

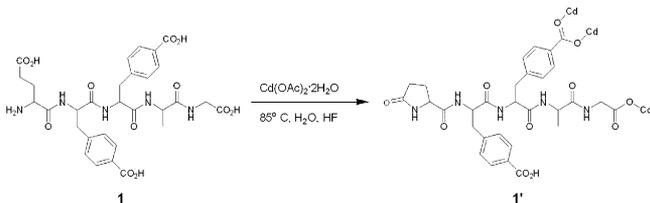
Crystalline Fibers of Metal–Peptide Double Ladders

Dani Peri,^{†,‡} Jim Ciston,[§] Felipe Gándara,^{†,‡} Yingbo Zhao,^{†,‡} and Omar M. Yaghi^{*,†,‡}[†]Department of Chemistry, University of California—Berkeley, Berkeley, California 94720, United States[‡]Kavli Energy NanoScience Institute at University of California—Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States[§]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Despite remarkable progress in the field of MOFs, structures based on long-flexible organic linkers are scarce and the majority of such materials rely on rigid linkers. In this work, crystals of a new metal–organic double ladder (MODL) are obtained by linking a pentapeptide (NH₂-Glu-*p*CO₂Phe-*p*CO₂Phe-Ala-Gly-OH) with cadmium acetate to produce a Cd(2-pyrrolidone-*p*CO₂Phe-*p*CO₂Phe-Ala-Gly)(H₂O)₃ framework. SEM and TEM analyses show the fibrous nature of the crystals and show that the infinite cadmium oxide rod secondary building units (SBUs) are aligned with the longitudinal axis of the nanofibers.

In the chemistry of metal–organic frameworks (MOFs) it is common to obtain crystalline products from the assembly of metal ions with rigid organic linkers.^{1–3} Thousands of such MOFs have been reported, with very few encompassing long-flexible organic linkers. It is widely believed that the difficulty in obtaining crystals increases with the length and flexibility of the linkers employed in the synthesis. In this report we show how a pentapeptide (Scheme 1) can be linked by cadmium,

Scheme 1. Reaction Scheme for Formation of MODL^a

^aDuring the reaction the Glu moiety undergoes an intramolecular cyclization.

crystallized into fibers, and then characterized by single-crystal X-ray diffraction (SXRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). We show that cadmium peptide double ladders propagate along the longitudinal axis of the fibers. The choice of peptide as a linker addresses the crystallization challenge stated above and may have the potential of making MOFs with biologically relevant interiors.

There are few crystalline MOFs incorporating flexible linkers. Several are made from tartaric acid derivatives, γ -cyclodextrin,

or *N*-(4-pyridylmethyl)-D/L-valine.^{4–6} Even though a number of MOFs with di- or tripeptide linkers are known, only a few are crystalline.^{7–12} To date, no reports of a crystalline pentapeptide or even a tetrapeptide MOF have been made. Herein we report a unique pentapeptide-based metal–organic double ladder (MODL).

Cadmium acetate dihydrate (8.8 mg, 0.033 mmol) and NH₂-Glu-*p*CO₂Phe-*p*CO₂Phe-Ala-Gly-OH (**1**; 4.2 mg, 0.064 mmol) were dissolved in 2 mL of deionized water with 5 μ L of hydrofluoric acid in a 4 mL scintillation vial (Scheme 1). The reaction mixture was placed under autogenous pressure at 85 °C. Needle-shaped crystals were collected after 5 days, filtered, and washed with 30 mL of water. The reaction produced transparent colorless needle-shaped crystals in a yield of 43% based on cadmium. The MODL was formulated and characterized by elemental microanalysis¹³ and X-ray single-crystal diffraction studies.

The MODL is constructed of two infinite cadmium chains linked by a pentapeptide in a double-ladder fashion which progress along the [010] axis of the unit cell (Figure 1). During the assembly process the Glu amino acid at the amine end of **1** reacted in an intramolecular fashion to form a 2-pyrrolidone moiety, as is evident from the crystal structure, to form **1'**

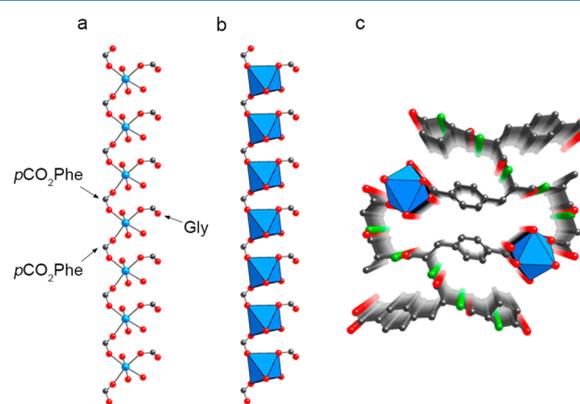


Figure 1. MODL structure: (a) Ball-and-stick representation of SBU; (b) SBU with Cd shown as polyhedra; (c) view of the crystalline 1D framework with inorganic SBUs linked together by **1'**. Color scheme: Cd, blue; C, gray; O, red; N, green. Hydrogen atoms are omitted for clarity.

Received: September 27, 2013

Published: November 20, 2013



(Scheme 1). **1'** binds to the SBU through the *p*CO₂Phe and Gly moieties, the former bridging between two cadmium ions and the latter coordinating in a monodentate fashion (Figure 2a).

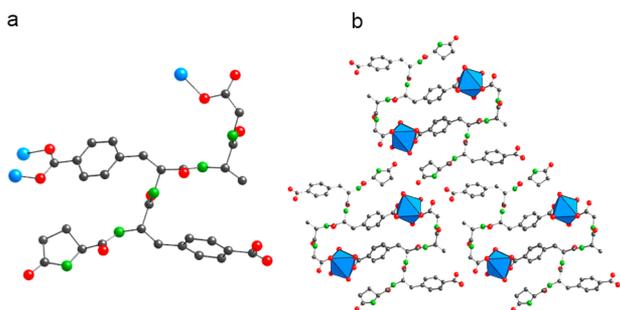


Figure 2. (a) Bridging of the *p*CO₂Phe moiety between two Cd ions and simultaneous binding of the Gly moiety in a monodentate fashion. (b) Three MODLs viewed along the [010] crystallographic axis, intermolecular hydrogen bonds between the double ladders producing the 3D ensemble. Color scheme: Cd, blue; C, gray; O, red; N, green. Hydrogen atoms are omitted for clarity.

Each cadmium ion has a pseudo-octahedral environment with three bound carboxylate moieties, two of which are of *p*CO₂Phe moieties that originate from two different linkers and another carboxylate which is of the Gly moiety of a third linker (Figure 1b) with Cd–O bond lengths that range between 2.24 and 2.30 Å. In addition, three water molecules coordinate to the cadmium center to complete the octahedral environment, with Cd–O bond lengths that range between 2.29 and 2.37 Å. The three water ligands bind in a meridional fashion with an angle of 174.5° between the two *trans* H₂O ligands and 87.0–91.3° between the two *cis* H₂O ligands.

A complex net of intramolecular and intermolecular hydrogen bonds (*vide infra*) stabilize the ensemble. Intramolecular hydrogen bonding between the amide bonds of the stacked **1'** linkers stabilizes the double ladder. In addition, intermolecular hydrogen bonding between water ligands and the carbonyl of the 2-pyrrolidone moiety, between the noncoordinating carboxylic moiety of the *p*CO₂Phe amino acid and the terminal carboxylate of **1'**, and between the amide of the 2-pyrrolidone moiety and the noncoordinating carboxylic moiety of the *p*CO₂Phe are donor–acceptor hydrogen pairs that act as a secondary hierarchical interaction in the construction of the macroscopic ensemble (Figure 2b).

SEM images of MODL (Figure 3a, b) show the fiberlike morphology of the particles. The fibers have an approximate diameter of 0.2–0.8 μm with a length of ca. 0.5 cm. After sonication of the sample for 3.5 h the nanofibers maintain their straight edge and relative high diameter-to-length ratio with a diameter of ca. 20–100 nm (Figure 3c, d). This observation led us to believe that there is a strong correlation between the macro shape of the fibers and the molecular structure of the double ladder, meaning that the longitudinal axis of the MODL and the [010] crystallographic axis align with the longitudinal axis of the fiber.

We investigated the hypothesis stated above by employing TEM imaging. This was done by obtaining a diffraction pattern and a visual image of the same nanofiber at the exact same orientation. Afterward, crystallographic planes and spacing such as the [010] plane with a 4.9 Å spacing were identified by matching the TEM-acquired diffraction pattern with the

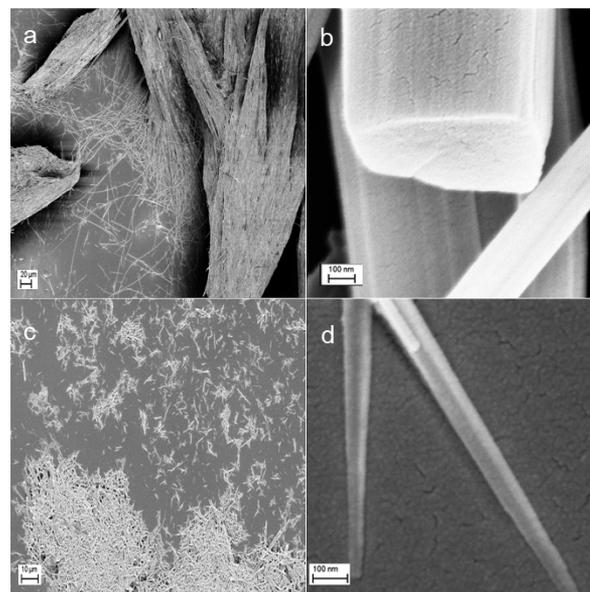


Figure 3. SEM images: (a) MODL fibers before sonication; (b) MODL fiber cross section showing a diameter of up to ca. 0.8 μm; (c) MODL after sonication for 3.5 h; (d) single particle after 3.5 h of sonication showing a diameter of ca. 20–100 nm.

calculated diffraction pattern of the single-crystal structure. In this way, as is evident from Figure 4, we found that the [010] planes are perpendicular to the longitudinal axis of the particle. Since the double ladders propagate along the [010] axis (with a value of 4.87 Å based on the unit cell parameters), we could unambiguously determine that the longitudinal axes of the fiber and of the double ladder are aligned (Figure 4c).

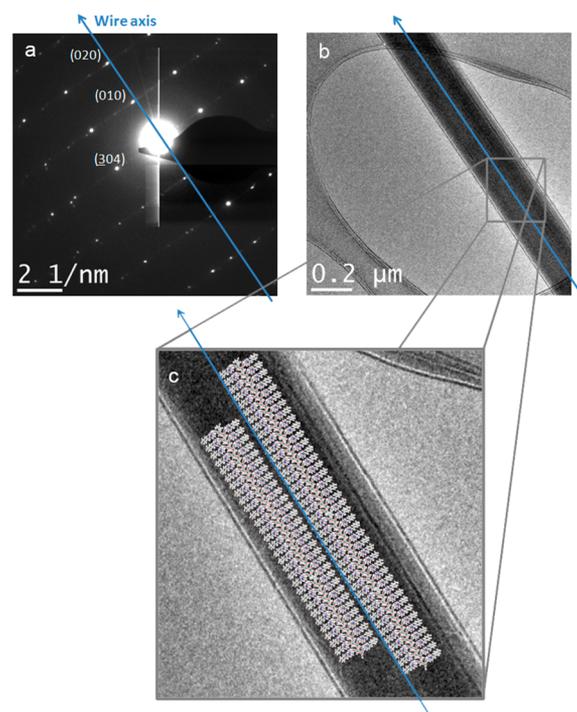


Figure 4. TEM studies: (a) diffraction pattern of a MODL nanofiber by TEM; (b) visual TEM image of the exact same nanofiber from (a); (c) cartoon of the MODL oriented within the nanofiber.

The unique combination of single-crystal X-ray diffraction studies combined with SEM and TEM studies provided us with the unambiguous determination that the double ladders propagate along the longitudinal axis of the nanofibers. Utilizing a pentapeptide that allows for strong and weak interactions in the construction of the ensemble provides new properties and potentially a top–bottom approach for the synthesis of such materials. The Glu and *p*CO₂Phe amino acids at the first and second positions of the pentapeptide, respectively, only take part in the secondary hierarchical structure by hydrogen bonding. Therefore, substituting these amino acids with other moieties could potentially produce double-ladder structures with alternative packing and properties.

■ ASSOCIATED CONTENT

📄 Supporting Information

Text, figures, and a CIF file giving details of the experiments, SEM and TEM images, and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*O.M.Y.: e-mail, yaghi@berkeley.edu; fax, 510-486-5846; tel, 510-643-5507.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-SC0001015. The TEM portion of this work was carried out at NCEM, which is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

■ REFERENCES

- (1) Stock, N.; Biswas, S. *Chem. Rev.* **2012**, *112*, 933–969.
- (2) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673–674.
- (3) Deng, H.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gándara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; Kazumori, H.; O’Keeffe, M.; Terasaki, O.; Stoddart, J. F.; Yaghi, O. M. *Science* **2012**, *336*, 1018–1023.
- (4) Sahoo, S. C.; Kundu, T.; Banerjee, R. *J. Am. Chem. Soc.* **2011**, *133*, 17950–17958.
- (5) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986.
- (6) Smaldone, R. A.; Forgan, R. S.; Furukawa, H.; Gassensmith, J. J.; Slawin, A. M. Z.; Yaghi, O. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 8630–8634.
- (7) Comotti, A.; Bracco, S.; Distefano, G.; Sozzani, P. *Chem. Commun.* **2009**, *3*, 284–286.
- (8) Perkins, C. M.; Rose, N. J.; Weinstein, B.; Stenkamp, R. E.; Jensen, L. H.; Pickart, L. *Inorg. Chim. Acta* **1984**, *82*, 93–99.
- (9) Rabone, J.; Yue, Y.-F.; Chong, S. Y.; Stylianou, K. C.; Bacsa, J.; Bradshaw, D.; Darling, G. R.; Berry, N. G.; Khimyak, Y. Z.; Ganin, A. Y.; Wiper, P.; Claridge, J. B.; Rosseinsky, M. J. *Science* **2010**, *329*, 1053–1057.
- (10) Anedda, R.; Soldatov, D. V.; Moudrakovski, I. L.; Casu, M.; Ripmeester, J. A. *Chem. Mater.* **2008**, *20*, 2908–2920.

(11) Lee, H.-Y.; Kampf, J. W.; Park, K. S.; Marsh, E. N. G. *Cryst. Growth Des.* **2007**, *8*, 296–303.

(12) Tiliakos, M.; Katsoulakou, E.; Terzis, A.; Raptopoulou, C.; Cordopatis, P.; Manessi-Zoupa, E. *Inorg. Chem. Commun.* **2005**, *8*, 1085–1089.

(13) Elemental micro analysis (%) Calcd for Cd(C₃₀H₃₁N₅O₁₁)(H₂O)₃: C, 44.81; H, 4.64; N, 8.71. Found. C, 44.62; H, 4.81; N, 8.86.