



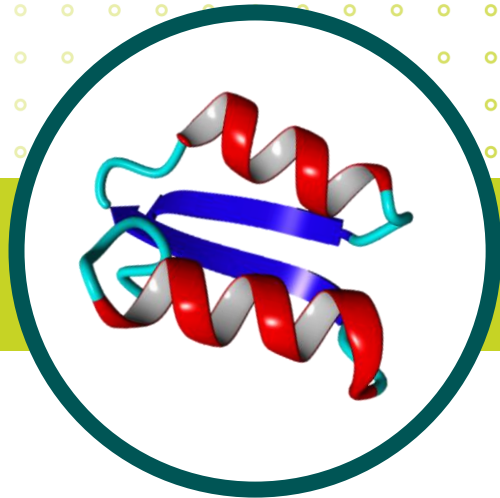
CARBOHYDRATES IN SUPRAMOLECULAR CHEMISTRY: SYNTHESIS, FOLDING, AND ASSEMBLY

Martina Delbianco

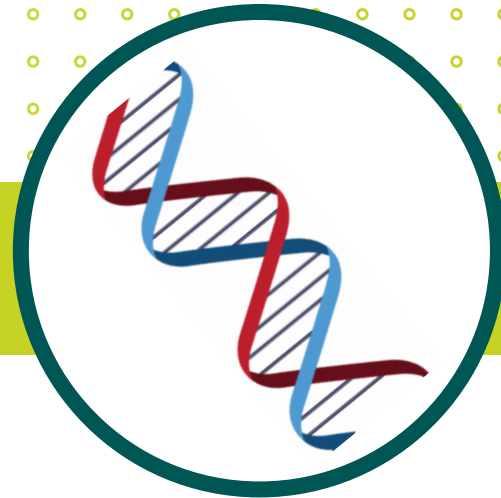




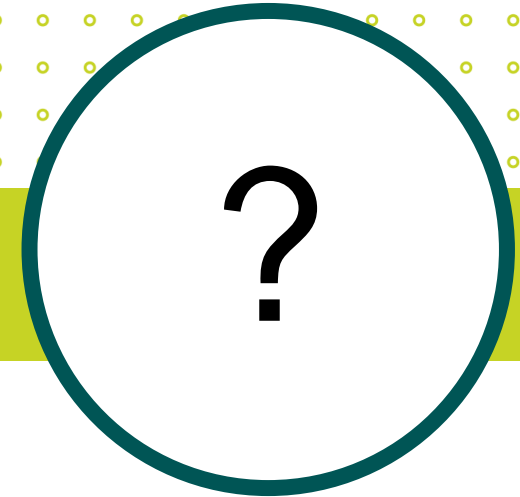
BIOPOLYMERS IN NATURE



Polypeptides



Polynucleotides



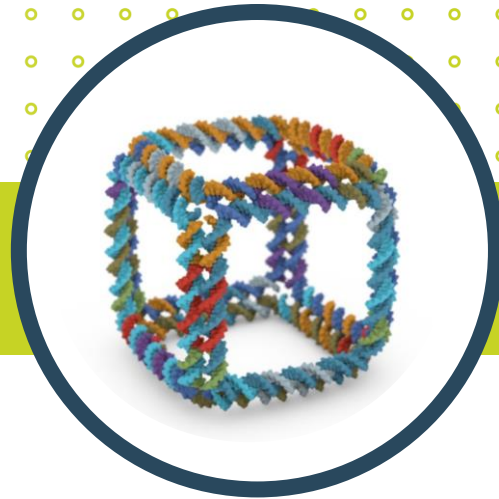
Polysaccharides



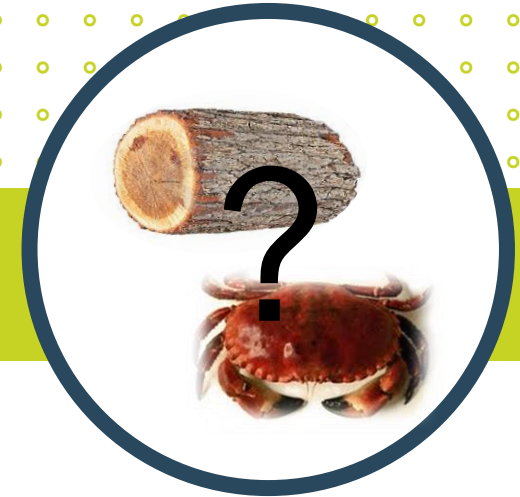
BIOPOLYMERS IN NANOTECHNOLOGY



**Polypeptides
nanotechnology**



**Polynucleotides
nanotechnology**



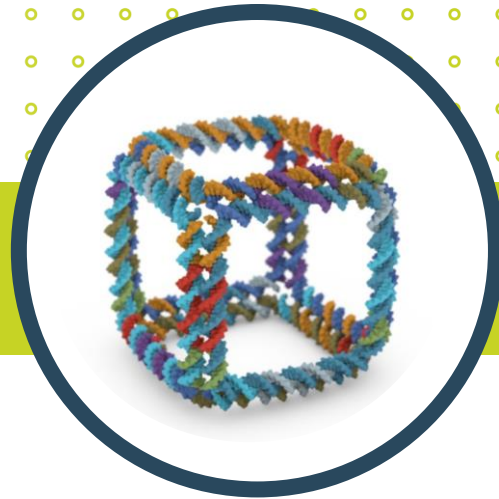
**Polysaccharides
untapped potential**



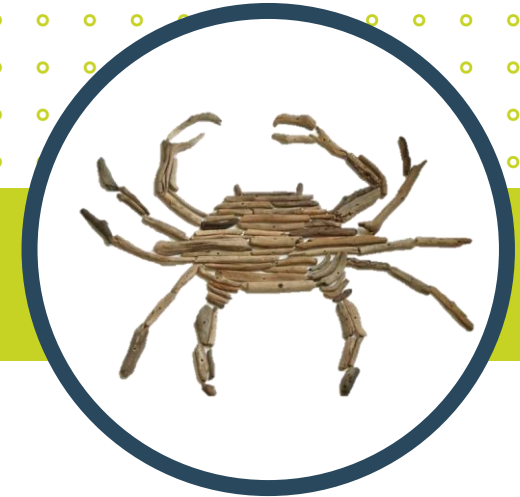
BIOPOLYMERS IN NANOTECHNOLOGY



**Polypeptides
nanotechnology**



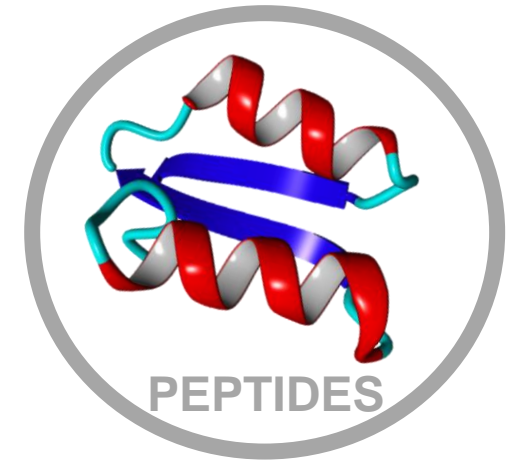
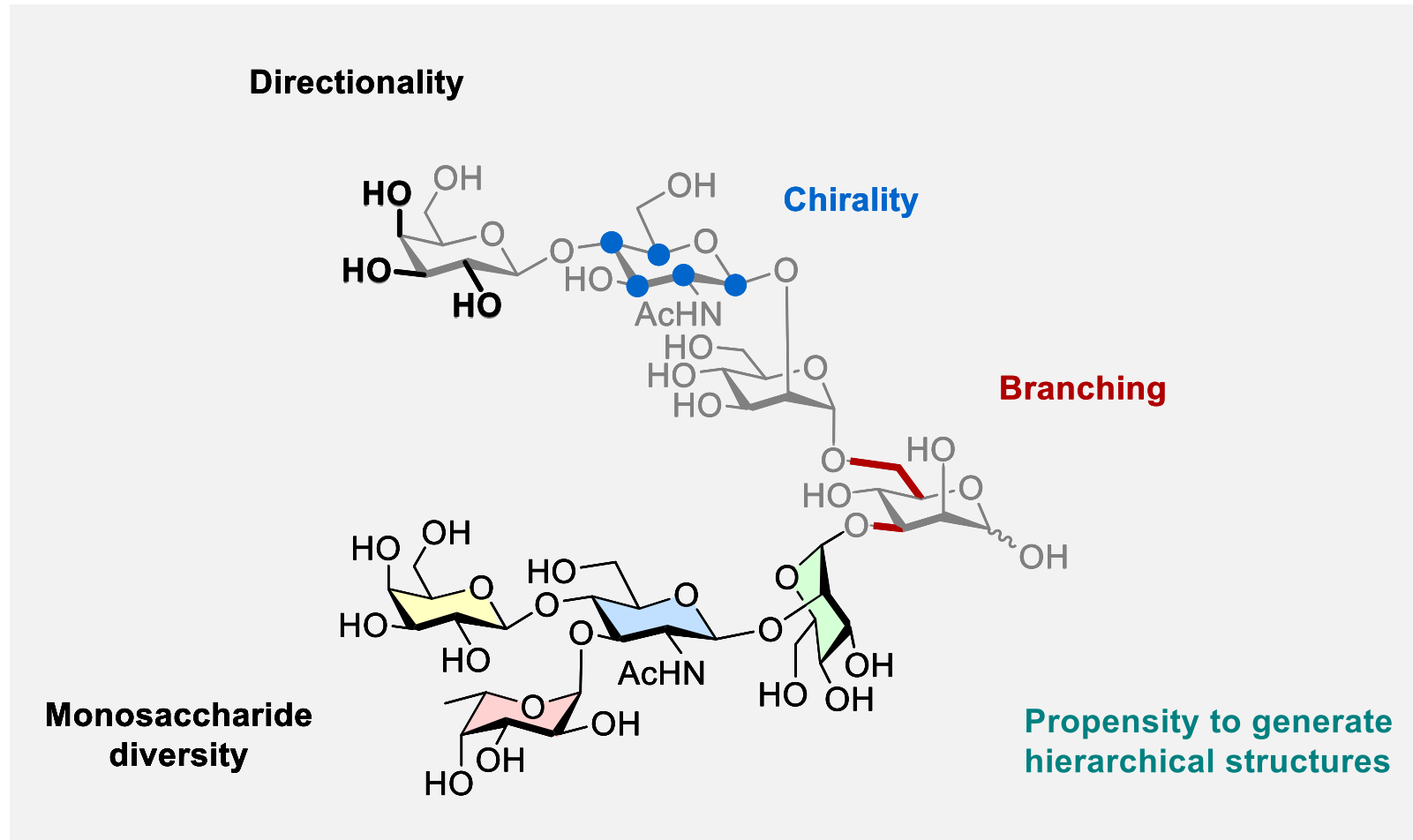
**Polynucleotides
nanotechnology**



**Polysaccharides
untapped potential**

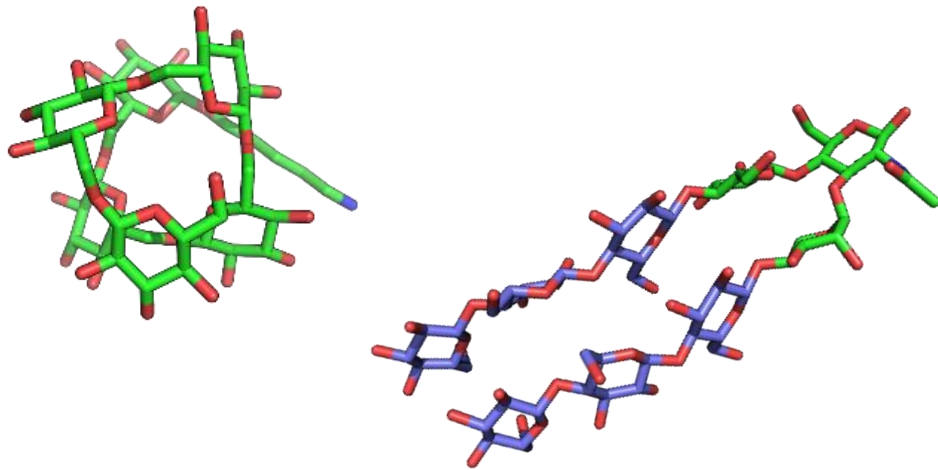


GLYCANS – OPPORTUNITIES AND CHALLENGES

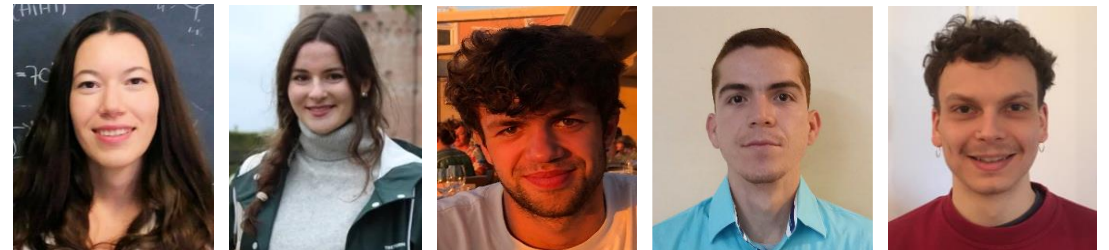
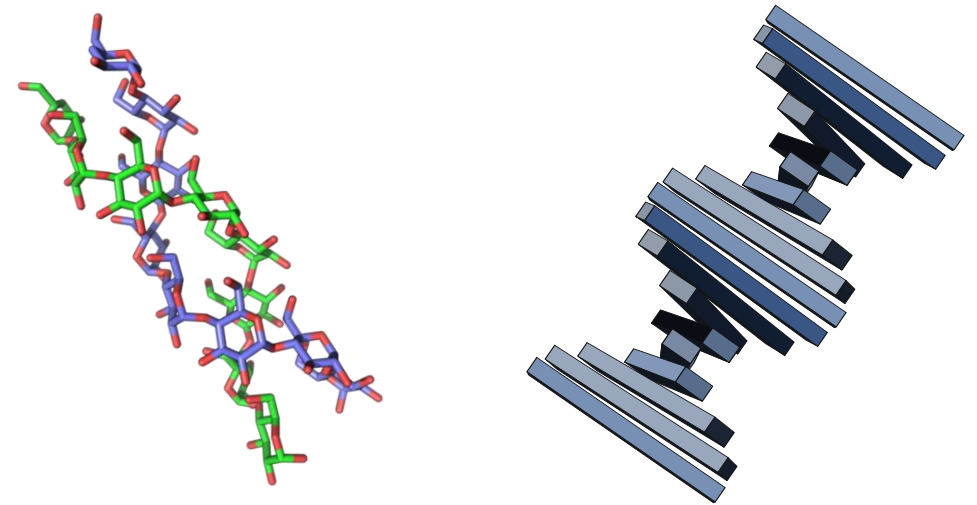


TWO BIG FUNDAMENTAL CHALLENGES

Can we design a glycan that **folds** into a defined conformation?

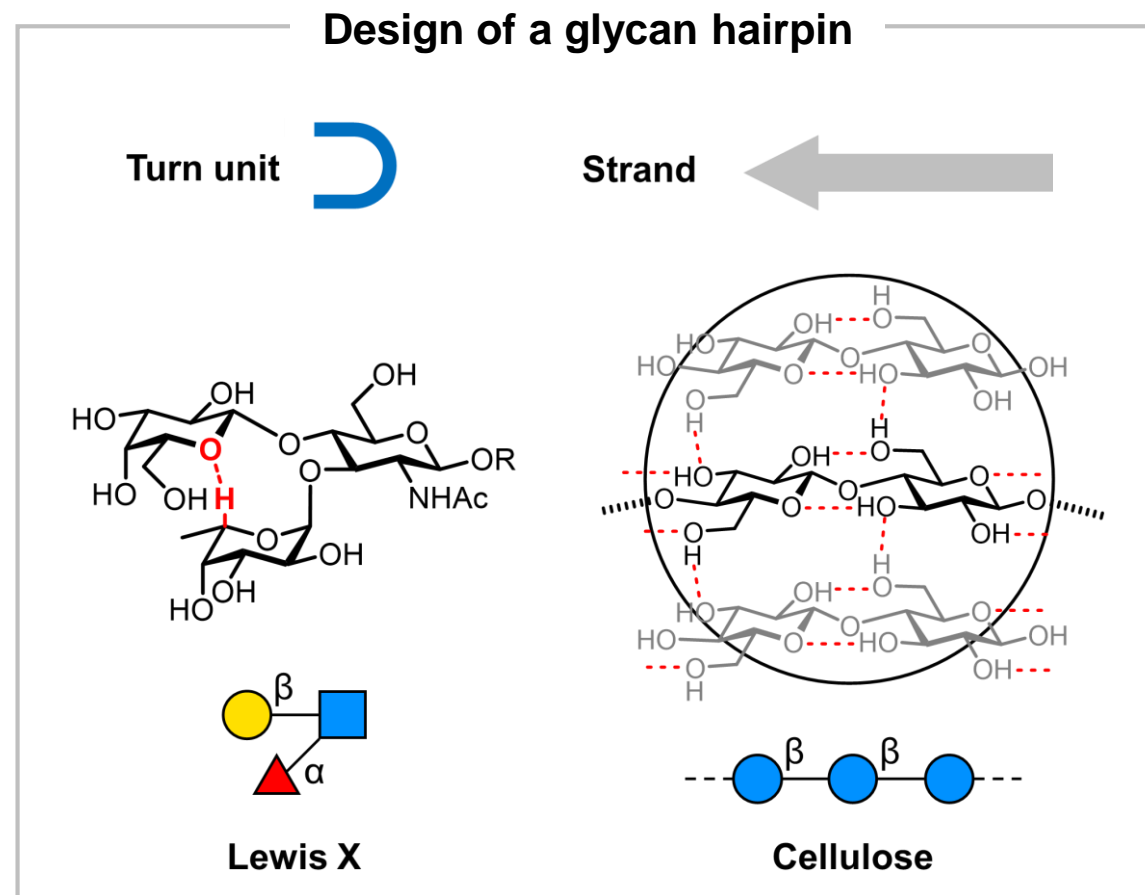
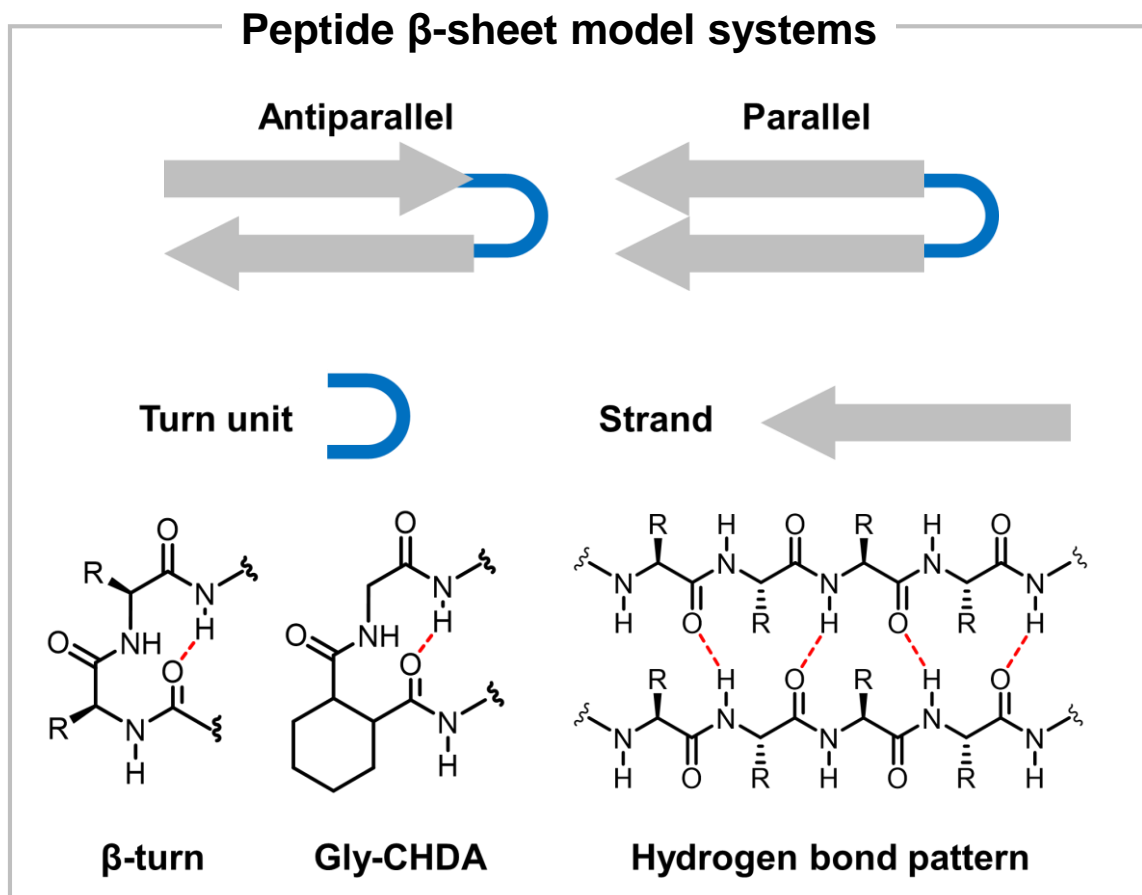


Can we design a glycan that **assembles** into a programmable architecture?



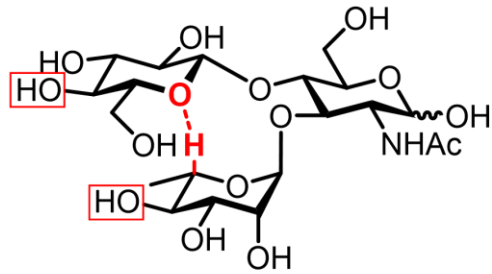
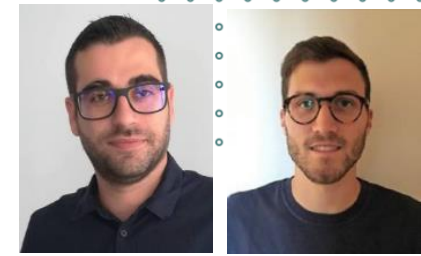


DESIGN OF A GLYCAN SECONDARY STRUCTURE

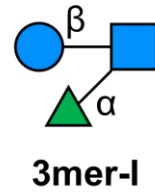


Nat. Chem., 2023, 15, 1461

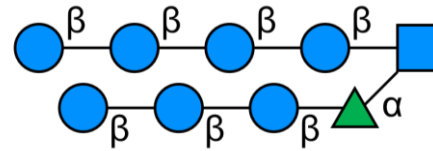
TARGET STRUCTURES



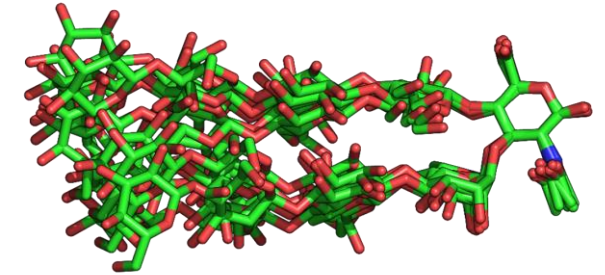
3mer-I



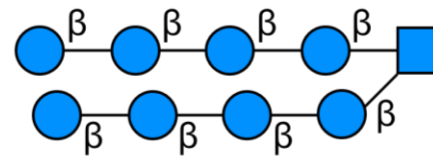
3mer-I



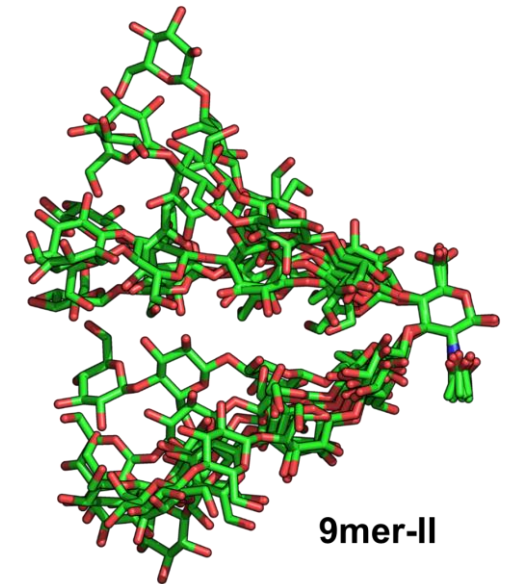
9mer-I



9mer-I



9mer-II



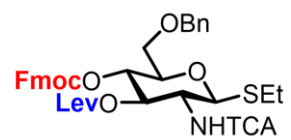
9mer-II

Nat. Chem., **2023**, 15, 1461

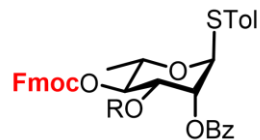
AUTOMATED GLYCAN ASSEMBLY (AGA)



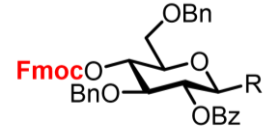
AGA



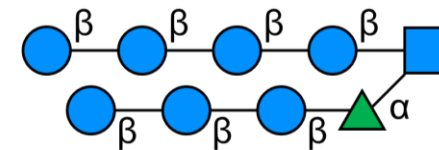
BB1



BB3a R=Bz
BB3b R=Bn



BB2a R = STol
BB2b R = OPO(OBu)₂

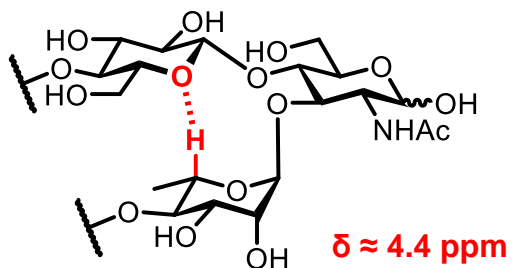
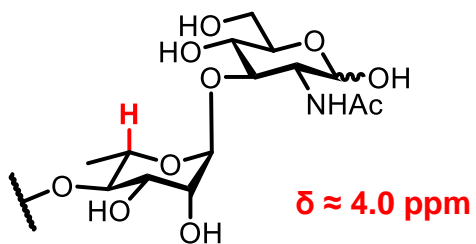


9mer-I



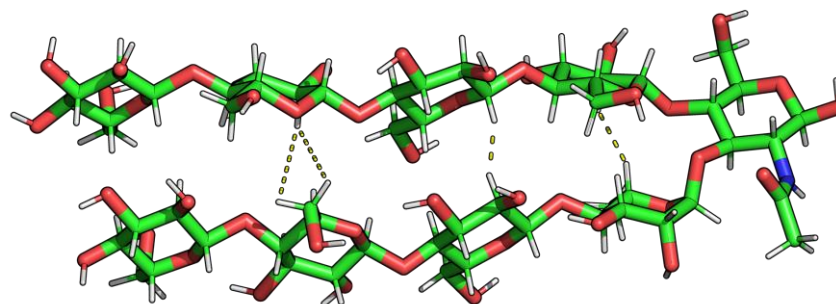
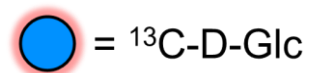
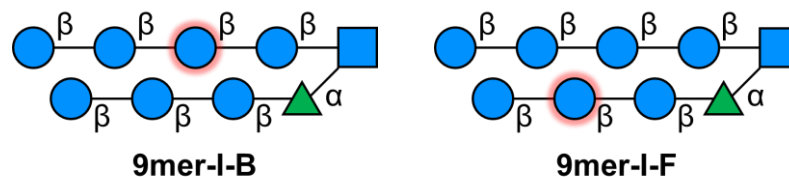
NMR STUDIES TO PROVE FOLDING

Non-conventional H-bond

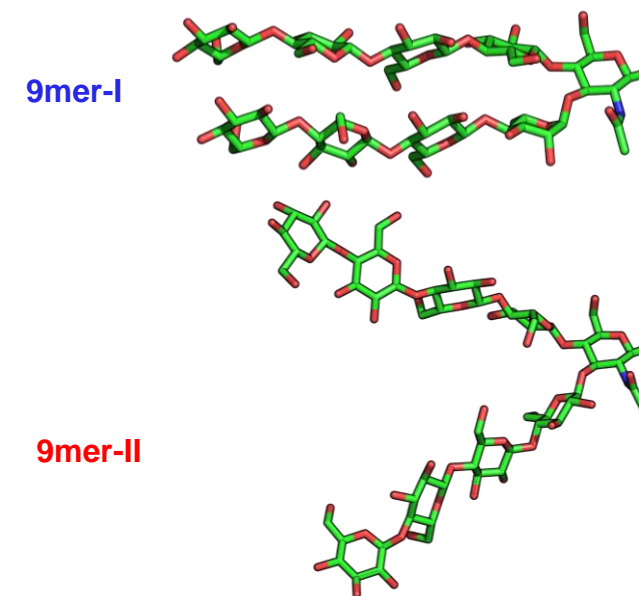
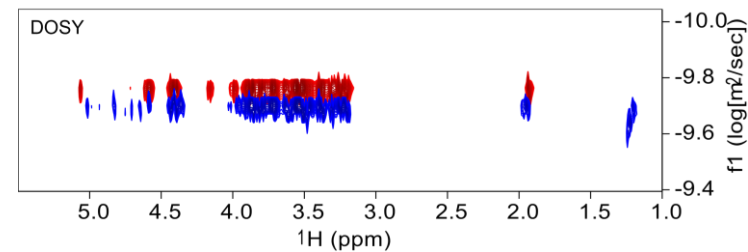


Downfield shift $\Delta\delta \approx 0.40 \text{ ppm}$

NOE analysis



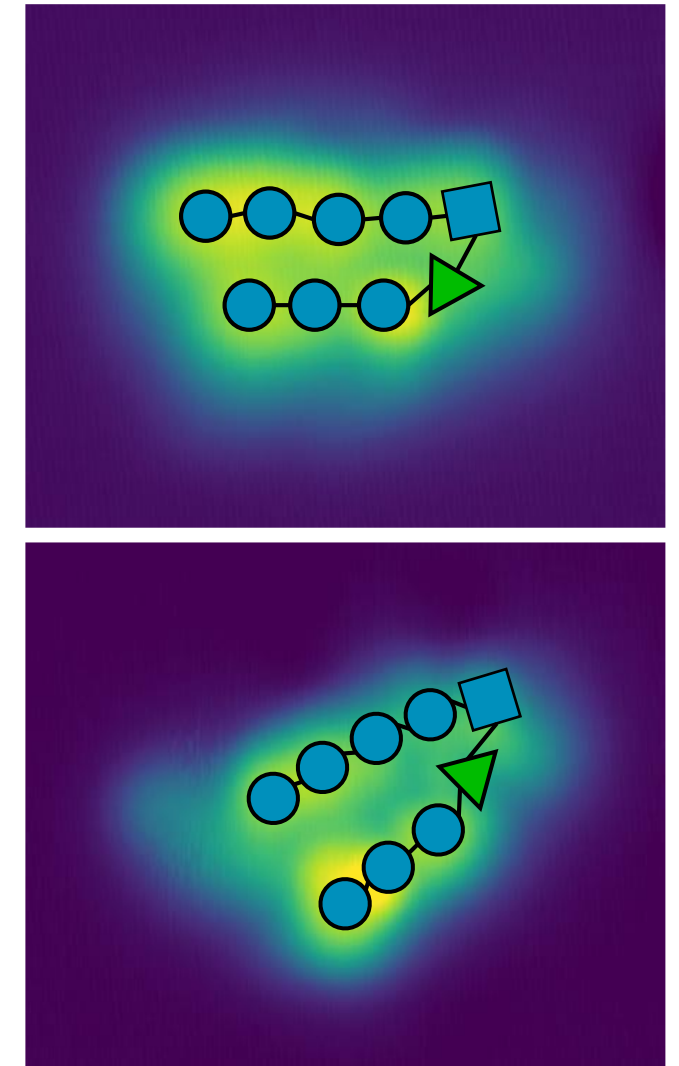
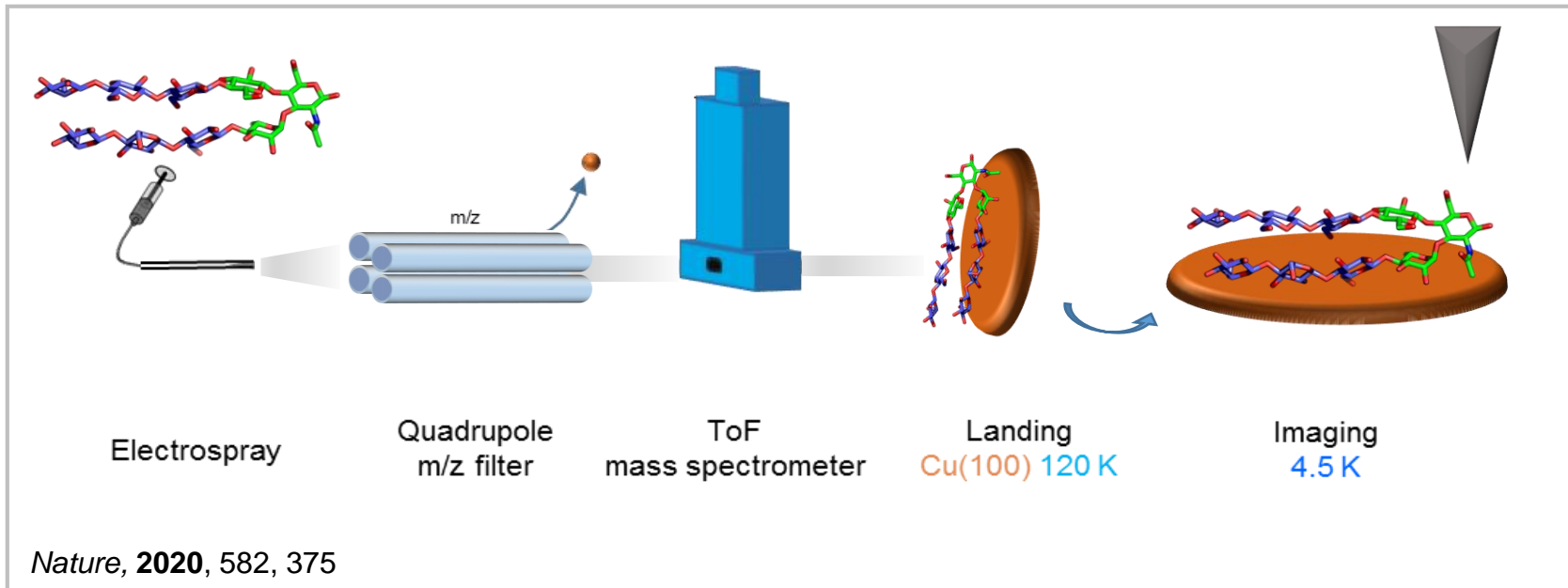
DOSY analysis



THE FIRST IMAGES OF A GLYCAN HAIRPIN

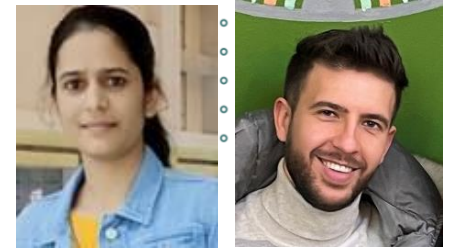
Ion beam deposition

Scanning tunneling microscopy

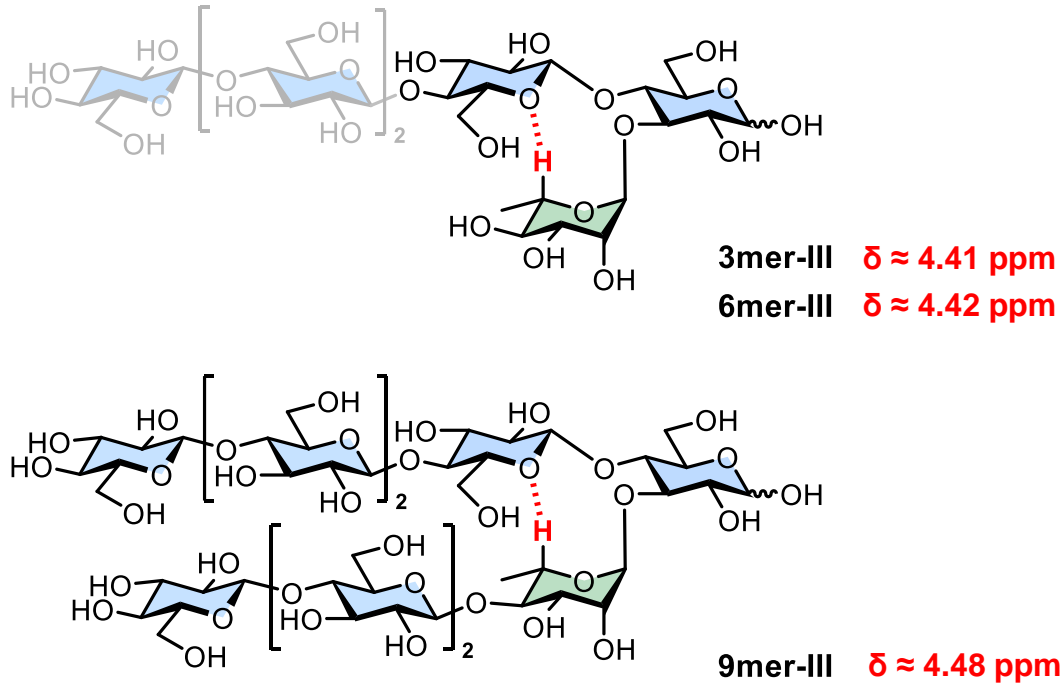


Dr Kelvin Anggara

DISSECTING THE CONFORMATIONAL STABILITY

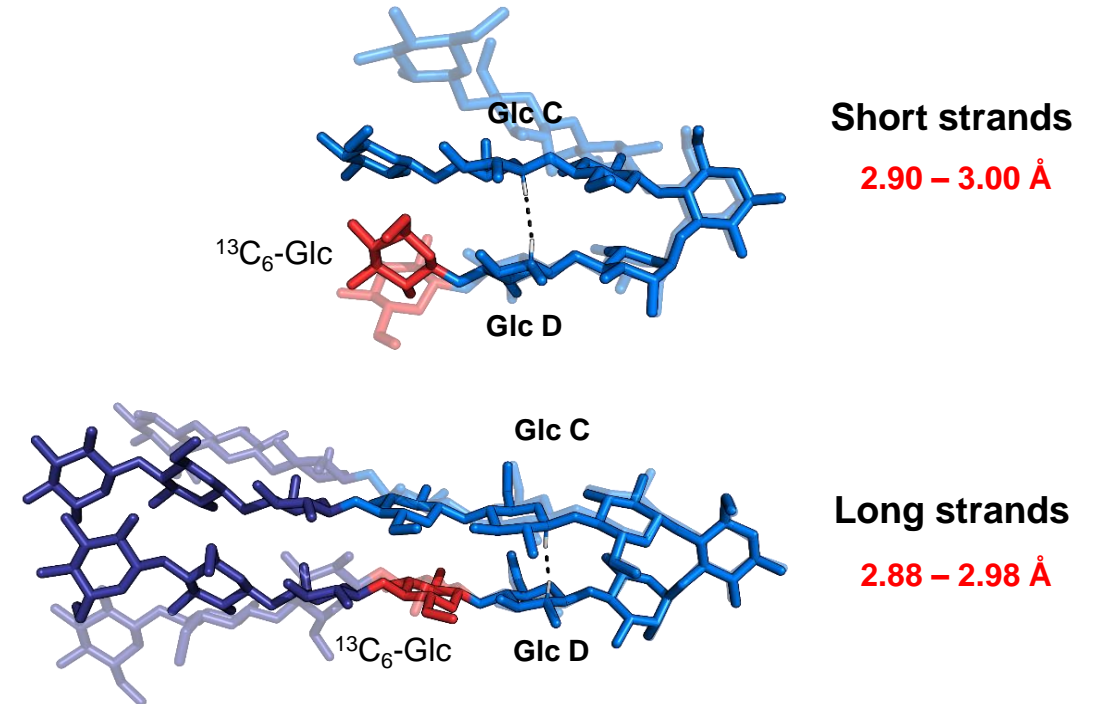


The effect of the strands



Glycan-glycan interactions can be used to rigidify glycan sequences

The effect of the strands length



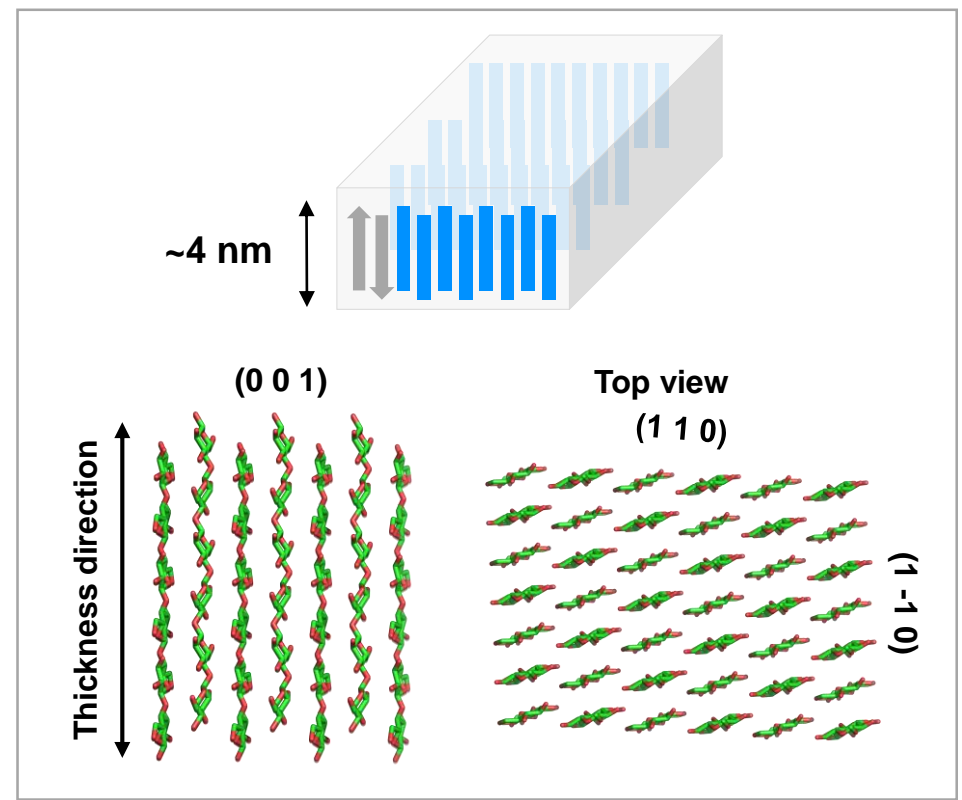
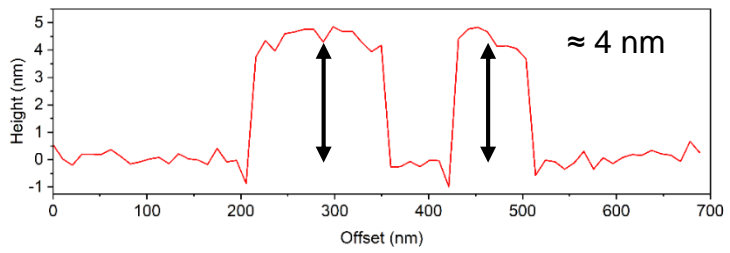
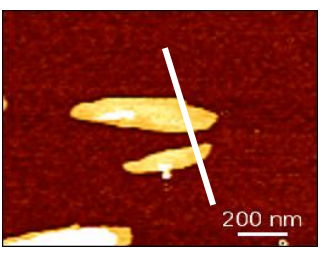
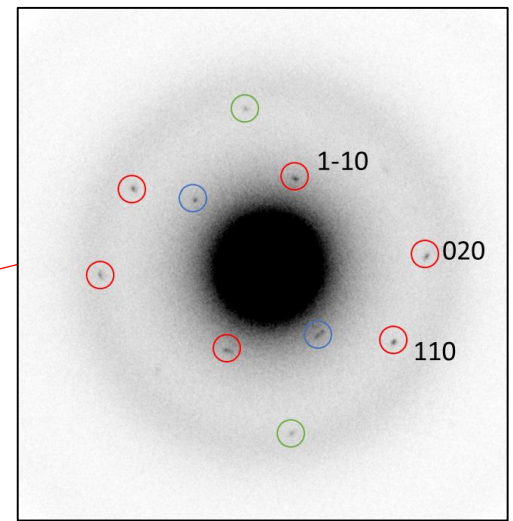
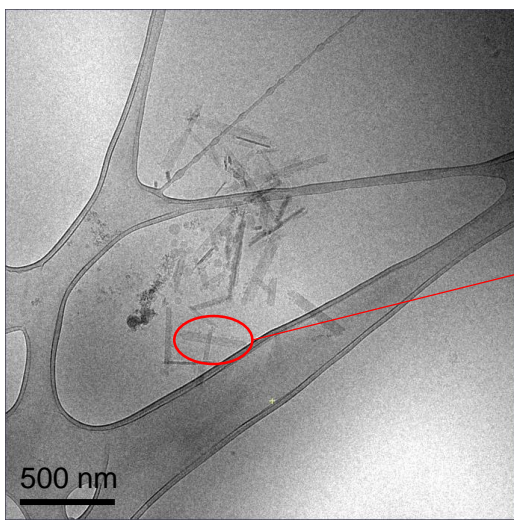
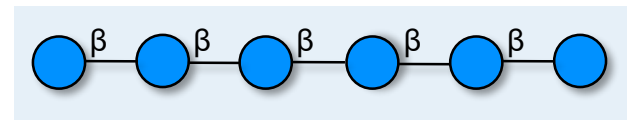
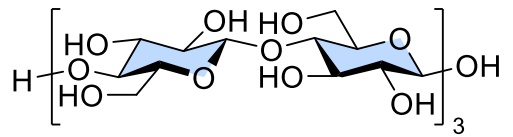
Small changes can influence the **stability of remote glycan motifs**

J. Am. Chem. Soc., 2024, 146, 6369

DESIGN OF A GLYCAN ASSEMBLY



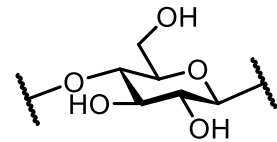
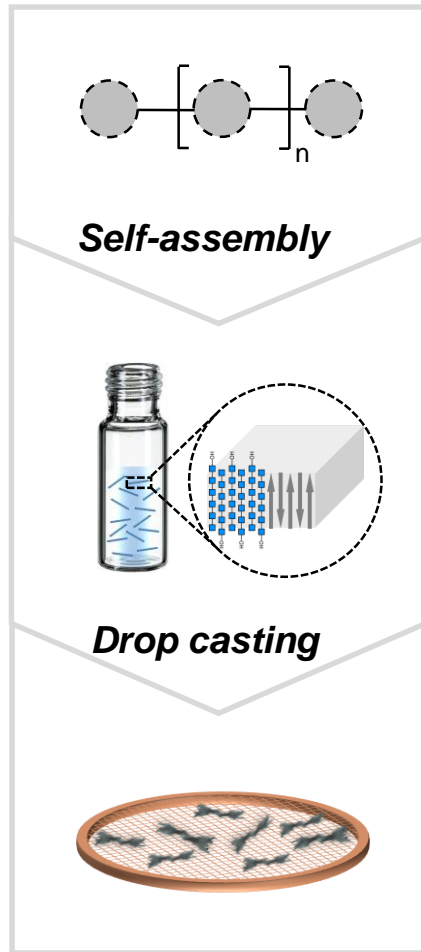
A₆



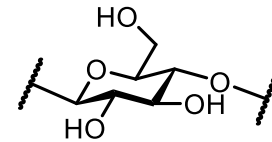
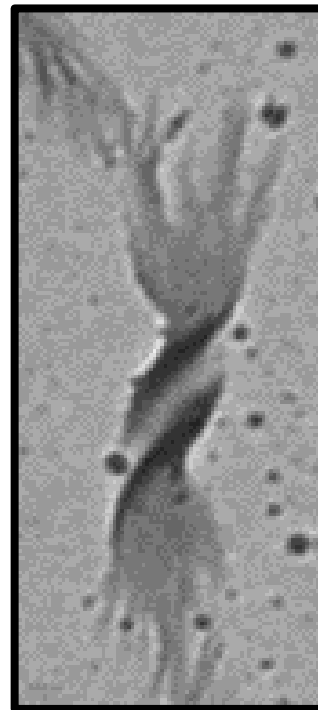
Dr Yu Ogawa (Cermav)

J. Am. Chem. Soc., 2022, 144, 12469

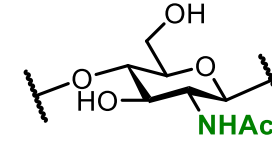
SYNTHETIC CHIRAL ASSEMBLIES



Right handed



Left handed



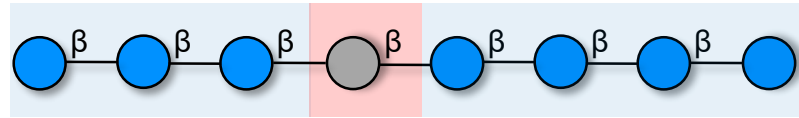
More twisted



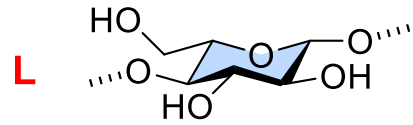
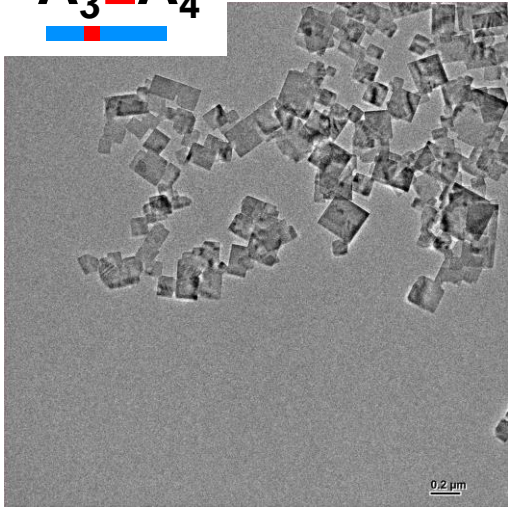
TOWARDS NEW SHAPES



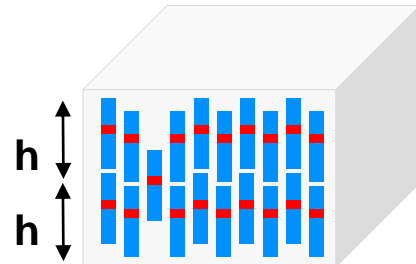
Modification within the core



A₃LA₄

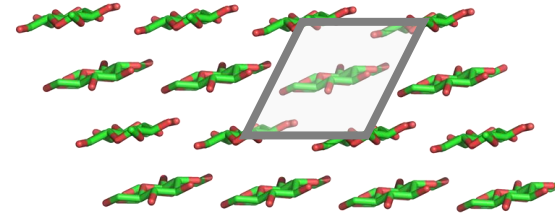


3D crystal

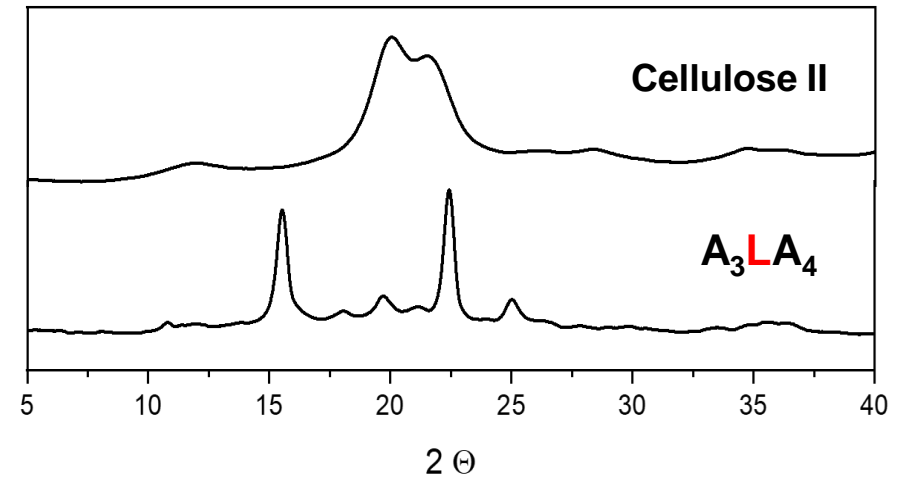
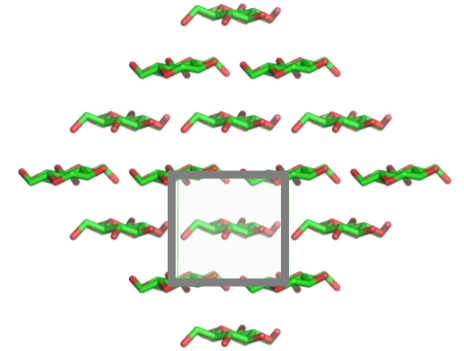


New allomorph - Cellulose IV_{II}

Cellulose II



Cellulose IV_{II}

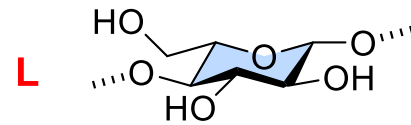
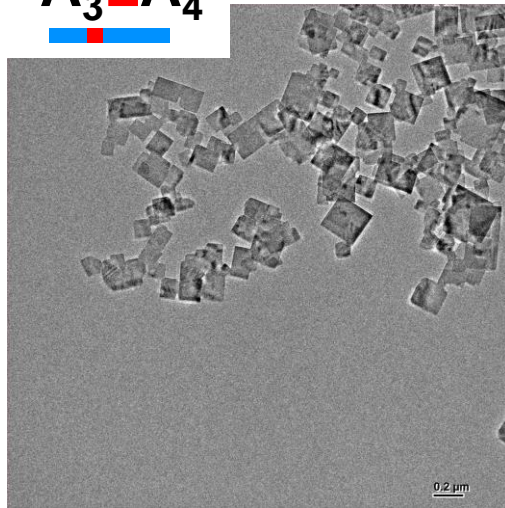
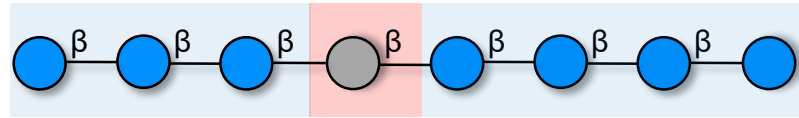


Angew. Chem. Int. Ed., **2023**, e202310357

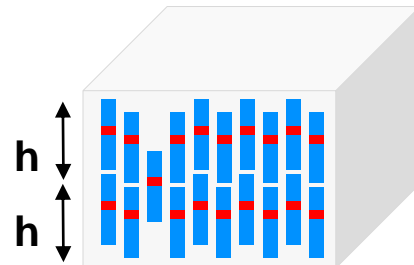
TOWARDS NEW SHAPES



Modification within the core

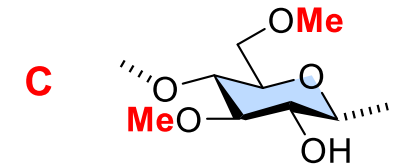
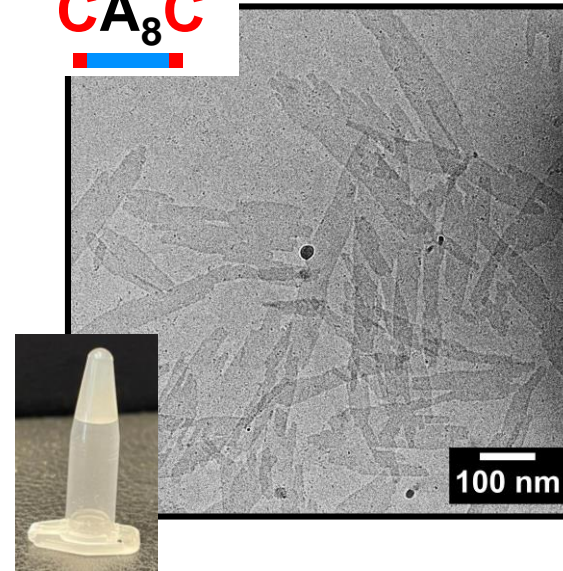
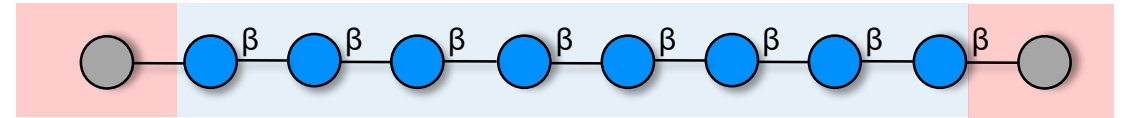


3D crystal

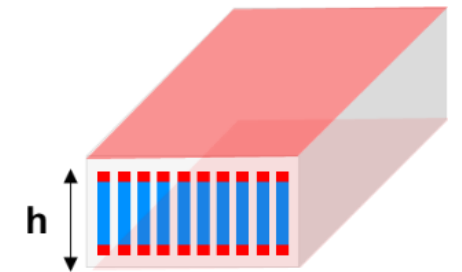


New allomorph - Cellulose IV_{II}

Modification at the surface



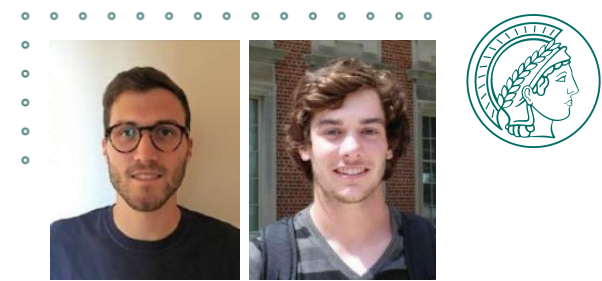
2D crystal



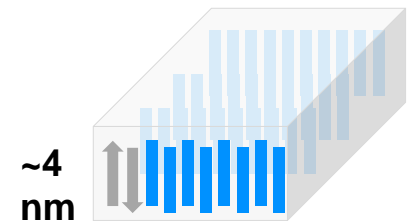
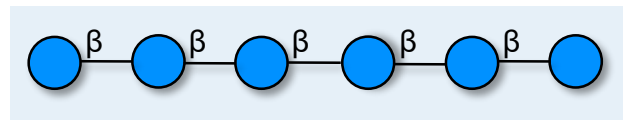
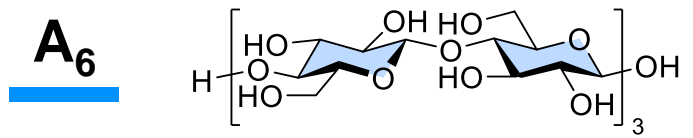
Supramolecular hydrogels

Angew. Chem. Int. Ed., 2023, e202310357

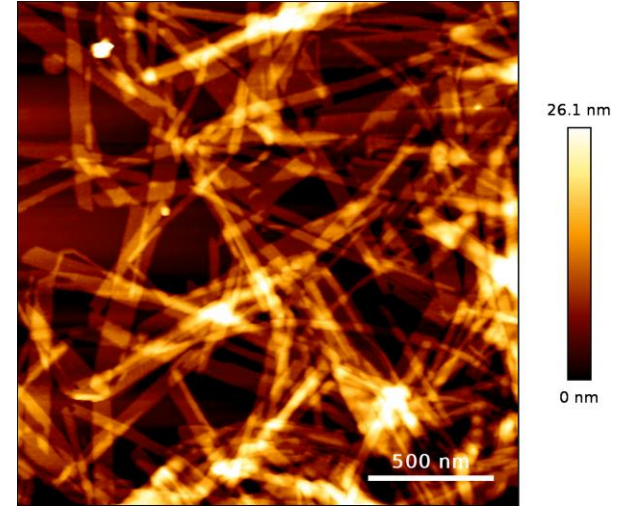
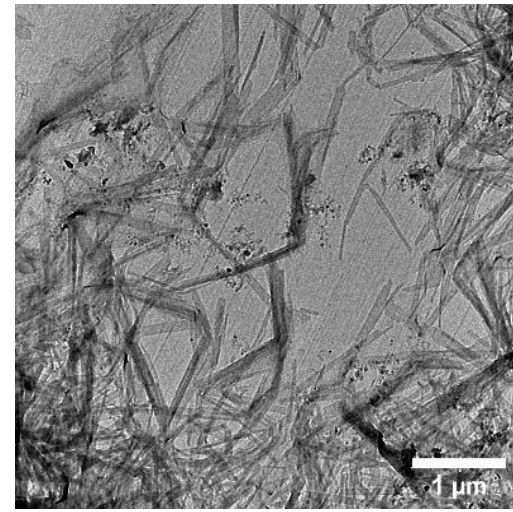
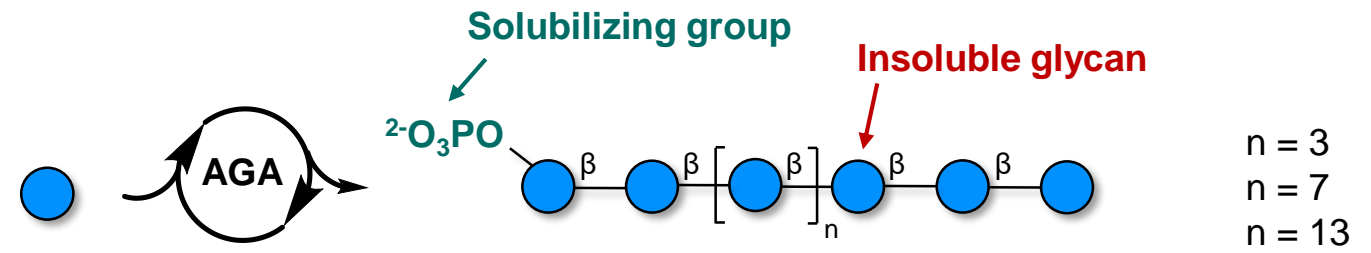
MAKING LONG CELLULOSE OLIGOMERS



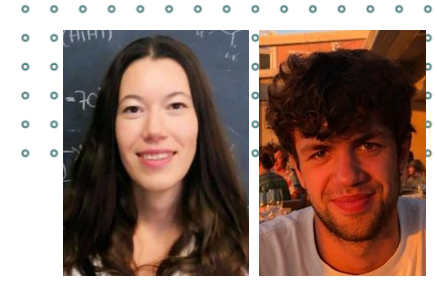
Assembly of A₆



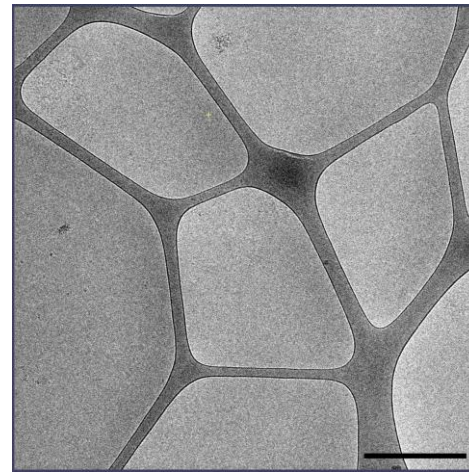
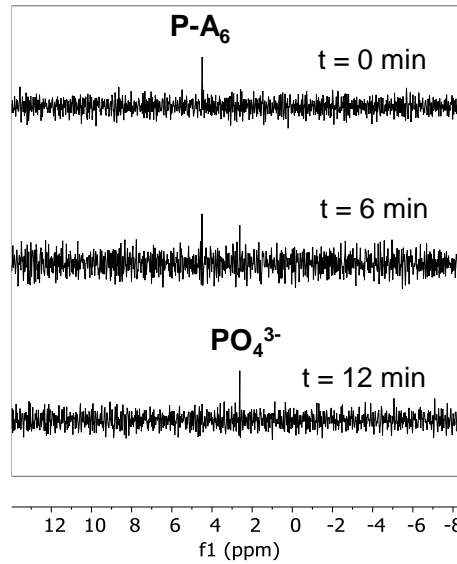
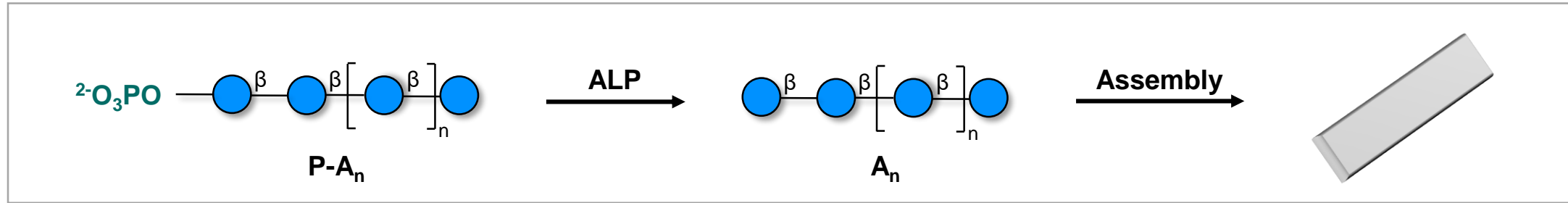
Can we go longer?



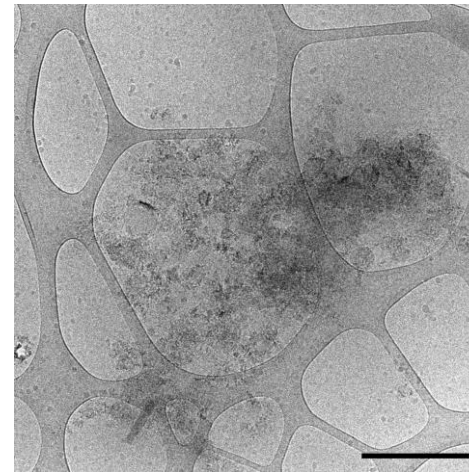
ACS Cent. Sci., 2024, 10, 138



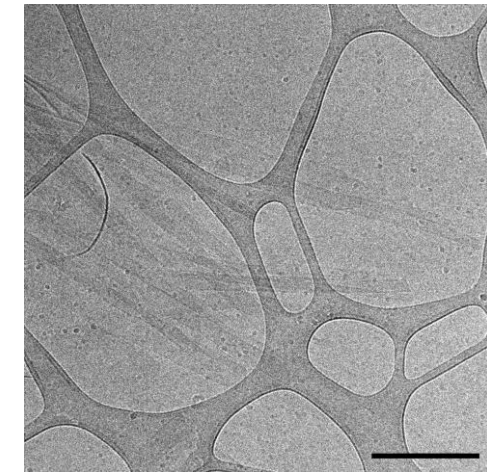
THE MECHANISM OF ETA



t = 5 min



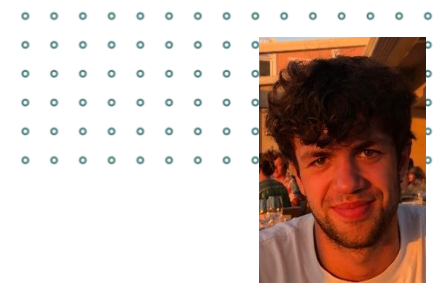
t = 1 h



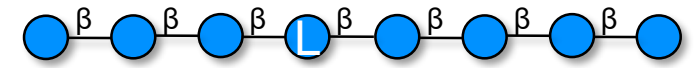
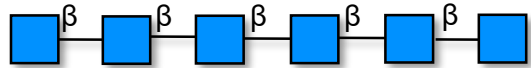
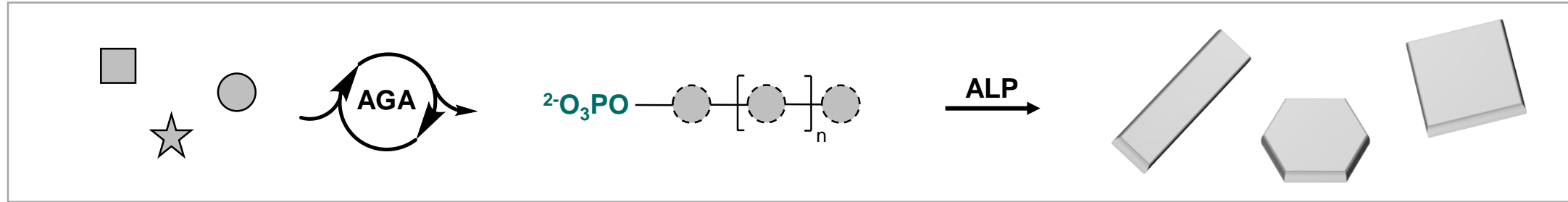
t = 24 h

Jia Hui Lim & Dr Yu Ogawa (Cermav)

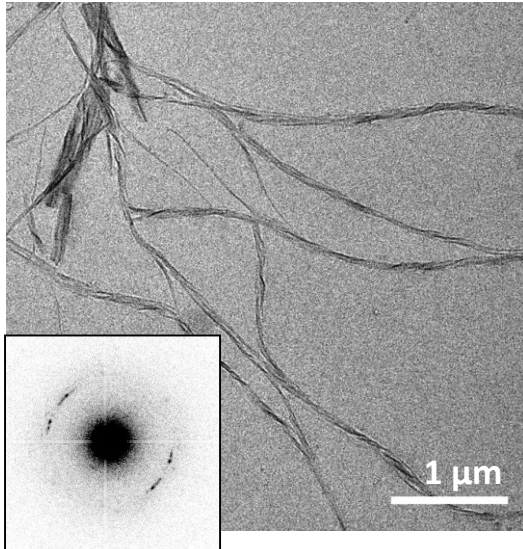
Angew. Chem. Int. Ed., 2024, accepted



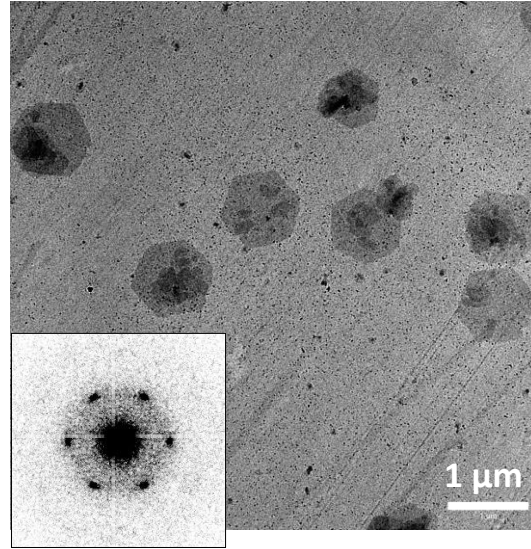
ENZYME-TRIGGERED ASSEMBLY



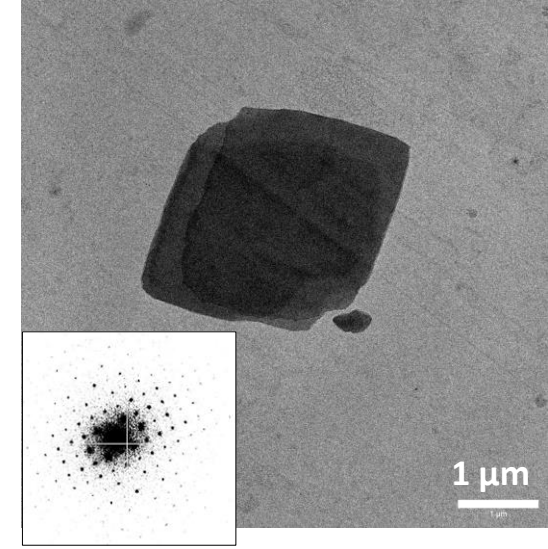
N_6



Y_{12}

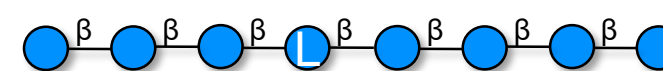
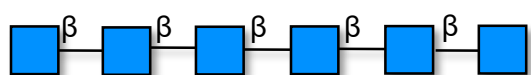
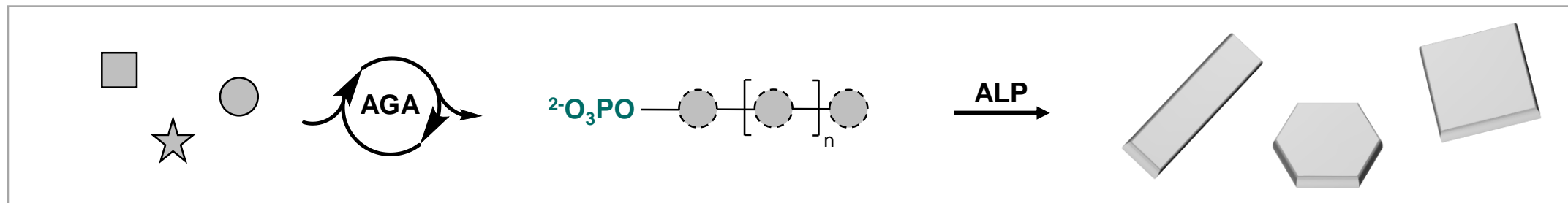
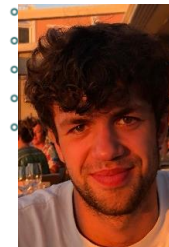


A_3LA_4

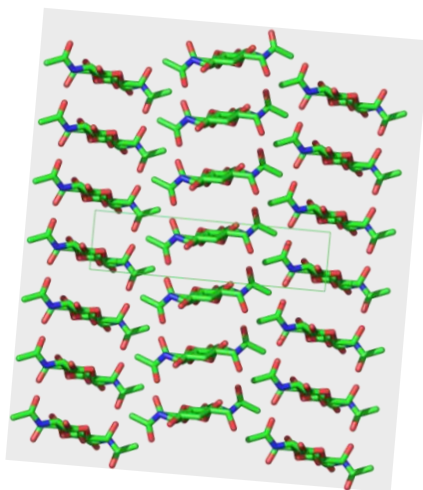


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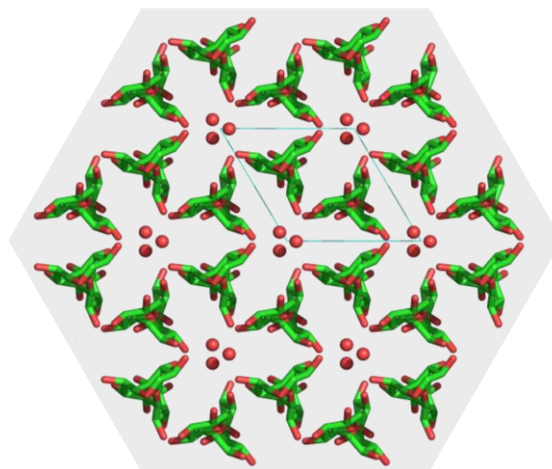
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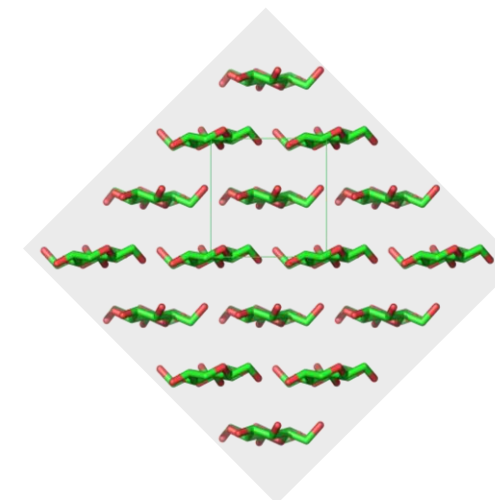
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Y_{12}



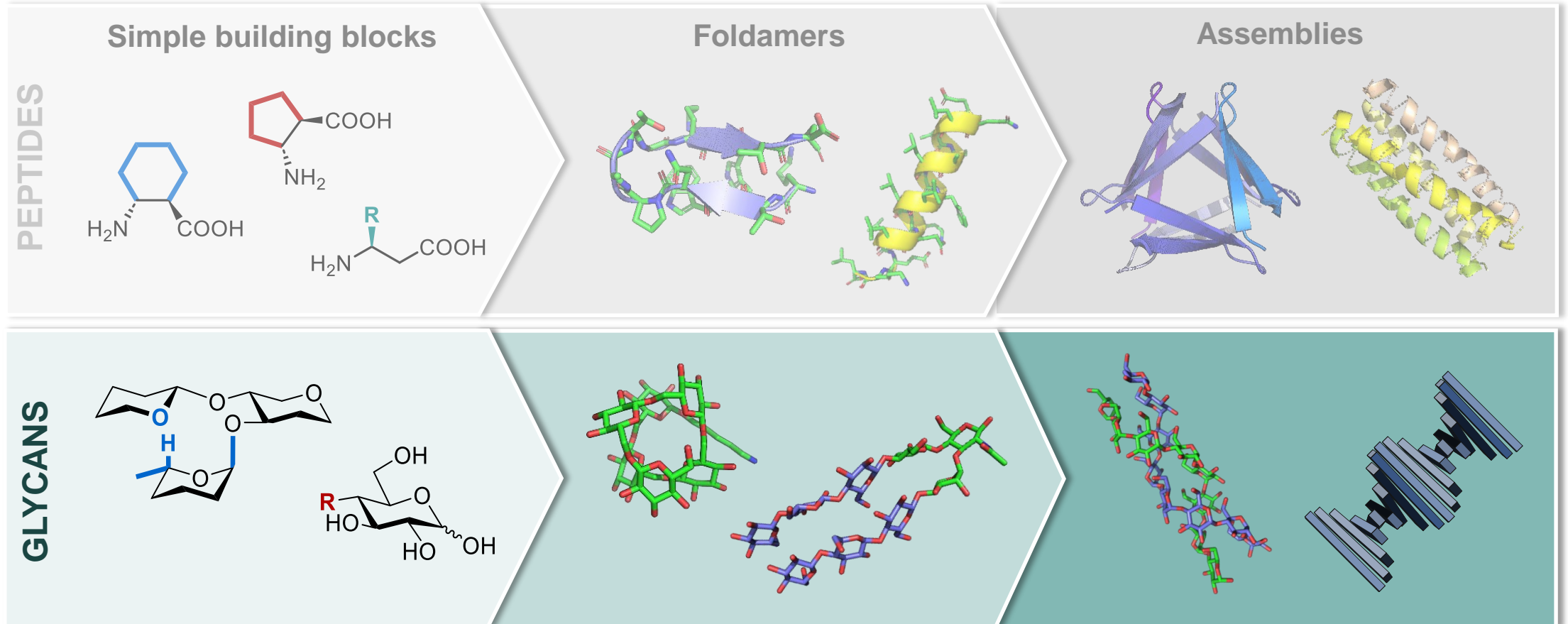
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OUR VISION



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Alumni

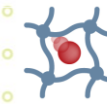
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Dr Soeun Gim
Dr Vittorio Bordoni
Prof. Yuntao Zhu
Dr Manish Chaube
Dr Denisa Vargová
Dr Theodore Tyrikos-
Ergas
Dr Giulio Fittolani
Dr Zhouxiang Zhao
Jaap Van Trijp

Collaborators

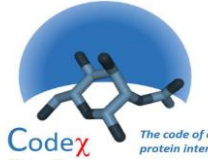
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Prof. Stephan Rauschenbach (Oxford)
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Dr Kelvin Anggara (MPI-FKF)
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The code of chito-
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