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Original Scientific Article

Omega Polynomial in a Combined Coronene-Sumanene Covering

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Abstract. A new graphene pattern, called CorSu, was designed by combining the patterns of coronene [6:6_6] and sumanene [6:$(5,6)_3$]. The energy of some small fragments of this lattice, functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, was evaluated at the level of semiempirical method PM3. The topology of the network is described in terms of Omega counting polynomial. Close formulas for calculating the Omega polynomial and the Cluj-Ilmenau index derived from this polynomial are given.

Keywords: counting polynomial, lattice, CI index, coronene, sumanene

INTRODUCTION

Several new carbon allotropes have been discovered and studied for applications in nano-technology, in the last twenty years, which can be assigned as the "Nano-era". The impact of the Nano-Science resulted in reduction of dimensions of electronic devices and increasing their performances, at a lower cost of energy and money. Among the carbon new structures, fullerenes (zero-dimensional), nanotubes (one dimensional), graphene (two dimensional) and spongy carbon (three dimensional) are the most studied.[1,2] The attention of scientists was also focused to inorganic compounds, a realm where almost any metal atom can form clusters, tubules or crystal networks, very ordered structures at the nano-level. Recent articles in crystallography promoted the idea of topological description and classification of crystal structures.[3–8] They present data on real, but also hypothetical lattices, designed by computer.

The present study deals with a hypothetical graphene patterned by coronene- and sumanene-like units, described in terms of Omega counting polynomial and evaluated as energy by the PM3 method. The Omega and related counting polynomials take account of the chemical nature of the atoms/vertices and topology of the lattices.

OMEGA POLYNOMIAL

Let $G(V,E)$ be a connected graph, with the vertex set $V(G)$ and edge set $E(G)$. Two edges $e = uv$ and $f = xy$ of G are called *codistant e co f* if they obey the following relation:[9]

$$d(v,x) = d(v,y) + 1 = d(u,x) + 1 = d(u,y) \qquad (1)$$

which is reflexive, that is, *e co e* holds for any edge e of G, and symmetric, if *e co f* then *f co e*. In general, relation *co* is not transitive; an example showing this fact is the complete bipartite graph $K_{2,n}$. If "*co*" is also transitive, thus an equivalence relation, then G is called a *co-graph* and the set of edges $C(e) := \{f \in E(G);\ f\ co\ e\}$ is called an *orthogonal cut oc* of G, $E(G)$ being the union of disjoint orthogonal cuts:

$$E(G) = C_1 \cup C_2 \cup ... \cup C_k,\ C_i \cap C_j = \varnothing,\ i \neq j\ .$$

Klavžar[10] has shown that relation *co* is a theta Djoković-Winkler relation.[11,12]

We say that edges e and f of a plane graph G are in relation *opposite, e op f,* if they are opposite edges of an inner face of G. Note that the relation *co* is defined in the whole graph while *op* is defined only in faces. Using the relation *op* we can partition the edge set of G into *opposite* edge *strips, ops.* An *ops* is a quasi-orthogonal cut *qoc*, since *ops* is not transitive.

Let G be a connected graph and S_1, S_2, ..., S_k be the *ops* strips of G. Then the *ops* strips form a partition of $E(G)$. The length of *ops* is taken as maximum. It depends on the size of the maximum fold face/ring F_{max}/R_{max} considered, so that any result on Omega polynomial will have this specification.

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Denote by $m(G,s)$ the number of *ops* of length s. The Omega polynomial[13-15] is defined as:

$$\Omega(G,x) = \sum_s m(G,s) \cdot x^s \quad (2)$$

Its first derivative (in $x = 1$) equals the number of edges in the graph:

$$\Omega'(G,1) = \sum_s m(G,s) \cdot s = e = |E(G)| \quad (3)$$

On Omega polynomial, the Cluj-Ilmenau [9] index, $CI = CI(G)$, was defined:

$$CI(G) = [\Omega'(G,1)]^2 - [\Omega'(G,1) + \Omega''(G,1)] \quad (4)$$

Within this paper, the main results refer to $F_{max}(6)$. If rings instead of faces are considered, the polynomial is different. The inclusion of hexagons lying "under" the bridge brings complications in the number and length of *ops*, particularly at the maximum length.

Data were calculated by an original program called Nano Studio,[16] developed at the TOPO Group Cluj.

LATTICE BUILDING

The lattice was built on the graphene sheet, of (6,3) tessellation, by decorating it with coronene-like flowers, having sumanene units as petals. The pattern, called CorSu,[17,18] can be described as: $\{[6:6_6],[6:(5,6)_3)]_6\}$, with vertices/atoms of degree 3 and 4, as shown in Figure 1.

This idea came out from the TOPO Group Cluj older studies on aromaticity,[2,19,20] in which circulene/flower units were proposed as extensions of the Clar[21,22] theory of aromaticity. Notice, the coronene and sumanene are molecules synthesized in the labs. It was also supported by the synthesis of several bowl-shaped molecules, inspired from the architecture of fullerenes and, more recently, by the direct synthesis[23] of fullerenes starting from open precursors. The design of various domains on the graphene sheet is nowadays a challenge study and practice.[24–27]

The pentagonal rings, possibly entering as local bridges over the graphite sheet by reactions like oxidation, amination, or carbene action, will force the geometry of graphene to a bowl-shaped one (Figure 1, the right hand column). The overall positive curvature depends on the bond length of the atoms involved in the bridges, it being as bowl-shaped as the atom covalent radius is smaller (see Table 1). The lattice appears as alternating positive (sumanene) and negative (coronene) curved domains.

MAIN RESULTS

Energetic and structural data

The graphene lattice patterned by CorSu repeat units was designed in the idea of coronene,[28] the circulene $[6:6_6]$, whose petals were replaced by sumanene[29,30] units $[6:(5,6)_3]$, two molecules appearing as domains in fullerenes. Data in Table 1, computed at the PM3 level of theory, show the fragments of the lattice, functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, as relatively stable ones, both as total energy per atom and HOMO-LUMO gap. The bond lengths are quite reasonable, slightly elongated than the normal values. In comparison, the total energy per atom (in kcal/mol) for C_{60} is –2722.45, while the gap is around 6.59 eV. The bridges defining the pentagonal rings of the sumanene units, will force the planar graphene to adopt a bowl-shaped form and the sp^2 carbon atom is supposed to shift to the sp^3 hybridization. In the whole, the lattice appears as a waved surface, with margins eventually positively curved (Figure 1) or launched to hyperbolic geometry. It can explain the corrugate surface of graphene, as shown by electronic microscopy.[27]

Calculations made on CorSu domains by using density functional-based tight binding method combined with the self-consistent charge technique, SCC-DFTB,[31,32] revealed relative energies among different structures showing the same trend as those computed by PM3, these results following to be detailed in a more chemically developed article.

Topology

The topology of the lattice is described here in terms of Omega polynomial. Two approaches will be presented in the following: (i) complete subdomain description and (ii) composition of monomer interactions.

Complete subdomain description (i)

This approach makes use of the symmetry properties of the repeat units/monomers.

Let the common edges be four edges that have a blue point in the centre, *i.e.*, the edges shared by two Sumanene units in a hexagonal domain of CorSu graphene sheet (Figure 2). Let W_n denote the number of common edges of the structure $CorSu_n$. Let r_k be the number of hexagons for the complete domain, $r_0 = 1$ and $r_k = r_{k-1} + 6k$. After solving the recurrence, it follows

$$r_k = 1 + 3k(k+1) \quad (5)$$

For a given n, there exist a unique index k, such that $CorSu_n$ has complete k layers, namely $r_k \le n < r_{k+1}$.

Table 1. Energy and structural data for two fragments of the hypothetical lattice CorSu

	Structure	Bond Length C–X (expressed in Å)	Total energy per Number of heavy atoms (expressed in kcal/mol)	HOMO-LUMO Gap (expressed in eV)
	CorSu_96–X			
1	O	1.52	–3271.32	5.950
2	C (CH2)	1.64	–2925.55	6.655
3	N (NH)	1.61	–3007.54	6.740
4	P (PH)	2.06	–2889.53	6.057
	CorSu_198–X			
5	O	1.52	–3289.57	8.776
6	C (CH_2)	1.62	–2889.05	8.603
7	N (NH)	1.58	–2967.23	8.143
8	P (PH)	2.05	–2853.45	6.590

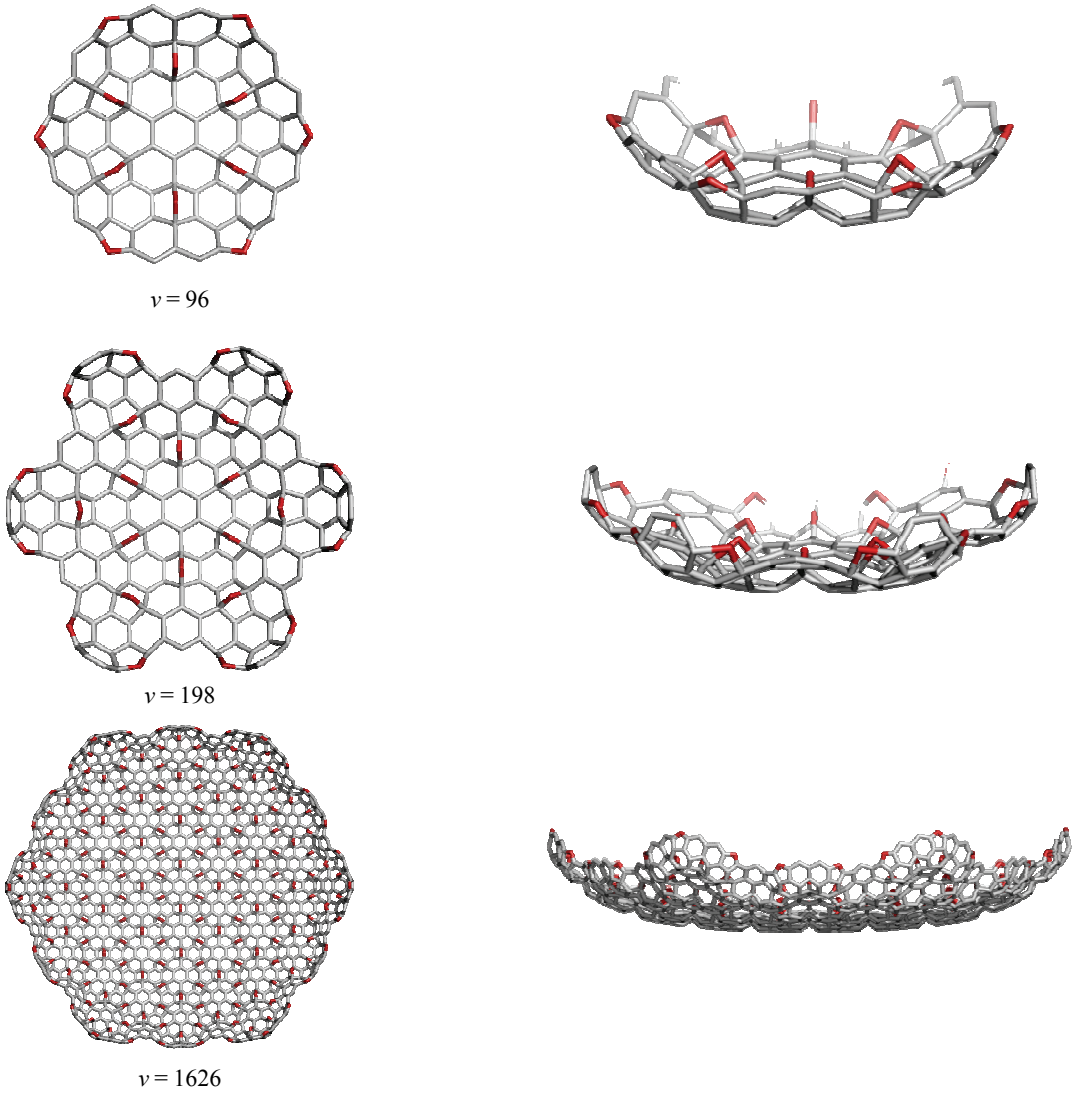

Figure 1. Hexagonal domains in the CorSu graphene sheet: top view (left hand column) and side view (right hand column).

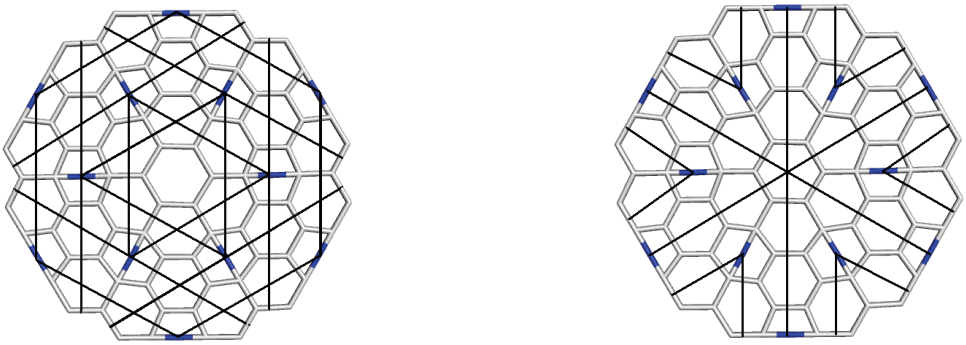

Figure 2. Calculation of Omega polynomial for hexagonal domains in the CorSu graphene sheet.

To compute the numbers W_n, we need to include *the common edges* for the complete r_k layers of hexagons, and the common edges between the hexagons from the last layer and those from the layer before the last one (every added hexagon can produce one or two common edges).

$$W_n = W_{r_k} + \left\lfloor \frac{n - r_{k-1}}{k} \right\rfloor + 2\left(n - r_{k-1} - \left\lfloor \frac{n - r_{k-1}}{k} \right\rfloor \right) + (n - r_{k-1} - 1) \quad (6)$$

For the special case when $n = r_k$, we need to add one more edge, and in this case we have

$$W_n = W_{r_k} + \left\lfloor \frac{n - r_{k-1}}{k} \right\rfloor + 2\left(n - r_{k-1} - \left\lfloor \frac{n - r_{k-1}}{k} \right\rfloor \right) + (n - r_{k-1}) \quad (7)$$

The Omega polynomial for the CorSu lattice of hexagonal domains is given by:

$$\Omega(CorSu_n, x) = a_n x + b_n x^2 + c_n x^3 + d_n x^6 \quad (8)$$

For the starting values, we have $a_0 = 24, b_0 = 12, c_0 = 24, d_0 = 3$ (see Figure 2). Each common edge reduces the coefficients a_n and b_n by 2 and 4, respectively. On the other hand, for c_n every common edge increases the coefficient by 2, and we need to subtract $6(W_n + 1 - n)$. Similarly, for the coefficient d_n we need to increase it by $3(W_n + 1 - n)$. Finally, we get

$$\Omega(CorSu_n, x) = (24n - 2W_n)x + (12n - 4W_n)x^2 + (24n + 2W_n - 6(W_n + 1 - n))x^3 + (3n + 3(W_n + 1 - n))x^6 \quad (9)$$

Data in Table 2 give examples of the application of relation (9), along with CI and the number of atoms and bonds.

For a parallelogram domain $CorSu_{p(a,b)}$, we have $a \times b$ hexagons, and the number of common edges in this structure is

$$W_{a,b} = (a-1)b + (2a-1)(b-1) = 3ab - 2a - 2b + 1 \quad (10)$$

The Omega polynomial is given by the formula:

$$\Omega(CorSu_{p(a,b)}, x) = (24ab - 2W_{a,b})x + (12ab - 4W_{a,b})x^2 + (24ab + W_{a,b} - 6(W_{a,b} + 1 - ab))x^3 + (3ab + 3(W_{a,b} + 1 - ab))x^6$$

After substituting $W_{a,b}$, the formula becomes

$$\Omega(CorSu_{p(a,b)}, x) = (-2 + 4a + 4b + 18ab)x + (-4 + 8a + 8b)x^2 + (-10 + 8a + 8b + 18ab)x^3 + (6 - 6a - 6b + 9ab)x^6 \quad (11)$$

Table 3 lists some examples of the application of relation (11), along with CI and the number of atoms and bonds.

Similarly, we can calculate the number of atoms, bonds and CI index

$$v(a,b) = 81ab + 10a + 10b - 5$$
$$e(a,b) = 126ab + 8a + 8b - 4$$
$$CI(a,b) = (126ab + 8a + 8b - 4)^2 - 108 + 108(a + b) - 504ab.$$

Composition of monomer interactions.

The Omega polynomial of a graph G can be decomposed in contributions of the graph fragments F_i:

Table 2. Omega polynomials of hexagonal domains $CorSu_n$ with CI index and the number of atoms and bonds

N	Omega	CI index	Atoms	Bonds
1	$24x + 12x^2 + 24x^3 + 3x^6$	18648	96	138
2	$46x + 20x^2 + 50x^3 + 6x^6$	73192	187	272
3	$66x + 24x^2 + 72x^3 + 12x^6$	160362	273	402
4	$86x + 28x^2 + 94x^3 + 18x^6$	281332	359	532
5	$106x + 32x^2 + 116x^3 + 24x^6$	436102	445	662
6	$126x + 36x^2 + 138x^3 + 30x^6$	624672	531	792
7	$144x + 36x^2 + 156x^3 + 39x^6$	839628	612	918
8	$164x + 40x^2 + 178x^3 + 45x^6$	1094758	698	1048
9	$184x + 44x^2 + 200x^3 + 51x^6$	1383688	784	1178
10	$202x + 44x^2 + 218x^3 + 60x^6$	1695916	865	1304
11	$222x + 48x^2 + 240x^3 + 66x^6$	2051406	951	1434
12	$240x + 48x^2 + 258x^3 + 75x^6$	2428146	1032	1560
13	$260x + 52x^2 + 280x^3 + 81x^6$	2850196	1118	1690
14	$278x + 52x^2 + 298x^3 + 90x^6$	3291448	1199	1816
15	$298x + 56x^2 + 320x^3 + 96x^6$	3780058	1285	1946
16	$316x + 56x^2 + 338x^3 + 105x^6$	4285822	1366	2072
17	$336x + 60x^2 + 360x^3 + 111x^6$	4840992	1452	2202
18	$354x + 60x^2 + 378x^3 + 120x^6$	5411268	1533	2328
19	$372x + 60x^2 + 396x^3 + 129x^6$	6013296	1614	2454
20	$392x + 64x^2 + 418x^3 + 135x^6$	6667786	1700	2584

Table 3. Omega polynomials of parallelogram domains p(a,b) with CI index and the number of atoms and bonds

a	b	Omega	CI index	Atoms	Bonds
1	1	$24x + 12x^2 + 24x^3 + 3x^6$	18648	96	138
1	2	$46x + 20x^2 + 50x^3 + 6x^6$	73192	187	272
1	3	$68x + 28x^2 + 76x^3 + 9x^6$	163648	278	406
1	4	$90x + 36x^2 + 102x^3 + 12x^6$	290016	369	540
1	5	$112x + 44x^2 + 128x^3 + 15x^6$	452296	460	674
2	2	$86x + 28x^2 + 94x^3 + 18x^6$	281332	359	532
2	3	$126x + 36x^2 + 138x^3 + 30x^6$	624672	531	792
2	4	$166x + 44x^2 + 182x^3 + 42x^6$	1103212	703	1052
2	5	$206x + 52x^2 + 226x^3 + 54x^6$	1716952	875	1312
3	3	$184x + 44x^2 + 200x^3 + 51x^6$	1383688	784	1178
3	4	$242x + 52x^2 + 262x^3 + 72x^6$	2440696	1037	1564
3	5	$300x + 60x^2 + 324x^3 + 93x^6$	3795696	1290	1950
4	4	$318x + 60x^2 + 342x^3 + 102x^6$	4302468	1371	2076
4	5	$394x + 68x^2 + 422x^3 + 132x^6$	6688528	1705	2588
5	5	$488x + 76x^2 + 520x^3 + 171x^6$	10395448	2120	3226

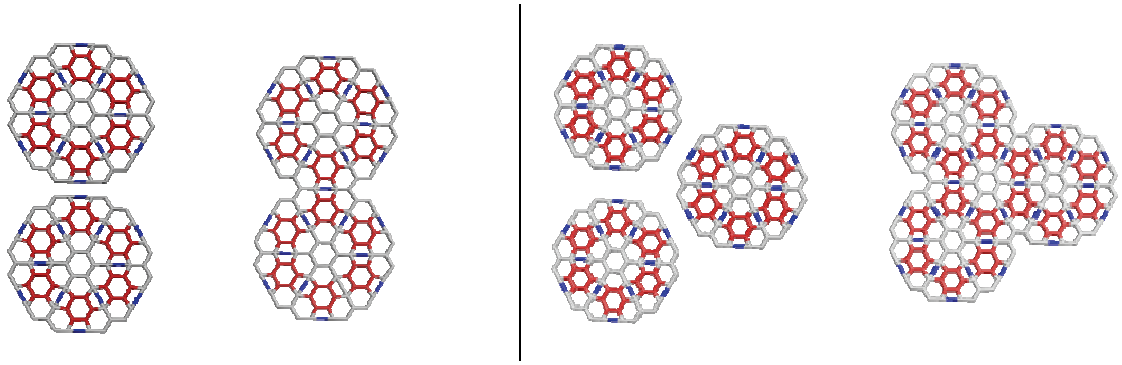

Figure 3. Interaction of units u in CorSu graphene: edge-type A (left) and vertex-type B (right).

Table 4. Defining the edge- and vertex-type interactions A, B and BX, respectively, in CorSu unit u: $\Omega(u) = 24x^1 + 12x^2 + 24x^3 + 3x^6$

Exponent	u	2 u	2 × u	A	3 u	3 × u	BX	B = BX – 3 A
1	24	46	48	–2	66	72	–6	0
2	12	20	24	–4	24	36	–12	0
3	24	50	48	2	72	72	0	–6
6	3	6	6	0	12	9	3	3

Table 5. Omega polynomial composition rules: examples

Unit	Composition
$A = -2x - 4x^2 + 2x^3$ $B = -6x^3 + 3x^6$ $u = 24x^1 + 12x^2 + 24x^3 + 3x^6$	
$CorSu_1 = 144x^1 + 36x^2 + 156x^3 + 39x^6$ $CorSu_2 = 372x^1 + 60x^2 + 396x^3 + 129x^6$ $CorSu_3 = 708x^1 + 84x^2 + 744x^3 + 273x^6$	$CorSu_1 = (u + 6u) + 12A + 6B$ $CorSu_2 = (7CorSu_1 + 12u) + 30A + 18B$ $CorSu_3 = (19CorSu_2 + 18u) + 48A + 30B$
$CorSu_{p(a,b)}$ (parallelogram domain)	$CorSu_{p(2,2)} = 4u + 2B + 5A$ $CorSu_{p(3,3)} = 9u + 8B + 16A$

$$\Omega(G = \cup F_i) = \sum_i \Omega(F_i) + \sum_i \Omega(I(F_i)), \qquad (12)$$

where $I(F_i)$ represent the "interactions" manifested between (among) two (or more, depending of the connectivity of actual) fragments F_i, *i.e.*, the ops strips which appear/disappear by the union of F_i.

The union/composition of F_i to form the whole G can be achieved as follows.

(i) The fragments F_i are united by *joining* "Jn" of the involved vertices by appropriate edges.

(ii)The fragments F_i are united by *identifying* "Id" of the actual superimposed subgraphs (points, edges, faces, *etc.*).

Examples of union by identification are given in Figure 3. Other cases will be discussed in future papers.

The edge- and vertex-type (of degree three) interactions are detailed in Table 4.

By combining the interactions of type A (edge) and B (vertex), any kind of domains in the *CorSu* lattice can be described, but in the following only regular hexagonal (the suffix *k* being the net parameter) and parallelogram-like (assigned by a suffix *p*(*a*,*a*)) domains will be considered. Table 5 provides some examples: *u* refers to the repeat unit of *CorSu* lattice.

CONCLUSIONS

A new graphene lattice, patterned by CorSu units, was functionalized by groups containing oxygen, carbon, nitrogen and phosphorus, and its stability evaluated at the level of semiempirical method PM3. The small fragments, taken into consideration, showed relatively good stability, as compared with the data for the well-known C_{60}. Further calculations, on various CorSu domains, by using density functional-based tight binding method combined with the self-consistent charge

technique, SCC-DFTB, revealed the same trend in their relative energies as those computed by PM3. The topology of the network is described in terms of Omega counting polynomial. The topological description can be used in structure elucidation analysis. Close formulas for calculating the polynomial and the Cluj-Ilmenau index derived from this polynomial were given.

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SAŽETAK

Omega polinom u kombiniranom koronensko-sumanenskom prekrivanju

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Kombiniranjem uzoraka koronena [6:6_6] i sumanena [6:$(5,6)_3$], skraćeno nazvanim CorSu, dizajniran je novi grafenski predložak/uzorak. Semiempirijskom metodom PM3 procijenjena je energija nekih malih fragmenata ove mreže s funkcionalnim skupinama koje sadrže kisik, ugljik, dušik i fosfor. Topologija mreže opisana je s pomoću Omega polinoma. Prikazane su i formule za računanje Omega polinoma i Cluj-Ilmenau indeksa, koji se izveden iz toga polinoma.