Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information for:

Biomineral-inspired growth of metal-organic frameworks in gelatin hydrogel matrices

Ashesh Garai, William Shepherd, Jia Huo and Darren Bradshaw*

E-mail: *D.Bradshaw@soton.ac.uk*

Additional figures and characterisation date:

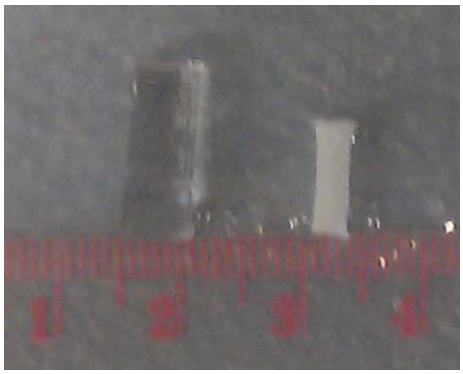

Figure S1. Digital photographs of a 5 wt% pure gelatin hydrogel pellet (left) and after soaking in EtOH (right). The shrinkage occurs due to partial gelatin insolubility in alcohol, and demonstrates that this does not occur due to the presence of ZIF-8.

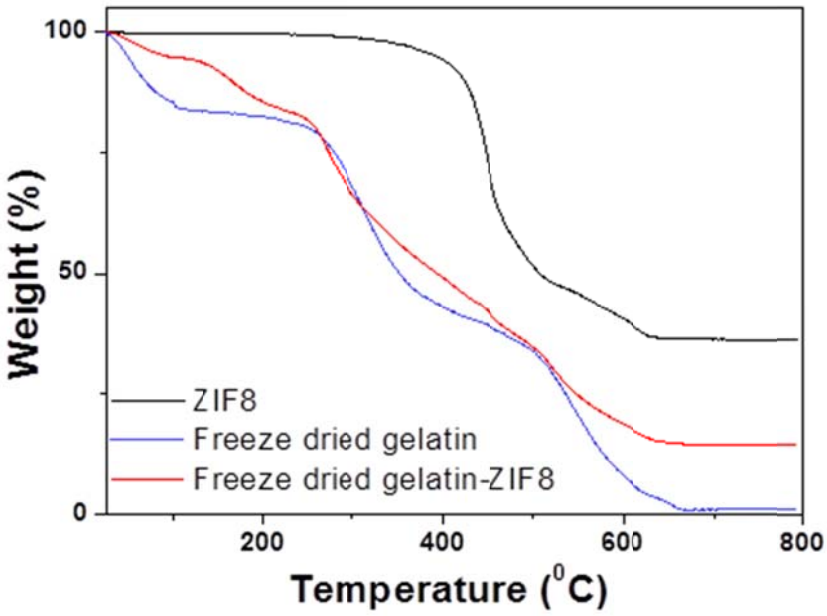

Figure S2. Thermogravimetric data of ZIF-8@gelatin composites compared to the individual components.

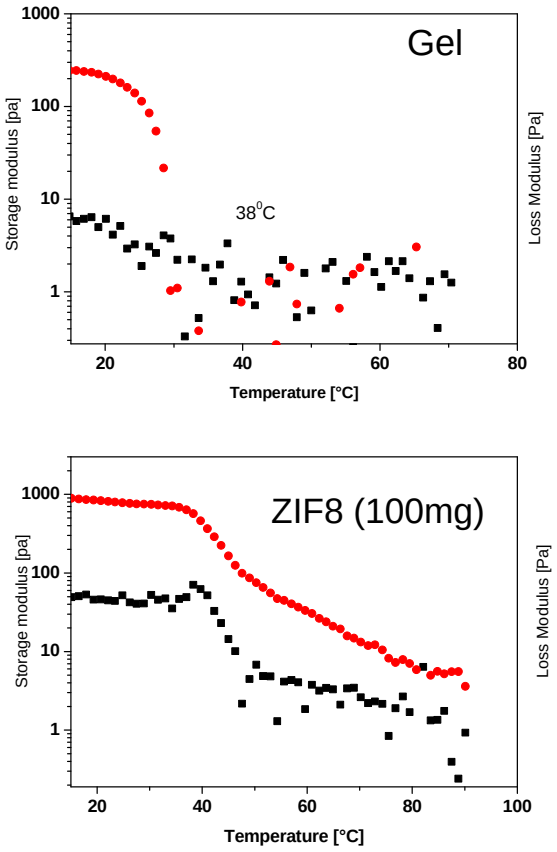

Figure S3. The oscillatory viscoelastic temperature ramp curve of pure 5 wt% gelatin gel and ZIF-8@gelatin composite (prepared from a starting amount of 100mg zinc nitrate hexahydrate) at a constant frequency of 1 Hz (red symbol– storage modulus, black symbol - loss modulus).

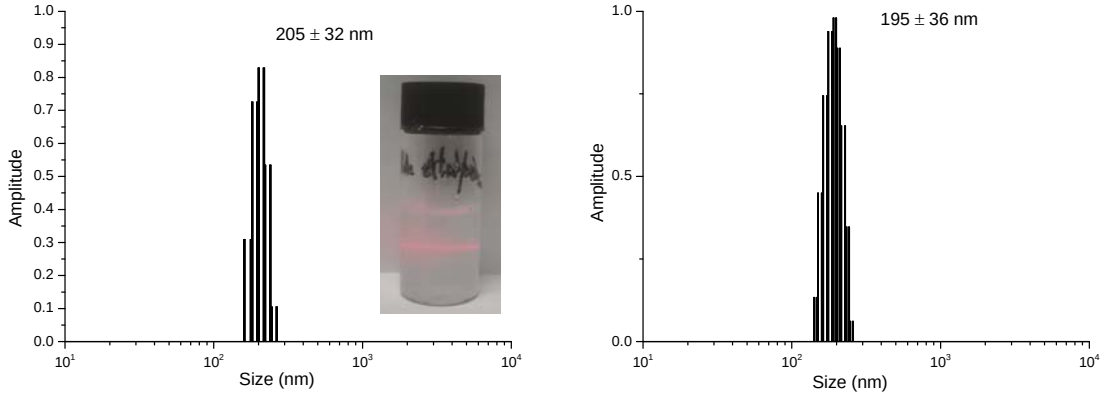

Figure S4. DLS data of a redispersed ZIF-8@gelatin composite after reaction for 24 hrs (left) and after standing for 2 months (right). The inset is a demonstration of the Tyndall effect by the (re)dispersed composite colloids.

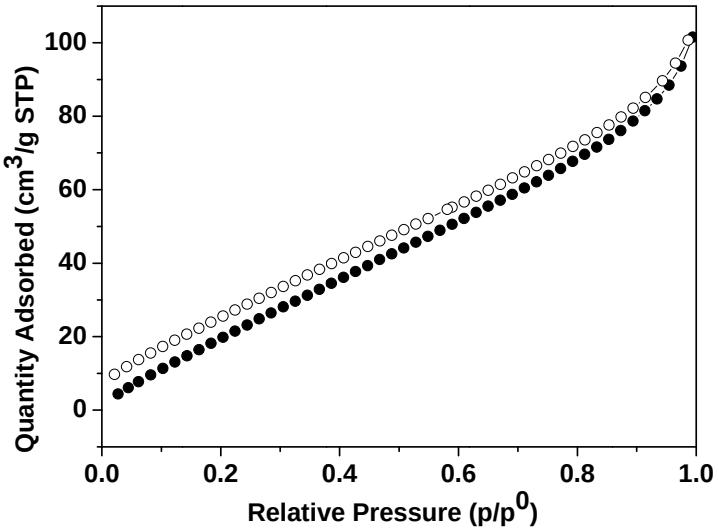

Figure S5. Nitrogen adsorption isotherm of ZIF-8@gelatin composite following redispersion and freeze-drying. The isotherm reveals no microporosity, consistent with the ZIF-8 particles being wholly embedded within the gelatin matrix.

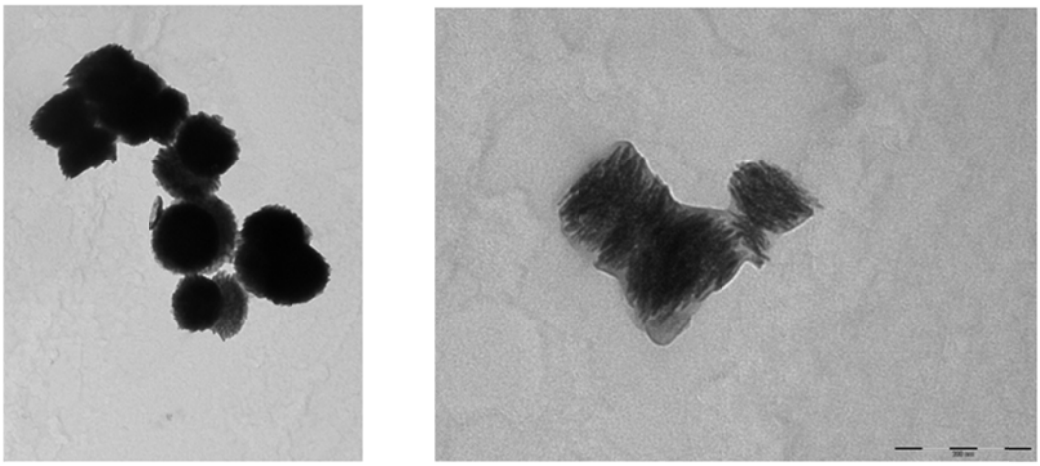

Figure S6. TEM images of ZIF-8@gelatin composites, prepared by pipetting 2-month old aqueous redispersions onto the grids.

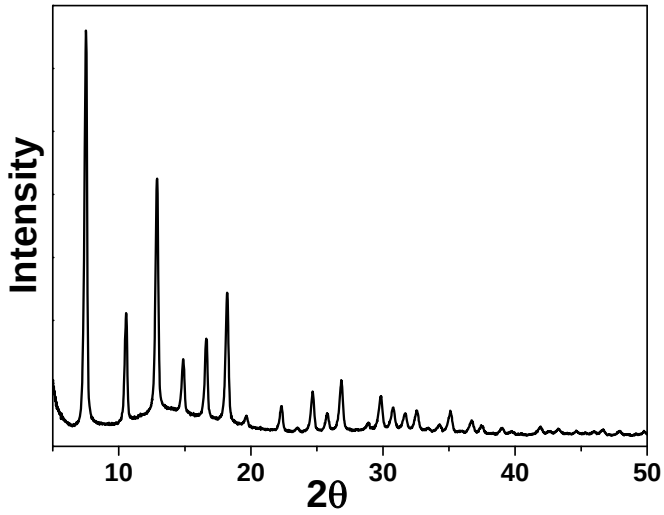

Figure S7. PXRD pattern of ZIF-8 recovered from ZIF-8@gelatin composites after removal of the biopolymer by repeated washing in hot water.

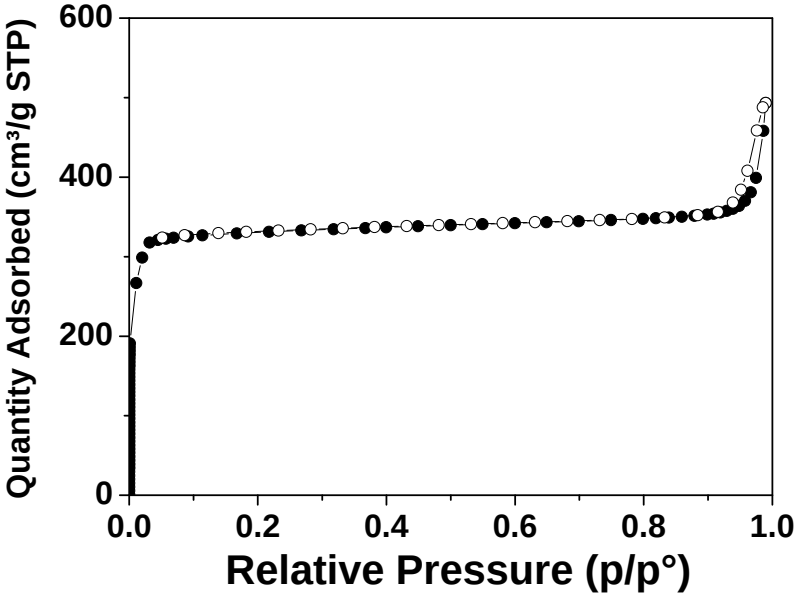

Figure S8. N_2 isotherm data for ZIF-8 recovered from ZIF-8@gelatin composites after removal of the biopolymer by repeated washing in hot water. The apparent BET surface area is 1350 m^2/g, and the upturn at high relative pressure is consistent with the small particle size previously observed by SEM.

Figure S9. Digital photographs of (a) Zn(II)@gelatin precursor pellets of varying Zn contents following soaking in ethanolic 2-MeIm solution for 24 hrs. b) Zn(II)@gelatin precursor pellets containing 40 mg of Zn following soaking in ethanolic 2-MeIm solution for varying periods of time.

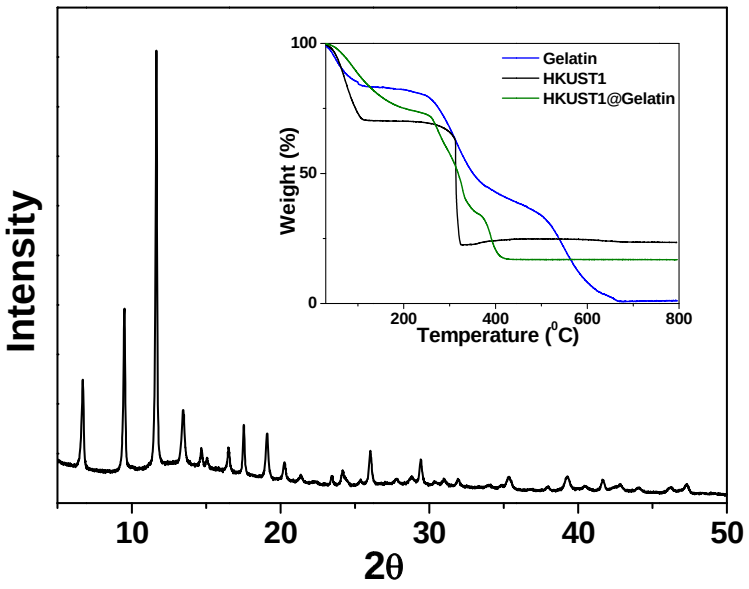

Figure S10. PXRD characterisation data of HKUST-1@gelatin composites; the inset shows TGA data and indicates a MOF content of 70% for the composite.

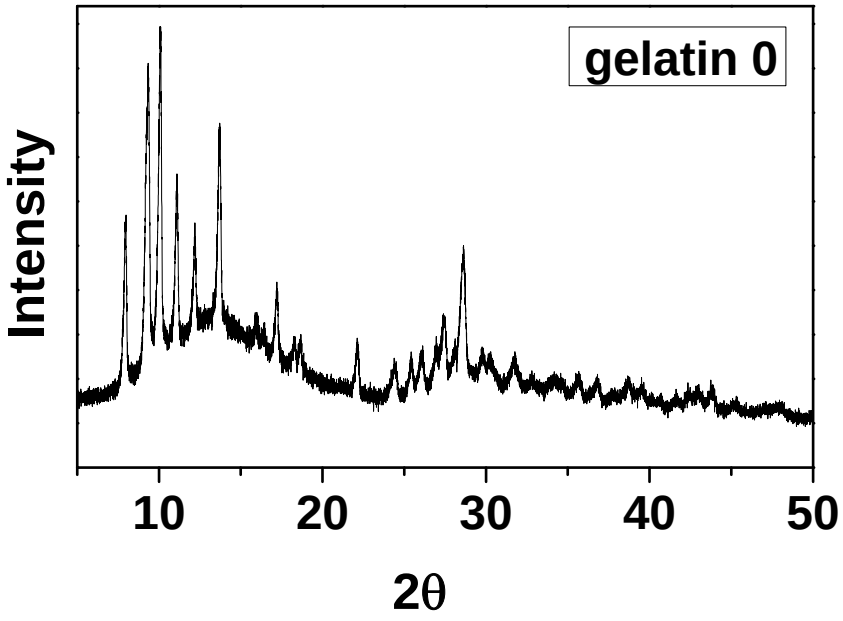

Figure S11. PXRD data of the product formed by the direct reaction between $Cu(OAc)_2$ and Na_3BTC in water in the absence of any gelatin. It is clear that no HKUST-1 formation has occurred, and the product is likely a mixture of the competing phases and other impurities.

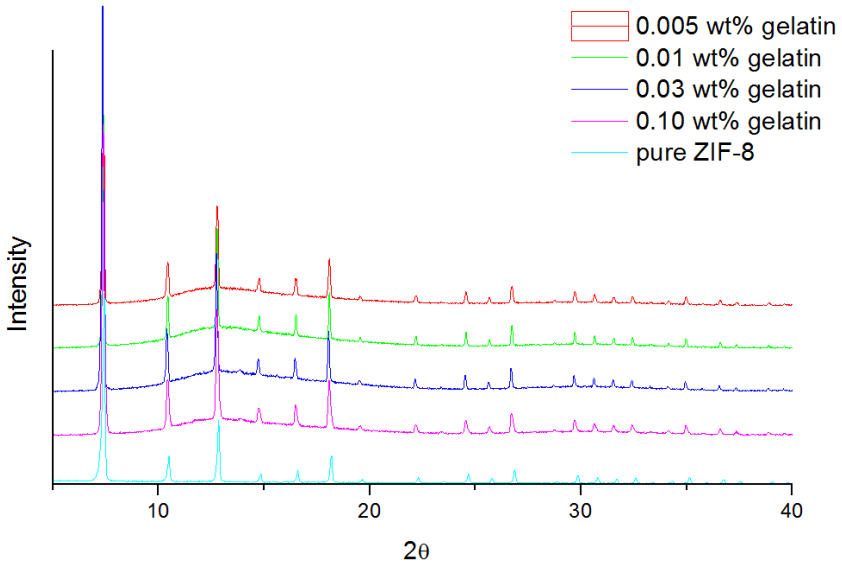

Figure S12. PXRD data of ZIF-8 prepared in the presence of small amounts of gelatin added as a soluble macromolecular additive. See also table S3.

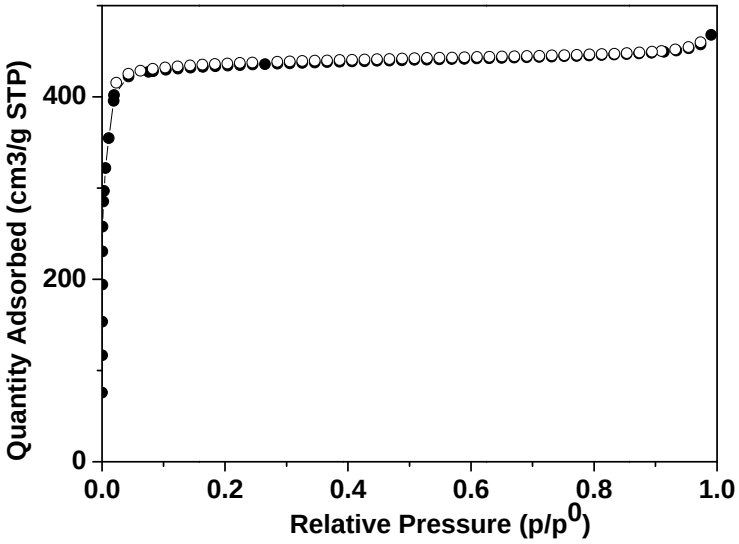

Figure S13. N_2 isotherm data for ZIF-8 crystals prepared in the presence of 0.1 wt% gelatin. The apparent BET surface area is 1281 m^2/g which is only slightly lower than previous reports for ZIF-8 nanoparticles.

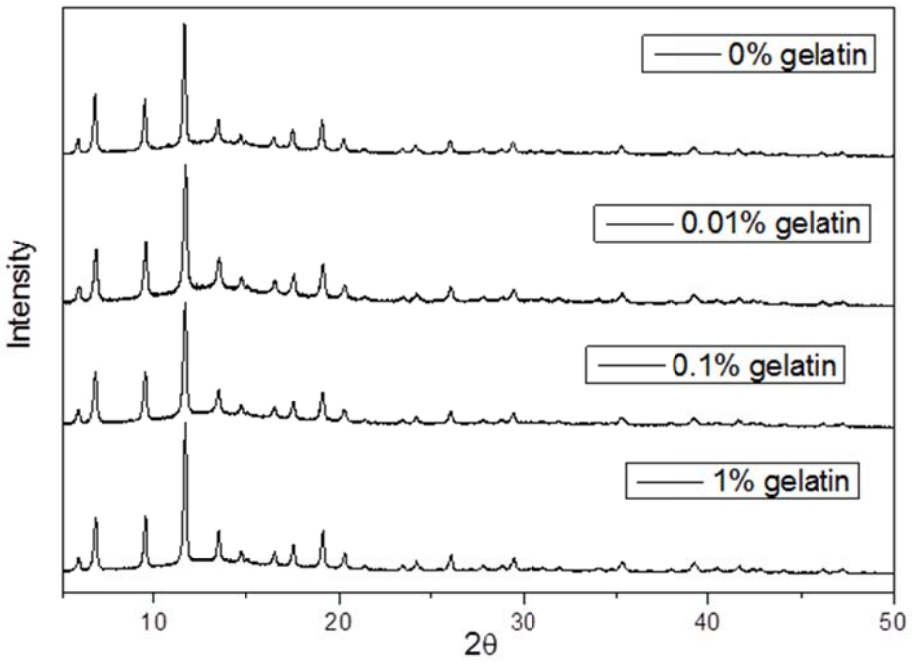

Figure S14. PXRD patterns of HKUST-1 prepared solvothermally at 120 °C in 50/50 EtOH/H_2O in the presence of gelatin as indicated.

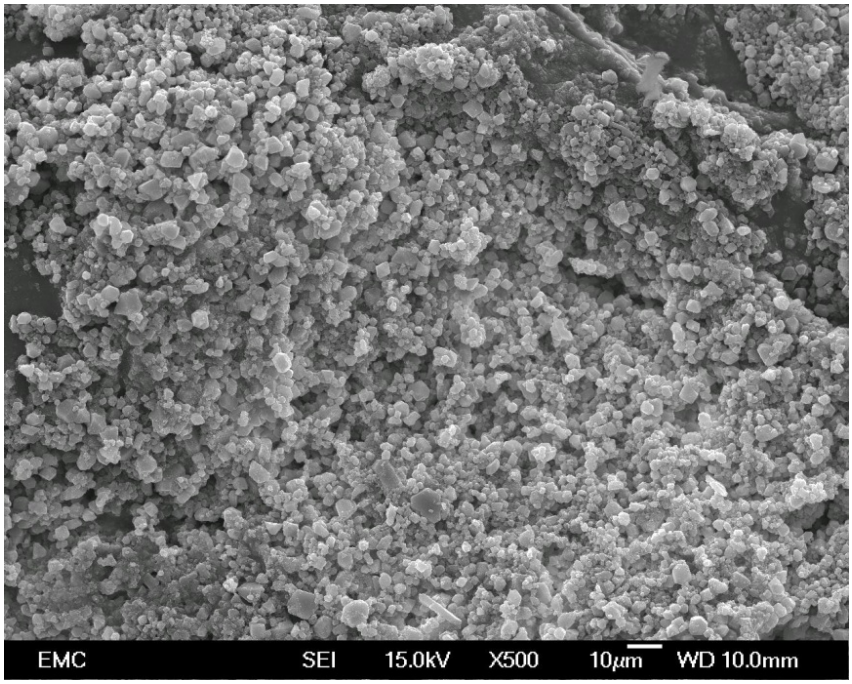

Figure S15. SEM image of HKUST-1 prepared solvothermally at 120 °C in 50/50 EtOH/H_2O in the presence of 0.1% gelatin, revealing a mesostructured aggregate of microparticles.

$mZnNO_3.6H_2O$ (mg)	m 2-MeIm (mg)	Particle size (nm)	Percent (%)
40	442	10.4	6.4
		103.88	73.9
		625.43	19.8
30	332	12.64	3.1
		129.65	51.1
		1621.69	45.9
20	221	0.18	0.9
		1.18	1.6
		11.47	9.5
		76.22	27.3
		204.62	45.2
		4063.63	15.5
10	111	2.52	0.4
		12.7	16.6
		47.55	27.7
		156.53	55.3
5	55	9.57	16
		30.54	25.2
		150.89	52
		1345.51	6.7

Table S1. DLS size distributions of redispersed ZIF-8@gelatin composite pellets prepared from precursor gels of varying Zn contents.

Soaking time (min)	Particle size (nm)	Percent (%)
10	6.65	9
	19.55	29.6
	95.44	40.9
	566.86	20.5
30	11.25	1.6
	104.2	15.4
	270.87	54
	4013	29
60	7.97	1.3
	42.02	5.1
	115.71	52.6
	1368.61	41
120	8.99	7.2
	68.66	36.6
	194.62	56.3
240	13.2	4.9
	104.02	74.6
	407.69	20.5
360	11.44	2.9
	99.06	38.2
	370.87	40.1
	3373.81	18.8
1440	10.4	6.4
	103.88	73.9
	625.43	19.8

Table S2. DLS size distributions of redispersed ZIF-8@gelatin composite pellets prepared from a 40 mg Zn@gelatin precursor gel and soaked in ethanolic 2-MeIm for various time periods.

Set no	Zinc nitrate (mg) in 1 ml water	2-methylmidazole (mg) in 7 ml water	Gelatin mg (%)	Particle size (average ± std) µm
Set 1	29	454	0	2.98 ± 1.49
Set 2	29	454	0.4 (0.005%)	2.15 ± 1.04
Set 3	29	454	0.8 (0.01%)	1.4 ± 0.3
Set 3	29	454	2.4 (0.03%)	1 ± 0.19
Set 4	29	454	8 (0.1%)	0.30 ± 0.09

Table S3. Synthesis conditions and particle size distributions determined from SEM images for ZIF-8 prepared in the presence of gelatin as a soluble additive.