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From Responsive Molecules to Interactive Materials

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"Taking lessons from Nature on our next journey into uncharted territories of molecular materials, we cannot avoid dreaming about the astonishing way living systems sense, function autonomously and respond to their environment." This quote, taken from the Vision Statement of the Nobel Laureate Ben Feringa, captures the essence of this Special Issue and provides a perfect starting point for this Editorial. Being able to sense the environment, process the information received, and respond in an autonomous fashion are important characteristics of biological systems. They allow them to self-regulate their activities, self-repair upon damage, and self-replicate – the quintessential hallmark of living systems. All these characteristics are dictated by communication between their constituents, e.g. signaling between cells, as well as interaction between the system and the environment. Mimicking such "embodied intelligence" in man-made materials yields a paradigm shift from responsive materials to ***interactive materials***, which will eventually give rise to adaptive systems and devices with "life-like" properties.

Interactive materials are driven by stimuli-responsive molecular building blocks that have to be (self-)assembled in order to translate the molecular-level property changes effectively to a desired function at the macroscopic scale. In order to succeed, the entire structural hierarchy from individual molecules and their supramolecular assemblies all the way to the resulting/emerging macroscopic systems and their associated functions has to be mastered. Once again, natural systems act as a great source of inspiration, providing many prominent examples of how molecular events are transduced and amplified to eventually culminate in vital biological functions that form the very basis of our existence. Work performed in and by cells is driven by molecular motor proteins, such as kinesin and dynein as well as myosin, whose movement is fueled chemically by hydrolysis of adenosine triphosphate. The vision event, in turn, is triggered by the universal biological photoswitch *cis*-retinal, which upon capturing a photon undergoes a structural change, kicking off a signaling cascade that eventually leads to a visual perception in the brain. The chemical fuels that drive these crucial biological processes

serve to sustain living organisms out of equilibrium, in a kinetic state of matter, in which covalent and noncovalent structures are continuously being formed, broken, and reformed. The resulting complex structural dynamics provides the basis for many biological functions, perhaps most importantly, the ability to respond and adapt.

This Special Issue deals with many of the aspects needed along the journey from responsive molecules towards interactive materials. This journey is guided by the principles learned from biological systems and machines. While synthetic materials may not fully match their biological counterparts in terms of complexity or sophistication, the remarkable collection of contributions by world-leading experts showcases the many faces of this vivid and exciting research field and its enormous future potential. We are especially proud to present several new contribution types, previously not featured in *Advanced Materials*. The *Vision Statements* by **Ben Feringa** (DOI: xxx) and **Peer Fischer** (DOI: xxx) provide overviews on the key concepts that guide us from single molecules to dynamic molecular assemblies, and eventually to applications such as autonomous soft robotics. The *Interviews* of **Takuzo Aida** (DOI: xxx) and **Samuel Stupp** (DOI: xxx), both among the pioneers in the field of supramolecular chemistry, provide the unique possibility to share some highlights along their journey to the forefront of contemporary materials science. Through the interview of **Dirk Broer** (DOI: xxx), the inventor of reactive mesogens, we gain insights into his views on the past and the future of stimuli-responsive liquid crystalline networks and functional coatings.

Other non-conventional article types introduced in this Special Issue are *Pros&Cons Articles* and *Viewpoints*. The former compares two widely used, yet orthogonal methodological approaches for addressing important goals in different areas of materials science. **Metin Sitti** and **Diederik Wiersma** (DOI: xxx) focus on magnetic *versus* optical actuation methods in mobile micro-robotics, as these two widely used stimuli sources have very distinct characteristics. **Rienk Eelkema** and **Andrij Pich** (DOI: xxx) compare the approaches of using non-covalent supramolecular networks *versus* covalent macromolecular networks in the

construction of functional hydrogels with advanced properties. In both contributions, specific areas where one approach outperforms the other can be identified. Nevertheless, merging the two seemingly opposing methodologies to yield additional synergies and degrees of control and tunability seems to be the choice for tomorrow. The Viewpoints, in turn, focus on some key concepts needed in the design of interactive materials. **Andreas Walther** (DOI: xxx) elaborates the differences between classical stimuli-responsive materials and next-generation materials that could be considered truly adaptive and interactive. **Joanna Aizenberg** and coworkers (DOI: xxx) discuss the concept of homeostasis in the context of synthetic materials, and how coupled feedback loops may conjure complex and emergent behavior. **Olli Ikkala** and coauthors (DOI: xxx) introduce synthetic model systems that algorithmically mimic classical conditioning, addressing a major challenge of "*allowing the interaction with the world to redefine the system itself so that it not only processes information, but also starts to learn*", as expressed by Peer Fischer in his Vision Statement.

The Issue also contains eight *Progress Reports* and five *Review Articles*, dealing with different aspects of molecular switches and machines and (inter)active materials and interfaces. **Alberto Credi** and his team (DOI: xxx) review the research on light-activated synthetic molecular machines. They point out that while several light-induced processes such as electron and proton transfer are underexploited as tools in molecular machinery, the aspect requiring the strongest research effort is the integration of molecular machines with their environment to produce macroscopic effects with potential value in practical applications. Putting molecular machines to work in concert in different kinds of stimuli-responsive materials is also the underlying theme for **Nicolas Giuseppone** and coworkers (DOI: xxx). They point out that only in few cases are systems made of molecular motors actuated in dissipative conditions, which would be needed in order to obtain autonomous materials with "life-like" properties. Dissipative self-assemblies, driven by chemically fueled reaction cycles, are further elaborated by **Thomas Hermans** *et al*. (DOI: xxx), painting a horizon where "life-like" materials with

inherently dynamic properties bridge the gap between inanimate and animate matter. Making and breaking (covalent) bonds in a reversible manner, alike in living matter, is also the topic of **Christopher Bowman** and coworkers (DOI: xxx) who exploit dynamic covalent chemistry in adaptive networks to yield stimuli-responsive, reworkable, and recyclable materials with the potential of replacing conventional thermosets in the future.

Light is the central theme in the contributions of the groups of **Stefan Hecht** (DOI: xxx) and **Rafal Klajn** (DOI: xxx). The former reviews different approaches of incorporating molecular photoswitches into various materials classes with different degrees of ordering, and the photoinduced effects that can be invoked therein. While reminding that to date, the only major commercial application of photoswitchable materials has been photochromic lenses for adaptive sunglasses, the authors are convinced that the future of molecular photoswitches is bright in the context of interactive materials with functions yet unimaginable today. The latter, in turn, describes the many ways of using light to control the assembly of nanoparticles of different kinds, outlining the future potential of such light-driven self-assemblies as well as the key challenges that still remain to be solved. In the future, the material will be the machine, as brought out in the comprehensive review by **Timothy White** and coworkers (DOI: xxx). They critically compare different kinds of stimuli-responsive materials in terms of their potential in soft actuators and robotics, highlighting the importance of the material itself to sense, respond autonomously, or even make decisions, all important attributes to interactive materials.

Incorporation of responsive molecules as active ingredients in (inter)active materials with different degree of ordering is highlighted in several contributions. **Oren Scherman** and coworkers (DOI: xxx) provide guidelines for the design principles of aqueous interactive materials, water being the prominent environment also for adaptive biological systems and prospective biomedical applications. The progress report of **Andreas Herrmann** and coauthors (DOI: xxx) on supercharged proteins and polypeptides illustrates that supercharging allows to control catalytic activity, and in combination with synthetic entities yields new materials for

thermotropic and lyotropic liquid crystals. The contribution of **Bart Jan Ravoo** and his team (DOI: xxx) deals with active interfaces displaying responsive wettability, permeability, or adhesion, pointing out that with the toolbox already available, the future application potential of (inter)active materials and surfaces is limited only by the imagination and creativity of scientists. Moving towards higher degree of order, several contributions focus on crystalline materials and their dynamic/responsive nature. **Pance Naumov** and coworkers (DOI: xxx) outline global performance metrics for dynamic molecular crystals, still a relatively underexplored class of materials as micro-actuators. Recent advances in light-responsive metal-organic frameworks and their applications are reviewed by **Christof Wöll** and coauthors (DOI: xxx). Finally, **Feihe Huang** and coworkers (DOI: xxx) review the work undertaken on macrocycle-based supramolecular crystalline materials, their structure-property relationships, and application prospects.

We are indebted to all the authors who have contributed to this Special Issue for their invaluable insights to eventually guide us to materials that are truly interactive – thank you very much! Moreover, we are thankful to the entire editorial team at *Advanced Materials* for their tremendous support and their willingness to experiment with the unconventional article types. We especially acknowledge Dr. Ulf Scheffler for seeding the idea of this Special Issue in Rehovot, Israel, in November 2018, and for all his help along the way. We realize that with one issue, it is only possible to scratch the surface of this multifaceted and rapidly expanding topic. Acknowledging this, we hope that this collection of articles will inspire the readers and provoke them to think of materials in ways that blur the borderline between synthetic and living systems. Posing questions which today may seem unconventional are usually the ones that disrupt the ways we think tomorrow. As George Bernard Shaw nicely phrased it: *"You see things; and you say 'Why?' But I dream things that never were; and I say 'Why not?"*

Arri Priimägi & Stefan Hecht

Biographies

Arri Priimägi studied physics in Tampere University of Technology (now Tampere University) and obtained his Ph.D. in 2009 from Helsinki University of Technology (now Aalto University), under the guidance of Prof. Matti Kaivola and Prof. Olli Ikkala. After Postdoctoral Fellowships at Tokyo Institute of Technology with Prof. Atsushi Shishido and Politecnico di Milano with Prof. Pierangelo Metrangolo, he was appointed to a tenure-track position at Tampere University in 2014, where he presently acts as a Professor of Chemistry. He leads a research group *Smart Photonic Materials*, focusing on functional soft matter, in particular light-active systems for photonic and soft-robotic applications.

Stefan Hecht studied chemistry at Humboldt-Universität zu Berlin and obtained his Ph.D. from the University of California at Berkeley in 2001, working under the guidance of Prof. Jean M. J. Fréchet. After establishing his own research group at Freie Universität Berlin and a subsequent position as a group leader at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, he returned to his *alma mater* in 2006 as the Chair of Organic Chemistry and Functional Materials. In August 2019, he became the Scientific Director of the DWI - Leibniz Institute for Interactive Materials in Aachen and holds the Chair of Macromolecular Chemistry at RWTH Aachen University. His research group is developing molecular systems with particular focus on utilizing photoswitches to control active and interactive materials, devices, and processes with light.