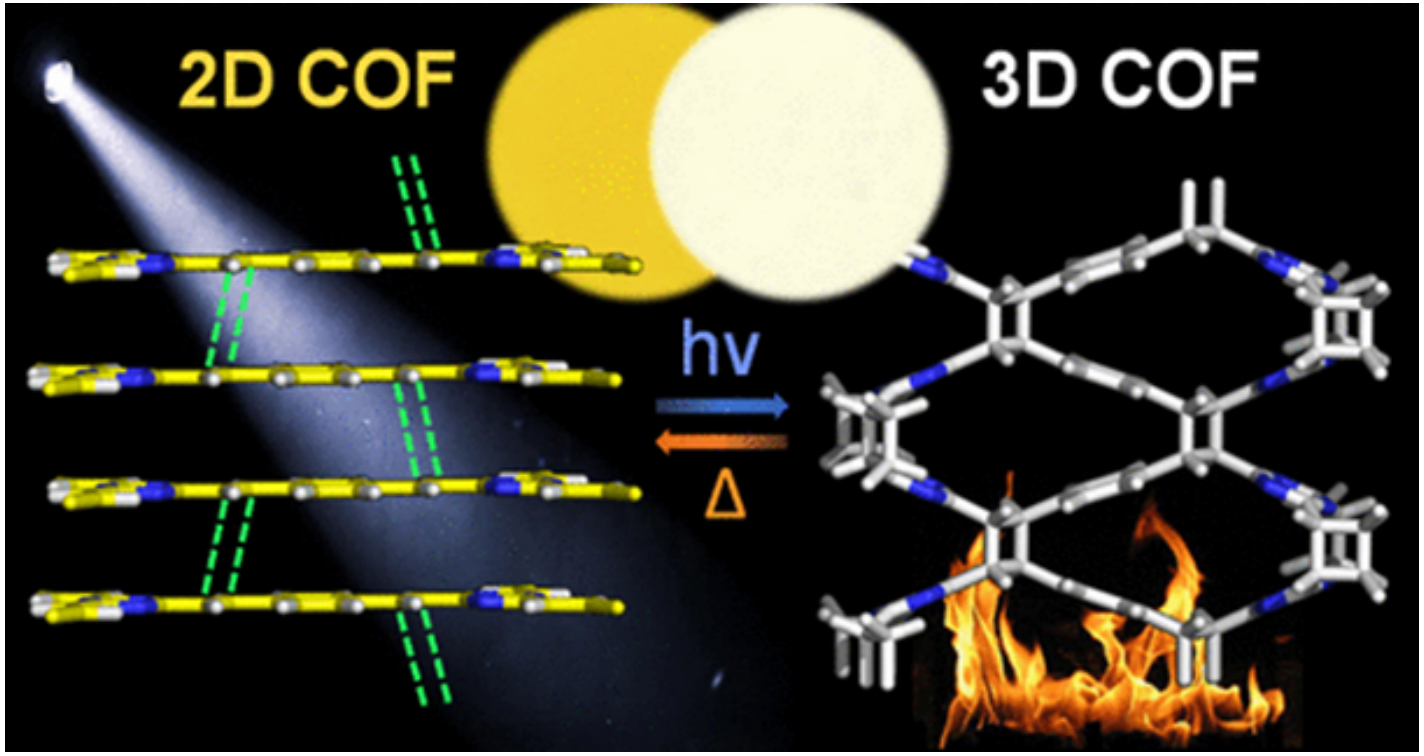
Conclusion



- So effectively We found a way to transform in between a 2D COF and a 3D COF
- Achieved these transformations while preserving the crystallinity

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Acknowledgments

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Cheng-Hao Liu
Dr. Afshin Dadvand
Ehsan Hamzehpoor
William Patterson
Antranik Jonderian
Dr. Robin S. Stein

Everyone in the lab

Thank you so much for listening!

CQMF Centre québécois sur les matériaux fonctionnels
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