ETH zürich

2025 Annual CMMRC Workshop – Washington DC, USA (online) – 02. October 2025

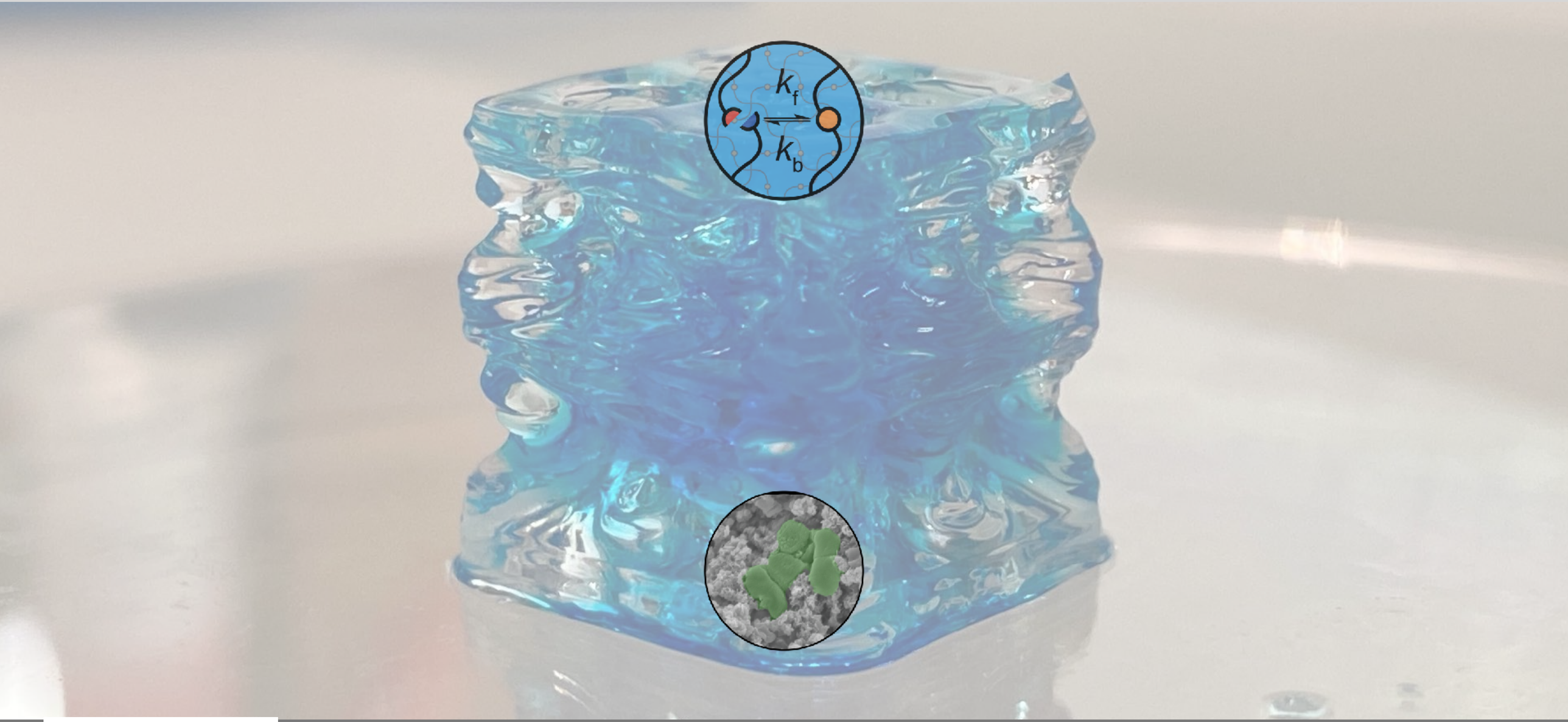
Dynamically reconfigurable network materials

Prof. Dr. Mark W. Tibbitt

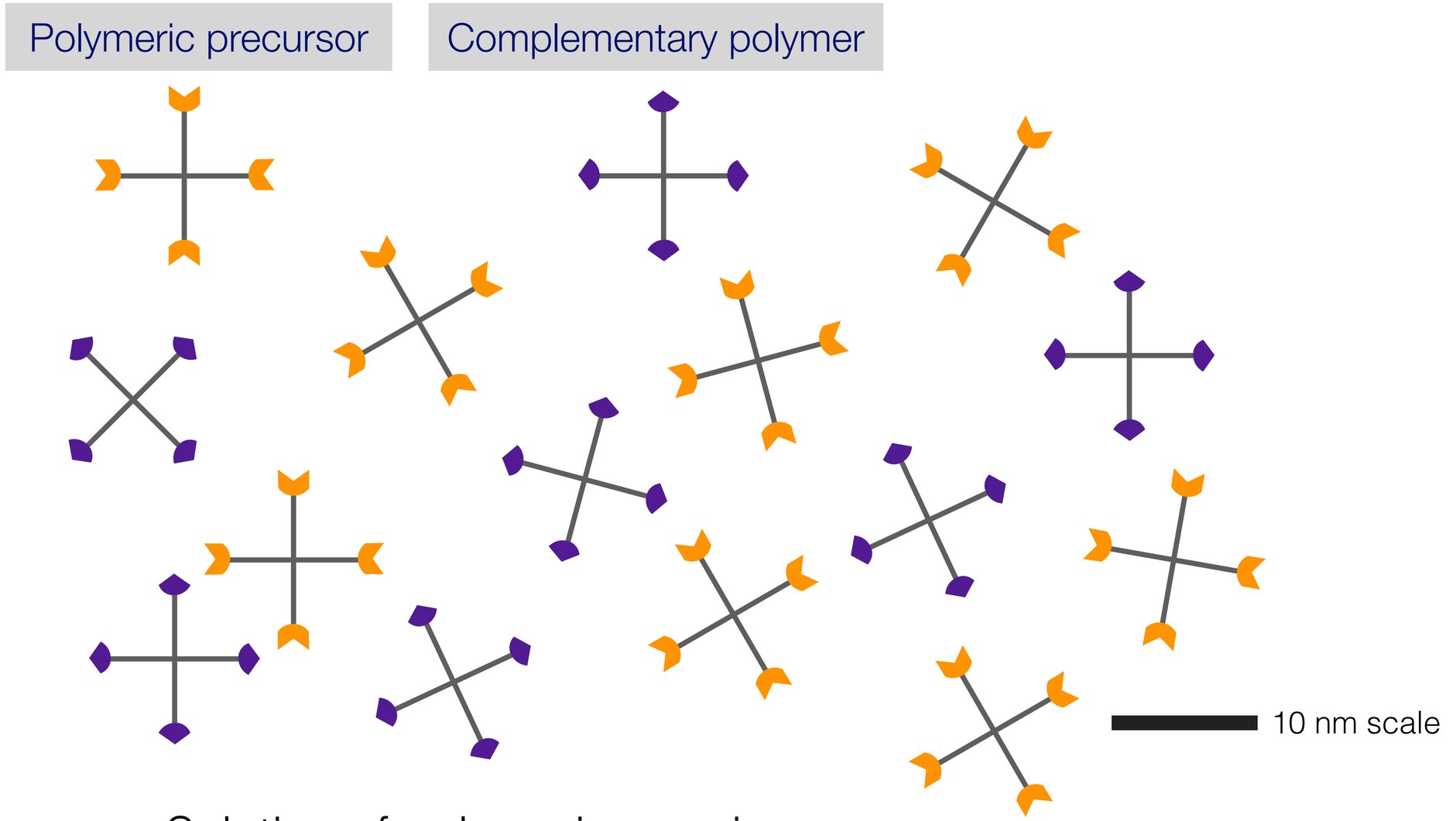
Biological materials that learn

https://www.youtube.com/watch?v=WQC0bXB4RQY

Materials that learn: a few important features



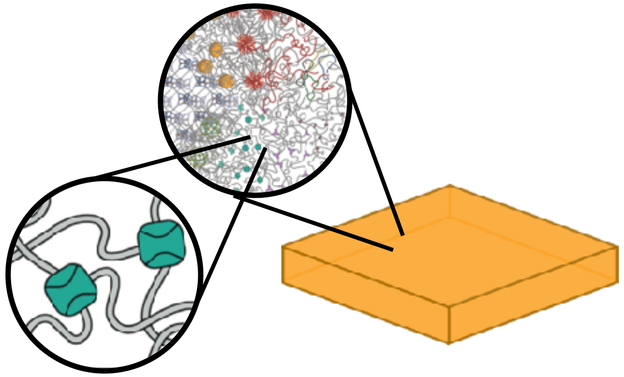
Polymer chains can be further cross-linked into networks



Solution of polymeric species

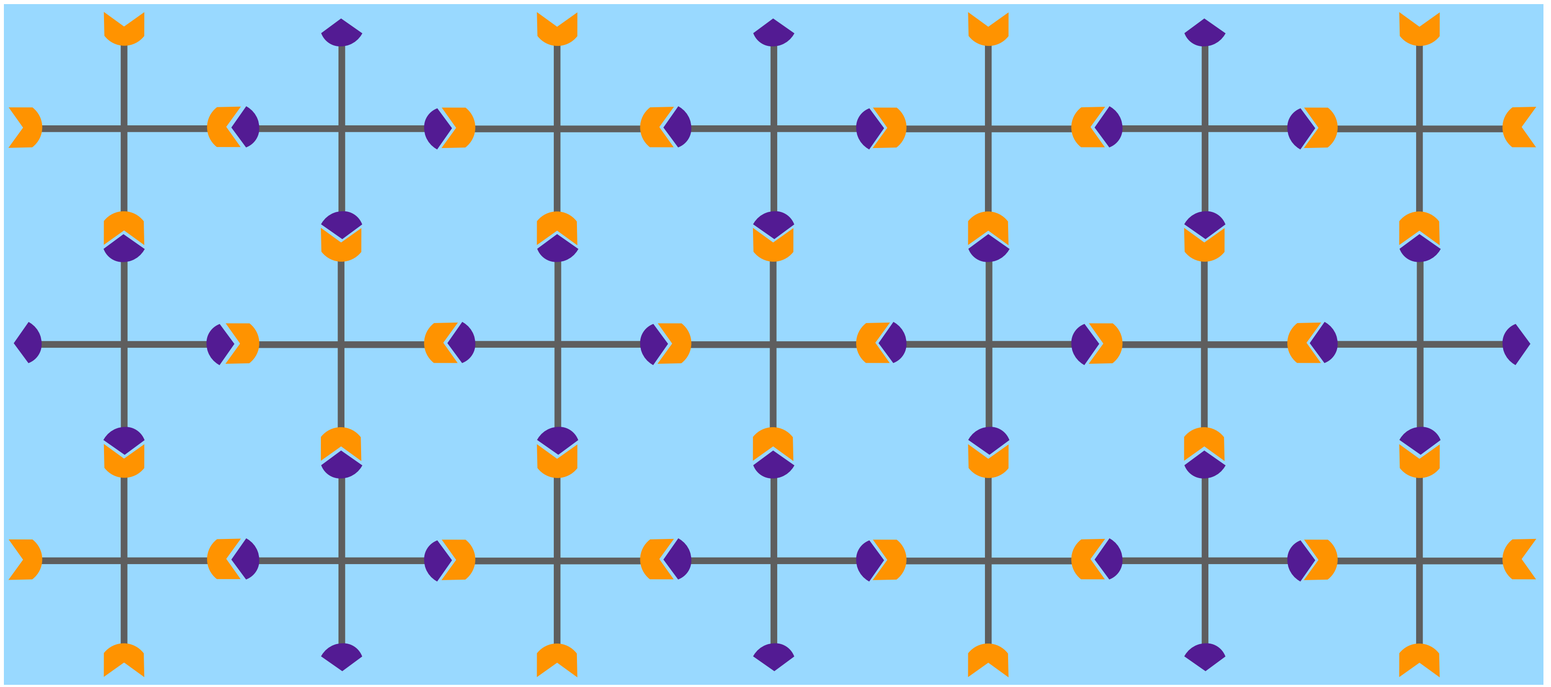
Polymer chains can be further cross-linked into networks

Viscoelastic insoluble network or gel



Elasticity

Swelling ***Durability***

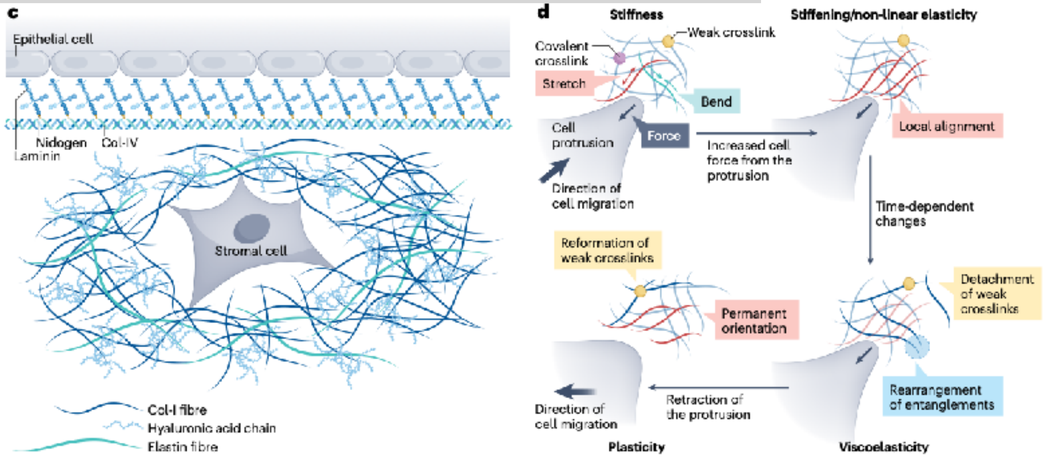


10 nm scale

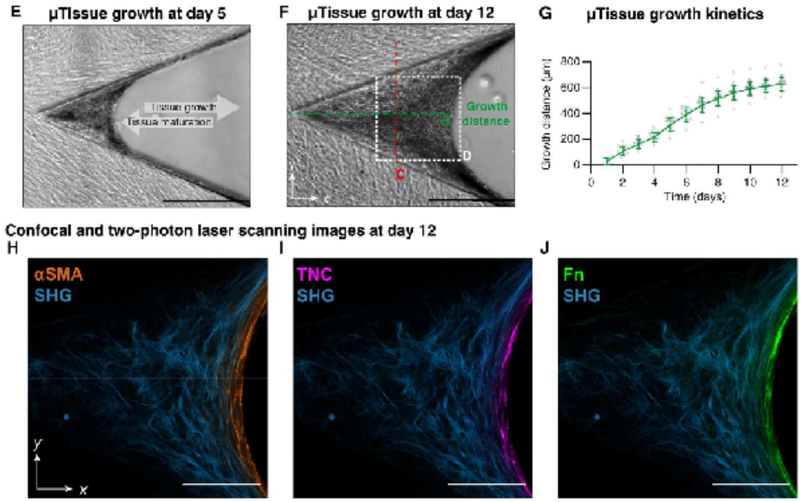
Gu Y. et al., *Angew. Chem. Int. Ed.*, **2020**, *59*, 5022

The extracellular matrix (ECM) as a driver of biological function

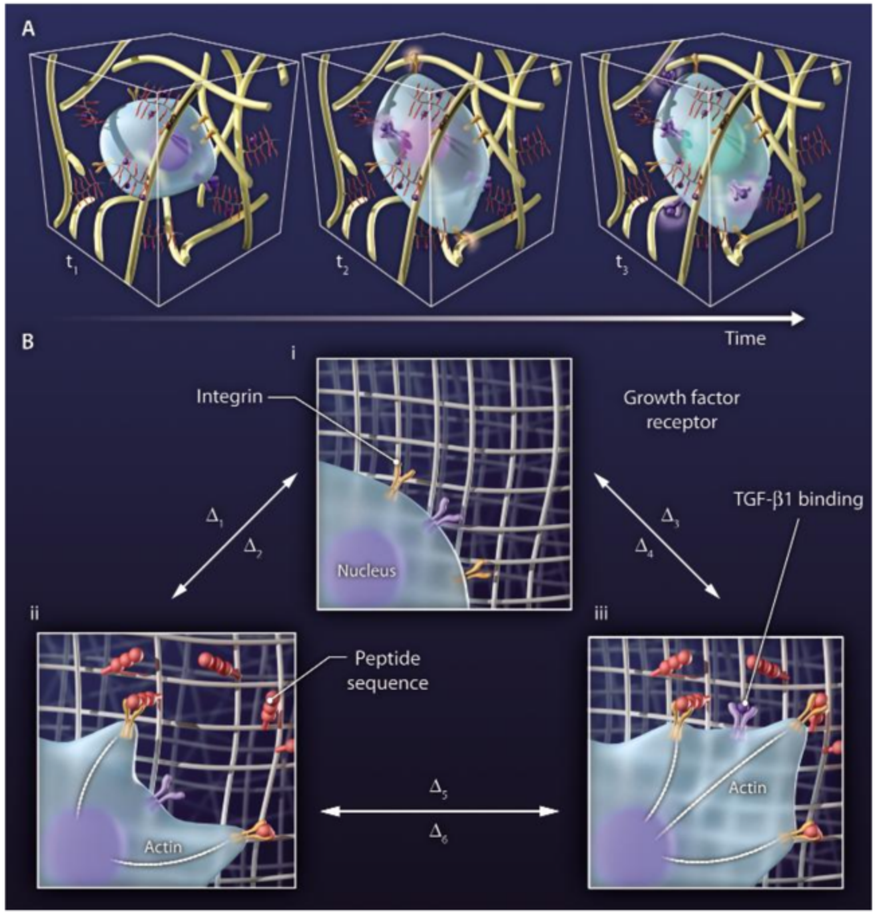
ECM properties influence cell function



At the single and multicellular level



Hydrogels as engineered ECM mimics

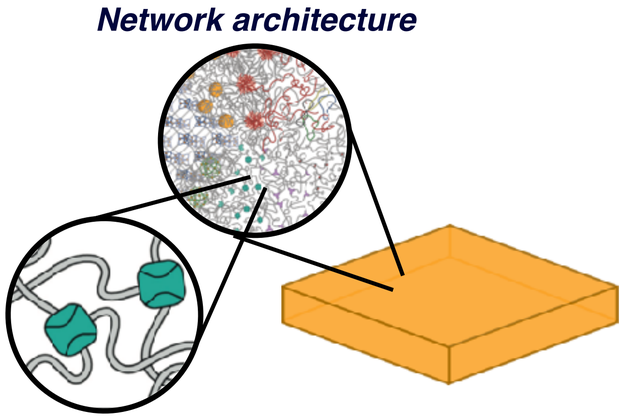


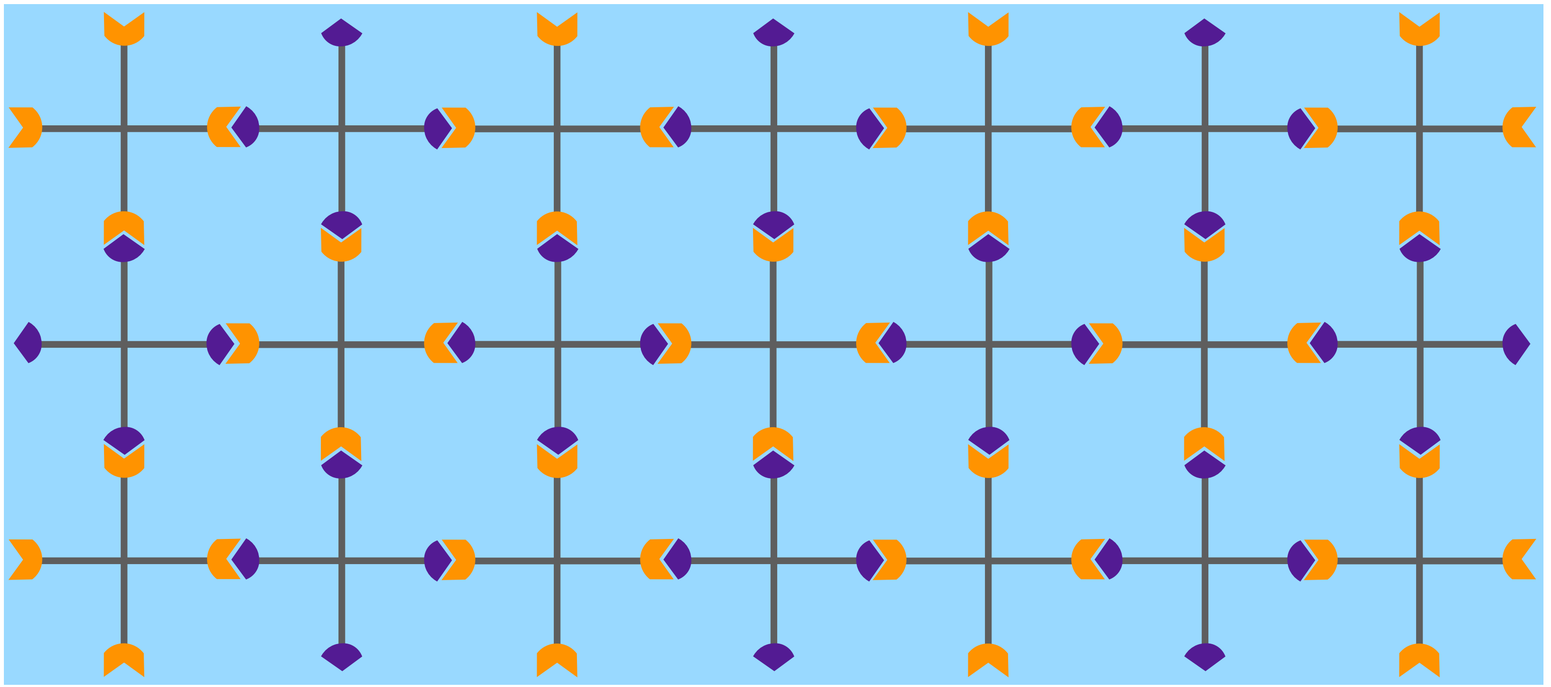
Moving from permissive scaffolds to materials that promote biological function and cooperate with biology

Saraswathibhatla, A. et al. *Nat. Rev. Mol. Cell Biol.*, **2023**, *24*, 495.
Benn M.C. et al. *Sci. Adv.*, **2023**, *9*, eadd9275.
Tibbitt M.W. and Anseth K.S. *Sci. Transl. Med.*, **2011**, *4*, 160ps24.

Polymer chains can be further cross-linked into networks

Viscoelastic insoluble network or gel





10 nm scale

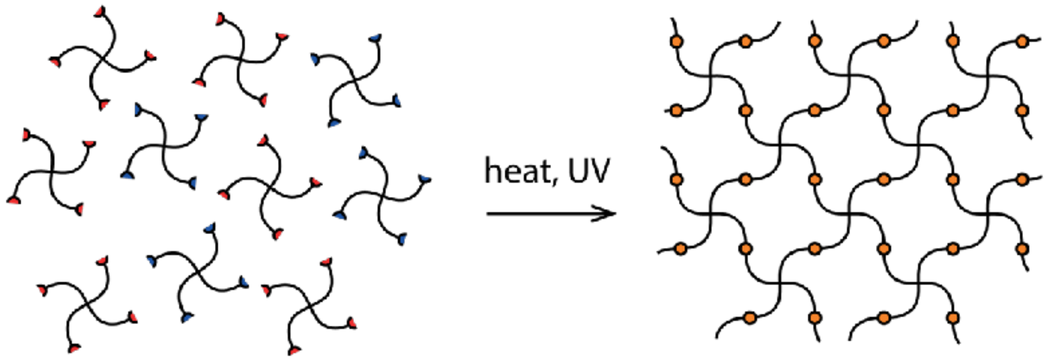
Elasticity

Swelling ***Durability***

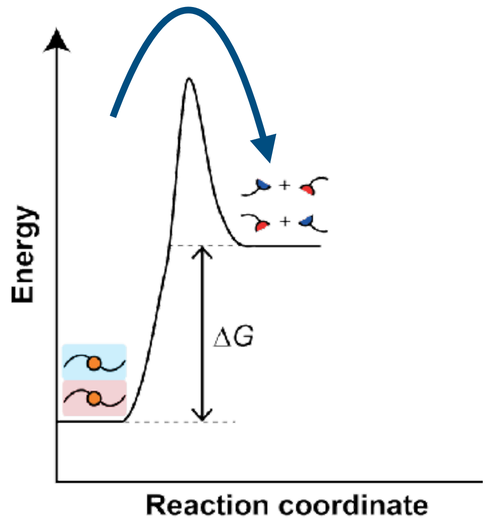
Polymer networks are traditionally engineered via **covalent linkages**.

Gu Y. et al., *Angew. Chem. Int. Ed.*, **2020**, *59*, 5022

Introducing engineered dynamics into polymer networks

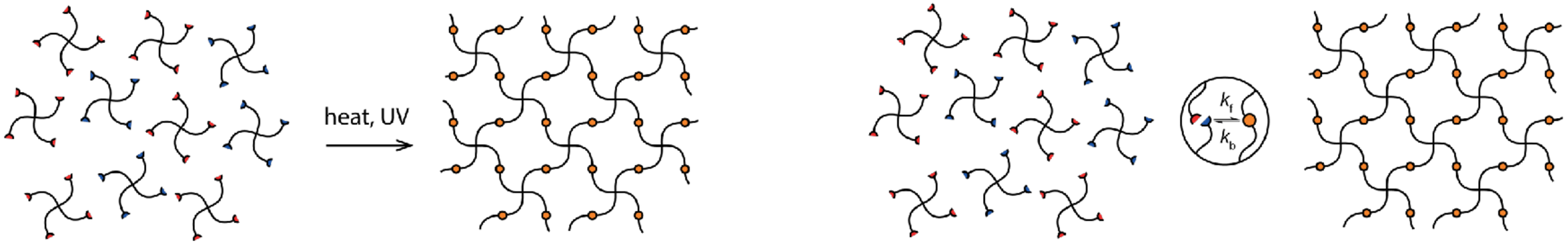


permanent networks



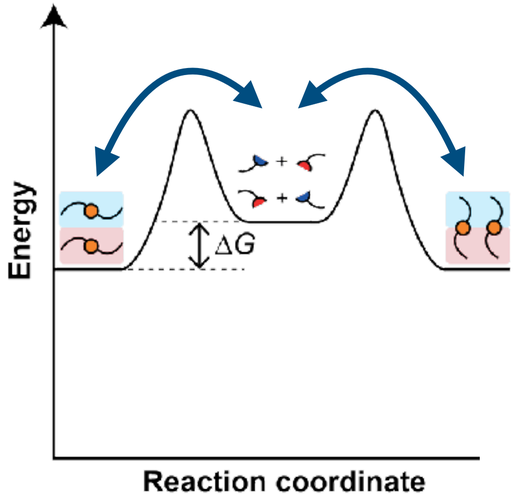
Marco-Dufort B. et al. *Mater. Today Chem.*, **2019**, *142*, 15371.
Webber M.J. and Tibbitt M.W. *Nat. Rev. Mater.*, **2022**, *7*, 541.

Introducing engineered dynamics into polymer networks



permanent networks

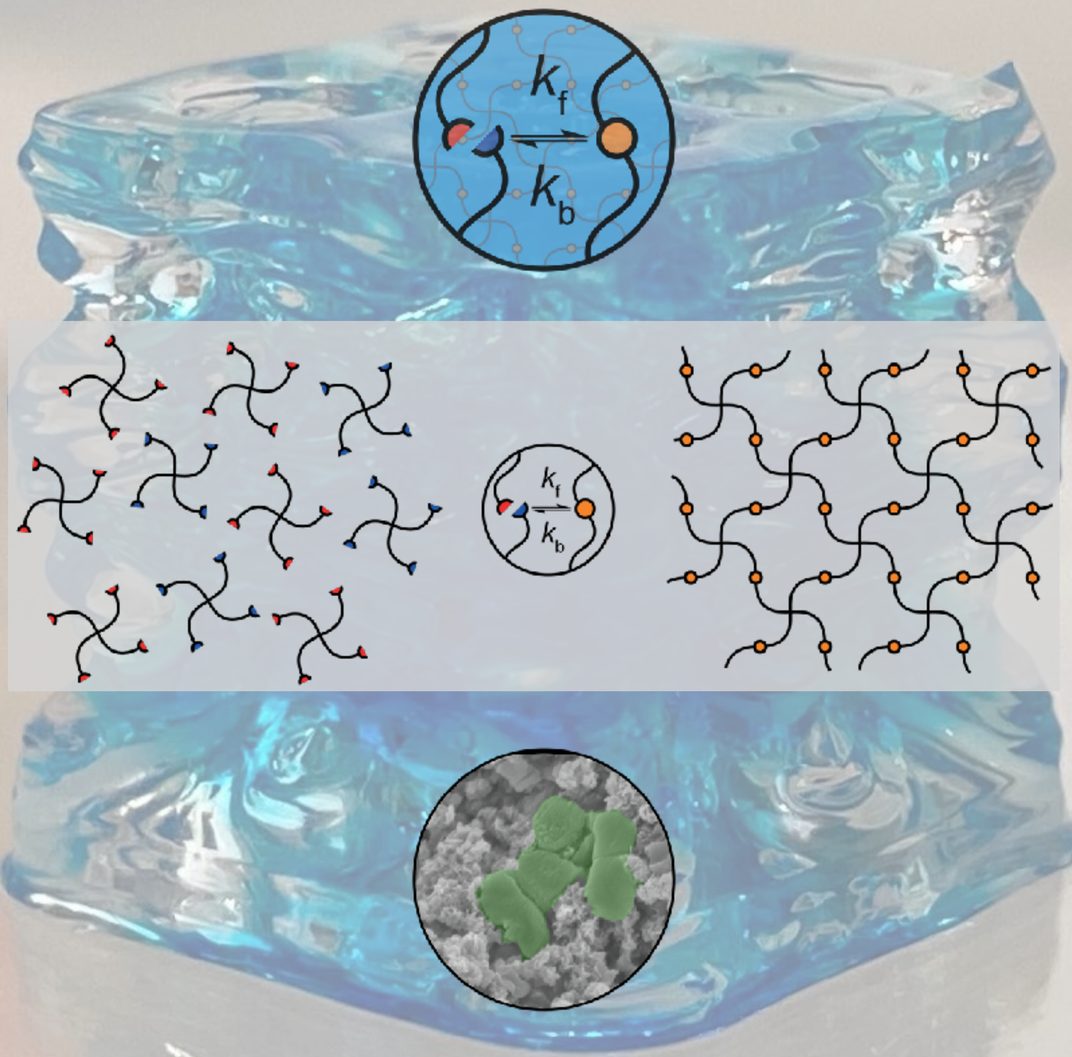
dynamic networks



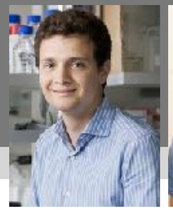
Reversible bonds enables dynamic exchange of the junctions in polymer networks.

Marco-Dufort B. et al. *Mater. Today Chem.*, **2019**, *142*, 15371.
Webber M.J. and Tibbitt M.W. *Nat. Rev. Mater.*, **2022**, *7*, 541.
Montarnal et al. *Science*, **2011**, *334*, 965.

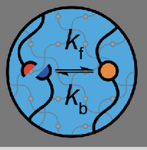
Materials that learn: a few important features



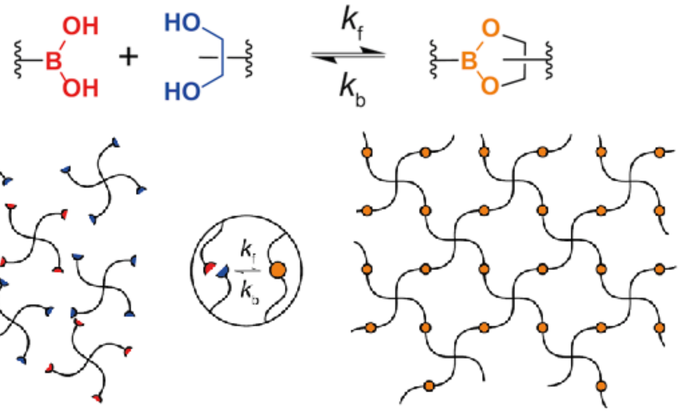
Model dynamic covalent networks using boronic-ester cross-links


Bruno Marco-Dufort

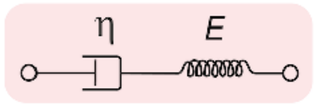

Lucien Cousin

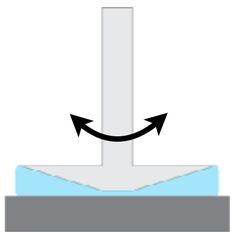


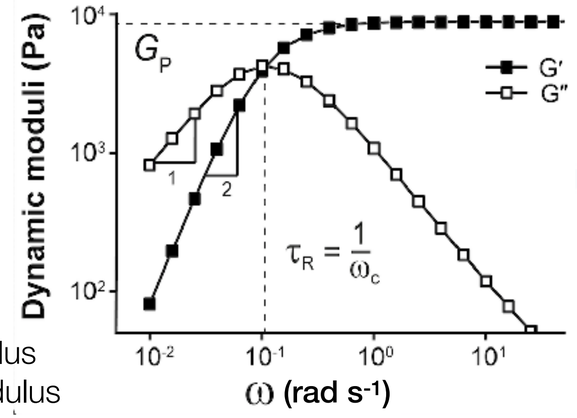
Moldable and self-healing, viscoelastic gel



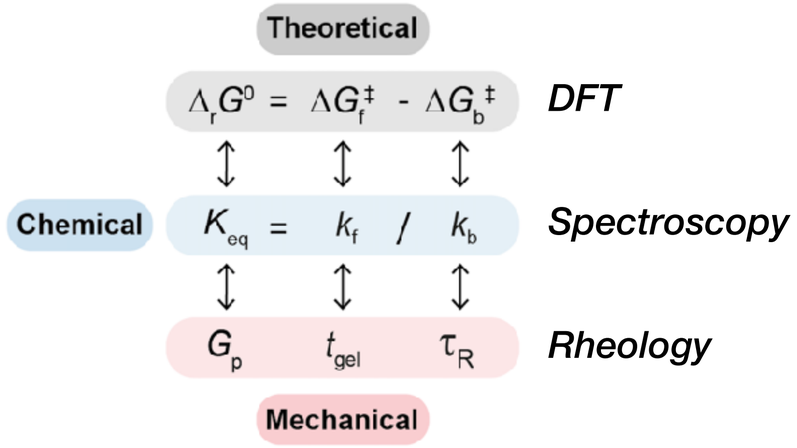
Maxwell material





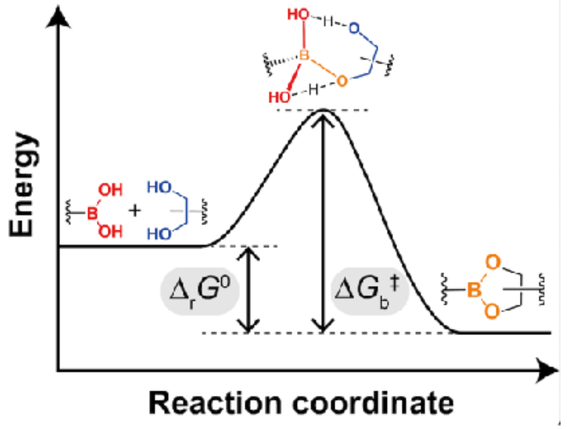


G′ - elastic modulus
G″ - viscous modulus



What features are enabled by dynamic covalent networks?

$$K_{eq} = \frac{k_f}{k_b} = \frac{[\text{boronic ester}]}{[\text{diol}][\text{boronic acid}]}$$

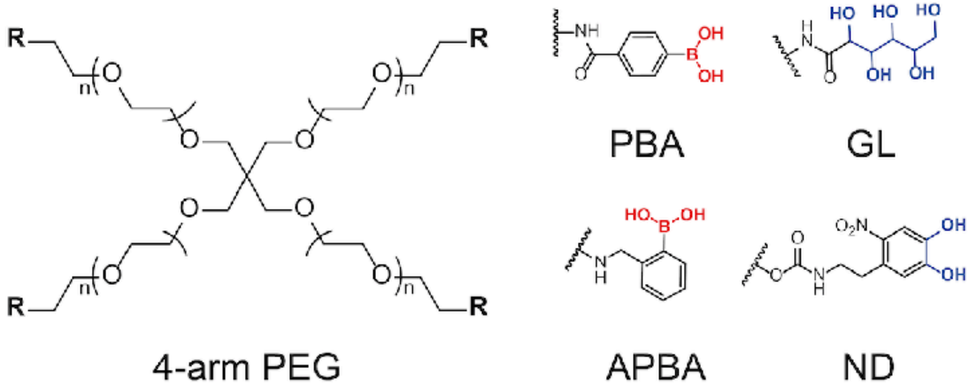


Original developments of boronic-ester based materials at ETH:
Deuel and Neukom. *Die Makromoleculare Chemie.* 1949.

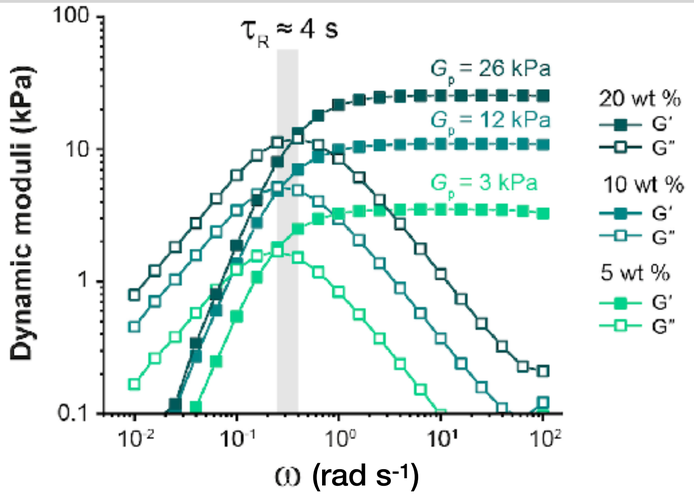
Marco-Dufort B., Tibbitt M.W. *Mater. Today Chem.*, **2019**, *12*, 16.
Marco-Dufort B., Iten R., Tibbitt M.W. *J. Am. Chem. Soc.*, **2020**, *142*, 15371.

Linking molecular properties to macroscale behavior in dynamic networks

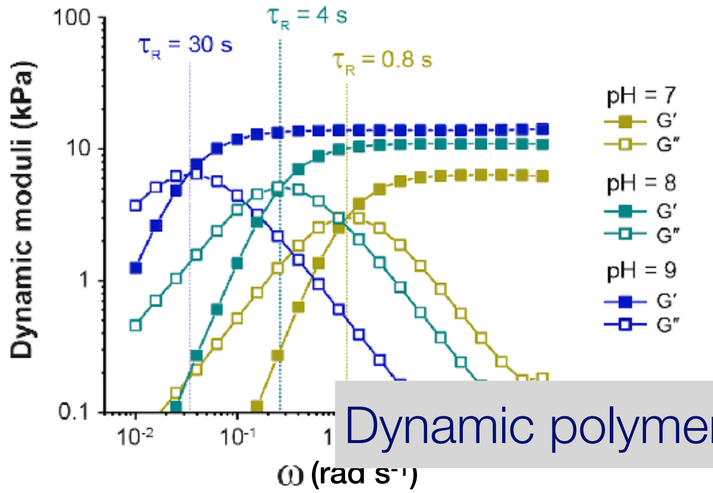
Material properties vary with [*c*], pH, and *T*

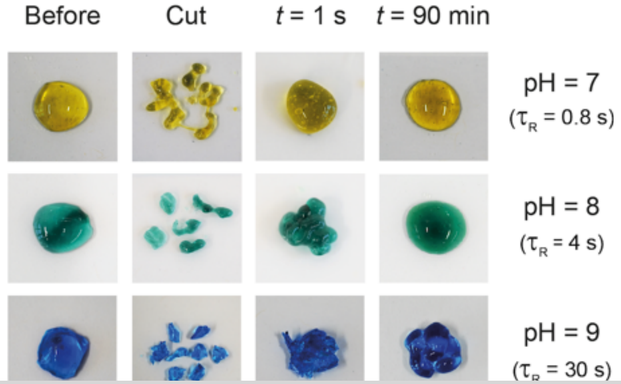


Plateau modulus scales with polymer concentration



Relaxation time and self-healing scale with pH



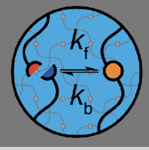


Dynamic networks enable **tunable modulus** and **flow properties** through environmental control of the dynamic chemical equilibrium.

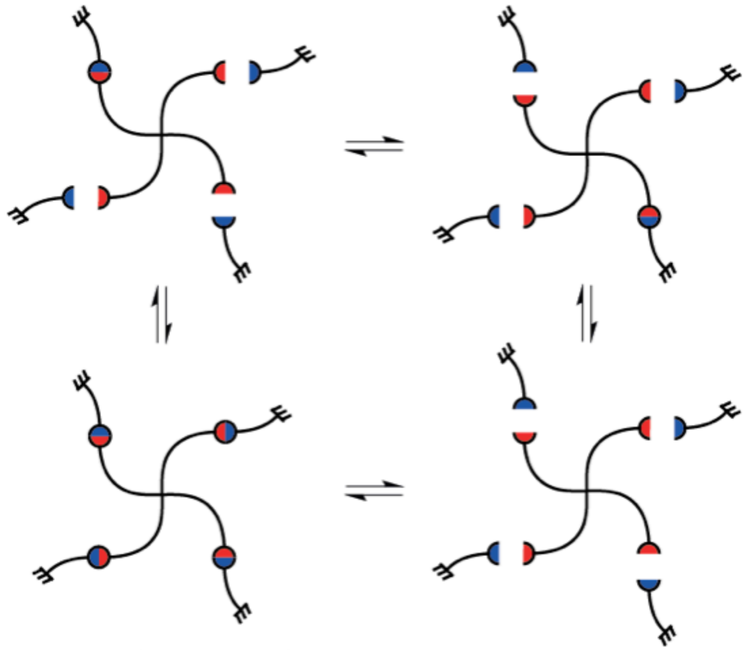
Dynamic polymer networks allow a high but **reduced number of DoFs**.

Marco-Dufort B., Iten R., Tibbitt M.W. *J. Am. Chem. Soc.*, **2020**, *142*, 15371.

Mechanical properties depend on entropy maximization in reversible polymer networks



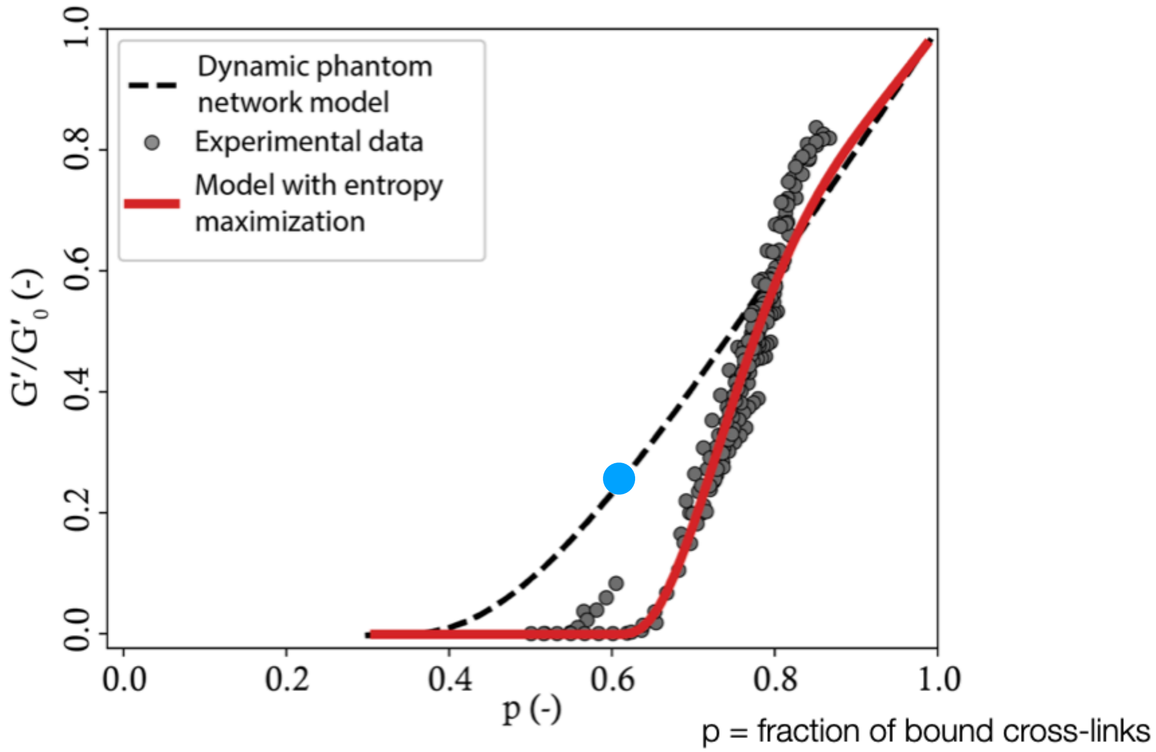
The ability to bind and unbind leads to additional **entropy maximization** in reversible polymer networks.



$$\frac{S}{k_B} = \log\left(\frac{N_A}{\sum_{i=0}^{4} i N_i}\right) - \sum_{i=0}^{4} \frac{N_i}{N_S} \log \frac{N_i}{N_S} + \sum_{i=0}^{4} N_i \binom{4}{i}$$

N_A = number of arms
N_S = number of stars
N_i = number of stars with i arms bound

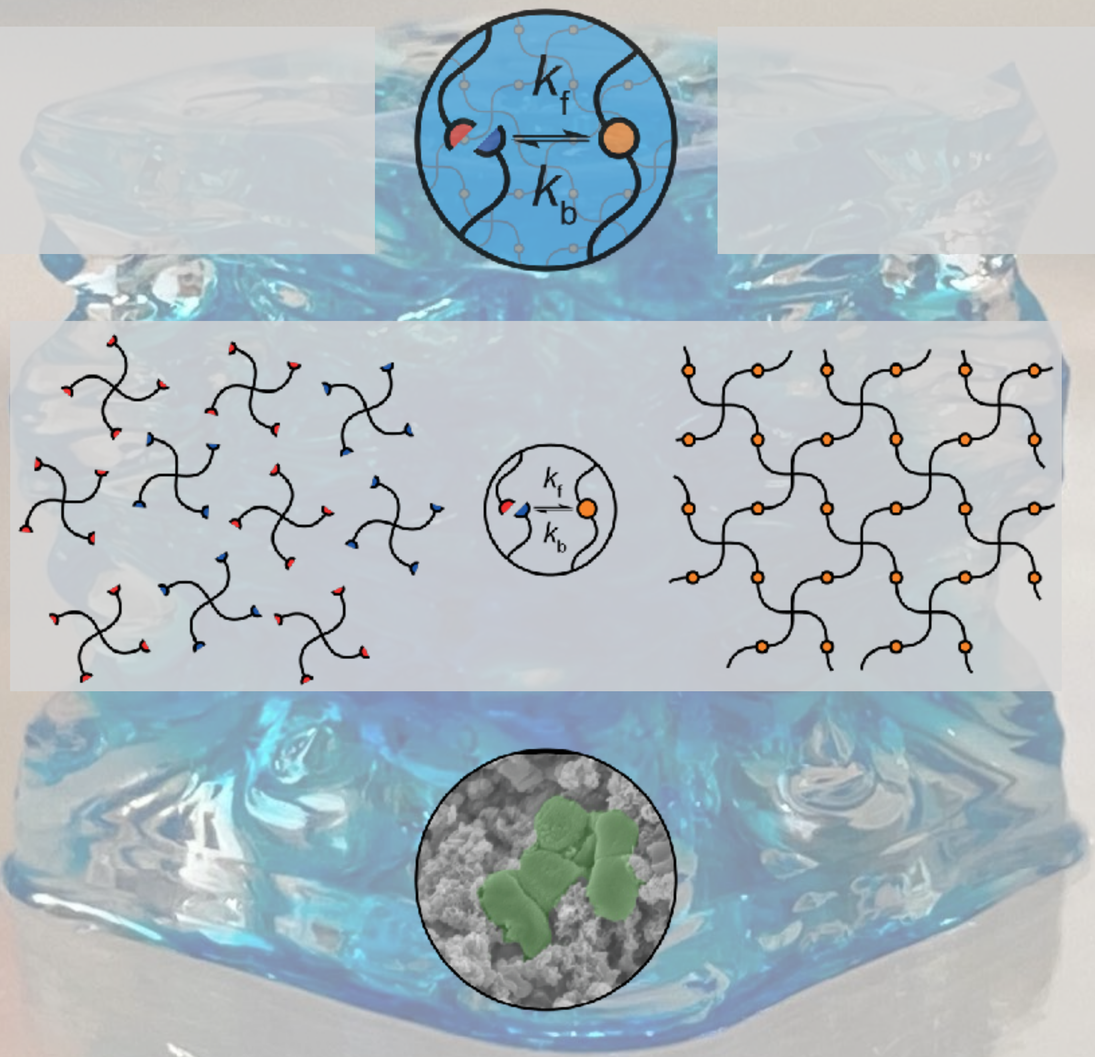
Modifying the dynamic phantom network model for **defect entropy describes network properties**.



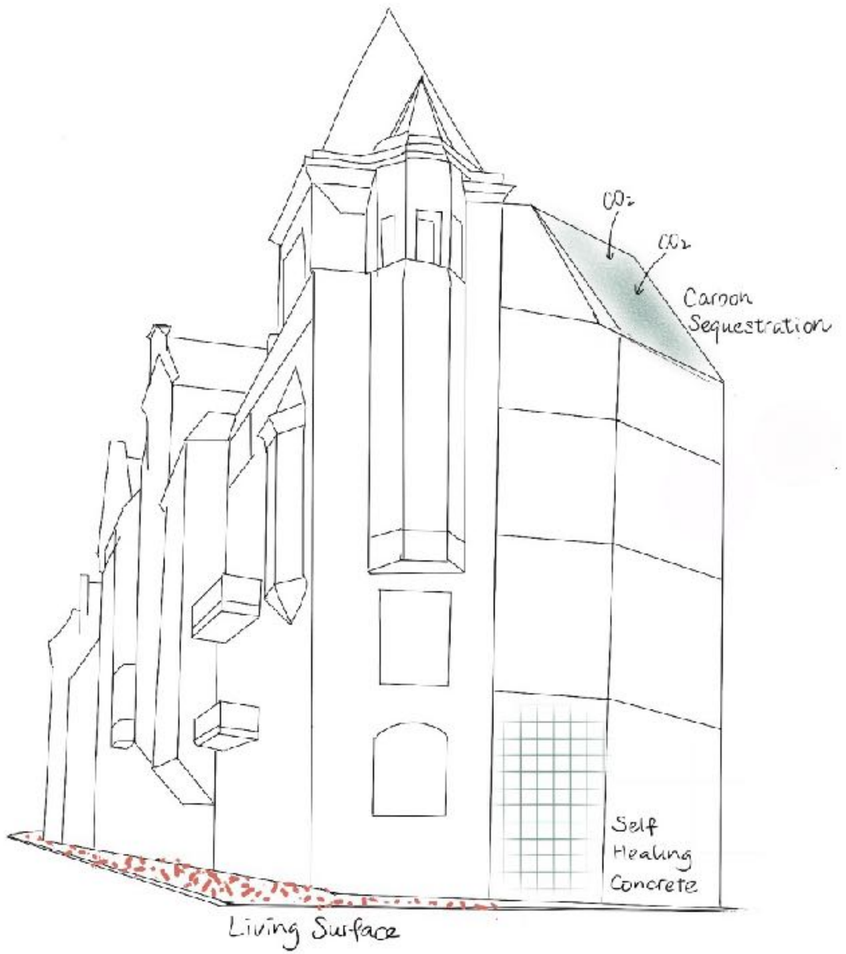
Chemical control over entropic states provides **multistability**.

Cousin L. et al. ***in preparation***.

Materials that learn: a few important features



Advanced engineering with living materials



Can we **integrate living functionality** into dynamic networks for more **perceptive**, **responsive**, and **functional** materials design?

alive
advanced engineering with living materials

Biohybrid Robots
R. Katzschmann

Zurich Joint
R. Müller

CliMa
U. Angst

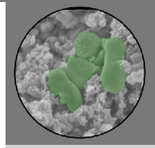
Drawings by Yifan Cui
Co-lead with Eleni Chatzi and in collaboration with 20+ professors at ETH Zurich

Dynamic networks support photosynthetic living materials

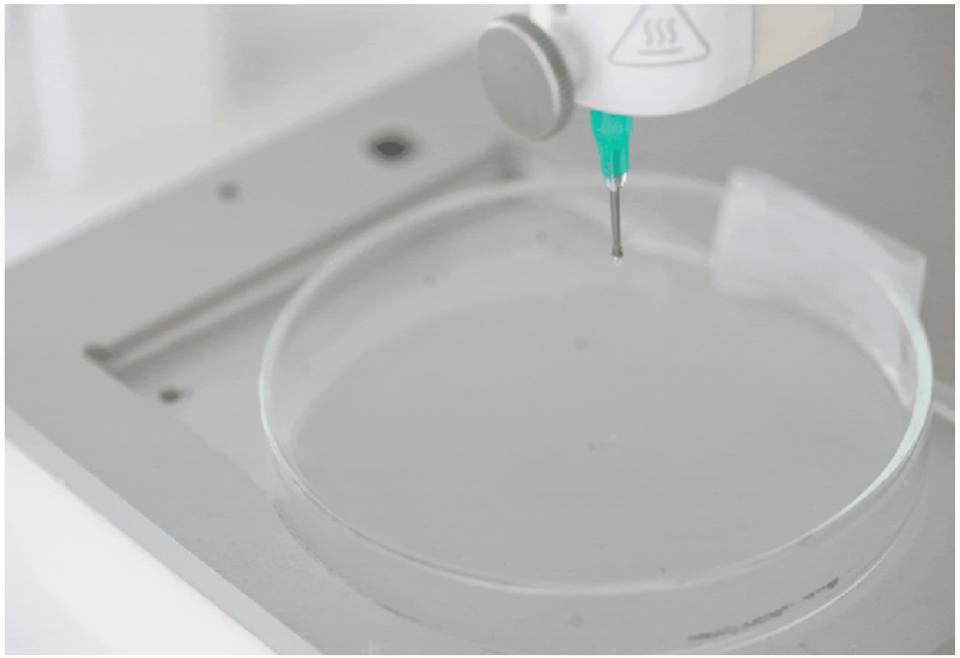

Yifan Cui


Dalia Dranseike

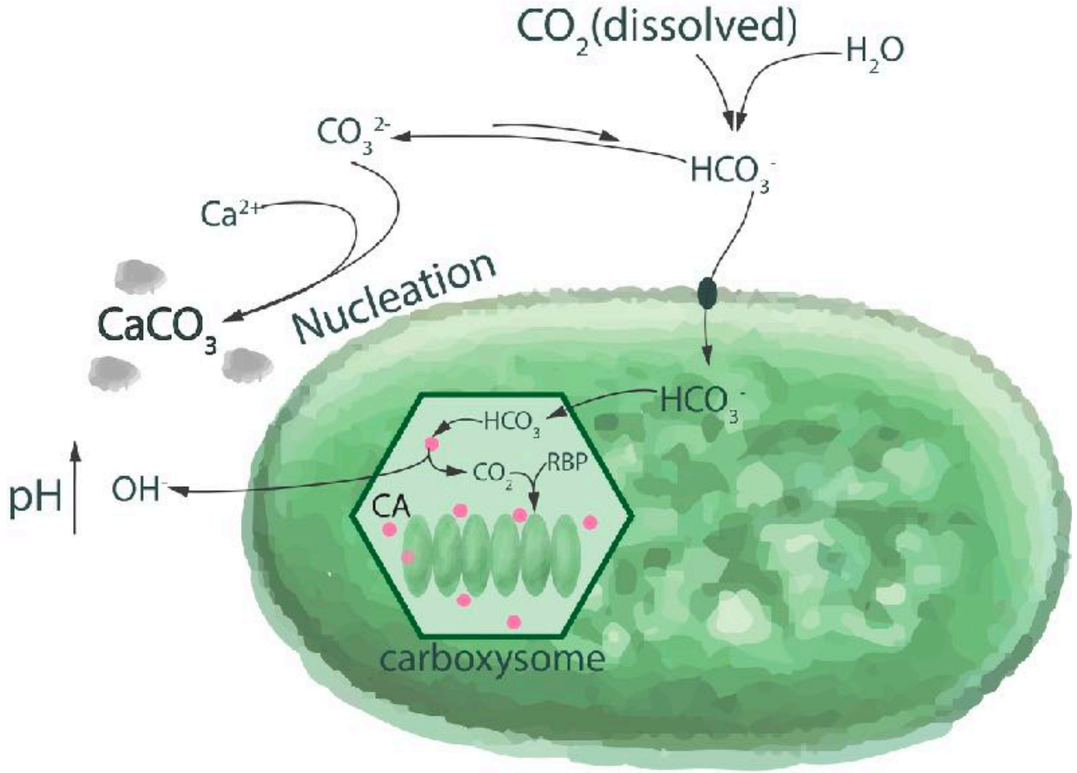

Andrea Ling



Direct ink writing of living materials



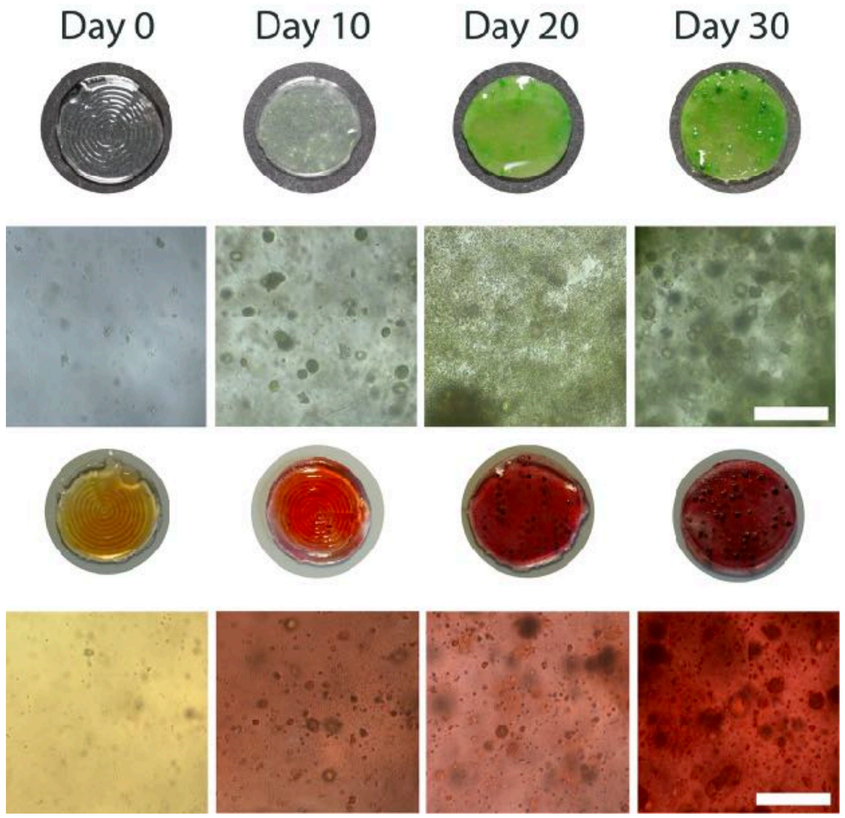
Microbially induced $CaCO_3$ precipitation



Synechococcus sp. PCC 7002

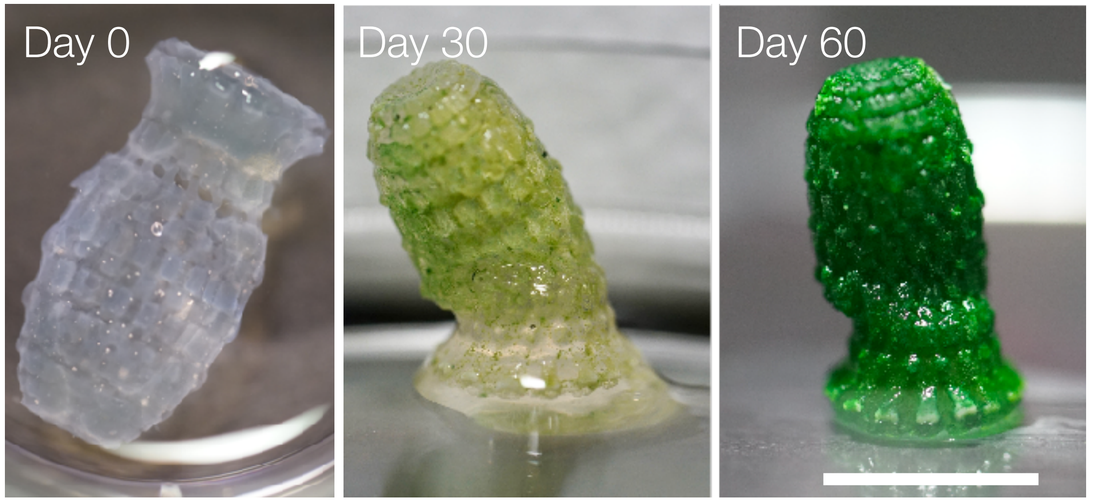
Photosynthetic living materials for dual carbon sequestration

Biomass growth and **mineral** deposition



Alizarin Red; Scale bar, 100 μm

Structures evolve with time to form living composites



*Immersed sample

Scale bar, 1 cm

Living sample

Living carbon sink →

Mineral deposits

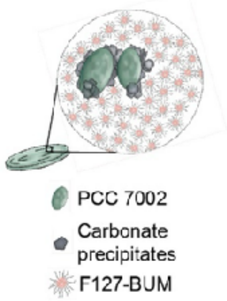
Living materials **perceive the outside world**, using light to sequester CO_2 and store it in mineral form.

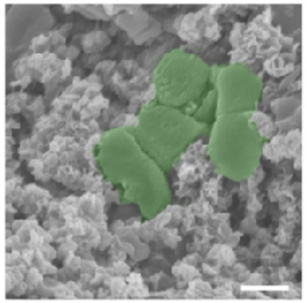
In collaboration with A. Studart (MATL), B. Dillenburger (ARCH) and J. Oakey (U. Wyoming)

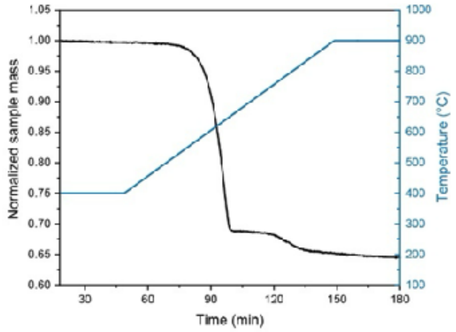
Dranseike D., Cui Y., et al. *Nat. Commun.*, **2025**, *6*, 3832.

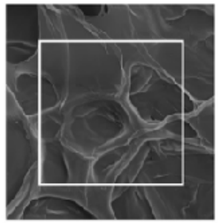
Photosynthetic living materials mechanically reinforce over time

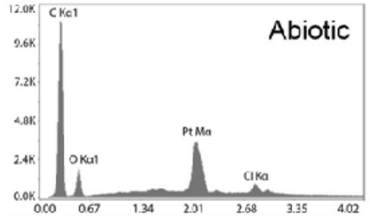
XRD and EDX confirm precipitate formation

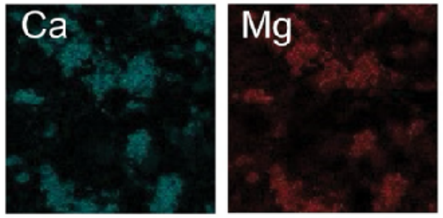


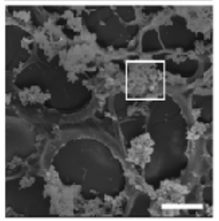


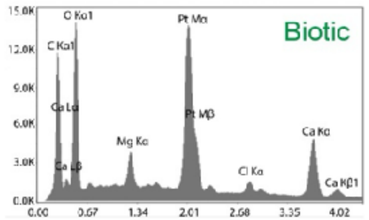


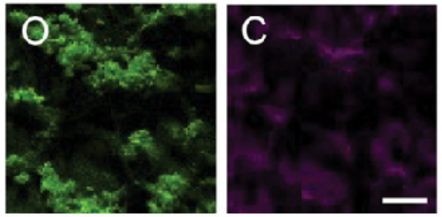




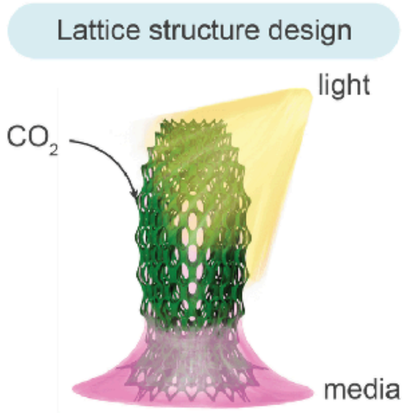


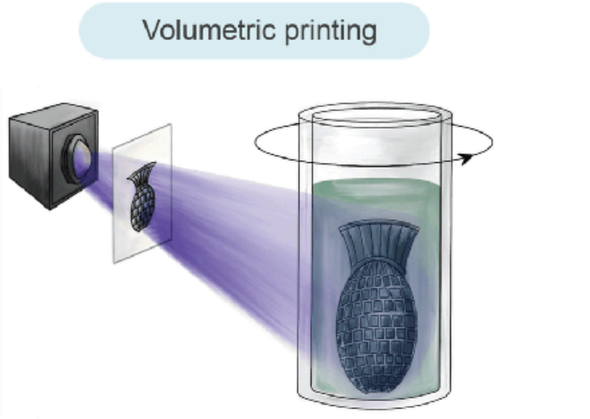


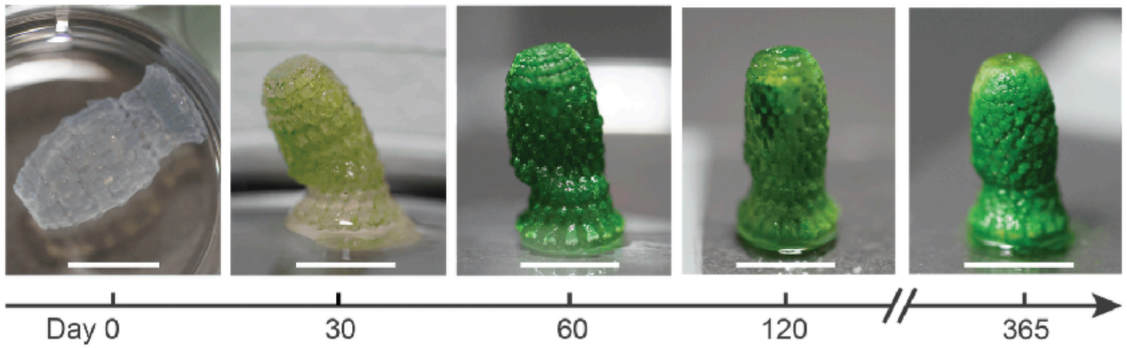




Structures remain viable for up to 1 year







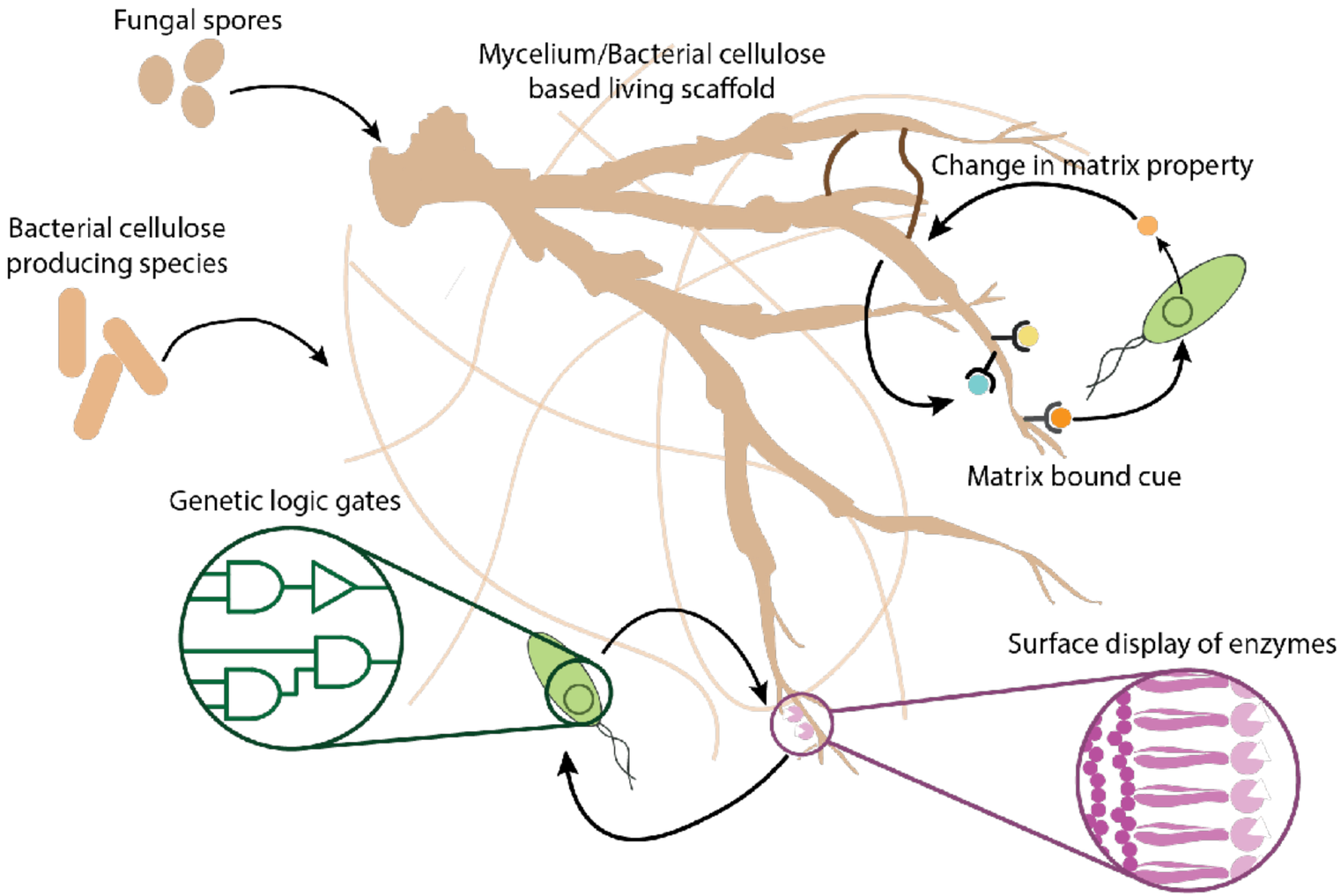
Scale bar, 1 cm

Soft, floppy material (like the baby elephant's trunk) **reinforces** over time to form a rigid structure.

XRD = X-ray diffraction analysis
EDX = Energy-dispersive X-ray spectroscopy

Dranseike D., Cui Y., et al. *Nat. Commun.*, **2025**, *6*, 3832.

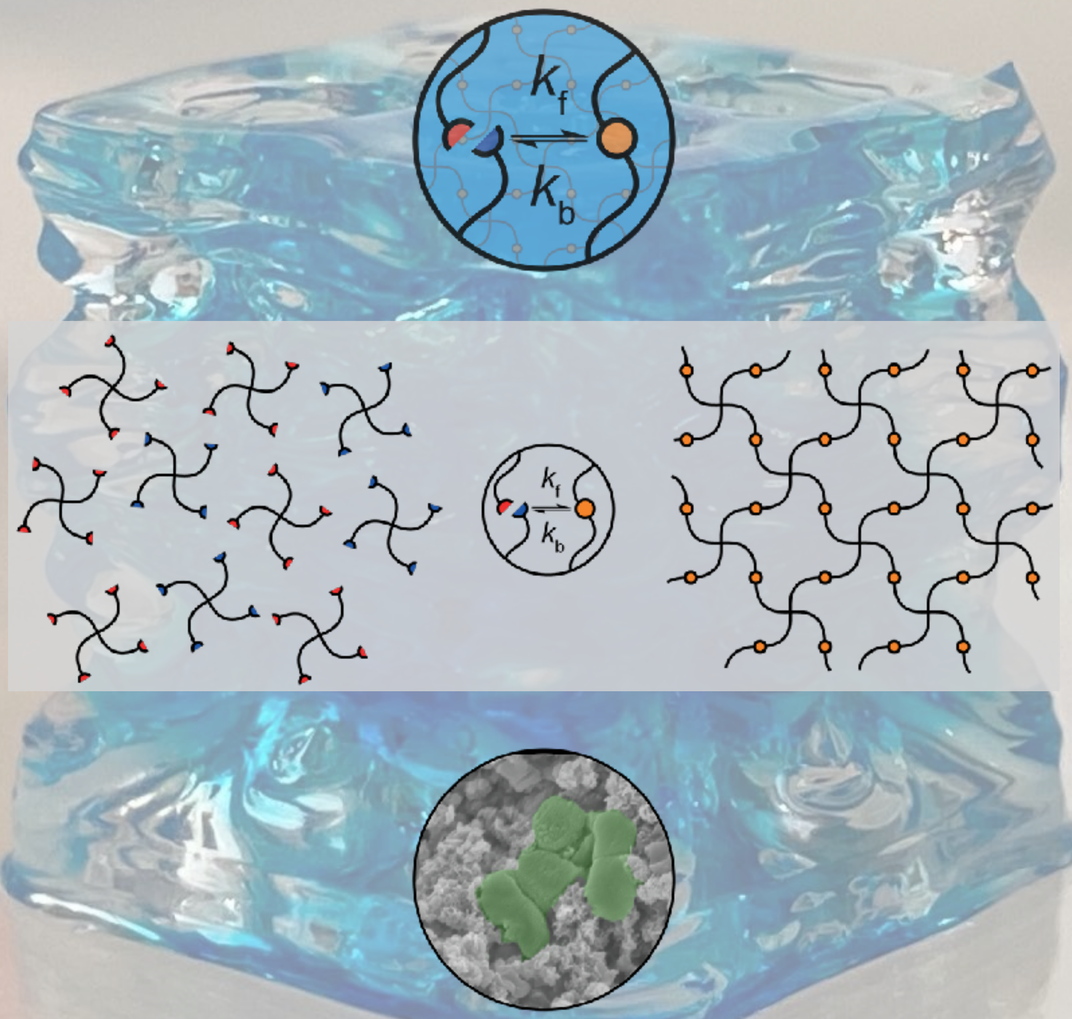
Can we expand on these ideas by coupling dynamic living and non-living materials?



Building toward living materials that **adapt** and **evolve** during their lifecycle.

Cui, Y., Tang, T.C., Tibbitt, M.W., Lu, T.K. ***in preparation.***

Materials that learn: a few important features



Macromolecular Engineering Laboratory

mtibbitt@ethz.ch

Current group:

Jonas Binz
Lucien Cousin
Yifan Cui
Filippo Cuni
Leslie Cunningham
Gabriela da Silva André
Börte Emiroglu
Yanmiao Fan
Florian Huwyler
Saumitra Joshi
Céline Labouesse
Shuo Li
Jaimie Mayner
Vlasis Mavrantzas
Stefan Mommer
Nika Petelinsek
Jaime Pietratuono Nepomuceno
Hannah Rasel
Apoorv Singh
Carolina Söll
Morris Wolf

Ann-Kathrin von Ammon
Peter Feusi

Collaborators:

Sabine Werner (BIOL)
Catharina Sanger
Edoardo Mazza (MAVT)
Costanza Giampetro
Anastasiya Martyts
David Norris (MAVT)
Valentina de Rosa
Christina Tringides (ITET)
Nako Nakatsuka (ITET)
Alessandra Curioni (U. Fribourg)
Jörn Dengjel (U. Fribourg)
Sibilla Sander
Gilles Weder (CSEM)
Markus Rimann (ZHAW)
Jan Vermant (MATL)
Rob Style (MATL)
André Studart (MATL)
Matt Webber (Notre Dame)
John Oakey (U. Wyoming)
Ori Bar-Nur (HEST)
Joel Zvick
Laura De Lorenzis (MAVT)
ALIVE Consortium
Eleni Chatzi (BAUG)
Heloise Ragelle (Roche)
Pierre-Alain Clavien (UZH)
Philipp Dutkowski (USZ)
Philipp Rudolf von Rohr (ETHZ)
Andrew deMello (CHAB)
Martin Ehrbar (USZ)
Jürg Dual (MAVT)
B. Dillenburger (ARCH)
Andrea Ling
Christian Wolfrum (HEST)
Lianggong Ding

Funding:

ETH zürich
Schweizerischer Nationalfonds
SKINTEGRITY.CH
LIVER 4LIFE
Wyss Zurich Translating Science into Life
Roche
NANOLY BIOSCIENCE
alive advanced engineering with living materials
Strategic Focus Area Advanced Manufacturing
Helmut Horten Stiftung
Innosuisse - Schweizerische Agentur für Innovationsförderung