

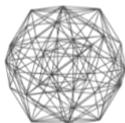
THE 2ND ANNUAL  
VIRTUAL  
SYMPOSIUM  $\frac{2}{0}$   
**SOLID-STATE**  
**ORGANIC**  
CHEMISTRY

Monday, May 24, 2021

Tuesday May 25, 2021



**MERCK**



Molecular Design Institute

NEW YORK UNIVERSITY

## Message from the Organizing Committee

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Welcome to the 2nd Annual Virtual Symposium on Solid-State Organic Chemistry! We're living in a time where the word "get-together" is almost taboo. As such, it has become difficult for the scientific community to unite in the collaborative spirit that is so ingrained in our identity. Scientific meetings have been postponed or canceled as most individuals are working remotely and unable to share their latest findings with the rest of the scientific community. The global pandemic has catapulted us into a new reality, a virtual reality, but despite the challenges, it also provides an opportunity to adapt to a new way of learning and thinking. Change is a means of fostering innovative and creative ideas, and at the heart of it, that is what science is all about.

Merck and NYU teamed up in May 2020 to organize a virtual symposium in the area of organic solid-state chemistry whereby graduate students and postdocs were invited to share their research with their peers from other institutions. This marked the inception of VS<sup>3</sup>OC. We are delighted to continue this new tradition with the 2nd annual VS<sup>3</sup>OC, a two-day symposium serving as a platform to share the research progress we've made in the field of solid-state organic chemistry. This year we're excited to have nearly doubled the number of participating research groups, making for a more diverse and expansive pot of research. Our program has also expanded to include two new events, a "meet and greet" social and a career panel hosted by Merck and Co.

We are ecstatic that you can join us. Thank you to all our speakers and all participants tuning in! It is your participation and contributions that have made this event a unique and exciting science get-together.

## List of Participating Institutions

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Jason Benedict, University at Buffalo, SUNY

Ying Diao, University of Illinois, Urbana Champaign

Elizabeth Elacqua, Penn State University

Lara Estroff, Cornell University

Travis Holman, Georgetown University

Bart Kahr, New York University

Alfred Lee, Merck & Co., Inc

Stephanie Lee, New York University

Vilmali Lopez-Mejias, University of Puerto Rico - Rio Piedras

Katherine Mirica, Dartmouth College

Leonard MacGillivray, University of Iowa

Jeffrey Rimer, University of Houston

Linda Shimizu, University of South Carolina

Calvin Sun, University of Minnesota

Jennifer Swift, Georgetown University

Lynne Taylor, Purdue University

Mike Ward, New York University

Lian Yu, University of Wisconsin-Madison

## List of Career Panelists and Affiliations

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### **Sara Koynov**

*Associate Principal Scientist, Center for Materials Science & Engineering  
Merck & Co., Inc.*

### **Anisha Patel**

*Director, Molecular & Materials Characterization  
Merck & Co., Inc.*

### **Ashish Punia**

*Associate Principal Scientist, Preformulation  
Merck & Co., Inc.*

### **Melissa Tan**

*Senior Scientist, Molecular & Materials Characterization  
Merck & Co., Inc.*

### **Narayan Variankaval**

*Executive Director, Small Molecule Analytical Research & Development  
Merck & Co., Inc.*

## Career Panel Session Moderators

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### **Andrew Brunskill**

*Principal Scientist, Preformulation  
Merck & Co., Inc.*

### **Lee Robison**

*Senior Scientist, Molecular & Materials Characterization  
Merck & Co., Inc.*

# Scientific Program

Day 1 (S1) – Monday, May 24 (Zoom Link: <https://nyu.zoom.us/j/99919047307>)

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Session Moderator: Alfred Lee, Merck and Co.,

- 12:45      Opening Remarks
- 12:55      **Wenchuan Ma**, University of Houston  
*Control of organic crystal nucleation by modifying the population of nucleation precursors*
- 13:25      **Chenguang Wang**, University of Minnesota  
*Computational Prediction of the Elastic Constants of Molecular Crystals*
- 13:55      **Steven Huss**, Penn State University  
*Furan-Derived Nanofibers: Synthesis, Characterization, and Reaction Optimization*
- 14:25      **Daniel Davies**, University of Illinois, Urbana Champaign  
*Direct Control of Cooperative Structural Transitions via Alkyl Chain Modification*

14:55      **Break**

Session Moderator: Tony Hu, New York University

- 15:05      **Nicholas Belloch**, Dartmouth College  
*Stimuli-Responsive Crystalline Materials for Temporary Adhesion*
- 15:35      **Francheska Reyes**, University of Puerto Rico  
*Pressure Dependent Polymorphic Phase Transformation in Solid Dispersions*
- 16:05      **Konrad Hedderick**, Cornell University  
*In-situ AFM Observation of Surface-Induced Coacervation Facilitating Localized Precipitation of Mineral Precursors from Dilute Solutions*
- 16:35      **Zoe Marr**, University at Buffalo, SUNY  
*The design and synthesis of photoswitchable diarylethene-based crystalline materials utilizing halogen bonding*
- 17:05      **Tony Hu**, New York University, Closing Remarks
- 17:10      Meet and Greet Event (see page 7)

Day 2 (S2) – Tuesday, May 25 (Zoom Link: <https://nyu.zoom.us/j/99919047307>)

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Session Moderator: Justin Newman, Merck & Co.,

- 13:00      Opening
- 13:10      **Jen Werner**, Georgetown University  
*Distinct desolvation pathways of four niclosamide solvates*
- 13:40      **Muhammad Saddam Hussain**, University of South Carolina  
*From Persistent Radicals to Conductivity: A Structure Property Investigation in a Series of Urea-tethered Halogenated Triphenylamines*
- 14:10      **Celymar Ortiz de Leon**, University of Iowa  
*From binary cocrystals to ternary cocrystals: supramolecular bridges, isomerism, and polymorphs*
- 14:40      **Alexandru Deac**, Purdue University  
*Effect of Solid-State Interactions on Dissolution Behavior of Amorphous Solid Dispersions*
- 15:10      **Break**

Session Moderator: Michael D. Ward, New York University

- 15:20      **Prashant Kumar Pandey**, Georgetown University  
*On the solid-state phase behavior and porosity of dimethoxypillar[5]arene*
- 15:50      **Aida Alaei**, New York University  
*Scaffold-directed solution-phase crystallization of emerging semiconductors*
- 16:20      **Xin Yao**, University of Wisconsin-Madison  
*Crystal Nucleation on the Surface of Molecular Liquids*
- 16:50      **Mike Ward**, New York University, Closing Remarks
- 17:00      Merck & Co., Career Panel  
(Zoom Link: <https://nyu.zoom.us/j/95947612078>)

## Meet and Greet Event

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In the spirit of scientific camaraderie and good old social mingling, we are excited to host a “Meet and Greet” event following Day 1 of VS<sup>3</sup>OC. There will be 14 breakout rooms available, each representing the institution of one of our speakers, who will also be present in their respected room. We encourage all attendees to join in the fun of meeting other participants and learn more about the incredible, diverse array of research. It is also a chance to meet our speakers in a smaller, more intimate setting. There is only one “rule” for our attendees: you can join any breakout room except for the one of your institution. We hope this will be a fun way to meet new folks, reconnect with colleagues, and enjoy a relaxed social hour. Everyone is welcome! Be sure to bring a drink and something to nibble on, as well!

# Presentation Abstracts



## Control of organic crystal nucleation by modifying the population of nucleation precursors

### Wenchuan Ma

University of Houston

William A. Brookshire Department of Chemical and Biochemical Engineering

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Numerous industrial tasks require suppression of nucleation. Elaborate structures can grow by precise nucleation control that consists of suppression of nucleation throughout and enhanced nucleation at a perfectly selected location. Robust suppression of nucleation cannot be understood or designed within the realm of classical theory. Strategies to suppress nucleation, however, naturally arise for two-step nucleation. Nucleation can be inhibited by disrupting the assembly of disordered precursors that host crystal nuclei or by engineering the cluster properties to constrain crystal nucleation.

For these studies, we employed hematin dissolved in octanol (with about 5 % water), a convenient model organic system. Hematin forms crystals elongated along their  $\tilde{c}$  crystallographic axis. In a supersaturated solution the scattered light intensity and the respective autocorrelation function  $G(\tau)$ , ( $\tau$  lag time) rapidly grow announcing fast nucleation of crystals. The addition of modifiers known to control hematin crystallization, heme-artesunate adduct (H-ARS), mefloquine (MQ), chloroquine (CQ), and pyronaridine (PY), invokes one of three outcomes: accelerated nucleation, suppressed nucleation, or no effect.

To explore the crystal nucleation precursors, we monitored hematin solutions with concentrations below the crystal solubility, in which crystallization is prohibited, with oblique illumination microscopy (OIM). Solution inhomogeneities are detected from the light that they scatter toward the objective lens. We apply a Stokes-Einstein procedure to the recorded Brownian trajectories of individual aggregates, extracted from sequences of OIM images and obtain the

aggregates' sizes. These behaviors of the hematin aggregates cohere with previous observations of mesoscopic solute-rich clusters of other organics, such as olanzapine, and numerous proteins. We conclude that the hematin aggregates are mesoscopic solute-rich clusters: independent of the solute concentration and steady in time; increases exponentially with the solute concentration as a consequence of the thermodynamic equilibrium between the clusters and the bulk solution. TEM observation of cluster-assisted nucleation and the parallel trends of additive activity on the cluster population and crystal nucleation support a mechanism of nucleation control employing additives that modulate the nucleation precursors.

Finally, we concluded the nucleation control strategy by manipulating the nucleation precursor clusters will proceed in three steps: (1) Test whether organic compounds of interest employ two step nucleation; (2) Combine experiments and molecular simulations to establish the mechanisms of formation of the nucleation precursors and define means to control them; and (3) Test whether variations in the populations of nucleation precursors in response to additives correlate with variations of the nucleation rate.



## Computational Prediction of the Elastic Constants of Molecular Crystals

### Chenguang Wang

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The mechanical properties of molecular crystals hold interest for both fundamental basic research and industrial applications. There has been a growing interest in exploring the crystal structure – mechanical properties relationship. Considering the low symmetry of molecular crystals, a complete experimental characterization of the mechanical properties of organic molecular crystals is challenging. Hence, computational approaches have gained much interest. Among the computational methods for estimating the elastic constants of molecular crystals, i.e., 1) quantum mechanical modeling of density functional theory (DFT), 2) force field (FF) methods, and 3) molecular dynamics (MD) simulations, the DFT and FF methods are the most commonly employed. The performance of both methods is affected by several factors. The calculated elastic constants (using an FF method), match well with the experimentally measured values of urea. Importantly, urea is predicted to be hard and brittle based on the dense 3D hydrogen bonding patterns and isotropic energy framework, which contradicts its high plasticity. On the other hand, the elasticity 3D map by both experimental and computational methods revealed large anisotropy of the mechanical property, explaining its high plasticity. Moreover, an accurate 3D elastic modulus map of a molecular crystal allows assessing the mechanical properties of specific crystal faces inaccessible by common experimental techniques, such as nanoindentation.

Because of its high computational efficiency, an accurate and reliable FF methods to predict the elastic constants of organic molecular crystals is highly

advantageous. Our work shows that the COMPASS FF with constant strain is a good starting point for further validation. A reliable computational method for elastic constants is an indispensable tool that complements the intermolecular energy calculation and nanoindentation study to better understand the structure – mechanical properties relationship of molecular crystals.



## Furan-Derived Nanofibers: Synthesis, Characterization, and Reaction Optimization

### Steven Huss

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Compared to traditional organic synthesis, pressure-mediated solid-state synthesis is an underexplored field which provides access to new reaction pathways that are challenging at ambient pressure. Carbon nanofibers are one-dimensional  $sp^3$  polymers produced by pressure-induced polymerization of unsaturated molecules at gigapascal pressures. Their columnar diamondoid structure allows them to pack in a pseudohexagonal crystalline lattice while also giving them a high predicted tensile strength and flexibility. Whereas a few examples of carbon nanofibers have been reported, the need for high initiation pressures ( $\geq 17$  GPa) to synthesize them precludes scalability and limits scope. Herein, we will discuss furan-derived carbon nanofibers, which are synthetically available at reduced pressures owing to furan's lessened aromaticity relative to other molecular precursors. Evidence of polymerization is observed in situ by X-ray diffraction and Raman spectroscopy. The diffraction of the furan nanofibers are consistent with atomistic simulations for crystals of furan nanofibers. MALDI-FT-ICR, CID fragmentation, and solid-state NMR each provide evidence that furan-derived nanofibers have formed through a series of [4+2] cycloaddition reactions. The reaction conditions are currently being optimized with use of UV light radiation and increased temperature.



## Direct Control of Cooperative Structural Transitions via Alkyl Chain Modification

**Daniel Davies**

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Cooperative phase transitions have shown to exhibit unique properties not typically accessible in semiconductor systems such as ultrafast kinetics bypassing large energy barriers and shape memory effects. Cooperative structure transition involves simultaneous, concerted displacement of molecules in a crystalline material, in stark contrast to the typical nucleation and growth mechanism occurring in a molecule-by-molecule fashion that often disrupt the material structural integrity. Cooperative transitions have acquired much attention in the research community for its low transition barrier, ultrafast kinetics, and structural reversibility. However, cooperative transitions are rarely observed in molecular crystals and the molecular design rules governing the presence of these cooperative transitions are still largely unknown. Recently, 2-dimensional quinoidal terthiophene (2DQTT-o-B), a high-performance organic semiconductor, was shown to have diverse polymorphic behavior. Along with structural diversity, 2 thermally triggered reversible phase transitions showed both cooperative and nucleation and growth mechanisms in the same system. In situ microscopy, single crystal and grazing incidence X-ray diffraction, and Raman spectroscopy suggested the cooperative transition occurred via a reorientation in the alkyl side chains causing a change in molecular tilt. The nucleation and growth transition, on the other hand, shows alkyl chain melting coupled with increased core interactions from an increased presence of biradical species, confirmed via in situ electron paramagnetic resonance spectroscopy. By adjusting the branching alkyl chain length, we show control over the presence of the cooperative transition. Moreover, we established synergistic effect

between alkyl chain melting and biradical concentration during the nucleation and growth transition. Through understanding how the molecular structure affects the transition mechanisms, we can establish design rules to target these polymorphic behaviors in organic semiconductors for novel electronic devices.

**S1.****Stimuli-Responsive Crystalline Materials for Temporary Adhesion****Nicholas Blelloch**

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The development of novel temporary adhesives—a fundamental challenge motivated by modern technological problems that demand new function—has the potential to enhance our current understanding of the fundamental structure–property relationships of molecular materials. This research provides the fundamental understanding required to rationalize the macroscopic physical and chemical properties of a material as a function of its chemical and crystal structures. Strategic application of supramolecular chemistry and crystal engineering principles has enabled the molecular design of temporary adhesives capable of bonding glass, metal, and plastic with lap shear forces in the MPa range. For context, double-sided scotch tape, a common temporary adhesive, has a lap shear strength of ~150 kPa. In addition, these materials are capable of rapid release of substrates on-demand without the use of solvent and/or mechanical force. Systematic investigation of the chemical structures of these materials indicate that intermolecular interactions present within a polycrystalline film determine its macroscopic behavior—namely its response to stress/strain, and its phase transitions. Furthermore, stimuli-responsive behavior, such as photo- or chemical-reactivity, may be encoded into temporary adhesives. Overall, this work improves our fundamental understanding of our ability to control the mechanical and adhesive properties of molecular solids through systematic investigation of their structure-property relationships.

**S1.**

## **Pressure Dependent Polymorphic Phase Transformation in Solid Dispersions**

**Francheska Reyes**

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The inadvertent occurrence of polymorphic phase transformations (PPT) of active pharmaceutical ingredients (APIs) during polymer-based melt formulation technologies such as hot melt extrusion (HME) and 3D printing (3DP), have been claimed to limit their applications to formulate solid dispersions with the API in the desired crystalline state (CSDs). Consequently, there is a need to understand the relationship between polymorphism and the critical process parameters (CPPs) of HME and 3DP to successfully implement them as alternative solid dosage formulation strategies for CSDs. In this study, the influence of the CPPs pressure, temperature, composition, and residence time were investigated on CSDs composed of the model compound flufenamic acid (FFA) and polyethylene glycol (PEG) by temperature-pressure simulated extrusion (TPS-E) utilizing a rheometer. The results reveal a 26% reduction in the average PPT induction time compared to temperature-simulated extrusion (70-100 °C) without pressure ( $3.0 \pm 0.3$  MPa). Yet, offline powder x-ray diffraction and Raman spectroscopy confirm that FFA form III, metastable above the transition point of 42 °C, can be obtained by TPS-E because the PPT induction time is longer than the average reported residence time in conventional extrusion processes (5 min). Moreover, it was demonstrated that thorough fundamental understanding of the thermodynamic and kinetic design space for the API-polymer system leads to polymorphic control in the produced CSDs. This will aid to broaden the application of HME and 3DP as formulation technologies for CSDs containing APIs prone to polymorphism, representing about 80% of all APIs.



## **In-situ AFM Observation of Surface-Induced Coacervation Facilitating Localized Precipitation of Mineral Precursors from Dilute Solutions**

**Konrad Hedderick**

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Many organisms control the precipitation of minerals at ambient conditions, using soluble ions as building blocks. A typical strategy for such crystallization processes in biological systems is via a multistep pathway, where a metastable initial phase will transform into the final, often thermodynamically stable phase. Even though the transformation of these intermediate phases has been intensively studied, it remains unclear how the initial metastable phase forms within the cellular context. A model system for such controlled biomineralization is the coccolithophore. These marine algae produce intricately calcite architectures for a variety of functions. These calcitic shells (termed coccoliths) form intracellularly at very low calcium concentrations. In this work, we use coccolithophore-derived and synthetic polymers to study, *in vitro*, the chemical interactions between calcium ions and organic macromolecules that precede coccolith formation. We use *in-situ* analyses, including cryo-electron tomography and liquid-cell atomic force microscopy, to study the interactions in bulk solution and on organic surfaces simultaneously. The results unveil a chemical process in which a functional surface induces the precipitation of a polymer–Ca dense phase, or a coacervate, at chemical conditions where precipitation in solution is kinetically inhibited. Such behavior demonstrates how organisms can form dense Ca-rich phases from the dilute concentrations of calcium in seawater and eventually within organelles. This Ca-rich phase can then transform into a mineral precursor in a subsequent step, without posing challenges to cellular homeostasis.

**S1.**

## **The design and synthesis of photoswitchable diarylethene-based crystalline materials utilizing halogen bonding**

**Zoe Marr**

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Diarylethenes (DAEs) are a class of photochromic molecules that have the ability to undergo a reversible isomerization induced by photoirradiation. DAEs are attractive, compared to other photochromes, because they are generally thermally stable, can possess high quantum yields, can be repeatedly cycled, and can undergo the photochromic reaction in the solid state. Incorporating DAEs into crystalline solid-state materials allows for the controlled transformation of both the physical and chemical properties via light, which is useful for applications such as optical memory, switches, and molecular machines.

In order to synthesize these crystalline architectures, the concept of crystal engineering, which is the design and controlled assembly of solid-state structures with desired properties through the understanding and manipulation of intermolecular interactions, is applied. Supramolecular synthons, structural units formed through intermolecular interactions like hydrogen and halogen bonds, are commonly utilized as the basis of these structures. Within the last five years, there has been a growing interest in using halogen bonding to control the formation of molecular assemblies as it has been shown that halogen bonded solid-state materials can exhibit a novel or an improved photoresponse. This presentation will describe recent progress towards establishing the relationship between halogen bond strength and its effects on the photophysical properties of the solid-state DAEs through the following steps: (1) Synthesis of the halogen-containing DAEs, (2) Computational modeling of the DAEs to determine their suitability for halogen bonding, and (3) Creation of halogen bonded co-crystals that systematically vary the strength of the intramolecular interactions followed by a study of their photoresponse.



## Distinct desolvation pathways of four niclosamide solvates

**Jen Werner**

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Small molecule crystalline hydrates and solvates have a variety of applications, ranging from pharmaceuticals to semiconductors. Although some types of hydrates and solvates may not have suitable stabilities for development, they can serve as important precursors which upon desolvation yield novel solvent-free phases that differ from those that can be obtained directly from solution growth. However, the ability to predict the mechanistic pathway and products of a desolvation reaction remains a challenge. The orally delivered pharmaceutical niclosamide (NCL) is considered an “Essential Medicine” by the World Health Organization as a treatment for parasite infections. It crystallizes in multiple forms, including two solvent-free polymorphs, two hydrates, and multiple solvates. Here we examine the kinetic and mechanistic aspects of solid state desolvation from four different NCL forms (two monohydrates, acetonitrile and methanol solvates) which differ in their topology but yield the same solvent-free form. Comparison of the different desolvation pathways from these four distinctly different precursors to the same final product phase provides insight into how the degree of structural similarity between the initial and final lattices defines the solid state transformation.



## From Persistent Radicals to Conductivity: A Structure Property Investigation in a Series of Urea-tethered Halogenated Triphenylamines

**Muhammad Saddam Hussain**

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Triphenylamines (TPAs) are known to form persistent organic radicals either by chemical, electrochemical or photoinduced oxidation. Typically, fully para-substituted TPAs capable of forming stable radical cations while partially substituted systems quickly degrade. Herein, we study the effects of solid-state organization on series of urea tethered halogenated TPAs **1** (X = H, Cl, Br, I) and compare their radical cation formation and persistence after UV-irradiation. These halogenated urea tethered TPAs were examined by single-crystal X-ray diffraction where their assembly was guided by three-centered urea hydrogen bonding interaction. The structures of **1H**, **1Cl**, and **1Br** adopted anti-parallel extended TPA conformation with an average TPA N...N distance of approximately 14 Å. The N...N separation was slightly longer in **1H** (14.1 Å) as compared with ~13.9 Å in **1Cl** and **1Br**. In contrast **1I**, which alone crystallized as an ethyl acetate hemi-solvate, adopts a U-shaped structure with a shorter N...N distance of 9.9 Å and exhibited both halogen and hydrogen bonding interactions. Although all compounds form photogenerated radical cations in solution, the structures quickly degrade. In contrast, supramolecular assembly enhanced the stability and persistence of the radicals, which appear to undergo charge recombination without degradation. Greater quantities of these radical cations are observed for **1Br** and **1H**. Theoretical calculations on single molecules and hydrogen-bonded dimers with time-dependent density functional theory (TD-DFT) suggest that the charge transfer (CT) is feasible upon UV-irradiation, favoring an intramolecular process for **1Br** versus an intermolecular CT process in

**11.** In addition, electrical charge coupling leads to faster charge recombination in **11** versus **1Br**. We are currently investigating the relationship of CT and radical formation with mobility and conductivity measurements as conductive assembled TPA have particular importance as hole transporters in organic solar cells.



## From binary cocrystals to ternary cocrystals: supramolecular bridges, isomerism, and polymorphs

**Celymar Ortiz de Leon**

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While co-crystallization remains an important tool for the development of functional materials, strategies for design and formation of more complex and higher order cocrystals are still a work in progress. Cocrystal formation relies on the assembly of the constituent molecules via noncovalent interactions to give rise to a lattice composed of two or more different molecules. The challenge in forming higher order cocrystals lies in balancing the increasing possible noncovalent interactions between the components. Herein we report the supramolecular construction of a ternary cocrystal involving resveratrol (resv), a nutraceutical, and 5-fluorouracil (5-fu), an important anticancer agent, with trans-bis(4-pyridyl)ethylene (bpe). Additionally, we discovered a polymorph of binary 4(5-fu)·(bpe) that exhibits rare supramolecular isomerism based on a subtle difference in the hydrogen bonding pattern. A ternary cocrystal involving phenazine (phe), resv, and bpe will also be discussed. Collectively, our work provides insight into the construction of higher order cocrystals.



## **Effect of Solid-State Interactions on Dissolution Behavior of Amorphous Solid Dispersions**

**Alexandru Deac**

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Amorphous solid dispersions (ASDs) are a formulation strategy for enabling the oral delivery of poorly soluble drugs. Up to 90% of compounds in development pipelines possess low aqueous solubility as categorized by the Biopharmaceutics Classification System. Despite their increased acceptance as a practical solution to increase the solubility and dissolution rate of poorly soluble drugs, ASDs have complicated dissolution behavior. Several researchers have shown that the release of drug from an ASD ceases above a critical drug load, termed the limit of congruency (LoC). Moreover, the LoC varies depending on the drug-polymer system and it can be as low as 5% w/w. In our work we have uncovered that strong drug-polymer interactions in the solid-state play a crucial role in decreasing the LoC by forming a relatively large insoluble phase. We hypothesize that this insoluble phase forms at the dissolution interface of an ASD, which then blocks the release of further drug and polymer. Our study highlights the importance of balancing the drug-polymer interaction strength when screening for polymers in ASD formulations.



## On the solid-state phase behavior and porosity of dimethoxypillar[5]arene

**Prashant Kumar Pandey**

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Pillar[n]arenes are a relatively new class of shape-persistent, tubular macrocycles that are receiving ever-increasing scientific interest because of their easy synthesis and exceptional host-guest binding properties. It is surprising, however, that rather less is known about the solid-state properties and phase behavior of the simplest and most accessible member of this family, dimethoxypillar[5]arene (**DMP5**). In its most abundant crystalline solvated form ( $\beta$ -solvent@**DMP5**), guest solvent molecules occupy isolated, tubular cavities. Given the shape-persistence of the macrocyclic structure, one can envision the existence of a “0D” porous guest-free crystalline form. Such a porous material would have commercial potential as the compound is available in high yields, in a single step, from commodity chemicals. This presentation will focus on on solid-state phase behaviour of **DMP5**. It was found to exist in three new polymorphic forms, including two empty crystalline non-porous phases,  $\alpha$ -**DMP5** and  $\gamma$ -**DMP5**, and an amorphous phase ( $\alpha$ -**DMP5**). All of these were found to transform to a  $\beta$ -xCO<sub>2</sub>@**DMP5** gas clathrate in the solid-state when pressurized with CO<sub>2</sub>. A partially CO<sub>2</sub>-occupied metastable  $\beta$ -phase,  $\beta$ -xCO<sub>2</sub>@**DMP5** (x  $\approx$  0.16) has been isolated and was demonstrated to be formally porous, exhibiting a CO<sub>2</sub> uptake capacity similar to the related, porous dihydroxypillar[5]arene compound. Single crystal structures of  $\alpha$ -**DMP5** and  $\beta$ -1.0CO<sub>2</sub>@**DMP5** were obtained. The ability of **DMP5** to selectively scavenge appropriate organic guest molecules will also be described.



## Scaffold-directed solution-phase crystallization of emerging semiconductors

**Aida Alaei**

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Directing the growth of solution processable organic and hybrid semiconductor crystals is of great interest to the emerging electronics community since optoelectronic properties can vary significantly along different crystallographic directions. Here we demonstrate a method to dictate the orientation of crystals with different growth habits by confining crystallization within scaffolds comprising nanopore or nanopillar arrays with feature sizes on the tens to hundreds of nanometer length scale. In particular, the size, shape, and orientation of organic semiconductor triisopropylsilylethynyl pyranthrene needle-like crystals and perylene platelike crystals grown via a continuous dip coating method were dictated by the scaffold geometry and processing conditions. Similar orientation and shape control were observed for metal-halide perovskite crystals grown from a two-step deposition onto porous anodized aluminum oxide scaffolds. The orientation of these crystals is optimized for light energy harvesting, with the fast charge transport direction of crystals aligned with the current flow direction in solar cell devices.



## Crystal Nucleation on the Surface of Molecular Liquids

**Xin Yao**

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Molecules on the surface of a liquid have a different environment from those in the bulk, showing preferred orientation, layering, and fast motion. The surface effect on crystal nucleation is potentially important whenever a crystallizing system has a free surface, e.g., water droplets in atmosphere, but there is virtually no quantitative information. We report that crystal nucleation is vastly faster on the surface of liquid D-arabitol than in its bulk, by 11 orders of magnitude on the per-molecule basis. Surface nucleation favors a different polymorph (II) than bulk nucleation (I), a consequence of the similarity of the surface molecular packing to the surface-nucleating polymorph. The enantiomer of D-arabitol, L-arabitol, shows identical phenomenon, while the racemate does not, supporting our conclusion. Our study highlights the importance of liquid surface in crystal nucleation.