Architecture of Heptagonal Metallo-macrocycles via Embedding Metal Nodes into Its Rigid Backbone

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INTRODUCTION

- Metal-organic macrocycles serve multiple purposes such as molecular recognition, anti-bacterial properties, and compound encapsulation, while also enabling the exploration of structure-property relationships at the nanoscale.

- Benzene rings are commonly used as the backbone, limiting the ligand arm angle to 60, 120, and 180 degrees, and it results in most metallo-macrocycles being limited to triangles and hexagons [1].

- Exploring the use of backbones with larger angles and constructing metallo-macrocycles with more than six edges is rare[2].

METHODOLOGY

- **Ligand backbone Synthesis:** Connected two different terpyridine(tpy)-based motifs leaving four bromide atoms for subsequent installation of terpyridine arms with an inner layer arms angle of 120° and outer layer arms angle of 144.7°.

- **Ligand Synthesis:** Ligand L1, L2, and L3 with four simple tpy arms were synthesized via a multi-fold Suzuki coupling reaction[2] on the backbone ligand 4 with a good yield (*Refer Figure 6*).

- **Metallo-macrocycle M1 self-assembly:** *D*irectly mixing the ligand L1 and $Zn(NO_3)_2$ in a stoichiometric ratio of 1:2 in CN_3CN/CH_3OH(v/v, 3/1). The mixture was stirred at 75°C for 8 hours, followed by adding saturated CH_3OH solution of Li(NTf2) to exchange counterpart anions.

- **Metallo-macrocycle M2 self-assembly:** The ligand L2, L3 and $Zn(NO_3)_2$ were mixed in DMF with stoichiometric ratio of 1:1:4. After 8 hours of refluxing, an excess amount of $Li(NTf_2)$ methanol solution was added to exchange the counterpart anions.

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RESULTS

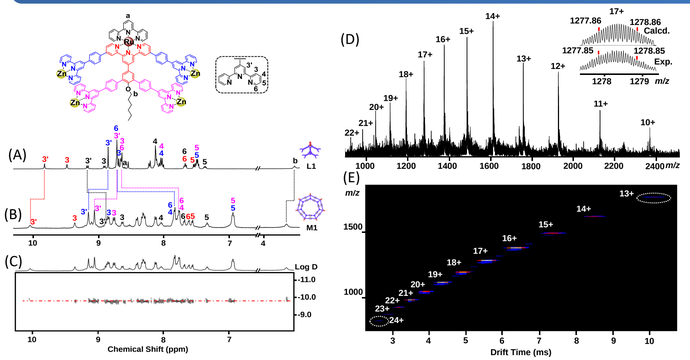

Figure 1: ^{1}H NMR spectra of(A) **L1** and (B) **M1** in CD_3CN. DOSY spectrum of (C)**M1** in CD_3CN (D) ESI-MS spectrum and (E) ESI-TWIM-MS plot of complex M1.

- ^{1}H NMR spectra provide information about: the **formation of the coordination bonds, self-assembly of a single product, and purity of the product**.

- The **molecular compositions of heptagonal supramolecule** was identified with the aid of electrospray ionization mass spectrometry (ESI-MS) and traveling-wave ion mobility mass spectrometry (TWIM-MS).

- Transmission electron microscopy (TEM) and ultra-high vacuum low-temperature scanning tunneling microscopy (UHV-LT-STM), were employed in this study to **achieve direct imaging and obtain detailed structural information of molecules at a single atomic level**.

Metallo- macrocycle M1:

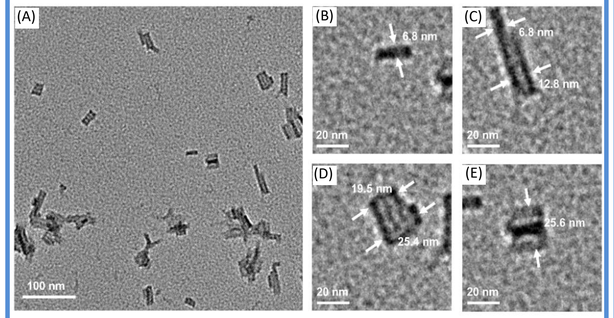

Figure 2: TEM images of nanotube structures formed by (A)**M1 at larger densities**; (B, C, D, E,) Enlarged nanotube TEM images with different degrees of aggregation formed by **M1.**

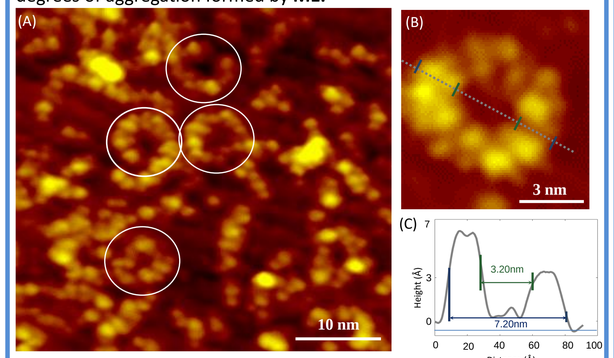

Figure 4: STM characterization of the complex **M1** on Au (111) surface. A large area STM image showing multiple complexes (A) **M1** (Imaging parameter: V_{bias} = 2 V and I = 110 pA). STM line profile measurements revealed the height and the size of the supramolecule (B), (C) **M1.**

Metallo- macrocycle M2:

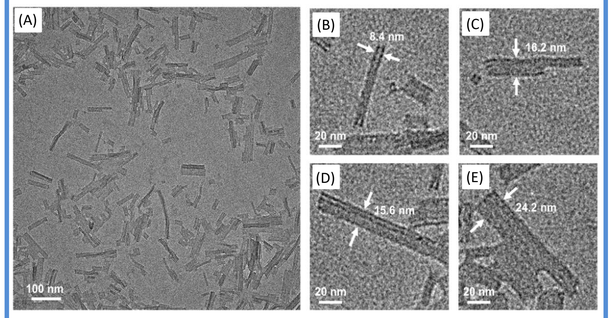

Figure 3: TEM images of nanotube structures formed by (A)**M2 at larger densities**; (B, C, D, E,) Enlarged nanotube TEM images with different degrees of aggregation formed by **M2.**

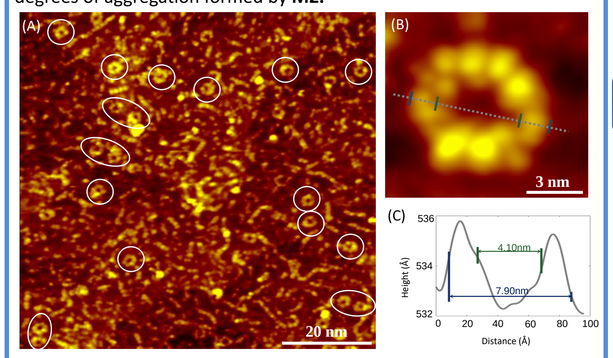

Figure 5: STM characterization of the complex **M2** on Au (111) surface. A large area STM image showing multiple complexes (A) **M2** (Imaging parameter: V_{bias} = 2 V and I = 110 pA). STM line profile measurements revealed the height and the size of the supramolecule (B), (C) **M2.**

SUPRAMOLECULE FRAMEWORK

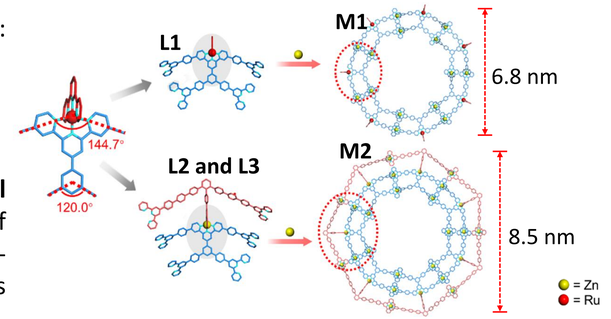

Figure 6. The framework of heptagonal metallo-macrocycle **M1** and **M2** and metal coordination node embedded in its backbone.

CONCLUSION

- By adjusting the ligand angle through the embedded coordination site at the backbone, successfully obtained concentric heptagonal metallo-macrocycles.

- The supramolecular M1 and M2 showed a strong tendency to form hierarchical self-assembled nanotube structures.

- Our findings indicate that UHV-LT-STM is an effective methodology for characterizing supramolecules at a single molecule level, providing more details of the molecular structure that is difficult to resolve by the resolution of TEM.

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