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Porous Materials

Modulation by Amino Acids: Toward Superior Control in the Synthesis of Zirconium Metal–Organic Frameworks

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Abstract: The synthesis of zirconium metal–organic frameworks (Zr MOFs) modulated by various amino acids, including L-proline, glycine, and L-phenylalanine, is shown to be a straightforward approach toward functional-group incorporation and particle-size control. High yields in Zr-MOF synthesis are achieved by employing 5 equivalents of the modulator at 120 °C. At lower temperatures, the method provides a series of Zr MOFs with increased particle size, including many suitable for single-crystal X-ray diffraction studies. Furthermore, amino acid modulators can be incorporated at defect sites in Zr MOFs with an amino acid/ligand ratio of up to 1:1, depending on the ligand structure and reaction conditions. The MOFs obtained through amino acid modulation exhibit an improved CO_2-capture capacity relative to nonfunctionalized materials.

Introduction

The metal–organic frameworks (MOFs) assembled from Zr_6–oxo cluster nodes and a polytopic carboxylate linker, pioneered by Lillerud and co-workers,[1] have emerged as promising porous materials for applications that range from gas storage and separation to catalysis and sensing. In addition to the chemical versatility offered by the organic linker, these Zr-based MOFs show a remarkable stability, partly attributed to the high degree of connectivity (i.e., up to 12 carboxylates/cluster) associated with the $\{Zr_6\}$ node.[1,2] Interestingly, the synthesis of such materials, exemplified by the UiO family[1] of MOFs, is commonly accomplished in the presence of a modulating agent, often a monocarboxylic acid (e.g., benzoic or formic acids).[3] It is likely that the modulator, used in excess, leads to a more controlled network growth through the initial formation of soluble monomeric $\{Zr_6(OH)_4(O)_4(RCOO)_{12}\}$ clusters, which then assemble through a slower dynamic exchange between the modulator and the linker units (Scheme 1). Indeed, the assembly of discrete isolated Zr_6–carboxylate clusters has been established as a valid route toward UiO-type MOFs.[4]

Thus, modulation is now commonly used to induce the higher levels of crystallinity and larger particle size often desired in several applications, including the possibility of a high-yield generation[3] of MOF particles of greater than 1 μm in size, which are desirable in chromatography and continuous flow chemistry. Acid modulation has also been key to achieving single crystals of Zr MOFs suitable for X-ray analysis, by aiding the rational design of new materials and their detailed structural characterization.[3,5] Despite these advances, the generation of X-ray-quality single crystals of Zr MOFs remains largely a trial-and-error enterprise. Interestingly, acid modulation in Zr-MOF synthesis has been recently shown to play a key role in the nature and quantity of the defects present in the Zr-MOF network. These defects, in turn, have come under an intense spotlight as potential sites for MOF functionalization,[3b,6] by complementing the covalent-linker modification approach.[7]

During the course of our own work on defect control and chemical modification in the UiO-family of MOFs, we reported that L-proline could be incorporated at missing-linker formate-capped defect sites by treating samples of UiO-67 (Scheme 2 A) with L-proline hydrochloride.[3b,8] This finding led us to ponder the possibility of obtaining Zr MOFs containing L-proline (or other amino acids) directly through modulation with the corresponding amino acid (Scheme 2 B). Independently and since 2015, Forgan and co-workers reported how they exploited the excellent modulating abilities of L-proline and studied the phenomenon of amino acid modulation.[9] It should also be mentioned that applications of L-proline in MOF design include the induction of supramolecular chirality in Zn-based MOF-5 crystals.[10]

Herein, we report our study on the effect of amino acids on the growth of Zr MOFs, including the exceptional modulating ability of L-proline. Through a series of optimization experiments, two protocols were identified for the use of a L-proline·HCl modulator in an exceptionally efficient generation of X-ray-quality single crystals. In addition, it was also found that amino acids can be incorporated at Zr-MOF defect sites, thus opening the door to new functional materials.

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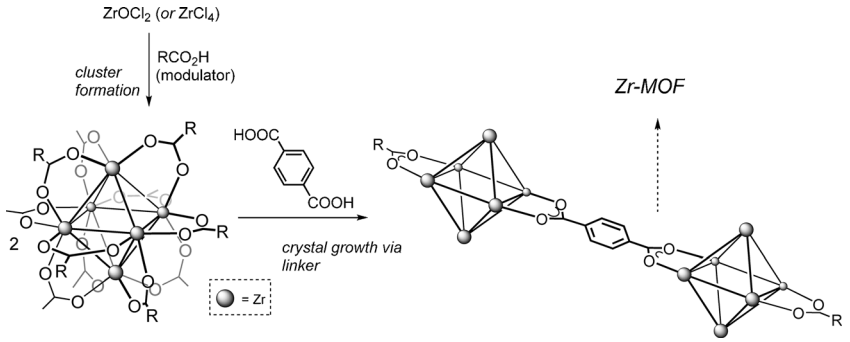
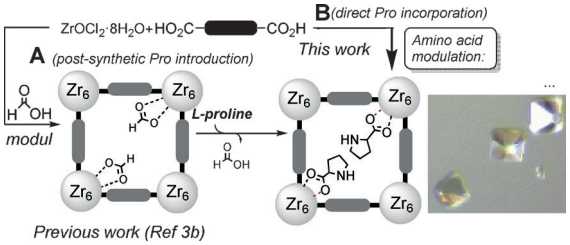
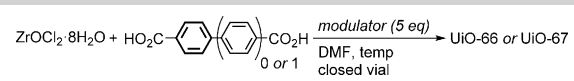


Scheme 1. The modulation phenomenon illustrated for the formation of the UiO-66 MOF.



Scheme 2. A) Anchoring of L-proline onto a Zr MOF.[3b] B) Amino acid-modulated MOF synthesis.

Table 1. Performance of three model amino acids as modulators (mod) for Zr-MOF synthesis.



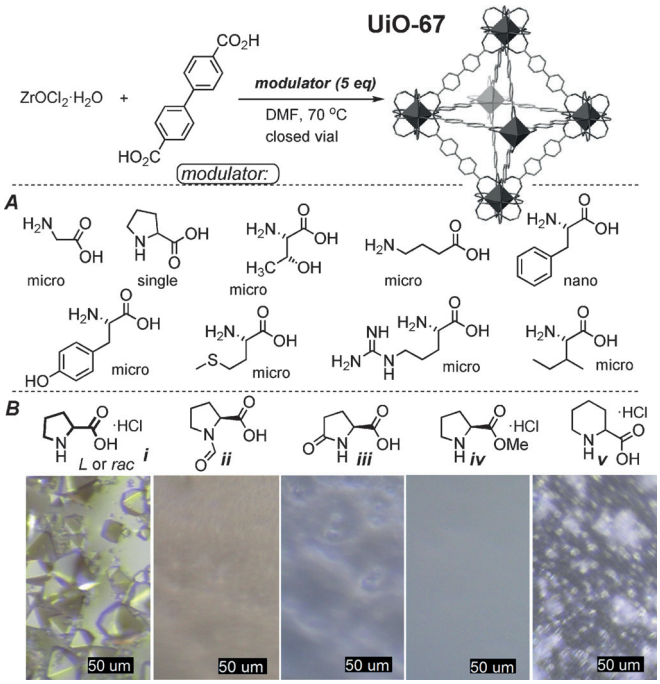
T [°C]	Amino acid	UiO-66 mod/L[a]	Range[b]	UiO-67 mod/L[a]	Range[b]
	L-Pro	0.5	micro[c]	0.12	micro[d]
120	Gly	1.0	micro	0.11	micro
	L-Phe	0.8	nano	0.14	nano
70	L-Pro	0.9	micro	<0.01	single

[a] Defined as amino acid/HO_2C-R-CO_2H (mmol/mmol). [b] Micro = 1–10 μm, nano = 40—300 nm. [c] Yield = 95%. [d] Yield = 90%.

Results and Discussion

For the modulated synthesis of MOFs, the solubility of the modulator acid in the reaction medium is likely a key factor for efficient growth of the 3D network. For several amino acids, including L-proline, the free-base form proved to be largely insoluble in DMF and showed a poor modulating ability in the preparation of Zr MOFs. Experimentally, the conversion of the amino acids into the corresponding hydrochloride salts proved crucial to ensure their solubility in DMF, thus enabling their use as modulators in the syntheses of Zr MOFs. Initial tests were conducted by exploring the growth of the isoreticular UiO-66 and UiO-67 pair in the presence of glycine (Gly), L-proline (L-Pro), and L-phenylalanine (L-Phe). Thus, a mixture of $ZrOCl_2 \cdot 8H_2O$ and the amino acid (5 equiv with respect to the linker) was dissolved in a mixture of DMF and aqueous HCl in a sealable vial; subsequently, a linker diacid (*para*-terephthalic or biphenyl dicarboxylic acid) was added to the reaction mixture and the vial was stored at 120 °C. Both UiO-66 and UiO-67 were readily obtained under these conditions, as determined by powder X-ray diffraction (PXRD), with particle sizes of less than 1 μm for L-phenylalanine and greater than 1 μm for glycine and L-proline (see Figures S1 and S2 in the Supporting Information). ^{1}H NMR spectroscopic analysis of the acid-digested samples (see the Supporting Information) showed a substantial and moderate level of amino acid incorporation into UiO-66 and UiO-67, respectively (Table 1). L-Proline was particularly efficient in this process, thus affording a high yield (≥90%) of the MOF in both cases. Importantly, the proline loading of 5 equivalents employed here was a fraction of the commonly used modulator amounts (≥30 equiv), in line with previous observations by Forgan and co-workers.[9] Nitrogen sorption on amino acid-modulated MOFs demonstrated the high porosity of the samples (see Figure S3 in the Supporting Information; BET surface area = 1270, 1220, and 1030 m^2g^{-1} for UiO-66Pro, UiO-66Gly, and UiO-66Phe, respectively), despite the high amino acid loading. This data is evidence that amino acids are not simply "stuck" inside the pores, but are likely present as a defect-capping structural elements. Moreover, the thermogravimetric analysis (TGA; see Figure S4 in the Supporting Information) shows a substantial linker deficiency in the studied samples. As a key observation, proline modulation at 70 °C, although much less efficient in terms of yield, led to the formation of X-ray-quality crystals of UiO-67 (Scheme 3A) on the walls of the reaction vial.

Intrigued by this ability to induce the growth of larger crystals at lower modulator loading, we tested a wider range of amino acids (Scheme 3A) as modulators of the formation of UiO-67 at 70 °C. This screen revealed that although several amino acids provide the desired MOF (see the results of the PXRD study; see Figure S5 in the Supporting Information), only proline (L- or *rac*-) appears to have the capacity to generate the material in a single-crystalline form. Thus, it would appear that the steric-/electronic-property balance in proline provides the right conditions for the slower growth of high-quality crystals. Additional experiments were carried out to pinpoint the structural parameters responsible for the unique modulation capacity of proline. The use of *N*-formylproline, detected during the proline-modulated Zr MOF synthesis (see below), did not yield single crystals (Scheme 3B, compare structures **1** and **2**). Similarly, very small particles were observed with py-



Scheme 3. A) Amino acid screen in the UiO-67 synthesis. B) Proline versus analogues in the modulated synthesis.

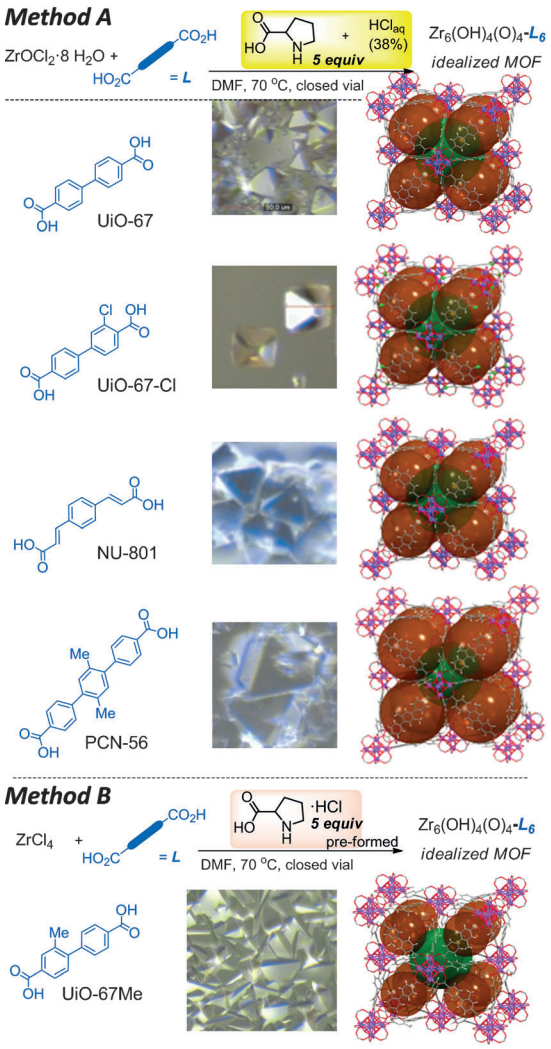


Figure 1. The ligand space explored in the present study for single-crystal growth under modulation with L-Pro (5 equiv).

roglutamic acid or proline methyl ester (Scheme 3B, structures **3** and **4**), thus indicating the participation of both the NH_2^+ and CO_2H moieties in the modulation phenomenon. The poorer MOF crystallinity registered with the next higher homologue of proline, namely, pipecolinic acid (Scheme 3B, structure **5**), was more surprising and suggests even more subtle conformational effects on modulating ability. On the other hand, switching from the hydrochloride to the trifluoroacetic acid salt of L-proline led to equally effective modulation (see Figure S6 in the Supporting Information).

As mentioned above, the generation of X-ray-quality crystals in Zr MOF is far from trivial, and proline modulation appears to constitute a promising "point of attack" in this endeavor. Thus, proline modulation was applied to a range of potential linker structures (Figure 1) under a set of conditions that involved the use of $ZrOCl_2{\cdot}8H_2O$ and the L-proline hydrochloride salt generated in situ (by using $HCl_{(aq)}$ in Method A; Figure 1). We were pleased to find that although MOF formation was observed in most cases tested, several of these MOFs were obtained as X-ray-quality single crystals (see Figure S7 in the Supporting Information). As a proof of concept and in addition to redetermination of the single-crystal structures of UiO-67 (reported recently, including by our group)[11,3b,5b,9e] and a methylated UiO-68 derivative (also known as PCN-56),[12] we prepared and determined the single-crystal structures of the previously unknown UiO-67Cl and NU-801 MOFs, synthesized from 1,4-benzenediacrylic acid (Figure 1, Method A). The structure of the latter had previously been determined by means of powder X-ray diffraction studies, and the new determination corroborates the previous findings.[2e]

Although a fivefold excess of L-proline was used to ensure optimal performance, single crystals could be achieved even with stoichiometric quantities of L-proline (see Table S3 in the Supporting Information), once again in sharp contrast to the classical protocols typically based on a large modulator excess ($\geq$30 equiv). However, dilution of the reaction mixture led to smaller particles when using 5 equivalents of L-proline (see Table S4 in the Supporting Information). For certain linkers, it was observed that conditions employed in Method A were still insufficient to provide crystals large enough for conventional structure determination. We speculated that minimizing the reaction water content (present through the zirconium(IV) hydrate source and also as a co-solvent for HCl) might further slow down the reaction, thus aiding the formation of larger crystals. Indeed, large single crystals of UiO-67Me and Zr–muconate were obtained by using the preformed isolated L-proline·HCl and anhydrous $ZrCl_4$, thus allowing for structure determination through single-crystal X-ray studies (see Method B in Figure 1 and Figure 2). In the context of the formation of a UiO-type network when using 2-methylbiphenylcarboxylic acid, it is interesting to mention the possibility of the alternative kinetically controlled ligand-deficient structure PCN-700 re-

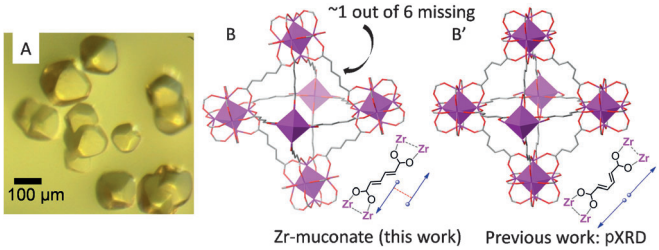
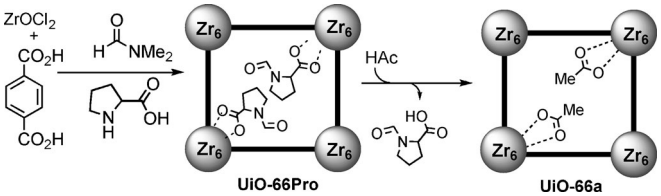


Figure 2. A) Crystal of Zr–muconate species obtained by using Method B and B) the single-crystal X-ray structure of this material. For comparison, the structure obtained by means of PXRD for the material synthesized from Zr_6–methacrylate[4] is shown as B′.

ported recently by Zhou and co-workers for a closely related 2,2′-dimethyl ligand.[13] As we see here (and as one might expect), it appears that the presence of just one 2-methyl substituent is insufficient to override the thermodynamic preference for a cubic UiO-67 structure.[13b] Interestingly, the muconate-derived framework presents a structure different from that previously determined from PXRD studies for the material synthesized by ligand exchange from preformed Zr_6–methacrylate clusters.[4] Although the reported structure featured the muconic acid in the s-*cis* conformation with a framework essentially identical (through disorder) to UiO-66 (Figure 2B′), the single-crystal structure of the material obtained here through proline modulation (Figure 2A, Method B) is constructed with linkers in the extended s-*trans* conformation. The loss of colinearity between the two RCO_2 coordination vectors is reflected in the lowering of the space-group symmetry to $Pn\bar{3}$, in a departure from from the $Fm\bar{3}m$ space group ubiquitous for this type of network. Specifically, the $\{Zr_6\}$ cluster now resides on a $\bar{3}$ site, which only imposes a crystallographic D_{3d} symmetry of a trigonal antiprism. The strut occupancy was refined to 0.82, which means that roughly 1 out of 6 muconate species is missing, in perfect agreement with the proline content obtained through ^{1}H NMR spectroscopic analysis of the acid-digested crystals (L-proline/ligand = 0.4:1; see Table S2 in the Supporting Information).

A second corollary of the use of amino acid modulators is the potential entry into amino acid-containing MOF structures. We found a roughly inverse correlation between amino acid incorporation and crystal size/quality (see Table 1 and Figure S2 in the Supporting Information). This outcome meant respectable levels (of up to 1:1 for L-Pro/ligand) of proline incorporation in the less-crystalline UiO-66, the Zr–muconate species synthesized at low temperature, and the batches of UiO-67 obtained at high temperature, thus opening a way to control the amino acid loading. The amino acid binding is assumed to be the normal carboxylate bidentate coordination, as seen in the crystal structure of the related discreet Zr_6–glycinate units.[14]

^{1}H NMR spectroscopic analysis of several acid-digested samples of UiO-66 and UiO-67 revealed that the amino acid is included as the *N*-formate form, presumably through reaction with DMF (see Figure 3, Scheme 4, and Figure S1 in the Supporting Information), a process that we determined for various



Scheme 4. UiO-66Pro formation with simultaneous L-proline formylation followed by substitution with acetate ions for defect-content confirmation.

amines to be assisted by the presence of a zirconium(IV) species. For example, heating a solution of benzylamine in DMF at 100 °C and in the presence of either UiO-66 or $ZrOCl_2{\cdot}8H_2O$ for 20 hours led to full conversion into *N*-formylbenzylamine.

The recent technique of quantitative defect capping exchange[3b] for a new anion was applied (Scheme 4) to confirm that the amino acid is chemically bound to the MOF (rather than being present as an insoluble amorphous admixture). Thus, a sample of UiO-66Pro, for which a ratio of proline/terephthalic acid of close to a 1:2 had been determined by NMR spectroscopic analysis, was immersed into a 4% AcOH solution in DMF for 20 hours and then thoroughly washed with DMF and acetone. PXRD studies of the resulting material showed retention of crystallinity (see Figure S12 in the Supporting Information) and nitrogen sorption demonstrated increased porosity (BET surface area = 1550 m^2g^{-1}; see Figure S13 in the Supporting Information) consistent with the substitution of formylprolinate with the lower FW acetate anion. Indeed, ^{1}H NMR spectroscopic analysis of the acid-digested resulting material showed a ratio of acetic acid/framework ligand of close to 1:2,

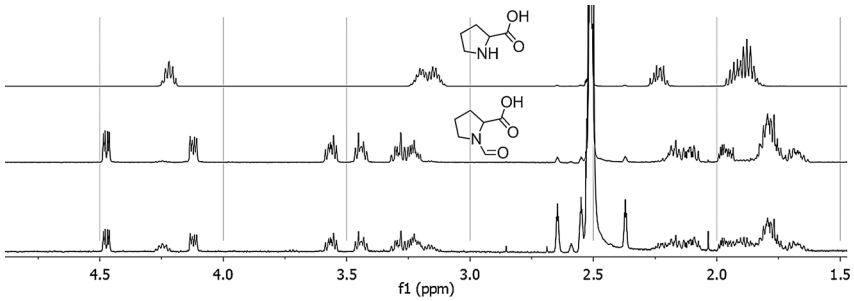


Figure 3. Fragment of the NMR spectra of proline (top), *N*-formylproline (middle), and proline-modulated UiO-66 (bottom).

thus demonstrating quantitative substitution of the modulator-capping defects with the new acid and lending further evidence for its position at the defect sites.

As a final note, we briefly tested the effect that the modulator would have on the carbon-capture capacity of the MOF (an aspect that has gained attention from the MOF community).[15] We employed samples of UiO-66 prepared on a multigram scale by using modulation with proline and benzoic acid. The former UiO-66Pro MOF (prepared at 120 °C) contained a ratio of *N*-formyl-L-proline/ligand of 0.5:1, whereas the latter UiO-66b MOF[3b] contained a ratio of benzoate/ligand of 0.8:1. Measurements showed (Figure 4) that even though UiO-66Pro

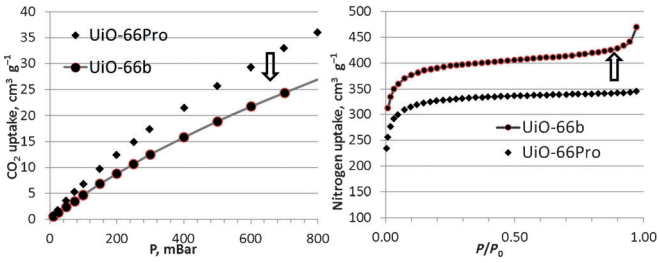


Figure 4. CO_2 sorption at 300 K (left) and nitrogen sorption at 77 K (right) for UiO-66Pro relative to UiO-66b.

is less porous than UiO-66b (BET surface area = 1270 and 1520 m^2g^{-1}, respectively), the CO_2 uptake of the latter MOF is 30% higher than the former MOF. We tentatively attribute this increase to a stronger interaction of CO_2 with the polar groups introduced through amino acid modulation. The CO_2-sorption capacity of UiO-66Pro is completely recovered after evacuation at room temperature.

The modulated growth of Zr MOFs was also tested in other solvents to suppress proline formylation. For environmental reasons, we are particularly interested in water, which was already demonstrated to work well for Zr-MOF syntheses.[16] We were pleased to find that water (and also DMSO; see Figures S15 and S16 in the Supporting Information) is compatible with amino acid modulation and provides highly crystalline UiO-66 grafted with non-formylated proline.

Conclusion

Amino acid modulation for Zr-MOF synthesis has been further developed as a straightforward way for functionality incorporation and particle-size control, complementing the work by Forgan et al. This method (especially with the use of proline) has provided Zr MOFs with increased particle size (from being micrometers in size to single crystals), which is important for applications in chromatography and flow chemistry and X-ray characterization. New Zr-MOF single-crystal structures were studied as a result. On the other hand, amino acid modulators can be incorporated into Zr MOFs at defect sites in ratios of the amino acid to the framework ligand of 0:1→1:1, as controlled by the ligand structure and reaction conditions. With the possibility of the installation of bigger biomolecules (i.e., peptides, etc.), straightforward opportunities are opened up for the design of new hybrid materials for separation and catalysis. Furthermore, our amino acid-modulated Zr MOFs demonstrated improved CO_2-capture capacity relative to nonfunctionalized materials.

Experimental Section

General experimental information and additional procedures are provided in the Supporting Information.

Method A for the amino acid-modulated Zr-MOF synthesis: Solid $ZrOCl_2{\cdot}8H_2O$ (485 mg, 1.51 mmol) and the amino acid modulator (7.53 mmol) were dissolved in a mixture of DMF (20 mL) and hydrochloric acid (37% 0.625 mL; for the conversion of the amino acid into a soluble salt) in a vial (the vial size was chosen in terms of total volume so that the vial was as full as possible) and the mixture was sonicated for 5 min. The dicarboxylic acid ligand (1.51 mmol) was added to the reaction mixture, which was further sonicated for an additional 5 min. The vial was sealed with a screw cap and was stored undisturbed in a temperature-controlled oven preheated to 120 or 70 °C, depending on the application requirements, such as yield/crystallinity/amino acid loading versus single crystals (Table 1) for 4 days. At this point, a part of the supernatant solution was decanted (the biggest single crystals formed on the walls of the reaction vessel), and the remaining resulting precipitate was separated by filtration or centrifugation (for nanocrystals) and washed with DMF (5×20 mL). For UiO-66Gly synthesis, DMF/water (3:2) was used for washing instead of DMF to remove the glycine byproducts. Each washing cycle consisted of the addition of DMF, stirring of the sample with a spatula to achieve a homogeneous suspension, allowing the mixture to repose for 30 min, and isolation of the precipitate. The same procedure was repeated with THF (5×20 mL). To remove the solvents from the pores (i.e., activation), the material was evacuated for 5 h at room temperature and then for 15 h at 120 °C at a ramp of 1 °C min^{-1}.

X-ray structure determination: The structures determined by X-ray diffraction studies during this study have been deposited in the Cambridge Structural database.[17]

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Keywords: amino acids · metal–organic frameworks · modulated synthesis · proline · zirconium

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[17] CCDC 1453411 – 1453416 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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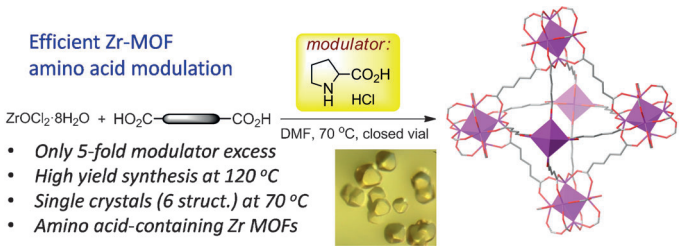

Controlled assembly: Zirconium metal–organic frameworks (Zr MOFs) are synthesized through amino acid modulation in a straightforward approach toward functional-group incorporation and particle-size control. This method provides a series of Zr MOFs with increased particle size and an improved CO_2-capture capacity relative to non-functionalized materials.

Porous Materials

O. V. Gutov, S. Molina, E. C. Escudero-Adán, A. Shafir**

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Modulation by Amino Acids: Toward Superior Control in the Synthesis of Zirconium Metal–Organic Frameworks