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UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

DynaMoMat
Dynamic Molecular Materials Laboratory

Centro Interdipartimentale Grandi Strumenti
CINQUANTA

Cristalli dinamici: la nuova frontiera dei materiali intelligenti

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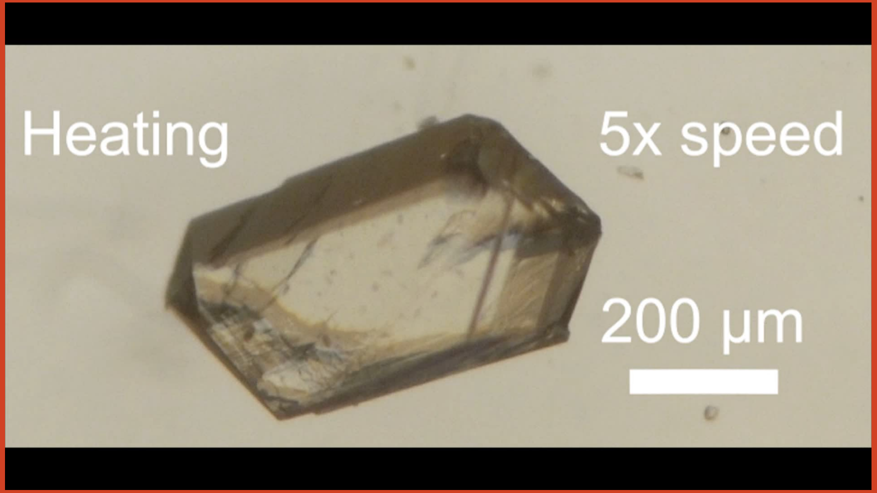
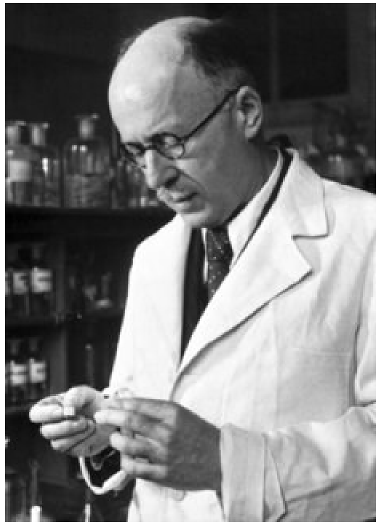
Dynamic Molecular Materials Laboratory,

Department of Life Sciences, UniMORE

07/11/2024 CIGS 50 anni

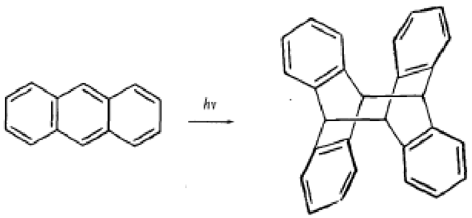


Crystals are dead! Long live to the Crystals!

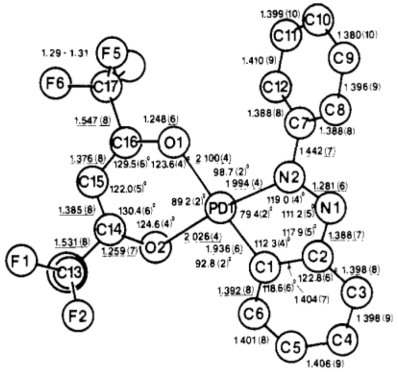


“Ein Kristall ist ein chemischer Friedhof”
(a crystal is a chemical graveyard)

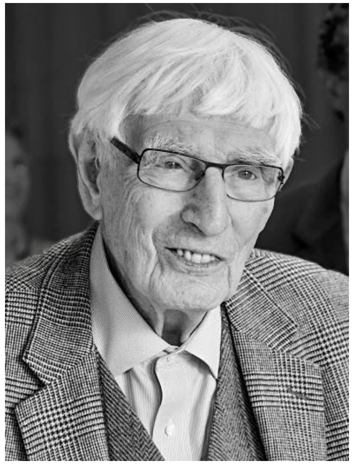
Leopold Ružička (1939 Chemistry Nobel Prize)

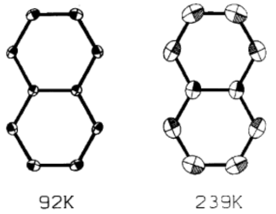


Schmidt, Pure Appl. Chem. 1971, 27, 647.



Etter et al. JACS, 1983, 105, 641.
Nat. Commun. 2014, 5, 4811.

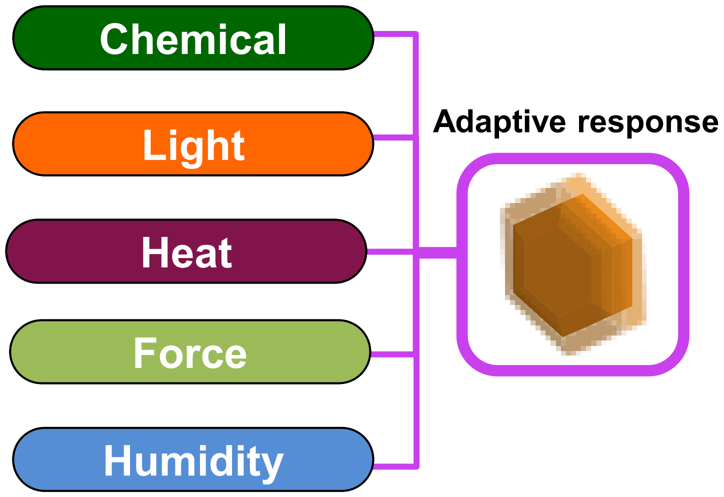




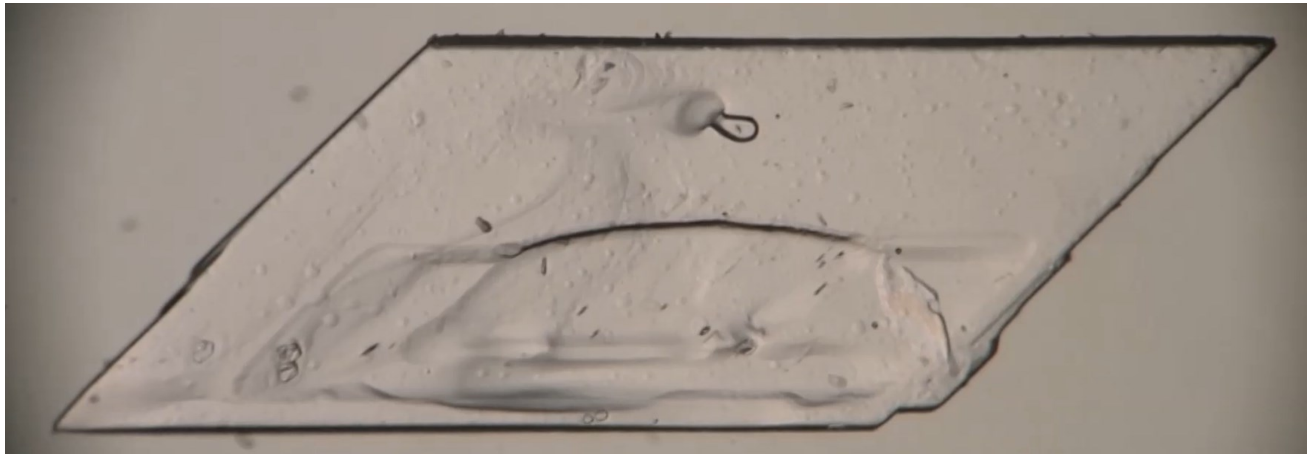
Dunitz et al . J. Phys. Chem., 1988, 92, 856.

Dynamic crystals?

Molecular crystals adapting to changes in external conditions.



JACS, 2020, 142, 13256
Chem. Soc. Rev., 2023, 52, 3098



Chemical science, 2019, 10 , 7327.

Dynamic crystals?

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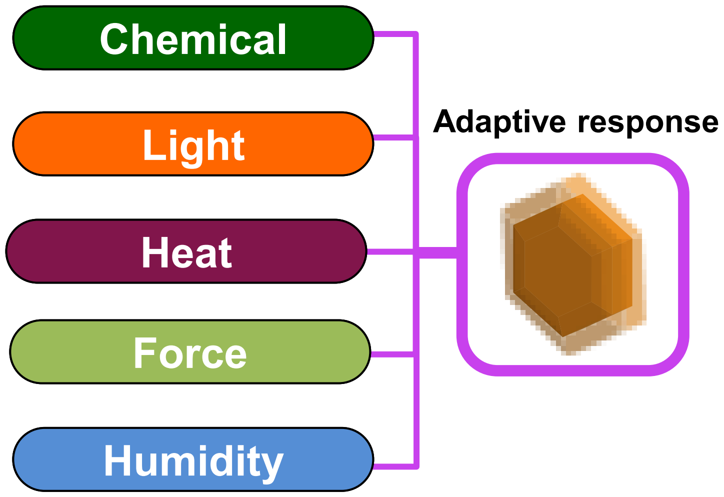
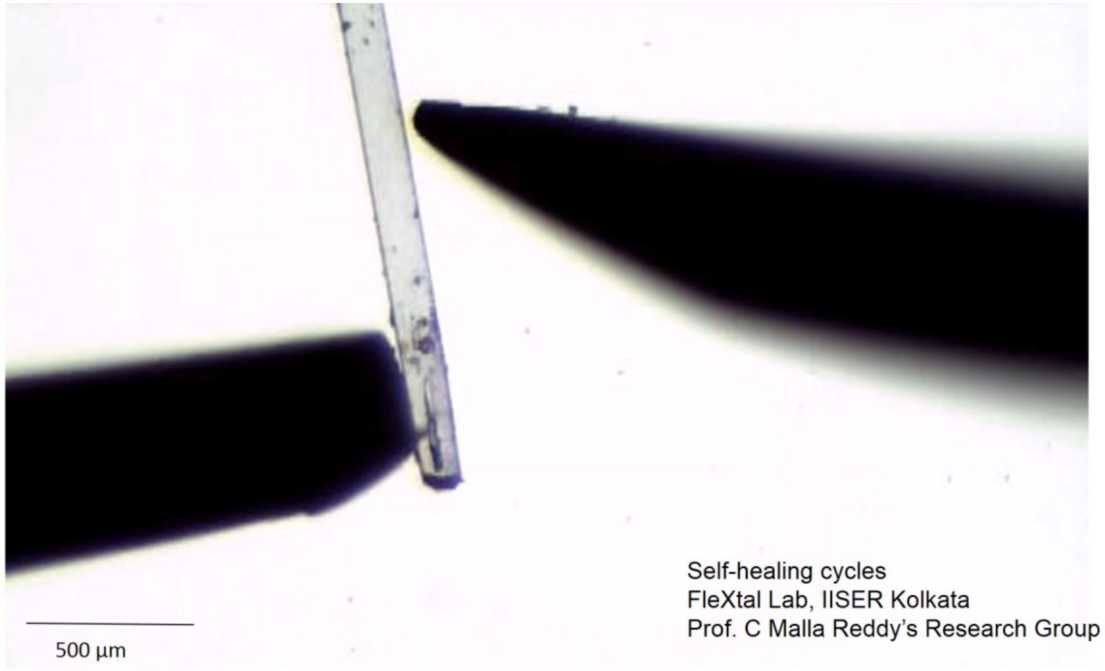


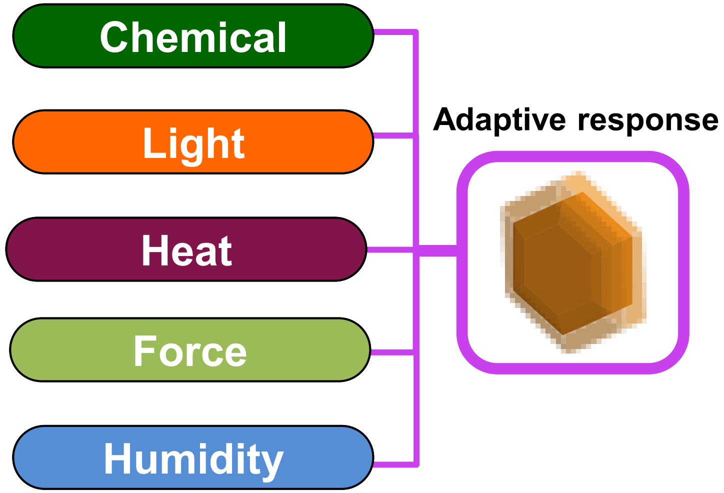
JACS, 2020, 142, 13256
Chem. Soc. Rev., 2023, 52, 3098



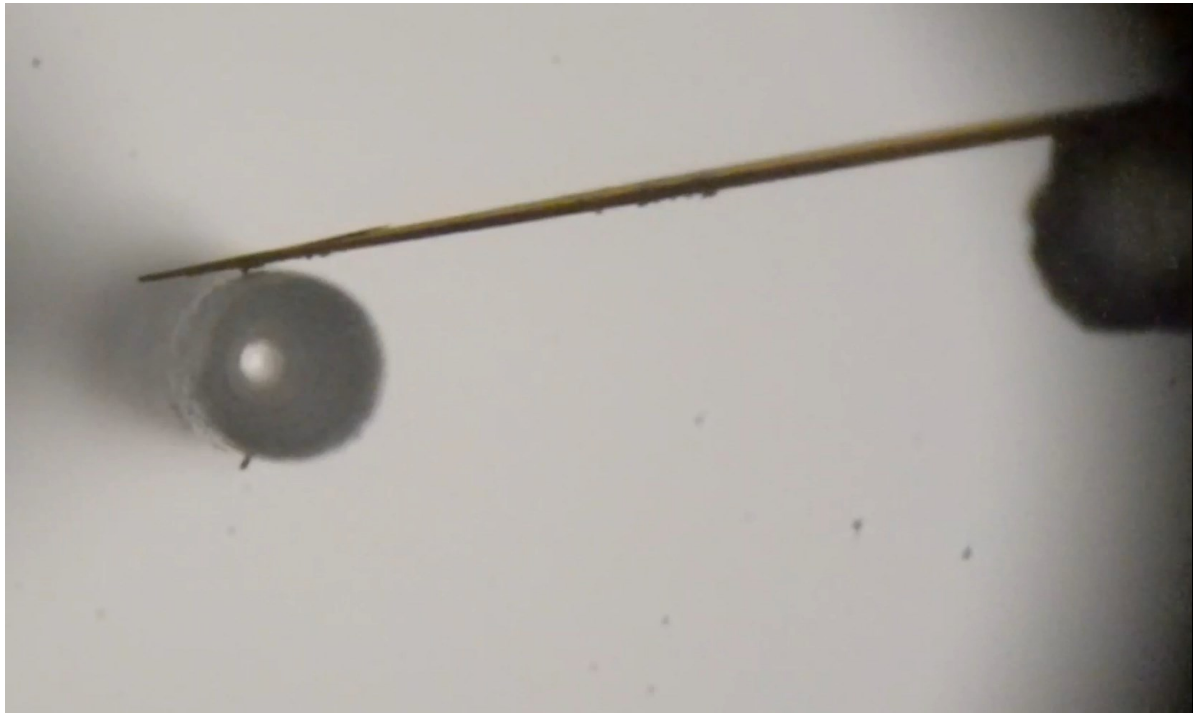
Science, 2021, 373, 321
Adv. Mater. 2022, 34, 2109374.

Dynamic crystals?

Molecular crystals adapting to changes in external conditions.



JACS, 2020, 142, 13256
Chem. Soc. Rev., 2023, 52, 3098

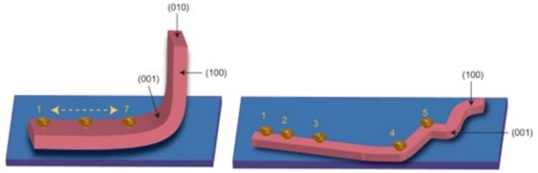


PNAS, 2021, 118, e2020604118
J. Am. Chem. Soc. 2019, 141, 14966

Why so interesting? Intelligent materials!

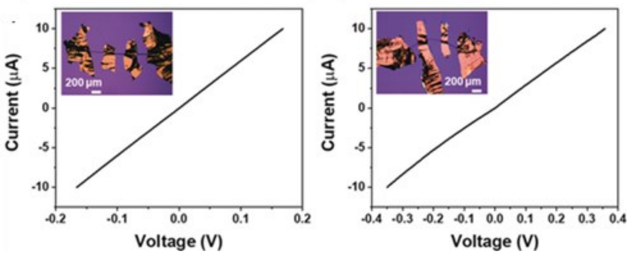
Ability of molecular crystals to shape-shift and adapt to changes in external conditions combining multiple functionality in a single-component system.

Tunable mechanics



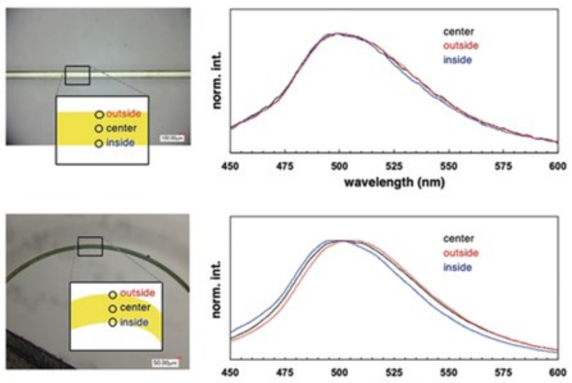
Nat. Chem. 2015, 7, 65.

Electronic properties



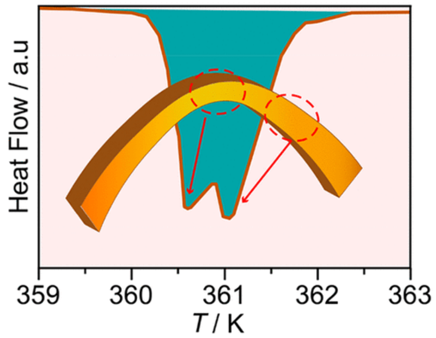
ACIE, 2020, 59, 16436.
Cryst. Growth Des. 2019, 20, 884.

Photophysical



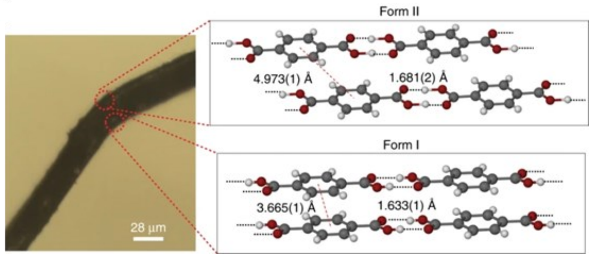
ACIE, 2020, 59, 16195.

Thermodynamics

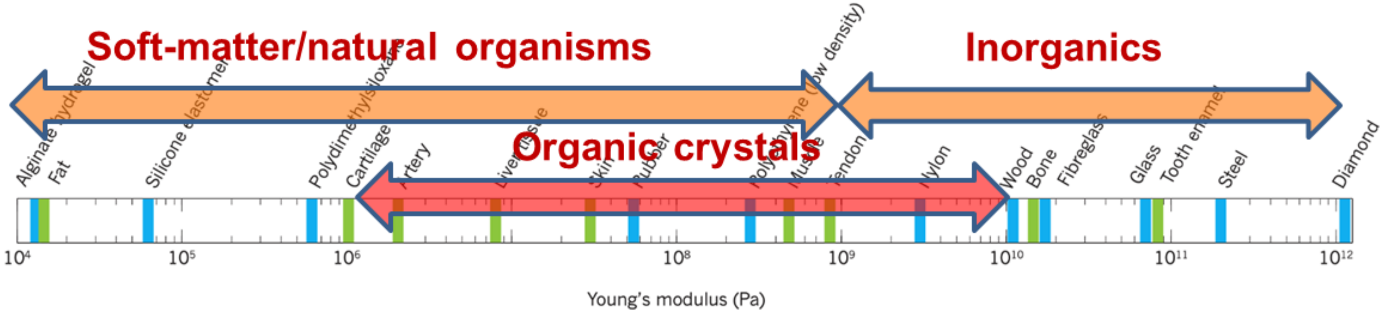


JACS, 2020, 142, 11219.

Crystal structure

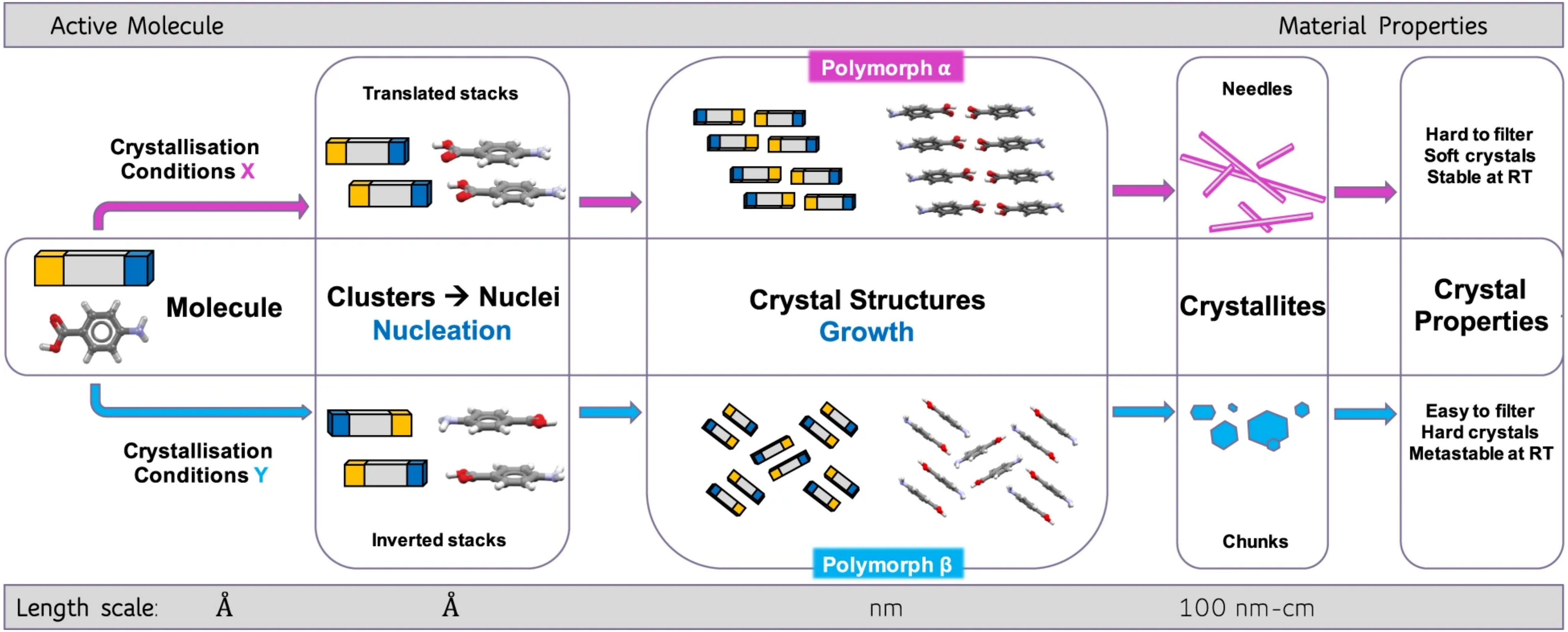


Nat. Comm. 2019, 10, 3723.



ACIE, 2018, 57, 8837.

Polymorphism in crystals



1 (supra)molecular building block, countless materials!

Impact on pharmaceuticals, organic electronics and optoelectronics, fertilizers, pigments, high-energy materials

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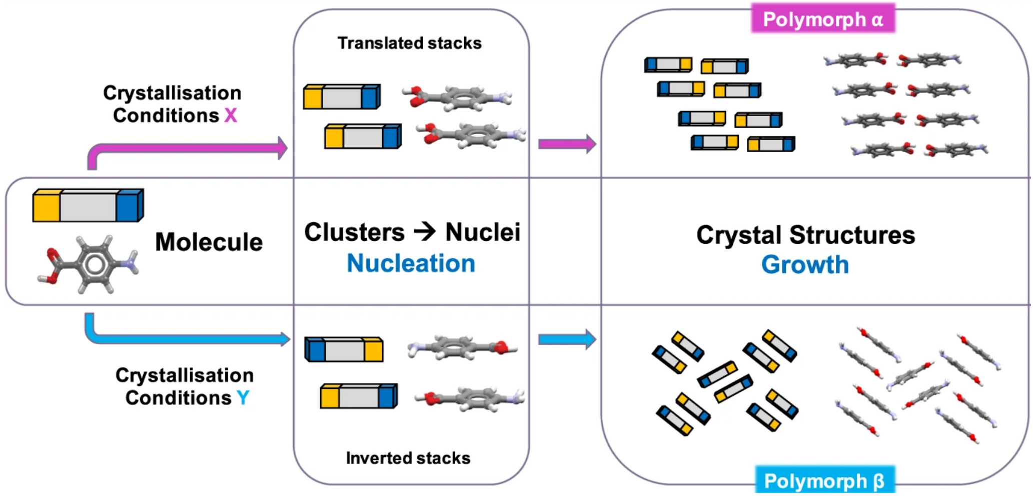
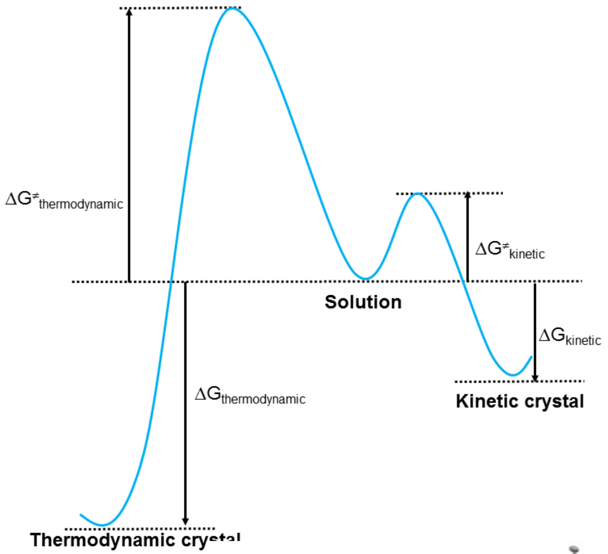
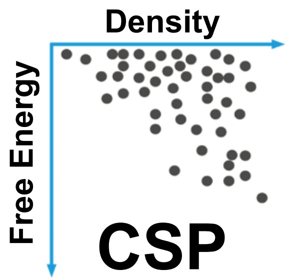
Commun. Chem. 2020, 3, 142.
CrystEngComm, 2019, 21, 2034.

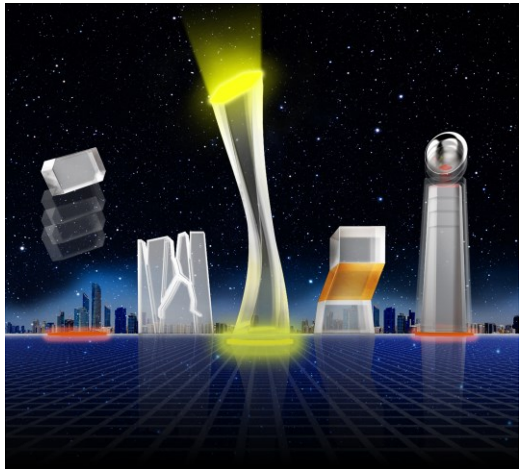
Discover and control polymorphs?

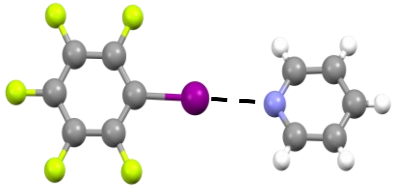


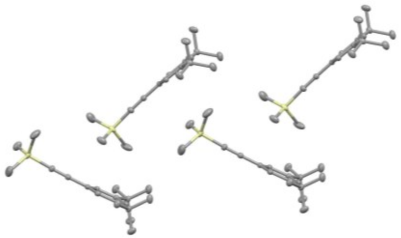


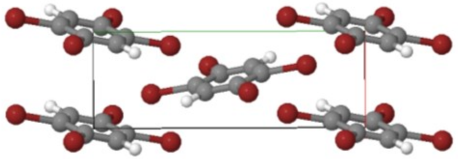


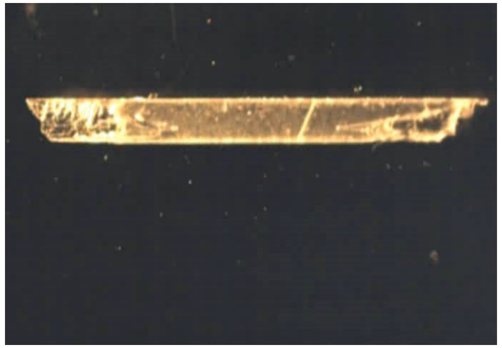
Why so difficult?











Structure

Properties ⟷ **Dynamics**

Commun. Chem. 2020, 3, 142.
J. Am. Chem. Soc. 2016, 138, 13298.
Chem. Sci 2019, 10, 1332.

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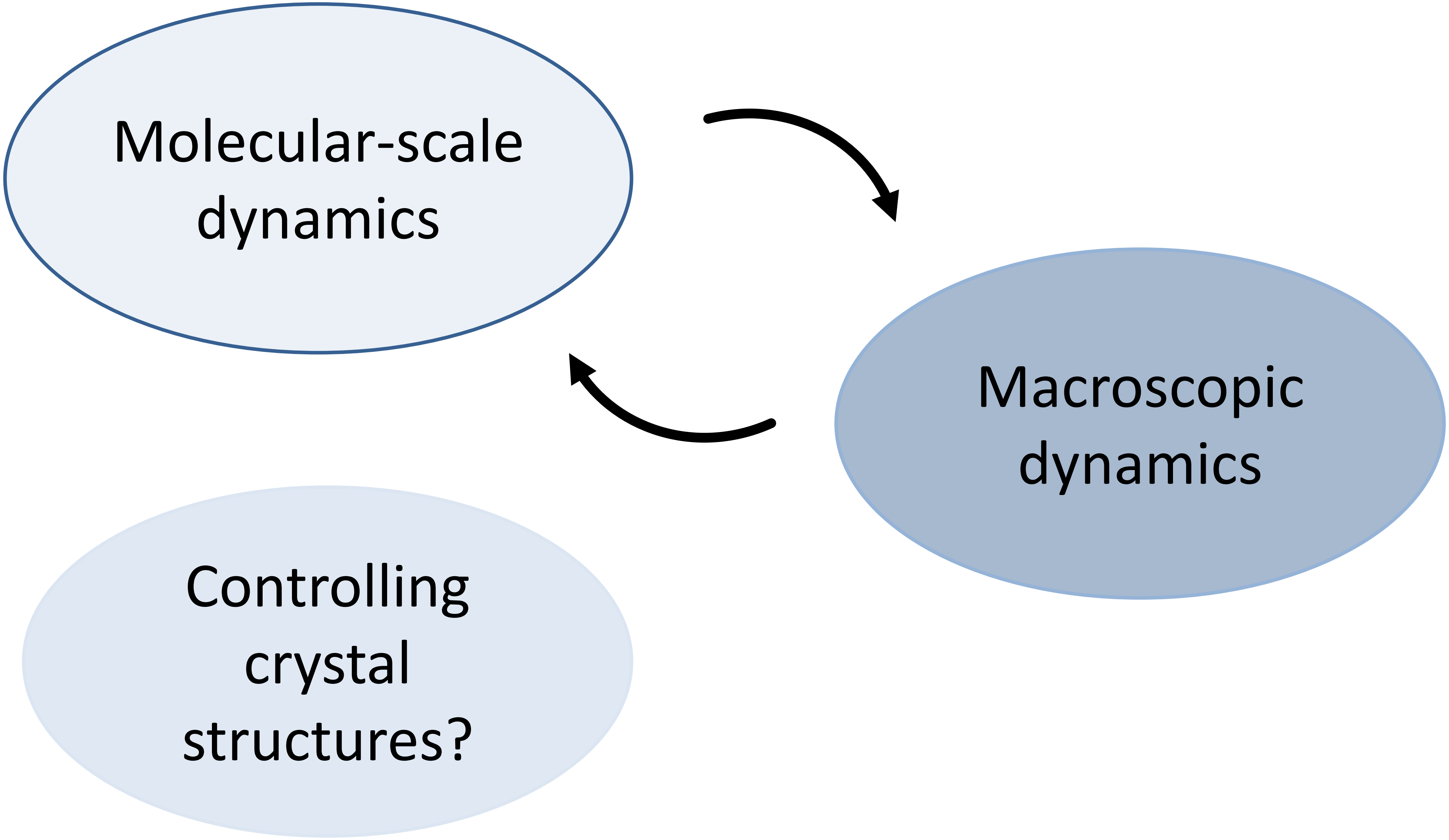
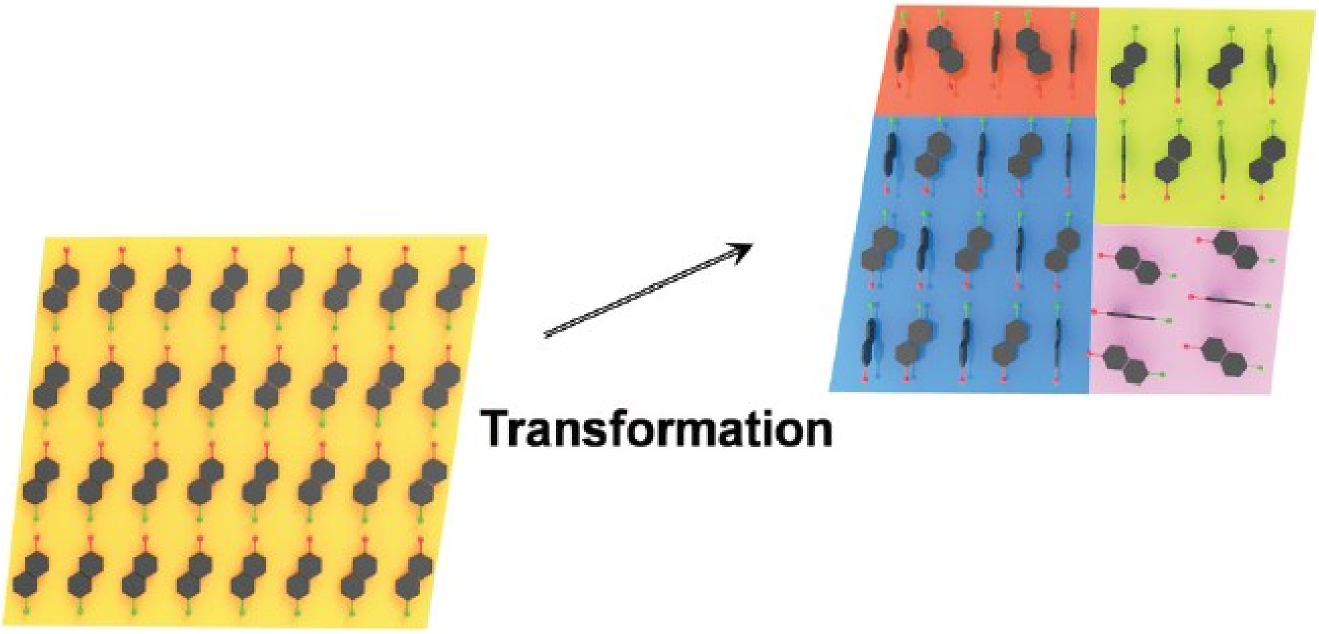

Molecular-scale dynamics
Macroscopic dynamics
Controlling crystal structures?

Solid-to-solid cooperative phase transitions



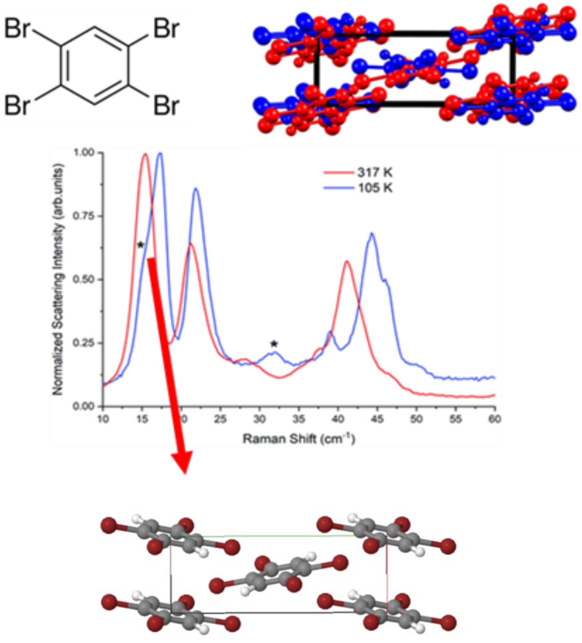
Nucleation and Growth

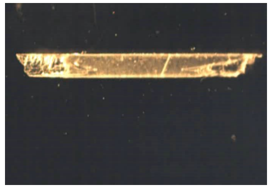
- Molecule by molecule
- Usually reconstructive / disruptive
- Large change in molecular packing
- No orientation correlation between pristine and transformed phases
- Slow kinetics and can be irreversible

Chem. Soc. Rev., 2020, 49, 8287.
J. Phys. Chem. Lett. 2023, 14, 1570-1577.
Manuscript submitted

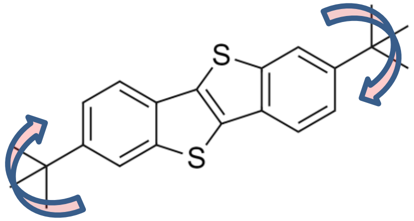
Building a model for cooperative phase transitions?

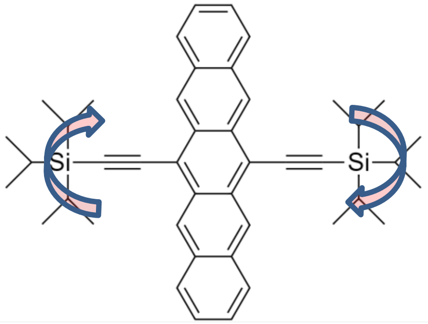
Phonon-driven transitions?

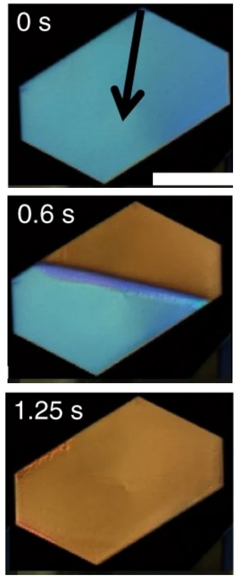


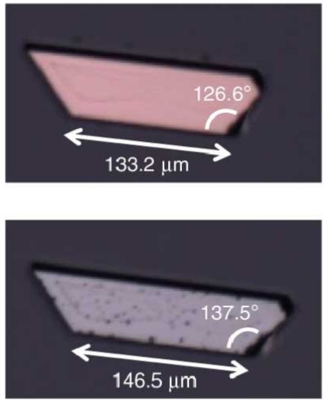


Chem. Sci., 2019, 10, 1332.



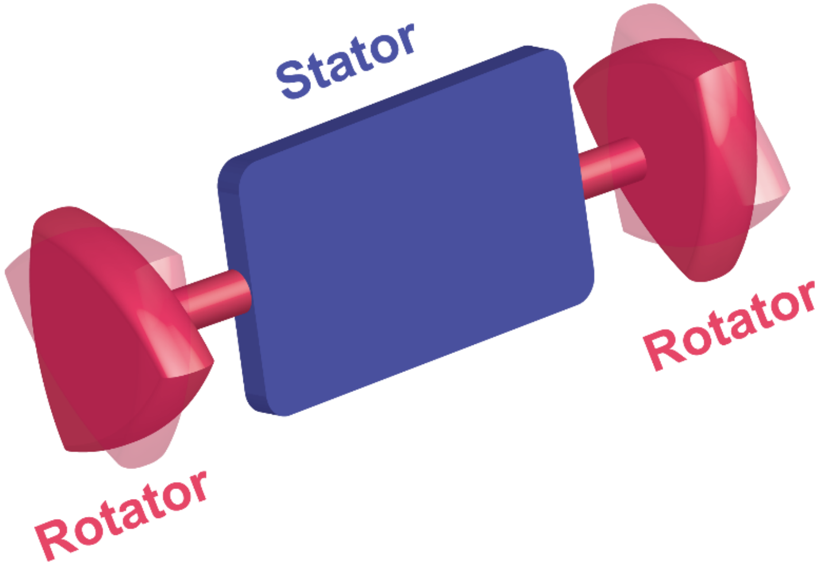






J. Phys. Chem. Lett. 2023, 14, 1570-1577
Nat. Commun. 2018, 9, 278

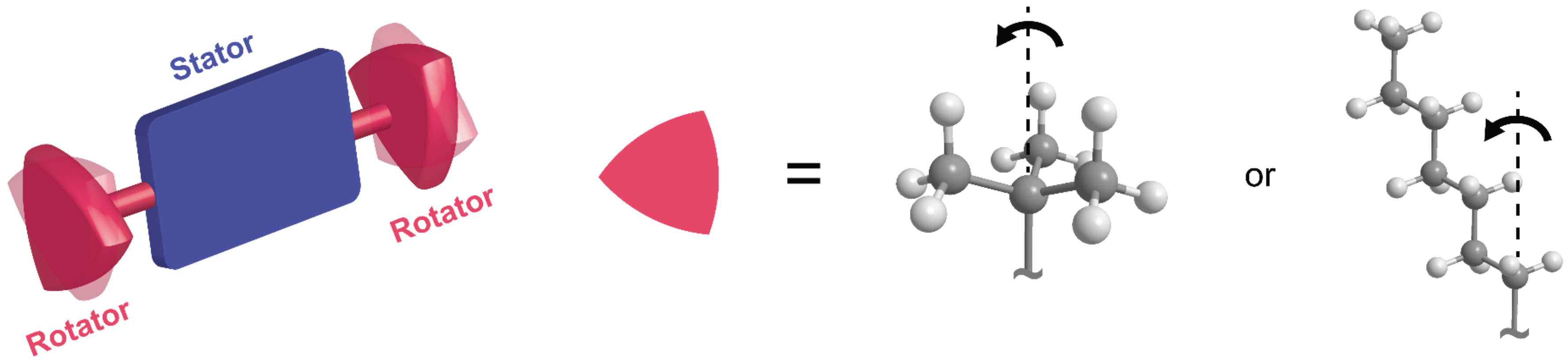
Aromatic rigid core

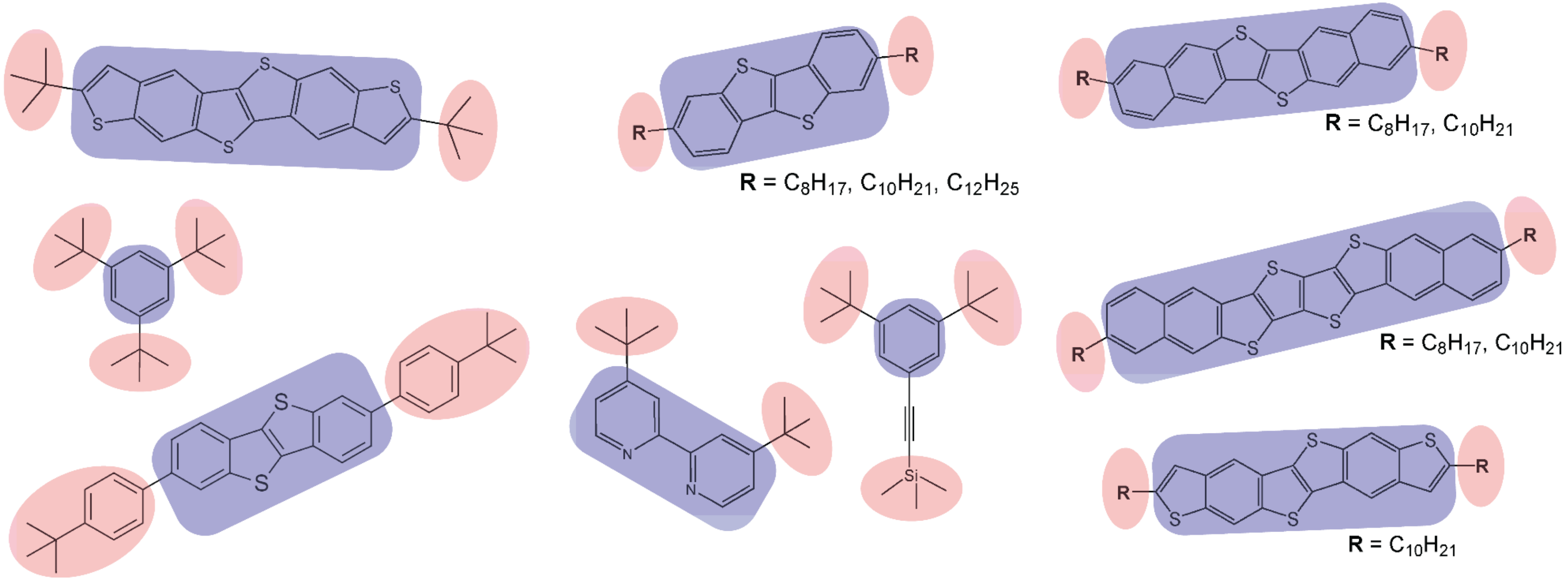


Rotating bulky/long side chains

JACS, 2015, 137, 15386
JACS, 2017, 139, 843
CrystEngComm, 2018, 20, 5872.

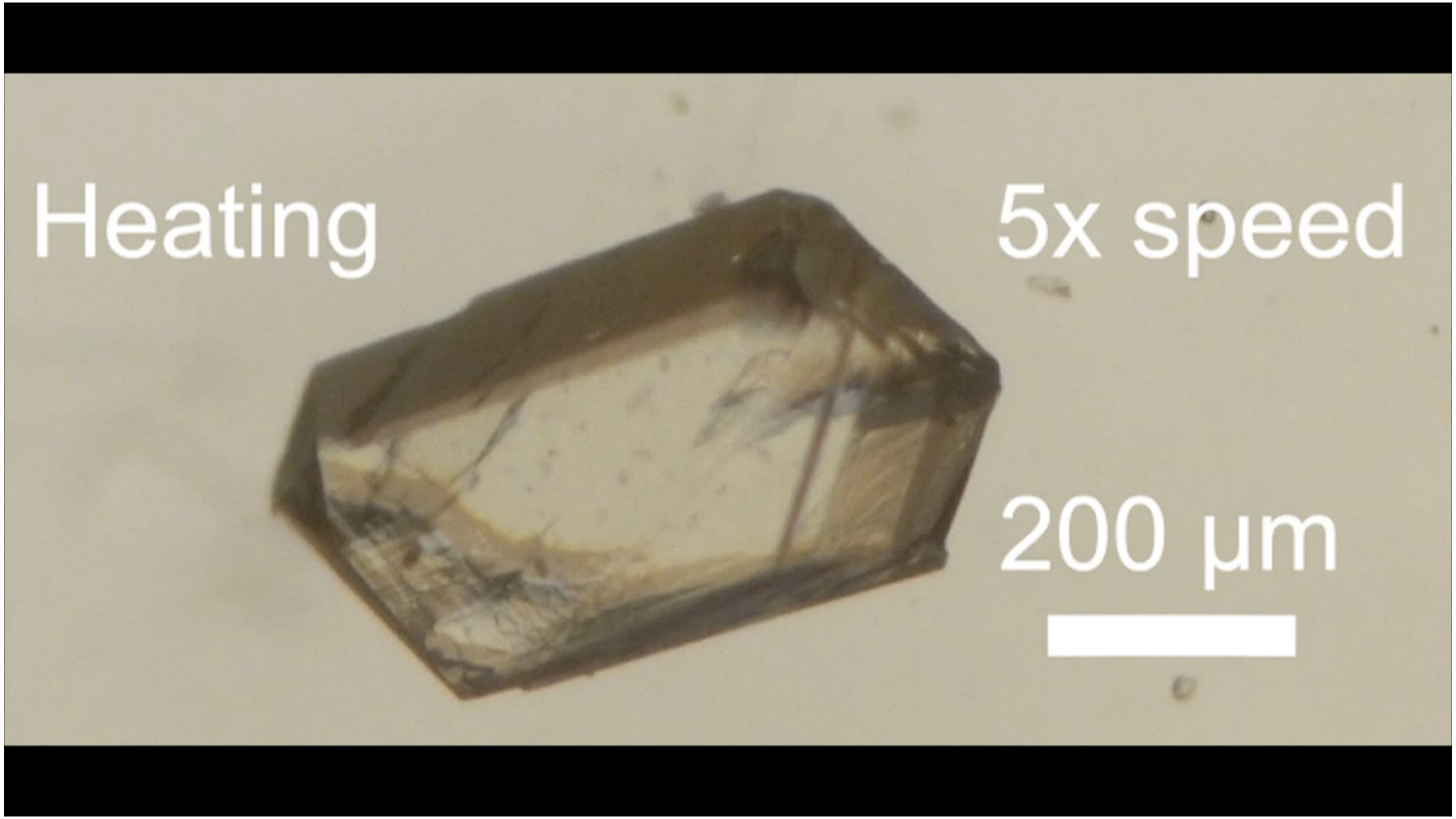
Generalized strategy?

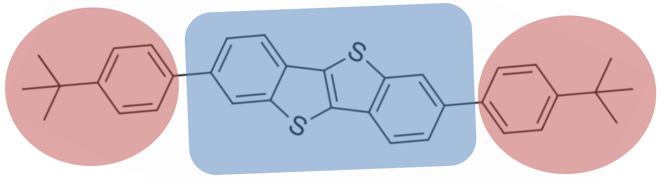




Nat. Chem. 2016, 8, 644-656
Nat. Commun. 2018, 9, 278
J. Am. Chem. Soc. 2024, just accepted

It works! More than 13 examples discovered!





Shapeshifting!

J. Am. Chem. Soc. 2024, just accepted

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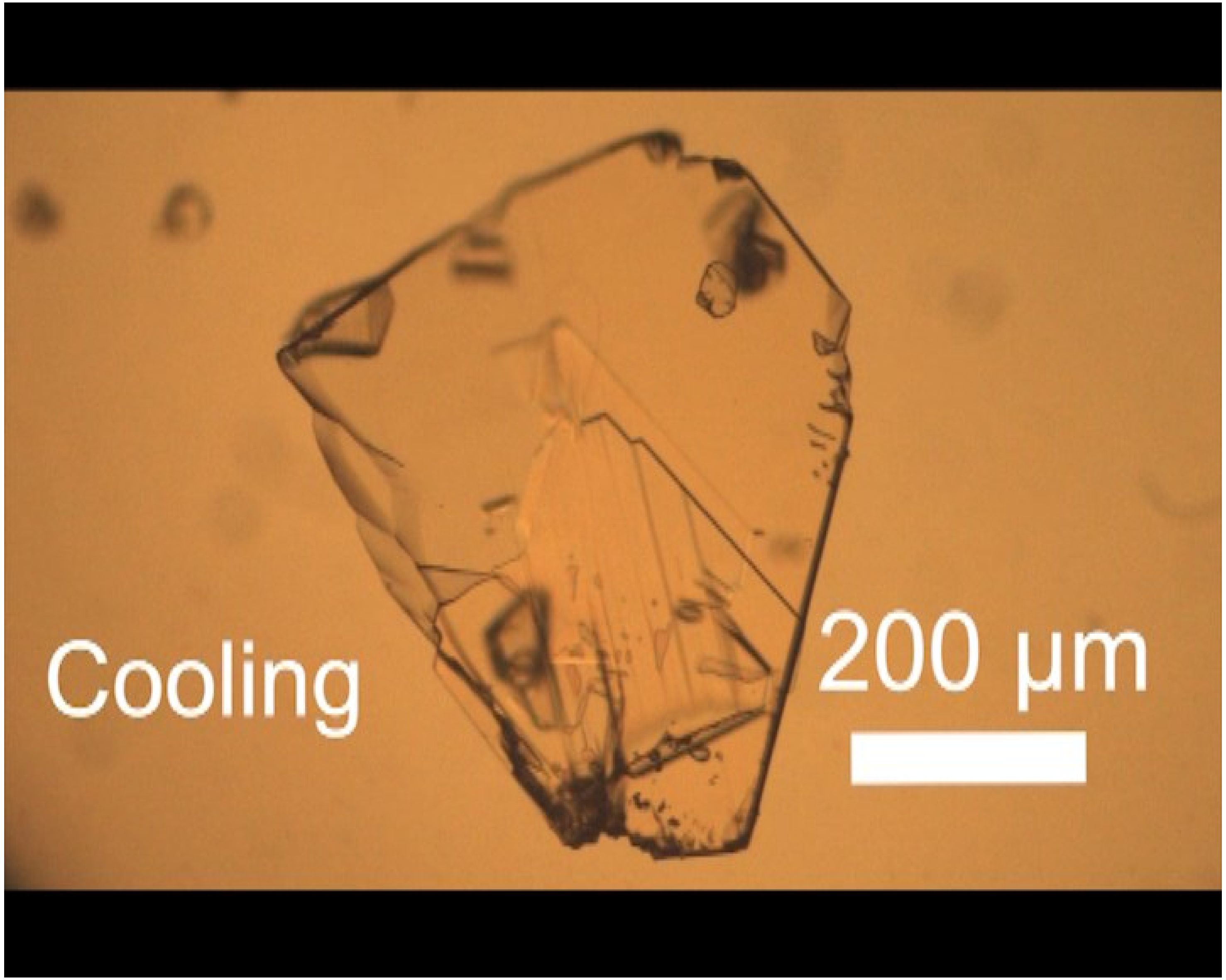
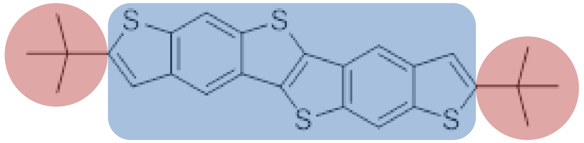
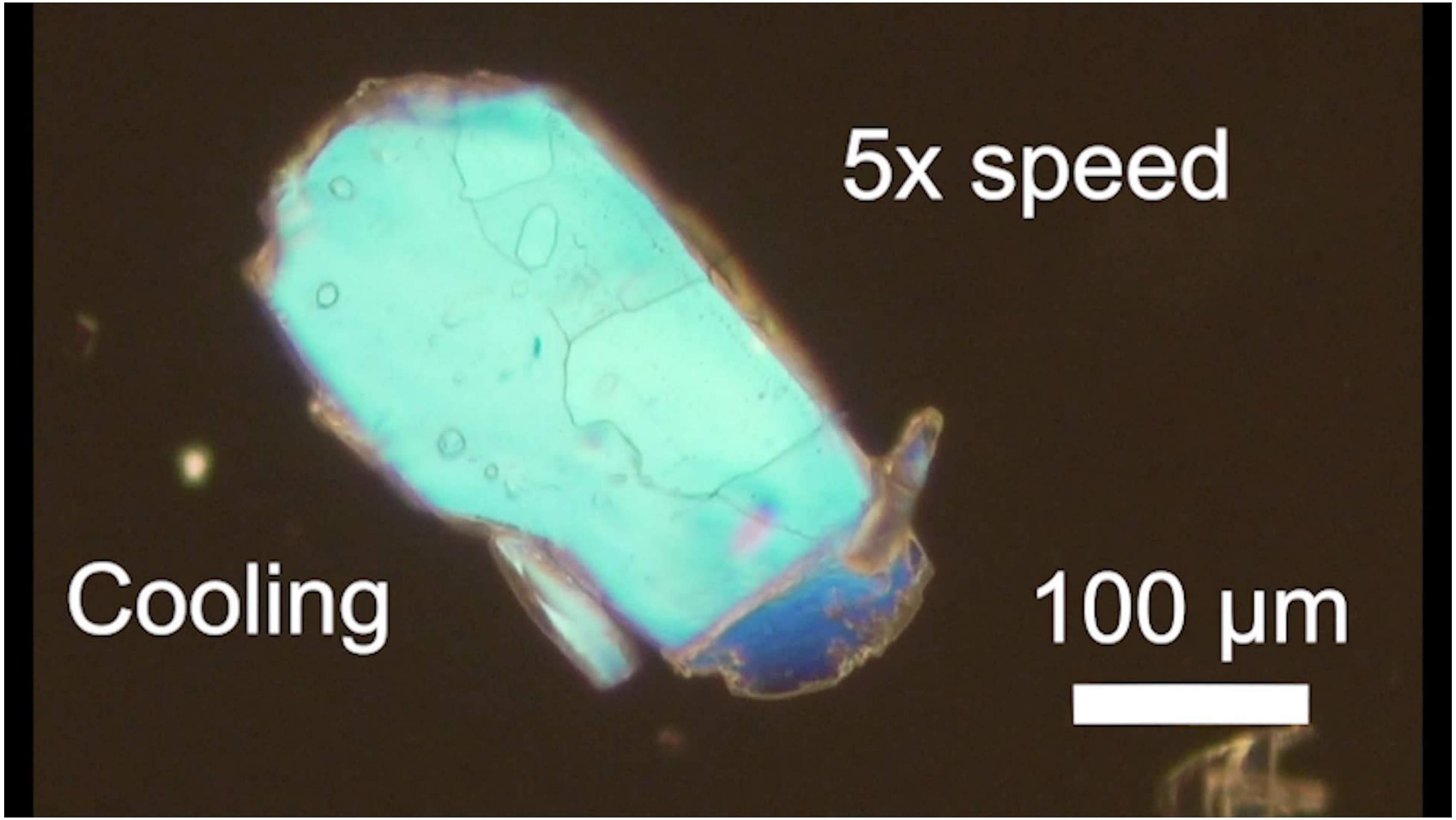


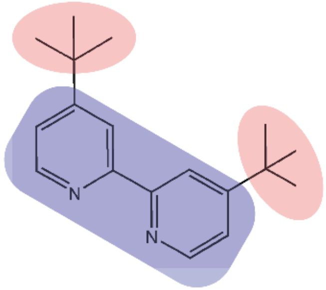


Jumping!

J. Am. Chem. Soc. 2024, just accepted

It works! More than 13 examples discovered!

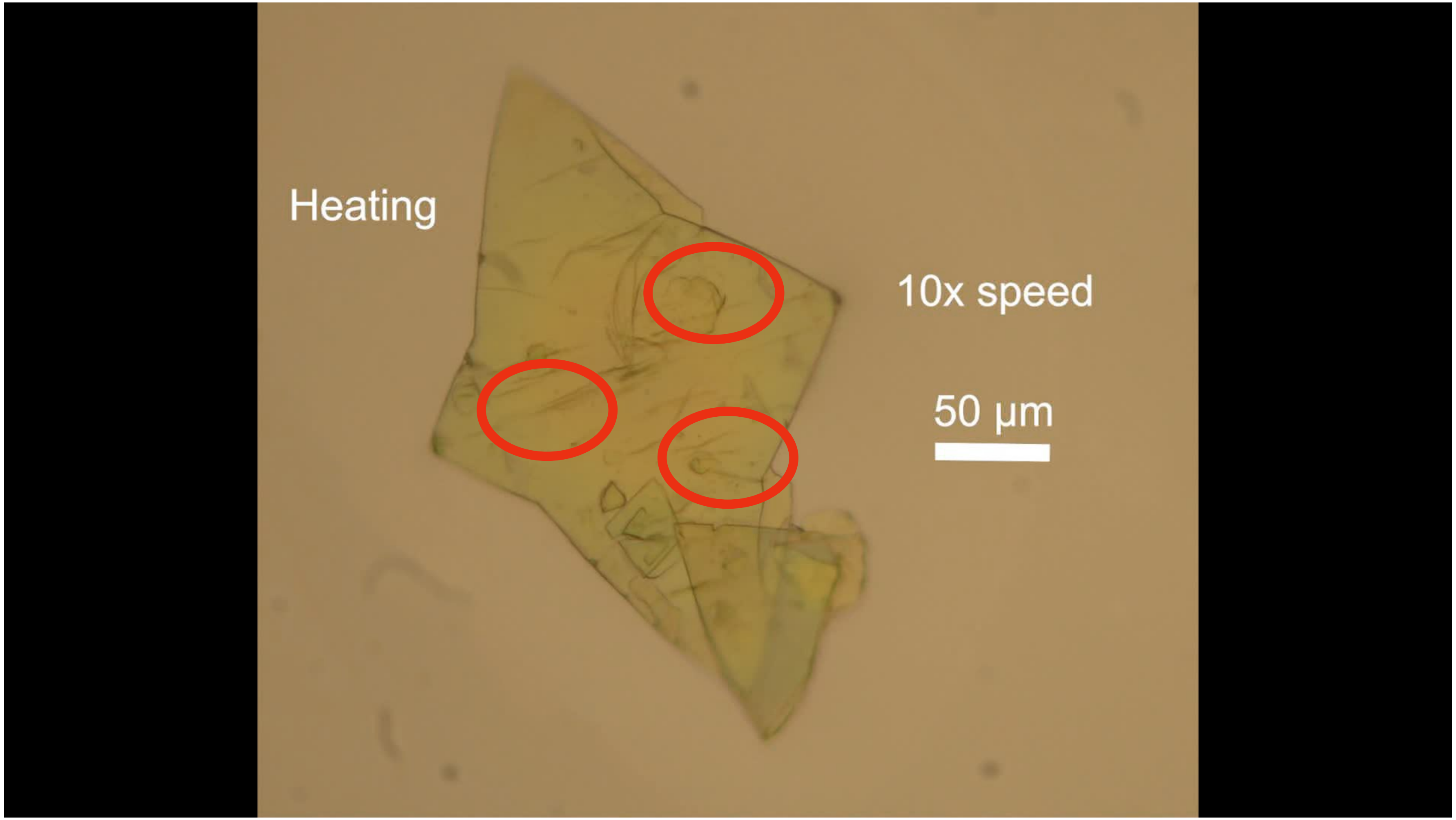


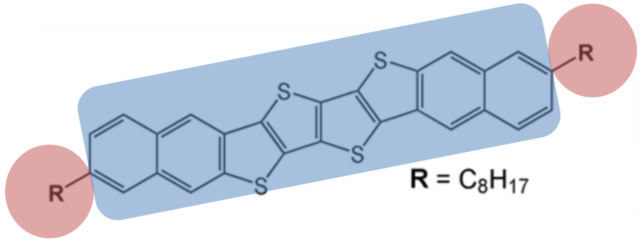


Phase front propagation!

J. Am. Chem. Soc. 2024, just accepted

It works! More than 13 examples discovered!

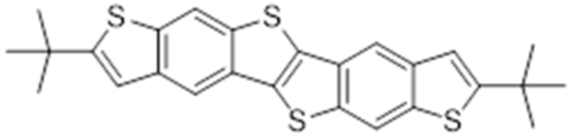


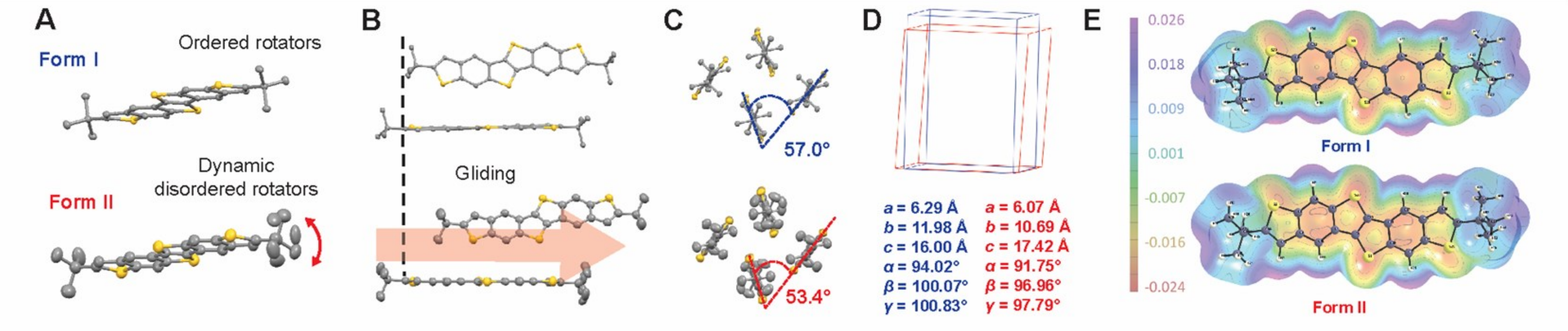


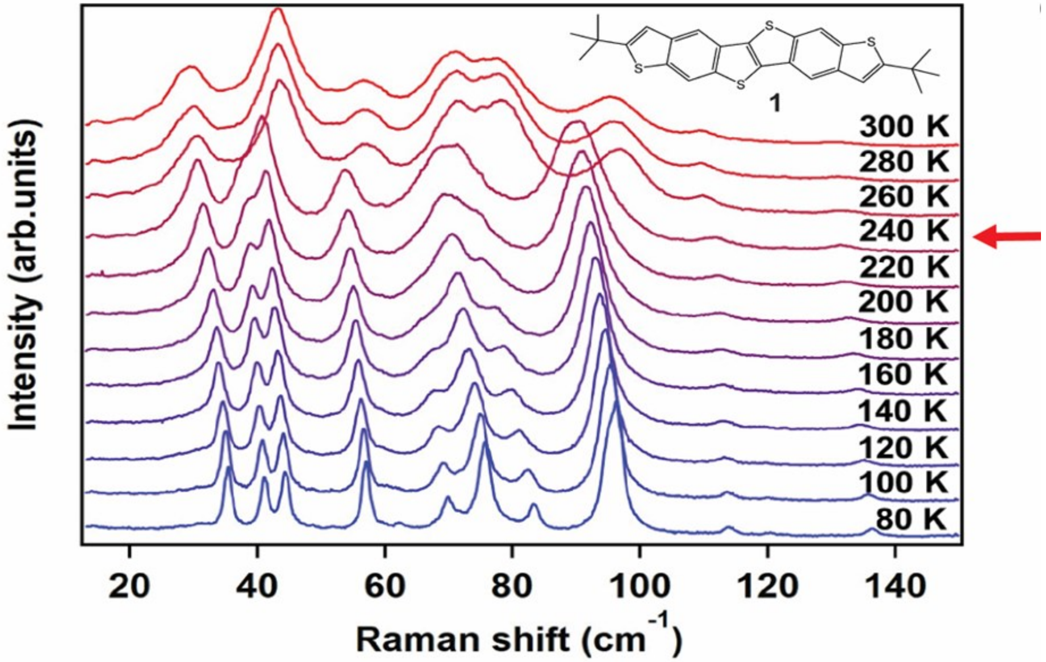
Shapeshifting
and
crack closure?

J. Am. Chem. Soc. 2024, just accepted

Order-disorder phase transition







Order-disorder phase transitions

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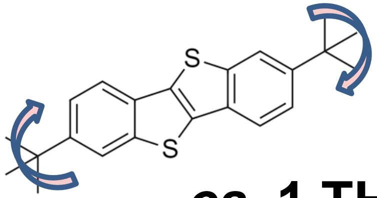
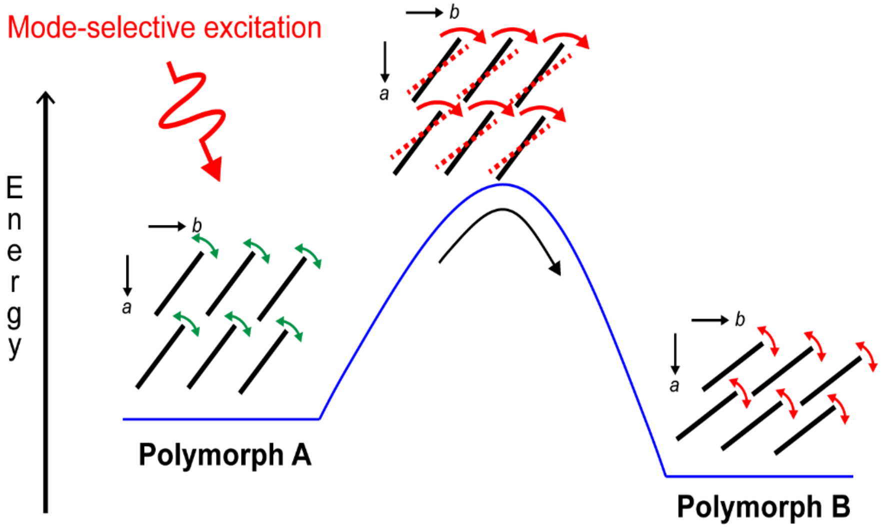
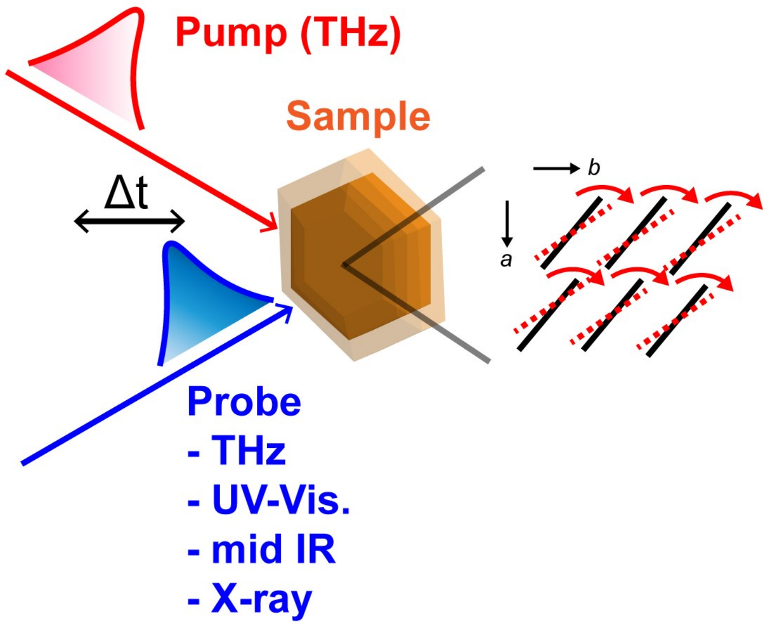
Programmable crystals?

Cooperative transitions seem to be driven by **specific phonon modes**, from molecular-scale motion to macroscopic dynamics.



***ca.* 1 THz (33 cm^{-1})**





Institut national de la recherche scientifique

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Jan-Chistoph Deinert

NATIONAL ACCELERATOR LABORATORY

Matthias Hoffmann

Keith Nelson

BROWN

Daniel Mittelman

Ankit Disa

Future directions

1) Phase transitions as a mean to control charge transport

2) Twisting polymorphic crystals

3) From bulk crystals to thin films and nanocrystals

4) Self-healing of organic electronics

5) Thermal management through order-disorder phase transitions

6) Non-volatile memories

NSF IRES 2420126

Michael T. Ruggiero

Deepak Venkateshvaran

GRANTOVÁ AGENTURA ČESKÉ REPUBLIKY

Standard Projects

24-12403S

Yves Geerts &
Guillaume Schweicher

UNIMORE

Stephanie Lee

Jarad Mason

Petr Brazda

The European Synchrotron

Stefano Checchia

Université libre de Bruxelles

Yves Geerts

Guillaume Schweicher

Rémy Jouclas

New York University Abu Dhabi

Panče Naumov

Durga Prasad Karothu

University of Mons

David Beljonne

Marco Bardini

THANK YOU!

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Strathclyde University

Alan R. Kennedy

Weizmann Institute of Science

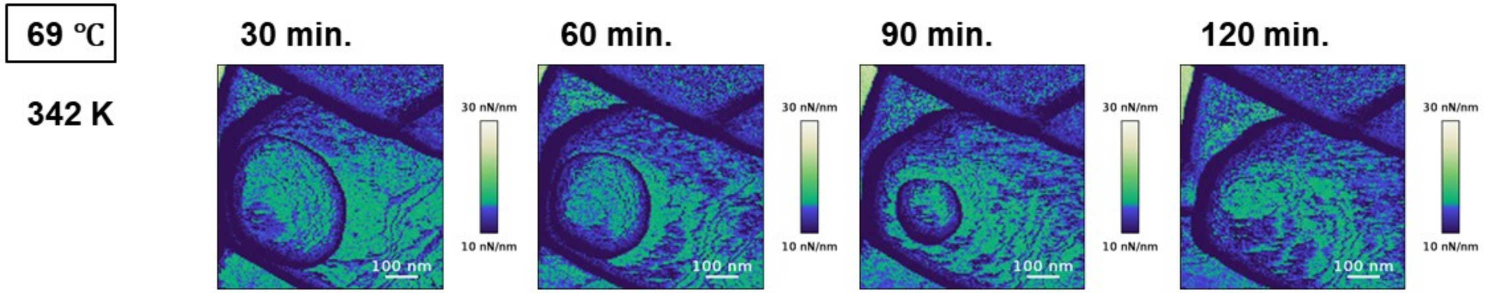
Omer Yaffe

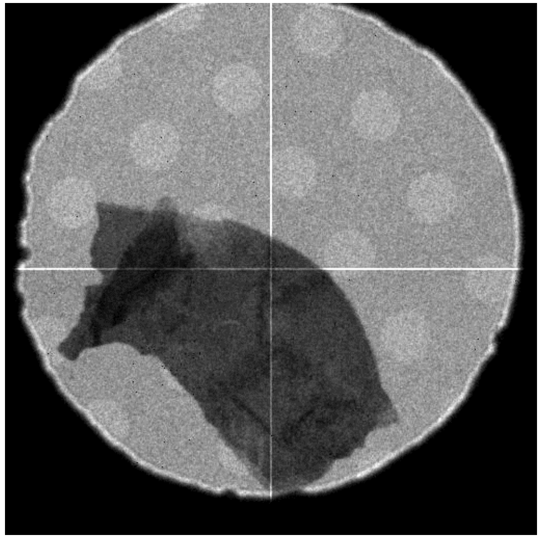
Maor Asher

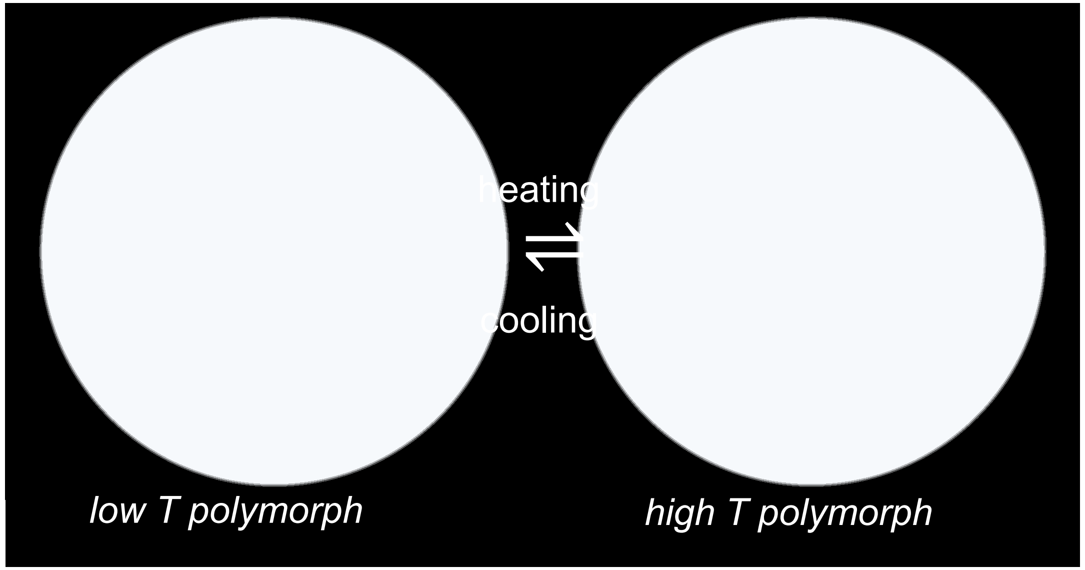
Rituraj Sharma

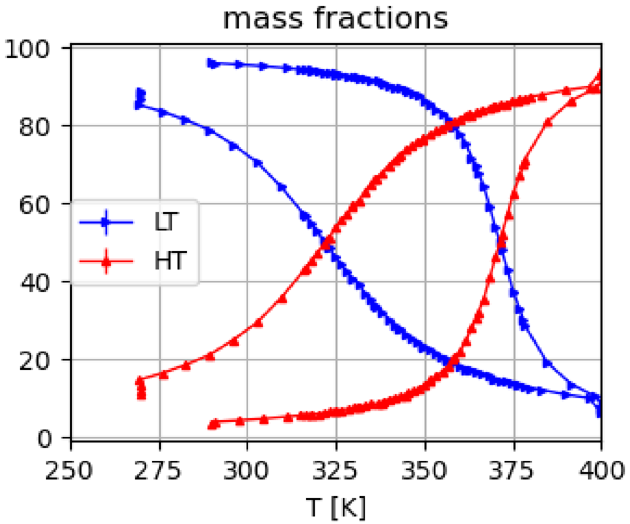
Grant agreement 801505

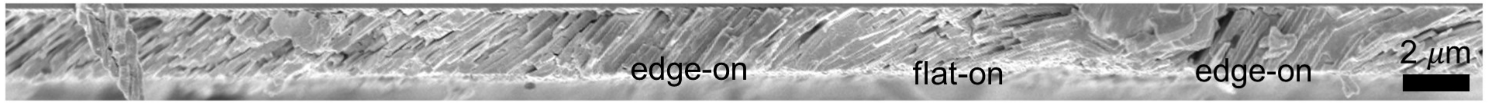
Future directions





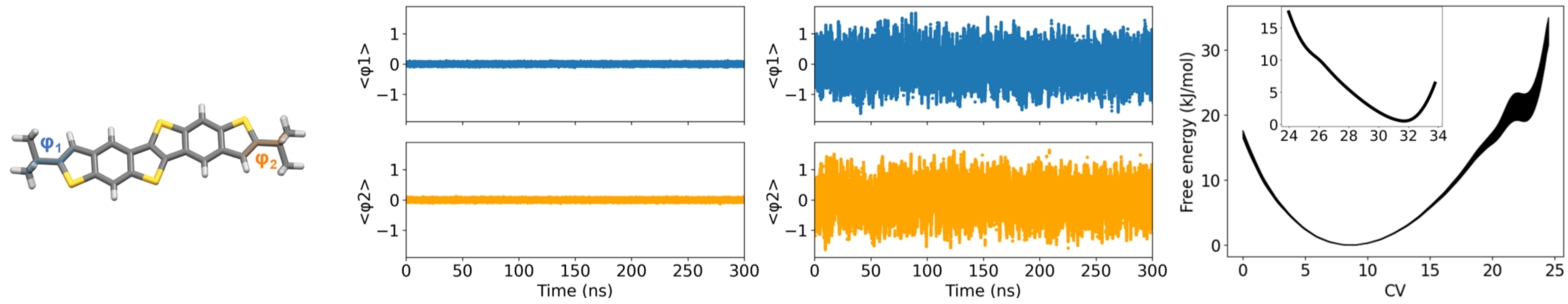


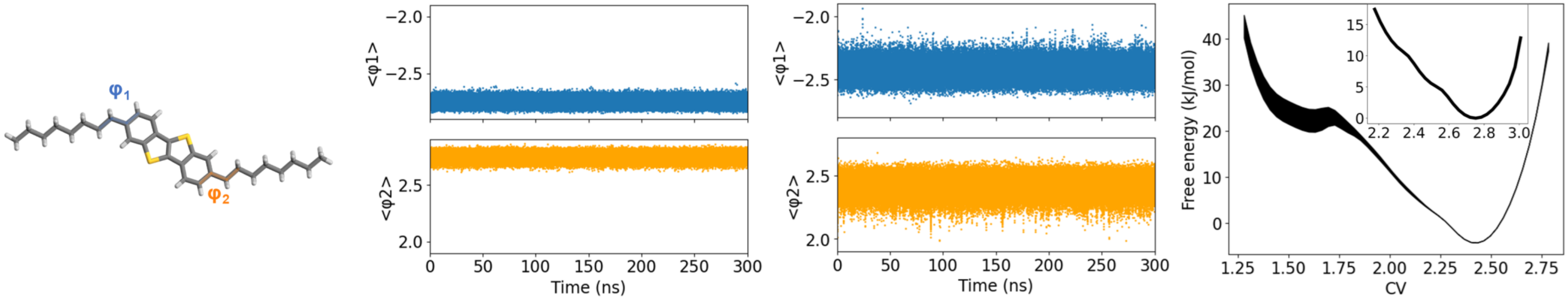




Molecular Dynamics

Emergence of multiple equilibrium positions

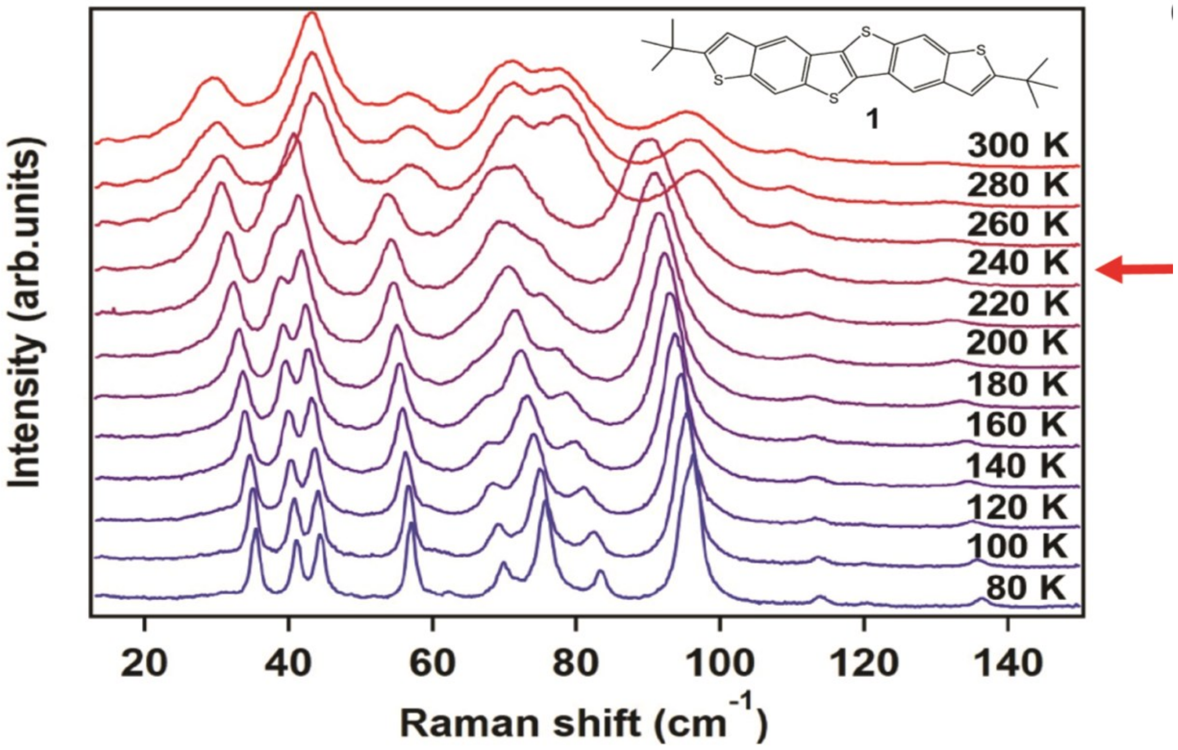


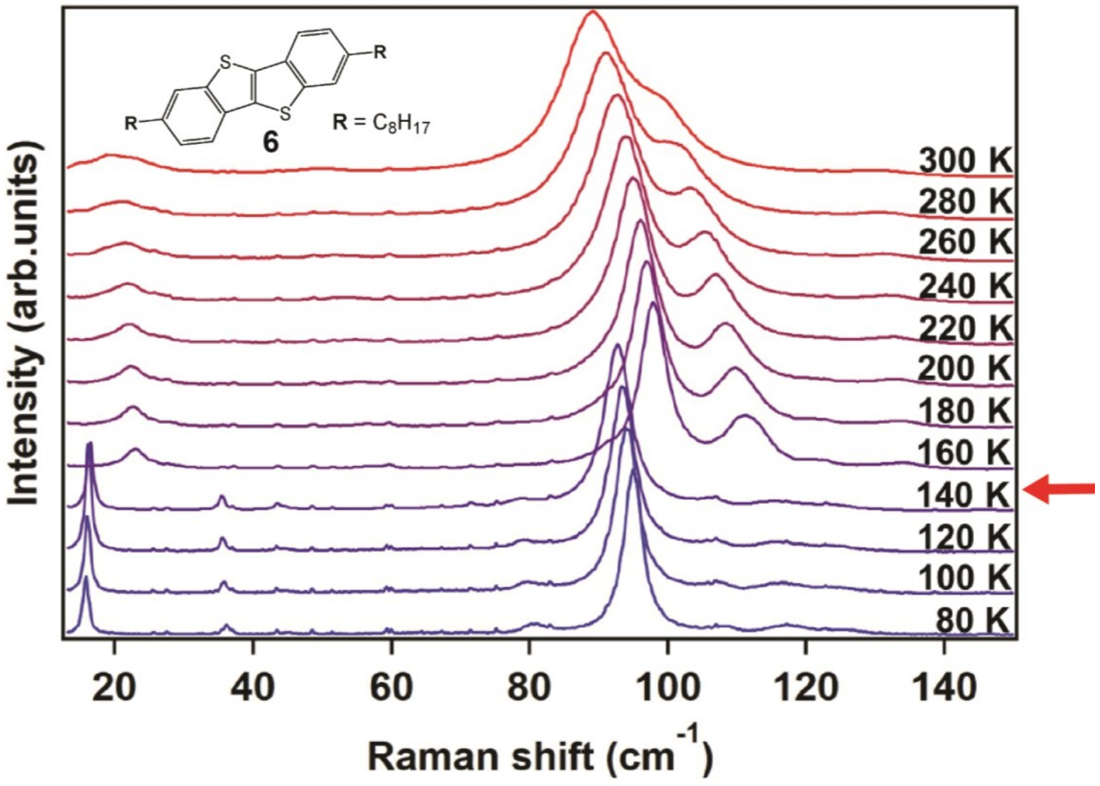


J. Am. Chem. Soc. 2024, just accepted

Order-disorder phase transition

Emergence of a liquid-like behavior





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