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Construction of Stable Helical Metal-Organic Frameworks with Conformationally Rigid "Concave Ligand"

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Abstract: A helical-shaped metal-organic framework was prepared using conformationally rigid tetratopic benzoic acid ligand with binding units pointing toward each other (concave ligand). To avoid the obvious intramolecular interactions between binding units, matching spacing groups was applied to introduce atropic repulsion, allowing the formation of extended frameworks for the first time. With this new ligand design, a helical-shaped MOF was successfully prepared with significantly improved air and moisture stability, providing a new strategy for ligand design toward porous material constructions.

With the high surface area and adjustable pore size, the metal-organic framework (MOF) has enjoyed its unique position in material science with many impressive applications in various research areas both in academic and industrial settings.^[1] Despite the numerous stellar MOFs synthesis, the general design of the organic ligands could be divided into two parts: A) binding domain and B) structural domain (skeleton).^[2] The combination of different metal ion binding patterns (clusters) and diverse organic skeletons assure the ability to access a large number of porous structures with versatile functionality.^[3] Based on the tremendous successes in ligand design and complex synthesis, the focus of MOF research shifts more toward practical applications in the past decade, with many promising systems developed including targeting gas separation/storage,^[4]energy storage,^[5] sensors,^[6] and heterogeneous catalysis.[7] Despite these tremendous progress, one may envision that the new ligand design principle remains as a critical factor in MOF research as it would provide a fundamentally different linkage strategy for porous material synthesis. Integration of the new design principle with other typical binding features, such as various secondary building units (SBUs) and different coordination

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clusters, will certainly result in new molecular architecture, which could further enrich the MOF research and applications.



Scheme 1. Ligand skeleton in MOF network synthesis

In general, to ensure the effective synthesis of polymeric network structures, the "open-arm" ligand design has been adopted in almost all reported MOFs. As shown in **Scheme 1A**, the binding units are positioned at the "convex" face of the ligand skeleton, allowing easy structure extension. Some representative MOFs with this "convex-ligand" design are ZJU-31^[8] and NU-1400.^[9] Not surprise, ligand skeletons with binding units pointing toward each other has not been widely applied in MOF synthesis due to the concern that the primary binding mode of this "concave ligand" is intramolecular coordination, preventing the formation of extended polymeric networks.

Besides the unfavored binding geometry, another major problem of "concave design" is the challenging synthesis of the ligand with crowded substitution all located on one side of the molecule.^[10] To ensure practical synthesis, easy access to ligand is one important feature in MOF chemistry.^[11] Based on conformation analysis and orthogonal functional groups synthesis design, herein, we report a new helical-MOF synthesis using properly designed concave ligand bearing atrop-repulsion, which effectively prevents the undesired intramolecular binding unit aggregation to ensure the polymeric network construction. To the best of our knowledge, this is the first example of MOF reported with the novel concave ligands design principle.

With good structural rigidity and easy functionalization ability, benzene has been widely applied as the backbone for ligand skeleton synthesis.^[12] One main challenge in preparing ligand with "concave" binding units is the need of a spatial "crowed" 1,2,3-tri-substituted building blocks that bear orthogonal reactive sites (selective reacting with C-2 over C-1 and C-3).^[10] To achieve MOF practical application, the readily available ligand with

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efficient synthesis (large scale and show steps) is crucial. With a strong interest in exploring this concave ligand design, we set a goal to develop a practical synthesis of 1,2,3-trisubstituted ligands through a modular approach. After exploring several different approaches, we identified the application of diazonium and halide as the orthogonal coupling units to achieve various concave-shape ligands (**6a-6c**) with high overall yields and capability in large scale productions. This modular synthetic route is summarized in **Figure 1**.



Figure 1. General synthetic route of concave ligand 6.

The synthesis starts from commercially available paramethyl aniline 1. Bromination followed by oxidation (diazonium formation) and iodination gave the 1,2,3-trisubstituted arene 3 in excellent yields and large scale (>100 gram). After screening various coupling conditions, combination Pd(dppf)₂Cl₂ catalyst and aryl bis-boronic acid (commercially available) was identified as the optimal conditions, giving the C-2 coupling products 4 in good yields. The resulting tetra bromoarene 4 were charged with typical Suzuki conditions followed by saponification to yield the tetra-acid 6 concave ligands. This synthesis has high efficiency with the overall yields >35%. Also, the design is based on the modular synthesis concept, where the different combinations of central linkers (various length and binding angle) and various binding arms could be easily prepared under similar conditions. Some alternative linkers (alkyne and heterocycles) and binding arms are currently under investigation in our lab.

To explore whether concave-shape ligands could be applied for MOF network construction, we put our focus on evaluating ligand 6 with three different central arene linkages. Compounds 6a-6c were prepared and applied in MOF synthesis. Although almost fifty MOF growing conditions have been tried under different combinations of cations, solvents, and acid additives, ligands 6b and 6c failed to give crystalline polymeric MOF so far. The competing intramolecular binding between the concave binding moieties could be problematic, which highlighted the significant challenges in constructing porous networks using the concave ligand design. Based on the structural conformation analysis, we hypothesized that ligand 6a could be used to overcome the intramolecular binding competition with the "atrop-repulsion".

As shown in **Figure 2A**, with a shorter linker, the two benzene at the side arms could encounter steric repulsion and push the two arenes away from each other.^[13] As the results, the two COOH binding units are twisted and prevent

the undesired intramolecular interactions. This atroprepulsion makes COOH in twisted conformation and available for the construction of extended networks. With this analysis, we put our efforts in synthesizing MOF using this twisted arm ligand **6a**. After exploring various MOF synthesis conditions, a colorless single crystal was obtained when treating **6a** with Cd(NO₃)₂.4H₂O in DMF and water mixture at 85 °C for 18 hours. After cooling the reaction mixture to room temperature, complex **6a-MOF-Cd** was obtained in 91% yield. The FT-IR spectra of the resulting MOF confirmed the disappearance of the carboxylic acid group at 3114 cm⁻¹ and coordinated carboxylate groups stretching at 1393 cm⁻¹ and 1527 cm⁻¹, indicating the coordination between carboxylates and metal cations (see **Fig S3**).









Figure 2. Helical MOF from concave ligand with atrop-repulsion

The single-crystal of **6a-MOF-Cd** was obtained which revealed the structure of **6a-MOF-Cd** as triclinic space group P-1 (a=10.615(8) Å, b=15.614(0) Å, and c=17.580(6) Å).^[14] As shown in **Figure 2B**, each asymmetric unit in **6a-MOF-Cd** consists of two Cd²⁺ and four concave ligands **6a**. The secondary building unit (SBU) contains two Cd with different coordination patterns. Cd₁ is bonded to six O atoms (two from DMF and three from **6a**, Cd₁-O distances:2.210-2.354 Å), whereas Cd₂ binds to seven O atoms (two from DMF and three from **6a**, Cd₂-O=2.209-2.438 Å). With this twisted concave ligand **6a** and two types of Cd clusters, a new 2D helical molecular architecture was formed. Two micropores

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were identified with sizes of 6.7 Å and 5.6 Å. The distance between the upper and lower hydrophobic edge of the 2D planar structure is 14.4 Å (Figure 2C). The topology of **6a-MOF-Cd** was abstracted to **3,3,4-c** using ToposPro.^[15] The ligand **6a** was simplified into two connected triangles with four carboxylates extending in different directions. After removing free solvent molecules in the crystal structure, the total void volume of **6a-MOF-Cd** was calculated and estimated to be 38.5 % by PLATON.^[16]

To confirm the phase purity, powder X-ray diffraction (PXRD) spectra of 6a-MOF-Cd was collected. The diffraction patterns of the tested samples and the calculated data from crystal structure were compared (Figure 3A). As shown in the crystal structure, the hydrophobic methyl groups on the edge of ligand 6a point to the upper and lower faces of the complex, forming a hydrophobic centered tube. This structure feature suggests the opportunity for future structure modification by introducing different functional groups at the methyl position for new network construction and applications. CO2 adsorption isotherms of 6a-MOF-Cd was recorded at 195 K. The Langmuir and Brunauer-Emmett-Teller (BET) surface area were calculated to be 465.89 and 283.69 m²g⁻¹ respectively. The maximum CO₂ uptake of 6a-MOF-Cd of 113.4 cm³g⁻¹ at P/P₀=0.95 was recorded (Figure 3D). Although this number is relatively low compared to other reported MOFs,^[4a,17] the introduction of atrop-repulsion in concave ligand for the successful synthesis of polymeric complexes representative provides a new design principle for MOF synthesis.

Besides the readily available synthesis, complex chemical and thermal stabilities are crucial for practical applications of any new MOFs. As many other MOF materials, the first stage of mass loss in 100-250 °C was caused by the release of non-bond solvents (DMF and water, etc). 6a-MOF-Cd was stable under vacuum of 110 °C for 12 hours. After the sorption experiment was carried out under CO₂ at 195K, the PXRD suggesting that the MOF framework remains the same. PXRD of the sample after heating to 200 °C showed the collapse of the framework. Based on the TGA result, the content of free DMF and water is 19.5%. The weight loss of the sample between 410-520 °C is 54%, which is the total amount of ligand 6a in the sample. After 520 °C, there is almost no significant weight loss, and the final residue is likely the CdO after metal oxidation and complex decomposition (Figure S6).

Due to water or solvent binding competition, the chemical stability of MOFs could be a concern, especially when treating MOFs in acid or basic aqueous solution. To our great satisfaction, this new MOF material from the concave ligand showed excellent stability in a wide range of solvents and large pH range. Soaking **6a-MOF-Cd** in different solvents (including water, MeOH, MeCN, THF, and DCM) for a week gave almost no decomposition of the complexes with PXRD signals remaining almost identical as the assynthesized MOF, demonstrating the excellent stability of this new class of MOFs in various solvents (**Figure 3B**). The acid and base stability was also investigated upon soaking

the complex in aqueous solutions at different pH for 24 hours. As shown in **Figure 3C**, the crystalline frameworks remain intact in a wide range of acidic and basic conditions (pH=2 to pH=12) and at high temperature (85 °C 24 hours). It is known in literature that COO-Cd could be very labile in aqueous due to the competing O-Cd binding. The excellent water and acid/base stability of this new MOF is very impressive and highlighted the clear advantage of this new concave ligand design in MOF formation.



Figure 3. A) PXRD patterns of 6a-MOF-Cd. B) Stability of 6a-MOF-Cd in organic solution. C) Stability of 6a-MOF-Cd in aqueous solution from pH=2 to pH=12. D) 195K CO₂ uptake of 6a-MOF-Cd

In conclusion, based on structure functional group orthogonal reactivity, we developed a facile synthesis of tetra-carboxylate bearing concave binding geometry. As the modular synthesis, various concave ligands containing different linkers and arms could be readily synthesized in gram scale. Through structure conformational analysis, we identified ligand 6a with atrop-repulsion to avoid intramolecular binding and successfully prepared the first polymeric 6a-MOF-Cd complexes bearing a concave ligand design. With the maximization of the A-1,3 repulsion effect, the concave ligand 6a can spirally extend in a twodimensional space to produce a chiral helical 2D-MOF molecular architecture. This new framework exhibited excellent solvent and acid-base stability owing to its hydrophobic surface. Based on this novel concave ligand design, derivatization on such ligands towards the development of new materials with the potential application is undergoing in our laboratory.

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Keywords: MOF • concave ligand • helical structure • acid-base stability

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