DOI: 10.1002/anie.200701684

Diamondoid Chemistry

Diamonds are a Chemist's Best Friend: Diamondoid Chemistry Beyond Adamantane

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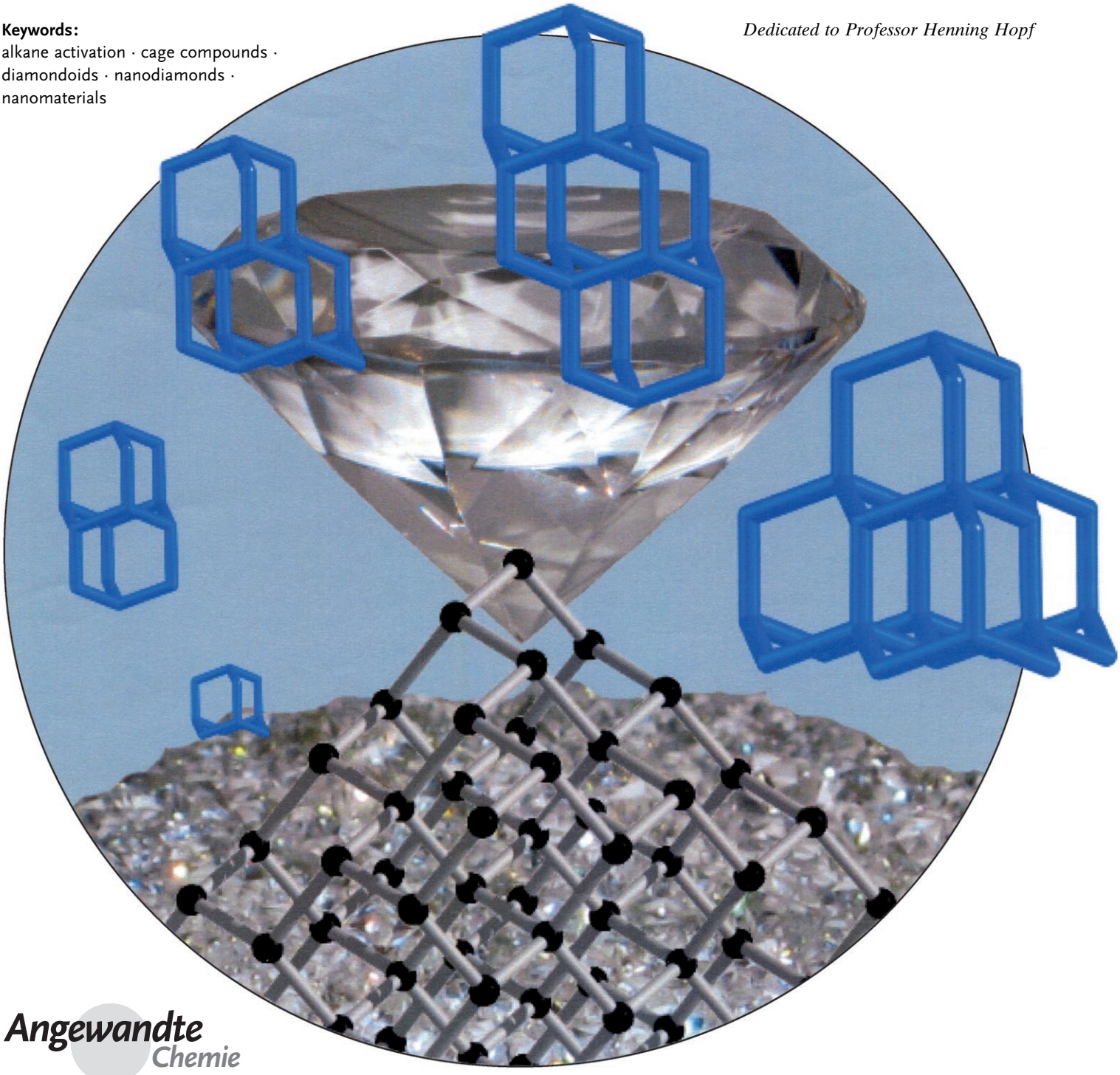
Keywords:
alkane activation · cage compounds · diamondoids · nanodiamonds · nanomaterials

Dedicated to Professor Henning Hopf



Marilyn Monroe knew that "diamonds are a girl's best friend" but, in the meantime, many chemists have realized that they are also extremely attractive objects in contemporary chemistry. The chemist's diamonds are usually quite small (herein: nanometer-sized "diamondoids") and as a result of their unique structure are unusual chemical building blocks. Since lower diamondoids (up to triamantane) have recently become available in large amounts from petroleum and higher diamondoids (starting from tetramantane) are now also accessible from crude oil new research involving them has begun to emerge. Having well-defined structures makes these cage compounds so special compared to other nanometer-scale diamonds. Selective and high-yielding synthetic approaches to the functionalization of diamondoids gives derivatives that can find applications in, for example, polymers, coating materials, drugs, and molecular electronics.

From the Contents

1. Introduction

For a scientist the worth of a diamond is not only measured by its weight in carats, the color, or the perfection of the stone but rather in its value as a material for research and technology. A diamond combines several very useful properties, such as extreme mechanical hardness, stability against chemical reagents, broad optical transparency, wide band gap, high radiation hardness, and high thermal conductivity.[1] Since diamond materials are known to have only a small or no adverse effect on living cells they can be used for biological, cosmetic, or medical applications.[2] For material scientists, physicists, and chemists the term nanodiamond (ND) is mostly associated with industrially processed single-crystalline diamonds, polycrystalline diamond films, or powders.[1,3,4] The term diamondoid ("diamantoid", German) was coined by Decker in 1924 during his attempts to synthesize diamonds.[5] Kleinfeller and Frercks used this term again in 1933 in their synthetic work towards diamondoid compounds;[6] they predicted the structure of the lowest diamondoid adamantane (**1**). Each of the diamondoids (alternatively named "polymantanes" by Balaban and Schleyer[7]) has a clearly defined structure (Figure 1). A simple, systematic classification and nomenclature of diamondoids was developed by Balaban and Schleyer.[7] The so-called Baeyer names of these compounds can be generated from a method created by Eckroth.[8] Since all diamondoids resemble parts of the hydrogen-terminated diamond lattice and because of their dimensions in the lower nanometer scale, these aliphatic hydrocarbon cage compounds are members of the carbon nanostructure family.

2. Diamondoids and Nanodiamonds

Shenderova et al. wrote that "*the term 'nanodiamond' is used to identify a variety of structures that include diamond crystals present in interstellar dust and meteorites, isolated diamond particles nucleated in the gas phase or on a surface, and nanocrystalline diamond films.*"[3] From the chemist's viewpoint this definition is problematic because those ND particles usually have a wide range of sizes that often exceed the nanometer scale. This lose definition was introduced at a time when higher diamondoids were not available. It is important to emphasize the difference because in contrast to nanodiamond powders, which are mixtures of isomers or even mixtures of compounds, diamondoids have a precisely defined structure. That is, they are chemically well defined, of high purity, and structurally well characterized. In view of many highly sensitive applications in medicinal chemistry and organic electronics this is an essential requirement. ND materials, such as films and especially powders, can be prepared commercially in ton quantities, for instance, by detonation or chemical vapor deposition (CVD) based techniques and have been explored by several groups in the past few years.[3,9] A major challenge is the purification of the crude ND powder. The powder can either be treated with oxidizing acid mixtures at higher temperatures,[10,11] directly converted into a fluorinated substrate with a H_2/F_2 mixture,[12] or reduced with $LiAlH_4$ or borane in THF.[13] For these

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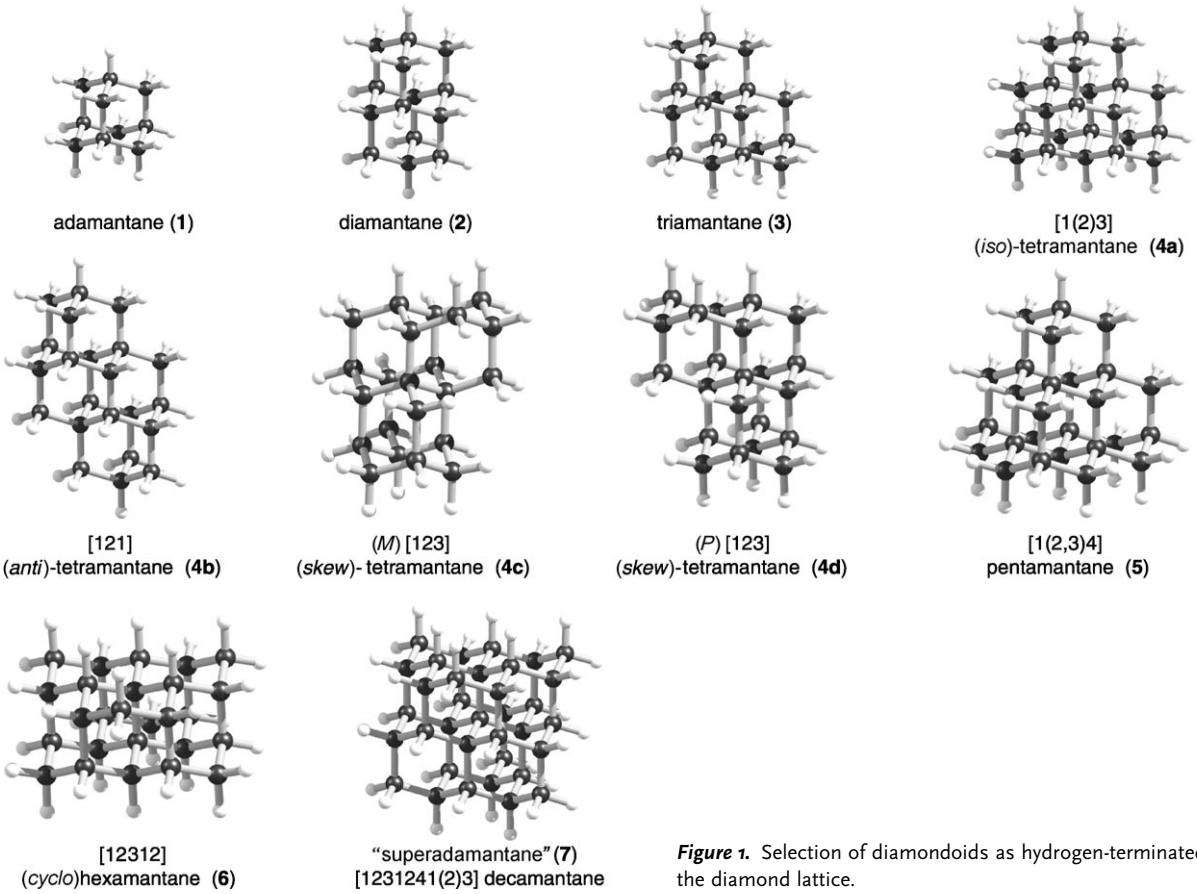
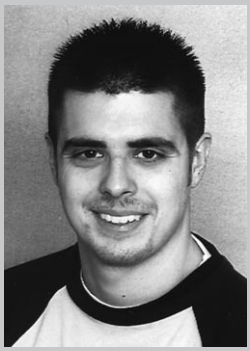


Figure 1. Selection of diamondoids as hydrogen-terminated parts of the diamond lattice.

"cleaned" powders several functionalization procedures have been developed. Loktev et al. treated ND powder with a mixture of HNO_3 and H_2SO_4 resulting in particles with carboxyl groups on the surface.[10] This substrate was treated with various reagents such as F_2, Cl_2, or H_2 and investigated by IR and X-ray photoelectron spectroscopy (XPS). In 2002 Tsubota et al. treated cleaned ND powder surfaces with benzoyl peroxides and investigated the resulting hydrogen abstraction by the benzoyl radical species.[11] Nakamura et al. used the photolysis of perfluoroazooctane to functionalize a diamond surface covered with keto- and carboxy groups.[14] Liu et al. showed in 2004 that it is possible to functionalize a fluorinated ND surface with various alkyl lithium compounds, diamines, and an amino acid (Scheme 1, top).[12,15] Recently Krüger et al. developed a procedure to synthesize silanized ND powders that can be linked to amino acids (Scheme 1, bottom).[13] Despite these advances in the functionalization the major disadvantage is the size and size distribution of NDs. Nakamura et al. as well as Tsubota et al. used commercially available "nanodiamond" powders with an average diameter of 0.5 μm,[11,14] whereas the ND powder used by Liu et al. had a "*tiny average particle size*" of approximately 3.5 nm,[12] which emphasizes the non-homogeneity of these materials.



Hartmut Schwertfeger was born in 1979 in Lahn-Giessen, Germany. He studied chemistry at the Justus-Liebig University Giessen (2001–2005) and received his degree in September 2006. During these studies in the group of P. R. Schreiner he worked on the preparation of functionalized diamantane derivatives. For his Ph.D. he is continuing his work on the selective functionalizations of diamantane and higher diamondoids.

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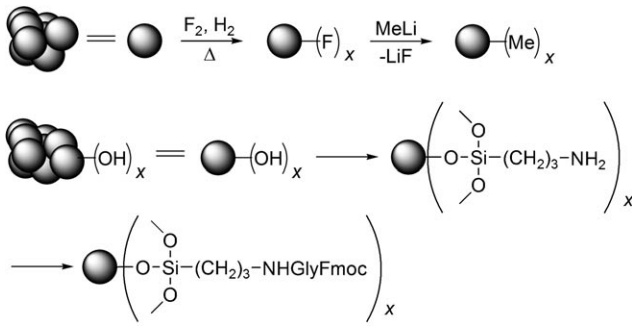

Scheme 1. Examples of functionalized nanodiamond powders (gray spheres).[12,13] Fmoc = (9*H*-fluoren-9-ylmethoxy)carbonyl.

Another problem is "… *the tight agglomeration of the nanodiamond primary particles, which hinders completely homogeneous surface functionalization and produces a rather broad aggregate size distribution*".[13] In the case of silanized and amino acid functionalized ND powder the agglomerates have "…*particle sizes in the range of several hundred nanometers* …".[13] These results show that nanodiamond powders are inhomogeneous and have a tendency to form agglomerates. This is in marked contrast to the diamondoids which can be prepared/extracted and functionalized selectively. Therefore it must be emphasized, that "diamondoids" are not the same as "nanodiamonds", irrespective of the fact that they are both nanomaterials. Owing to the increasing number of members of the carbon nanostructure family and without an exact classification system[3,16] incorporating all of them in a proper way, the term "nanodiamond" remains rather imprecise.

3. Origin and Synthesis of Diamondoids

Naturally occurring diamondoids can be isolated from crude oil, natural gas, and other hydrocarbon-rich materials. Adamantane[17] (**1**) and Diamantane[18] (**2**) were both discovered from the same crude oil near Hodonin, Czechoslovakia in 1933 and 1966, respectively. Since no methods for isolating and purifying **1** and **2** were developed, studying diamondoids from oil was not considered further for a long time. This situation changed around 1990 when the Mobil Oil Corporation filed several patents describing the separation of diamondoids from oil and gas. The impetus for developing these separation techniques was that diamondoids and some of their derivatives "… *cause problems during production and refining of hydrocarbonaceous minerals, particularly natural gas, by condensing out and solidifying, thereby clogging pipes and other pieces of equipment*".[19] Although Mobil Oil filed patents with methods to extract the diamondoids,[19,20] they quickly realized that these compounds "… *are themselves valuable products*".[19] As a consequence Mobil Oil filed patents concerning the recovery and purification of diamondoids from gas and oil[21] and the company began working on different utilizations of them (e.g. polymers, fuel additives).[22] By the end of 1995, diamondoids up to hexamantanes had been shown to exist in petroleum,[23,24] but these higher adamantologues could not be isolated. Lin and Wilk already suspected that "… *higher analogues of polymantanes, …, are also present in Nature*".[24] The proposal that diamondoids occur in all petroleum sources[25] was demonstrated by Dahl et al. in 2003 through the isolation and identification of 21 different higher polymantanes by HPLC techniques.[26] Dahl et al. also provided structural proof for cyclohexamantane (**6**), which is a disc-shaped large diamondoid.[27] The larger diamondoids and also the "*adamantane-of-adamantanes*" or "*superadamantane*" (**7**), which has not yet been isolated, were studied by Shen et al. in 1992 using computational methods.[28] The third possible source of diamondoid hydrocarbons after oil and natural gas are sediments, from which **1** and **2** could be identified along with other hydrocarbons.[29] From this point of view it would be interesting to know if diamondoids also occur in other hydrocarbon-rich materials, such as kimberlite rocks. A novel method for generating diamondoids has been published by Wei et al.[30] Their approach uses sediments or kerogen macromolecules. The hydrous pyrolysis of these in the presence of mineral catalysts, which are common in sedimentary rocks,[31] results in the formation of lower diamondoids. This result shows that acidic minerals, such as, aluminosilicates promote the formation of diamondoids. These results strengthen the proposal that, in nature, diamondoids may form through Lewis acid assisted rearrangements. Giruts et al. showed recently that **1** and **2** can be generated by thermal cracking of high-molecular-mass fractions from crude oils.[32] Since the lower diamondoids (**1**–**3**) are now available in kilogram and higher diamondoids in multigram quantities from MolecularDiamond Technologies[33] novel and exciting applications may be developed.[34,35]

Diamondoids can also be synthesized in the laboratory. Adamantane (**1**) was first prepared by Prelog and Seiwerth in 1941.[36] In 1957 Schleyer published a simple preparation of **1** through a so-called stabilomeric rearrangement of tetrahydrodicyclopentadiene by Lewis acids.[37] This chemistry has already been well reviewed.[38] At the XIXth International Congress of Pure and Applied Chemistry in London in 1963 Prelog used the then unknown second diamondoid as the congress emblem and encouraged the participants to consider its synthesis by writing in the foreword of the book of abstracts that "*The Synthesis of the Congress Emblem, …, is*

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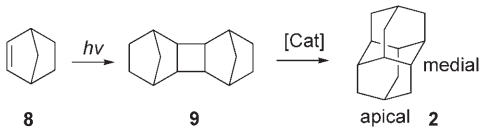
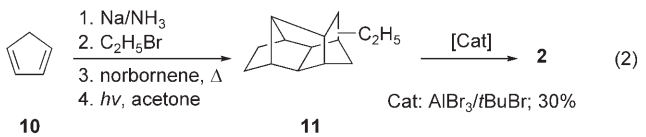
suggested as a challenging objective for the participants in the Congress."[39] Consequently Prelog named this molecule "congressane."[40] Two years later, Cupas et al.[39] published the first synthesis of congressane through a [2+2] photodimerization of norbornene (**8**) followed by stabilomeric rearrangement with $AlCl_3$;[41] unfortunately, the yield was only 1% [Eq. (1), method a].



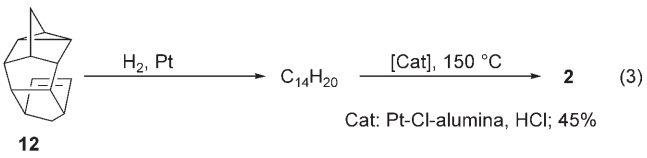
(1)

Cat:
a) $AlCl_3$; 1%
b) $AlBr_3$/*t*BuBr; 10–11%

In 1966 Vogl et al., who worked on hexaoxodiamantanes, proposed to abandon the word congressane and to rename the molecule diamantane (**2**) (Böttger also used the name "diamantane" once in his work for adamantane in 1937[42]) and the further diamondoids should be tri-, tetra-, etc to reflect the logical sequence of diamondoids.[43] Gund et al. first improved the norbornene dimer (**9**) synthesis [Eq. (1), method b] and found an even more convenient precursor that made the second diamondoid "*... as readily available as adamantane*" [Eq. (4), method a].[44,45] This method uses "Binor-S" (**13**) as the starting material[46] which was hydrogenated to give the desired $C_{14}H_{20}$ composition.[44] (other precursors were also tested but are not so readily available and high yielding as **13** [Eq. (2) and (3)][44,47].) Rearrangement of the tetrahydro Binor-S by various methods resulted in the formation of **2** [Eq. (4), methods b–d][47,48] or its derivatives.[47–49]

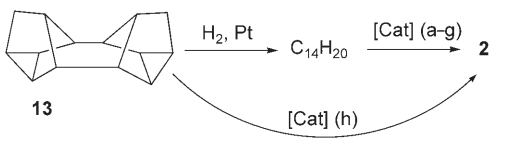


(2)



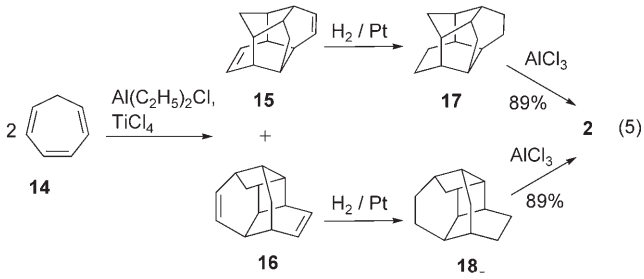
(3)

The mechanism for the formation of **2** from various pentacyclotetradecanes was investigated by Gund et al. in 1975 using computer-assisted theoretical analysis.[50] Kulazhanov et al. studied several catalyst systems for the hydrogenation of **13** and could show that platinum is the only metal catalyst to give a full conversion of **13**.[51] Olah et al. used superacids as well as a mixture of $NaBH_4/CF_3SO_3H$ to catalyze the rearrangement of **13** and tetrahydro Binor-S and give nearly quantitative yields of **2** [Eq. (4), methods e–h].[52,53] Turecek et al. used a cycloheptatriene dimerization catalyzed by titanium complexes, followed by hydrogenation and isomerization to prepare **2** in high yield [Eq. (5)].[54,55]



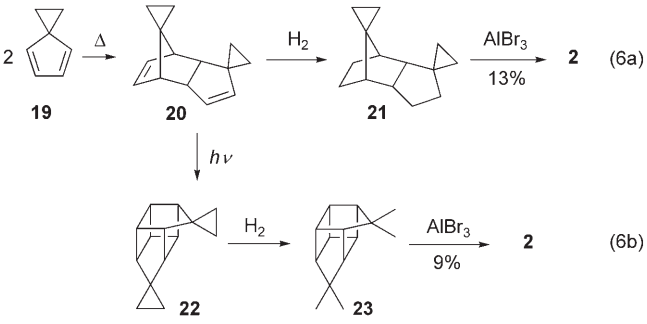
(4)

Cat:
a) $AlBr_3$, CS_2 or cC_6H_{12}; 60–75%
b) Pt-Cl-alumina, HCl, 150 °C; 70%
c) CH_2Cl_2, $AlCl_3$; 82%
d) H_2SO_4, 60 °C; 10%
e) $B(OSO_2CF_3)_3$, Freon-113; 99%
f) CF_3SO_3H-SBF_5 (1:1); 98%
g) CF_3SO_3H-$B(OSO_2CF_3)_3$ (1:1); 98%
h) $NaBH_4$, CF_3SO_3H, Freon-113; 99%



(5)

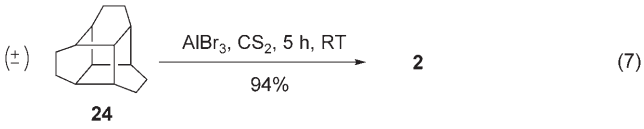
A very interesting but unfortunately very low yielding synthesis of **2** was shown by Khusnutdinov et al. in 1988 in which the dimerization of spiro[2.4]hepta-4,6-diene was followed either by a direct hydrogenation/isomerization or photochemical [2+2] reaction and hydrogenation/isomerization [Eq. (6a,b)].[56]



(6a)

(6b)

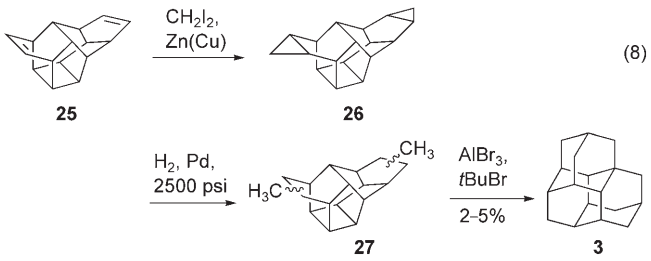
Nakazaki et al. synthesized **2** by rearrangement of D_3-tritwistane which is also a pentacyclotetradecane [Eq. (7)].[57]



(7)

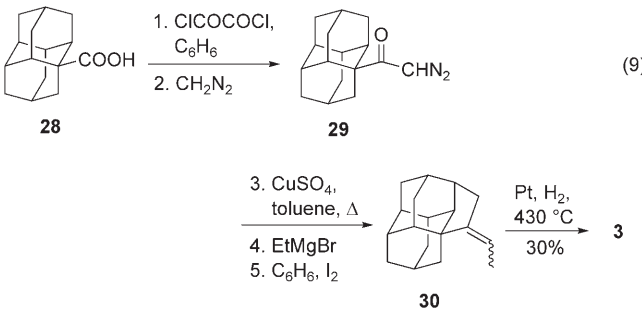
Another pathway is the stepwise elaboration from **1** developed by Fărcaşiu et al. in 1977.[58] This method is in principle a route to synthesize even higher diamondoids but it is not practical owing to the many steps required. Takhistov et al. used phenylcyclopentane and phenylcyclohexane to prepare methyl and dimethyldiamantanes.[59] Grubmüller et al. showed that the opposite approach, the dealkylation of methyldiamantanes and even triamantane (**3**), also leads to the formation of **2**.[60] Another interesting, if still theoretical pathway, for the preparation of higher diamondoids should be mentioned at this point, because it was one of the earliest ones. In 1970 Fujimoto et al. proposed that "*... polyamantane might be produced by the electrocyclic polymerization of p-quinodimethane...*" but this to our knowledge has never been tried.[61]

The third member of this logical series, triamantane (**3**) was synthesized by Williams et al. by the cyclopropanation of a cyclooctatetraene dimer followed by reductive cleavage of both cyclopropane rings and isomerization.[62] The yield of **3** was very low and varied between 2–5% in the final step [Eq. (8)].



(8)

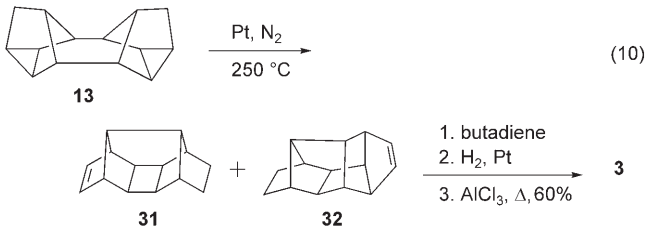
A higher yielding synthesis based on rearrangements was published in 1975 by Burns et al. who started from 1-diamantanecarboxylic acid (**28**) that gave **3** through a so-called "*single homologation*" in low yield [Eq. (9)].[63]



(9)

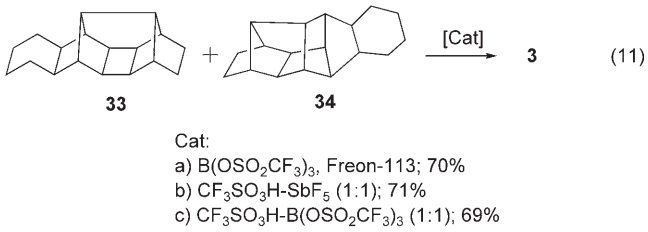
An even better synthesis for **3** was discovered by Hamilton et al. when heating **13** on a platinum catalyst in the absence of hydrogen gas,[64,65] which results in the formation of cyclic monoolefins that undergo Diels–Alder reactions with butadiene. Hydrogenation/Lewis acid rearrangement gave **3** with moderate yield [Eq. (10)].

By changing the diene from butadiene to isoprene it was possible to isolate various methyl derivatives of **3**.[65] This kind



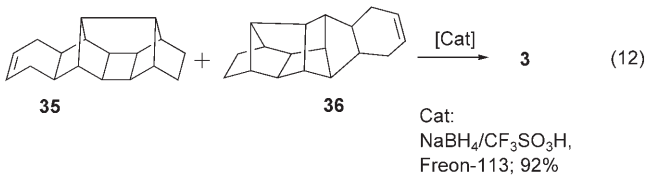
(10)

of reaction pathway was studied in more detail by Kafka et al. by using various Lewis acids for the isomerization of **13**;[66,67] the products of the Diels–Alder reaction with the resulting hexacyclic olefins were also studied.[68] Farooq et al. showed that it is also possible to catalyze the rearrangement of heptacyclooctadecanes with superacids and to get a 70% yield of **3** [Eq. (11), methods a–c].[52]



(11)

Even heptacyclooctadecenes can be converted into **3** in high yields by using $NaBH_4/CF_3SO_3H$ [Eq. (12)].[53]

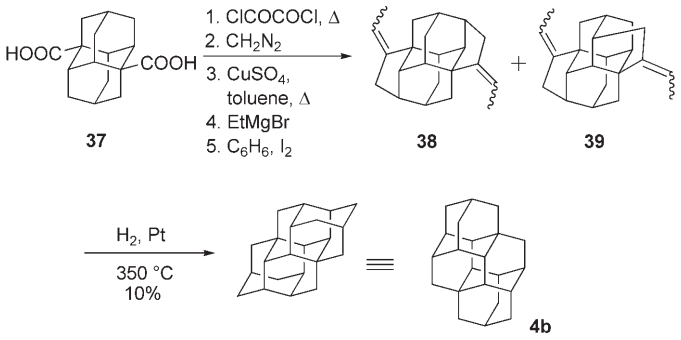


(12)

As with **2**, computational studies on the triamantane rearrangement were conducted by Tanaka et al. in 1983.[69]

The next logical member of the diamondoid series is tetramantane (**4**) which already exists as three isomers (*iso*-tetramantane (**4a**), *anti*-tetramantane (**4b**), and two enantiomeric *skew*-tetramantanes (**4c**, **d**)). Its synthesis was attempted by Schleyer et al. "*... by the same Lewis acid rearrangement approach successful for the lower members of the series*,"[70] but this was unsuccessful; their resulting molecule was called "*a Bastard Tetramantane*" (or short bastardane).[70,71] The only tetramantane isomer synthesized to date is *anti*-tetramantane (**4b**; Scheme 2).[72] Burns et al. used the same approach (now a "*double homologation*") as for **3** and utilized 1,6-diamantanedicarboxylic acid (**37**) as the starting material. The X-ray analysis confirmed the structure of **4b**.[73]

For a general review on adamantane (**1**) and higher diamondoid rearrangements as well as a review of synthetic



Scheme 2. Synthetic route to *anti*-tetramantane (**4b**).[72]

approaches for higher diamondoids see the articles by McKervey and by Verbrugge who called these cage molecules strange organic compounds.[74]

4. Diamondoids as New Building Blocks

The availability of diamondoids from natural resources initiated studies in to their use as building blocks for a large variety of applications. Their geometrical shapes (Figure 1) and the possible "transcription" of bulk-diamond properties, such as extreme hardness, and thermal conductivity, to diamondoids has drawn a lot of attention towards these molecules. This line of thinking receives an important justification through the fact that Badziag et al. could show that nanometer-sized diamonds are actually more stable than graphites of similar sizes.[75]

Several groups have been studying the electronic structures of diamondoids[76] and one key result is that diamondoids should have negative electron affinities (NEA).[77] Yang et al. could show that this NEA exists for **4b**.[78] "*This opens up to the possibility of coating surfaces with diamondoids to produce new electron-emission devices.*"[77] It is well known that functionalization is an essential condition for any application. Therefore our work concentrates on the development of methods to functionalize these aliphatic cage compounds selectively.

5. Functionalization of Diamondoids

5.1. Adamantane

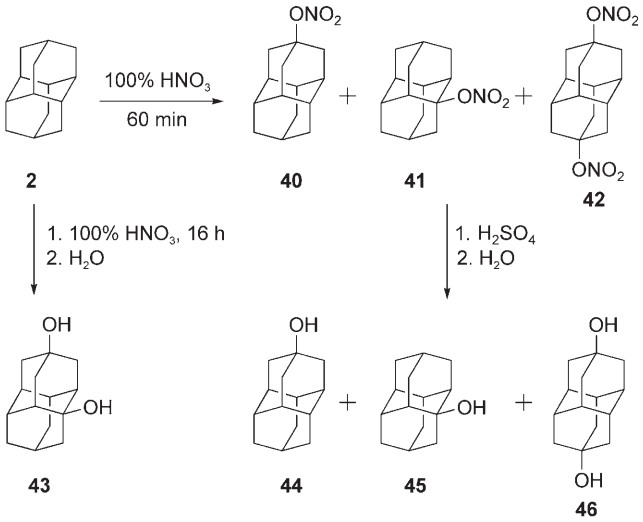
Adamantane (**1**) chemistry has been studied and reviewed very extensively in the last 50 years.[38,79] Owing to the fact that the smallest diamondoid has only one kind of tertiary and one kind of secondary carbon atoms its functionalization is easy, in terms of selectivity, compared with the higher adamantologues. For instance, it is possible to prepare derivatives of **1** with four different substituents in the tertiary positions.[80] These compounds are chiral but difficult to separate, because of their near spherical shape. Recent mechanistic studies of adamantane as a model helped rationalize and predict the behavior of higher diamondoids in the presence of radical, electrophilic, and oxidative reagents.[81]

5.2. Diamantane

Diamantane (**2**) is more challenging when it comes to its selective functionalization because it has two different types of tertiary C–H bonds. These compose the six "medial" positions of the central cyclohexane and the two "apical" positions [see Eq. (1)]. The first functionalization of diamantane (**2**) was accomplished by Gund et al. who were able to prepare a dozen new compounds.[82] Diamantane chemistry has been well reviewed by Janku and Burkhard[83] who covered the literature from 1965 to January 1988. Some aspects are briefly repeated herein because they lay the ground for our explorations of selective diamondoid C–H functionalization methods. Arguably, the best precursors for subsequent functional group transformations are the bromide and alcohol derivatives of diamantane (**2**). The bromination reactions have been studied by various groups and it was shown that seven different quaternary bromo derivatives could be synthesized and characterized.[47,82,84–98] Secondary geminal bromides were studied by Burkhard et al. in 1988.[99] Even though the preparation of the tertiary bromo derivatives is in principle a simple preparative task, the separation of mixtures and especially the selective synthesis of the apical derivatives is rather difficult and the yields are very low. Recently published results show that the most stable diamantane cation is the one with the positive charge located close to the geometrical center of the cage (this result holds for all other diamondoids).[91] Therefore the only bromides that can readily be prepared are the mono- and bisaxial ones which can be prepared in good yields without the use of Lewis acids. For large-scale production, however, the bromination route seems rather cumbersome.

Much more readily available are the alcohols of **2**. All the literature procedures for the preparation of alcohols either modify diamantane derivatives (e.g., hydrolysis of bromides or chlorides)[47,48,82,86–89,95,97,98,101–104] or use **2** directly as the starting material.[105–108] There is also additional literature that deals with characterization[84,109] and the possible equilibration of the monoalcohols **44** and **45** (Scheme 3).[110,111] Unfortunately the yields of the direct hydroxylation methods of **2** by Jones et al. with lead(IV) salts,[105] Olah's bis(trimethylsilyl)peroxide synthesis,[108] and Leddy's pathway using permanganates[106] are oftern low or require the use of metal complexes.[107] Our group also developed a method for the direct hydroxylation of diamantane (**2**) using *m*-chloroperbenzoic acid but the conversion (43%) and the yields (23% for **45** and 4% for **44**) are also not high enough to prepare large amounts of alcohols.[91]

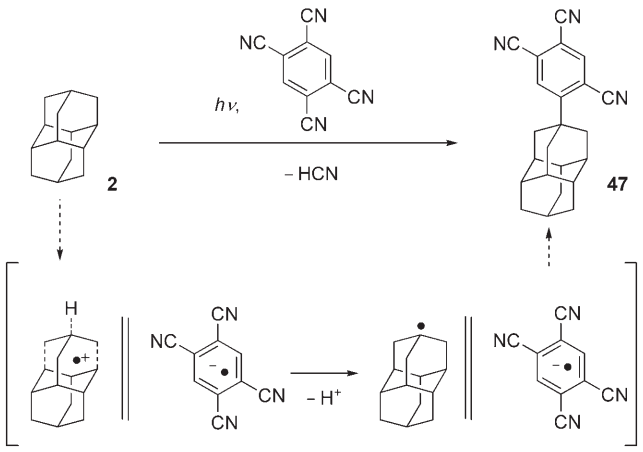
A more convenient approach for the hydroxylation of diamondoids is the nitroxylation and subsequent hydrolysis.[112] Especially our direct nitroxylation of **2** and isomerization in sulfuric acid is high-yielding (over 90% total yield) and can even be conducted easily on a 200-g scale (Scheme 3, right pathway).[100,113] The nitroxy derivatives are generated through a hydrogen-coupled electron transfer from a nitronium nitrate and they are hydrolyzed to the respective alcohols.[91] The major advantage of this method is that by varying the reaction parameters the yield of each alcohol (**43**–**46**) can be changed. Long reaction times during the nitro-



Scheme 3. Alcohol derivatives of diamantane (**2**) by oxidation using 100% nitric acid.[100]

xylation give the dialcohol **43** with 50% yield, while shorter reaction times allow the preparation of mono alcohols. With short reaction times for the treatment with sulfuric acid more of the monosubstituted alcohols (e.g., up to 44% of **44** and 24% of **45**) form. By increasing the reaction time, the bisapical alcohol **46** can be prepared in up to 78% yield. This is, to our knowledge, the only reaction that gives the apical derivatives with very high yield and is halogen-free.

Fluoro[92,114] chloro,[47,48,86,91,92,96,99,104,111,115] and iodo[91,92,116] derivatives of **2** were also prepared and characterized. The well-studied[117] alkyl derivatives are available by Grignard coupling,[82,86,92,95,118] or by methylation with diazomethane under UV-radiation.[119] Photochemistry was not only used to prepare alkyl compounds but was also the method of choice by Tabushi et al. to prepare acetyl derivatives.[102] Irradiation was also used by our group to demonstrate that the selective functionalization of diamantane (**2**; and higher diamondoids) is also possible when radical cations are involved (Scheme 4).[91] The single-electron transfer (SET) photooxidation of **2** with 1,2,4,5-tetracyanobenzene (TCB) gives the

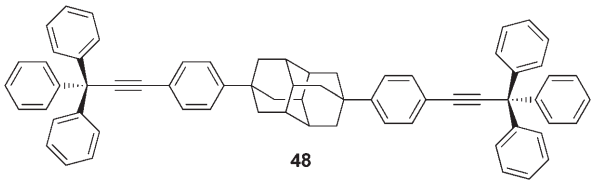


Scheme 4. Photooxidation of **2** with tetracyanobenzene is 100% selective.[91]

apically substituted derivative **47** exclusively (at low conversion).

Very interesting derivatives for pharmacological applications are acetamides[82,86,91,94,116,120–122] that can be hydrolyzed under acidic or basic conditions to the respective amines.[82,86,94,116,121,122] Another possible way of preparing amines is the hydrogenation of the azides,[90] and a direct amination with $NCl_3/AlCl_3$ was also attempted but is low-yielding.[123] A common feature of all these methods is that they do not allow the preparation of large quantities. Just recently our group was able to solve this problem and amines can easily be prepared from the alcohols in two steps in high yields.[124] These amino derivatives are important compounds in terms of further functionalization, especially for the preparation of peptides. The best counterparts for a peptide bond are arguably carboxylic acids. These diamantane carboxylic acids,[82,86–88,97,98,125,126] their methyl esters,[84,88,98,101] acyl chlorides,[127] acetic acids derivatives,[128] and their bromine- or hydroxy-substituted derivatives[84,87,101,129] have been prepared and studied very intensively by various groups in the past few years.

Karlen et al. used **2** as a stiff spacer in molecular gyroscopes **48** (Scheme 5).[130] The structure of **48** in

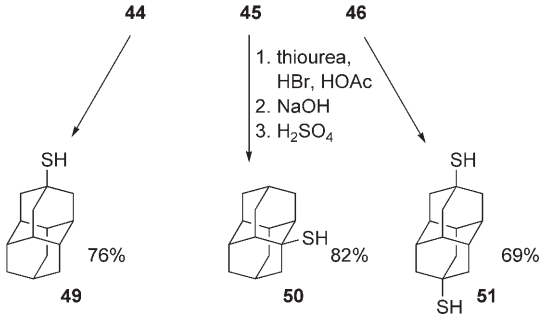


Scheme 5. Diamantane moiety in a "molecular gyroscope".[130]

Scheme 5 emphasizes both the stiffness of the carbon framework and the 180° angle in **2** that is a welcome linear building block not only as a mechanochemical device, but also as a spacer, for example, in polymers. In the early 1990s the group around Malik, Archibald, and Baum worked on new polymers based on ethynyl diamantane derivatives[93,131] and the condensation of the dimethylester of 4,9-diamantanedicarboxylic acid with, for example, 2,5-diamino-1,4-benzenedithiol.[98] Chern and co-workers used **2** as a rigid spacer and linked its carboxylic acid, amine, and phenyl derivatives with the corresponding components to prepare polyimides, polymaleimides, polyamides, and polyesters.[94,122,125,127,132,133] In 2004, Dang et al. synthesized polyarylenether ketones with **2** as the structural unit.[134] Diamantane polymers have been covered in a review by Meador.[135] Even though some of these polymers show very interesting features, such as high-subglass transition temperatures or low dielectric constants, none of them seems to have been used in practice.

The rigid three-dimensional structure of diamondoids is not only useful in polymers but is also of interest, for example, for the preparation of thin-layer coatings. To attach diamondoids to noble-metal surfaces, such as gold (forming of self-assembled monolayers (SAMs)), thiol derivatives are the best choice. The first preparation of thiol derivatives of **2** was published by Cahill in 1990 using bromo derivatives as

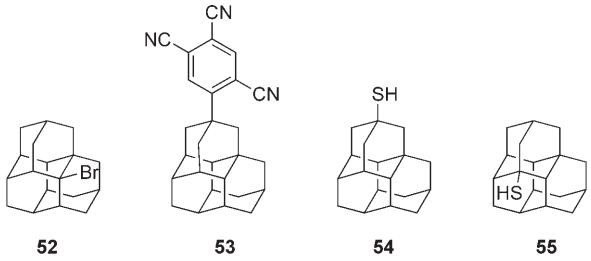
starting materials.[123] Even though the yields were quite good, the disadvantage of this procedure lies in the necessity of using bromo derivatives as starting materials. By using our high-yielding procedure for preparing medial, apical, and bisapical alcohols of **2** very selectively, our group was able to synthesize diamantane thiols (and higher adamantologues) in good yields from these alcohols (Scheme 6).[136]



Scheme 6. Preparation of diamantane thiols from the corresponding tertiary alcohols.[136]

5.3. Triamantane

Triamantane (**3**) is the first diamondoid that has a quaternary carbon atom. There are also four different tertiary positions and three non-equivalent methylene groups, which make functionalizations rather challenging. Even though **3** can be synthesized in high yields from various precursors [Eq. (8)–(12)], only a few derivatives are known. Hollowood et al. described the preparation and characterization of bromo and hydroxy derivatives by bromination, Lewis acid rearrangements, and hydrolysis.[137] Leddy et al. used various permanganates for the synthesis of hydroxy derivatives of **3**.[106] Kafka et al. prepared triamantanones, alcohols, and a carboxylic acid derivative through various oxidation methods (nitric acid, sulfuric acid, chromium trioxide, etc.) of **3**.[67,138,139] Besides these few functionalization reactions, other groups investigated **3** in terms of "*low-frequency light scattering*",[140] "*room temperature specific heat anomaly*",[141] phase transitions,[142] Raman spectra,[143,144] the partial molal volume of bromo triamantane[145] and strain/substituent effects on ^{13}C chemical shifts.[95,146] Further chemical functionalization studies were undertaken by our group resulting in new selective methods for the preparation of bromides (e.g., **52**), mono- and bisalcohols, tricyanophenyl (**53**), acetyl and acetate derivatives (Scheme 7).[100,147] We were also able to prepare the highly valuable thiol derivatives **54** and **55** (Scheme 7).[136]

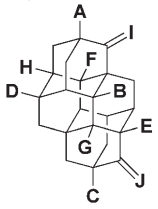


Scheme 7. Examples of triamantane (**3**) derivatives synthesized by our group.[136,147]

5.4. Tetramantane

The functionalization of any of the four isomers had not been described prior to our work, and we recently prepared a variety of *anti*-tetramantane (**4b**) derivatives (Table 1).[147] Even though **4b** also has four different types of tertiary carbon atoms and three non-equivalent methylene C–H bonds, the observed selectivities are much higher than for **3**. As with triamantane (**3**), various bromides, mono- and bisalcohols, and acetate derivatives were synthesized.[100,147] Oxidation of **4b** and an alcohol to ketones was accomplished

Table 1: *anti*-Tetramantane (**4b**) derivatives synthesized by our group.[100,136,147]



4b

A	H	H	Ac	Ac	OAc	OAc	H	OH	OH	H	H	OH	OH	H	H	TCP[a]	H	OH	H	SH	H	SH
B	Br	H	H	H	H	H	OH	H	H	H	H	OH	H	H	H	H	H	H	H	H	SH	H
C	H	H	H	Ac	H	OAc	H	H	OH	H	H	H	H	H	H	H	H	H	H	H	H	SH
D	H	H	H	H	H	H	H	H	H	OH	H	H	H	H	H	H	H	H	H	H	H	H
E	H	H	H	H	H	H	H	H	H	H	OH	H	H	H	H	H	H	H	H	H	H	H
F	H	Br	H	H	H	H	H	H	H	H	H	H	H	H	OH	H	H	H	H	H	H	H
G	H	Br	H	H	H	H	H	H	H	H	H	H	OH	OH	OH	H	H	H	H	H	H	H
H	H	H	H	H	H	H	H	H	H	H	H	H	H	OH	H	H	H	H	H	H	H	H
I	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	O	H_2	H_2	H_2	H_2	H_2
J	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	H_2	O	O	O	H_2	H_2	H_2

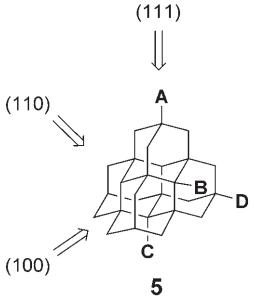
[a] TCP = tricyanophenyl.

together with the selective photoacetylation.[147] Thiols of *anti*-tetramantane (**4b**) were also synthesized.[136] Owing to the stick-like shape of this molecule and the selective functionalization possibilities (bisapical thiols and alcohols), it is a very useful building block for many applications of diamondoids. Theoretical studies of the molecular structure and Raman spectra of **4** have been conducted by Chang et al.[143]

5.5. Pentamantane

Of the possible ten pentamantanes only the [1(2,3)4] pentamantane (**5**) has been functionalized.[148] This molecule has a pyramidal shape that allows it to fully cover a metal surface, particularly suitable for this are its thiol derivatives. Pentamantane (**5**) has a size of approximately 0.8 nm and is the simplest centrosymmetric hydrocarbon which has the (111) face of diamond (Table 2).[148] In terms of functionalization, we managed to prepare different bromo, hydroxy, nitroxy, and thiol derivatives (Table 2). The SET oxidation of **5** with TCB gave, as expected, exclusively the peripheral product. Interestingly, these reactions are more selective than for triamantane (**3**) and *anti*-tetramantane (**4b**).

Table 2: Pentamantane (**5**) with a (111) diamond face and its derivatives.[148]



5

A	H	H	H	H	OH	Br	ONO_2	OH	Br	TCP[a]	SH
B	H	H	Br	OH	H	H	H	H	H	H	H
C	Br	OH	Br	OH	H	H	H	H	H	H	H
D	H	H	H	H	H	H	ONO_2	OH	Br	H	H

[a] TCP = tricyanophenyl.

5.6. Higher Diamondoids

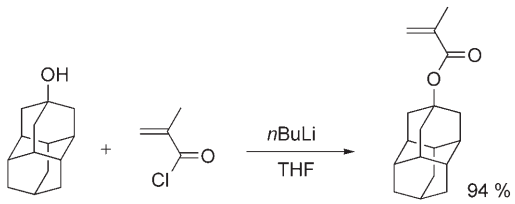
To our knowledge no diamondoids other than the *anti*-tetramantane (**4**) and pentamantane (**5**) have been functionalized to date. Just recently, DFT studies of **6** were undertaken by Richardson et al.[149] that confirmed our earlier results.[91] We are currently working on the functionalization of **4a**, **4c**, **4d**, and cyclohexamantane (**6**).

6. Applications of Diamondoids

Since a broad variety of diamondoids is now readily available from various natural sources in sizable quantities, many applications (only a few can be mentioned herein) may be envisaged because of their unique structures and properties. Spectroscopic studies of IR,[150] Raman,[151] and vibrational[152] behavior were investigated recently and the results "*... may strengthen a possible detection of this family of compounds in different astrophysical objects, ...*".[150] This would demonstrate that diamondoids are not only present on Earth but also in interstellar space (diamonds on the nanometer scale have already been found in meteorites[153]). Owing to their high stability under extreme conditions diamondoids were used as internal standards for liquefaction studies of coal.[154] Chen et al.[155] used diamondoids for estimating the age of mature crude oils and they introduced the so-called methyl-diamondoid indices for **1** and **2** that also allow geochemical studies of petroleum, molecular fossils, biodegradation models, and source rocks.[156] Dahl et al.[25] showed that the "*... diamondoid concentrations increase in a predictable fashion with increasing temperature*", and "*... the possibility of using their concentrations as a measure of oil destruction.*"[157] Hence diamondoids can be used as "fingerprints" for petroleum products, such as natural gas condensates or gasoline.[158,159] These GC/MS methods rely on the fact that other biomarkers, such as terpenes and steranes, are removed from the original crude oil during the refining process, but the much smaller and far more stable diamondoids are concentrated in the petroleum products.[159] That diamondoids can be destroyed under certain conditions was published by Wei et al. who investigated the "*fate of diamondoids in coals and sedimentary rocks*".[160] They could show that "*... at high temperatures, diamondoids are cracked into aromatic hydrocarbons, gases, and pyrobitumen, and that aromatic hydrocarbons are possibly the most stable compounds occurring in petroleum*".[160]

Adamantane (**1**) is well established as a building block for many pharmacologically active compounds (for example, in drugs against Parkinson's and Alzheimer's diseases).[161] However, only a few derivatives of the higher diamondoids have been explored for pharmaceutical uses. Heyd et al. showed in 1982 that derivatives of **1** and **2** are hypobetalipoproteinemic agents.[162] Upjohn filed patents where aniline derivatives of **1** and **2** are used as "*... hypolipidemic agents, particularly hypocholesteremic...*".[163] Mobil Oil investigated several different compounds of **1** and **2** for pharmaceutical use and showed that these derivatives "*... have antiviral activity against HIV.*"[164] Chevron also tested some diamondoid derivatives which exhibit therapeutic activity in the treatment of neurological disorders.[165] Derivatives of **1** and **2** were used by Hodek et al. for the inhibition of different cytochrome P450s and some showed "*... a high selectivity and inhibition potency...*".[166] Other possible diamantane (**2**) derivatives were studied by Chern's group as anticancer agents.[133,167] Even though none of these results have given rise to an actual medicament, we think that the amine- and peptide-functionalized derivatives should be investigated further for pharmaceutical uses.

With the aim of making polymers containing diamondoid compounds our group developed an easy, high-yielding procedure to prepare the methacrylates of diamantane, with the substituent in the apical position (Scheme 8).[168] The



Scheme 8. Preparation of 4-diamantyl methacrylate.[168]

combination of properties from polymethacrylates and the diamondoids is expected to result in some desirable properties such as high glass-transition temperatures, scratch-proof features, etc. In addition to our synthetic work, recently Ghosh et al.[169] used diamondoids as additives for polypropylene and polycarbonate, and Chevron[35] tried using them as nucleating agents for the manufacturing of thermoplastics. Ghosh et al. could show that diamondoids are "*... capable of modifying some thermomechanical properties of polymers without sacrificing other properties, as is often the case with larger filler inclusions.*"[169] In comparison to other polymer "additives" the role of diamondoids is not fully explored but the present results show that polymantanes (especially the functionalized ones) will probably give rise to materials with the above mentioned desirable properties.

The thiol derivatives of **4b** and **5**, such as *anti*-tetramantane-6-thiol (**58**), can be attached to gold surfaces (Figure 2 top).[78] Another interesting combination consists of the two

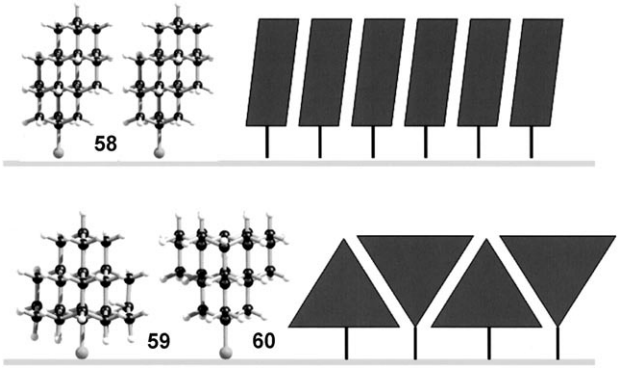


Figure 2. Thiol derivatives of **4b** and **5** on of a gold surface (gray horizontal line).

different pentamantane thiol derivatives **59** and **60**, because of their "trigonal-pyramidal shape" which would result in the surface being totally covered by a tight packing of diamondoids (Figure 2 bottom).

Another promising application for diamondoid dithiol derivatives is their use in single-molecule conduction junctions, which are under investigation because of their potential as nanoscale molecular interconnections.[170,171] These systems promise to act as switches, gates, or transport elements that "*... may help to minimize computer circuit dimensions and enhance performance.*"[170] Figure 3 shows *anti*-tetramantane-dithiol (**61**) between two gold electrodes as such a single-molecule junction.

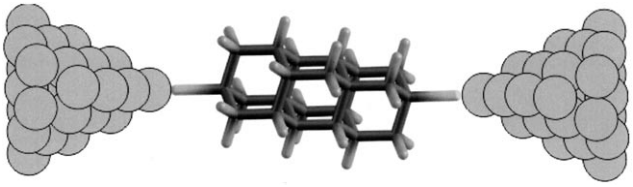
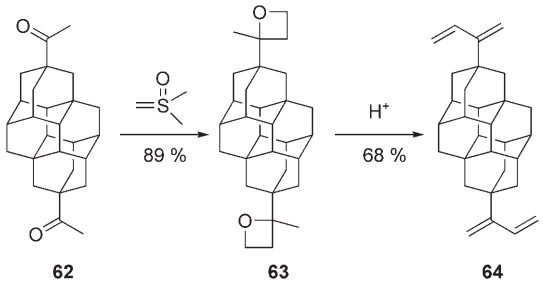


Figure 3. *Anti*-tetramantane-dithiol (**61**) as a single-molecule conduction junction between two gold electrodes (gray spheres).

Just recently our group was able to prepare diamondoids selectively functionalized with 1,3-dienes.[172] These compounds can readily be obtained from the respective ketones in a two-step procedure involving the intermediate formation of oxetanes (Scheme 9). By this procedure mono- and



Scheme 9. Two-step procedure for the preparation of 1,3-dienes.[172]

bisdienes of **1**, **2**, **3**, **4b**, and **5** were prepared and characterized. The 1,3-dienes are an ideal addition to our previous prepared thiol derivatives because they offer the possibility to be used for the formation of diamondoid SAMs on silicon surfaces via a [2+4] cycloaddition.[173]

7. Conclusion and Outlook

Since diamondoids are now readily available from crude oil in sizeable quantities this class of organic compounds is (again) under intense investigation. In comparison to other (hydro)carbon materials in the nanometer scale, such as nanodiamond powders, nanotubes, or fullerenes, these structurally well-defined hydrogen-terminated polymantanes are a long-known but at the same time a new class of so-called "nanomaterials". Several high-yielding functionalization reactions for the synthesis of alcohols, 1,3-dienes, thiols, acetates, have been developed and these transformations can be conducted in a highly selective fashion that is amenable to large-scale preparations. Intriguingly, the tertiary C–H bond functionalization selectivity increases with the size of the diamondoids. The three-dimensional rigidity and their stability in comparison to other carbon modifications on the nanometer scale makes them ideal compounds for applications, such as surface protection, rigid-fiber preparation, or as

molecular interconnections. Further research on the lower diamondoids as inexpensive starting materials will lay the ground for the preparation of even higher functionalized diamondoids such as the "superadamantane" (**7**).

MolecularDiamond Technologies, Chevron Technology Ventures is gratefully acknowledged for partial support of this research.

Received: April 17, 2007
Revised: July 10, 2007
Published online: December 14, 2007

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