

Synthetic, 'inorganic DNA' as a means to high-density molecular electronics



Matthew Kapelewski

Penn State University, Email: mtk180@psu.edu

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Introduction

Molecular electronics is one of the fastest growing fields in modern science, and with good reason. Computers have become a part of the everyday lives of a majority of people around the globe, largely in part to the integrated circuit, seen in Figure 1. They have completely changed the way in which we communicate, do business, and learn. Constant advancement in such a field is highly desirable, as the benefits to such advancement abound. Unfortunately, the current silicon-based economy in the computer industry can only go so far, as there is a lower limit to the size of silicon based parts. Quantum computing and molecular assemblies provide an opportunity to surpass this silicon-imposed limit. Moore's Law is a description of a trend exhibited in computers since approximately 1965; this "law" states that the number of transistors that can be placed on an integrated circuit doubles every two years. Computer chip makers wishing to push Moore's Law to and beyond the current limits need to have the ability to shrink components within their systems to the molecular and atomic level.

A novel approach to doing exactly this is by using individual molecules as current-carrying structures. While in its infancy relative to other fields of science, molecular computing and single-molecule computer components are becoming a more realistic way to accomplish the miniaturization necessary for advancement. Molecules such as carbon nanotubes, seen in Figure 2, and $\text{Mo}_6\text{S}_3\text{I}_6$ [1] nanotubes promise to reduce the cost of these computer chips extensively if they can effectively be implemented as molecular computational tools. Such low-cost,

molecular computer chips would have far-reaching applications, from increasing computing power to better serve the ever-expanding infrastructure of the internet, to providing ultra-affordable technology to impoverished people around the globe.

Proposed "iDNA" architecture and formation of such structures through self-assembly

Paramount to this reduction in size is control of the formation of such structures. Self-assembly is an attractive option, as mass quantities of molecular wires can easily and quickly be synthesized by virtue of the fact that the molecules will assemble themselves in the desired arrangement. The prototypical molecule to look at as a basis for self-assembly is DNA, which has obviously been succeeding as a self-assembling structure since the dawn of life. Using DNA as a model, we have begun synthesizing novel compounds that are based, in theory, on the structure of DNA. Stoichiometric coordination of metal atoms to the pyridine-based ligands in Figure 3 can be used in place of hydrogen bonding in DNA to facilitate the self-assembly of this "inorganic DNA," or "iDNA." The structure of some basic types of these self-assembling molecules can be seen in Figure 4. In essence, we have a chain of "base pairs" that each have a certain number of nitrogens in them in pyridine rings, which can use their lone pair of electrons to chelate to a metal atom placed nearby. An example of this chelation can be seen in Figure 5.

The pyridine based ligands are self-complementary;



Figure 1: An example of an integrated circuit used in a computer

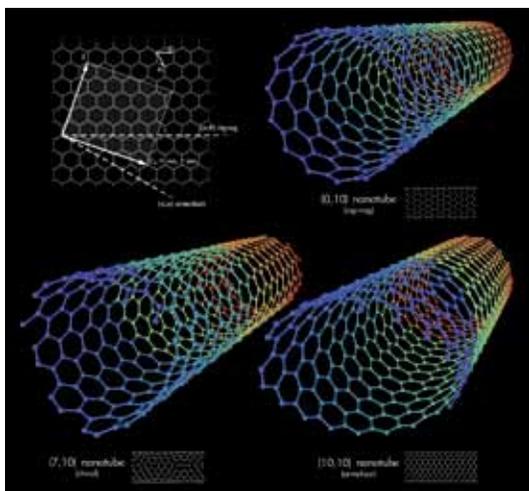


Figure 2: Different types of carbon nanotubes

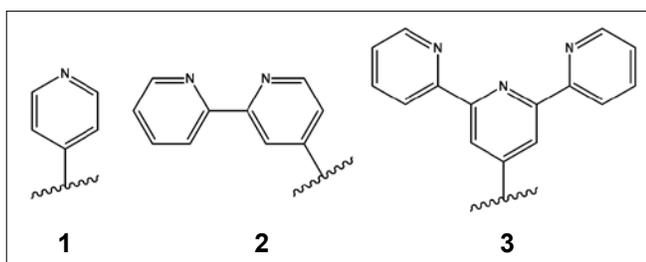


Figure 3: Pyridine (1), bipyridine (2), and terpyridine (3) ligands

this creates the self-assembly that is a critical part of this process. The structure of the ligands is that the pyridine and pyridine derivatives bind to a polyamide backbone. These monomers are then linked through deprotection and coupling to form di- and tripeptides, and longer oligomers. As an example, a pyridine-bipyridine-terpyridine tripeptide could be formed. This would bind in an antiparallel, self-complementary arrangement

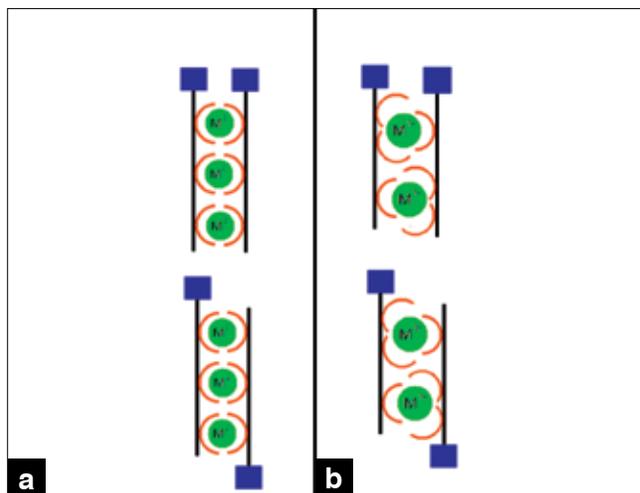


Figure 4: Alignment of ligands with (a) tetracoordinate and (b) hexacoordinate metals.²

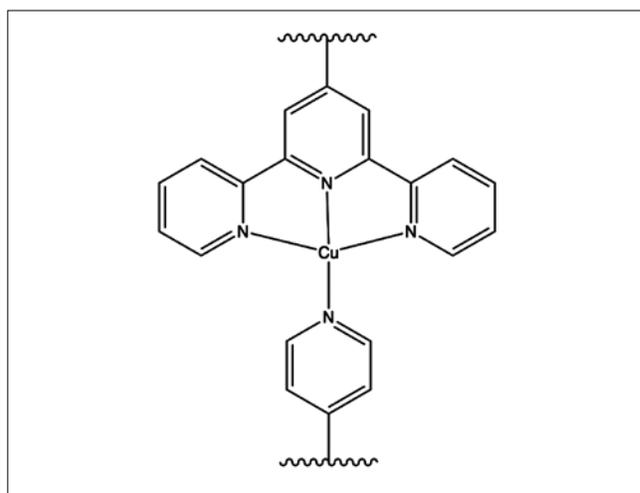


Figure 5: Terpyridine and pyridine ligands bonding to a copper atom

to produce the complex.^[2] This occurs because each of the three metal atoms that are being used has four coordination sites where the lone pair of electrons from a nitrogen atom can bind. The single pair in the pyridine will line up with the three pairs in the terpyridine to give four total pairs, while the two bipyridine ligands will align to give another four electron pairs. This is a system in which self-complementary chains of pyridine-based ligands form molecular wires, which can function as redox systems for multi-electron transport. Due to the structure of the molecules, electrons could hop from metal atom to metal atom down the center of the wire, effectively transporting them in one-dimension and creating a flow of electrons that constitutes a current.

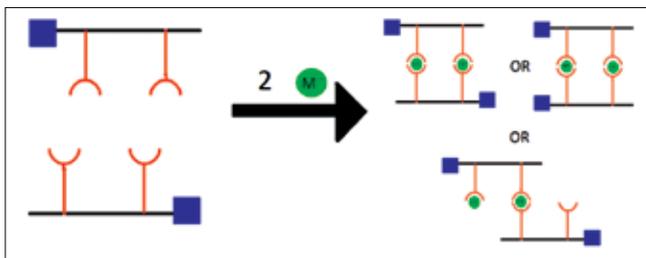


Figure 6: Formation of several isomers from basic iDNA building blocks^[3]

Separation of isomers

This setup of a molecular wire using electron hopping to carry current is a long-term goal, however. At this point, the project is still in its early stages, as the systems being studied are primarily di- and tripeptide systems. We have been synthesizing these self-complementary structures and examining their properties. One of the most prominent problems with the synthesis of these simple iDNA structures, as well as longer molecular wires based on this architecture, are possible isomers that can result from variations in the synthesis. Such isomers are important because they directly affect the physical and electronic properties of the compounds. It can be seen in Figure 6, that even the simplest building blocks, such as the two bipyridine dimers and tetracoordinate metal atom, can isomerize in multiple ways. The bottom product in Figure 6 could terminate at any length, yielding many different compounds. The difference between the other two products in Figure 6 is subtler, as the only difference is in the parallel or antiparallel arrangement of the strands. This isomerization problem manifests itself even more as the complexity of the system increases with the addition of longer strands or heterometallic complexes. Since only certain isomers of the complex are desirable, it is important to have the ability to separate these compounds in some way. Using a specific solvent system (5 ACN:2 H₂O:1 KNO₃) in a high performance liquid chromatography (HPLC) system, we are able to separate these compounds based on charge in a reverse-phase silica column. This process is able to

separate most of the isomers that are created, since they will have varying amounts of charged metal atoms in them. Analysis of the separation of the products of a synthesis can possibly assist in the creation of a more controlled synthesis of the desired isomer (in most cases, the antiparallel, controlled length chain).

Conclusion

The need for novel ways to increase computing speed is crucial to the advancement of the computing industry beyond silicon. Self-assembling molecular wires are one possible solution to achieve this. Although time is needed, this research in molecular, self-assembling wires is making strides toward achieving this goal and thus opening up new possibilities for computing power, which would benefit people around the globe.

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References

1. Vrbancic D, *et al* *****kindly provide rest of author names*****. Air-stable monodispersed Mo₆S₃I₆ nanowires. *Nanotech* 2004;15:635-8.
2. Gilmartin BP, Ohr K, McLaughlin RL, Koerner R, Williams ME. Artificial oligopeptide scaffolds for stoichiometric metal binding. *J Am Chem Soc* 2005;127:9546-55.
3. Myers CP, Gilmartin BP, Williams ME. Aminoethylglycine-Functionalized Ru(bpy)₃²⁺ with pendant bipyridines self-assemble multimetallic complexes by Cu and Zn coordination. *Inorg Chem* 2008;47:6738-47.

About the Author

Matthew Kapelewski, Penn State University, Email: mtk180@psu.edu

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