

# Cocrystallizing polymers with small molecules: towards a new class of organic supermolecules

Dritan Hasa<sup>1\*</sup>, Elvio Carlino<sup>2</sup>, Antonietta Taurino<sup>3</sup>, Dejan-Krešimir Bučar<sup>4</sup>

\*lead presenter: dhasa@units.it

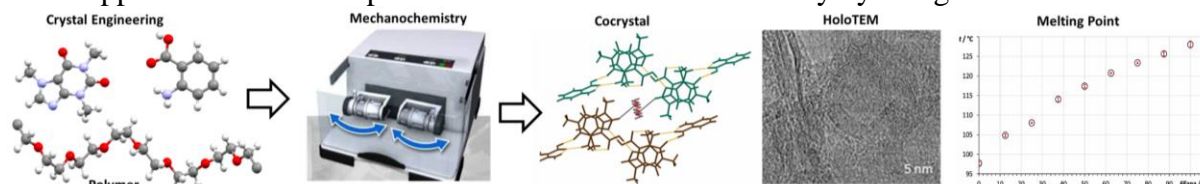
1 Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

2 Institute of Crystallography, National Research Council of Italy, IC-CNR  
Via Amendola 122/O, 70126 Bari, Italy

3 Institute for Microelectronics and Microsystems, National Research Council of Italy, IMM-CNR, Via Monteroni, I-73100 Lecce, Italy

4 Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AH, United Kingdom

The synthesis of cocrystals, solids that combine several different molecular entities within the same crystalline lattice is a rapidly growing branch of supramolecular chemistry, bringing the engineering of new crystalline forms to a higher level of refinement and versatility compared to single-component molecular solids [1]. Through identifying reliable crystal engineering strategies, cocrystallization technology offers versatile avenues for the design and preparation of new solid forms that have tunable physical properties [2]. Modulating the properties of crystalline solids through engineering of their supramolecular interactions promoted remarkable advances in several areas of chemistry. Such a remarkable tool, however, has been so far applied for the development of advanced materials mainly by using small molecules.



Recently, we used crystal engineering strategies for obtaining cocrystals made from small molecules and polymers; this latter class of materials has so far been sidestepped in crystal engineering efforts, mostly owing to the overwhelming difficulties related to their crystallization. Specifically, we reported how the cocrystallization of polyethylene glycol generates solids with enhanced thermal stability without compromising the mechanical flexibility of the polymer, while isomorphous replacement of one of the cocrystal components enables the formation of solid solutions with melting points that can be readily fine-tuned over a practically wide temperature range [3].

This presentation has particular focus on the effect of preparation techniques on the solid-state characteristics of such materials investigated by advanced XRD and novel atomic resolution direct HoloTEM imaging and simulations [3,4]. Some relevant examples already available in literature will be also mentioned, and our most recent results will be presented.

## References

[1] Bučar DK. Engineering molecular crystals: backbreaking, yet gratifying. *Cryst Growth Des.* 2017;17(6) 2913–2918.

[2] Corpinot MK, Bučar DK. A practical guide to the design of molecular crystals. *Cryst Growth Des.* 2019;19(2) 1426–1453.

[3] Germann LS et al. Modulating thermal properties of polymers through crystal engineering. *Angew Chem Int Ed.* 2023; accepted (doi.org/10.1002/anie.202212688).

[4] Carlino E. In-Line Holography in Transmission Electron Microscopy for the Atomic Resolution Imaging of Single Particle of Radiation-Sensitive Matter, *Materials* 2020;13, 1413.