Stoichiometric Control of Multiple Different Tectons in Coordination-Driven Self-Assembly: Preparation of Fused Metallacyclic Polygons

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Research Interests:

- Unsaturated reactive intermediates like vinyl cations and unsaturated carbenes.
- Polyvalent iodine chemistry and in particular alkynyl iodonium salts and derived chemistry.
- Supramolecular chemistry and self-assembly: coordination based directional bonding paradigm to self-assemble and study pre-designed metallacycles and metallacages such as cuboctahedra, dodecahedra etc.

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Ph.D., 1966, University of California, Berkeley
NIH Postdoctoral Fellow, 1967-68, Princeton University.
Preparation of Fused Metallacyclic Polygons
Self-Recognition in the Coordination Driven Self-Assembly of 2-D Polygons

Inorg. Chem. 2004, 43, 5335-5338
Self-Assembly of 2-D Polygons

Synthesis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Building blocks</th>
<th>Ratio</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 + 2 + 4</td>
<td>2:3:5</td>
<td>5 + 6 (75%)</td>
</tr>
<tr>
<td>B</td>
<td>1 + 3 + 4</td>
<td>2:4:6</td>
<td>5 + 7 (72%)</td>
</tr>
<tr>
<td>C</td>
<td>2 + 3 + 4</td>
<td>3:4:7</td>
<td>6 + 7 (80%)</td>
</tr>
<tr>
<td>D</td>
<td>1 + 2 + 3 + 4</td>
<td>2:3:4:9</td>
<td>5 + 6 + 7 (73%)</td>
</tr>
</tbody>
</table>
Self-Assembly of 2-D Polygons

$^{31}$P{¹H} and ¹H NMR, and ESI-MS of 5 and 6
Self-Assembly of 2-D Polygons

$^1$H NMR of 5-7

ESI-MS of 5-7
Coordination-Driven Self-Assembly of Three-Dimensional $M_3L_2$ Polyhedra

Acetone-$d_6$ /D$_2$O 1:1
55 °C for 48 - 72 h

*Org. Lett.* 2007, 9, 1561-1564
3-D Polyhedra

$^{31}\text{P}^{(1\text{H})}$ and $^{1\text{H}}$ NMR spectra of 4 and 5
3-D Polyhedra

ESI-MS of 4 and 5
3-D Polyhedra

$^{31}\text{P}^{(1}\text{H})$ and $^{1}\text{H}$ NMR spectra of 8 and 9
Size Selective Self-Sorting: 2-D

Acetone-$d_6$ /D$_2$O 1:1
60–65 °C for 45 - 65 h

Size Selective Self-Sorting: 2-D

ESI-MS of 5 and 6

1 h

7 h

21 h

45 h

31P{1H} and 1H NMR spectra of Rectangles 5 and 6

A: [R_L-2NO_3]^{2+}
B: [R_S-2NO_3]^{2+}
C: [R_L-3NO_3]^{3+}
D: [R_S-3NO_3]^{3+}
Size Selective Self-Sorting: 3-D

Acetone-$d_6$/D$_2$O 1:1
65–70 °C for 24 h
Size Selective Self-Sorting: 3-D

$^{31}\text{P} \{^1\text{H}\}$ and $^1\text{H}$ NMR spectra of 11 and 12

A: $[\text{DTP}_S\cdot2\text{NO}_3]^{2+}$
B: $[\text{DTP}_L\cdot3\text{NO}_3]^{3+}$
C: $[\text{DTP}_S\cdot3\text{NO}_3]^{3+}$
D: $[\text{DTP}_L\cdot4\text{NO}_3]^{4+}$

ESI-MS of 11 and 12
Self-Selection in the Self-Assembly of Isomeric Supramolecular Squares from Unsymmetrical Ligands

CD$_3$NO$_2$, r.t., 24 h

J. Org. Chem. 2008, 73, 6580-6586
Supramolecular Squares from Unsymmetrical Ligands

Partial $^{31}$P{¹H} (a) and ¹H NMR (b) spectra of 5, 6, and 7
Second-Order Self-Organization: Exploring the Limits of Self-Selection

(A) \( \text{1} + \text{2} \xrightarrow{<} \text{6} \)

(B) \( \text{3a} + \text{3b} \xrightarrow{<} \text{3h} + \text{3c} \)

(C) \( \text{4a} + \text{5a} \xrightarrow{7} \text{4c} \)

A. Acetone-\(d_6/\text{CD}_2\text{Cl}_2\) 1:1, r.t., 18 h
B. \(\text{CD}_2\text{Cl}_2\), r.t., 18 h
C. Acetone-\(d_6/\text{D}_2\text{O}\) 1.2:1, 55-60 °C, 18 h

Second-Order Self-Organization

31P{1H} and 1H NMR spectra of DB24C8/ferrocene mixed rhomboid ESI-MS (suggestive of homotopic preference)
Second-Order Self-Organization

ESI-MS of dandron assemblies, suggestive of a statistical mixture of homotopic and heterotopic assemblies
Second-Order Self-Organization

$^{31}$P{$^1$H} and ESI-MS spectra of mixed functionality rectangles, suggestive of increasing self-organization from a roughly statistical mixture to a highly amplified homomeric mixture.
Second-Order Self-Organization

$^{31}\text{P}^{1\text{H}}$ (full and close-up) and ESI-MS spectra of mixed functionality rectangles, suggestive of nonstatistical and statistical distribution
Fused Metallacyclic Polygons

Preparation

\[ \text{CD}_2\text{Cl}_2, \text{r.t.}, 18 \text{ h} \]

\[ \text{J. Am. Chem. Soc. 2009, 131, 12028-12029.} \]
Fused Metallacyclic Polygons

Calculated (top, blue) and experimental (bottom, red) ESI-MS spectra (5+) and molecular force field models of (A) double triangle 4, (B) double rhomboid 7, and (C) triple rhomboid 8

Diffusion coefficient:
Solvent: acetone: dichloromethane: (1:1)
The diffusion coefficient of 8 is $3.26 \pm 0.015 \times 10^{-6}$ cm$^2$/s
The diffusion coefficient of 7 is $5.22 \pm 0.03 \times 10^{-6}$ cm$^2$/s
Fused Metallacyclic Polygons

A) $^1$H and B) $^{31}$P{$^1$H} NMR spectra of 4, and 7
Fused Metallacyclic Polygons

A) $^1$H and B) $^{31}$P{$^1$H} NMR spectra of 8

ESI-MS of triple rhomboid 8
Fused Metallacyclic Polygons

Conclusions

New self-assembled fused metallacyclic polygons have been synthesized through stoichiometric and structural control of multicomponent mixtures of different pyridyl donors and platinum acceptors.

Single supramolecular species can be formed from multicomponent self-assembly and that the shape of the product polygons can be controlled simply by changing the ratio of individual components.