Supplementary Information for "An EXAFS study of the Formation of a Nanoporous Metal-Organic Framework: Evidence for the Retention of Secondary Building Units During Synthesis" S. Surblé, F. Millange, C. Serre, G. Férey and R. I. Walton

All EXAFS spectra were modelled using the program EXCURV98 in which rapid curved wave theory[1] is used to calculate EXAFS spectra from a user inputted structural model. Phase shifts were calculated within EXCURV98 with exchange potentials calculated using the Hedin-Lunqvist model and ground state potentials calculated using the von Barth method. Shell occupation numbers were initially fixed at the expected crystallographic values, and Debye-Waller factors allowed to vary in least squares refinements (along with interatomic distances and the Fermi energy) to model the amplitude of the k^3-weighted EXAFS signal: these values are reprorted in Tables S1 and S2. This allowed interpretation of the data from the amorphous materials studied (see text) . In a further refinement cycle, shell occupation numbers were included in refinement, as reported in Table S3. In order to reduce the total number of refined parameters to a statistically valid value,[2] the total number of shells was reduced to three: this allowed the existence of the trimer iron cluser core to be tested. Note that for all reported parameters, errors quoted on refined interatomic distances are statistical and the true experimental errors on refined distances are ± 0.02 Å. For the Debye-Waller factor ($A = 2\sigma^2$), the true error on this parameter, which includes the effect of both thermal and static disorder , is ± 10%. Crystallographic interatomic distancse quoted are average values, and the values quoted for MIL-89 are taken from the structurally related MIL-88, which contains the same SBUs but linked by fumarate anions. The goodness of fit is reported as two values:

$$\mathrm{R\%} = \left(\int \left|\chi_i^{calc}(k) - \chi_i^{\exp}(k)\right| k^3 \mathrm{d}k \Big/ \int \left|\chi_i^{\exp}(k)\right| k^3 \mathrm{d}k\right) \times 100$$

$$\text{Fit-index} = = \sum_i \left(k^3\left(\chi_i{}^{calc}(k) - \chi_i^{\exp}(k)\right)\right)^2 .$$

1. S.J. Gurman, N. Binsted and I. Ross,. *J.Phys.C.* 1984, **17**, 143.

2. P.A. Lee, P.H. Citrin, P. Eisenberger and B.M. Kincaid, *Rev. Mod. Phys.*, 1981, **53**, 769.

Table S1: Refined EXAFS structural parameters from the crystalline materials Fe(III) acetate and MIL-89, with crystallographic values for comparison, and three of the amorphous materials isolated during the crystallisation.

Material	Shell	Shell Occupation Number	Average Interatomic Distance / Å	Debye-Waller Factor/ Å^2	R_{cryst} / Å	R% / Fit-index
Iron(III) acetate	O	6	2.007(3)	0.022(1)	1.911	17.89 / 0.00013
	C	4	3.010(10)	0.009(2)	2.996	
	Fe	2	3.232(21)	0.029(10)	3.279	
	O	4	3.308(16)	0.008(18)	3.340	
	O/C	8	4.487(14)	0.023(4)	4.317 (4C) / 4.500 (4O)	
MIL-89	O	6	2.002(3)	0.016(1)	1.949	21.58 / 0.00022
	C	5	3.001(20)	0.033(9)	2.952	
	O	2	3.219(19)	0.001(4)	3.182	
	Fe	2	3.358(25)	0.013(5)	3.340	
	O	2	3.549(67)	0.010(14)	3.468	
1 hr amorphous	O	6	2.004(3)	0.018(1)		20.71 / 0.00021
	C	5	3.009(22)	0.040(10)		
	O	2	3.224(21)	0.001(3)		
	Fe	2	3.358(23)	0.014(6)		
	O	2	3.560(51)	0.008(9)		
2 hr amorphous	O	6	2.006(4)	0.012(1)		25.36 / 0.00028
	C	5	3.010(23)	0.035(9)		
	O	2	3.202(20)	0.000(4)		
	Fe	2	3.356(21)	0.010(5)		
	O	2	3.527(41)	0.003(6)		
3 hr amorphous	O	6	2.005(5)	0.021(1)		25.99 / 0.00032
	C	5	3.010(28)	0.041(14)		
	O	2	3.219(40)	0.001(10)		
	Fe	2	3.378(58)	0.015(15)		
	O	2	3.556(90)	0.006(22)		

Table S2: Refined EXAFS structural parameters from a solution of Fe(III) acetate in methanol and the reaction solution used to prepare MIL-89. See footnotes on Table S1 for explanation of these parameters.

Material	Shell	Shell Occupation Number[a]	Average Interatomic Distance / Å[b]	Debye-Waller Factor / Å^{2}[c]	R% / Fit-index[e]
Iron(III)	O	6	2.013(3)	0.018(1)	20.47 / 0.00017
acetate trimer	C	4	2.996(10)	0.010(2)	
in methanol	Fe	2	3.246(41)	0.028(3)	
	O	4	3.290(22)	0.013(3)	
	O/C	8	4.510(18)	0.023(6)	
Reaction	O	6	2.052(7)	0.019(1)	38.68 / 0.00078
solution	C	4	3.031(38)	0.012(13)	
	Fe	2	3.220(57)	0.021(24)	
	O	4	3.326(48)	0.004(5)	
	O/C	8	4.559(43)	0.024(13)	

Table S3: Refined EXAFS structural parameters from the crystalline materials Fe(III) acetate and MIL-89, with crystallographic values for comparison, three of the amorphous materials and the solutions studied. In this case shell occupation numbers were included in the refinement, with the number of refined shells reduced to three to lower the total number of refined parameters.

Material	Shell	Shell Occupation Number	Average Interatomic Distance / Å	Debye-Waller Factor/ Å^2	R_{cryst} / Å	R% / Fit-index
Iron(III) acetate	O	5.2(2)	2.000(3)	0.018(1)	1.911	20.04/0.00018
	C	1.5(5)	2.998(14)	0.004(5)	2.996	
	Fe	1.4(4)	3.321(6)	0.011(3)	3.279	
MIL-89	O	5.6(2)	2.001(3)	0.015(1)	1.949	21.54/0.00021
	C	1.5(6)	2.963(16)	0.004(6)	2.952	
	Fe	2.2(6)	3.316(7)	0.017(4)	3.340	
1 hr amorphous	O	5.6(2)	2.004(3)	0.017(1)		19.89/0.00018
	C	1.4(5)	2.971(16)	0.005(5)		
	Fe	2.2(5)	3.311(6)	0.016(3)		
2 hr amorphous	O	5.5(2)	2.006(4)	0.017(1)		23.41/0.00025
	C	1.2(5)	2.957(17)	0.003(6)		
	Fe	1.9(6)	3.314(7)	0.016(4)		
3 hr amorphous	O	5.6(3)	2.002(4)	0.020(2)		29.74/0.00035
	C	1.7(7)	2.973(19)	0.008(6)		
	Fe	2.9(1.2)	3.316(11)	0.027(8)		
Iron(III) acetate in methanol	O	5.0(2)	2.008(3)	0.014(1)		21.91/0.00019
	C	2.3(6)	2.988(12)	0.007(4)		
	Fe	2.2(7)	3.322(8)	0.021(5)		
Reaction Solution	O	4.6(5)	2.046(9)	0.014(3)		46.87/0.0010
	C	0.3(1.4)	3.024(229)	0.006(73)		
	Fe	0.9(7)	3.331(16)	0.007(8)		