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# Chemistry in a Materials World

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The past decades have witnessed great advances in methods of organic synthesis. Future progress will also depend on crystallographic control combined with the use of translational symmetries, which are typically found in inorganic solid-state phases. With the shift in attention from unnatural hydrocarbon molecules and their physics toward natural products and their biology, however, one has lost sight of the physical properties of organic matter and of the chemist's unique ability to "synthetically" tune such characteristics.

Society regards chemistry with suspicion, while at the same time defining urgent needs regarding future technologies. Physicists and engineers have hurried to take on these challenges, raised a stellar amount of funding, and made optimistic promises. What is overlooked is that many of the applied materials are far from perfect. A few good examples come to mind when looking at lithium-ion batteries and fuel cells, important pillars of future electromobility. Graphite, used as the anode in such batteries, has a low charge-storage capacity. Inorganic materials are superior, but suffer from morphological instabilities arising from the great volume changes upon ion uptake and release. On the other hand, fuel cells employ Nafion membranes, which hardly match the needs in terms of stability, proton conduction, and water retention. Furthermore, platinum serves as the catalyst for oxygen reduction, yet the world does not have enough of this precious metal to equip the envisaged number of electrically powered cars.

Moving on to more sophisticated functions, silicon has proven to be a unique semiconductor that will dominate the fields of electronics and photovoltaics for the foreseeable future. Nevertheless, the requirements for further miniaturization may pave the way for the expanded use of new semiconductors such as graphene nanoribbons. These materials are fabricated by physicists through the unzipping of carbon nanotubes. Not surprisingly, in view of the harsh fabrication methods, the resulting materials lack structural perfection and control over the band structure, even if researchers speak of "smooth" edges. Are all these unsolved scientific and technical challenges not motivation enough for chemists to offer their superior abilities in synthesis and join the materials field?

> ***A redirection of chemistry toward materials and their properties would need an increased sense of structural complexity***

The transition from an organic compound to a material results in a defined macroscopic state of matter such as a thin film, a fiber, an ordered mesophase, or nanostructured morphology. Synthesis and processing must be combined in a unified approach and this integration may often include supramolecular order. Conjugated organic macromolecules as a representative case are characterized by their properties of light emission and charge-carrier transport. For electronic devices, these polymers are cast into thin films from solution, and what makes them unique is their ability to form defined nanostructures upon blending. Donor–acceptor polymers with alternating arrays of electron-rich and electron-deficient building blocks play a key role as low-band-gap light absorbers in photovoltaics and as semiconductors with high charge carrier mobility in field-effect transistors. Not only would the synthesis of these compounds be impossible without modern methods of transition-metal-catalyzed carbon–carbon coupling, but they also define challenges for synthetic rigor such as strict avoidance of structural defects, control of molecular weight and polydispersity, as well as scrupulous removal of catalysts. Additionally, there is significant room for creative structural modifications and deeper mechanistic studies of polymer growth.

What is still in its infancy is the controlled transition of these macromolecules to a desired mode of their solid-state packing. Before taking on this challenge and focusing on organic solids, one must consider the specifics of inorganic (solid) materials synthesis with an emphasis on catalysts made from metals, metal oxides, or intermetallic compounds. The issues here are different from those of organic synthesis since the varying phase stabilities and widths of binary, ternary, or even more complex compositions often lead to inhomogeneities in stoichiometry and microstructure. This diversity, which becomes particularly severe in multicomponent equilibria, severely limits the predictability of inorganic materials synthesis.

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Returning to the supramolecular features of organic macromolecules, how would one enforce the desired lamella-type packing of conjugated chains and their orientation with respect to the substrate surface? Morphologies are indeed influenced by the choice of building blocks and alkyl substitution, but the deposition of a conjugated polymer film remains complex when considering processes such as nucleation, phase formation, and wetting–dewetting. Also, one may well end up in kinetically trapped, unfavorable conformations and packing modes away from equilibrium states.

Let us not only consider organic one-dimensional polymers, but also their two-dimensional variants such as graphene. Graphene has exciting physical properties, but whether it holds promise for future technologies remains to be shown—regardless of the enormous amount of funding the field presently receives. Methods of graphene fabrication thus hold a decisive position. Graphene can be obtained by mechanically or electrochemically assisted exfoliation of single layers from bulk graphite, or by reduction of graphene oxide dispersions, both representing "top-down" protocols. Alternatively, there is the chance of a "bottom-up" synthesis of graphene by making polycyclic aromatic hydrocarbons larger and larger, finally into the micrometer range. Both approaches differ in "ease" of experimental procedures, available quantities, structural perfection, and processability of the material, but they could well be combined to create synergies.

In the quest for alternative energy technologies, solutions to the problems outlined above can be found with new materials. Hybrid materials, in which inorganic nanoparticles are wrapped up in graphene shells, combine high charge-storage capacity with morphological stability, and thus utilize the "best of both worlds" for next-generation batteries. In fuel cells, nitrogen-doped graphene sheets can outperform platinum as catalysts for oxygen reduction, if their fabrication succeeds in optimizing the location and electronic nature of the nitrogen centers as well as the porosity for mass transport. Nanostructured metal oxides are suitable catalysts for sustainable hydrogen production by photocatalytic water splitting, but their rational design, as mentioned above, is often hampered by the lack of control over the complex composition. A multitude of characteristics must be optimized, such as band-edge alignment, surface energetics, and optical absorption. Furthermore, growth of these materials may require control outside the thermodynamic regime, a situation that was invoked above for the deposition of conjugated polymers from solutions onto surfaces.

### Chemists must not become amateur physicists, but must be able to discuss the problems at hand

Thus, it appears that chemistry and materials science could mutually benefit from a closer interaction if a few conditions were fulfilled: 1) Chemists should use their structural imagination, knowledge of structure–property correlations, experimental skill, and theoretical background, but direct these powerful tools to materials and their properties. 2) Such a redirection would need an increased sense of structural complexity in which bulk properties of solids, and not only of molecules in solution, are studied. Interfaces can often play a decisive role. 3) In so doing, chemists must not become amateur physicists, but must be able to discuss the problems at hand and identify the methods needed for interdisciplinary efforts. 4) Evaluating the function of a material must be carried out in a device. This is a complex system including a multitude of components, and the "weakest" member of this chain could severely limit performance. 5) At the institutional level, academic research should lower the borders between disciplines both inside and outside chemistry, as well as educate scientists in a multidisciplinary spirit.

Chemists are under increasing pressure to explain their contributions to the public. This could be straightforward since there is no new technology without improved materials, especially in fields of immense societal importance such as energy, health, water, or sustainability. These materials must be made, and it is the chemist who knows how to do it, from which the leading role of chemistry for future developments can easily be derived. But why is chemistry more and more relegated to the back seat when driving toward new technologies? To begin with, the trouble with industrial research and development is that the players have timidly lost their sense of invention and that they trust engineering more than chemical imagination. The other problem is that chemists often view structural beauty as a higher goal than functionality of a molecule or material. Function does not necessarily mean practical or commercial application. To avoid becoming an enabling science, chemistry must define its own conceptual novelty. A few characteristic cases come to mind, such as 1) organic synthesis in the solid state, after immobilization on surfaces, or in nano(micro)reactors, 2) supramolecular design and morphology control for transport processes, 3) fabrication of three-dimensional porous structures with atomically precise voids and inner surfaces, 4) replication and self-healing of organic macromolecules, or 5) new concepts for inorganic catalyst materials to gain a deeper understanding of the prevailing active sites and abandon the notion of static catalysts in favor of chemical dynamics. I am fully aware that the reader may want to add further, probably much more relevant examples. These could well be regarded as "grand challenges" of chemistry that would have enormous consequences, but interestingly enough, they all contain ingredients of materials science. Their essence is a focus on structural and functional complexity over a wide length scale from atoms to the macroscopic state as well as over a broad range of time scales.

### Why is chemistry more and more relegated to the back seat when driving toward new technologies?

What should be added is that this definition of chemistry is equally relevant for physics and biology, and is thus far from “nonnatural”. For biomedical applications, there are both molecular and supramolecular challenges. An example of the former case is photocrosslinking of biodegradable and biocompatible polymers that furnish porous networks as scaffolds for tissue engineering. As to the latter case, sequence regulation of different segments of macromolecular architectures endows programmability not only to self-assembly processes, but also to folding, molecular recognition, biodegradability, and therapeutic delivery. Just as for the assembly of synthetic semiconductor molecules, formulation, delivery, and release of drugs require control over weak intermolecular forces and their stimulus-induced changes. Other examples are virus-mediated uptake of foreign DNA to encode a therapeutic protein, which depends on complex formation between polyelectrolytes, and the cell-type selective, “targeted” delivery of cytotoxic anticancer drugs. This delivery can be optimized by precise tuning of host–guest interactions to bind membrane proteins and initiate cellular uptake.

This Editorial is a personal view that is thus open for the reader’s conflicting arguments and outlooks, and it is written at a time when chemists all over the world discuss the future of their science. They need a critical reflection of the state-of-the-art and an open mind for unexpected developments, but materials will definitely gain more and more importance.

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