Modeling of Nanomolecular and Reticular Architectures with Sixfold Grooved Programable Interlocking Disks

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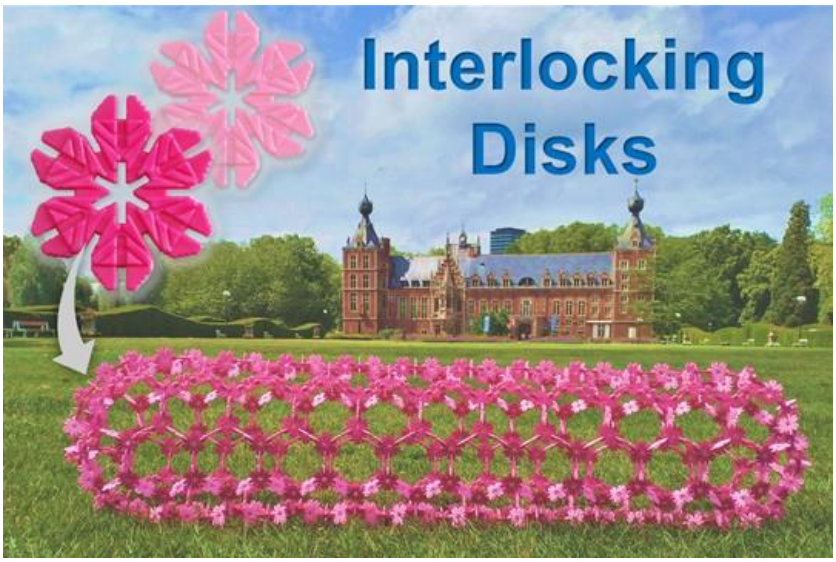
ABSTRACT

Single-type, 6-fold symmetrically grooved and commercially accessible interlocking disks (ILDs) have been used for modeling of sp^2 hybridized carbon-based nanoarchitectures, complex polyhedral and reticular material models. In the case of carbon-based nanoarchitectures we showcase that the primary ILDs can be directly used for representing individual atoms and bonds. Further on, the spatial connectivity of the primary ILDs can be extended by assembly of symmetrical secondary building units (SBUs). The constructed (deci)meter scale models are robust, light, scalable and suitable for classroom demonstrations. The ILDs technique is also suitable for use in workshop for facile discovery-based learning of nanomolecular structure, showing promise in wider use in the broader chemistry curriculum.

GRAPHICAL ABSTRACT



KEYWORDS

Demonstrations; Group Theory/Symmetry; Hands-On Learning/Manipulatives; Inorganic Chemistry; Materials Science; Molecular Modeling; Molecular Properties/Structure

Over the past century there have been significant efforts in development of simple and intuitive molecular modeling hands-on manipulatives that facilitate discovery-based learning, classroom demonstrations and enhance spatial reasoning, which are all necessary for comprehending complex molecular architectures and crystal structures.[1–4] Classical modeling toolkits relying on reusable ball-like and stick-like primary building units (PBUs) that easily interlock or interscrew, often provide an oversimplified view on molecular complexity, while retaining essential information on the local atomic coordination. However, as molecular and material complexity increases, complex physical models of molecular geometries involving large number of centers with varying coordination geometries are required. This motivates search for universal interlocking building blocks that are light, scalable, inexpensive and globally accessible. Attempts in this direction have started already in the 1930s, when it was proposed to use single type of polyhedral ball-like connector that can interlock with multiple sticks representing atoms and bonds respectively.[5] These type of models were shortly abandoned, but the interest in them reemerged in the 1970s due to the teaching demands of structural inorganic chemistry.[6,7] The concept of using single type polyhedral connector with multiple interlocking sites was excelled by the development of the so called "zometools".[8,9] The later methodology can be easily used in designing of robust complex polyhedral and reticular architectures, however high retail costs and trade embargos limit the application of this technique around the globe.

Development of alternative modeling approaches based on inexpensive or cost-effective building units such linearly interlocking "legoidal" building blocks have shown to be useful in modeling of complex nanoelectronics architectures,[10] at the same time the "legoidal" building blocks are too rigid and inflexible to have any broader application in stereochemistry.[11] Complex polyhedral topologies with relevance to inorganic chemistry have been designed based on inexpensive and commercially accessible materials such as paper,[12,13] straws,[14,15] beads,[16] and bottle caps,[17,18] however preparing models with these building blocks requires substantial manual effort and time while the components used for modeling often cannot be reused in a damage-free manner.

Inspired by these challenges, we have recently reported a new technique that relies on single type 8-fold symmetrically grooved commercially accessible plastic interlocking disks (ILDs) toy.[19] These building units are originally designed for training the motor skills of little children, however, intelligent use can

afford facile construction of versatile polyhedral and reticular architectures with relevance to modern inorganic and structural chemistry (e.g. zeolites, metal-organic frameworks, polyoxometalates and other). The 8-fold ILD (i.e. ILD^8) was chosen for our first study as it has high number of grooves that allow many different connectives which is reflected by the high number of secondary building units that can be designed, featuring coordination geometry different than that of the primary IDL^8. However, the ILD^8 has limitation in achieving planar coordination angles such as 60^O referring to sp^2 hybridized carbon centers. Although this in principle can be circumvented by use of large SBUs, the constructed models unnecessarily use numerous ILD components, which prompted study of ILDs with different number of grooves.

In this work, we showcase the use of commercially accessible, six-fold symmetrically grooved interlocking plastic disks resembling the form of flowers or snowflakes to which we commonly refer to as "ILD^6" where the superscript 6 reflects the number of grooves (Figures 1 and S1). The ILD^6 can adopt different spatial coordination which can be further used in "programming" complex structure such as models of polynuclear sp^2 hybridized carbon-based architectures (e.g. fullerenes and nanotubes) or reticular topologies with relevance to mesoporous framework materials. These aspects are summarized over the next sections.

PBUs and Structure Classification

The ILD^6-type building blocks are accessible as single type material with a diameter of 43 mm and a mass of 2.4 ± 0.1 g and thicknesses of ca. 3.5 mm. A single ILD^6 can connect with up to six other ILD^6, providing internal bite angles as multiples of 60° (i.e., 60, 120, and 180°). To enhance systematic description, the six grooves in a single ILD^6 can be enumerated from 1 to 6 (Figure 1a). Constructions of SBUs based on a central ILD^6 that directly connects between two and six ILD^6 can adopt many configuration modes. Among these, the linear ILD^6-(1,4) and the trigonal-binding ILD^6-(1,3,5) reminiscent of bond and sp^2 hybridized carbon centers respectively are the most important (Figure 1b). Removal of a single ILD^6 from the ILD^6-(1,3,5) leads to an "unsaturated" bent ILD^6-(1,3) linking mode that if used in construction of polygons or polyhedral and exhibits an unsaturated site for further connectivity (Figure 1b).

Discrete structures based on ILD^6-(1,3,5) and ILD^6-(1,4) lead to "saturated" with many polygonal faces, reminiscent of fullerene or nanotube topologies. Combinations of ILD^6-(1,3,5) and ILD^6-(1,3) can lead to high symmetry SBUs which are useful in construction of infinite networks. Examples of each of these aspects are provided over the next two sections. The authors also note that for construction of the models shown herein it is essential to have a disk rather than other symmetrically comparable building blocks (see Figure S2 and comment therein).

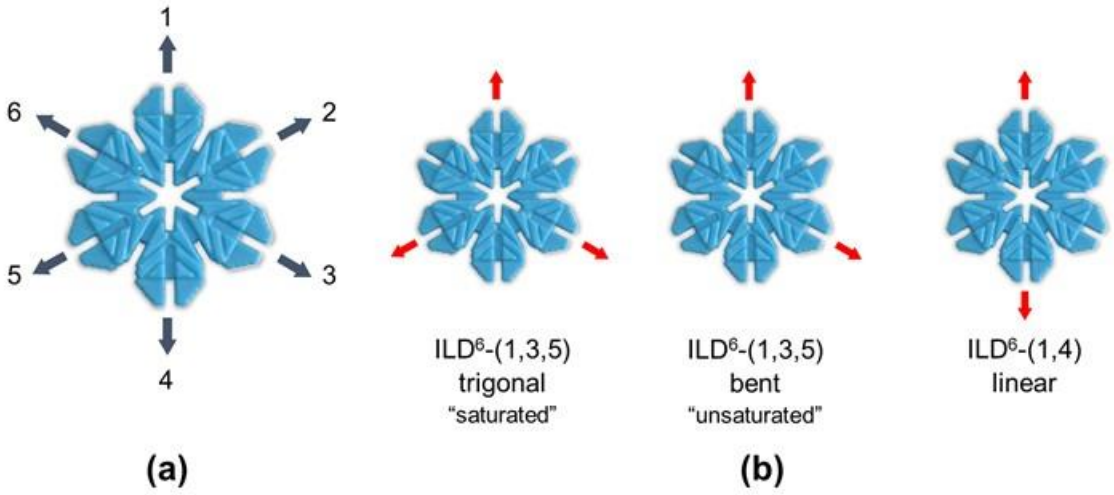


Figure 1. (a) Enumeration of the grooves in a single ILD^6. (b) Important symmetrical connectivity modes associated with a single ILD^6.

Modeling of Discrete "Saturated" Polyhedra

Carbon fullerenes are one of the most impactful chemical topologies and most commonly modeled systems in chemical and nanoscience education.[11,17–30] Combination of ILD^6-(1,3,5) and ILD^6-(1,4) can lead to an infinite honeycomb network reminiscent of single layer graphene structure (see Figure S3). However, as it is difficult to infinitively combine the building blocks, eventually models of patches of graphene ribbons are constructed that exhibit "unsaturated" ILD^6-(1,3,5) or ILD^6-(1,3) termini.

By exerting mild strain, pentagonal rings comprised of ILD^6-(1,3,5) and ILD^6-(1,4) units can be constructed (see Box S1 and S2). Interlocking of these pentagons with ILD^6-(1,4) units leads to models to truncated icosahedron topology that is reminiscent of the C_{60} fullerene model in rather facile manner. The produced C_{60} models are very robust and enduring, which makes them suitable for long term static

models. By exchanging the linear ILD^6-(1,4) with longer {ILD^6-(1,4)}$_n$ where n is an odd number (e.g. 3, 5, 7 etc.), one can linearly upscale the size of the constructed C_{60} fullerenes, however one should be aware that the longer linking units gradually add structural elasticity, in other words, they compromise the robustness found among the lower ILD containing models (see Figure S4). However, if the single linear ILD^6-(1,4) are retained, construction of high-nuclearity fullerene entities such as the theoretically relevant C_{180} fullerene[32,33] or single walled nanotube assemblies that provide fascinating perspective in the interior of these materials are achievable (See Figure 2.c,d and Figure S5). All these assemblies are (deci)meter scale, which makes them suitable for demonstrations in large classrooms or auditoria (Figure S6).

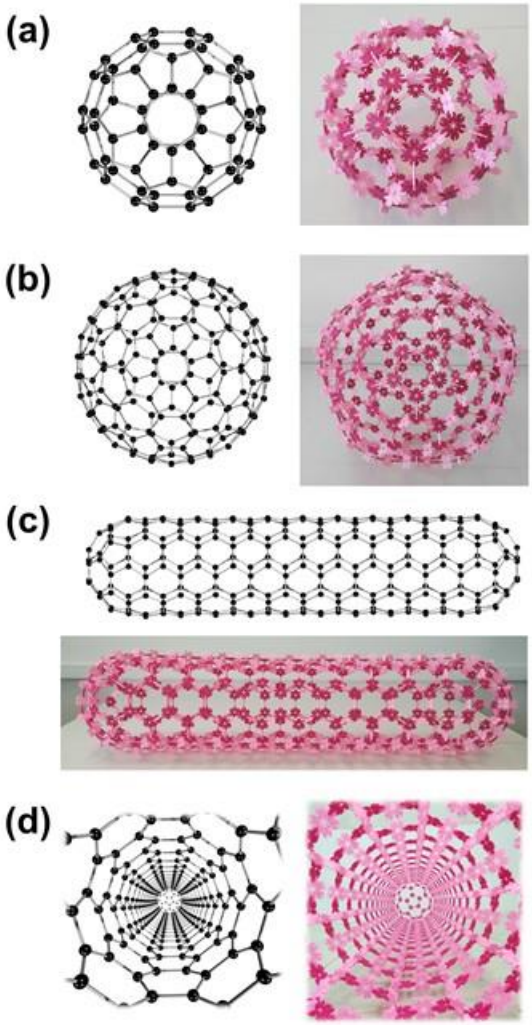


Figure 2. ILD^6 based modes of: (a) C_{60}; (b) C_{180}; (c) outer look of the Zigzag carbon nanotube mode made of 250 C-centers; (d) insider look in a zig zag carbon nanotube. C-centers are depicted by violet trigonally connected ILDs, while the C-C bonds are depicted by pink linearly connecting ILDs.

The construction of the C_{60} models takes 10-15 minutes for experienced chemist with no previous knowledge of the ILD technique and 20-30 minutes for non-chemists and persons of wide age ranges, previously unfamiliar to the ILD technique. The rapid construction timing and optical elegance is very crucial for effective discovery-based learning of carbon-based nanomaterials which we successfully implemented as a workshop during the Open Chemistry Department Day at KU Leuven (see Figure 3).

Figure 3. Photo highlights of the on first open workshop on building fullerene, nanotube and graphene models organized at the department of Chemistry at KU Leuven on 19 May 2019.

Modeling of "Unsaturated" Polyhedra and Reticular Networks

Combination of ILD^6-(1,3,5) and ILD^6-(1,3) in an unstained manner leads to the formation of four-fold antiprism-like connecting SBU with an overall D_{4d} symmetry point group and "ILD formula" {[ILD^6-(1,3,5)]$_4$[ILD^6-(1,3)]$_4$}. Two of such units can interconnect with four other ILD^6-(1,3) leading to the cuboctahedral SBU {[ILD^6-(1,3,5)]$_8$[ILD^6-(1,3)]$_{12}$} with an overall O_h symmetry point group to which we shortly refer to as CUB (see Figure 4.a).

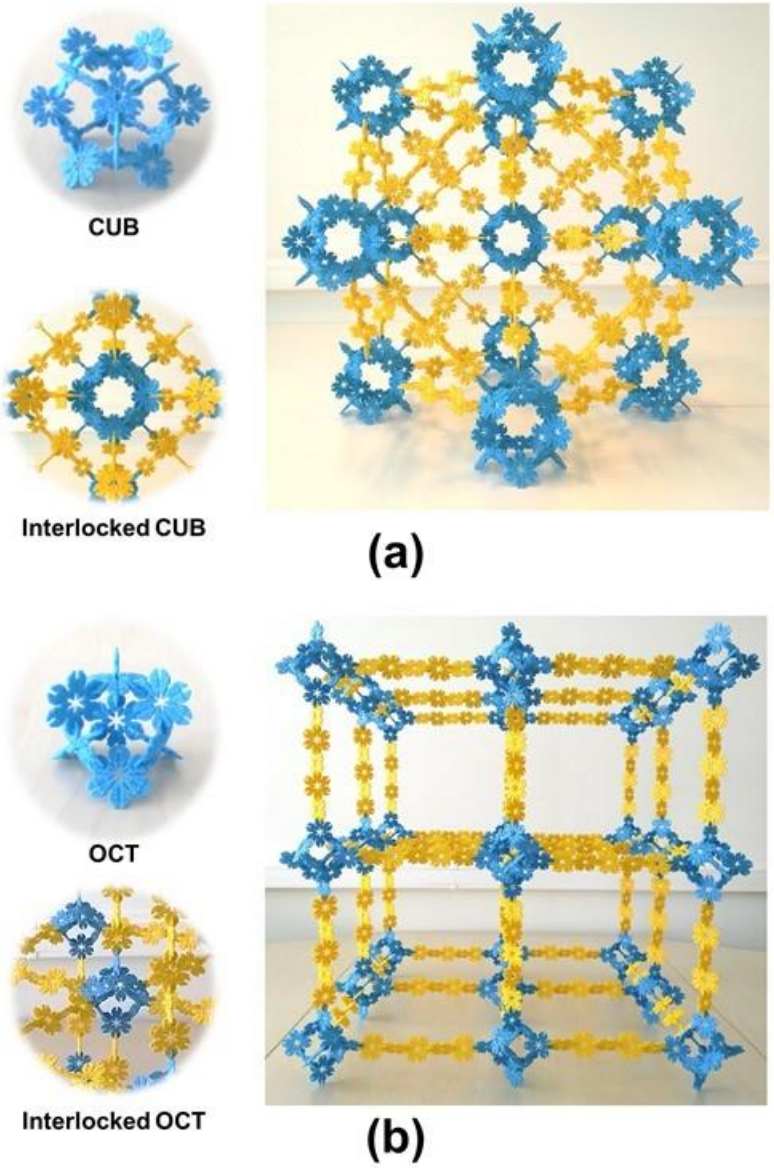


Figure 4. Fragments of reticular networks linked using [$ILD_6(1,4)$] linking SBUs (yellow) interconnected with (a) OCT and (b) CUB SBUs (blue).

This CUB SBU built of ILD^6 can provide spatial tetrahedral, square planar, dodecahedral and other intermediate connectivity, which are reminiscent to that made of ILD^8 with formula $\{[ILD^8\text{-}(1,3)]_{12}\text{-}[ILD^8\text{-}(1,3,5,7)]_6\}$. In essence the two CUB SBUs are comparable with a major difference that the CUB made of ILD^8 for its construction requires two PBUs less per unit, while ILD^6 has an easily accessible interior. To demonstrate the utility of the CUB connector we have constructed a segment of a reticular network

evocative of the connectivity in the metal organic framework UiO-66[34] and of the face-centered cubic crystal system typical for metals.

By introducing strain during the cyclization of ILD^6-(1,3,5) and ILD^6-(1,3) PBUs one can easily form three-fold of five-fold antiprism-like connecting SBU with an overall D_{3d} and D_{5d} symmetry point groups respectively. These unsaturated polygonal assemblies can be stepwise grown to polyhedral platonic solids, the tetrahedral {[ILD^6-(1,3,5)]$_4$[ILD^6-(1,3)]$_6$} and the dodecahedral {[ILD^6-(1,3,5)]$_{20}$[ILD^6-(1,3)]$_{30}$}. The tetrahedral {[ILD^6-(1,3,5)]$_4$[ILD^6-(1,3)]$_6$} SBU provides an octahedral connectivity and in essence it is comparable with the OCT SBU built of ILD^8 (see Figure 4.b). Its preparation is however far more facile and requires three times less PBUs, and as such it is a very convenient for use as an octahedral connector or for building primitive cubic crystal systems. On the other hand, the dodecahedral {[ILD^6-(1,3,5)]$_{20}$[ILD^6-(1,3)]$_{30}$} SBU may not have a direct utility in classical stereochemistry, however, it is worth nothing that it can be used as a basis for modeling of the 120-cell Coxeter polytope as shown recently by us,[35] which has relevance in understanding non-crystallographic groups[36] and the need of existence of Higgs particles.[37]

Summary and Outlook

In this work we presented the potential of the 6-fold symmetrically grooved ILDs in the learning of complex topological principles relevant in inorganic and nanomolecular chemistry and we discussed how the symmetry of the PBUs affects the ILD programmability and the accessible structural space. We have showcased that single type ILD^6 building blocks can be intelligently assembled into robust models resembling carbon fullerene and nanotubular architectures. Modeling of such architectures was found to be an excellent activity for promoting science by organization of hands-on activity workshop during Chemistry department open day. The facile and intuitive use of the ILDs during the workshop exemplified with minimal construction errors (see SI) together with the power to construct high symmetry and nuclearity architectures may provide secondary school and higher-education chemistry educators with a convenient toolkit to introduce topics related to cluster symmetry, solid state packing and reticular chemistry. During the work with the ILD^6, we recognized that strain exerted by the primary ILDs can provide a foundation for a personal “fingertips-feeling” that can help the user to develop

consciousness of the steric factors that go beyond classical Bayer strain theory[38,39] and effectively govern the formation of nanomaterials. The construction of large-scale models opens further demands for developing of ILD based helical molecular models with biological relevance. Further facilitation in terms of intuitive use of the ILDs may be achieved by combinations of complementary n-fold symmetrically grooved PBUs, which is currently explored by us.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

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