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Determination of Zhang-Zhang Polynomials for Various Classes of Benzenoid Systems: Non-Heuristic Approach

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Abstract

We employ a graphical proof-oriented tool, ZZDecomposer, to discover formal derivations of Zhang-Zhang (ZZ) polynomials for various families and subfamilies of benzenoid structures including tripods, zigzag-edge coronoids fused with a starphene, oblate rectangles $Or(m,2)$, hexagons $O(2,2,n)$, $O(2,3,n)$, and $O(3,3,n)$, and multiple zigzag chains $Z(4,n)$, $Z(5,n)$, $Z(6,n)$, $Z(7,n)$, $Z(8,n)$, and $Z(9,n)$. Current derivations are based on formal graph decompositions of the analyzed structures. The decompositions provide appropriate recurrence formulas, which are subsequently solved, yielding closed-form expressions for the ZZ polynomials. We hope that in addition to many new basic facts about ZZ polynomials of some important classes of benzenoids, the current study will provide the researchers who are interested in mathematical graph theory with a practical guide to the ZZDecomposer functionality and will enable and facilitate their research.

1. Introduction

In a series of two recent papers [1, 2] we suggested a collection of techniques applicable for finding closed form of Zhang-Zhang (ZZ) polynomials for various subfamilies of catacondensed and pericondensed polycyclic benzenoid compounds. The presented techniques were based on a structural analysis of the ZZ polynomials for the smallest members $(n = 1, 2, 3, \ldots)$ of a given subfamily of structures. The main goal of the analysis was discovering the underlying algebraic structure of the ZZ polynomial for the studied subfamily and expressing its algebraic coefficients as functions of the index n. The discovered ZZ polynomial formulas were subsequently tested for a large number of analogous structures in order to verify their validity. Our approach, though practically useful and yielding ready-to-use algebraic formulas, had one serious methodological drawback. Namely, the ZZ polynomials for a given entire subfamily of benzenoid compounds were derived from the analysis of a finite number of its members. Therefore, it is not impossible that for an appropriately large value of n, the discovered formulas stop to be valid and produce erroneous results. An interesting example of such a situation would be the case of cyclotomic polynomials $\Phi_n(x)$, [3] for which an analogous analysis based on the first 104 members of this class would suggest that all their coefficients are equal to $+1$ or -1. This pattern first breaks for $\Phi_{105}(x)$, where the coefficients for x^7 and x^{41} are -2. [4] Such a situation is very unlikely in our heuristic analysis taking into account the structural similarities detected between the ZZ polynomials for subsequent members in the series, relatively small number of parameters used to generate the final formulas (substantially smaller than the number of analyzed series members), and numerous final tests of the discovered formulas against the ZZ polynomials of big isostructural compounds computed using formal recursive decomposition techniques. Nevertheless, despite of their structural beauty and apparently correct form, most of the ZZ polynomial formulas discovered by us in [1] and [2] are pure conjectures, which remain to be formally established using standard proof techniques, similarly as it was been done for other topological indices derived using formal interpolation techniques. [5, 6]

In the current study we attempt to correct for the aforementioned omission using a specialized, proof-oriented, graphical computer environment (ZZDecomposer) developed recently in our group. ZZDecomposer is capable of performing interactive decompositions of

ZZ polynomials for an arbitrary benzenoid structure and enabling one in this way to conduct a formal proof of the derived formulas. This tool, described in detail in the prequel [7] to the current paper and distributed free of charge (http://qcl.ac.nctu.edu.tw/zzdecomposer), is applied here for performing formal proofs for the heuristically discovered formulas presented in our previous work [1, 2]. The preceding publication [7] used ZZDecomposer to give formal derivations (or re-derivations) of the ZZ polynomial formulas for the four well-known families of benzenoid structures: multiple-segment polyacene chains $L(m,n)$, zigzag-edge coronoids $ZC(n,m,l)$, fenestrenes $F(n,m)$, and parallelograms $M(m,n)$. These proofs were mainly meant as an illustration of capabilities of ZZDecomposer designed to introduce a freshman user to this new software. Here, we use ZZDecomposer to give formal proofs for further six families of benzenoid structures: tripods $T(n,m,l)$, structures $S(n)$ of Randić [1, 8-11], zigzag-edge coronoids fused with a starphene $ZCS(n,m,l)$, oblate rectangles $Or(m,2)$, hexagons $O(2,2,n)$, $O(2,3,n)$, and $O(3,3,n)$, and multiple zigzag chains $Z(4,n)$, $Z(5,n)$, $Z(6,n)$, $Z(7,n)$, $Z(8,n)$, and $Z(9,n)$. These formal derivations are new. The approach used here will be further generalized to other families of benzenoid structures treated in detail in our next publications due to the complexity of the underlying theory. First two of these publications, giving a general, closed-form formula for chevrons $Ch(k,m,n)$ and generalized chevrons $Ch(k,m,n_1,n_2)$ [12] and for prolate rectangles $Pr(m,n)$ and generalized prolate structures $Pr([m_1,m_2,\ldots,m_n],n)$ [13] accompany this paper. The remaining classes, including general classes of multiple zigzag chains $Z(m,n)$, ribbons $Rb(k,m,n)$ and generalized ribbons $Rb(m_1,n_1,m_2,n_2)$, [14] and oblate rectangles $Or(m,n)$, require somewhat more involved theory and will be published shortly. In our opinion, the structures posing most serious problems for finding closed-form of their ZZ polynomials are hexagon benzenoids $O(k,m,n)$, for which all our attack attempts remained in vain except for a few of their subfamilies.

2. Review of available closed-form formulas for the ZZ polynomials of benzenoid structures

In our recent two studies [1, 2], we have reported a number of heuristically discovered formulas for the ZZ polynomials of various classes of benzenoid structures. Namely, we have reported general closed-form formulas for the ZZ polynomials of 14 families of benzenoid structures: polyacenes $L(n)$, single armchair chains $N(n)$, multiple-segment polyacene chains $L(m,n)$, zigzag-edge coronoids $ZC(n,m,l)$, fenestrenes $F(n,m)$, linear and cyclic polyphenyles $P(n)$ and $AC(n,m,l)$, tripods $T(n,m,l)$, starphenes $St(n,m,l)$, hammers $H(n)$, zigzag-edge coronoids fused with a starphene $ZCS(n,m,l)$, parallelograms $M(m,n)$, prolate rectangles $Pr(m,n)$, and generalized prolate structures $Pr([m_1,m_2,m_3,\dots,m_n],n)$. For some of these structures, formal proofs of the results obtained by us were already available. The formulas for the ZZ polynomials of $L(n)$, $N(n)$, $L(m,n)$, and $St(n,m,l)$ were provided in the seminal papers by Zhang and Zhang. [15-18] The formulas for the ZZ polynomials of $ZC(n,m,l)$ and $F(n,m)$ were given originally by Guo, Deng, and Chen [19] with a small technical lapse, which was corrected in [20]. The ZZ formula for the parallelograms $M(m,n)$ was derived by Gutman and Borovićanin. [21] To our best knowledge, no formal proofs are available for the remaining families of structures.

In addition to the general closed-form formulas for the ZZ polynomials for the 14 above-listed families, the ZZ polynomial formulas for 14 subfamilies of pericondensed benzenoid structures: multiple zigzag chains $Z(m,2)$, $Z(m,3)$, $Z(m,4)$, $Z(m,5)$, $Z(4,n)$, $Z(5,n)$, and $Z(6,n)$, hexagons $O(2,2,n)$ and $O(3,3,n)$, chevrons $Ch(2,2,n)$ and $Ch(3,3,n)$, ribbons $Rb(m,m,2)$ and $Rb(m,m,3)$, and oblate rectangles $Or(m,2)$, were also reported in our recent studies [1, 2]. No formal proofs of these results are available in the literature. Formal derivation of ZZ polynomials of oblate rectangles $Or(m,1)$ was offered by Gutman, Fortula, and Balaban [22]; unfortunately, this result cannot be easily generalized to other subfamilies of oblate rectangles. However, the ideas behind this proof stimulated us to start our work on ZZ polynomials and design the ZZDecomposer graphical environment presented in the current series of papers [7, 12-14]. It should also be mentioned here that a collection of ZZ polynomials for generalized multiple zigzag chains $Z(2,[n_1,n_2])$ and $Z(3,[n_1,n_2,n_3])$ was offered by Chen, Deng, and Guo [23], but the resulting formulas are very lengthy and cumbersome for immediate everyday use, and do not give much insight in the internal structure of these subfamilies of benzenoids. We believe that additional analysis can cast these equations in much shorter and more structured form.

It is also appropriate to mention here that general recurrence formulas for the structures $S(n)$ of Randić [1, 8-11] and for the multiple zigzag chains $Z(m,n)$ were offered [1, 2], but solving these recurrences proved to be exceedingly difficult. For the structures $S(n)$, a satisfactory expression for the ZZ polynomials could be obtained in terms of an appropriate generating function, [1] while for the $Z(m,n)$, the two-dimensional recurrence could not be solved at that time. [2]

It is clear that some of the closed-form ZZ polynomial formulas for various benzenoid systems are known and used, but no formal demonstration of their correctness has been presented. A good example here can be the closed-form expressions for the ZZ polynomials of prolate rectangles $Pr(m,n)$ given by Zhang and Zhang [15, 17], where a formal proof is replaced by the "it is easy to see" argument. The reported here program, ZZDecomposer, gives us a convenient tool for performing formal derivations (or re-derivations in some cases) of the known ZZ polynomial formulas for the discussed earlier families and subfamilies of benzenoid structures and for discovering the ZZ polynomials for various new classes of benzenoids, which did not permit such a discovery until now.

3. ZZ polynomials of the $S(n)$ structures of Randić

The formal proof of the recurrence formula found in [1] for the $S(n)$ structures of Randić [1, 8-11] starts here with the analysis of a finite member of this family, $S(8)$. Recursive decomposition of $S(8)$ in the way presented in **Figure 1** shows that the ZZ polynomial of $S(8)$ can be represented in two equivalent forms:

$$\mathrm{ZZ}(S(8),x)=(1+x)\mathrm{ZZ}(S(7),x)+\mathrm{ZZ}(Sa(7),x) \tag{1}$$

if the decomposition is terminated after the first step or

$$\mathrm{ZZ}(S(8),x)=(2+x)\mathrm{ZZ}(S(7),x)+(1+x)\mathrm{ZZ}(Sa(5),x) \tag{2}$$

if the decomposition is terminated after the second step. Provided that $n > 3$ both equations can be immediately generalized to the case of $S(n)$, which is associated with the fact that the part of the structure $S(8)$ located inside the gray shaded boxes in **Figure 1** does not take an active part in the decomposition process and in principle can be arbitrarily long. The generalized equations

$$\mathrm{ZZ}(S(n),x)=(1+x)\mathrm{ZZ}(S(n-1),x)+\mathrm{ZZ}(Sa(n-1),x) \tag{3}$$

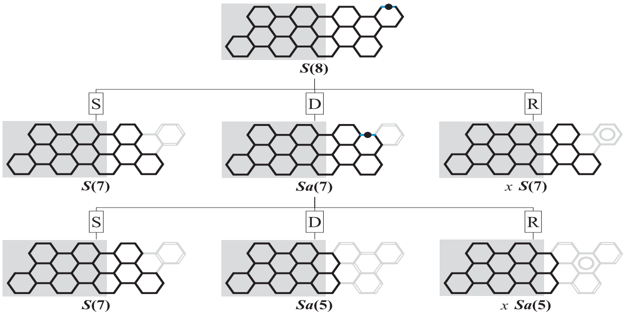

Figure 1. A convenient graph decomposition of the structure $S(8)$. The gray shaded area is passive in the decomposition process and thus can be of arbitrary length, allowing one to generalize the decomposition to an arbitrary structure $S(n)$ and

and

$$\mathrm{ZZ}\left(S(n),x\right)=(2+x)\mathrm{ZZ}\left(S(n),x\right)+(1+x)\mathrm{ZZ}\left(Sa(n-3),x\right) \tag{4}$$

constitute a convenient departure point for the proof, which is based on the elimination of the ZZ polynomials of the structure $Sa(n-3)$ from Eq. (4). Slight modification of Eq. (3)with the index n replaced by $n-2$, gives

$$\mathrm{ZZ}\left(Sa(n-3),x\right)=\mathrm{ZZ}\left(S(n-2),x\right)-(1+x)\mathrm{ZZ}\left(S(n-3),x\right) \tag{5}$$

This formula, when substituted in Eq. (4) produces the formula of the ZZ polynomial of $S(n)$ agreeing with Eq. (24) of [1]

$$\begin{aligned}\mathrm{ZZ}\left(S(n),x\right)=&(2+x)\,\mathrm{ZZ}\left(S(n-1),x\right)+(1+x)\,\mathrm{ZZ}\left(S(n-2),x\right)\\&-(1+x)^2\,\mathrm{ZZ}\left(S(n-3),x\right).\end{aligned} \tag{6}$$

Solution to this recurrence equation has quite simple form given by

$$\mathrm{ZZ}\left(S(n),x\right)=\sum_{i=1}^{3}\frac{R_i^2(1+x)-1}{2R_i^3(1+x)^2-R_i^2(1+x)-1}\cdot\frac{1}{R_i^n} \tag{7}$$

where R_1, R_2, and R_3 are the solutions to the polynomial equation

$$R_i^3(1+x)^2-R_i^2(1+x)-(2+x)R_i+1=0 \tag{8}$$

Unfortunately, algebraic roots of this equation have rather complex and lengthy form, making the evaluation of the ZZ polynomial of $S(n)$ using Eq. (7) quite a cumbersome and time-consuming process. Yet, Eq. (7) can be conveniently used for determining the total number of Clar covers for the structures $S(n)$. This value can be easily obtained by substituting $x = 1$ in Eq. (7), which evaluates to

$$\frac{1}{5}+\frac{1-2\left(\frac{\sqrt{5}}{4}-\frac{1}{4}\right)^2}{\left(2+\sqrt{5}-12\left(\frac{\sqrt{5}}{4}-\frac{1}{4}\right)^2\right)\left(\frac{\sqrt{5}}{4}-\frac{1}{4}\right)^n}+\frac{1-2\left(\frac{\sqrt{5}}{4}+\frac{1}{4}\right)^2}{\left(2-\sqrt{5}-12\left(\frac{\sqrt{5}}{4}+\frac{1}{4}\right)^2\right)\left(-\frac{\sqrt{5}}{4}-\frac{1}{4}\right)^n} \tag{9}$$

The recurrence formula given by (6) can be also solved in terms of an appropriate generating function

$$GF(t,x)=\sum_{k=0}^{\infty} ZZ(S(k),x)\cdot t^k \tag{10}$$

which can be computed using standard methods with MAPLE [24] or obtained directly from Eq. (6) by multiplying both sides by t^n and summing the resulting formula over all non-negative integers, yielding

$$GF(t,x)=\frac{1-(1+x)\cdot t^2}{1-(2+x)\cdot t-(1+x)\cdot t^2+(1+x)^2\cdot t^3} \tag{11}$$

with the boundary conditions given by $ZZ(S(1),x)$, $ZZ(S(2),x)$, and $ZZ(S(3),x)$ listed in Eq. (23) of [1]. To get a useful expression for the ZZ polynomials of $S(n)$, we expand the generating function in the following way

$$\begin{aligned} GF(t,x) &= \frac{1-(1+x)t^2}{(1+x)^2t^3-(1+x)t^2-(2+x)t+1} \\ &= (1-(1+x)t^2)\cdot\sum_{l=0}^{\infty}(-1)^l\left((1+x)^2t^3-(1+x)t^2-(2+x)t\right)^l \\ &= (1-(1+x)t^2)\cdot\sum_{l=0}^{\infty}\sum_{k=0}^{l}\sum_{m=0}^{k}(-1)^m\binom{l}{k}\binom{k}{m}\cdot t^{k+l+m}\cdot(1+x)^{k+m}\cdot(2+x)^{l-k} \end{aligned} \tag{12}$$

The triple summations can be rearranged by the following sum identity

$$\sum_{l=0}^{\infty}\sum_{k=0}^{l}\sum_{m=0}^{k} t^{k+l+m}\cdot \mathrm{A}_{k,l,m} = \sum_{n=0}^{\infty} t^{n} \sum_{k=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \sum_{l=0}^{\left\lfloor \frac{n-2k}{3} \right\rfloor} \mathrm{A}_{l+k,n-2l-k,l} \tag{13}$$

where $\lfloor \cdots \rfloor$ denotes the floor function, into the following closed-form formula

$$\begin{aligned} GF(t,x) &= (1-(1+x)t^2)\sum_{n=0}^{\infty} t^{n} \sum_{k=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \sum_{l=0}^{\left\lfloor \frac{n-2k}{3} \right\rfloor} (-1)^{l} \binom{n-2l-k}{l+k}\binom{l+k}{l}\cdot(1+x)^{2l+k}\cdot(2+x)^{n-3l-2k} \\ &= 1+\sum_{n=1}^{\infty} t^{n} \sum_{k=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \sum_{l=0}^{\left\lfloor \frac{n-2k}{3} \right\rfloor} (-1)^{l} (1+x)^{2l+k}(2+x)^{n-3l-2k} \frac{n-2l-2k}{n-2l-k}\binom{n-2l-k}{l}\binom{n-3l-k}{k} \end{aligned} \tag{14}$$

The series of transformations leading to the final equation is quite complex and involves multiple change of summation indices and a number of binomial identities; we skip the intermediate steps showing here only the final result. Comparison of the second line of Eq. (14) with Eq. (10) shows that the ZZ polynomial of the structure $S(n)$ for $n \geq 1$ is given by

$$ZZ\left(S(n),x\right) = \sum_{k=0}^{\left\lfloor \frac{n}{2} \right\rfloor} \sum_{l=0}^{\left\lfloor \frac{n-2k}{3} \right\rfloor} (-1)^{l} (1+x)^{2l+k}(2+x)^{n-3l-2k} \frac{n-2l-2k}{n-2l-k}\binom{n-2l-k}{l}\binom{n-3l-k}{k} \tag{15}$$

Numerical experiments show that Eq. (15) is correct. It is quite possible that further transformations of this equation may simplify it significantly; this task is not attempted here.

4. ZZ polynomials of tripods $T(n, m, l)$

The formal derivation of the ZZ polynomial for tripods $T(n, m, l)$ is most conveniently initiated with the analysis of the case with $m = 1$. The ZZ polynomial for such a "hockey stick" structure, $T(n, 1, l)$, was derived originally by Zhang and Zhang (one of initial conditions to Eq. (4.4) of [17]) and formally by us (**Figure 6** of [7]); it is given by

$$\mathrm{ZZ}\left(T(n,1,l),x\right) = (x+1) + \mathrm{ZZ}\left(L(n-1),x\right)\cdot \mathrm{ZZ}\left(L(l-1),x\right), \tag{16}$$

For $m > 1$, a possible graph decomposition of $T(n, m, l)$ is shown in **Figure 2**. It can be seen that the ZZ polynomial of $T(n, m, l)$ has the following formula

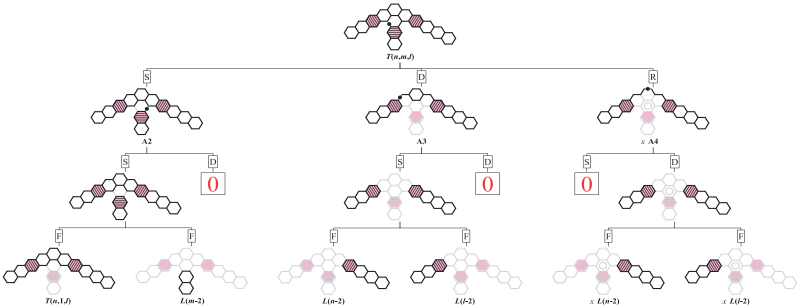

Figure 2. A convenient graph decomposition of a tripod $T(n,m,l)$.

$$ZZ\big(T(n,m,l),x\big)=\big[ZZ\big(T(n,1,l),x\big)\cdot ZZ\big(L(m-2),x\big)\big]\\ +(x+1)\cdot\big[ZZ\big(L(l-2),x\big)\cdot ZZ\big(L(n-2),x\big)\big]. \tag{17}$$

Substituting Eq. (16) into Eq. (17) produces the resulting ZZ polynomial of $T(n,m,l)$ identical to the formula given by Eq. (27) of [2]

$$ZZ\big(T(n,m,l),x\big)=\big[ZZ\big(L(m-2),x\big)\cdot ZZ\big(L(n-1),x\big)\cdot ZZ\big(L(l-1),x\big)\big]\\ +(1+x)\cdot\big[ZZ\big(L(m-2),x\big)+ZZ\big(L(n-2),x\big)\cdot ZZ\big(L(l-2),x\big)\big] \tag{18}$$

5. ZZ polynomials of zigzag-edge coronoid fused with starphene $ZCS(n,m,l)$

The ZZ polynomial of zigzag-edge coronoid fused with starphene $ZCS(n,m,l)$ is definitely the most complicated formula obtained in our previous study. [2] Here, we present its formal derivation, which turns out to be a fairly complicated process. A partial graphical decomposition of $ZCS(n,m,l)$ is shown in **Figure 3**. After a number of decomposition steps, the ZZ polynomial of $ZCS(n,m,l)$ can be represented as a sum of ZZ polynomials of 14 intermediate structures

$$ZZ\big(ZCS(n,m,l),x\big)=(1+x)\cdot ZZ\big(F_1(n,m,l),x\big)+\sum_{i=2}^{14}ZZ\big(F_i(n,m,l),x\big) \tag{19}$$

Ten of the intermediate structures are easily identified

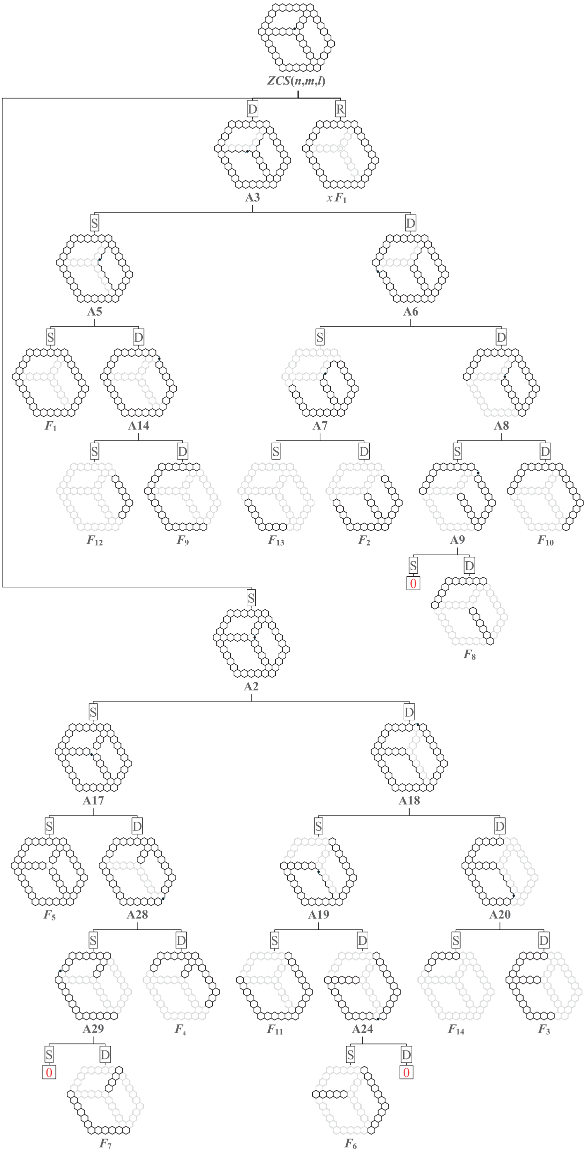

Figure 3. A recursive decomposition of $ZCS(n,m,l)$ used in text to derive a closed form formula for the ZZ polynomial of this structure.

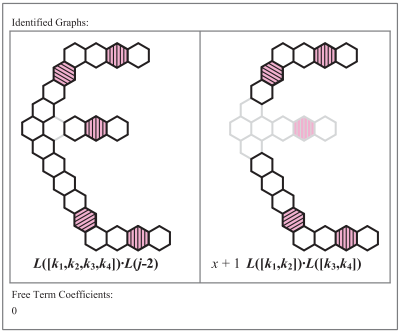

Figure 4. The width-mode decomposition of $TD([k_1, k_2, k_3, k_4], j)$

$F_1 = ZC(n, m, l)$		
$F_6 = L(n-1) \cdot L([m, l])$	$F_7 = L(l-1) \cdot L([m, n])$	$F_8 = L(m-1) \cdot L([l, n])$
$F_9 = L([n, m, l, n])$	$F_{10} = L([l, n, m, l])$	$F_{11} = L([m, l, n, m])$
$F_{12} = L([m-2, l-2])$	$F_{13} = L([m-2, n-2])$	$F_{14} = L([n-2, l-2])$

The remaining four intermediate structures are new. Structures F_2, F_3, and F_4 belong to the same family; they can be called "tridents" owing to their shape. The ZZ polynomial of a most general trident $TD([k_1, k_2, k_3, k_4], j)$ is given by

$$\begin{aligned} ZZ\big(TD([k_1,k_2,k_3,k_4],j),x\big) &= ZZ\big(L([k_1,k_2,k_3,k_4]),x\big)\cdot ZZ\big(L(j-2),x\big) \\ &+(1+x)\cdot ZZ\big(L([k_1,k_2],x\big)\cdot ZZ\big(L([k_3,k_4]),x\big) \end{aligned} \tag{20}$$

as can be easily seen from the decomposition performed in **Figure 4** with the width-mode ZZDecomposer. Thus, we have

$$F_2 = TD\big(\big[m-2,n,l,m-2\big],m-1\big) \tag{21}$$

$$F_3 = TD\big(\big[n-2,m,l,n-2\big],n-1\big) \tag{22}$$

$$F_4 = TD\big(\big[l-2,n,m,l-2\big],l-1\big) \tag{23}$$

The remaining intermediate structure, $F_5(n, m, l)$, is almost as complex as the original structure $ZCS(n, m, l)$ and requires a separate decomposition. The highly-symmetric products of its recursive decomposition obtained with the width-mode ZZDecomposer are shown in **Figure 5**. The resulting ZZ polynomial formula is given by

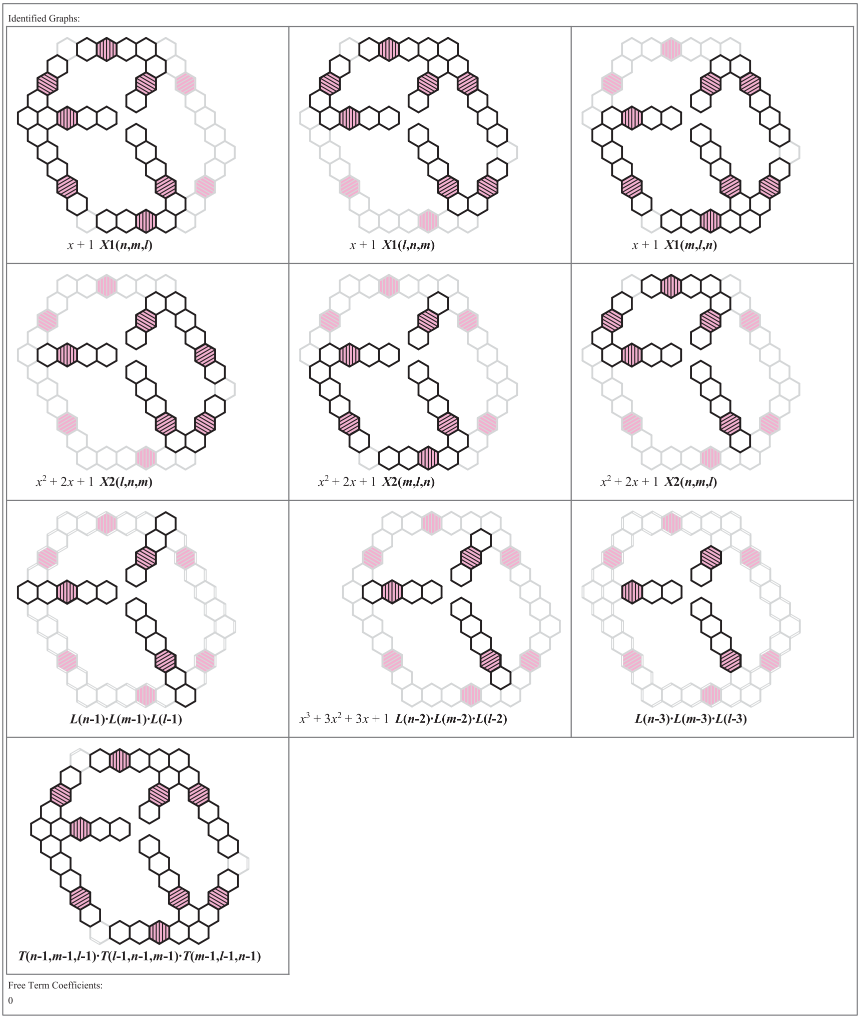

Figure 5. Decomposition products of $F_5(n,m,l)$ obtained with the width-mode ZZDecomposer.

$$\begin{aligned}
\mathrm{ZZ}\left(F_5(n,m,l),x\right) = {} & \mathrm{ZZ}\left(T(n-1,m-1,l-1),x\right)\cdot \mathrm{ZZ}\left(T(l-1,n-1,m-1,x\right)\cdot \mathrm{ZZ}\left(T(m-1,l-1,n-1),x\right) \\
& +(x+1)\cdot\left[\mathrm{ZZ}\left(X_1(n,m,l),x\right)+\mathrm{ZZ}\left(X_1(m,l,n),x\right)+\mathrm{ZZ}\left(X_1(l,n,m),x\right)\right] \\
& +(x+1)^2\cdot\left[\mathrm{ZZ}\left(X_2(n,m,l),x\right)+\mathrm{ZZ}\left(X_2(m,l,n),x\right)+\mathrm{ZZ}\left(X_2(l,n,m),x\right)\right] \\
& +(x+1)^3\cdot\left[\mathrm{ZZ}\left(L(n-2),x\right)\cdot \mathrm{ZZ}\left(L(m-2),x\right)\cdot \mathrm{ZZ}\left(L(l-2),x\right)\right] \\
& +\mathrm{ZZ}\left(L(n-1),x\right)\cdot \mathrm{ZZ}\left(L(m-1),x\right)\cdot \mathrm{ZZ}\left(L(l-1),x\right) \\
& +\mathrm{ZZ}\left(L(n-3),x\right)\cdot \mathrm{ZZ}\left(L(m-3),x\right)\cdot \mathrm{ZZ}\left(L(l-3),x\right)
\end{aligned} \tag{24}$$

where $X_1(k_1, k_2, k_3)$ and $X_2(k_1, k_2, k_3)$ are defined as

$$X_1(k_1,k_2,k_3) = T(k_1-1,k_2-1,k_3-1)\cdot L([k_1-2,2,k_2-2])\cdot L([k_3-2,2,k_2-2]) \tag{25}$$

$$X_2(k_1,k_2,k_3) = L(k_2-2)\cdot L([k_1-2,2,k_3-2])\cdot L([k_1-2,2,k_3-2]) \tag{26}$$

with the dot representing the union of disconnected structures. Direct substitution of the ZZ polynomials of all intermediate structures to Eq. (19) produces the ZZ polynomial of the structure $ZCS(n, m, l)$ equivalent to Eqs. (65) and (66) of [2], completing the formal derivation presented here. The complexity of the underlying intermediate structures and their abundance partially explain the complexity of the $ZCS(n, m, l)$ ZZ polynomial formula; it is rather unlikely that it can be further simplified into substantially shorter form.

6. ZZ polynomials of multiple zigzag chains $Z(4, n)$, $Z(5, n)$ and $Z(6, n)$

The two step decomposition of the multiple zigzag chain $Z(4, n)$ shown in **Figure 6** yields a recursion formula for its ZZ polynomial in the following form

$$\begin{aligned} \mathrm{ZZ}(Z(4,n),x) = {} & \mathrm{ZZ}(Z(4,n-1),x) + (1+x)\cdot \mathrm{ZZ}(Z(3,n-1),x) \\ & + x\cdot(1+x)\cdot \mathrm{ZZ}(L(n-1),x)^2 + \mathrm{ZZ}(M(2,n),x)\cdot \mathrm{ZZ}(L(n),x) \\ & + x\cdot \mathrm{ZZ}(M(2,n-1),x)\cdot \mathrm{ZZ}(L(n-1),x) \end{aligned} \tag{27}$$

This decomposition, similarly to many others appearing in this study later, relies heavily on **Theorem 7** of [12], which states that the ZZ polynomial of two fused parallelograms is equal to the product of their ZZ polynomials. The structure obtained by fusing two parallelograms is represented in the following figures as $M(m, n)||M(m', n')$ to stress the parallel alignment of the parallelograms or as $M(m, n) \cdot M(m', n')$ to stress the essentially disconnected character of such a composite structure. Eq. (27) can be telescopically folded to yield

$$\begin{aligned} ZZ(Z(4,n),x) = {} & ZZ(M(2,n),x)\cdot ZZ(L(n),x) + (1+x)\sum_{k=0}^{n-1} ZZ(Z(3,k),x) \\ & + (1+x)\sum_{k=0}^{n-1} ZZ(M(2,k),x)\cdot ZZ(L(k),x) + x\cdot(1+x)\cdot \sum_{k=0}^{n-1} ZZ(L(k),x)^2 \end{aligned} \tag{28}$$

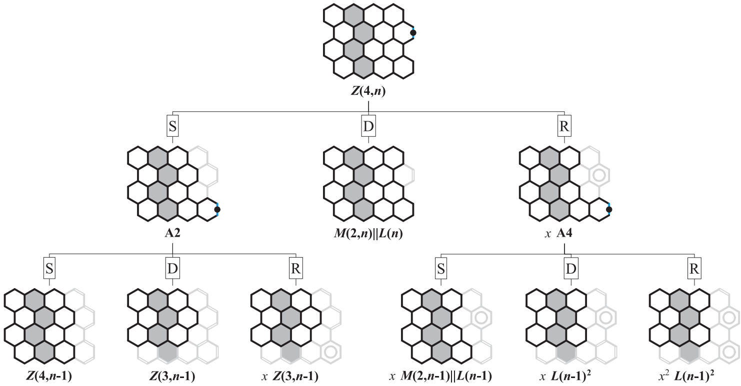

Figure 6. Graph decomposition of $Z(4,n)$. Each shaded hexagon represents schematically a horizontal polyacene of length $n-3$.

Since $Z(3,k) = Ch(2,2,k)$, the ZZ polynomial of $Z(3,k)$ is given by Eq. (15) of [12] as

$$ZZ\left(Z(3,k),x\right) = ZZ\left(L(k),x\right)^2 + (1+x)\cdot\sum_{l=0}^{k-1} ZZ\left(L(l),x\right)^2 \tag{29}$$

Direct substitution of this formula to Eq. (28) produces a closed formula for the ZZ polynomial of $Z(4,n)$ expressed in terms of ZZ polynomials of the simplest building blocks, polyacenes $L(k)$ and parallelograms $M(2,k)$

$$\begin{aligned} ZZ\left(Z(4,n),x\right) = {} & ZZ\left(M(2,n),x\right)\cdot ZZ\left(L(n),x\right) \\ & +(1+x)\sum_{k=0}^{n-1} ZZ\left(M(2,k),x\right)\cdot ZZ\left(L(k),x\right) \\ & +(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k} ZZ\left(L(l),x\right)^2 \end{aligned} \tag{30}$$

which can be further simplified using relation (58) to

$$\begin{aligned} ZZ\left(Z(4,n),x\right) = {} & ZZ\left(M(2,n),x\right)\cdot ZZ\left(L(n),x\right) \\ & +(1+x)\sum_{k=0}^{n-1} ZZ\left(M(2,k),x\right)\cdot ZZ\left(L(k),x\right) \\ & +(1+x)^2\sum_{k=0}^{n-1}(n-k)\cdot ZZ\left(L(k),x\right)^2 \end{aligned} \tag{31}$$

This form is already suitable for numerical evaluation of $ZZ(Z(4,n),x)$, but direct substitution of $ZZ(M(2,k),x)$ and $ZZ(L(k),x)$ after substantial algebraic manipulations yields much more compact and quite surprising formula

$$\begin{aligned} ZZ\left(Z\left(4,n\right),x\right) &= \sum_{k=0}^{4}\left(1+x\right)^{k}\left[\binom{3}{k}\binom{n}{k}+n\binom{3}{k-1}\binom{n}{k-1}+\binom{0}{k-4}\binom{n+2}{k}\right] \\ &= ZZ\left(M\left(3,n\right),x\right)\cdot ZZ\left(L\left(n\right),x\right)+\binom{n+2}{4}\left(1+x\right)^{4} \end{aligned} \tag{32}$$

which is consistent with Eq. (44) of [2], justifying the previous heuristic reasoning.

Analogous three level decomposition of the multiple zigzag chain $Z(5,n)$ yields the decomposition products shown in **Figure 7** and produces a recursion formula for its ZZ polynomial in the following form

$$\begin{aligned} ZZ\left(Z\left(5,n\right),x\right) = {} & ZZ\left(Z\left(5,n-1\right),x\right)+ZZ\left(M\left(2,n\right),x\right)^{2} \\ & +x\cdot ZZ\left(M\left(2,n-1\right),x\right)^{2}+2\left(1+x\right)\cdot ZZ\left(Z\left(4,n-1\right),x\right) \\ & +\left(1+x\right)^{2}\cdot ZZ\left(Z\left(3,n-1\right),x\right) \\ & +2x\cdot\left(1+x\right)\cdot ZZ\left(M\left(2,n-1\right),x\right)\cdot ZZ\left(L\left(n-1\right),x\right) \\ & +x\cdot\left(1+x\right)^{2}\cdot ZZ\left(L\left(n-1\right),x\right)^{2} \end{aligned} \tag{33}$$

which can be telescopically folded and simplified to yield

$$\begin{aligned} ZZ\left(Z\left(5,n\right),x\right) = {} & ZZ\left(M\left(2,n\right),x\right)^{2}+\left(1+x\right)\sum_{k=0}^{n-1}ZZ\left(M\left(2,k\right),x\right)^{2} \\ & +2\left(1+x\right)\sum_{k=0}^{n-1}ZZ\left(L\left(k\right),x\right)\cdot\left[ZZ\left(M\left(2,k\right),x\right)+ZZ\left(M\left(3,k\right),x\right)\right] \\ & +\left(1+x\right)^{3}\sum_{k=0}^{n-1}\left(n-k\right)\cdot ZZ\left(L\left(k\right),x\right)^{2}+2\left(1+x\right)^{5}\binom{n+2}{5} \end{aligned} \tag{34}$$

This form can be again suggested for numerical computations. Direct substitution of ZZ polynomials of $M(2,k)$ and $L(k)$ produces a lengthy expression containing sums of double and triple products of binomial coefficients that could be simplified to

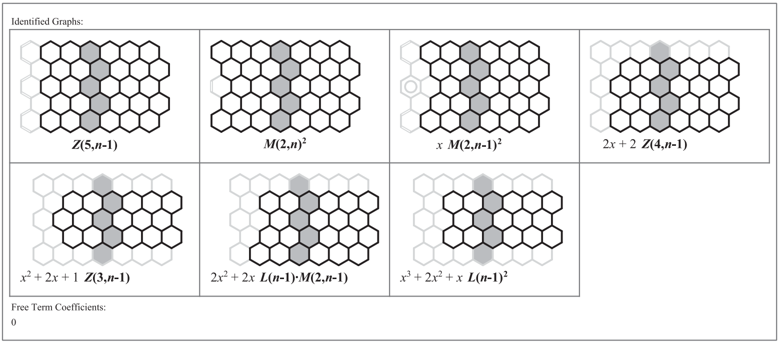

Figure 7. Decomposition products of $Z(5,n)$ obtained with the width-mode ZZDecomposer. Each shaded hexagon represents schematically a horizontal polyacene of length $n-6$.

$$\begin{aligned} ZZ\left(Z(5,n),x\right) &= \sum_{k}^{5}\binom{5}{k}\binom{n}{k}(1+x)^k + 6\binom{n+1}{2}(1+x)^2 \\ &+\left(20\binom{n+1}{3}+\binom{n+1}{2}\right)(1+x)^3 + \left(27\binom{n+1}{4}+7\binom{n+1}{3}\right)(1+x)^4 \\ &+\left(15\binom{n+1}{5}+9\binom{n+1}{4}+\binom{n+1}{3}\right)(1+x)^5 \end{aligned} \tag{35}$$

This formula is consistent with the heuristically derived ZZ polynomial of $Z(5,n)$ given by Eq. (45) of [2].

Analogous technique can be employed for deriving the ZZ polynomial of $Z(6,n)$. The three-level decomposition process, yields the decomposition products shown in **Figure 8** and produces the following recursion formula

$$\begin{aligned} ZZ\left(Z(6,n),x\right) &= ZZ\left(Z(6,n-1),x\right) + (1+x)\cdot ZZ\left(Z(3,n),x\right)\cdot ZZ\left(M(2,n),x\right) \\ &+(1+x)\cdot ZZ\left(Z(4,n-1),x\right)\cdot ZZ\left(L(n-1),x\right) \\ &+(1+x)^2\cdot ZZ\left(Z(3,n-1),x\right)\cdot ZZ\left(L(n-1),x\right) \\ &+(1+x)\cdot ZZ\left(Z(5,n-1),x\right) + (1+x)\cdot ZZ\left(Z(4,n-1),x\right) \\ &+(1+x)^2\cdot ZZ\left(Z(3,n-1),x\right) - x\cdot(1+x)\cdot ZZ\left(M(2,n),x\right)\cdot ZZ\left(L(n),x\right) \\ &-x\cdot(1+x)\cdot ZZ\left(Z(3,n),x\right) + x\cdot(1+x)^2\cdot ZZ\left(L(n),x\right) \end{aligned} \tag{36}$$

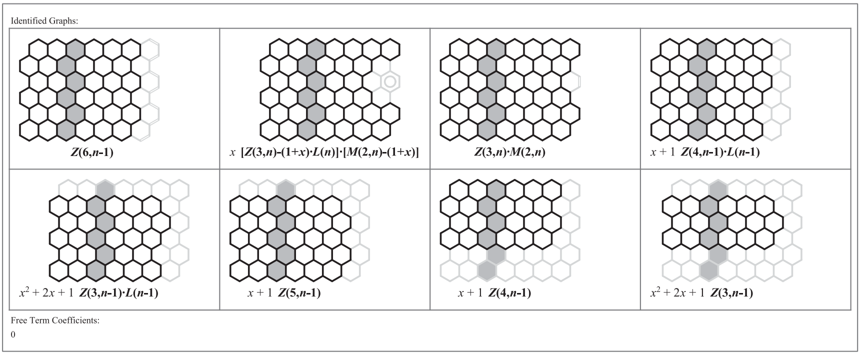

Figure 8. Decomposition products of $Z(6,n)$ obtained with the width-mode ZZDecomposer. Each shaded hexagon represents schematically a horizontal polyacene of length $n-6$.

After telescopic folding and extensive algebraic manipulations analogous to those described earlier for $Z(4,n)$ and $Z(5,n)$, it is possible to cast this equation in the following binomial-based form

$$\begin{aligned} ZZ\left(Z\left(6,n\right),x\right) = {} & \sum_{k}^{6}\binom{6}{k}\binom{n}{k}(1+x)^{k} + 10\binom{n+1}{2}(1+x)^{2} + \left(48\binom{n+1}{3}+4\binom{n+1}{2}\right)(1+x)^{3} \\ & + \left(102\binom{n+1}{4}+30\binom{n+1}{3}\right)(1+x)^{4} \\ & + \left(116\binom{n+1}{5}+72\binom{n+1}{4}+8\binom{n+1}{3}\right)(1+x)^{5} \\ & + \left(60\binom{n+1}{6}+62\binom{n+1}{5}+17\binom{n+1}{4}+\binom{n+1}{3}\right)(1+x)^{6} \end{aligned} \qquad (37)$$

which agrees with the heuristically-derived Eq. (46) given by us previously in [2].

The presented here method gives a ready-to-use technique of developing closed-form ZZ polynomial formulas for multiple zigzag chains with larger values of m. It is easy to show that the ZZ polynomial of $Z(7,n)$ is given by

$$\mathrm{ZZ}\big(Z(7,n),x\big)=\sum_{k=0}^{n}\mathrm{ZZ}\big(Z(3,k),x\big)^{2}+x\cdot\sum_{k=1}^{n}\Big(\mathrm{ZZ}\big(Z(3,k),x\big)-(1+x)\cdot\mathrm{ZZ}\big(L(k),x\big)\Big)^{2}$$
$$+2\cdot(1+x)\sum_{k=0}^{n-1}\Big[\mathrm{ZZ}\big(Z(5,k),x\big)\cdot\big(\mathrm{ZZ}(L(k),x)+1\big)\Big]$$
$$+(1+x)^{2}\sum_{k=0}^{n-1}\Big[\mathrm{ZZ}\big(Z(3,k),x\big)\cdot\big(\mathrm{ZZ}(L(k),x)+1\big)^{2}\Big] \tag{38}$$

which can be readily transformed into a working equation given by

$$\mathrm{ZZ}\big(Z(7,n),x\big)=1+7n\cdot(1+x)+3n\cdot(6n-1)(1+x)^{2}+\frac{5}{6}n(13n-1)(2n-1)(1+x)^{3}$$
$$+\frac{n}{3}(4n+1)(10n^{2}-10n+1)(1+x)^{4}$$

$$+\frac{n}{10}(n-1)(2n-1)(22n^{2}-12n+1)(1+x)^{5}$$
$$+\frac{n}{90}(n-1)(2n-1)(34n^{3}-45n^{2}+23n-3)(1+x)^{6}$$
$$+\frac{n}{2520}(n-1)(2n-1)(68n^{4}-136n^{3}+133n^{2}-65n+18)(1+x)^{7} \tag{39}$$

analogous to Eqs. (44), (45), and (46) given in [2] for $Z(4,n)$, $Z(5,n)$, and $Z(6,n)$. Similar working equations for $Z(8,n)$ and $Z(9,n)$ obtained in the same manner are given by

$$\mathrm{ZZ}\big(Z(8,n),x\big)=1+8n(1+x)+\frac{7}{2}n\cdot(7n-1)(1+x)^{2}+n(37n^{2}+1-18n)(1+x)^{3}$$
$$+\frac{5n}{24}(5n-1)(29n^{2}-25n+2)(1+x)^{4}$$
$$+\frac{n}{30}(n-1)(421n^{3}-339n^{2}+76n-4)(1+x)^{5}$$
$$+\frac{n}{80}(n-1)(301n^{4}-480n^{3}+275n^{2}-60n+4)(1+x)^{6}$$
$$+\frac{n}{2520}(n-1)(1385n^{5}-3249n^{4}+3275n^{3}-1695n^{2}+440n-36)(1+x)^{7}$$
$$+\frac{n}{40320}(n-1)(1385n^{6}-4155n^{5}+5967n^{4}-5009n^{3}+2656n^{2}$$
$$-844n+144)(1+x)^{8} \tag{40}$$

$$
\begin{aligned}
\mathrm{ZZ}\big(Z(9,n),x\big) = {} & 1+9n\cdot(1+x)+4n\cdot(8n-1)(1+x)^2+\frac{7}{6}n\cdot(50n^2-21n+1)(1+x)^3 \\
& +\frac{n}{2}(6n-1)(20n^2-15n+1)(1+x)^4 \\
& +\frac{n}{6}(220n^4-350n^3+160n^2-25n+1)(1+x)^5 \\
& +\frac{n}{45}(n-1)(2n-1)(308n^3-264n^2+55n-3)(1+x)^6 \\
& +\frac{n}{840}(n-1)(2n-1)(1300n^4-2124n^3-1295n^2-303n+18)(1+x)^7 \\
& +\frac{n}{2520}(n-1)(2n-1)(496n^5-1172n^4+1228n^3-673n^2 \\
& \qquad +193n-18)(1+x)^8 \\
& +\frac{n}{11340}(n-1)(2n-1)(124n^6-372n^5+547n^4-474n^3+265n^2 \\
& \qquad -90n+18)(1+x)^9
\end{aligned}
\tag{41}
$$

Unfortunately, the presented here derivations have not brought us much closer to the main goal of our analysis, i.e., finding a general closed formula for the ZZ polynomial of a general multiple zigzag chain $Z(m,n)$. Substantial research effort in our group is devoted to this topic and we hope to shed more light on this issue in one of the forthcoming publications.

7. ZZ polynomial of oblate rectangle $Or(m,2)$

Closed form of ZZ polynomial for the oblate rectangle $Or(m,2)$ can be formally derived in the following way. The recursive decomposition of $Or(6,2)$ shown in **Figure 9** shows how to express its ZZ polynomial in terms of ZZ polynomials of a shorter oblate rectangle $Or(5,2)$, multiple zigzag chains $Z(5,5)$ and $Z(4,5)$, intermediate rectangles $R(3,6)$ and $R(3,5)$ [11], and a pentagon $D(2,3,5)$. It is clear that the fragments of the studied structures located in the shaded gray areas are passive in the decomposition process and can in principle be of arbitrary length without changing the decomposition scheme. Therefore, it is obvious that the presented decomposition of $Or(6,2)$ can be immediately generalized to a general oblate rectangle $Or(m,2)$ yielding the following recurrence formula

$$ZZ(Or(m,2),x) = ZZ(Or(m-1,2),x) + ZZ(R(3,m),x) + (1+2x)\cdot ZZ(R(3,m-1),x) \\ +x\cdot(1+x)\cdot ZZ(Z(5,m-1),x) + x\cdot(1+x)\cdot ZZ(Z(4,m-1),x) \\ +(1+x)\cdot ZZ(D(2,3,m-1),x) \qquad (42)$$

which can be telescopically folded to the following form

$$ZZ(Or(m,2),x) = ZZ(R(3,m),x) \\ +2(1+x)\sum_{k=0}^{m-1} ZZ(R(3,k),x) + x\cdot(1+x)\sum_{k=0}^{m-1} ZZ(Z(5,k),x) \\ +x\cdot(1+x)\sum_{k=0}^{m-1} ZZ(Z(4,k),x) + (1+x)\sum_{k=0}^{m-1} ZZ(D(2,3,k),x) \qquad (43)$$

The ZZ polynomial of the pentagon $D(2,3,k)$ is given by Eq. (54). The ZZ polynomial of the last missing puzzle, the intermediate rectangle $R(3,n)$ can be derived as follows. The decomposition process shown in **Figure 10** for $R(3,6)$ can be immediately generalized on the base of the same arguments as for $Or(m,2)$ to a general intermediate rectangle $R(3,n)$ yielding the following recurrence formula

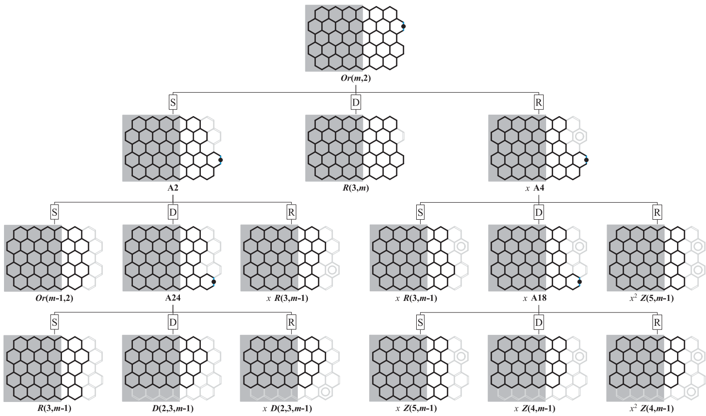

Figure 9. Decomposition tree of $Or(m,2)$. The shaded area is passive in the decomposition process and therefore it can be practically of arbitrary length.

$$ZZ(R(3,n),x) = ZZ(R(3,n-1),x) + ZZ(Z(5,n),x) + (1+x)\cdot ZZ(D(2,3,n-1),x) \\ +x\cdot ZZ(Z(5,n-1),x) + x\cdot(1+x)\cdot ZZ(Z(4,n-1),x) \qquad (44)$$

which can be telescopically folded to give

$$ZZ\left(R(3,n),x\right)=ZZ\left(Z(5,n),x\right)+(1+x)\sum_{k=0}^{n-1}ZZ\left(D(2,3,k),x\right)$$
$$+(1+x)\sum_{k=0}^{n-1}ZZ\left(Z(5,k),x\right)+x\cdot(1+x)\sum_{k=0}^{n-1}ZZ\left(Z(4,k),x\right) \quad (45)$$

Substitution of the ZZ polynomial formulas for $D(2,3,k)$ and $R(3,n)$ into Eq. (43) allows us to express the ZZ polynomial of $Or(m,2)$ solely in terms of the ZZ polynomials of $Z(5,n)$ and $Z(4,n)$, suggesting that the multiple zigzag chains $Z(m,n)$ may play an important role in the general theory of ZZ polynomials for pericondensed benzenoids in addition to the parallelograms $M(m,n)$. The resulting formula reads

$$ZZ\left(Or(m,2),x\right)=ZZ\left(Z(5,m),x\right)$$
$$+\sum_{k=0}^{m-1}\left[(2m-2k-1)(1+x)^2+2(1+x)\right]\cdot ZZ\left(Z(5,k),x\right) \quad (46)$$
$$+2\sum_{k=0}^{m-1}\left[\binom{m-k}{2}(1+x)^3+\binom{m-k}{1}(1+x)^2\right]\cdot ZZ\left(Z(4,k),x\right)$$

Direct substitution of ZZ polynomials for $Z(5,n)$ and $Z(4,n)$ given by Eqs. (35) and (32) yields the ZZ polynomial in the basis of $(1+x)^k$ monomials; the final formula justifies the heuristically derived Eq. (58) given by us previously in [2]. Note finally that analogous technique to that presented here can be applied for derivation of ZZ polynomials for $Or(m,3)$, $Or(m,4)$, $Or(m,5)$, etc, but the complexity of final formulas and the number of intermediate

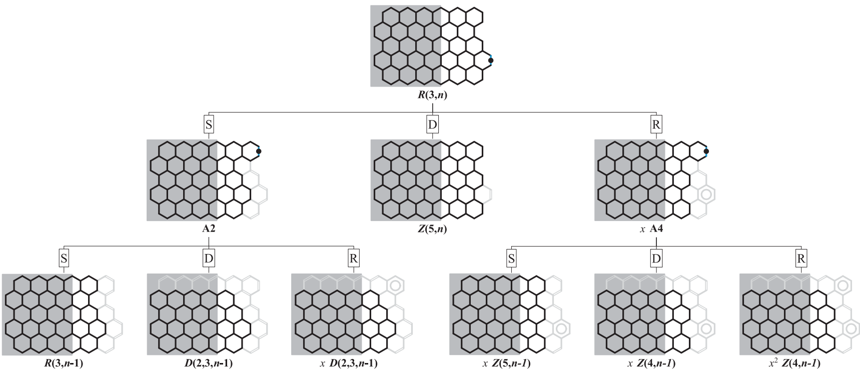

Figure 10. Decomposition tree of $R(3,n)$. The shaded area is passive in the decomposition process and therefore it can be practically of arbitrary length.

structures is anticipated to be substantially larger.

8. ZZ polynomials of hexagons $O(2,2,n)$, $O(2,3,n)$ and $O(3,3,n)$

The closed-form ZZ polynomial formulas for the $O(2,2,n)$ and $O(3,3,n)$ hexagons are reported in [2]. Despite of their quite structured form, the discovered formulas do not provide much insight in the general theory of ZZ polynomials of the $O(m,k,n)$ hexagons. Here we present formal derivation of these equations together with analogous derivation of ZZ polynomial for the $O(2,3,n)$ hexagons. The presented derivations partially explain the intrinsically complex structure of the ZZ polynomial formulas for hexagons.

The first two steps of a recursive decomposition of the $O(2,2,n)$ hexagon are shown in **Figure 11**. (The shaded benzene units are a symbolic representation of a segment of the hexagon $O(2,2,n)$ of width $n-5$; clearly, the width of this symbolic segment is immaterial for the presented here decomposition.) The first step of the decomposition process yields a recursive equation for the ZZ polynomial of $O(2,2,n)$ given by

$$ZZ\left(O(2,2,n),x\right)=ZZ\left(O(2,2,n-1),x\right)+ZZ\left(Ch(2,2,n),x\right)+x\cdot ZZ\left(Ch(2,2,n-1),x\right) \quad (47)$$

where $Ch(2,2,n)$ is a chevron structure with the ZZ polynomial given by Eq. (39) of [2]; the second step of the recursive decomposition shown in **Figure 11** suggest how one could obtain such a formula. Eq. (39) of [2] is generalized to an arbitrary chevron structure $Ch(k,m,n)$ in [12]. The resulting formal formula reads

$$\begin{aligned}ZZ\left(Ch(k,m,n),x\right)&=ZZ\left(M(k-1,n),x\right)\cdot ZZ\left(M(m-1,n),x\right)\\&+(1+x)\sum_{i=0}^{n-1}ZZ\left(M(k-1,i),x\right)\cdot ZZ\left(M(m-1,i),x\right)\end{aligned} \quad (48)$$

Eq. (47) can be telescopically folded with the boundary condition $ZZ(O(2,2,0),x)=1$ to yield

$$ZZ\left(O(2,2,n),x\right)=ZZ\left(Ch(2,2,n),x\right)+(1+x)\sum_{k=0}^{n-1}ZZ\left(Ch(2,2,k),x\right) \quad (49)$$

which, upon substituting with Eq. (48), gives

$$ZZ\left(O(2,2,n),x\right)=ZZ\left(M(1,n),x\right)^2 +2(1+x)\sum_{k=0}^{n-1}ZZ\left(M(1,k),x\right)^2 +(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}ZZ\left(M(1,l),x\right)^2 \tag{50}$$

Explicit evaluation of this expression with $ZZ(M(1,k),x) = ZZ(L(k),x) = k(1+x)+1$ gives in the basis of the $(1+x)^i$ monomials the following formula

$$ZZ\left(O(2,2,n),x\right)=(1+x)^4\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}l^2+(1+x)^3\left[\sum_{k=0}^{n-1}2k^2+\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}2l\right] +(1+x)^2\left[n^2+\sum_{k=0}^{n-1}4k+\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}1\right]+(1+x)\left[2n+\sum_{k=0}^{n-1}2\right]+1 \tag{51}$$

which agrees and justifies, upon evaluation of all the sums, the previously derived heuristic Eq. (35) of [2]. The algebraic complexity of the coefficients c_i in this expansion clearly explains the difficulties associated with finding general closed form of the coefficients c_i in the previous study; as we will see further, the complexity is even more severe for other hexagons, $O(2,3,n)$ and $O(3,3,n)$. In our opinion, the resulting Eq. (50) can be a convenient

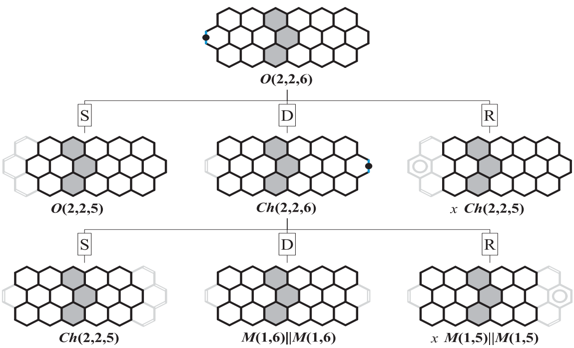

Figure 11. Graph decomposition of $O(2,2,n)$. Each shaded hexagon represents schematically a horizontal polyacene of length $n-5$.

departure point for further simplification of the obtained here formula; direct substitution of the ZZ polynomial of the parallelogram $M(m,n)$ in the hypergeometric form as given by

Eq. (5) of [12] and explicit evaluation of the sums may lead to much more compact representation, possibly also in hypergeometric form.

The recursive decomposition of $O(2,3,n)$, shown in **Figure 12**, is almost identical as for $O(2,2,n)$. The first step of the recursive decomposition produces a recurrence equation for the hexagon $O(2,3,n)$ given by

$$\mathrm{ZZ}\big(O(2,3,n),x\big)=\mathrm{ZZ}\big(O(2,3,n-1),x\big)+\mathrm{ZZ}\big(D(2,3,n),x\big)+x\cdot\mathrm{ZZ}\big(D(2,3,n-1),x\big) \tag{52}$$

where $D(2,3,n)$ is a regular four-tier strip usually referred to as pentagon [11]. Eq. (52) can be telescopically folded with the boundary condition $ZZ(O(2,3,0),x)=1$, yielding

$$\mathrm{ZZ}\big(O(2,3,n),x\big)=\mathrm{ZZ}\big(D(2,3,n),x\big)+(1+x)\sum_{k=0}^{n-1}\mathrm{ZZ}\big(D(2,3,k),x\big) \tag{53}$$

The closed-form formula for the ZZ polynomial of a general regular pentagon $D(k,m,n)$ is not known, but it is relatively easy to obtain the formula for $D(2,3,n)$ as suggested by the second step of the recursive decomposition shown in **Figure 12**. The resulting recurrence formula

$$\mathrm{ZZ}\big(D(2,3,n),x\big)=\mathrm{ZZ}\big(D(2,3,n-1),x\big)+\mathrm{ZZ}\big(Z(4,n),x\big)+x\cdot\mathrm{ZZ}\big(Z(4,n-1),x\big) \tag{54}$$

where $Z(m,n)$ is a multiple zigzag chain, can be again telescopically folded with the boundary condition $ZZ(D(2,3,0),x)=1$ giving

$$\mathrm{ZZ}\big(D(2,3,n),x\big)=\mathrm{ZZ}\big(Z(4,n),x\big)+(1+x)\sum_{k=0}^{n-1}\mathrm{ZZ}\big(Z(4,k),x\big) \tag{55}$$

This formula can be substituted in the expression for the ZZ polynomial of $O(2,3,n)$ yielding an expression analogous to Eq. (49)

$$\begin{aligned}\mathrm{ZZ}\big(O(2,3,n),x\big)&=\mathrm{ZZ}\big(Z(4,n),x\big)\\&\quad+2(1+x)\sum_{k=0}^{n-1}\mathrm{ZZ}\big(Z(4,k),x\big)+(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\mathrm{ZZ}\big(Z(4,l),x\big)\end{aligned} \tag{56}$$

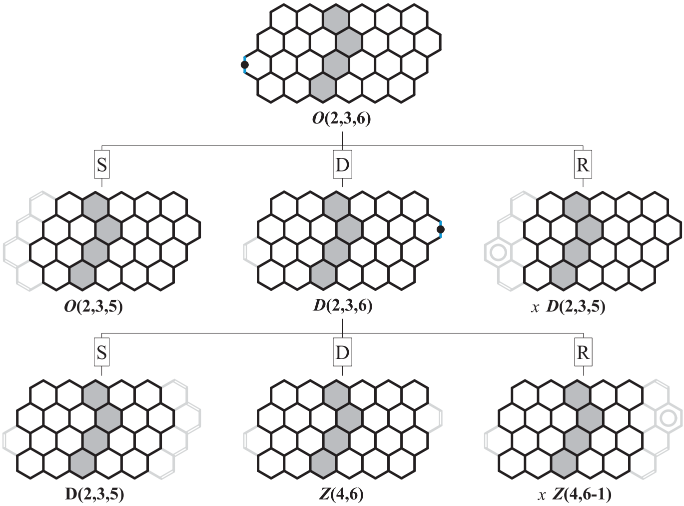

Figure 12. Graph decomposition of $O(2,3,n)$. Each shaded hexagon represents schematically a horizontal polyacene of length $n-5$.

Substituting into this equation the ZZ polynomial of $Z(4,n)$ given by Eq. (31) gives

$$\begin{aligned} ZZ\left(O(2,3,n),x\right) = {} & ZZ\left(M(2,n),x\right)\cdot ZZ\left(L(n),x\right) \\ & +3(1+x)\sum_{k=0}^{n-1} ZZ\left(M(2,k),x\right)\cdot ZZ\left(L(k),x\right) \\ & +3(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k-1} ZZ\left(M(2,l),x\right)\cdot ZZ\left(L(l),x\right) \\ & +(1+x)^3\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l-1} ZZ\left(M(2,m),x\right)\cdot ZZ\left(L(m),x\right) \\ & +(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k} ZZ\left(L(l),x\right)^2 + 2(1+x)^3\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l} ZZ\left(L(m),x\right)^2 \\ & +(1+x)^4\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l-1}\sum_{j=0}^{m} ZZ\left(L(j),x\right)^2 \end{aligned} \tag{57}$$

which can be greatly simplified using the following set of combinatorial identities

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k} F(l) = \sum_{k=0}^{n-1}\binom{n-k}{1} F(k) \tag{58}$$

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k-1} F(l) = \sum_{k=0}^{n-1}\binom{n-k-1}{1} F(k) \tag{59}$$

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l}F(m)=\sum_{k=0}^{n-1}\binom{n-k}{2}F(k) \quad (60)$$

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l-1}F(m)=\sum_{k=0}^{n-1}\binom{n-k-1}{2}F(k) \quad (61)$$

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l-1}\sum_{j=0}^{m}F(l)=\sum_{k=0}^{n-1}\binom{n-k}{3}F(k) \quad (62)$$

$$\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\sum_{m=0}^{l-1}\sum_{j=0}^{m-1}F(l)=\sum_{k=0}^{n-1}\binom{n-k-1}{3}F(k) \quad (63)$$

giving the most compact formula for the ZZ polynomial of $O(2,3,n)$ in the following form

$$\begin{aligned} ZZ(O(2,3,n),x) &= ZZ(M(2,n),x)\cdot ZZ(L(n),x) \\ &+\sum_{l=0}^{1}\sum_{k=0}^{n-1}ZZ(M(1+l,k),x)\cdot ZZ(L(k),x)\sum_{j=1}^{3}\binom{2+l}{j+l-1}\binom{n-k-l}{j-l}(1+x)^{j+1-l} \end{aligned} \quad (64)$$

Explicit substitution of ZZ polynomials for $M(2,n)$ and $M(1,n)=L(n)$ and evaluation of the sums produces a working equation for $O(2,3,n)$ given by

$$\begin{aligned} ZZ(O(2,3,n),x) &= 1+6n(1+x)+3n(3n-2)(1+x)^2+\frac{2}{3}n(8n-7)(n-1)(1+x)^3 \\ &+\frac{n}{12}(n-1)^2(17n-28)(1+x)^4+\frac{n}{6}(n-1)^2(n-2)^2(1+x)^5 \\ &+\frac{n}{144}(n-3)(n-1)^2(n-2)^2(1+x)^6 \end{aligned} \quad (65)$$

Formal derivation of the ZZ polynomial for the hexagons $O(3,3,n)$ closely follows analogous processes for the hexagons $O(2,2,n)$ and $O(2,3,n)$ presented above. The first step of the recursive decomposition shown in **Figure 13** produces a recurrence equation for the hexagon $O(3,3,n)$ given by

$$ZZ(O(3,3,n),x)=ZZ(O(3,3,n-1),x)+ZZ(D^j(3,n),x)+x\cdot ZZ(D^j(3,n-1),x) \quad (66)$$

where $D^j(3,n)$ is an auxiliary intermediate structure usually referred to as an oblate pentagon [11]. Eq. (66) can be telescopically folded with the boundary condition $ZZ(O(3,3,0),x)=1$, yielding

$$ZZ(O(3,3,n),x)=ZZ(D^j(3,n),x)+(1+x)\sum_{k=0}^{n-1}ZZ(D^j(3,k),x) \quad (67)$$

The closed-form formula for the ZZ polynomial of a general oblate pentagon $D^j(k,m,n)$ is not known, but it is relatively easy to obtain the formula for $D^j(3,n)$ as suggested by the

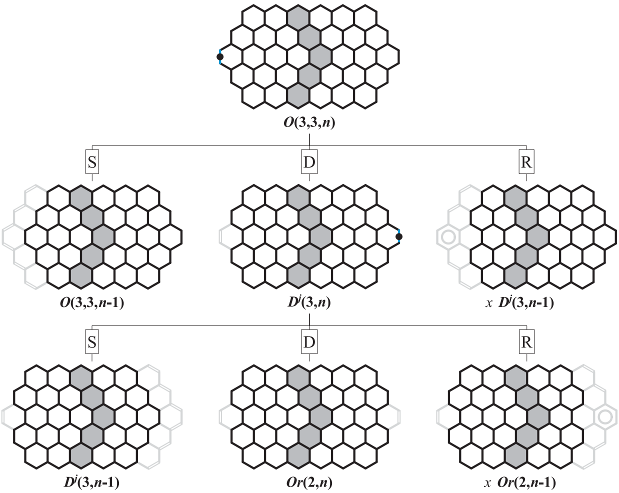

Figure 13. Graph decomposition of $O(2,3,n)$. Each shaded hexagon represents schematically a horizontal polyacene of length $n-5$.

second step of the recursive decomposition shown in **Figure 13**. The resulting recurrence formula

$$ZZ\left(D^j(3,n),x\right)=ZZ\left(D^j(3,n-1),x\right)+ZZ\left(Or(2,n),x\right)+x\cdot ZZ\left(Or(2,n-1),x\right) \tag{68}$$

where $Or(m,n)$ is an oblate rectangle structure, can be again telescopically folded with the boundary condition $ZZ\left(D^j(3,0),x\right)=1$ giving

$$\mathrm{ZZ}\left(D^j(3,n),x\right)=\mathrm{ZZ}\left(Or(2,n),x\right)+(1+x)\sum_{k=0}^{n-1}\mathrm{ZZ}\left(Or(2,k),x\right) \tag{69}$$

This formula can be substituted in the expression for the ZZ polynomial of $O(3,3,n)$ yielding an expression analogous to Eqs. (56) and (49)

$$\begin{aligned}\mathrm{ZZ}\left(O(3,3,n),x\right)=&\ \mathrm{ZZ}\left(Or(2,n),x\right)\\&+2(1+x)\sum_{k=0}^{n-1}\mathrm{ZZ}\left(Or(2,k),x\right)\\&+(1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\mathrm{ZZ}\left(Or(2,l),x\right)\end{aligned} \tag{70}$$

Substituting into this equation the ZZ polynomial of $Or(n,2)$ given by Eq. (46) gives

$$\begin{aligned}\mathrm{ZZ}\left(O(3,3,n),x\right) = 1 + 9n(1+x) + \frac{9}{2}n(5n-3)(1+x)^2 + \frac{n}{6}(149n^2-249n+106)(1+x)^3 \\ + \frac{n}{6}(n-1)^2(86n-103)(1+x)^4 + \frac{n}{6}(n-1)^2(28n^2-89n+72)(1+x)^5 \\ + \frac{n}{360}(n-1)(n-2)(316n^3-1464n^2+2201n-1059)(1+x)^6 \\ + \frac{1}{420}\binom{n}{3}(236n^4-1784n^3+4921n^2-5749n+2430)(1+x)^7 \\ + \frac{1}{840}\binom{n}{4}(105n^4-838n^3+2427n^2-2918n+1272)(1+x)^8 \\ + \frac{n}{8640}(n-1)^2(n-2)^3(n-3)^2(n-4)(1+x)^9\end{aligned} \quad (71)$$

which agrees with the heuristically derived Eq. (37) of [2].

9. Conclusion

We have presented formal derivations of ZZ polynomials for various families and subfamilies of benzenoid structuress using the semi-automatic computer environment (ZZDecomposer) recently developed in our group. [7] The formal derivations presented here justify the general formulas obtained previously [1, 2] for various classes of benzenoids using heuristic reasoning. Current derivations are based on formal graph decompositions of the analyzed structures, which yield appropriate recurrence formulas, which are subsequently solved, yielding closed-form expressions for the sought ZZ polynomials. In most cases, the recurrences are solved using telescopic folding. We hope that in addition to many new basic facts about ZZ polynomials of some important classes of benzenoids, the current study will provide the researchers who are interested in mathematical graph theory with a practical guide to the ZZDecomposer functionality and will enable and facilitate their search for the general ZZ polynomial formulas of benzenoids.

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