

# Reticular Chemistry and New Materials

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The societal problems we face today in climate change, clean energy, clean air, clean water, food, and health impact everyone on our planet. Solutions to these will require innovations in materials to bring about a more sustainable and resilient future. Some progress in understanding the basic science underlying these problems is being made and it is beginning to drive the invention and discovery of new materials. However, currently there is a gap between the materials we require and our ability to realize them. This is largely attributed to the fact that traditionally making extended chemical structures has been a trial-and-error activity with very little design expressed on the outcome of solid-state synthesis. This changed with the emergence of reticular chemistry, defined as the chemistry of linking molecular building blocks by strong bonds to make extended structures. As elaborated below this new chemistry laid the foundations for making atomically precise structures, which also could be chemically modified by design. The extension of reticular chemistry to linking nanoparticles and biological molecules, further widened the complexity and scope of the building blocks amenable to reticulation, thereby, ushering a new era in making new materials where the chemists' dream around the idea that 'if you think it, you can make it' becomes a reality (see attached figure).

Challenges also exist in the characterization of such extended structures when single crystalline samples are not accessible. Diffraction techniques have evolved to provide means of determining chemical connectivity of crystals in the nano-size regime. I wish to remark that even after addressing the design, synthesis, and characterization challenges, the study of materials properties is only the first step in determining the suitability of the material for a target application. It is becoming increasingly important that we as chemists must integrate into our research what might be termed the innovation cycle. This is the fundamental research which goes into not just molecules linked into materials but also materials form factors and their integration into systems (i.e., innovation cycle is molecule to material to engineering to system to society). These require expanding our knowledge beyond molecules and materials to encompass basic engineering principles. Since the materials we make can be designed with precision, study of the various parts of the innovation cycle provides a feedback loop between the molecular properties and system performance. It is worth noting that intensive research into each component of the innovation cycle has been carried out, but the science and engineering required for integrating these by *a priori* remains underdeveloped.

Attaining the knowledge to execute the innovation cycle in an orchestrated and correlated fashion and the speed in implementing it for a new material and application, will significantly speed up discovery and thereby scaling impact. We suggest that computation including artificial intelligence and machine learning will be critical to achieving these objectives, and without a meaningful coupling of the innovation cycle to modern computational tools, we will not capitalize on the potential the building block approach brings to the discovery of materials and their properties at the peril of society. Reticular

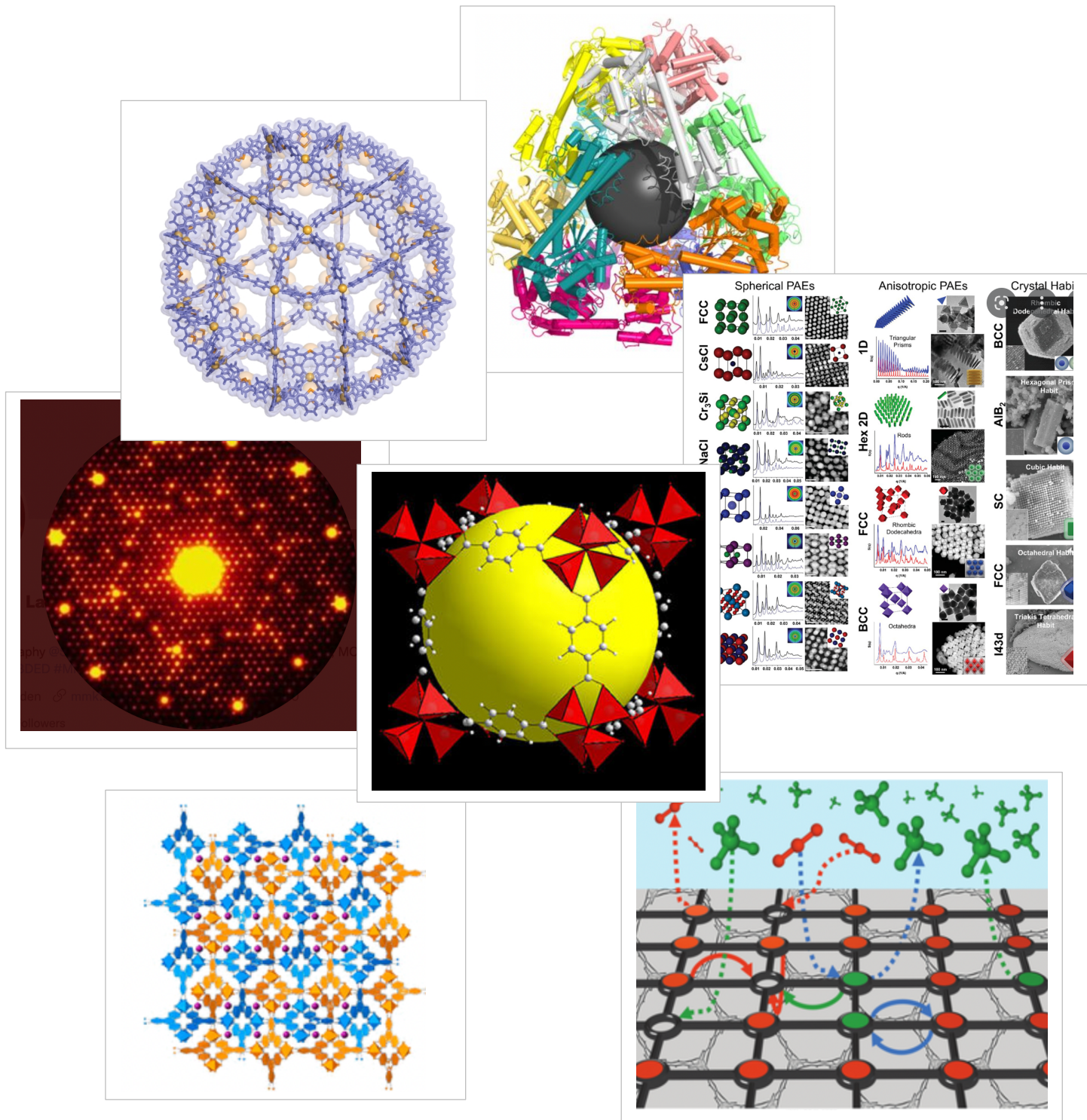
chemistry's logical approach involving the use of molecular or nano-sized building blocks is ideally suited for extending chemistry to engineering and computer science to effectively solve societal problems. This background provides the context for the presentations to be given at our symposium titled 'Reticular Chemistry and New Materials' at the 100<sup>th</sup> Anniversary of the Solvay Conference. The focus here will be on the basic ideas of reticulating crystalline extended chemical structures incorporating molecules, nanoparticles, and proteins as building blocks.

Every extended structure can be divided into linkers and nodes. The linkers join two chemical entities together (2-connected) and the node is 3- or more connected. The compositions of these can vary widely from simple to complex molecules, nanocrystals, and proteins. When such building blocks are linked together, the point at which they join is called the linkage. This is the 'glue' that allows the building blocks to stay together in the resulting extended structure. Such building blocks are necessarily large chemical entities to allow for expression of directionality and therefore design. This inevitably leads to open structures, an aspect that has led to ultra-porous crystals and consequently many applications in the fields stated at the outset.
















































When geometric building blocks are reticulated an important question arises that pertains to which structure among the almost infinite number of possible structures would result from the synthesis. A working hypothesis has been that if the building blocks are highly symmetric, it is the most symmetric structures which would result from the synthesis. Thus, for each combination of building block geometries, a few structures would be considered as reasonable targets. As the building blocks become progressively less symmetric, the possibilities are vastly increased. Presently, most structures made in reticular chemistry belong to those listed in the attached Table.

Diversity in this chemistry is achieved by varying the building block geometries, composition, size, and connectivity. Further diversification comes from the linkage variation and addition of functional groups to decorate the interior of the resulting structures. When multiple metal ions or functional organic groups (variants) are incorporated into a specific structure the diversity space increases exponentially. Although the nature of the functional groups or metal ions and their ratios in the structure are known, their spatial arrangements are unknown. However, the heterogeneous arrangements of these variants give a chemical rich environment capable of operating better than the sum of the parts. This scenario is conceptually related to DNA, where the nucleotides are superimposed and covalently linked to a repeating backbone: the variants in the reticulated structure are also bound to the ordered backbone to give sequences of variants running along the entire crystal structure. This 'complex order' is the basis a whole new and extensive chemical space whereby the reticulated structure properties are no longer discrete states but in fact they represented on a continuum of states. The implications of complex order of this type are that substrates can sample many different micro chemical environments to be bound and/or transformed.

In all these systems (synthetic and biological) the space encompassed by the reticulated structure is useful in selective binding and storage of guest molecules such as hydrogen, carbon dioxide, water, organics, and drug molecules. It has also been used for catalysis and installment of molecular machines. Given the precision with which structures can be reticulated, the extensive diversity of this chemical space, and the new powerful computational tools, it is not inconceivable that we will be able to design new materials representing concept transfer from biology. Specifically, materials capable of multiple functions and that can operate in parallel and in sequence, materials constructed from compartments that are open to each other, yet operate independently or synergistically, and materials programmed to sort and count molecules.



Clockwise starting at eleven o'clock: Makoto Fujita's large cage, Todd Yeate's protein cage, Chad Mirkin's nanocrystal assemblages, Joachim Sauer's accurate computations and prediction, Arne Thomas' silicon based organic framework, Xiaodong Zou's advanced electron diffraction techniques for nanocrystals, and center is Omar Yaghi's metal-organic framework. This collage illustrates the establishment of the building block approach to the synthesis of new materials and the evolving important role of computation and diffraction techniques in illuminating this chemistry.

Building unit 1 \ Building unit 2	2-c Linear	3-c Triangle	4-c Square	4-c tet	6-c Hexagon	6-c oct
3-c Triangle	 srs	 bwt, pyo, srs-b, ths-b	 fjh, fmj, gee, iab, yac, yao	 asn, ept, ofp	 cys, dnf*	 anh, ant, apo, brk, cep*, cml, czz, eea, qom, rti, tsx, zzz
4-c Square	 nbo, lvt, rhr	 pto, tbo	 cev, cdl, cdm, cdm, cds, cdz, mot, muo, qdl, qzd, ssd, sse, ssf, sst	 pts	 nts	 myd, ybh
4-c tet	 dia, lcs, qtz, sod	 bor, ctu	 fgl, mog, pds, pth, pli, ptr, ptt	 brl, byl, cag, cbt, coe, crb, fel, lom, kea, lon, pdl, qtz-b, sca, tpd, ucn	-	 alw, bix, cor, ing, spl, toc
6-c Hexagon	 hxg	 cys, dnf	 she	-	 hxg-b	-
6-c oct	 pcu, bcs, crs, reo	 pyr, spn	 soc	 gar, iac, ibd, toc	-	 pcu-b, bcs-b
6-c trp	 lcy, acs	 ceq, dag, fmz, hwx, moo, sab, sit, ydq	 stp	 fsi, hea, tpt	 htp	 nia
8-c cub	 bcu	 the	 scu, csq, sqc	 flu	-	 ocu
12-c cuo	 fcu	 sky	 ftw	 edc	-	-
12-c ico	-	-	-	 ith	-	-
12-c hpr	-	 aea	 shp	-	-	-
12-c tte	-	 ttt	-	-	 mgc	-
24-c tro	-	-	-	 twf	-	-

Tabulation of the resulting structures from combination of geometric building units. Unfilled squares indicate no chemical structures have been made for those geometries. This applies to networks of molecules, nanocrystals and proteins.

## FURTHER READING

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