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Diamondoids – The Molecular Lego of Biomedicine, Materials Science and Nanotechnology

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A Brief Description of Diamondoids

Diamondoids are a peculiar class of organic molecules with unique structures and properties. Diamondoid molecules (AKA polymantanes, adamantologs) are cage-like, ultra stable, saturated hydrocarbons. The basic repetitive unit of diamondoids is a ten-carbon tetracyclic cage system called "adamantane" (Figure 1a). Adamantane consists of cyclohexane rings in 'chair' conformation. These molecules are called "diamondoids" because their carbon-carbon framework is completely, or largely, superimposable on the diamond lattice (Figure 2). Diamondoids show unique properties due to their exceptional atomic arrangements. The discovery of adamantane cage in 1933 [1] and its direct synthesis in 1957 [2] has turned this diamondoid and its derivatives into readily available compounds with numerous applications. Since 1960, the interest in practical applications of diamondoid molecules has steadily increased [3]. Diamondoids are presently molecular building blocks for biomedicine, materials science and nanotechnology that enable the design and manufacturing of nanometer-scale structures programmed to have virtually any desired shape and properties [4-6].

Diamondoids were first discovered in petroleum [1] and since there has been limited progress in synthesizing them there have been continuous efforts in exploring them in petroleum and other fossil fuels [7-10]. The presence of diamondoids in fossil fuels has become much more than a chemical curiosity and has advanced to be a resourceful instrument in biomedicine, materials science, and nanotechnology [6].

It has also been of major interest to discover the tremendous ways of derivativizing these molecules to do wonders in biomedicine, materials science and in the emerging field of nanotechnology [4-6]. The presence of chirality is an important feature in many diamondoids. The vast number of structural isomers and stereoisomers is another property of diamondoids. For instance, octamantane possesses hundreds of isomers in five molecular weight classes. The octamantane class with formula $C_{34}H_{38}$ and molecular weight 446 has 18 chiral and achiral isomeric structures. Furthermore, there is unique and great geometric diversity within these isomers. For example, rod-shaped diamondoids (with the shortest one being 1.0 nm long) and disc-shaped and screw-shaped diamondoids (with different helical pitches and diameters) have been recognized [11]. For diamondoids and derivatives property predictions and characterizations in addition to variety of experimental techniques which are reported in [6] the quantum mechanical abinito methods are being utilized [12-16].

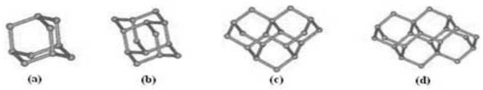

Figure 1: Molecular structures of lower diamondoids: (a): Adamantane (b): Diamantane (c): Triamantane (d): Anti- isomer of Tetramantane.

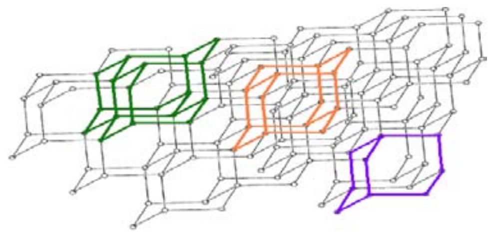

Figure 2: Structures of adamantane, diamantane and triamantane superimposed over the three-dimensional diamond network.

Diamondoid-based derivatives are used to fight cancer, Alzheimer's disease as well as viral, bacterial, and parasital infectious diseases. Utilization of diamondoids in synthesis of high temperature polymers, in polymer nanocomposites, and in crystal engineering are some of their major applications in materials science. Due to their six or more linking groups (Figure 3), diamondoids and derivative family of compounds (with over 20,000 variants) are the best candidates for templates and molecular building blocks in nanotechnology such as molecular self-assmbly (Figure 4), in design of NEMS and MEMS, in nanodrug delivery and targeting, in DNA-directed assembly nanostructure formation (Figure 5), and in host-guest chemistry.

Diamondoids have very high melting points as compared with other hydrocarbons and organic molecules. Diamondoids have negative electron affinities and they are transparent to visible light and high electrical insulating properties as diamond. Since diamondoids

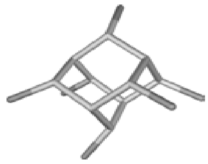

Figure 3: Six linking groups of adamantane [17].

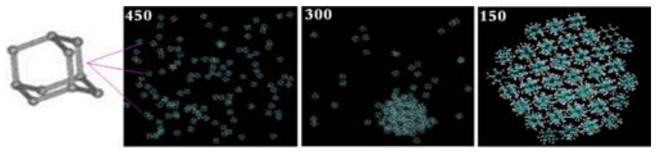

Figure 4: Self-assembly snapshots of 125 molecules of the adamantane, as temperature, in degrees Kelvin, is decreased [18,19].

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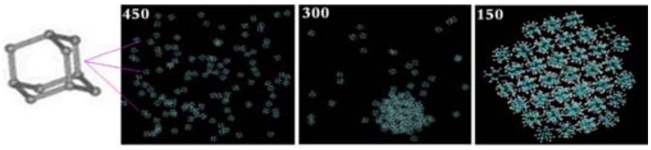

Figure 5: Diamondoid-DNA cube-shaped nanostructured assembly: (i) Green dotted lines showing hydrogen bonding between complementary sequences. (ii) Electrostatic potential surface of the cube-shaped nanostructure, where the red regions bear negative partial charges whereas the positive sites are colored in blue. (iii) The Corey-Pauling-Koltun model of the same nanostructure reflecting the square shape of each face [20,21].

also possess low strain energy, they are more stable and stiff, resembling diamond in a broad sense. They possess superior strength-to-weight ratio.

Biomedical Applications of Diamondoids and Derivatives

There have been great research interest and activities in understanding how diamondoid molecules interact with living systems, how these interactions could be useful in their biomedical applications, and characteristics of these molecules as tools for diagnosis and cell metabolism screening.

Among all diamondoids, adamantane and its derivatives have been most widely used for drug design.Starting from the late 50's and early 60's, the hydrophob ic nature associated with the compact and highly symmetrical structure of the adamantane molecule have attracted researches interested in the discovery of structurally unprecedented drugs, such as polyhaloadamantane pesticides [22]; and new or improved biological activities conferred by a caged moiety attached to known bioactive substances, such as orally active hypoglycemic sulfonylureas [23]. It is also known that adamantly group changes the properties of known drugs or provides an important pharmacophore for the design of new drugs [24].

Diamondoid derivatives in drug delivery and drug targeting, especially for the fact that due to their lipophilicity / hydrophobicity they can easily pass through blood-brain barrier. Adamantane nucleus, which is present in all adamantane derivatives, might be responsible for their ability to penetrate into the blood-brain barrier (BBB) and their accumulation in the CNS. Their applications for pharmacophore-based drug design, for drug delivery and drug targeting systems is a new matter of considerable importance [6].

Already diamondoids are used to design drugs in fighting infectious diseases like Influenza Viruses and HIV, bacterial infections like Gram-positive bacteria and MTB (*Mycobacterium tuberculosis*), and parasitic infection treatments like antimalarial drugs. Fighting cancer with diamondoids derivatives is another important application of these interesting compounds. Among such derivatives adaphostin retinoid derivative, is used for chemotherapy and exert selective antiproliferative and cytodifferentiating effects. These actions are of special interest in the search for new antineoplasic agents. Neuroprotective effect of memantine (a derivative of asamantane) and some other diamondoids derivatives for Alzheimer`s disease is another important set of biomedical applications of these compounds. Design of new antidotes to counteract the effect of a poison by diamondoid derivatives is an additional important application of these substances. A number of adamantane derivatives possess hypoglycemic action. And they are used as drugs fordiabetes treatments. In conclusion,

Antiviral drug
Cages for drug delivery
Crystal engineering
Designing molecular capsules
Design of new antidotes
Diamondoid-DNA nanoarchitectures
Drug delivery (they can easily pass through blood-brain barrier due to their lipophilicity / hydrophobicity)
Drug targeting
Fighting infectious viral diseases (influenza etc.)
Fighting infectious bacterial diseases (tuberculosis, etc.)
Fighting infectious parasitic diseases (malaria, etc.)
Fighting cancer (new antineoplasic agents)
Gene delivery
Hypoglycemic action (drugs fordiabetes treatment, etc.)
In designing an artificial red blood cell, called Respirocyte
In host-guest chemistry and combinatorial chemistry
MEMS
Molecular machines
Molecular probe
Nanodevices
Nanorobotics
Nanofabrication
Nanocomposites
Nanomodule
NEMS
Neuroprotective effect (for Alzheimer`s disease, etc.)
Organic MBBs in formation of nanostructures
Pharmacophore-based drug design
Polymer, co-polymers
Positional assembly
Power cells overcharge protecting compounds
Preparation of fluorescent molecular probes
Prodrugs
Rational design of multifunctional drug systems and drug carriers
Self-assembly: DNA directed self-assembly, host-guest chemistry
Shape-targeted nanostructures
Synthesis of supramolecules with manipulated architecture
The only semiconductors which show a negative electron affinity
Microelectronics (thermally conductive films in integrated circuit packaging, low-k dielectric layers in integrated circuit multilevel interconnects, thermally conductive adhesive films, thermally conductive films in thermoelectric cooling devices, passivation films for integrated circuit devices (ICs), and field emission cathodes)

Table 1: Major Applications of Diamondoids and Derivatives.

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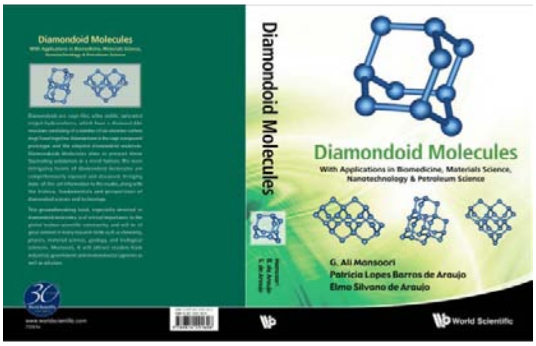

Figure 6: Diamondoid molecules with applications in biomedicine, materials science, nanotechnology and petroleum science [6].

diamondoids derivatives are an important family of compounds able to render diverse, strong, and sometimes unique biological properties to a multitude of drug classes. As many of these molecules are still in initial development phases, it will not be; surprising if a considerable amount of new cage compounds start to be a good addition to our medical supplies in a near future [6].

In Table 1 we report an alphabetical list of applications of diamondoids in biomedicine, materials science, nanotechnology. Diamondoids are fascinating molecules with interesting and promising applications as molecular lego in biomedicine, materials science, and nanotechnology. Recently a book (Figure 6) was published in which the details of diamondoids sources, properties and applications were reported.

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