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Note

Effect of ligand flexibility on coordination-driven self-assembly of Pt(II) metallacycles

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ABSTRACT

The effect of ligand flexibility on the self-assembly of Pt(II) metallacycles was investigated. Three diazopyridyl ligands with different flexibilities were used to synthesize three nanoscale supramolecular complexes via Pt(II) mediated self-assembly. With comparatively less flexible ligands, 4,4′azobispyridine (**2**) and pyridine-4-carbaldehyde azine (**3**), formation of [3+3] molecular triangles was observed; in contrast, the most flexible of the three ligands, pyridine-3-carbaldehyde azine (**4**), yielded the [2+2] molecular rhomboid. All three complexes were characterized by multinuclear NMR (^{1}H and ^{31}P) and HR-ESI-MS, and the structure of complex **7** was further established by X-ray crystallography. These studies clearly showed that increased ligand flexibility entropically favors the formation of smaller metallacycles as the ligand can reduce angular strain through bending or conformational change.

1. Introduction

Self-assembly is a fundamental strategy employed in nature to construct elegant and intricate molecular machinery, enabling the evolution of life. This type of self-assembly is adaptable to molecular manufacturing, i.e. processes that are designed to synthesize advanced materials with specific properties and functions that are determined by controlling the shape, form, and distribution of the individual building blocks. In recent years, coordination driven self-assembly has been employed for the synthesis of a large assortment of supramolecular entities. This approach has proven to be a particularly powerful tool for the construction of supramolecular two-dimensional (2-D) and three-dimensional (3-D) structures with well-defined shapes and sizes [1]. Among the two-dimensional species are squares [2], rectangles [3], parallelograms [4], rhomboids [5], and polygons of higher symmetry [6]. Many of these ensembles are finding applications in areas such as host–guest chemistry [7], chemosensing [8], and cavity controlled catalysis [9]. In contrast to the variety of higher order 2-D structures, one of the simplest, the triangle, has proven to be rare [10]. Despite their simplicity, molecular rhomboids are also much less commonly encountered [11].

An ideal equilateral molecular triangle would be assembled from three equal linear linking units in combination with three equal 60° angular fragments. Since there are no appropriate metal complexes of common co-ordination number with a 60° angle, less than ideal metalla-triangles might be derived from a combination of distorted angular components with angles wider than 60° (typically ca 90°) and linear linkers with angles narrower than 180°.

The self-assembled structures of more flexible linkers are less easy to predict and have a tendency to form undesirable polymers. However, flexible linkers may allow the generation of *pseudorigid assemblies* [12] through shape distortion to obtain more thermodynamically stable conformations. Aromatic N-heterocycles have been used as building blocks for supramolecular compounds due to their electronic and steric properties [13]. In addition to being capable of connecting metal centers, aromatic N-heterocycles can provide π-back bonding. Similarly, N-donor symmetrical polypyridyl ligands have been widely used to construct molecular self-assemblies. Ligands incorporating the diaza group R–C=N–N=C–R have been used due to their luminescence properties [14], and pyridine-4-carbaldehyde azine is a potential bridging ligand for the construction of supramolecular complexes [15].

Herein, we report a systematic study of the edge length effect on the formation of self-assembled metallacycles by varying ligand flexibility. The new self-assembled triangles and rhomboid were utilized 90° metal acceptor in conjunction with various flexible N-donor ligands. These molecular entities were based on a directional bonding approach and formed without templates, and were not in noticeable equilibrium with other macrocyclic species. In addition to single crystal X-ray analysis, all three assemblies were characterized using multinuclear NMR and ESI-MS.

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2. Experimental

2.1. Materials and methods

The 90° Pt(II) acceptor **1** was synthesized according to previously published methods [16]. 4-Aminopyridine, 3-aminopyridine, sodium hypochlorite, and hydrazine hydrate were purchased from Aldrich and were used without further purification. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker 300 (^{1}H, 300 MHz; ^{31}P, 121.48 MHz) spectrometer. ^{1}H and ^{31}P chemical shifts (δ) are reported in ppm and are referenced to residual solvent peaks. Melting points were determined using a Laboratory Devices "Mel-Temp".

2.2. Single-crystal X-ray crystallography

Diffraction data from a single crystal of **7** mounted on a loop were collected at 100 K on an ADSC Quantum 210 CCD diffractometer using synchrotron radiation (λ = 0.90000 Å) at the Macromolecular Crystallography Beamline 6B1, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods, and refinements were carried out with full-matrix least-squares on F^2 with appropriate software implemented in the SHELXTL program package: $C_{53}H_{85}F_{12}N_9O_{15}P_4Pt_2S_4$, M = 1958.60, Orthorhombic, $Pna2_1$ (No. 33), a = 38.990(8) Å, b = 20.006(4) Å, c = 9.531(2) Å, V = 7435(3) Å^3, Z = 4, T = 100 K, μ(synchrotron) = 6.468 mm^{-1}, ρ_{calc} = 1.750 g cm^{-3}, 34283 reflections measured, 10571 unique (R_{int} = 0.1329), R_1 = 0.0781, wR_2 = 0.2032 for 9155 reflections ($I > 2\sigma(I)$), R_1 = 0.0891, wR_2 = 0.2171 (all data), GOF = 1.070, Flack = 0.000(9), 893 parameters and 308 restraints. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

2.3. Synthesis of donors

2.3.1. Synthesis of ligand **2**

A cold solution of 4-aminopyridine (5.00 g in 100 ml water) was added dropwise to a solution of 10% NaOCl (300 ml), and the mixture was stirred at 0 °C to yield an orange precipitate. After filtration, the aqueous phase and the precipitate were extracted with diethyl ether. The ether phases were combined and then dried over $MgSO_4$. The crude 4,4′-azobispyridine product had a trans/cis ratio of 37:1 as determined by the integration of ^{1}H NMR signals. After column chromatography on silica gel, the pure, red colored trans-4,4′-azobispyridine was obtained [17].

Yield **3**: 8.00 g, 77%, ^{1}H NMR (CD_3NO_2, 300 MHz, ppm) δ 8.85–8.83 (d, 2H, Py-H$_\alpha$), 7.79–7.77 (d, 2H, Py-H$_\beta$).

2.3.2. Synthesis of donors **3** and **4**

4-Pyridinecarboxaldehyde (4.494 g, 4 ml, 40 mmol) or 3-pyridinecarboxaldehyde (4.494 g, 4 ml, 42 mmol) was dissolved in ethanol (15 ml), followed by the dropwise addition of hydrazine hydrate (1.032 g, 1 ml, 21 mmol). Two drops of formic acid were added, and the mixture was stirred at room temperature for 24 h. The resulting yellow crystalline solid was filtered and washed with ethanol/hexane (1:1) several times and then dried in air [18].

Yield **3**: 3.150 g, 85%, ^{1}H NMR (CD_3NO_2, 300 MHz, ppm) δ 7.78–7.75 (d, 4H, Py-H$_\beta$), 8.57 (s, 2H, CH=N), 8.72–8.70 (d, 4H, Py-H$_\alpha$).

Yield **4**: 2.688 g, 64%, ^{1}H NMR ($(CD_3)_2CO$, 300 MHz, ppm) δ 9.05 (s, 2H, Py-H$_\alpha$), 8.77–8.69 (pyridyl), 8.77 (s, 2H, CH=N), 8.32, 8.29 (d, 2H, pyridyl), 7.54–7.50 (dd, 2H, pyridyl).

2.4. Self-assembly of triangles **5** and **6** and rhomboid **7**

2.4.1. Self-assembly of **5**

A nitromethane-d_3 (0.6 ml) solution of Pt(II) acceptor **1** (2.176 mg, 0.003 mmol) and 4,4′-azobispyridine **3** (0.552 mg, 0.003 mmol) was stirred at room temperature for 30 min. After 30 min, the NMR of the clear pink-orange solution showed the formation of a single discrete assembly. Diethyl ether was added to precipitate the final product as an orange colored solid.

Yield: 91%, MP; 250 °C (decomposed), *Anal.* Calc. for $C_{72}H_{114}F_{18}N_{12}O_{18}P_6Pt_3S_6$: C, 31.55; H, 4.19; N, 6.13. Found: C, 31.72; H, 4.21; N, 5.91%. ^{1}H NMR (CD_3NO_2, 300 MHz, ppm); δ 9.1 (d, 4H, Py-H$_\alpha$), 8.09 (d, 4H, Py-H$_\beta$), 2.0 (m, 36H, PCH_2), 1.3 (m, 54H, $PCH_2\mathbf{CH_3}$), ^{31}P{^{1}H}NMR (CD_3NO_2, 121.4 MHz, ppm); δ 12.965 (s). MS (ESI) for **5** ($C_{72}H_{114}F_{18}N_{12}O_{18}P_6Pt_3S_6$): 1220.9 [M−2OTf]$^{2+}$.

2.4.2. Self-assembly of triangle **6**

The flexible bipyridyl donor ligand, pyridine-4-carbaldehyde azine **2** (0.4 mg, 0.002 mmol), and the Pt(II) 90° acceptor **1** (1.4 mg, 0.002 mmol) were accurately weighed into a glass vial. CD_3NO_2 (0.5 ml) was added, and the reaction mixture was stirred at room temperature. After stirring for 2 h, the homogenous yellow solution was transferred into an NMR tube to measure the ^{1}H and ^{31}P NMR spectra. A pure pale yellow solid was obtained after removing the solvent under a flow of N_2.

Yield: 95%, MP; 272 °C (decomposed), *Anal.* Calc. for $C_{78}H_{120}F_{18}N_{12}O_{18}P_6Pt_3S_6$: C, 33.23; H, 4.29; N, 5.96. Found: C, 33.42; H, 4.09; N, 5.81%. ^{1}H NMR (CD_3NO_2, 300 MHz, ppm), δ 8.03–8.01 (d, 4H, Py-H$_\beta$), 8.63 (s, 2H, CH=N), 9.02–9.00 (d, 4H, Py-H$_\alpha$), 2.0 (m, 36H, PCH_2), 1.3 (m, 54H, $PCH_2\mathbf{CH_3}$), ^{31}P{^{1}H}NMR($(CD_3)_2CO$, 121.4 MHz, ppm); δ −0.873 (s). MS (ESI) for **6** ($C_{78}H_{120}F_{18}N_{12}O_{18}P_6Pt_3S_6$): 1260.4 [M−2OTf]$^{2+}$.

2.4.3. Self-assembly of rectangle **7**

Metal acceptor **1** (1.5 mg, 0.002 mmol) and flexible linker pyridine-3-carbaldehyde azine (0.4 mg, 0.002 mmol) were placed in a 2 dram vial equipped with a magnetic stirring bar. Then, 0.3 ml of acetone was added, and the reaction mixture was stirred at room temperature for 4 h. The transparent pale yellow solution was layered with ether and kept overnight for slow diffusion of the diethyl ether. White, needle shaped crystals were obtained, which were carefully washed several times with ether and then dried under vacuum.

Yield: 96%, MP; 280 °C (decomposed), *Anal.* Calc. for $C_{52}H_{80}F_{12}N_8O_{12}P_4Pt_2S_4$: C, 33.23; H, 4.29; N, 5.96. Found: C, 33.01; H, 4.10; N, 5.77%. ^{1}H NMR ($(CD_3)_2CO$, 300 MHz, ppm); δ 9.74 (s, 2H, Py-H$_\alpha$), 9.11 (s, 2H, CH=N), 9.22 (d, 2H, pyridyl), 8.46 (d, 2H, pyridyl), 7.81–7.77 (dd, 2H, pyridyl), 1.8 (m, 24H, PCH_2), 1.3 (m, 36H, $PCH_2\mathbf{CH_3}$). ^{31}P{^{1}H} NMR($(CD_3)_2CO$, 121.4 MHz, ppm); δ 0.059(s). MS (ESI) for **7** ($C_{52}H_{80}F_{12}N_8O_{12}P_4Pt_2S_4$): 477.5 [M−3OTf]$^{3+}$.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Self-assembly of molecular triangles and rectangle

To explore the effect of ligand flexibility on the synthesis of self-assembled motifs, a systematic study using ligands of differing length and flexibility was carried out. The new supramolecular self-assemblies **5**–**7** were prepared in high yields by stirring 90° Pt(II) acceptor **1** with the donors **2**–**4**, respectively, in a 1:1 M ratio in CD_3NO_2 or $(CH_3)_2CO$ at 298 K (Scheme 1).