A Note on Construction of Giant Molecules: A Study of Fractals in Chemistry

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Abstract
We discuss the construction of two giant molecular fractals composed of fullerene molecules at the vertices of a truncated square graph. The dimension analysis shows the formation of the famous Vicsek fractals. Eigen-spectrum analysis of the planer graph of the basic building blocks has been reported.

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Introduction

In the last few decades, the research on novel large nano-structures has gained a tremendous momentum [1]. One kind of idea is to building up larger structures starting from a relatively smaller molecular unit as proposed for the icosahedral borane unit [2] with some pursuit of this idea- and another natural base building block [3] is C_{60}. An extension of this idea is to form a larger structure by repeating a smaller structure over and over resulting in a formation of fractal nano-structure as investigated for C_{60} or benzenoid like multi-coronoids by Klein or Trinajstić [4-8].

A fractal is a geometrical figure that consists of an identical motif repeating itself on an ever reduced scale [9]. If the replication is exactly the same at every scale, it is called a self-similar pattern. A nice example of a self-similar pattern is a tree with a trunk that separates into two branches and again those branches separate into two other smaller side branches and so on. As a result we get a fractal tree. The difference between fractals and other geometric patterns is due to the dimensional scaling of the fractals which changes at the scale at which it is measured. This has been discussed by Mandelbrot in his seminal book *"The fractal Geometry of Nature"* in reference to the length of British coastline [10]. Actually, in 1904, mathematician Helge von Koch gave an example of a curve without a tangent anywhere [11]. Replication of the curve in ever reducing scale produces Koch fractal (Fig. 1) and the same idea can be used to express the British coastline.
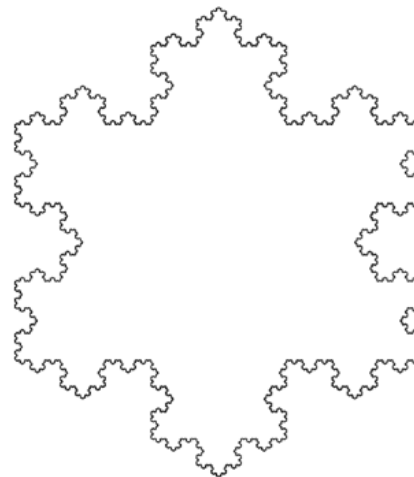

Fig. 1. Schematic outline of the Koch fractal.

In this work, we take fullerene C_{60} unit as a replacement of carbon centers of *N*-membered cyclic systems, resulting in the formation of the fullerene-*N*-cyclic systems. These systems are taken as the basic building block for constructing the fractal molecular structures.

A discussion on fullerene is due here. Geometrically C_{60}-fullerene is a truncated icosahedron with 12 isolated pentagons. A schematic diagram of icosahedron symmetry is shown in figure 2. It is evident that a truncated icosahedral C_{60} can attach another six such C_{60} unit at opposite positions along $\pm x$-, $\pm y$-, and $\pm z$-directions on the C_{60} framework [12]. This symmetry property has been used in the present work.
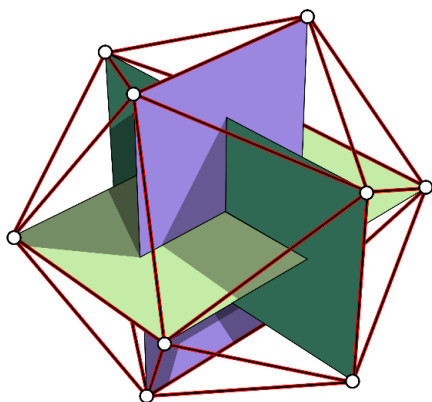

Fig. 2. Schematic diagram of an icosahedron showing the construction and symmetries of the geometry (Figure courtesy Wikipedia).

The theoretical basis for the construction of the molecular fractals relates to the study of complex networks involved in many fields of study, such as, physics, chemistry, biology, computer sciences etc. [13-15]. These studies help in understanding diverse dynamical processes defined on different networks [16-18]. The major dynamical process, which has been applied in various areas of science, is random walk on a network [19]. In various studies it has been established that the random walk on a network, more specifically scale-free networks, can be described by appropriate transition matrix. Thereby the study of eigenvalue spectra for transition matrix and corresponding adjacency matrix of the fractals is very much useful for understanding the behavior of various-real world systems.

Construction of Giant Molecular Fractals

We have used two different types of building blocks for constructing two different molecular fractals. In one case a basic square is subdivided into nine smaller squares in a 3×3 grid and then four corner squares are removed leaving the middle square and the other four squares above, below, left and right to the middle one. Thus forming the basic building block for the first type of molecular fractal (Figure 3). Repetition of this unit results in the formation of famous Vicsek fractal (Figure 4).
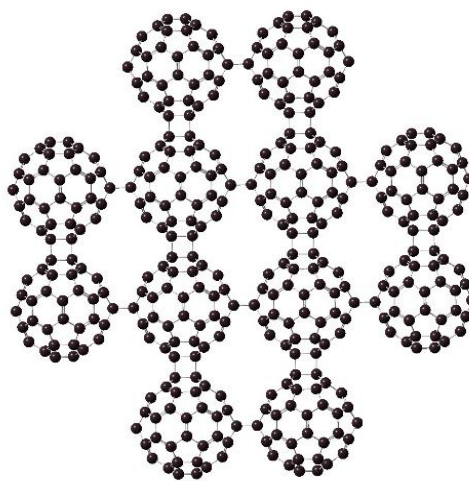

Fig. 3. Basic building block of the molecular fractal composed of Fullerene *N*-cyclic (*N* = 12) systems with fullerenes substituting each lattice point of a truncated square.
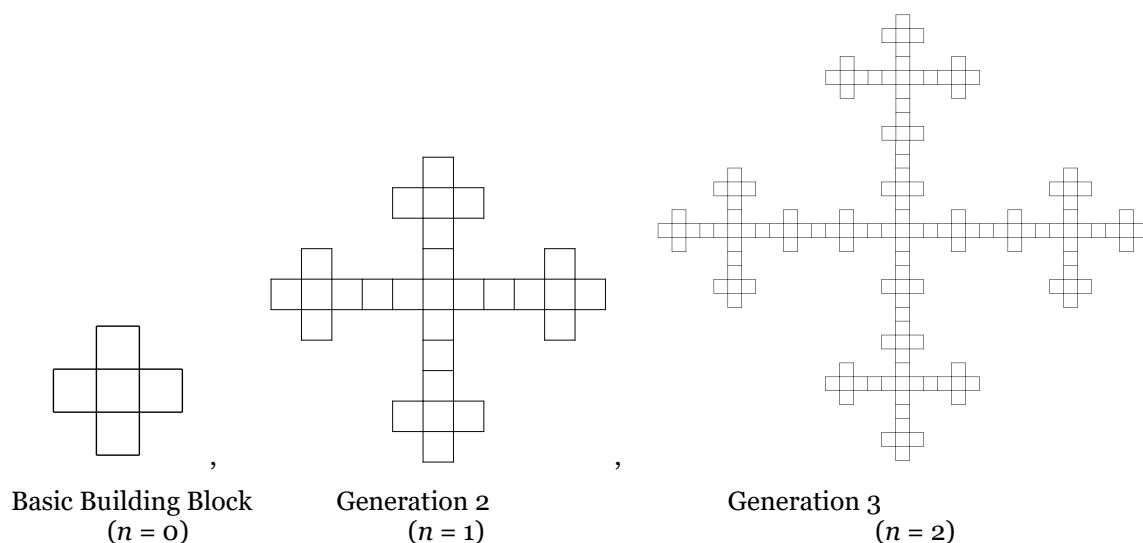
Fig. 4. Construction of Viksek fractal. More iterations after the first three iterations shown here will result in more complete form of the fractal.

In the second case, the basic building block is slightly different from that discussed before. The building block is shown in figure 5. A close inspection of the figure reveals that in this case the basic square has been subdivided into a 5×5 square grid and then some of the squares has been deleted in such a way that a middle 3×3 square grid remains intact with four other squares attached to it from above, below, left and right. A schematic representation of the stages of generations of the fractal using the building block has been shown in figure 6.
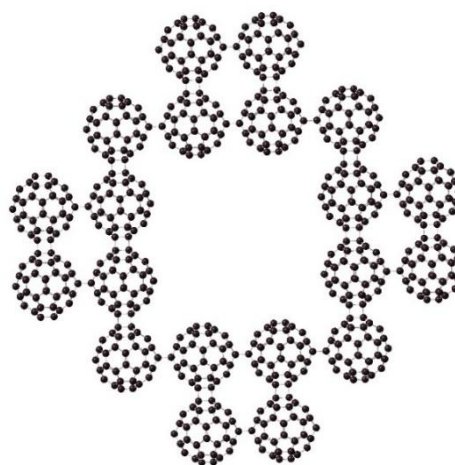

Figure 5. Fullerene N-cyclic (N = 20) system with fullerene substituting each carbon center in cyclobutane.
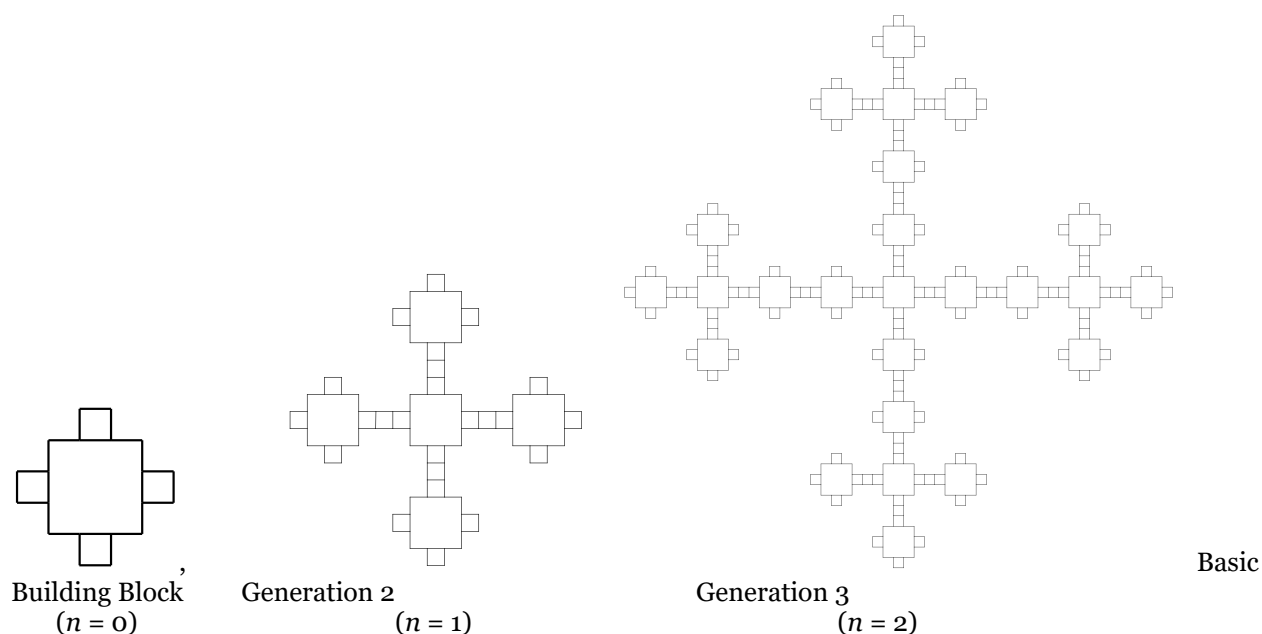
Building Block   Generation 2   Generation 3   Basic
(*n* = 0)   (*n* = 1)   (*n* = 2)

Figure 6. Graphical representation of the construction of the second fractal with the building block as shown in figure 5.

Discussion

Construction of the fullerene-*N*-cycle building blocks are done using UFF- molecular mechanics method in Gaussian 09 suit of programs [20]. Because of limited computational resources, even a semi-empirical calculation becomes exceedingly difficult.

Discussion

We formulate the general stoichiometric formula of the constructed fractals. For the first case, we start with a square graph subdivided in a 3×3 grid. As already mentioned, removal of corners of this square graph ends up leaving a planer graph of 12 and 20 lattice points for 1st type and 2nd type Vicsek fractal, respectively. All those points are occupied by fullerene moieties. Thus in the first generation (*n* = 0) one gets $C_0 = 12$ (1st type) and $C_0 = 20$. Furthermore, recursive construction gives $C_{n+1} = 5C_n$, for both the cases.

Evidently a very nice self-similar fullerene-*N*-cyclic molecular fractal is possible. The only challenge is its actual synthesis. However, degree of fractality of these molecular fractals can be easily determined following Mandelbrot's general ideas [4]. For the Vicsek fractal, the fractal dimension *D* is estimated to be 1.46497 applying a box-counting method [6].

For the second case, the mass of fullerene-*N*-cyclic system scales of the order of $\sim 5^N$, while their linear extension scales $\sim 3^N$, so that their overall density in 2-dimensional space goes as

$$\sim 5^N /(3^N)^2 = (5/9)^N \rightarrow 0. \qquad (1)$$

A *fractal* dimension *D* is obtained by demanding that the *D*-dimensional density give a finite non-zero result, which is to say

$(5^N / 3^N)^D = (5/3^D)^N$ is to remain non-zero and finite as $n \to \infty$. That is, $5/3^D = 1$ or

$$D = \log 5 / \log 3 \cong 1.46497.$$

(2)

A somewhat interesting fact comes out from the above discussion. In 2-dimnsional space these fractals show zero area as $N \to \infty$, while their perimeters remain finite. From the value of D, one can visualize that, if these molecular fractals can be prepared, they would be sparse for manifesting extension in 2-dimensional space.

A graph theoretical discussion of the basic building block of the said fractals is necessary at this point. We construct the following adjacency matrices $(\overline{\overline{\mathbf{A}}}_1^{(n)})$ of the basic ($n = 1$) building block for the first (denoted by the subscript '1') and second (denoted by the subscript '2') fractal system.

The eigen-spectrum analysis of the adjacency matrices (Eqn (3)) shows the eigenvalues and their corresponding degeneracies (Table 1). From Table 1 one observes that both the basic building blocks of the fractals are bipartite in nature with bipartivity measure $\beta(G) = 1$, where we have used the following relation [21], Eqn (4),

$$\beta(G) = \frac{\sum_j^n \cosh(\lambda_j)}{\sum_j^n \cosh(\lambda_j) + \sum_j^n \sinh(\lambda_j)}$$

(4)

for measuring the bipartivity measure $\beta(G)$ of the said fractals. A Fortran 77 program code has been prepared for diagonalization of the corresponding matrices.

$$\overline{\overline{\mathbf{A}}}_1^{(1)} = \begin{pmatrix}
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 \\
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0
\end{pmatrix}$$ and

$$\overline{\overline{\mathbf{A}}}_2^{(1)} = \begin{pmatrix}
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
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0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}.$$

(3)

Table 1: Eigenspectrum analysis of the basic building blocks of the two fractal systems.

Fractal System	Term	Eigenvalue	Degeneracies
I	λ_1	0	4
	λ_2	$\sqrt{3}$	2
	λ_3	$-\sqrt{3}$	2
	λ_4	1	1
	λ_5	-1	1
	λ_6	3	1
	λ_7	-3	1
II	λ_1	0	4
	λ_2	2	1
	λ_3	-2	1
	λ_4	$\dfrac{\sqrt{10}-\sqrt{2}}{2}$	2
	λ_5	$-\dfrac{\sqrt{10}-\sqrt{2}}{2}$	2
	λ_6	$\dfrac{\sqrt{10}+\sqrt{2}}{2}$	2
	λ_7	$-\dfrac{\sqrt{10}+\sqrt{2}}{2}$	2
	λ_8	-2.481	1
	λ_9	-0.689	1
	λ_{10}	1.170	1
	λ_{11}	-1.170	1
	λ_{12}	0.689	1
	λ_{13}	2.481	1

Conclusion

In this work, construction of two molecular fractals have been demonstrated. Although a number of studies [22] have been conducted on the dynamics of these types of fractals, in particular, Vicsek fractals manifested in hyper-branched polymers, study on energetics is lacking. Hence systematic study on the stability of these type of fractals may be of future interest. Furthermore, graph theoretical treatment shows that these types of fractals should be fully bipartite in nature. Thereby, study of these fractals may open up new routes for studying more complex network systems.

Acknowledgement

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