Supporting information for

Controlled biomimetic crystallization of ZIF-8 particles by amino acids

Kang Liang,* Raffaele Ricco, Cara M. Doherty, Mark J. Styles, and Paolo Falcaro*

To whom correspondence should be addressed.

E-mail: kang.liang@csiro.au, paolo.falcaro@csiro.au

Materials

20 natural amino acids (alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, and valine) and 2-methylimidazole (HmIm) were purchased from Sigma Aldrich (Australia). Zinc acetate dihydrate was obtained from Alfa Aesar (Australia). All other reactants were purchased from Sigma-Aldrich and used without further modification.

Methods

Biomimetic crystallization of ZIF-8 using amino acids. HmIm (263 mg) and glycine (20 mg) were combined and dissolved in deionised water (20 mL) in a glass beaker. To another glass beaker zinc acetate dihydrate (176 mg) was dissolved in deionised water (20 mL). The two solutions were then combined and the solution slowly turned cloudy. The reaction mixture was left at room temperature for 10 min. The products were centrifuged and washed in ethanol three times. Different amino acids were adjusted according to the same molar amount with glycine.

Characterisation techniques

Synchrotron XRD data were collected using the powder diffraction beamline at the Australian Synchrotron.[1] An X-ray beam energy of 16.82 keV ($\lambda = 0.736828$ Å) was selected, and diffraction patterns were collected between 5 to 85.5° 2θ using the high-resolution Mythen detector.[2] The diffraction patterns were acquired in pairs in order to eliminate the gaps between the modules of the Mythen detector. These diffraction pattern pairs were merged using the program CONVAS2[3] and analysed using the Rietveld method. An empirical model for the instrument was derived based on data collected from a sample of LaB_6 (NIST SRM 660b) mixed with diamond powder.

For the purposes of comparison with existing literature, all the XRD data presented here have been scaled to the wavelength of Cu Kα radiation ($\lambda = 1.54059$ Å).

Scanning electron microscopy (SEM) was used to investigate the particle morphology using a Philips XL30 Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive X-ray detector (EDS, Oxford Instruments).

ICP analyses were performed using a Varian ICP-OES spectrometer model 730-ES, operating in simultaneous wavelengths scanning. The ion concentrations were calculated from comparison with a suitable calibration curve.

^{1}H-NMR measurements were conducted on a Bruker BioSpin Avance^{III} NMR spectrometer operating at 500 MHz (11.7 T magnet), using D_2O as solvent; the decrease of the CH_3 integral at 2.2-2.3 ppm of HmIm was monitored against the unaffected CH_3 signal at 1.7-1.8 ppm of the acetate ion (internal standard), and used to calculate the amount of free 2-methylimidazole vs. time. The spectra were collected every 59 seconds, for a reaction time of 10 minutes for each experiment.

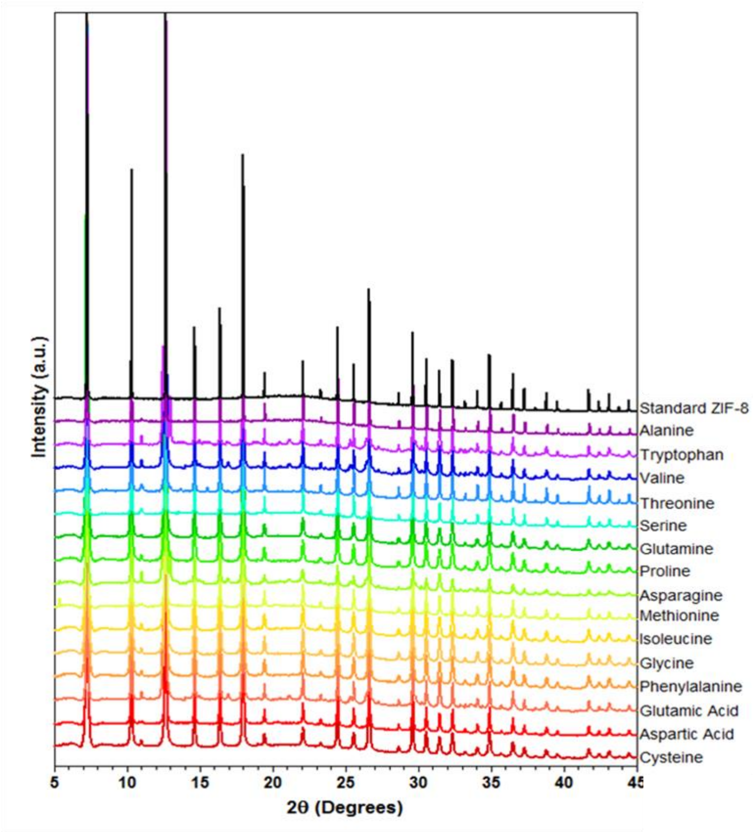

Figure S1. Synchrotron PXRD patterns of ZIF-8 synthesized using various amino acids.

Calculation of ZIF-8 particle number

Assuming the particles are spherical, volume of a spherical particle:

Eq. 4: $V_{NP} = \frac{4}{3}\pi r^3$

Volume of the total amount of ZIF-8:

Eq. 5: $V_{TOT} = \frac{mass}{density}$

Number of particles:

Eq. 6: $N_{NP} = \frac{V_{TOT}}{V_{NP}} = \frac{3*mass}{4*density*\pi*r^3}$

Table S1. NMR estimation of the amount of ZIF-8 produced using various amino acids (mg/ml reaction mixture).

Amino acid	Estimated amount of ZIF-8 (mg/mL) by NMR
Alanine	2.69
Methionine	3.47
Valine	4.01
Leucine	2.97
Isoleucine	3.52
Proline	4.17
Phenylalanine	2.52
Tryptophan	3.12
Tyrosine	n/a
Glycine	2.71
Serine	3.01
Cysteine	1.75
Threonine	1.88
Asparagine	2.48
Glutamine	2.79
Lysine	n/a
Arginine	n/a
Histidine	n/a
Aspartic acid	0.33
Glutamic acid	2.24

Table S2. ICP estimation of the amount of ZIF-8 produced using various amino acids (mg/ 40 ml reaction mixture).

Amino acid	Estimated total amount of ZIF-8 (mg/40 mL) by ICP
Alanine	67.53
Methionine	75.95
Valine	49.93
Leucine	74.87
Isoleucine	72.27
Proline	56.29
Phenylalanine	68.57
Tryptophan	62.95
Tyrosine	n/a

Glycine	68.07
Serine	69.20
Cysteine	36.22
Threonine	61.70
Asparagine	68.87
Glutamine	73.84
Lysine	n/a
Arginine	n/a
Histidine	n/a
Aspartic acid	33.20
Glutamic acid	46.29

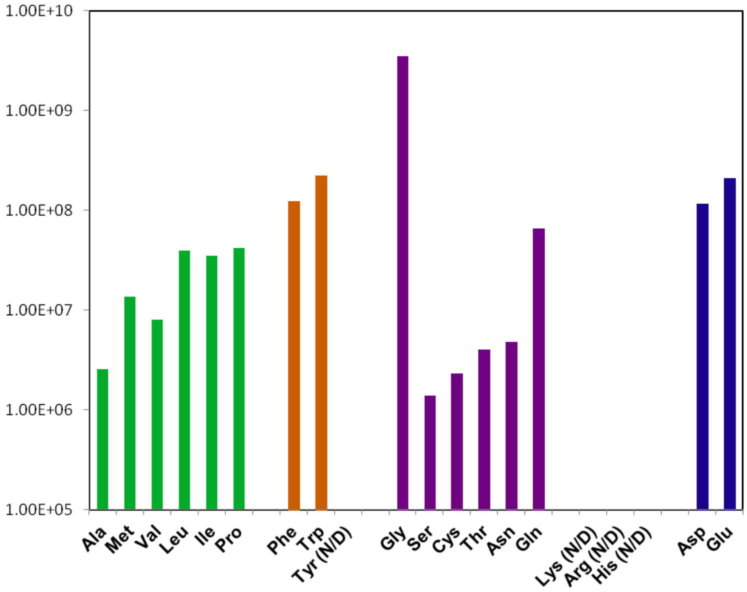

Figure S2. ICP estimation of the number of ZIF-8 particles per mL reaction mixture prepared using different natural amino acids.

References

1 K. S. Wallwork, B. J. Kennedy and D. Wang, in *AIP Conference Proceedings*, eds. J. Choi and S. Rah, Amer Inst Physics, Melville, 2007, vol. 879, pp. 879–882.

2 A. Bergamaschi, A. Cervellino, R. Dinapoli, F. Gozzo, B. Henrich, I. Johnson, P. Kraft, A. Mozzanica, B. Schmitt and X. Shi, *J. Synchrotron Radiat.*, 2010, **17**, 653–668.

3 M. R. Rowles, *Powder Diffr.*, 2010, **25**, 297–301.