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## COMMUNICATION

## Di-triazole boat conformation leads to metal-organic nanotube while chair conformation leads to coordination polymer

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**Aliphatic-cored di-1,2,4-triazole ligands form both a metal-organic nanotube (MONT) and a coordination polymer upon reaction with silver nitrate. Control of the conformation of the cyclohexane ring between the triazoles determines the reaction outcome where a boat (formed from bicyclo[2.2.2]octane) yields a MONT while a chair (formed from cyclohexane) yields the coordination polymer.**

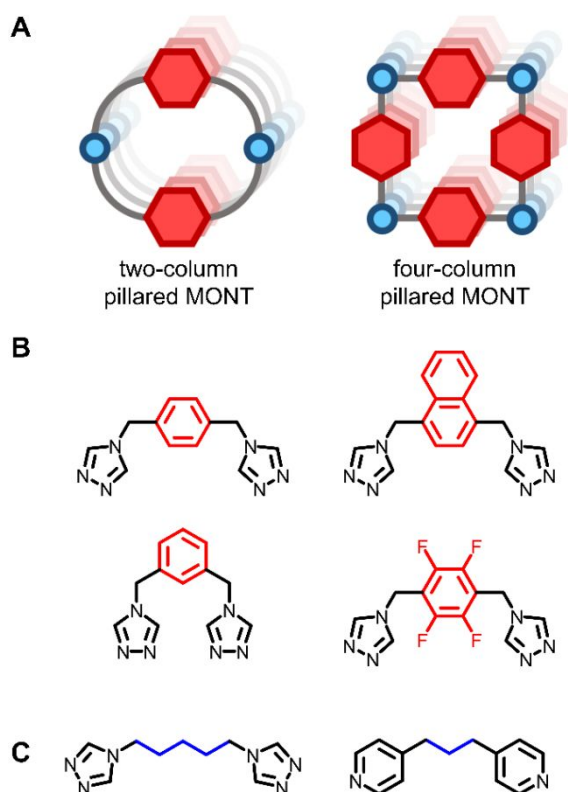
### Introduction

Metal-organic nanotubes (MONTs) are one-dimensional materials which contain organic ligands and metal clusters forming tubular structures.<sup>1</sup> MONTs are anisotropic like carbon nanotubes (CNTs), but, critically, they are highly tuneable like metal-organic frameworks (MOFs), since a wide variety of organic linkers can be utilized to both control the pore size<sup>2</sup> and the functionality of the resulting material.<sup>3,4</sup> For these reasons, MONTs are now moving into numerous applications, including host-guest chemistry,<sup>5,6</sup> gas adsorption<sup>7</sup> and separations,<sup>8,9</sup> and chemical sensors.<sup>10-13</sup>

Currently, the most common general strategy to synthesize MONTs is through molecular assembly by forming two- or four-column pillared MONTs (Fig. 1A).<sup>1, 7, 14-21</sup> In this approach, one or two ligands are reacted with a metal salt in a solvothermal process which leads to homogenous materials on a bulk scale. Although a wide variety of functional groups have been designed to bind the ligands to different metals, intriguingly the cores for many of the ligands are actually very similar.

Ligands for two- and four-column pillared MONT structures are normally assembled with aryl-cored moieties which frequently yield  $\pi$ - $\pi$  interactions between the tubular structures.<sup>1,12, 19</sup> For example, our previous research has focused on two-column pillared MONT formations with double-

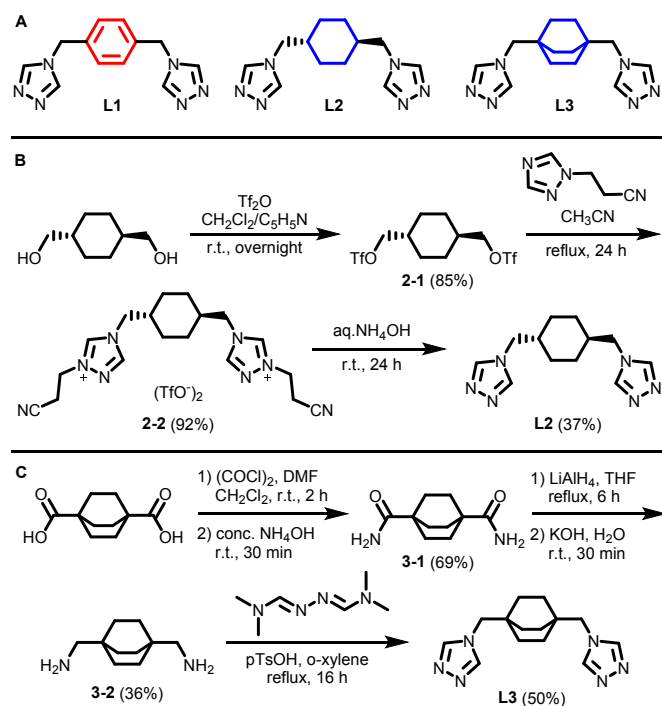
hinged di-1,2,4-triazole ligands that contains aryl units (Fig 1B).<sup>7, 17-21</sup> These ligands form a two-column pillared MONT with phenyl or naphthyl moieties arranged between the tubes. Four-column pillared MONT structures are also synthesized with aryl and bi-aryl linkers which gives rigidity to organic pieces for their tube formations.<sup>22-25</sup> These previous results raise the question if aryl or  $\pi$ -conjugation systems are required for MONT formation and whether non-planar or “ $\pi$ -lacking” cored ligands can assemble MONT in analogous geometries.



**Fig 1.** (A) Schematic diagram for 2- and 4-column pillared MONTs formation style: red hexagons and blue circles represent ligands and metal connecting nodes, respectively; (B) Previously published MONT ligands with  $\pi$ -conjugated system (highlighted in red) and (C) Aliphatic ligands (highlighted in blue) show only coordination polymer structures.

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**Scheme 1.** (A) Ligands **L2** and **L3** contain aliphatic cores compared with the phenyl-cored **L1**; (B) and (C) synthesis of new **L2** and **L3** ligands, respectively.

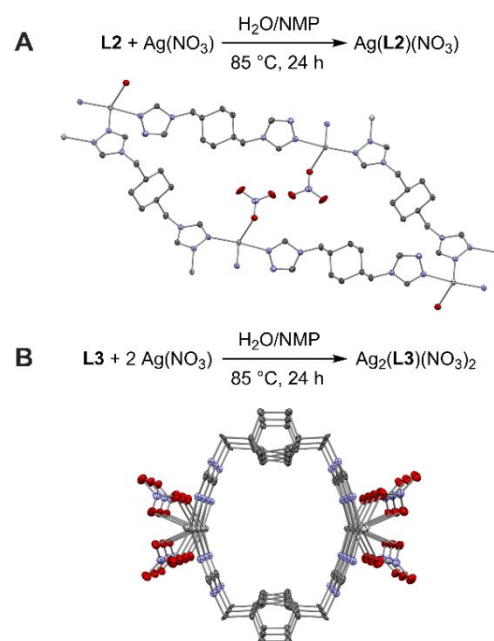
Indeed, aliphatic-cored ligands with the same functional groups for metal binding have been synthesized and reported for metal-organic coordination structures (Fig. 1C). For example, 1,5-di(4*H*-1,2,4-triazol-4-yl)pentane forms only coordination polymers or MOFs.<sup>26, 27</sup> Alternatively, 1,3-bis(4-pyridyl)propane has been reported as a ligand for a tube-like structure when reacted with silver(I) ion.<sup>28</sup> Nevertheless, its structure shows a non-porous material which cannot be classified as a MONT. To our knowledge, there are only two reports of two- or four-column pillared MONT structures without a fully  $\pi$ -conjugated core structure (such as benzene or pyridine), but each of these has limitations. In the first case, cyanide is employed as a bridging ligand, but it provides only a 2 Å pore, which is too short for many applications.<sup>23</sup> More importantly, there is no way to tune cyanide for specific pore sizes or properties. In the second case, Zhao and Zhang prepared a two-column pillared zinc MONT with a core bridging linker which contained both an aryl and non-aryl unit in the same ligand.<sup>29</sup> Therefore, understanding the effect of  $\pi$ - $\pi$  interaction of the ligand to MONT formation is essential for further ligand development.

In this manuscript, we have designed aliphatic-cored di-1,2,4-triazole linkers **L2** and **L3** as “ $\pi$ -lacking” ligands for MONT synthesis to compare with previously synthesized **L1** ligand (Scheme 1A). These new ligands provide fascinating insights into the design principles for MONT formation. If the central ring follows a chair conformer, then a coordination polymer is formed, but when the central cyclohexane is forced into a boat conformer, then a 2-pillared MONT is synthesized. These results demonstrate how it is possible to prepare MONTs that lack  $\pi$ - $\pi$  interactions in between the linkers.

## Results and Discussion

Despite their structural similarity, ligands **L2** and **L3** were prepared through disparate paths. Ligand **L2** was synthesized via a three-step synthesis (Scheme 1B). *Trans*-1,4-cyclohexanediol was reacted with trifluoromethanesulfonic anhydride modified from the reported procedure<sup>30</sup> to give **2-1** in 85% yield. The second step was adapted from Horváth, whereby addition of 1,2,4-triazole-1-propanenitrile to the dielectrophile compound **2-1**, provides **2-2** in 92% yield.<sup>31</sup> Concentrated  $\text{NH}_4\text{OH}$  removed the propanenitrile group, leaving **L2**, which was crystallized in 2-propanol in 37% yield. In contrast, ligand **L3** was synthesized via functional group interconversion strategies (Scheme 1C). Compound **3-1** was prepared by an adaptation from a previously reported two-step one-pot synthesis<sup>32</sup> by converting bicyclo[2.2.2]octane-1,4-dicarboxylic acid to acid chloride with oxalyl chloride, followed by amidation with  $\text{NH}_4\text{OH}$  to obtain the diamide compound **3-1** in 69% yield. Compound **3-1** was reduced with  $\text{LiAlH}_4$  to produce diamine compound **3-2** in 36% yield. The 1,2,4-triazole was formed using *N,N'*-bis(dimethylaminomethylene)hydrazine followed by crystallization in 2-propanol to give **L3** in 50% yield. All compounds were characterized with NMR and IR spectroscopies, high-resolution mass spectrometry, and in some cases single crystal X-ray diffraction (SCXRD) studies (see ESI for spectra).

Ligands **L2** and **L3** were reacted with silver nitrate under similar conditions that led to previously reported 2-pillared MONT formation with **L1**.<sup>7, 20</sup> Solutions of 2 mM **L2** in *N*-methyl-2-pyrrolidone (NMP) and 4 mM  $\text{AgNO}_3$  in water were prepared and heated separately at 85 °C. Then, 10 mL of **L2** and  $\text{AgNO}_3$  solutions were mixed and heated at 85 °C for 24 hours (Fig. 2A). The reaction generated crystals which were removed from the reaction mixture, washed with methanol and water, and then



**Fig 2.** Syntheses and single crystal X-ray structures of (A)  $\text{Ag}(\text{L2})(\text{NO}_3)$  and (B)  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$

dried to obtain  $\text{Ag}(\text{L2})\text{NO}_3$  in 54% yield. The same reaction was performed with **L3** and silver nitrate to obtain  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  in 35% yield (Fig. 2B). The solid crystals obtained from each reaction were analysed by SCXRD, powder X-ray diffraction (PXRD), IR, and elemental analysis (see ESI).

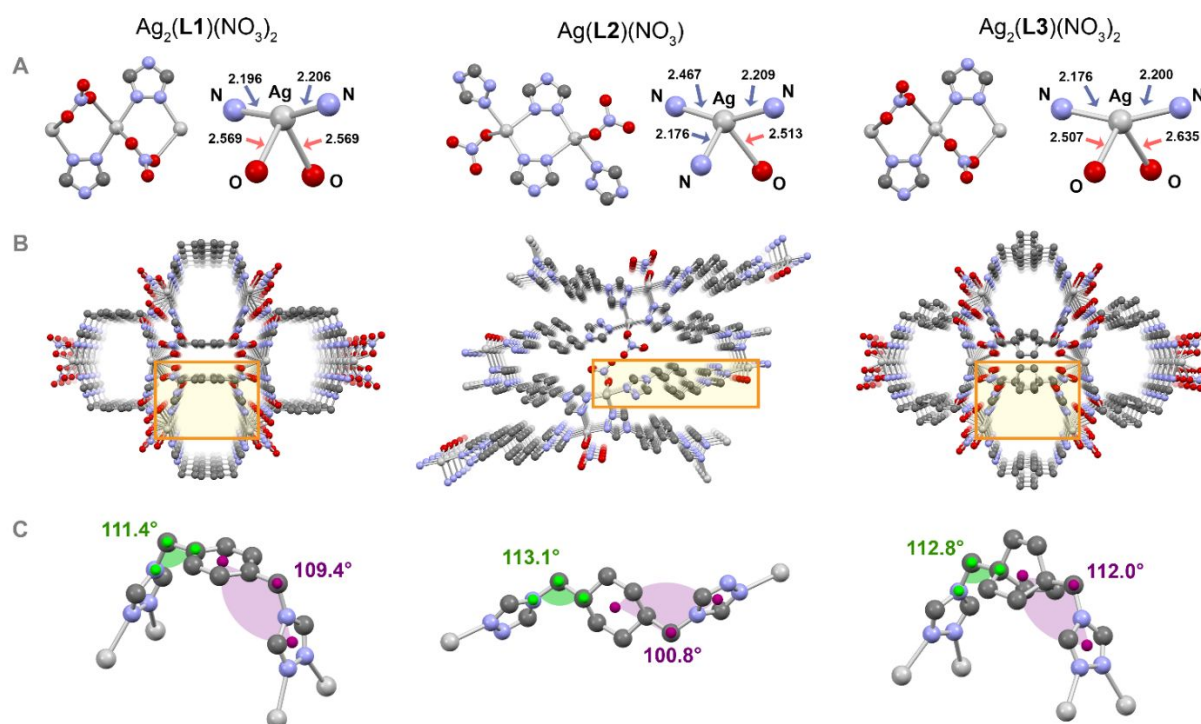
SCXRD studies confirmed the differences in structure of metal-organic materials formed from the two ligands and silver nitrate. Notably, **L2** and **L3** are almost the same size as **L1**, so they could form isostructural MONTs. Instead, cyclohexane-cored ligand **L2** yielded a two-dimensional coordination polymer,  $\text{Ag}(\text{L2})(\text{NO}_3)$  (Fig. 2A). Conversely, the bicyclo[2.2.2]octane-cored ligand **L3** yielded the MONT,  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  (Fig. 2B). These two materials were analysed with powder X-ray diffraction which showed correlated patterns with the simulated PXRD patterns from single crystal structures of  $\text{Ag}(\text{L2})(\text{NO}_3)$  and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$ , demonstrating that the single crystals selected match the bulk phase (see ESI).

The MONT formed from **L3** is remarkably similar to the one reported from **L1**. Crystal structure parameters of  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  with its  $C2/c$  space group are almost identical to previously reported  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$  (Table S2).  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  provides a wider  $a$  and narrower  $b$  axes with pore dimensions of  $9.38 \text{ \AA} \times 9.88 \text{ \AA}$ , while  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$  is  $8.96 \text{ \AA} \times 10.60 \text{ \AA}$ . Notably, the X-ray structures show the same connectivity at the silver centre where there are two bonds to triazole and two bonds to nitrate (Fig. 3A). All Ag–N and Ag–O bond distances of  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  are similar to the MONT  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$  MONT.

On the other hand, the coordination polymer  $\text{Ag}(\text{L2})(\text{NO}_3)$  is strikingly different from the two MONTs. Each silver atom binds

to three triazoles and one nitrate, which is different from  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$ 's and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$ 's silver-ligand bonds (Fig. 3A). In addition, one triazole of  $\text{Ag}(\text{L2})(\text{NO}_3)$  shows only a single nitrogen bound to a silver atom, which is different from other triazoles in these structures, and leads to a longer Ag–N bond distance (Fig. 3A).

To investigate the reason behind these phenomena, the geometric properties of the organic ligands within each structure were analysed to demonstrate the relative importance of bond angles between core moieties and triazole. In particular, the dihedral angles of N–C/C–N bonds between methylene bridges and triazoles to determine which may be the key to MONT formation (Fig. 3B and 3C). The C–C–N bond angles for  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$ ,  $\text{Ag}(\text{L2})(\text{NO}_3)$ , and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  are all with 1 degree of  $112.2^\circ$ . However, their core centroid–C–triazole centroid angles vary considerably.  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$  and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  share centroid angles that are near  $112^\circ$ , which is consistent with the C–C–N angle, but  $\text{Ag}(\text{L2})(\text{NO}_3)$  has a core centroid–C–triazole centroid angle of  $101^\circ$ . Moreover, dihedral angles of N–C/C–N bonds between methylene bridges and triazoles for  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$  and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  are around  $6^\circ$ , which causes those ligands to arrange in a *syn* formation, while  $\text{Ag}(\text{L2})(\text{NO}_3)$ 's is  $180^\circ$  which leads to an *anti* alignment. The key distinction between **L2** and **L3** is that the chair conformation of **L2** leads to core centroid–C–triazole centroid angles that are inconsistent with MONT formation on silver, while **L3** in a boat conformation effectively mimics the geometry of the central aryl unit of **L1** even though there is no  $\pi$ -system in **L3**.



**Fig 3.** Crystal structures of  $\text{Ag}_2(\text{L1})(\text{NO}_3)_2$ ,  $\text{Ag}(\text{L2})(\text{NO}_3)$  and  $\text{Ag}_2(\text{L3})(\text{NO}_3)_2$  show (A) metal-organic bonding around silver atoms, nitrate anion, and triazole units with bond distances. (B) crystal packing of MONTs and coordination polymer with orange boxes highlighting portion shown below. (C) Highlighted portion with bond angle comparison between C–C–N and centroid–C–centroid of core–methylene–triazole, indicated as green and purple dots, respectively.

Finally, Hirshfeld surface analysis allowed us to evaluate the intermolecular interactions among all metal-organic coordination structures. One key finding for this analysis is that the MONTs  $\text{Ag}_2(\mathbf{L1})(\text{NO}_3)_2$  and  $\text{Ag}_2(\mathbf{L3})(\text{NO}_3)_2$  have  $\pi$ - $\pi$  interactions between triazole units which was not found in  $\text{Ag}(\mathbf{L2})(\text{NO}_3)$  (Fig. S34). Yet given that all three materials contain the same triazole moiety, this is not the driving force for formation of a MONT versus a coordination polymer.

## Conclusion

We have synthesized and characterized the new ligands **L2**, with a cyclohexane core, and **L3**, with a bicyclo[2.2.2]octane core, neither of which have  $\pi$ -conjugation. These ligands react with silver nitrate under solvothermal conditions to form a coordination polymer and a MONT, respectively. The solid materials have been characterized with SCXRD, the bulk phase confirmed with PXRD, and the structures compared with previously reported  $\text{Ag}_2(\mathbf{L1})(\text{NO}_3)_2$ . Ligand **L3** yielded a MONT that is isostructural to the MONT formed by **L1**.  $\text{Ag}_2(\mathbf{L3})(\text{NO}_3)_2$  is the first example of a MONT that contains an aliphatic core linker. For this 2-pillared system with silver, the key discovery is that the ring centroid–C–ring centroid needs to be approximately  $112^\circ$  to form a MONT, but, in fact,  $\pi$ - $\pi$  stacking is not required for MONT formation. These insights in structural design will be utilized to prepare additional MONTs with aliphatic cores.

## Author Contributions

P.N.: Data curation, Formal Analysis, Investigation, Writing – original draft; D.M.J.: Conceptualization, Formal Analysis, Funding acquisition, Investigation, Methodology, Supervision, Visualization, Writing – original draft, Writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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