Supporting Information

# Molecular islands at the liquid-solid interface

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**Experimental section**

The synthesis of DBA-OC13 was previously reported.[1-3] 1-Phenyloctane was purchased from Tokyo Chemical Industry and used without further purification. All STM experiments were conducted at ambient condition (temperature: 20-25 °C; humidity: about 40%), on highly oriented pyrolytic graphite (HOPG) (grade ZYB, Advanced Ceramics Inc., Cleveland, OH, USA) surface, using an Agilent system. Before each experiment, the HOPG was freshly cleaved using scotch tape. The tips were mechanically cut from the Pt/Ir (80%/20%, diameter: 0.25 nm) wire. The structural models of the hexagonal porous structures formed by DBA-OC13 were built using Materials Studio 7.0, based on the high-resolution STM images. Using the same software, the intermolecular interaction energies were determined via Dreiding force field calculations.

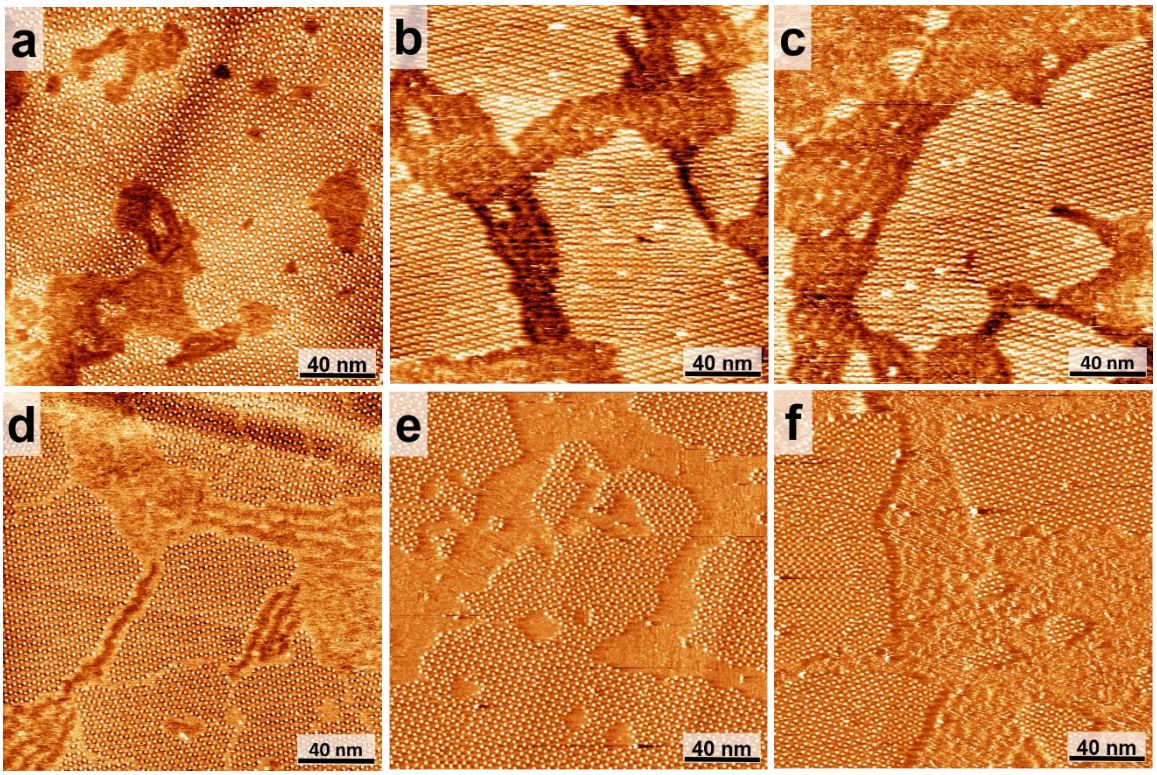


**Fig. S1.** Large-scale STM images for DBA-OC13 at the 1-phenyloctane-HOPG interface. Concentration: $1.0 \times 10^{-6}$ M. Scanning parameters: $V_s = -0.20$ V, $I_t = 200$ pA.

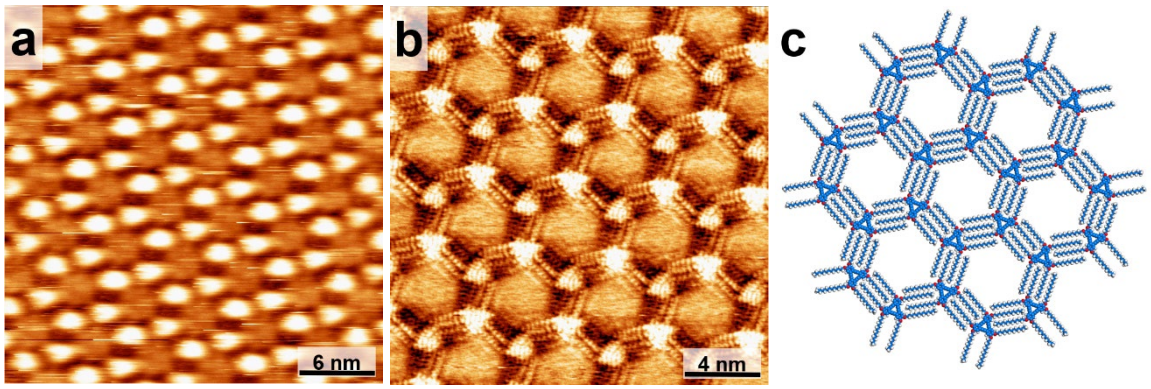


**Fig. S2.** (a, b) High-resolution STM images for DBA-OC13 at the 1-phenyloctane-HOPG interface to show the hexagonal porous structure. Concentration: $1.0 \times 10^{-6}$ M. Scanning parameters: $V_s = -0.20$ V, $I_t = 200$ pA. (c) Structural model for the hexagonal porous structure.

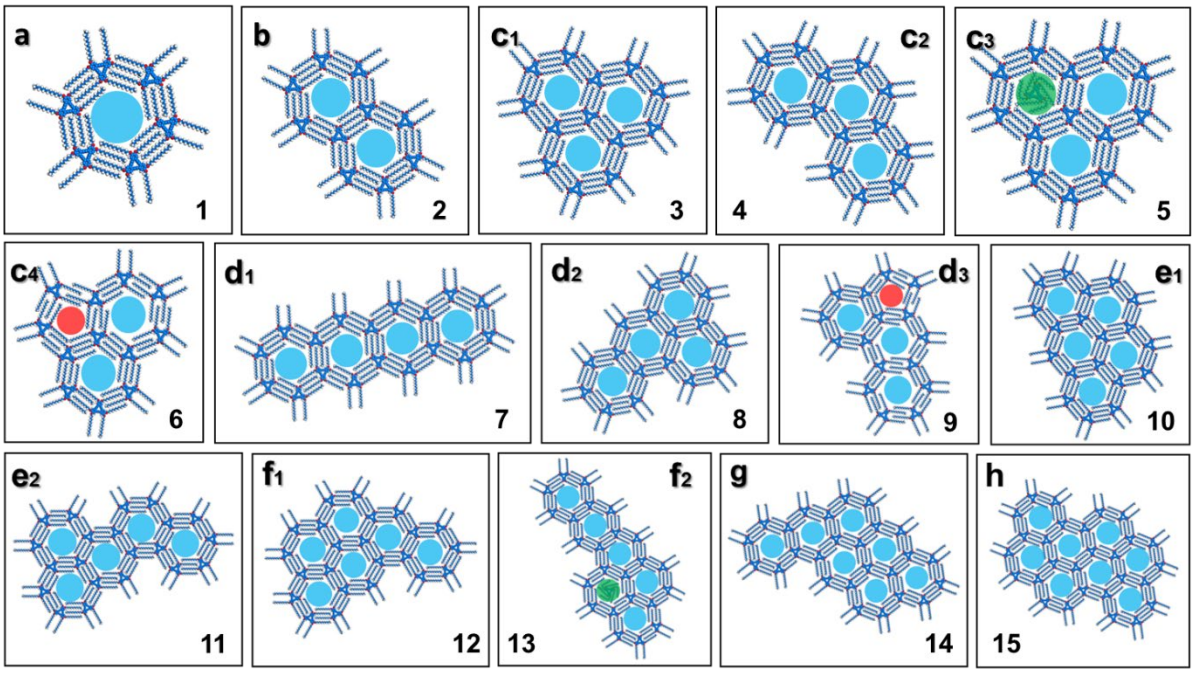


**Fig. S3.** Structural models numbered from 1 to 15, corresponding to the STM images in Fig. 2 in the main text. The normal hexagon pores are indicated by blue circles, while the host-guest and pentagon pores are indicated in green and red colors.

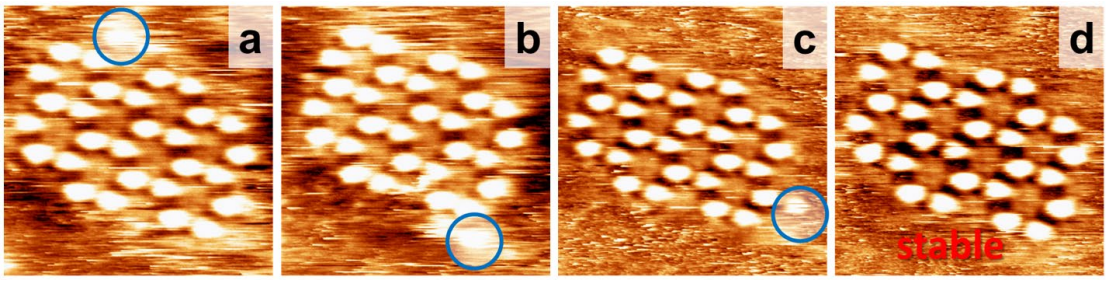


**Fig. S4.** Successive images of a molecular island that contains 8 pores. The dynamic molecules are indicated by blue circles. Time interval between two adjacent images is 3 min. Scanning parameters: $V_s = -0.20$ V, $I_t = 200$ pA.

**Force field calculations**

All simulations and calculations were performed using the Materials Studio 7.0 software, using the Dreiding force field. This force field was selected because it is able to properly describe the intermolecular interactions.[4, 5] The intermolecular interactions were calculated without HOPG. For patterns No. 1-15, the calculation details are shown below, in Table S1.

**Table S1.** Calculation detail of the intermolecular interactions.

| pattern | type | $E_{molecule}$ (kJ mol$^{-1}$) | $N$ | $E_{total}$ (kJ mol$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$ per pore) | $\Delta E$ (kJ mol$^{-1}$ per molecule) |
|---|---|---|---|---|---|---|
| 1 | a | 876.0 | 6 | 4744.1 | −511.9 | −85.3 |
| 2 | b | 876.0 | 10 | 7812.6 | −474.0 | −94.7 |
| 3 | $c_1$ | 876.0 | 13 | 10119.6 | −422.8 | −97.6 |
| 4 | $c_2$ | 876.0 | 14 | 10919.7 | −448.1 | −96.0 |
| 5 | $c_3$ | 876.0 | 14 | 11079.1 | −395.0 | −84.6 |
| 6 | $c_4$ | 876.0 | 12 | 9480.6 | −343.8 | −86.0 |
| 7 | $d_1$ | 876.0 | 18 | 13978.6 | −447.3 | −99.4 |
| 8 | $d_2$ | 876.0 | 17 | 13185.3 | −426.7 | −100.4 |
| 9 | $d_3$ | 876.0 | 16 | 12605.7 | −352.6 | −88.1 |
| 10 | $e_1$ | 876.0 | 19 | 14681.7 | −392.5 | −103.3 |
| 11 | $e_2$ | 876.0 | 21 | 16262.1 | −426.8 | −101.6 |
| 12 | $f_1$ | 876.0 | 23 | 17783.3 | −394.1 | −102.8 |
| 13 | $f_2$ | 876.0 | 25 | 19563.9 | −389.4 | −93.4 |
| 14 | g | 876.0 | 25 | 19249.3 | −378.7 | −106.0 |
| 15 | h | 876.0 | 28 | 21556.0 | −371.5 | −106.1 |

*$N$ represents the total number of molecules in the molecular island.*

*$E_{total}$ represents the energy of the whole system.*

*$E_{molecule}$ represents the energy of a DBA molecule.*

$$\Delta E_{total} = E_{total} - N \times E_{molecule}$$

$$\Delta E_{(per\ molecule)} = \Delta E_{total}/N$$

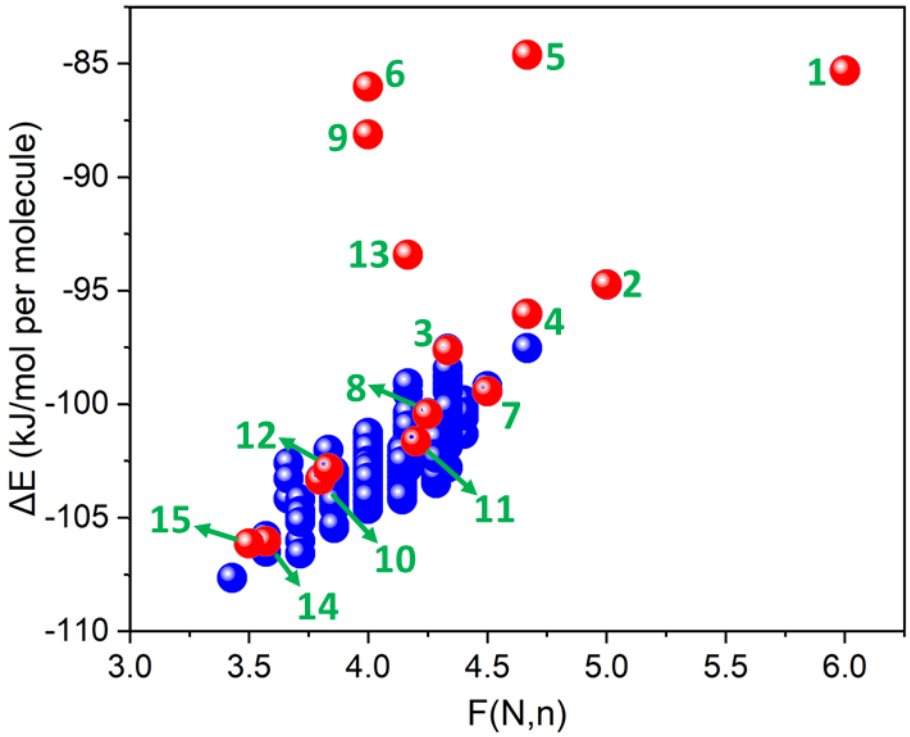


**Fig. S5** Intermolecular interaction energies for the 244 molecular islands (blue points) corresponding to n < 8, and pattern 1-15 (red points), expressed per molecule. Many data points overlap. The pattern number is indicted in green (see Fig. 2 in the main text and Table S1). Pattern number 5, 6, 9, 13, and 15 don't belong to the modeled 244 modeled islands as they contain defects (pattern 5, 6, 9, and 13) or contain more than 7 pores (pattern 15).

**Simulated schematic diagrams for the possible molecular islands in the case of n = 1−7.** All the models are listed according to their longest hexagon pore line. For ease of distinguishing, the hexagon pores are in different colors. In a row of pores, the connected seven, six, five, four, three, two and one molecules are in cyan, orange, yellow, purple, green, blue and red (Fig. S6), respectively.

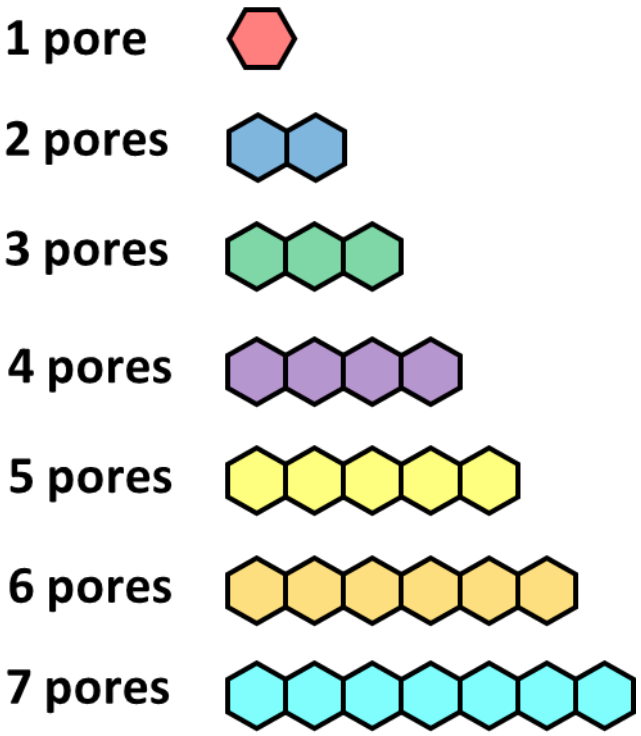


**Fig. S6.** Models for the connected seven, six, five, four, three, two and one molecules, in cyan, orange, yellow, purple, green, blue and red, respectively.

**The 244 possible molecular islands:**

## n = 1

1-1
N=6

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## n = 2

2-1
N=10

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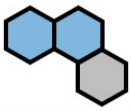
## n = 3

3-1
N=14

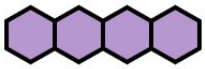
3-2
N=13



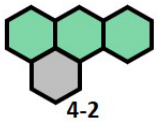
3-3
N=14

---

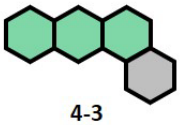
## n = 4



4-1
N=18



4-2
N=17



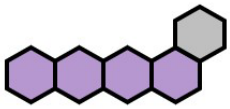
4-3
N=18

4-4
N=16

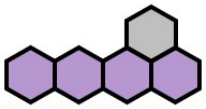
---

## n = 5

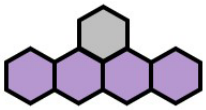
5-1
N=22



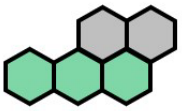
5-2
N=22



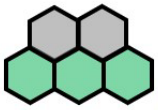
5-3
N=21



5-4
N=21



5-5
N=20



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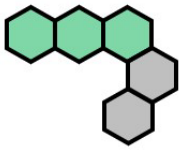
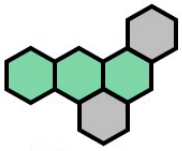
N=19



5-7
N=22



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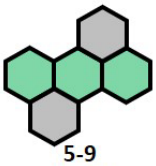

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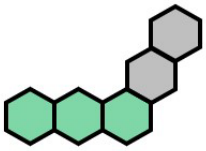

5-10
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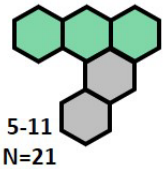

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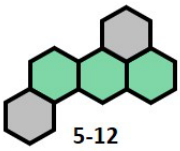

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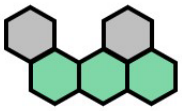

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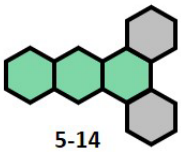

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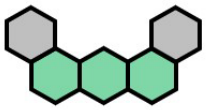

5-15
N=22

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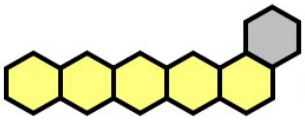
# n = 6

6-1
N=26



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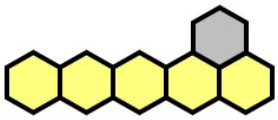

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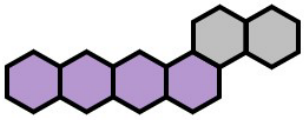
N=25

6-4
N=25



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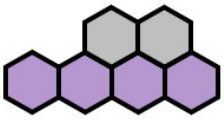

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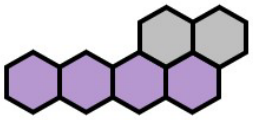

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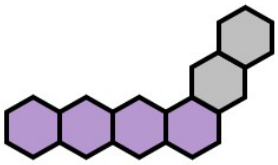

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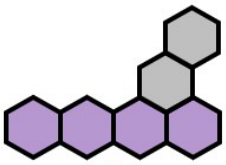

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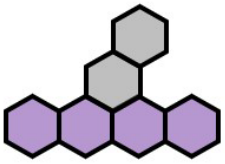

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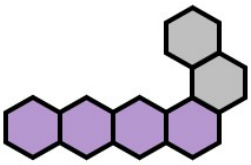

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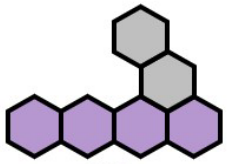

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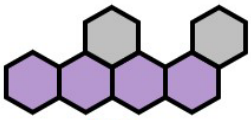

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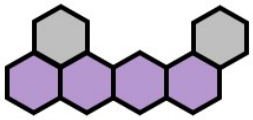

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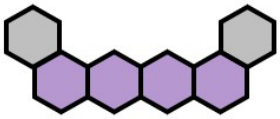

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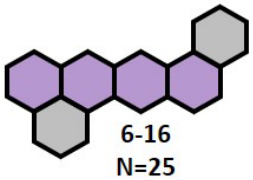

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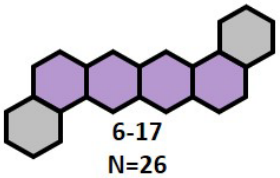

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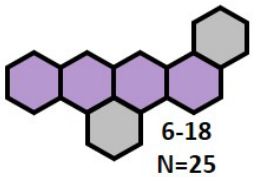

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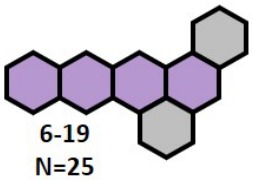

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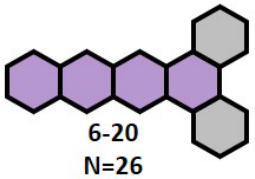

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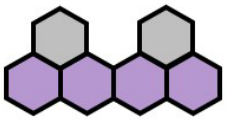

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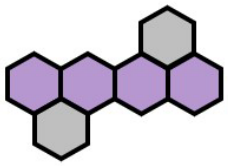

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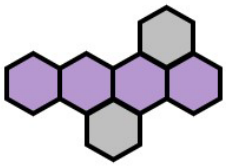

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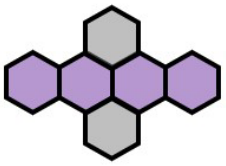

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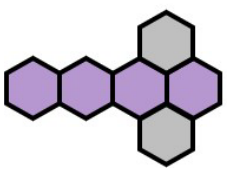

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6-26
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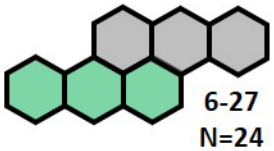

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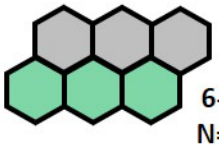

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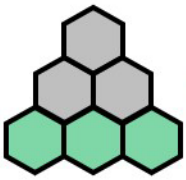

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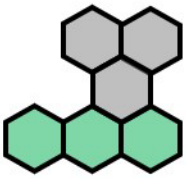

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6-31
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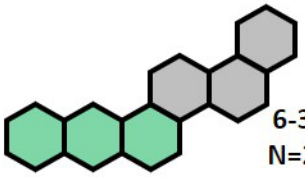

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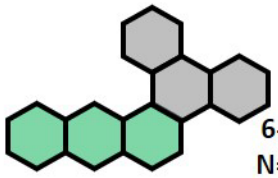

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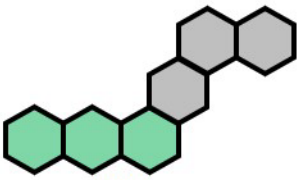

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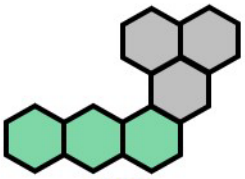

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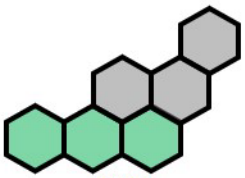

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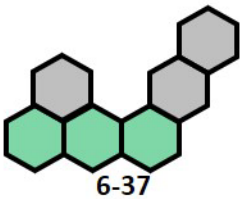

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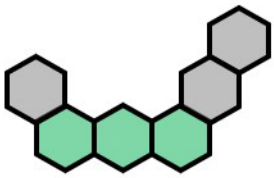

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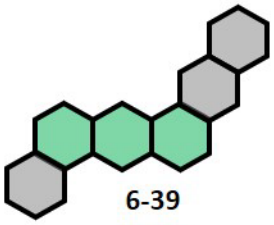

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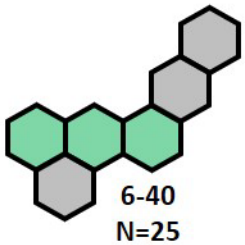

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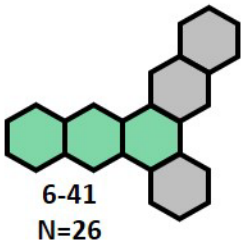

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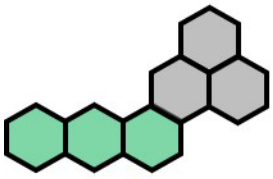

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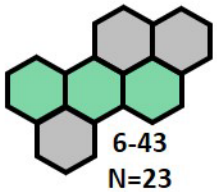

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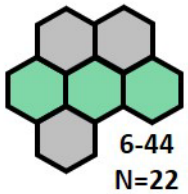

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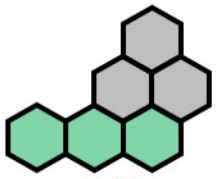

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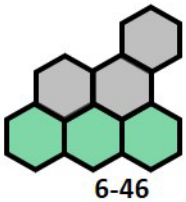

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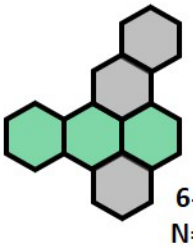

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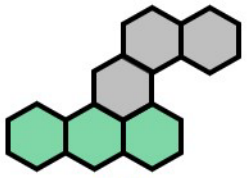

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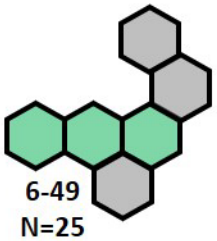

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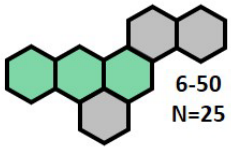

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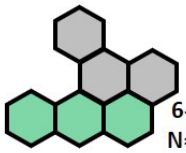

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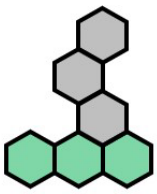

6-52
N=25

6-53
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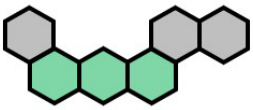

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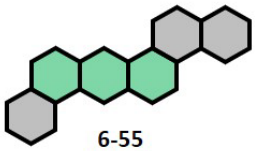

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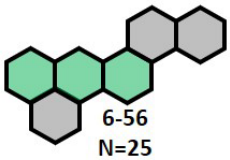

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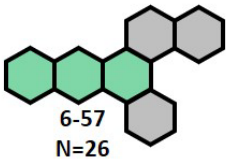

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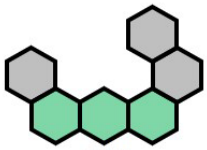

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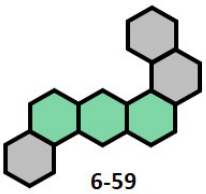

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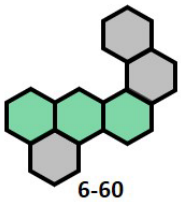

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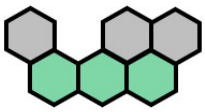

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N=24

6-62
N=24

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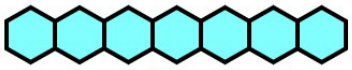

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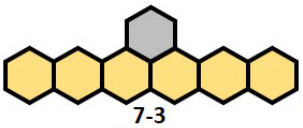
7-2
N=29



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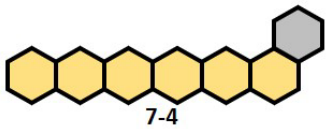
N=29



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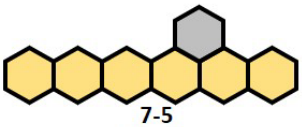

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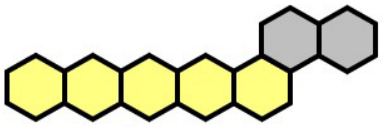

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7-7
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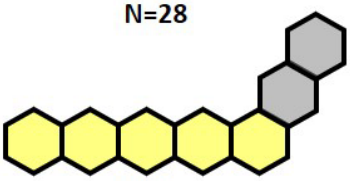
7-8
N=27

7-9
N=27



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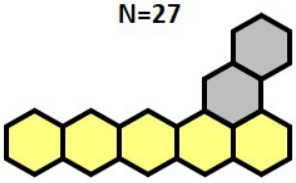

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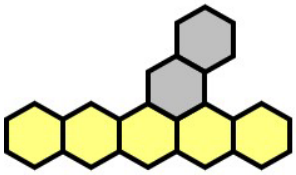

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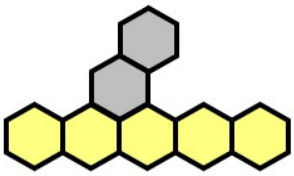

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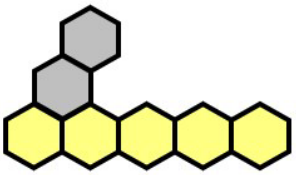

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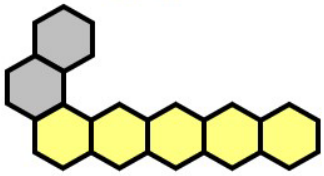

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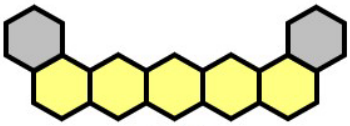
7-16
N=29

7-17
N=29

7-18
N=29



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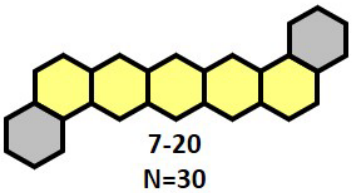

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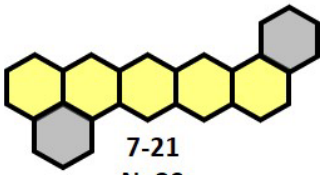

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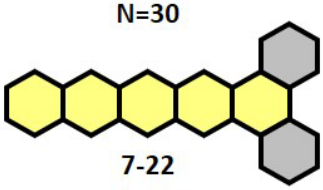

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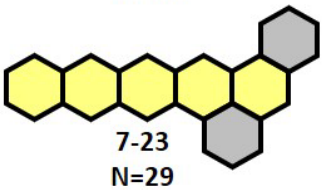

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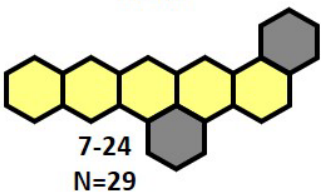

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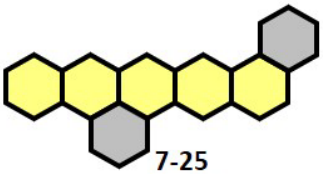

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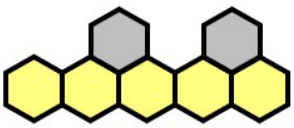

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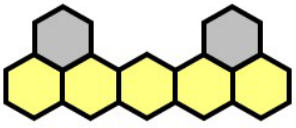

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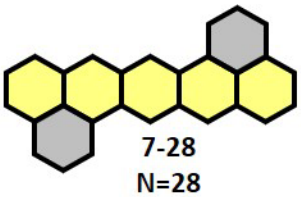

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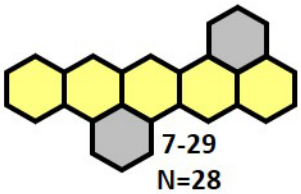

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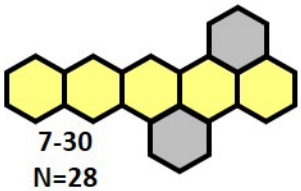

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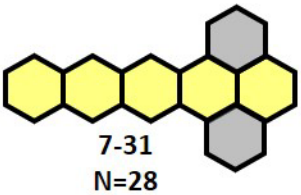

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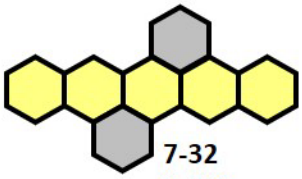

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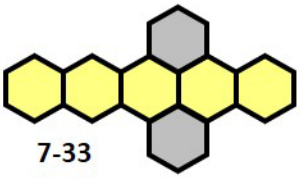

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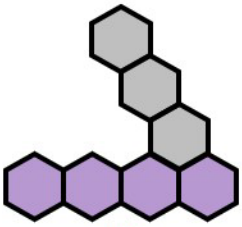

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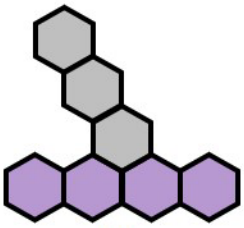

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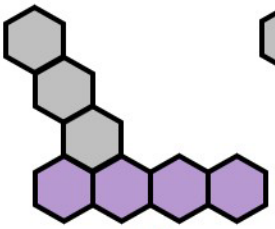

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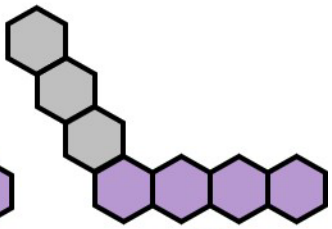

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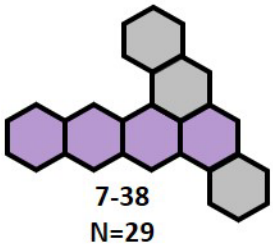

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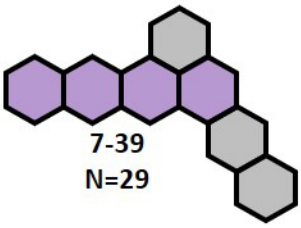

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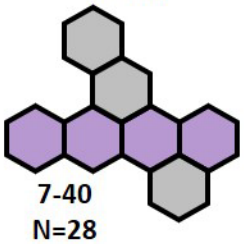

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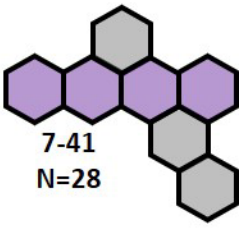

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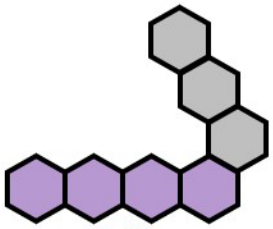

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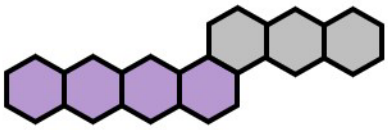

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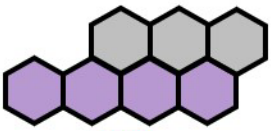

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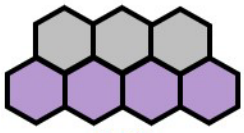

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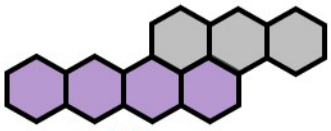

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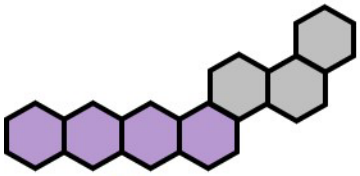

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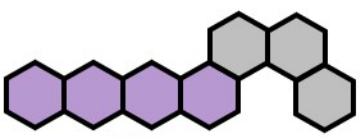

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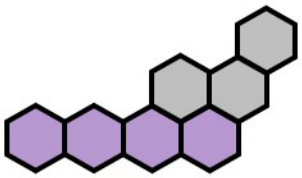

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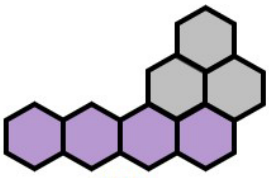

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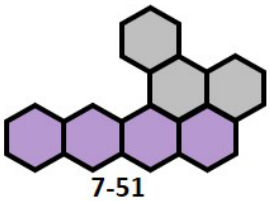

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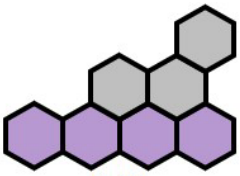

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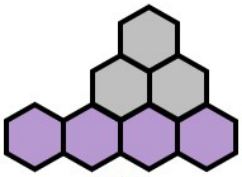

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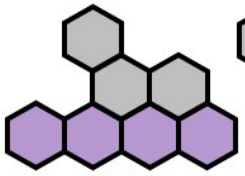

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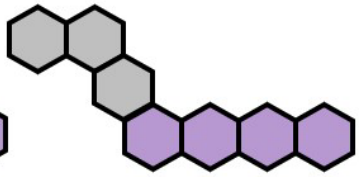

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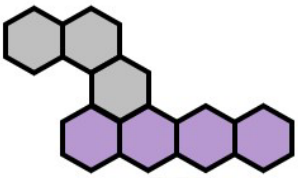

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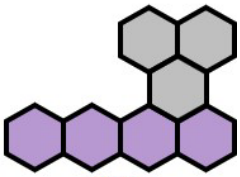

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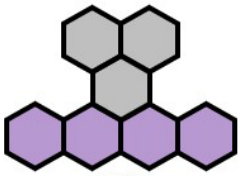

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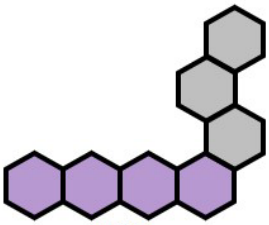

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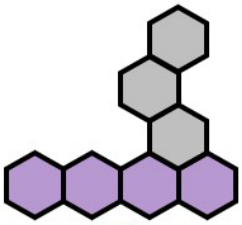

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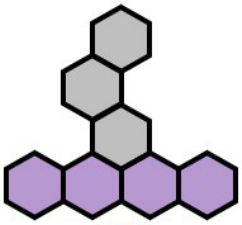

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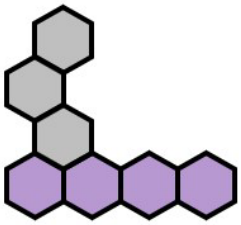

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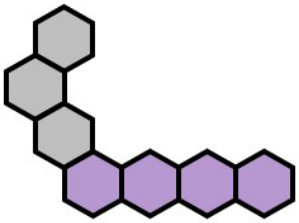

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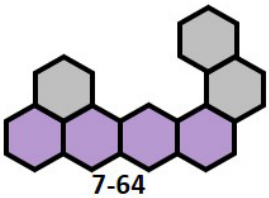

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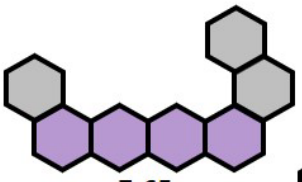

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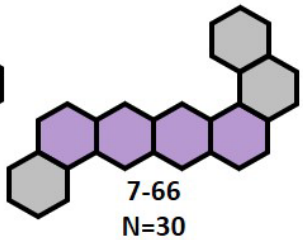

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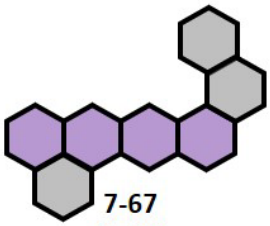

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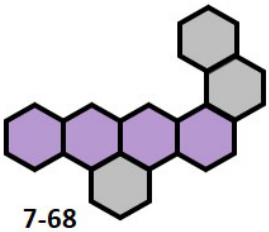

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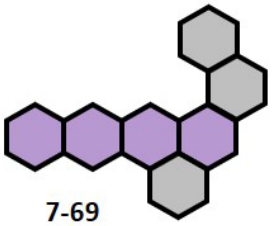

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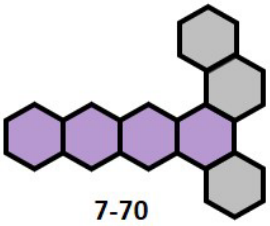

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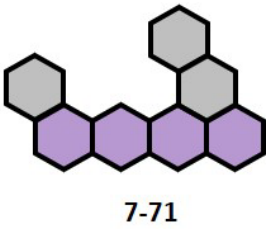

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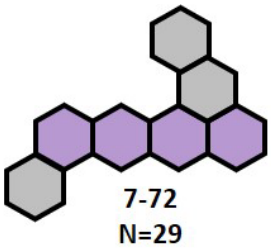

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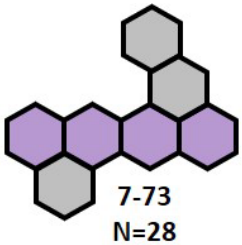

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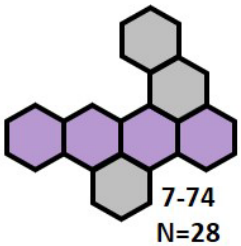

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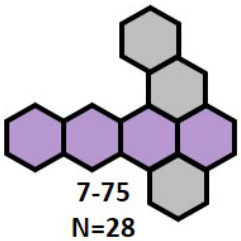

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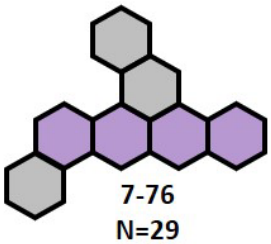

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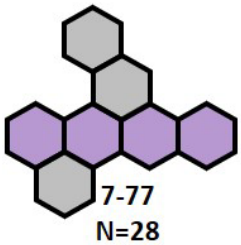

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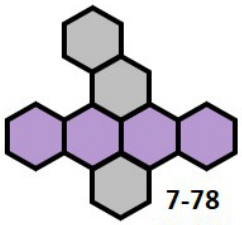

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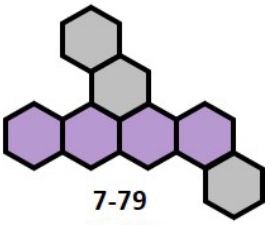

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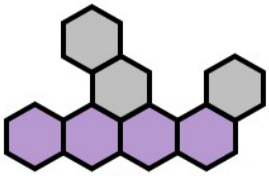

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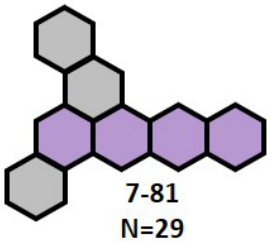

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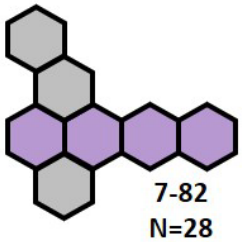

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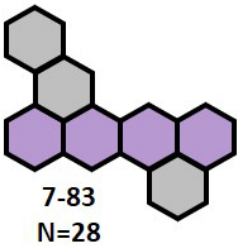

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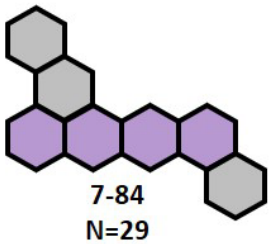

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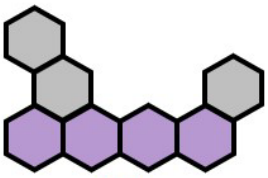

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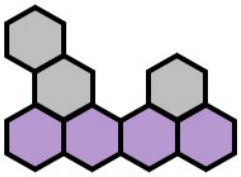

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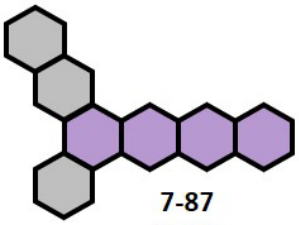

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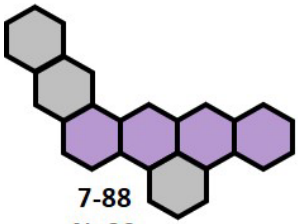

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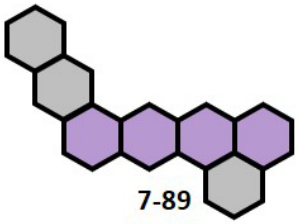

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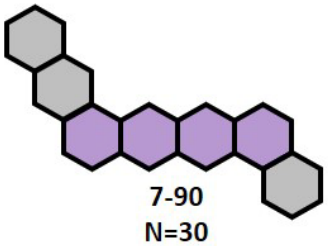

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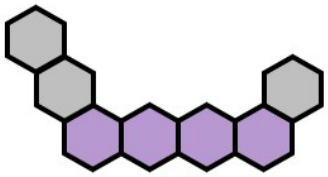

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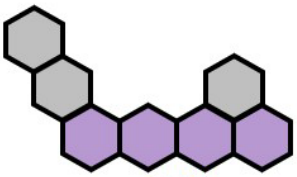

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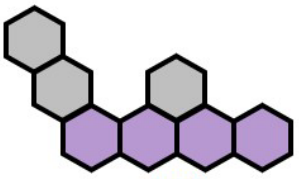

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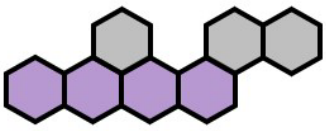

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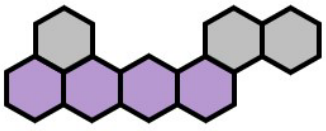

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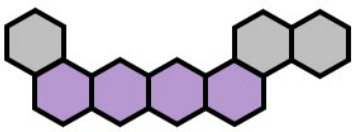

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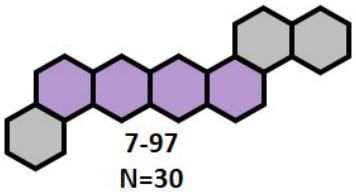

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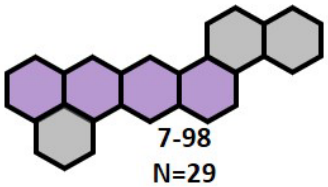

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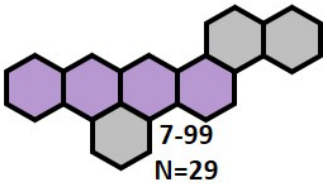

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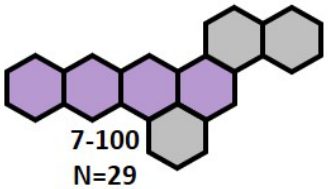

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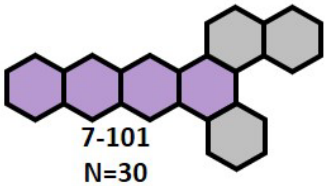

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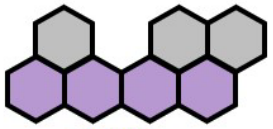

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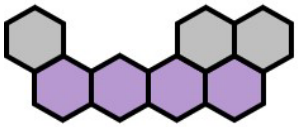

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N=28

7-104
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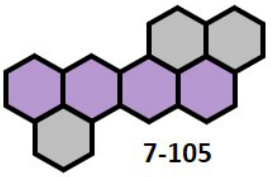

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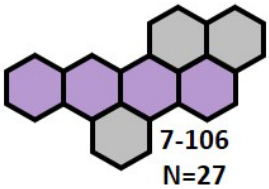

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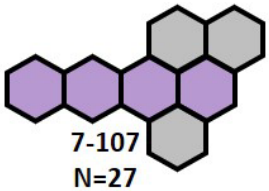

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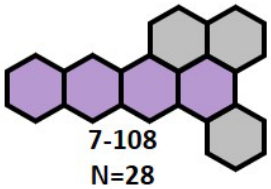

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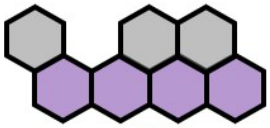

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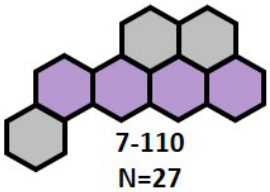

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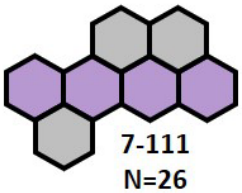

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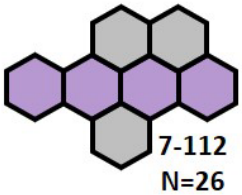

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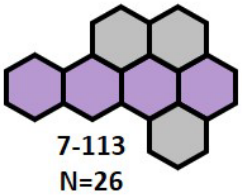

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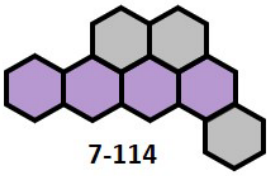

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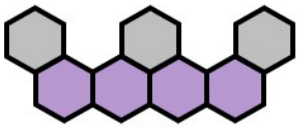

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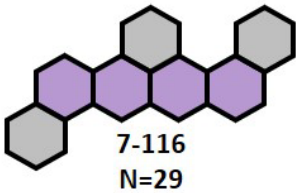

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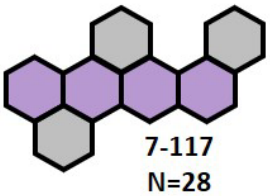

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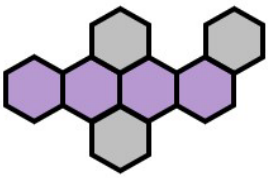

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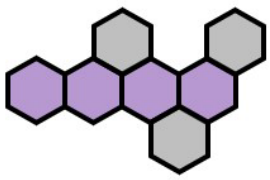

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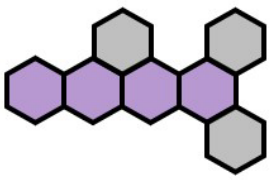

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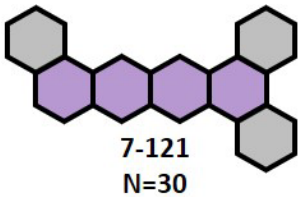

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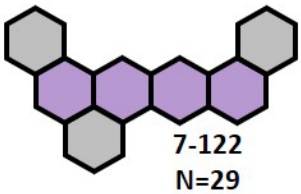

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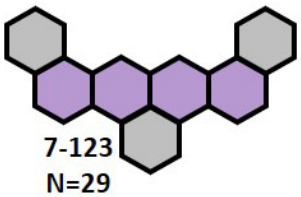

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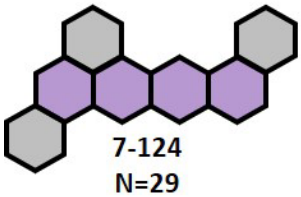

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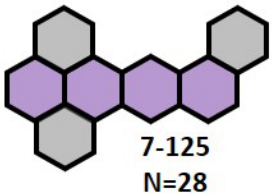

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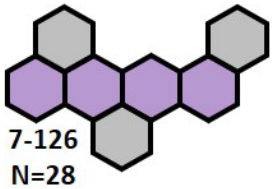

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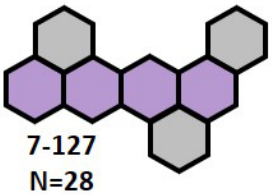

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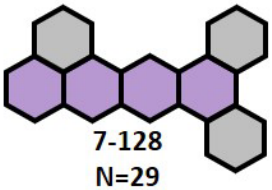

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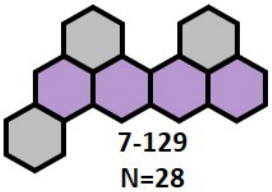

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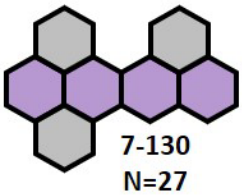

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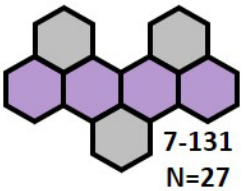

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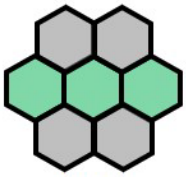

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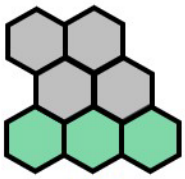

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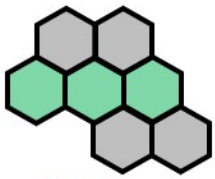

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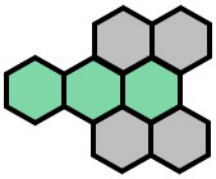

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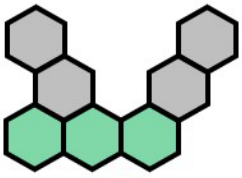

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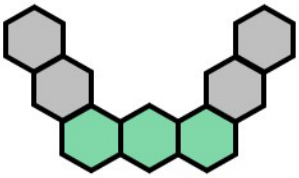

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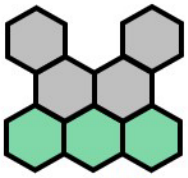

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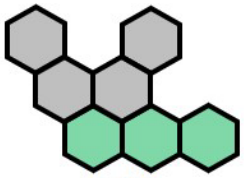

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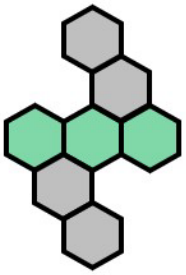

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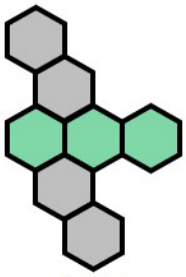

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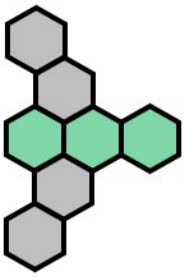

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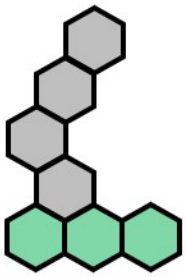

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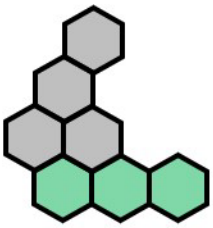

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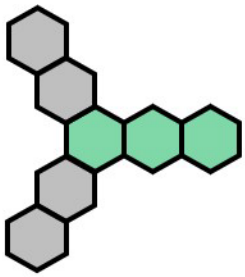

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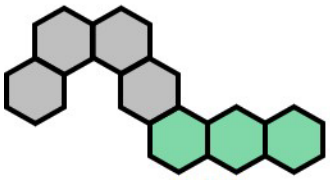

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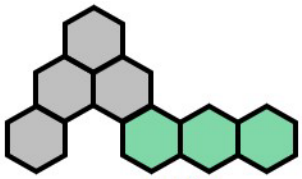

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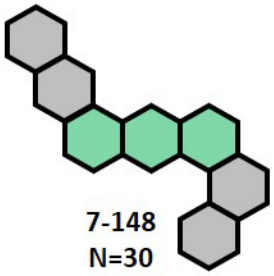

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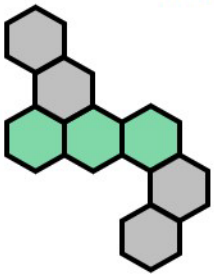

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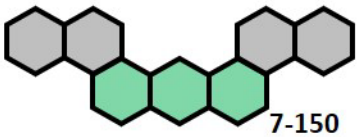

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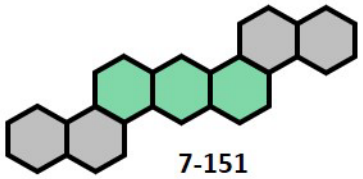

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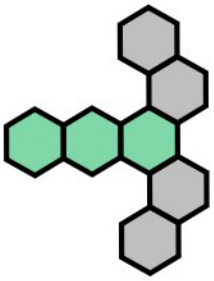

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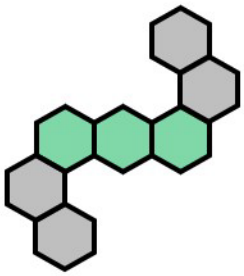

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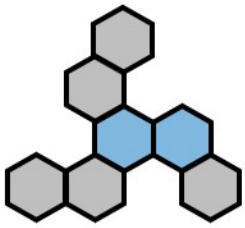

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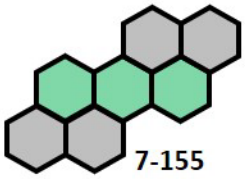

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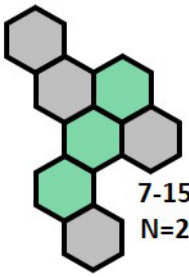

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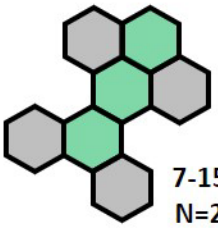

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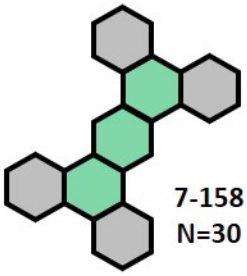

7-158
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