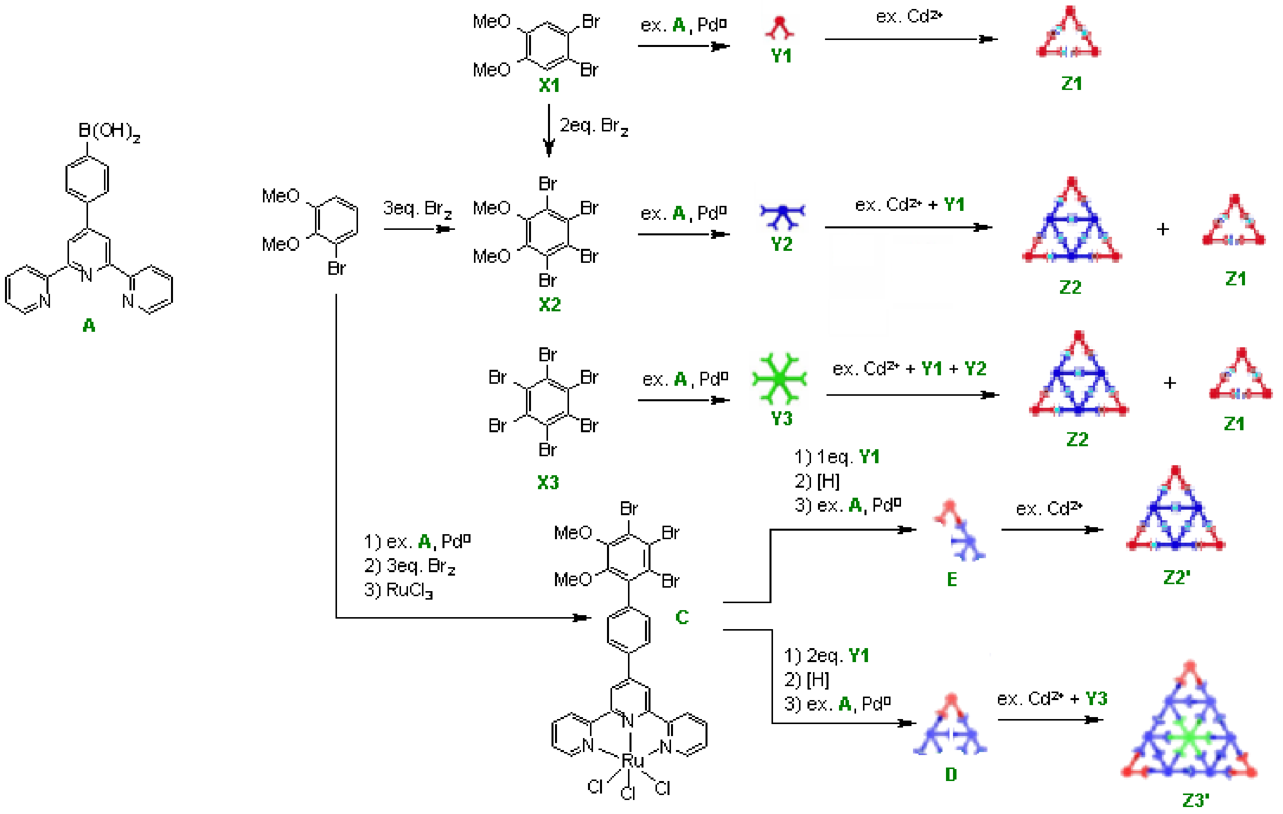
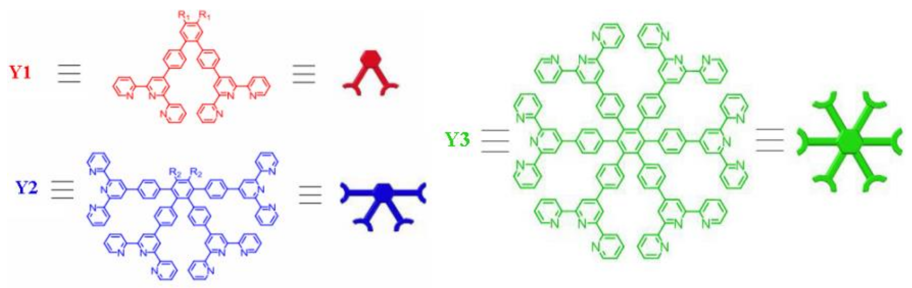
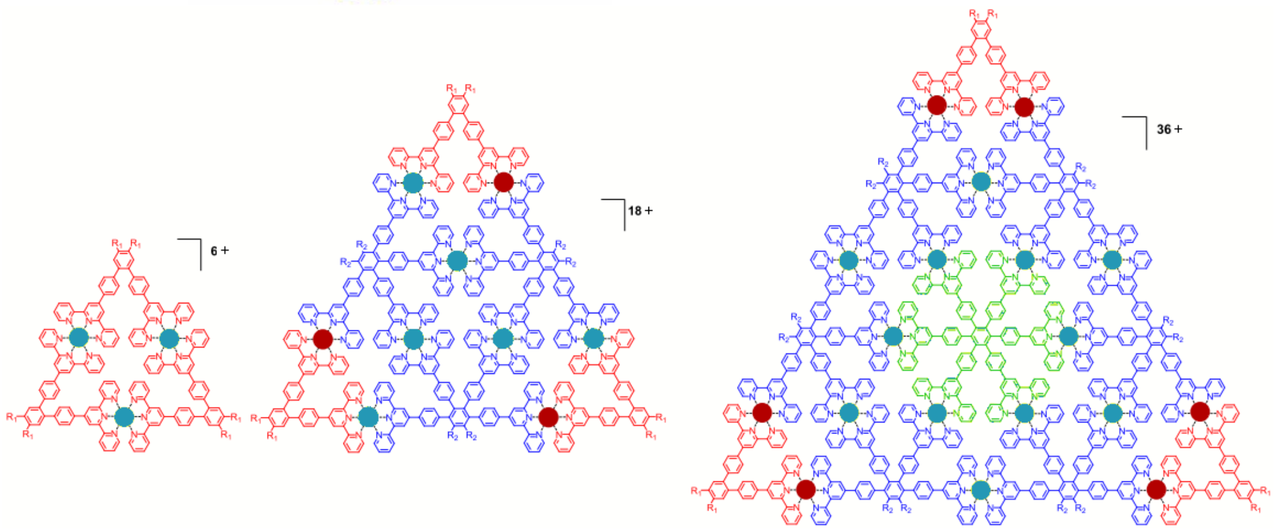
National Student Team Contest (first stage)
Solution of task 4. Nanopuzzles

1. To complete the triangles, **X1** must be the *ortho*-dibrom derivative. Single isomer of **Z1** yields only the shown below **X1**:





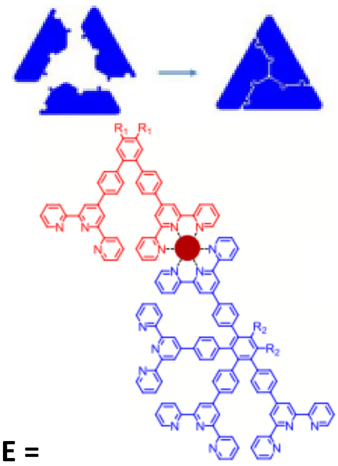


Z1, Z2, Z3 – all the circles = Cd,
Z2', Z3' – red circles = Ru, blue circles = Cd ($R_1 = R_2$ = OMe).

$$3\mathbf{Y1} + 3Cd^{2+} = \mathbf{Z1}^{6+}$$
$$3\mathbf{Y1} + 3\mathbf{Y2} + 9Cd^{2+} = \mathbf{Z2}^{18+}$$
$$3\mathbf{Y1} + 3\mathbf{Y2} + \mathbf{Y3} + 18Cd^{2+} = \mathbf{Z3}^{36+}$$

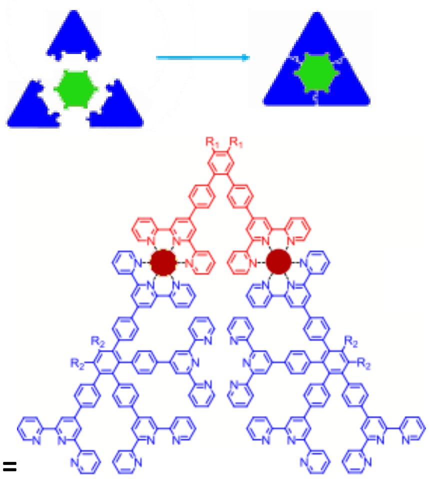
2. The main idea is to assemble **Z2'** and **Z3'** so that there are less other ways for the initial fragments to connect (the main problem of synthesis of **Z2** and **Z3**):

E + Cd^{2+} → **Z2'**



E =

D + **Y3** + Cd^{2+} → **Z3'**



D =

Ru is used to "glue" smaller fragment together and to fix them after reduction to Ru^{2+}, because it forms very strong bonds with terpyridine fragments which survive cross coupling conditions. Cd^{2+} is used because it binds quite reversibly so big fragments could assemble in the right way.

To obtain **Z2'** from **C** the same reactions as for **Z3'** are used, except 1eq.**Y1** is used at the first step and only single Cd^{2+} is used at the final self-assembly step.

3. Rough estimation of triangle size (A_Z). Consider all the bonds to be of the same length as the aromatic C-C bond (0.14 nm), then the hexagon diagonal is 2 C-C bond lengths. Add to the circumscribed around triangle circle diameter ($D = 2 \cdot A_Z/\sqrt{3}$) 2 C-C bond lengths (to roughly account for OMe groups).

$A_{Z1} = 18 \cdot 0.14 = 2.52$ nm	D_{Z1} = **3.2** nm
$A_{Z2} = 34 \cdot 0.14 = 4.76$ nm	D_{Z2} = **5.8** nm
$A_{Z3} = 50 \cdot 0.14 = 7$ nm	D_{Z3} = **8.4** nm