Supporting Information

Empirical modeling of material composition and size in MOFs prepared with ligand mixtures

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Contents

S1. General conditions

Starting materials, if commercially available, were purchased and used as such. *N,N*-dimethylformamide (DMF), was distilled before using. All reagent solutions were filtered through a 0.45 µm PTFE 25mm Syringe Filter. IR spectra were recorded using FT-IR ATR. Microscopic images were taken using Stereoscopic Microscope LEICA M165 FC. DRX powder spectra were performed on a BRUKER AXS D5005 powder diffractometer (Cu radiation, 40 kV, 30 mA, 0.05 steps, 6 s). ^{1}H magnetic resonance (NMR) spectra were recorded at 300 MHz. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual deuterated dimethyl sulfoxide. All calculations were carried out with the Gaussian 09 suite of programs.[1] Initially, density functional theory[2] calculations (DFT) have carried out using the B3LYP[3] exchange-correlation functionals, together with the standard 6-31G** basis set, in gas phase.[4] Subsequently, since the reactions are carried out in polar solvents, the inclusion of solvent effects have been considered by using a relatively simple self-consistent reaction field (SCRF) method,[5] based on the polarizable continuum model (PCM) of Tomasi's group.[6] Geometries have been fully optimized with PCM. As solvent we have used N,N-dimethylformamide.

S2. Detailed synthesis conditions

All the MOF synthesis were performed at 80ºC during 72h at atmospheric pressure. Mother solutions of **1**, **2** and **$Zn(NO_3)_2{\cdot}6H_2O$** were prepared. **1**, **2** and **$Zn(NO_3)_2{\cdot}6H_2O$** were dissolved in the total amount of DMF needed for a 2 mL/vial. The proportion L:Zn was always constant at 78,3:100 µmol

Table S1. Conditions for all the MOF crystals synthesis.

Vial	Percentage (%)		Amount (µmol)			Volume of DMF solution (mL)		
	1	**2**	**1**	**2**	**Zn^{2+}**	**1**	**2**	**Zn^{2+}**
1	100	0	78,3	0	100	1	0	1
2	90	10	70,5	7,8	100	0,9	0,1	1
3	80	20	62,7	15,7	100	0,8	0,2	1
4	70	30	54,8	23,5	100	0,7	0,3	1
5	60	40	47,0	31,3	100	0,6	0,4	1
6	50	50	39,2	39,2	100	0,5	0,5	1
7	40	60	31,3	47,0	100	0,4	0,6	1
8	30	70	23,5	54,8	100	0,3	0,7	1
9	20	80	15,7	62,7	100	0,2	0,8	1
10	10	90	7,8	70,5	100	0,1	0,9	1
11	0	100	0	78,3	100	0	1	1
TOTAL			430,8	430,8	1100	5,5	5,5	11
10 replays			4308	4308	11000	55	55	110

Stock solutions of **1** and **2** (861.6 µmol) in freshly distilled DMF (11 mL) and 2200 µmol of **$Zn(NO_3)_2{\cdot}6H_2O$** in 22 mL of freshly distilled DMF were prepared. Then, then volume established in each vial was taken, containing the exactly amount required for each one keeping global volume at 2 mL.

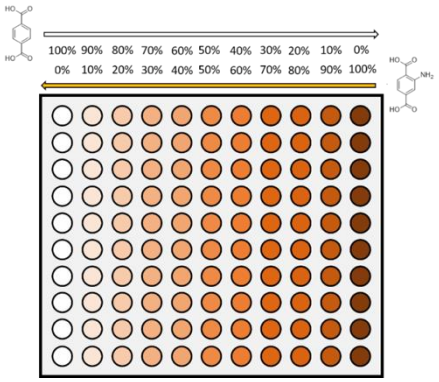


Figure S1. Representation of the methodology to synthesize all the MOF crystals.

Table S2. Yields for the corresponding materials (%), 3 independent experiences (of a pool of 5 samples), average yield and standard deviation. Samples were exchanged 3xDMF and then 3x$CHCl_3$ prior to activation under vacuum at 120 ^oC.

Material	Test 1	Test 2	Test 3	Average	SD
MOF-5	55,8	74,0	70,0	66,4	10,0
10%	53,6	79,6	78,6	70,4	15,1
20%	57,6	82,1	84,0	74,4	15,1
30%	62,4	78,6	76,7	72,4	9,1
40%	56,8	77,2	69,4	67,5	10,7
50%	54,4	66,1	63,1	61,1	6,3
60%	53,5	63,7	59,9	58,9	5,4
70%	51,8	57,6	57,6	55,4	3,8
80%	51,6	54,4	51,6	52,3	1,8
90%	48,9	58,9	57,0	54,6	5,8
IRMOF-3	48,8	53,8	47,2	49,3	3,9

S3. ^{1}H-NMR of digested MOFs

8 mg of activated MOF (employed for yield measurements) were digested and dissolved with sonication in 1 mL of 4% NaOD/D_2O solution. The digestion solution was used directly for ^{1}H-NMR.

Table S3. Content of amino terephtalic acid (**2**) for the corresponding materials (%), 3 independent experiences, average yield and standard deviation.

Material	Test 1	Test 2	Test 3	Average	SD
MOF-5	0	0	0	0,00	0,00
10%	7	7	5	6,33	1,15
20%	21	13	12	15,33	4,93
30%	29	22	20	23,67	4,73
40%	35	35	33	34,33	1,15
50%	42	40	36	39,33	3,06
60%	49	50	50	49,67	0,58
70%	58	60	63	60,33	2,52
80%	68	72	62	67,33	5,03
90%	82	85	84	83,67	1,53
IRMOF-3	100	100	100	100,00	0,00

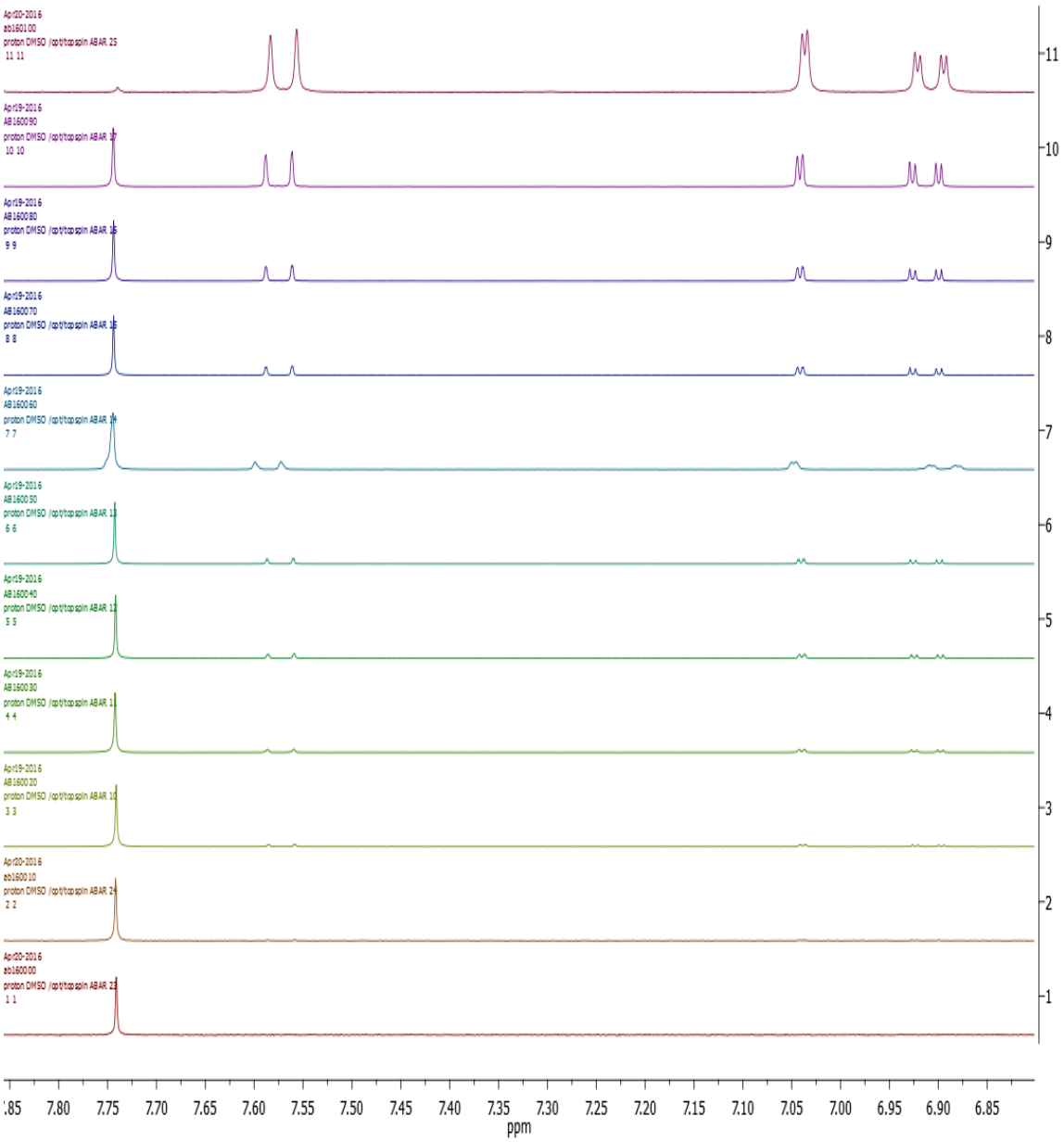


Figure S2. Representative ^{1}H-NMR spectra of dissolved crystals of each series.

S4. IR spectra of MOF crystals

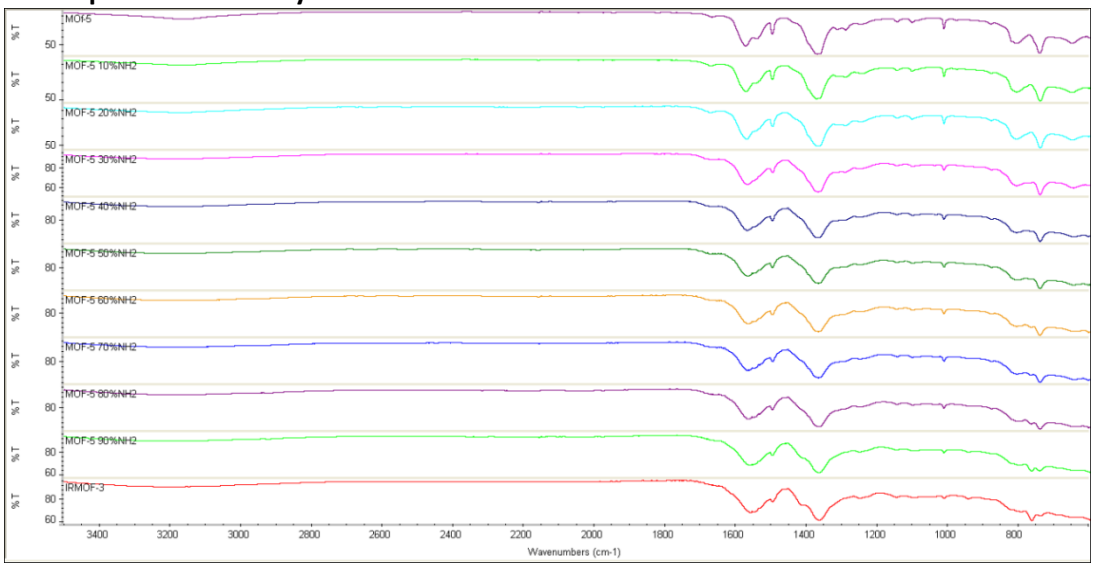


Figure S3. IR spectra of all MOF crystals

S5. Crystal's measurements (in mm)

	MOF-5	EXP 1	EXP 2	EXP 3		10%	EXP 1	EXP 2	EXP 3		20%	EXP 1	EXP 2	EXP 3
Average	**0,1078**	0,12	0,07	0,07	**Average**	**0,1091**	0,08	0,10	0,16	**Average**	**0,2816**	0,20	0,29	0,41
SD	**0,0258**	0,15	0,07	0,07	**SD**	**0,0286**	0,11	0,09	0,12	**SD**	**0,0959**	0,33	0,18	0,20
		0,13	0,08	0,11			0,07	0,11	0,13			0,35	0,29	0,33
		0,12	0,11	0,11			0,12	0,08	0,12			0,31	0,35	0,20
		0,09	0,12	0,09			0,15	0,11	0,08			0,33	0,22	0,29
		0,12	0,11	0,11			0,16	0,08	0,07			0,31	0,27	0,31
		0,10	0,08	0,13			0,12	0,11	0,07			0,33	0,31	0,24
		0,11	0,10	0,14			0,08	0,11	0,08			0,37	0,35	0,22
		0,09	0,11	0,08			0,10	0,11	0,10			0,10	0,18	0,18
		0,11	0,11	0,09			0,07	0,15	0,09			0,39	0,35	0,27
		0,07	0,11	0,07			0,11	0,13	0,12			0,31	0,10	0,18
		0,10	0,09	0,16			0,15	0,13	0,07			0,20	0,20	0,27
		0,07	0,12	0,14			0,16	0,12	0,14			0,37	0,27	0,22
		0,11	0,13	0,13			0,12	0,13	0,13			0,31	1,02	0,33
		0,11	0,16	0,16			0,11	0,11	0,08			0,29	0,29	0,33
		0,16	0,12	0,15			0,15	0,15	0,15			0,29	0,20	0,31
		0,07	0,13	0,07			0,08	0,11	0,11			0,37	0,22	0,22
		0,16	0,09	0,16			0,09	0,11	0,11			0,20	0,22	0,20
		0,11	0,11	0,12			0,08	0,15	0,10			0,18	0,31	0,12
		0,11	0,14	0,08			0,08	0,07	0,13			0,35	0,35	0,24
		0,10	0,08	0,11			0,16	0,19	0,11			0,43	0,20	0,29
		0,10	0,11	0,15			0,11	0,16	0,08			0,29	0,47	0,22
		0,08	0,11	0,09			0,09	0,07	0,12			0,27	0,33	0,20
		0,09	0,12	0,07			0,12	0,06	0,15			0,27	0,33	0,18

0,16	0,11	0,11
0,09	0,11	0,12
0,07	0,07	0,11
0,08	0,11	0,10
0,11	0,13	0,08
0,07	0,09	0,07
0,07	0,12	0,08
0,13	0,11	0,15
	0,13	0,12
	0,13	0,11
	0,11	0,10
	0,11	0,09
	0,09	
	0,13	
	0,09	
	0,12	
	0,12	
	0,16	
	0,07	
	0,10	

0,08	0,09	0,13
0,19	0,10	0,08
0,12	0,11	0,11
0,11	0,10	0,10
0,14	0,09	0,10
0,08	0,05	0,14
0,16	0,05	0,08
0,10	0,15	0,12
0,12	0,09	0,08
0,12	0,12	0,11
0,10	0,11	0,11
0,13	0,11	0,11
	0,11	0,11
	0,07	0,07
	0,05	0,10
	0,11	

0,31	0,31	0,22
0,20	0,37	0,20
0,18	0,27	0,27
0,29	0,31	0,29
0,31	0,24	0,27
0,29	0,31	0,22
0,43	0,24	0,20
0,31	0,29	0,31
0,31	0,35	0,31
0,35	0,31	0,29
0,27	0,24	0,35
0,39	0,20	0,18
0,31	0,16	0,20
0,31	0,41	0,27
0,27	0,27	0,27
0,27		0,29

	30%	**EXP 1**	**EXP 2**	**EXP 3**
Average	**0,4418**	0,45	0,29	0,41
SD	**0,1489**	0,57	0,18	0,20
		0,61	0,31	0,65
		0,65	0,37	0,57
		0,41	0,41	0,49
		0,57	0,45	0,61
		0,57	0,39	0,57
		0,45	0,20	0,61
		0,45	0,22	0,45
		0,57	0,29	0,53
		0,53	0,33	0,49
		0,61	0,51	0,57
		0,53	0,41	0,53
		0,41	0,51	0,49
		0,49	0,31	0,41
		0,41	0,20	0,41
		0,49	0,22	0,33
		0,57	0,24	0,41
		0,57	0,39	0,41
		0,41	0,45	0,37
		0,37	0,47	0,53

	40%	**EXP 1**	**EXP 2**	**EXP 3**
Average	**0,7432**	1,00	1,13	1,40
SD	**0,2708**	0,73	0,80	1,20
		0,87	0,67	1,00
		0,67	0,67	0,93
		0,93	1,20	0,67
		0,67	1,13	1,07
		0,80	0,53	1,20
		0,60	0,40	1,13
		1,00	0,60	1,00
		0,93	0,27	0,73
		0,87	0,47	0,47
		1,20	0,80	0,67
		0,80	0,73	0,73
		0,80	0,40	0,80
		1,33	0,60	0,73
		0,87	0,33	0,67
		0,80	0,40	1,20
		0,67	0,80	0,73
		1,00	0,73	0,80
		0,60	0,67	0,40
		0,93	1,00	0,80

	50%	**EXP 1**	**EXP 2**	**EXP 3**
Average	**1,2432**	1,48	2,00	0,97
SD	**0,3310**	1,16	0,97	1,55
		1,03	1,94	0,97
		1,16	1,35	1,29
		0,84	1,10	1,16
		0,71	1,42	1,29
		1,48	1,61	1,16
		1,29	1,35	0,52
		0,77	1,81	1,29
		0,90	1,10	1,29
		1,29	1,16	0,84
		1,10	1,29	0,90
		1,35	1,42	1,23
		1,03	1,68	1,87
		1,74	0,97	1,55
				1,10
				1,74
				1,03
				0,90
				0,77
				1,16

0,53	0,41	0,53		0,53	0,47	0,87				1,55
0,33	0,31	0,41		0,93	0,47	0,93				
0,49	0,33	0,37		1,07	0,33	0,80				
0,73	0,31	0,49		0,93	0,84	0,87				
0,45	0,29	0,61		0,67	0,60	1,07				
0,57	0,69	0,20		0,87	0,52	0,80				
0,53	0,48	0,61		0,93	0,68	1,07				
0,53	0,53	0,53		0,87	0,60	0,60				
0,57	0,71	0,41		0,33	0,44	1,20				
0,33	0,31	0,61		0,40	0,44	1,27				
0,57	0,20	0,82		0,40	0,40	0,67				
0,49	0,20	0,49		0,67	0,44	0,80				
0,53	0,22	0,82		0,33	0,40	0,87				
0,37	0,22	0,53		0,80	0,40	0,93				
0,53	0,24	0,57		0,93	0,52	0,73				
0,53	0,22	0,53		0,73	0,44	1,47				
0,41	0,41	0,61		0,53	0,36	1,13				
0,37	0,18	0,37		0,53	0,44	1,00				
0,57	0,20	0,33		0,27	0,44	1,33				
0,61	0,10	0,45		0,53	0,68	0,93				
0,49	0,20	0,45		0,73	0,48	0,80				
0,61	0,20	0,45		0,87	0,36	0,67				
0,69	0,24	0,41		0,47	0,32	0,93				
0,65	0,14	0,45		1,13	0,48	0,67				
0,41	0,16	0,41		0,40	0,52	0,67				
0,45	0,22	0,37		0,40	0,36	0,93				
0,61	0,22	0,33		0,93	0,36	1,20				
0,37		0,73		0,73	0,48	1,07				
0,65		0,53				0,80				
		0,57								

	60%	**EXP 1**	**EXP 2**	**EXP 3**		**70%**	**EXP 1**	**EXP 2**	**EXP 3**		**80%**	**EXP 1**	**EXP 2**	**EXP 3**
Average	**1,1707**	1,68	1,94	1,23	**Average**	**1,2353**	2,32	1,94	1,94	**Average**	**1,2057**	1,61	1,55	2,19
SD	**0,3473**	1,55	1,29	1,16	**SD**	**0,3800**	1,29	1,61	1,68	**SD**	**0,3604**	1,61	1,68	1,10
		1,42	1,81	1,03			1,68	1,68	1,16			1,55	1,29	1,16
		1,48	0,97	1,48			1,48	1,29	1,61			1,29	0,97	1,55
		1,55	1,29	0,97			1,61	1,29	1,61			1,42	1,10	1,48
		1,74	1,10	1,42			0,97	0,58	1,55			1,35	1,29	1,48
		1,55	1,35	1,87			0,90	1,16	1,48			1,23	1,16	1,23
		1,23	1,61	1,29			0,90	0,97	1,29			0,90	0,97	0,71
		1,29	1,29	1,35			1,35	0,84	1,94			0,97	0,90	0,52
		0,84	0,77	1,42			1,29	1,61	1,16			1,10	0,97	0,90
		0,77	1,16	1,55			1,10	1,61	1,29			0,77	1,23	1,81
		0,84	1,03	1,29			1,68	1,48	1,03			0,90	1,94	1,35

1,29	1,16	0,90		1,03	0,97	1,23		0,77	0,97	1,23
0,65	0,97	1,10		1,35	0,52	0,90		0,77	0,52	1,42
0,77	0,71	1,29		0,84	0,97	0,84		1,33	1,03	0,90
0,77	1,10	1,55		1,29	0,84	1,03		1,33	1,03	0,90
0,65	0,84	0,71		1,61	0,65	0,71		1,44	0,90	1,03
1,16	0,58	0,65		1,74	0,97	1,16				1,03
0,52		1,16		0,71	1,35	1,23				2,06
1,42		0,90		0,71	1,03	1,16				
		0,77		0,84	1,23	0,97				
		0,90		1,03		0,65				
		0,90				1,23				
		1,55				1,03				
						1,81				

	90%	EXP 1	EXP 2	EXP 3		IRMOF-3	EXP 1	EXP 2	EXP 3
Average	**1,1931**	1,42	1,29	1,29	**Average**	**1,3160**	1,42	1,42	1,61
SD	**0,3461**	1,35	1,29	1,29	**SD**	**0,2896**	1,16	1,55	1,23
		1,29	1,35	1,35			1,10	0,77	1,29
		0,90	1,29	1,29			1,10	1,35	1,35
		0,84	1,35	1,35			1,16	1,10	1,29
		1,23	1,23	1,23			1,03	1,29	1,16
		1,03	1,16	1,16			0,71	0,97	1,29
		0,84	1,03	1,03			1,03	1,03	1,35
		0,97	1,03	1,03			1,16	0,97	1,61
		0,90	1,23	1,23			1,16	2,10	2,00
		1,16	1,29	1,29			1,03	1,29	1,29
		0,97	0,97	0,97			1,29	1,42	1,35
		1,10	0,90	0,90			1,55	1,74	1,29
		0,97	1,03	1,03			1,61	1,61	1,03
		0,90	1,16	1,16			1,48	1,58	
		0,97	0,77	0,77			1,29	1,89	
		1,29	0,39	0,39					
		0,71	0,65	0,65					
		0,90	0,77	0,77					
		2,00	1,23	1,23					
		1,48	1,94	1,94					
		1,48	1,68	1,68					
		1,16	1,42	1,42					
		0,97	1,29	1,29					
			1,63	1,63					
			1,74	1,74					
			2,00	2,00					

S6. Experimental growth kinetics

Independent vials containing 100% of **1** and **2**, respectively, were put into the oven at 80ºC by 0, 16, 24, 36, 48, 60 and 72 hours. After these times, the remaining DMF was filtered (PTFE filter, 0.2 μm pore) and 0.5 ml of the filtered solution was added to 0.5 mL of HCl (1 M). The corresponding solution was analysed directly by ICP.

Table S4. Content of Zn(II) (ppm), 3 independent experiences, average yield and standard deviation.

	sample 1	sample 2	sample 3	Average	SD
MOF 5 16	3678.0	3731.0	3685.0	3698.0	28.8
MOF 5 24	3311.0	3288.0	3264.0	3287.7	23.5
MOF 5 40	2814.0	2740.0	2857.0	2803.7	59.2
MOF 5 48	2645.0	2799.0	2771.0	2738.3	82.0
MOF 5 72	2651.0	2775.0	2605.0	2677.0	87.9

	sample 1	sample 2	sample 3	Average	SD
MOF 3 16	3664.0	3684.0	3777.0	3708.3	60.3
MOF 3 24	3739.0	3708.0	3643.0	3696.7	49.0
MOF 3 40	2713.0	2890.0	2750.0	2784.3	93.4
MOF 3 48	2717.0	2796.0	2856.0	2789.7	69.7
MOF 3 72	2757.0	2673.0	2610.0	2680.0	73.7

S7. Microscopic images of MOF crystals

Highlighted images of MOF crystals (percentage of **2** is indicated).

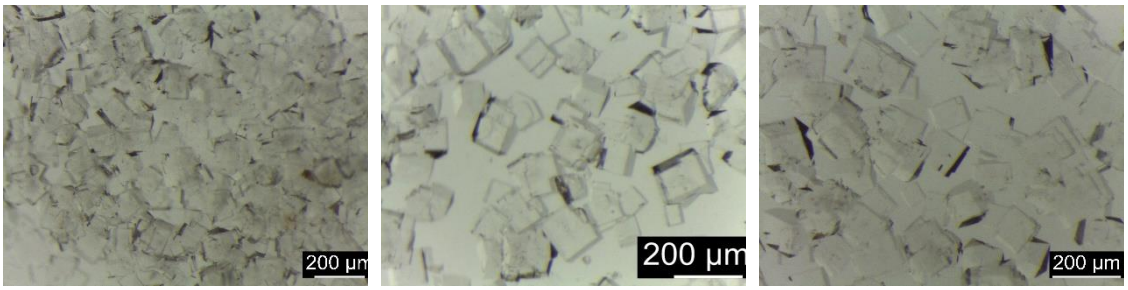


Figure S4: 0% (MOF-5)

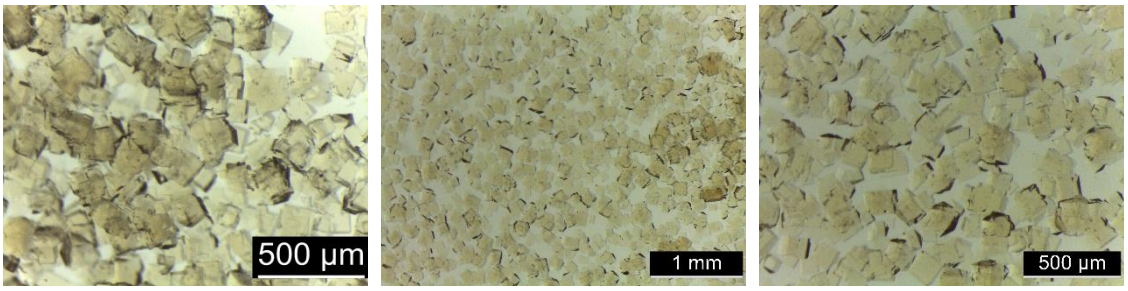


Figure S5: 10%

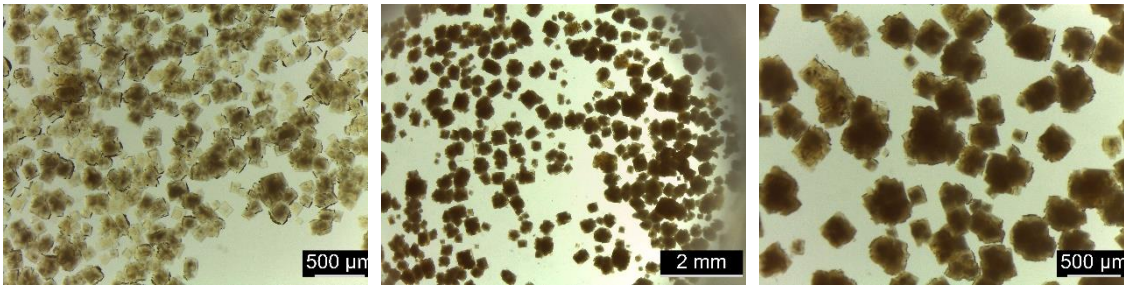


Figure S6: 20%

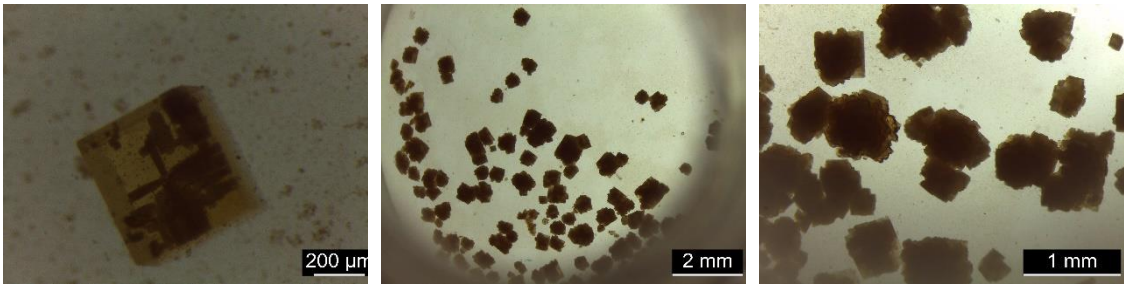


Figure S7: 30%

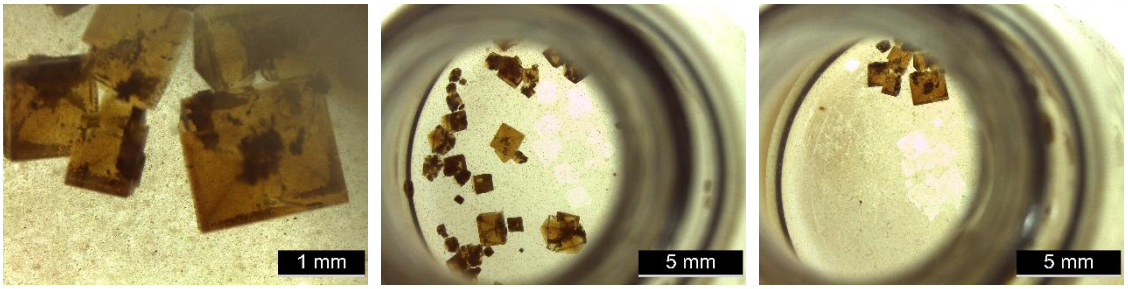


Figure S8: 40%

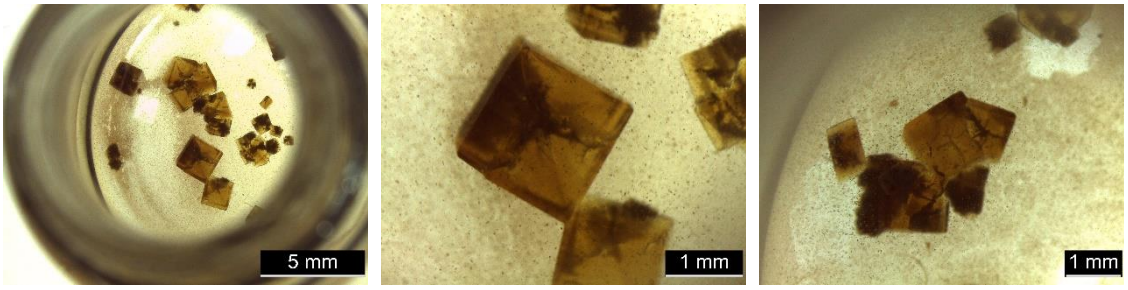


Figure S9: 50%

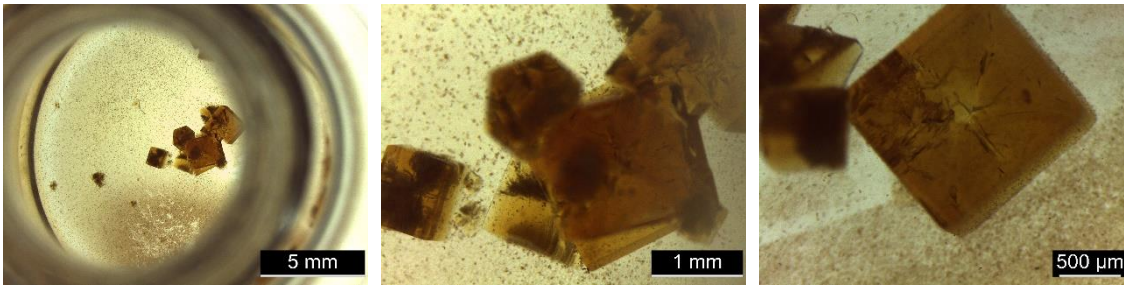


Figure S10: 60%

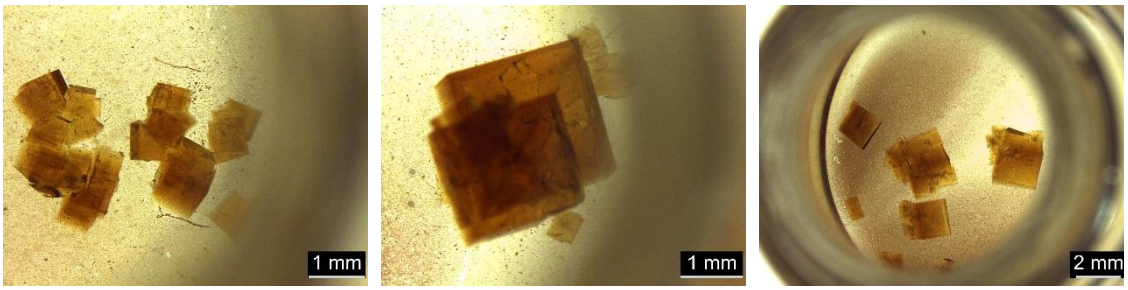


Figure S11: 70%

Figure S12: 80%

Figure S13: 90%

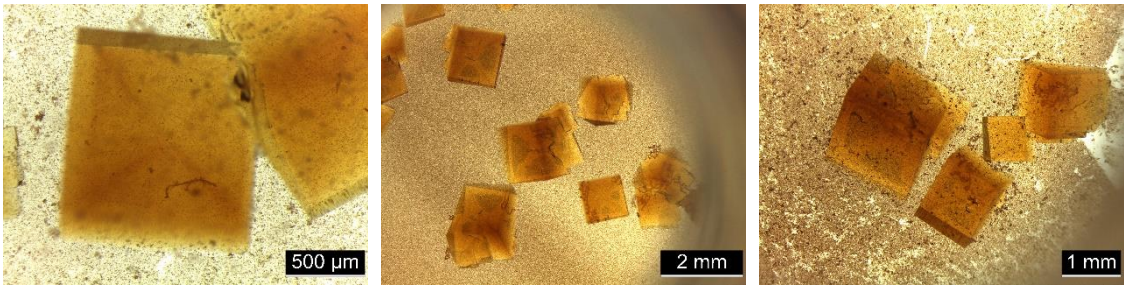


Figure S14: 100% (IRMOF-3)

S8. PXRD

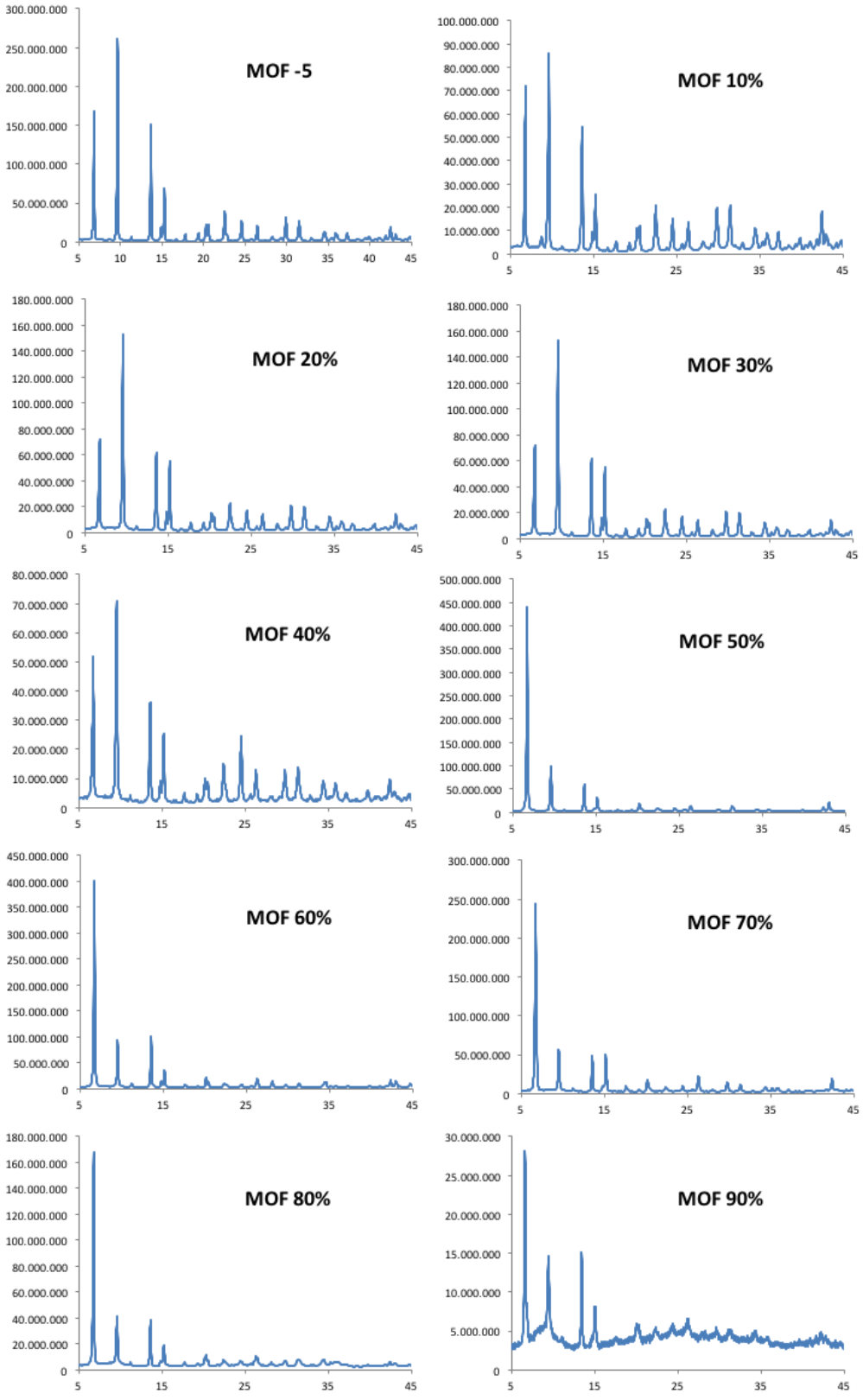


Figure S15: PXRD from MOF-5 until MOF 90% of ligand **2** sample

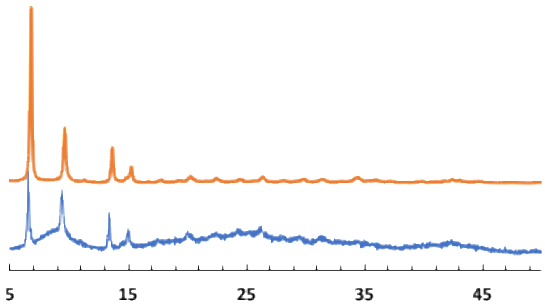


Figure S16: PXRD of IRMOF-3 Obtained under reported condtions (big crystlas, blue line) and 10 fold synthesis (orange).

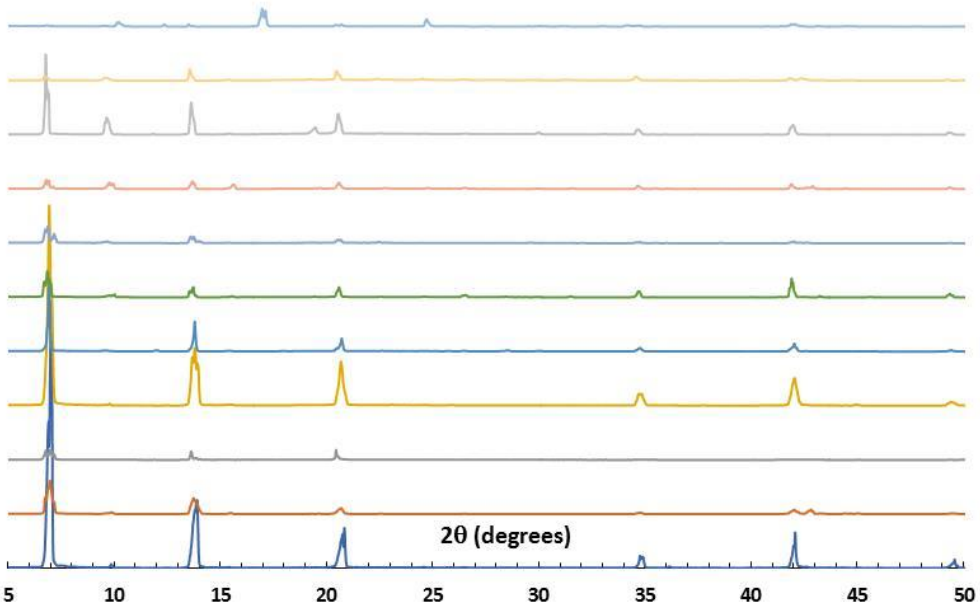
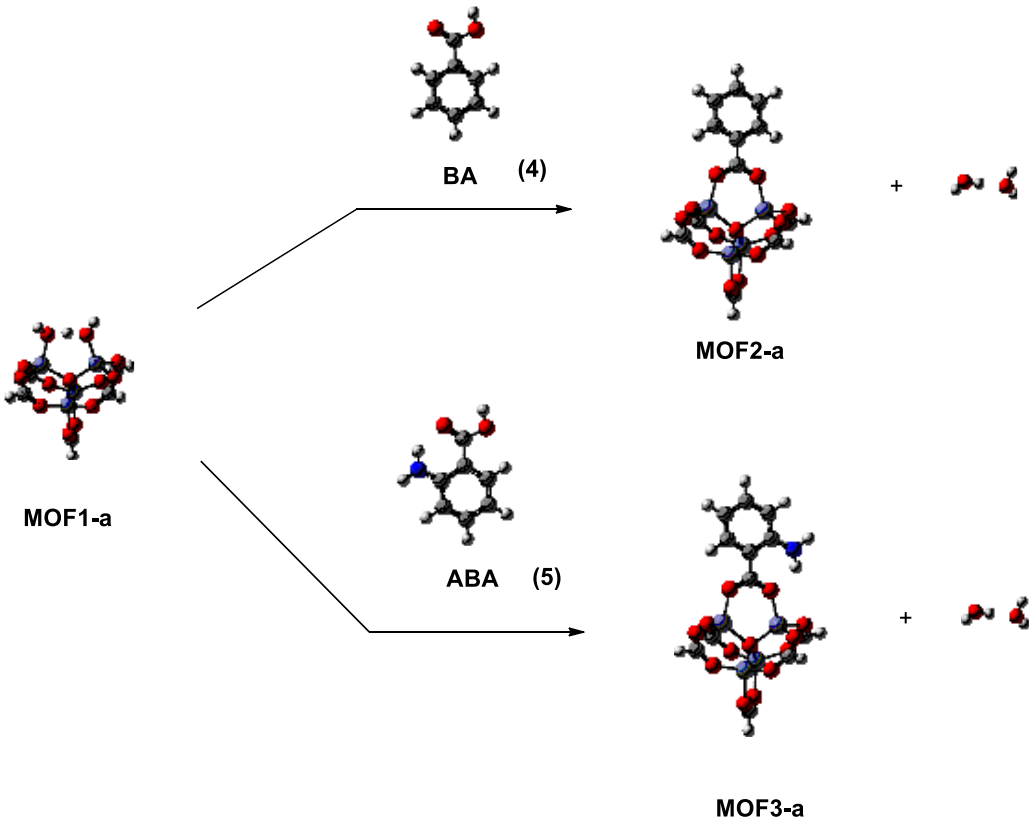


Figure S17: PXRD of DMF immersed crystals from IRMOF-3 (top) to MOF-5 (bottom).

S9. Theoretical calculations of structures

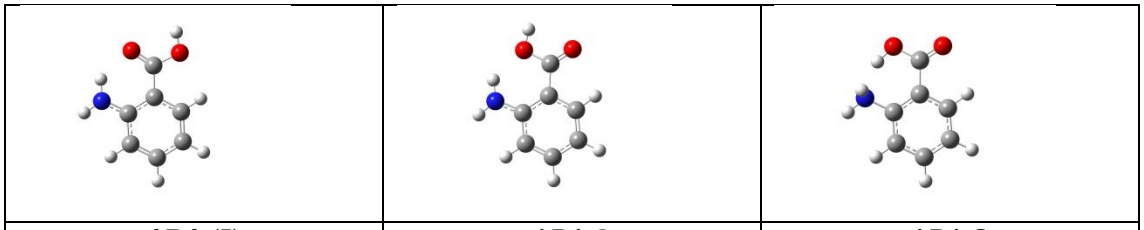


Scheme S1: Transformation of MOF1-a in MOF2-a or MOF3-a.

Table S5. B3LYP/6-31G** total energies (*E*, au) and relative energies (Δ*E*, kcal/mol) of species involved in the transformation of **MOF1-a** in **MOF2-a / MOF3-a** and in the transformation of **MOF1-b** in **MOF2-b / MOF3-**b.

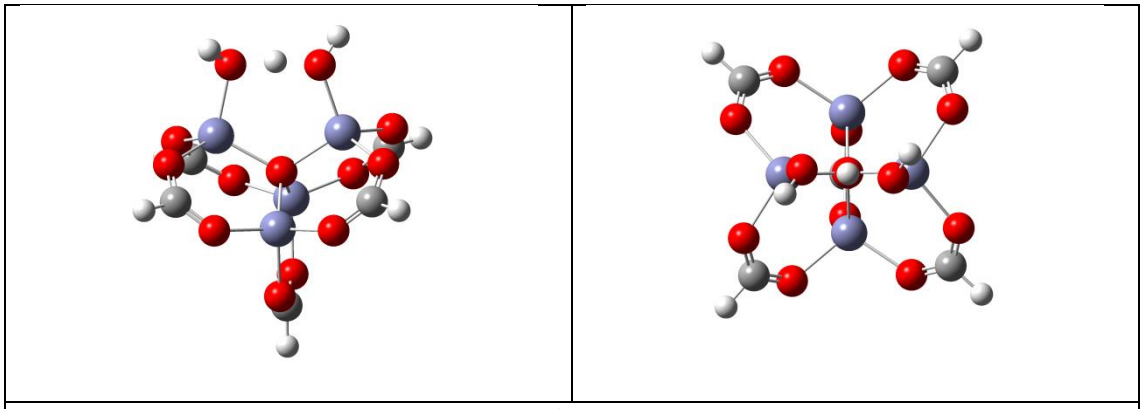
	gas-phase		N,N-dimethylformamide	
	E(a.u.)	ΔE(kcal/mol)	E(a.u.)	ΔE(kcal/mol)
BA (**4**)	-420,835432		-420,842222	
ABA (**5**)	-476,201325	0,00[a]	-476,209131	
ABA-2	-476,196342	3,13[a]		
ABA-3	-476,188532	8,03[a]		
2H2O	-152,851505		-152,863528	
MOF1-a	-8290,344699		-8290,383602	
MOF1-a+BA	-8711,180131		-8711,225823	
MOF2-a	-8558,331757		-8558,369128	
MOF2-a+2H2O	-8711,183262		-8711,232656	
(MOF2-a+2H2O)-(MOF1-a+BA)		-2,0		-4,3
MOF1-a+ABA	-8766,546025		-8766,592732	
MOF3-a	-8613,695076		-8613,734186	
MOF3-a+2H2O	-8766,546581		-8766,597714	
(MOF3-a+2H2O)-(MOF1-a+ABA)		-0,3		-3,1
MOF1-b	-9445,709492		-9445,747381	
MOF1-b+BA	-9866,544924		-9866,589603	
MOF2-b	-9713,696853		-9713,733000	
MOF2-b+2H2O	-9866,548358		-9866,596528	
(MOF2-b+2H2O)-(MOF1-b+BA)		-2,2		-4,3
MOF1-b+ABA	-9921,910817		-9921,956511	
MOF3-b	-9769,059927		-9769,097940	
MOF3-b+2H2O	-9921,911433		-9921,961468	
(MOF3-b+2H2O)-(MOF1-b+ABA)		-0,4		-3,1

[a] Three conformations have been calculated for o-aminobenzoic acid. The most stable is indicated as ABA.

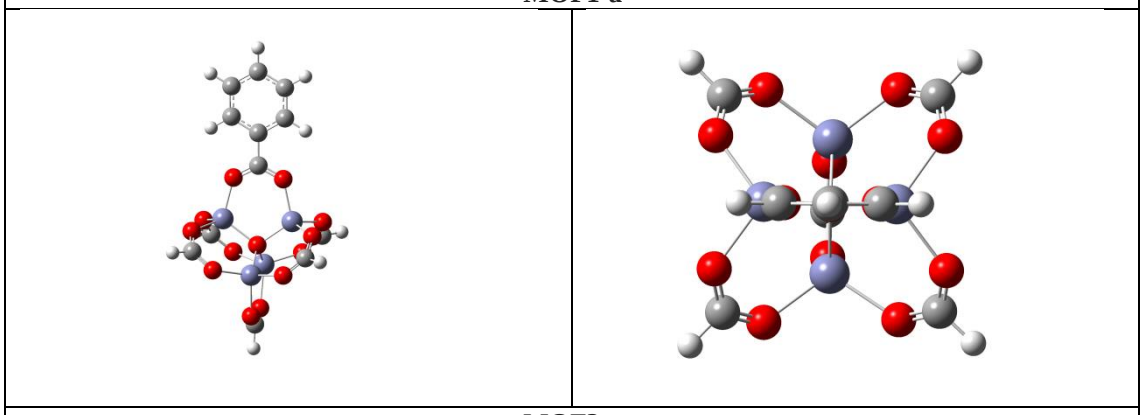


ABA (5)	ABA-2	ABA-3

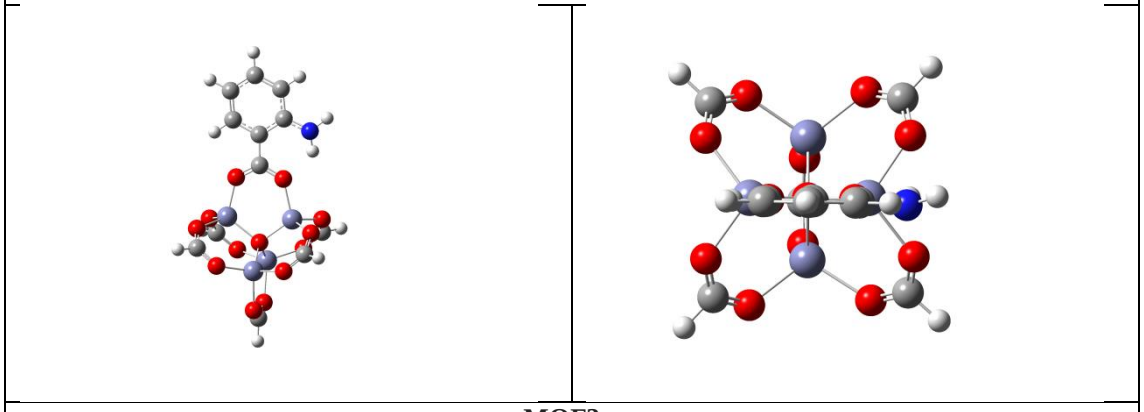
Figure S18: Three conformations of the o-aminobenzoic acid.



MOF1-a



MOF2-a



MOF3-a

Figure S19: Different views of **MOF1-a, MOF2-a** and **MOF3-a**.

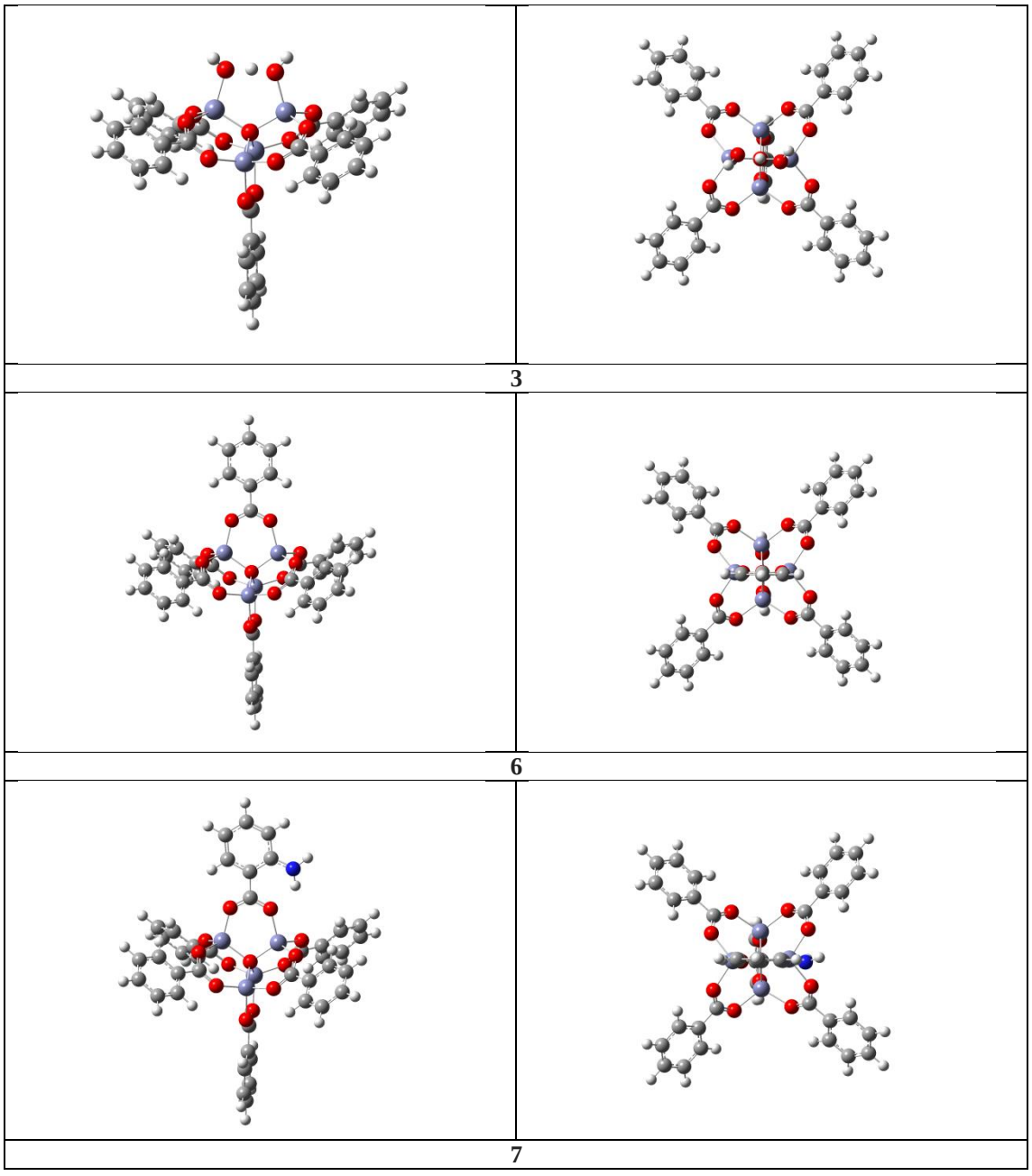


Figure S20: Different views of **3**, **6** and **7.**

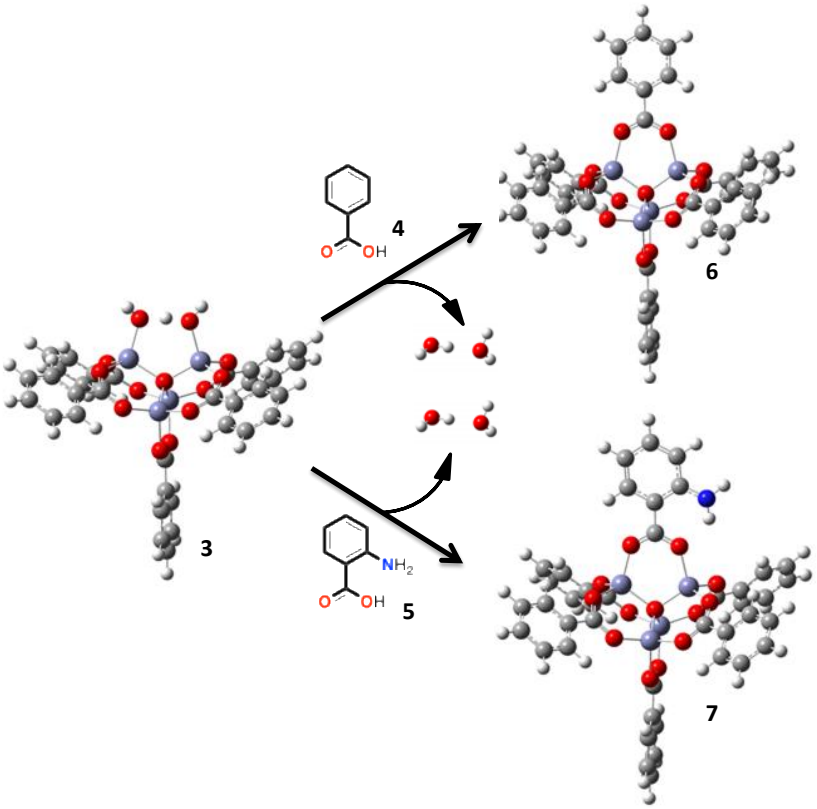


Figure S21: Model reagent **3**, composed by five benzoic acid unities and the Zn(II) oxo-cluster (Zn_4O) bearing H_2O and OH^- at the free position, is reacted with benzoic acid (**4**) or 2-amino benzoic acid (**5**) giving **6** and **7** as model products

S10. Logistic model

$$Y = Y_{min} + \frac{Y_{max} - Y_{min}}{1 + e^{-n(x-B)}}$$

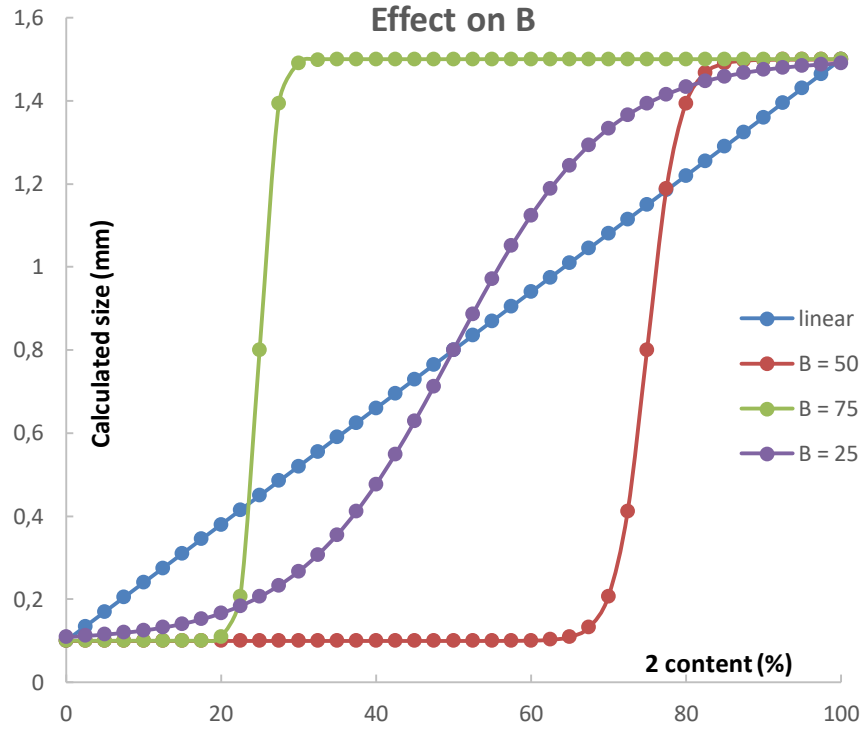


Figure S22: Effect of B on the logistic model.

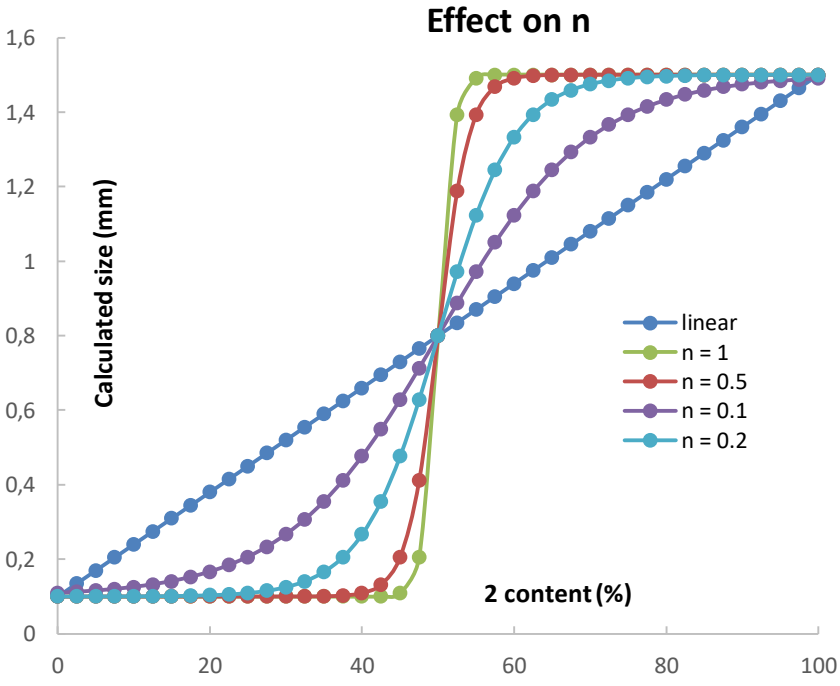


Figure S23: Effect of n on the logistic model.

S11. Beta incomplete function

$$\beta(x|a,b) = \frac{\int_0^x p^{a-1}(1-p)^{b-1}dp}{\int_0^1 p^{a-1}(1-p)^{b-1}dp}$$

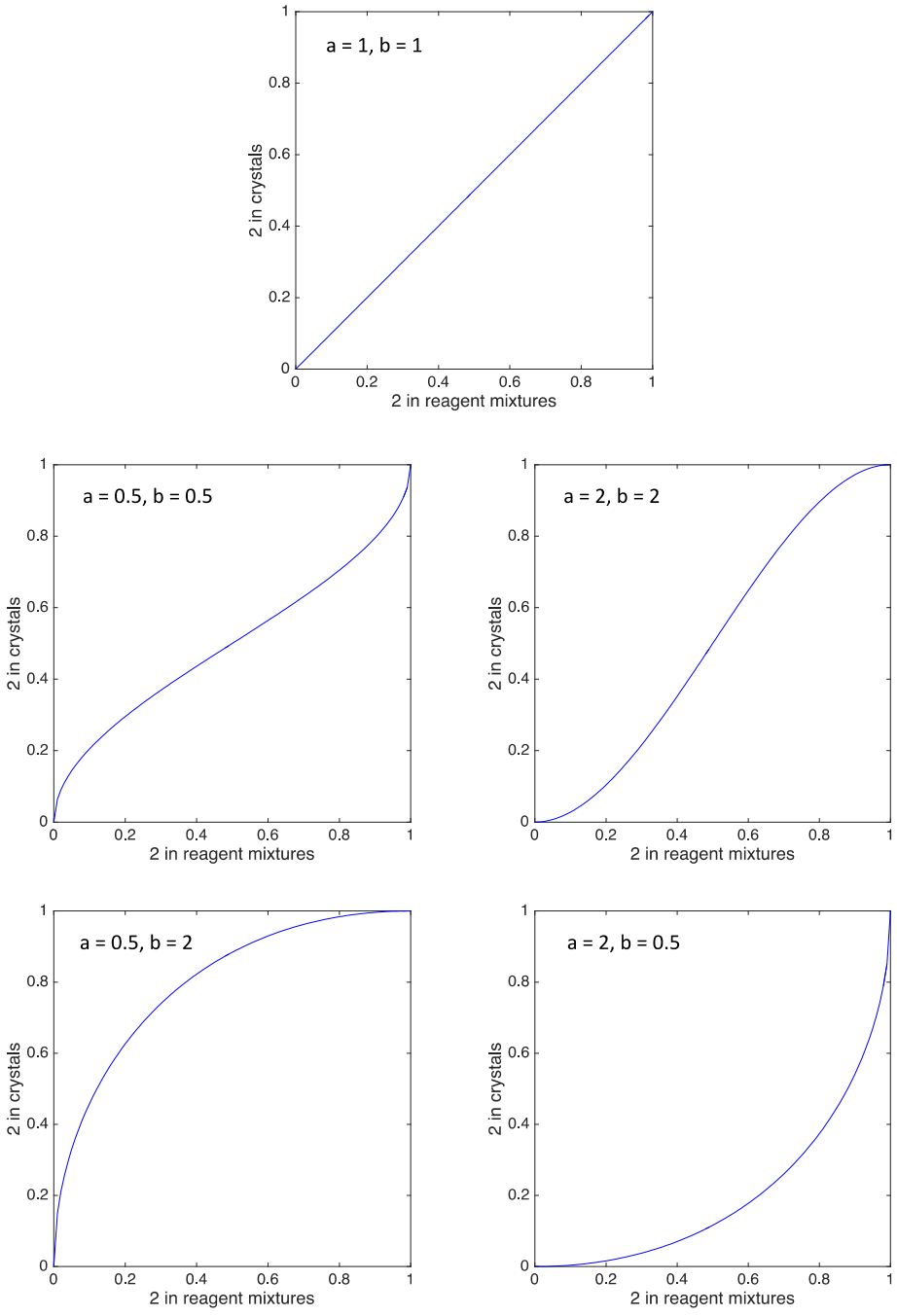


Figure S24: Shape of Beta incomplete function according to different a/b parameter values.

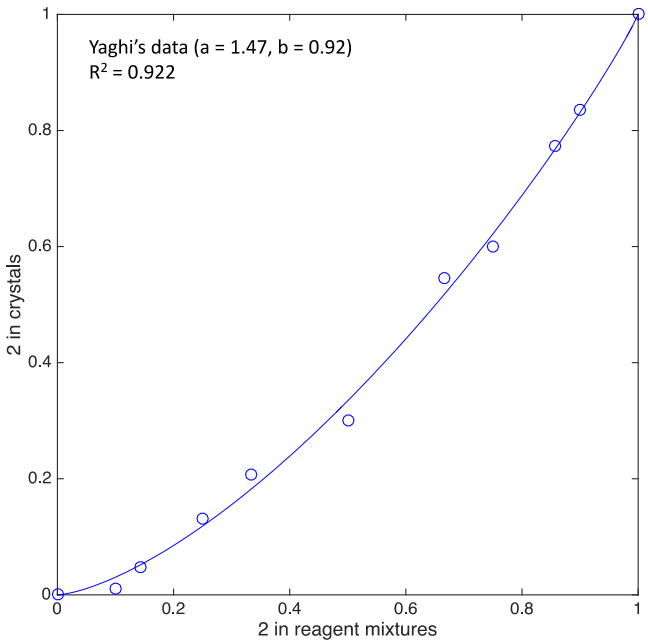


Figure S25: Fitting of Beta incomplete function to data obtained from Yaghi's results (MOF-5/IRMOF-3 mixtures obtained in diethylformamide at 100 ºC and 48 h.[7]

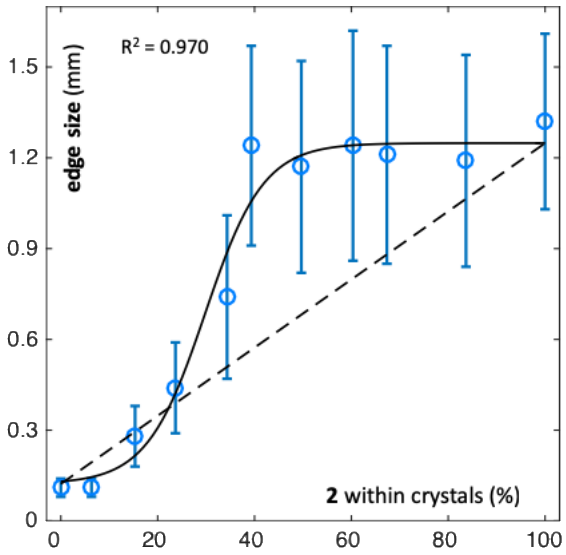


Figure S26: Crystal edge size vs. within concentration of ligand **2** (as a ratio). Solid line fits data (average values), while dashed line is the linear trend. Error bars correspond to standard deviations and indicate size dispersion of each sample. Parameters fitted: x_{50} = 29.8% and n = 16.6 over average values, with y_{min} = 0.123 mm and y_{max} = 1.248 mm.

S12. References

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