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Editorial

Lattice Dynamics: The Unexplored Multidimensional Dynamic Playground of Molecular Crystalline Materials

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Once considered rigid, static, and unreactive, molecular crystals are increasingly recognized as exhibiting a rich set of atomic dynamics, which in many cases result in materials with adaptive responsiveness to external stimuli, such as light, heat, and mechanical stress. This paradigm shift has prompted a new area of research on dynamic crystalline systems that are now recognized as ideal building blocks for a broad range of functional materials with switchable properties, such as mechanical, optical, optoelectronic, electronic, magnetic, structural properties, and dynamic behaviors ranging from the nanoscale (e.g., molecular reorientation and isomerization) up to the macroscopic scale (e.g., bulk crystals jumping, deformation, shape-shifting).[1−3] Lattice dynamics arising from atomic, molecular, and collective vibrations are believed to be at the core of this complex and multidimensional functional landscape—even though clear connections between local and long-range vibrations, structures, and functions are far from being understood. In this context, this Virtual Special Issue (VSI) in *Crystal Growth & Design* aims to highlight the latest efforts to elucidate the role of lattice dynamics for the design, development, and characterization of new dynamic molecular crystals with unexplored properties. In this editorial, the guest editors of the VSI have highlighted ongoing and emerging trends, and future outlooks of this exciting field to spur the interest of the community, with the hope to stimulate new multidisciplinary and collaborative efforts of researchers around the world to uncover the role of lattice dynamics in dictating the properties and functions of crystalline dynamic materials.

Untangling the Role of Lattice Dynamics in Porous Materials. Porous crystalline materials, such as metal−organic frameworks (MOFs), covalent-organic frameworks (COFs), and porous organic crystals, possess a broad range of dynamic behaviors, from local intra-/intermolecular motions to global lattice dynamics that can be precisely engineered and tuned by carefully designing the individual building blocks and the associated self-assembly process, taking advantage of host−guest interactions, and/or by exposing the materials to specific external stimuli, e.g., light, temperature, and pressure.[4] Even though porous crystals possess a rich dynamic landscape, there is still a fundamental lack of understanding of the role that lattice dynamics play in driving the structure and modulating the final physicochemical properties of the materials, including guest uptake, mechanical flexibility, and structural transitions. This calls for a robust multidisciplinary effort, combining materials science, physical organic chemistry, ultrafast science, and computational chemistry, to shed light on the inherently dynamic structure−property relation embedded in this class of compounds.[5]

Lattice Dynamics and the Mechanical Properties of Molecular Crystals. It has been well documented that molecular crystals have a wide range of mechanical properties, from extremely hard and rigid, as shown for some simple zwitterionic amino acids, to soft and mechanically compliant systems undergoing all kind of deformations, such as plastic and elastic bending, coiling, twisting.[6] The vast gamut of mechanical properties places organic crystals between inorganic materials and soft matter for applications ranging from soft-robotics, flexible electronics and optoelectronics, and robust fatigue-resistant functional materials.[7] In-depth analysis of the intermolecular interactions governing molecular crystalline packing has constituted the starting point to rationalize the connection between crystal structure and mechanical properties, and to consequently devise efficient crystal engineering strategies to predict and modulate the mechanical behavior of organic crystals through molecular engineering. While this approach has proved efficient, it does not take into account the complex lattice dynamics of crystalline systems and results in a static picture of the mechanical behavior of these materials. In this context, there is a clear need to shed light on the connections between lattice vibrations, crystal structures, and the mechanical features of molecular crystals in order to understand, characterize, and modulate their mechanical properties.[8]

Charge Transport and Lattice Dynamics. The studies on crystalline organic semiconductors have been burgeoning thanks to their easy processability, low cost, lightweight, high tunability, and inherent mechanical flexibility-making them ideal candidates for a broad range of electronic and optoelectronic applications.[9−11] However, the success of this class of materials is jeopardized by low charge carrier mobilities that rarely exceed 10 $cm^2\ V^{-1}\ s^{-1}$, making it difficult for them to compete with their inorganic counterparts.[12,13] To overcome these limitations, controlling and reducing dynamic structural disorder has been identified as a key parameter to suppress detrimental electron−phonon coupling and, hence, to

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increase the charge transport properties of organic semiconductor crystals.[14,15] To do so, preliminary studies have highlighted how molecular, crystal, and lattice dynamics engineering strategies can be devised to suppress specific low-frequency vibrations (below 100 cm^{-1}) that are highly excited at room temperature and seem to be responsible for most of the detrimental dynamic disorders of organic semiconductors.[16,17] However, the field is still in its infancy, and major interdisciplinary efforts combining chemists, solid state physicists, and materials scientists will be needed tackle this challenge.

Controlling Polymorphism via Lattice Dynamics. Despite major efforts to understand, control, and predict crystal forms and their polymorphic transitions, the fundamental question of whether a molecular crystalline system will be polymorphic remains unanswered.[18] The discovery of new polymorphs is still phenomenologically rooted in McCrone's famous statement that the number of crystal forms known for a given compound is proportional to the time and money spent in research on that compound leading to time-consuming, costly, and energy-demanding polymorph screenings.[19] Crystal structure prediction conducted in tandem with experimental screening has recently shown the power of using theory and experiment to predict and isolate crystal polymorphs.[20,21] A few recent reports have demonstrated that peculiar cooperative solid-to-solid phase transitions seem to be driven by specific molecular motions and phonons, hinting at the potentially general, but still unexplored, role of lattice dynamics to control polymorphism based on the design of the starting building blocks and their dynamic features. This often-overlooked concept is now opening new research directions in crystal engineering.[22,23]

■ CONCLUSIONS

The VSI has received many excellent contributions exploring several exciting aspects of dynamic crystals and lattice dynamics such as stimuli-responsive organic crystals, mechanical features of crystalline systems, vibrational spectroscopy, polymorphism, and dynamic porous materials. This is proof of the growing interest of the scientific community in trying to shed light on the inherent dynamic nature of molecular solids to drive their structures, physicochemical properties, and functions. We hope that this outstanding collection of works will further stimulate cross disciplinary collaborations to tackle this complex multidimensional challenge and then to exploit molecular and lattice motions to design new crystalline materials with tailored dynamic functions.

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Notes

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■ REFERENCES

(1) Garcia-Garibay, M. A. Crystalline molecular machines: encoding supramolecular dynamics into molecular structure. *Proc. Nat. Acad. Sci.* **2005**, *102*, 10771−10776.

(2) Sato, O. Dynamic molecular crystals with switchable physical properties. *Nat. Chem.* **2016**, *8*, 644−656.

(3) Naumov, P.; Karothu, D. P.; Ahmed, E.; Catalano, L.; Commins, P.; Mahmoud Halabi, J.; Al-Handawi, M. B.; Li, L. The Rise of the Dynamic Crystals. *J. Am. Chem. Soc.* **2020**, *142*, 13256−13272.

(4) Hernández-Santiago, E.; Espinosa-Rocha, J.; Galicia-Badillo, D.; Rodríguez-Molina, B. Local and global dynamics in organic soft porous crystals. *Matter* **2024**, *7*, 408−429.

(5) Krause, S.; Milić, J. V. Functional dynamics in framework materials. *Commun. Chem.* **2023**, *6*, 151.

(6) Awad, W. M.; Davies, D. W.; Kitagawa, D.; Mahmoud Halabi, J.; Al-Handawi, M. B.; Tahir, I.; Tong, F.; Campillo-Alvarado, G.; Shtukenberg, A. G.; Alkhidir, T.; Hagiwara, Y.; Almehairbi, M.; Lan, L.; Hasebe, S.; Karothu, D. P.; Mohamed, S.; Koshima, H.; Kobatake, S.; Diao, Y.; Chandrasekar, R.; Zhang, H.; Sun, C. C.; Bardeen, C. J.; Al-Kaysi, R. O.; Kahr, B.; Naumov, P. Mechanical properties and peculiarities of molecular crystals. *Chem. Soc. Rev.* **2023**, *52*, 3098−3169.

(7) Karothu, D. P.; Mahmoud Halabi, J.; Ahmed, E.; Ferreira, R.; Spackman, P. R.; Spackman, M. A.; Naumov, P. Global Analysis of the Mechanical Properties of Organic Crystals. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202113988.

(8) Ruggiero, M. T.; Sibik, J.; Orlando, R.; Zeitler, A.; Korter, T. M. Measuring the Elasticity of Poly-l-Proline Helices with Terahertz Spectroscopy. *Angew. Chem., Int. Ed.* **2016**, *55*, 6877−6881.

(9) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. Charge Transport in Organic Semiconductors. *Chem. Rev.* **2007**, *107*, 926−952.

(10) Wang, C.; Dong, H.; Jiang, L.; Hu, W. Organic semiconductor crystals. *Chem. Soc. Rev.* **2018**, *47*, 422−500.

(11) Bronstein, H.; Nielsen, C. B.; Schroeder, B. C.; McCulloch, I. The role of chemical design in the performance of organic semiconductors. *Nat. Rev. Chem.* **2020**, *4*, 66−77.

(12) Fratini, S.; Nikolka, M.; Salleo, A.; Schweicher, G.; Sirringhaus, H. Charge transport in high-mobility conjugated polymers and molecular semiconductors. *Nat. Mater.* **2020**, *19*, 491−502.

(13) Bulgarevich, K.; Horiuchi, S.; Takimiya, K. Crystal-Structure Simulation of Methylthiolated *Peri*-Condensed Polycyclic Aromatic Hydrocarbons for Identifying Promising Molecular Semiconductors: Discovery of 1,3,8,10-tetrakis(methylthio)peropyrene Showing Ultrahigh Mobility. *Adv. Mater.* **2023**, *35*, 2305548.

(14) Selezneva, E.; Vercouter, A.; Schweicher, G.; Lemaur, V.; Broch, K.; Antidormi, A.; Takimiya, K.; Coropceanu, V.; Brédas, J.-L.; Melis, C.; Cornil, J.; Sirringhaus, H. Strong Suppression of Thermal Conductivity in the Presence of Long Terminal Alkyl Chains in Low-Disorder Molecular Semiconductors. *Adv. Mater.* **2021**, *33*, 2008608.

(15) Illig, S.; Eggeman, A. S.; Troisi, A.; Jiang, L.; Warwick, C.; Nikolka, M.; Schweicher, G.; Yeates, S. G.; Henri Geerts, Y.; Anthony, J. E.; Sirringhaus, H. Reducing dynamic disorder in small-molecule organic semiconductors by suppressing large-amplitude thermal motions. *Nat. Commun.* **2016**, *7*, 10736.

(16) Schweicher, G.; D'Avino, G.; Ruggiero, M. T.; Harkin, D. J.; Broch, K.; Venkateshvaran, D.; Liu, G.; Richard, A.; Ruzié, C.; Armstrong, J.; Kennedy, A. R.; Shankland, K.; Takimiya, K.; Geerts, Y. H.; Zeitler, A. J.; Fratini, S.; Sirringhaus, H. Chasing the "Killer"

Phonon Mode for the Rational Design of Low-Disorder, High-Mobility Molecular Semiconductors. *Adv. Mater.* **2019**, *31*, 1902407.

(17) Banks, P. A.; D'Avino, G.; Schweicher, G.; Armstrong, J.; Ruzié, C.; Chung, J. W.; Park, J.-I.; Sawabe, C.; Okamoto, T.; Takeya, J.; Sirringhaus, H.; Ruggiero, M. T. Untangling the Fundamental Electronic Origins of Non-Local Electron−Phonon Coupling in Organic Semiconductors. *Adv. Funct. Mater.* **2023**, *33*, 2303701.

(18) Cruz-Cabeza, A. J.; Feeder, N.; Davey, R. J. Open questions in organic crystal polymorphism. *Commun. Chem.* **2020**, *3*, 142.

(19) McCrone, W. C. *Polymorphism in Physics and Chemistry of the Organic Solid State*; Wiley-Interscience, 1965; Vol. *2*, pp 725−767.

(20) Neumann, M. A.; van de Streek, J.; Fabbiani, F. P. A.; Hidber, P.; Grassmann, O. Combined crystal structure prediction and high-pressure crystallization in rational pharmaceutical polymorph screening. *Nat. Commun.* **2015**, *6*, 7793.

(21) Taylor, C. R.; Mulvee, M. T.; Perenyi, D. S.; Probert, M. R.; Day, G. M.; Steed, J. W. Minimizing Polymorphic Risk through Cooperative Computational and Experimental Exploration. *J. Am. Chem. Soc.* **2020**, *142*, 16668−16680.

(22) Chung, H.; Dudenko, D.; Zhang, F.; D'Avino, G.; Ruzié, C.; Richard, A.; Schweicher, G.; Cornil, J.; Beljonne, D.; Geerts, Y.; Diao, Y. Rotator side chains trigger cooperative transition for shape and function memory effect in organic semiconductors. *Nat. Commun.* **2018**, *9*, 278.

(23) Zaczek, A. J.; Catalano, L.; Naumov, P.; Korter, T. M. Mapping the polymorphic transformation gateway vibration in crystalline 1,2,4,5-tetrabromobenzene. *Chem. Sci.* **2019**, *10*, 1332−1341.

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