materials

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Article

Phase-Selective Microwave Assisted Synthesis of Iron(III) Aminoterephthalate MOFs

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1. Microwave-assisted solvothermal synthesis

Table S1. Letter codes for the resulting products of the following MW synthesis.

Letter Code	Resulting Reaction Product
A	MIL-53(Fe)-NH_2
B	MIL-88B(Fe)-NH_2
C	MIL-101(Fe)-NH_2
X	Amorphous
D	Fe_2O_3

Table S2. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3{\cdot}6H_2O/H_2BDC\text{-}NH_2$/HCl in water (V H_2O = 4 mL, T = 100 °C, t = 5 min). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3{\cdot}6H_2O$ (mg)	$FeCl_3{\cdot}6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	HCl 1 M (mL)	HCl: Fe	Result*
MW 1-01	21.6	0.08	14.48	0.08	1	0.02	0	0	**C**
MW 1-02	54	0.2	36.2	0.2	1	0.05	0	0	**C** + **A**
MW 1-03	108	0.4	72.4	0.4	1	0.1	0	0	**A** + **C**
MW 1-04	216	0.8	144.8	0.8	1	0.2	0	0	**A**
MW 1-05	54	0.2	36.2	0.2	1	0.05	0.05	0.25	**C** + **A**
MW 1-06	54	0.2	36.2	0.2	1	0.05	0.1	0.5	**C** + **A**
MW 1-07	54	0.2	36.2	0.2	1	0.05	0.15	0.75	**A** + **C**
MW 1-08	54	0.2	36.2	0.2	1	0.05	0.2	1	**A**

* In the case of mixture, the first letter is the major phase

Table S3. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$/HCl in water (V H_2O = 4 mL, T= 150 °C, t= 5 min and $^{(\bullet)}$ t= 30 min). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3$ $6H_2O$ (mg)	$FeCl_3$ $6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	HCl 1 M (mL)	HCl: Fe	Result *
MW 2-01	21.6	0.08	14.48	0.08	1	0.02	0	0	C + A
MW 2-02	54	0.2	36.2	0.2	1	0.05	0	0	A + C
MW 2-03	108	0.4	72.4	0.4	1	0.1	0	0	A
MW 2-04$^{(\bullet)}$	108	0.4	72.4	0.4	1	0.1	0	0	A
MW 2-05	216	0.8	144.8	0.8	1	0.2	0	0	A
MW 2-06	54	0.2	36.2	0.2	1	0.05	0.1	0.5	C + A

* In the case of mixture, the first letter is the major phase

Table S4. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL. T= 150 °C. t= 5 min). The resulting phases are indicated by the letter assigned in Table S1.

Sample name	$FeCl_3 \cdot 6H_2O$ (mg)	$FeCl_3$ $6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	HCl 1 M (mL)	HCl: Fe	Result
MW 3-01	21.6	0.08	14.48	0.08	1	0.02	0	0	B
MW 3-02	54	0.2	36.2	0.2	1	0.05	0	0	B
MW 3-03	108	0.4	72.4	0.4	1	0.1	0	0	B
MW 3-04	216	0.8	144.8	0.8	1	0.2	0	0	B

Table S5. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of assigned in Table S1. the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL. T= 150 °C. t= 5 min). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3 \cdot 6H_2O$ (mg)	$FeCl_3$ $6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	HCl 1 M (mL)	HCl: Fe	Result
MW 3-05	216	0.8	36.2	0.2	0.25	0.2	0	0	B
MW 3-06	216	0.8	72.4	0.4	0.5	0.2	0	0	B
MW 3-07	216	0.8	217.2	1.2	1.5	0.2	0	0	B
MW 3-08	216	0.8	289.6	1.6	2	0.2	0	0	B

Table S6. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, [Fe] =0.1 M, ligand:metal = 1:1). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3 \cdot 6H_2O$ (mg)	$FeCl_3$ $6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	T (°C)	Time (min)	Result
MW 3-09	108	0.4	72.4	0.4	1	0.1	100	5	**B**
MW 3-10	108	0.4	72.4	0.4	1	0.1	100	10	**B**
MW 3-11	108	0.4	72.4	0.4	1	0.1	100	20	**C**
MW 3-12	108	0.4	72.4	0.4	1	0.1	100	30	**C**
MW 3-13	108	0.4	72.4	0.4	1	0.1	150	10	**B**
MW 3-14	108	0.4	72.4	0.4	1	0.1	150	20	**B**
MW 3-15	108	0.4	72.4	0.4	1	0.1	150	30	**B**
MW 3-16	108	0.4	72.4	0.4	1	0.1	180	5	**B**
MW 3-17	108	0.4	72.4	0.4	1	0.1	180	10	**D**
MW 3-18	108	0.4	72.4	0.4	1	0.1	180	20	**D**
MW 3-19	108	0.4	72.4	0.4	1	0.1	180	30	**D**

Table S7. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in DMF (V DMF = 4 mL. T = 150 °C. ligand:metal = 1:1). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3$ $6H_2O$ (mg)	$FeCl_3$ $6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	T (°C)	Time (min)	Result*
MW 4-01	21.6	0.08	14.48	0.08	1	0.02	150	5	X
MW 4-02	54	0.2	36.2	0.2	1	0.05	150	5	**C** + **B**
MW 4-03	108	0.4	72.4	0.4	1	0.1	150	5	**B** + **C**
MW 4-04	216	0.8	144.8	0.8	1	0.2	150	5	**C** + **A**
MW 4-05	21.6	0.08	14.48	0.08	1	0.02	150	30	**C**
MW 4-06	54	0.2	36.2	0.2	1	0.05	150	30	**C** + **B**
MW 4-07	108	0.4	72.4	0.4	1	0.1	150	30	**B** + **C**
MW 4-08	216	0.8	144.8	0.8	1	0.2	150	30	**A** + **C**

* In the case of mixture, the first letter is the major phase

Table S8. Mass, mol and molar ratios, and dispensed amounts for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2/HCl$ in DMF (V DMF = 4 mL. T = 150 °C. t = 5 min). The resulting phases are indicated by the letter assigned in Table S1.

Sample Name	$FeCl_3 6H_2O$ (mg)	$FeCl_3 6H_2O$ (mmol)	$H_2BDC\text{-}NH_2$ (mg)	$H_2BDC\text{-}NH_2$ (mmol)	Ligand: Metal	[Fe] (M)	HCl 1 M (mL)	HCl: Fe	Result*
MW 4-10	54	0.2	36.2	0.2	1	0.05	0	0	C + B
MW 4-11	54	0.2	36.2	0.2	1	0.05	0.1	0.5	B
MW 4-12	54	0.2	54.3	0.3	1.5	0.05	0	0	C + B
MW 4-13	54	0.2	54.3	0.3	1.5	0.05	0.1	0.5	B

* In the case of mixture, the first letter is the major phase

2. PXRD patterns

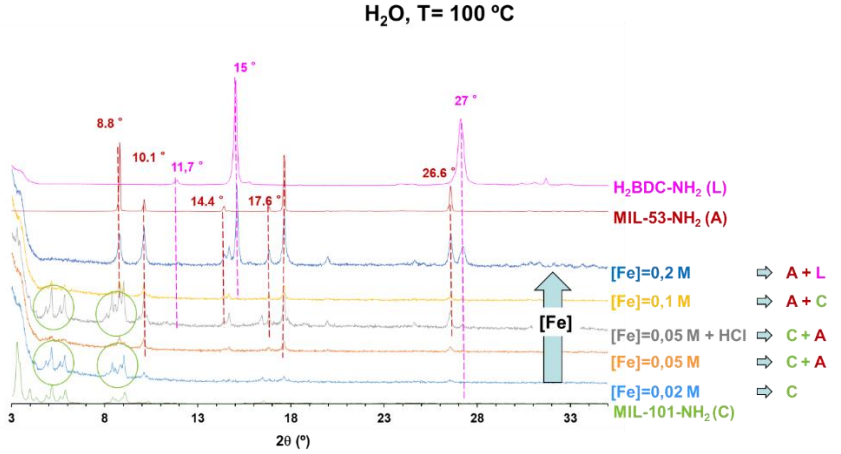

Figure S1. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2/HCl$ in water (V H_2O = 4 mL, T = 100 °C, t = 5 min) after activation with EtOH, compared to simulated MIL-101-NH_2 (green), MIL-53-NH_2 (red) and $H_2BDC\text{-}NH_2$ (pink).

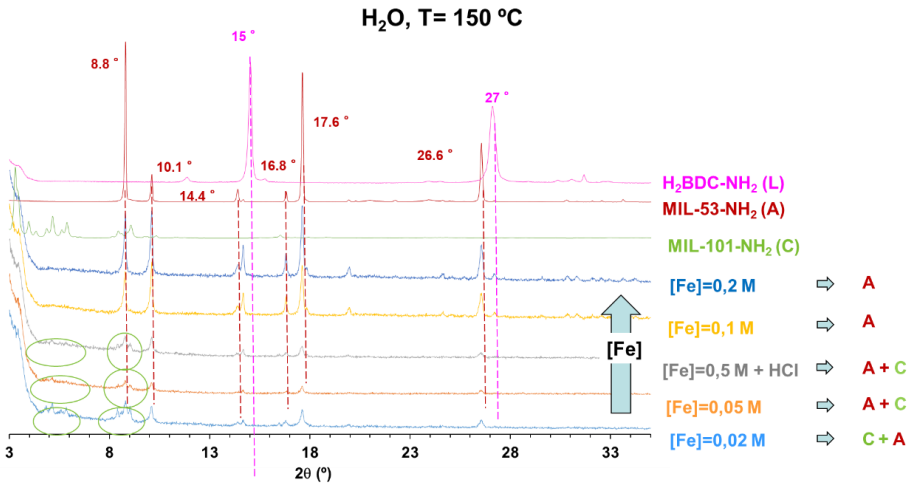

Figure S2. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2/HCl$ in water (V H_2O = 4 mL, T = 150 °C, t = 5 min) after activation with EtOH, compared to simulated MIL-101-NH_2 (green), MIL-53-NH_2 (red) and H2BDC-NH_2 (pink).

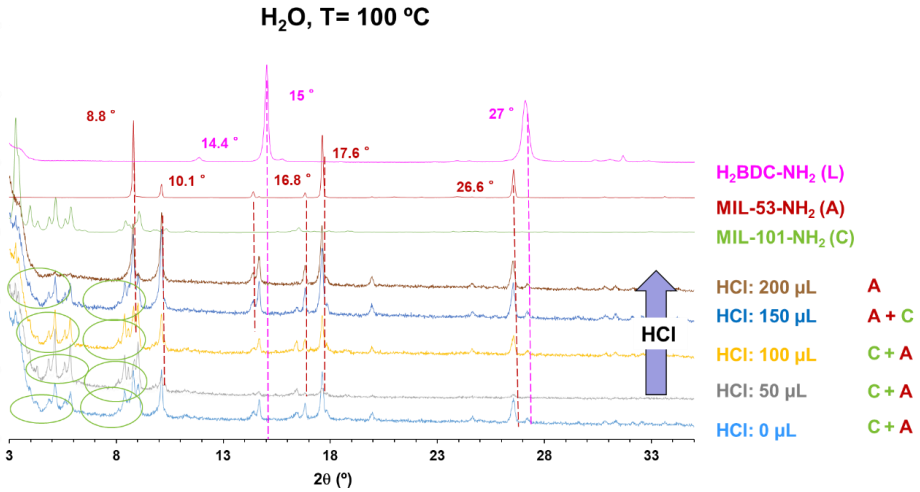

Figure S3. PXRD patterns for the MW investigation of the system $FeCl_3{\cdot}6H_2O/H_2BDC\text{-}NH_2/HCl$ in water (V H2O = 4 mL, T = 100 °C, t = 5 min, [Fe] = 0.05 M) after activation with EtOH, compared to simulated MIL-101-NH_2 (green), MIL-53-NH_2 (red) and H2BDC-NH_2 (pink).

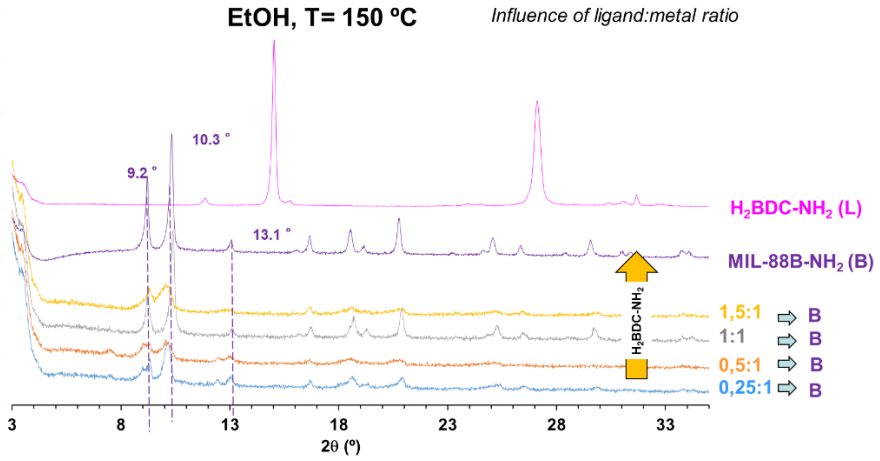

Figure S4. PXRD patterns for the MW investigation of the system $FeCl_3{\cdot}6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 150 °C, [Fe] = 0.2 M, t = 5 min) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple) and $H_2BDC\text{-}NH_2$ (pink).

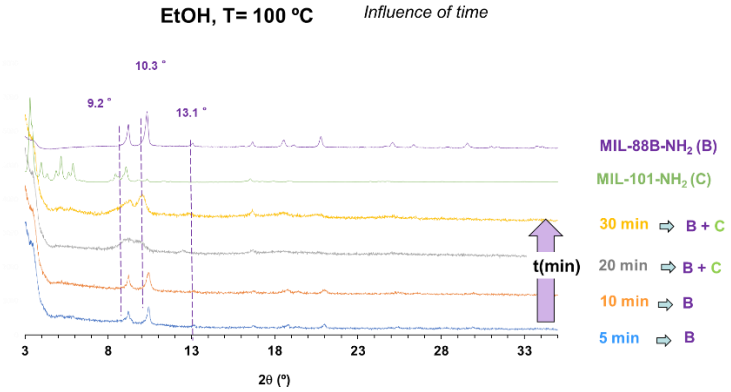

Figure S5. PXRD patterns for the MW investigation of the system $FeCl_3{\cdot}6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 100 °C, [Fe] = 0.1 M,) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple) and MIL-101-NH_2 (green).

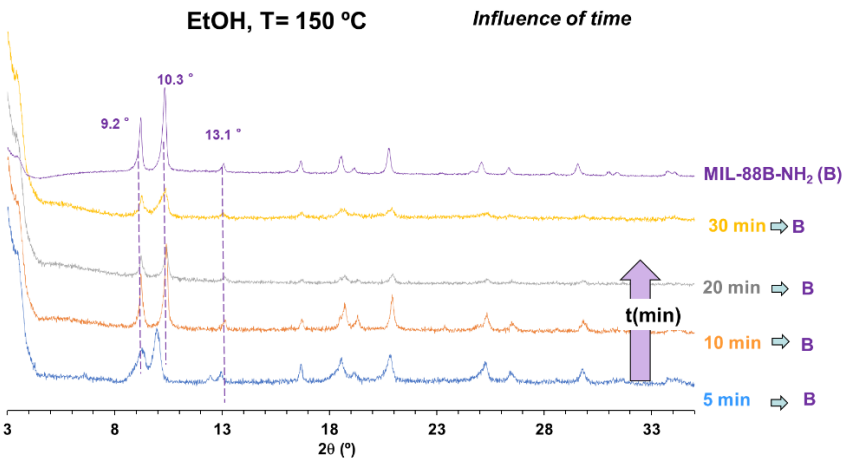

Figure S6. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 150 °C, [Fe] = 0.1 M,) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple).

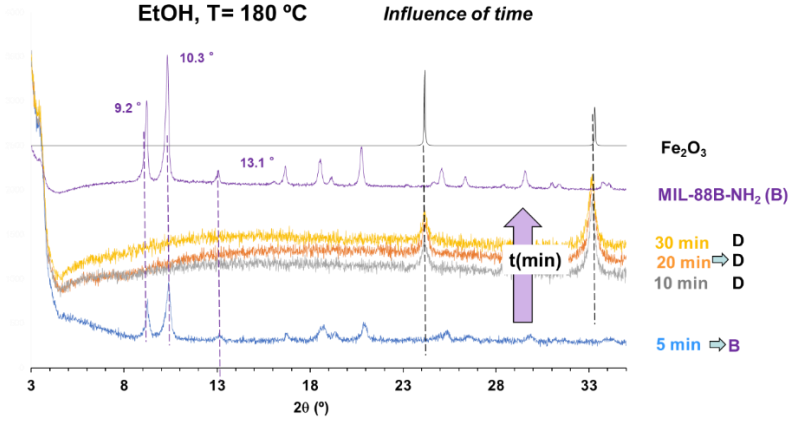

Figure S7. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 180 °C, [Fe] = 0.1 M,) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple) and Fe_2O_3 (black).

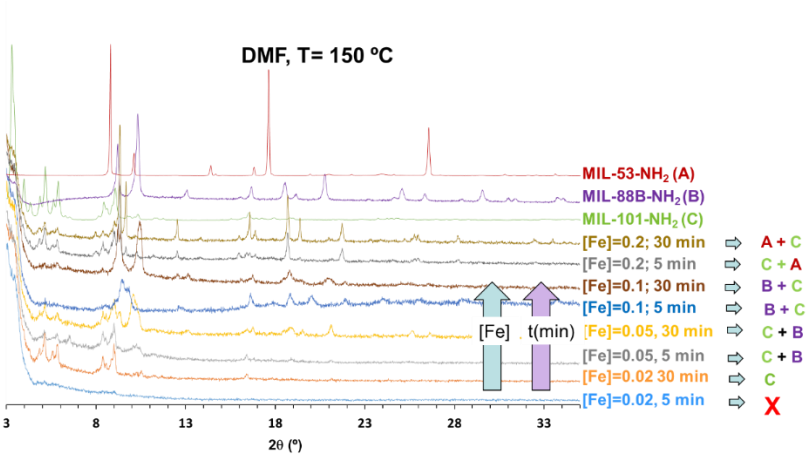

Figure S8. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in DMF (V DMF = 4 mL, T = 150 °C, ligand:metal = 1:1) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple) and MIL-101-NH_2 (green).

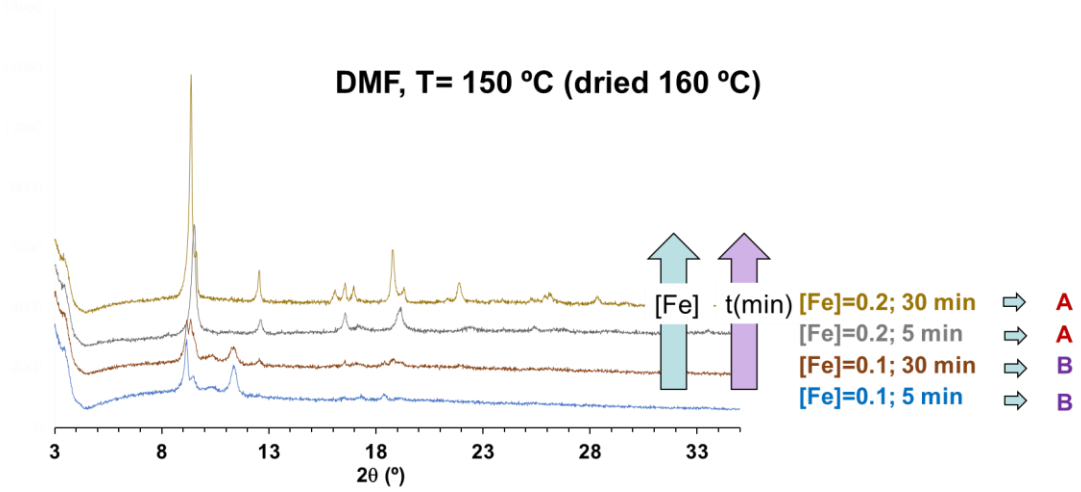

Figure S9. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in DMF (V DMF = 4 mL, T = 150 °C, ligand:metal = 1:1) after activation with EtOH and dried at 160 °C, for better discriminating between the different Fe-BDC-NH_2 MOF phases.

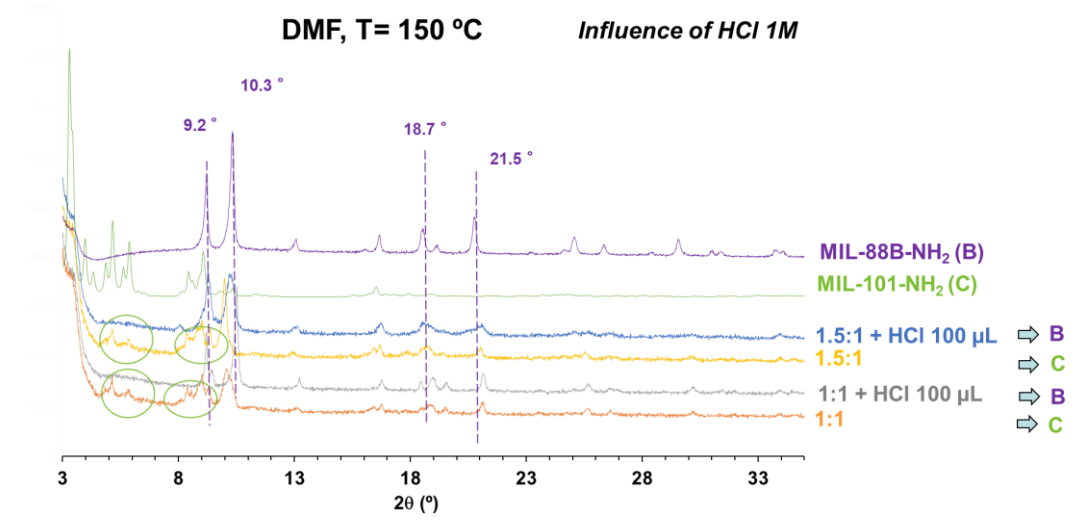

Figure S10. PXRD patterns for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$/HCl in DMF (V DMF = 4 mL, T = 150 °C, t = 30 min) after activation with EtOH, compared to simulated MIL-88B-NH_2 (purple) and MIL-101-NH_2 (green).

3. Particle size and reaction yield

Table S9. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in water (V H_2O = 4 mL, T = 100 °C, t = 5 min).

[Fe] (M)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0.02	450 ± 200	0.25 ± 0.01	~100(*)	3850	C
0.05	190 ± 70	0.32 ± 0.01	~100(*)	5400	C + A
0.1	450 ± 150	0.20 ± 0.06	~100(*)	8700	C + A
0.2	260 ± 70	0.11 ± 0.02	70	10400	A

* remaining ligand found prior activation due to poor $H_2BDC\text{-}NH_2$ solubility in water

Table S10. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in water (V H_2O = 4 mL, T= 150 °C, t= 5 min).

[Fe] (M)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0.02	300 ± 85	0.20 ± 0.11	~100(*)	2950	**C** + **A**
0.05	300 ± 90	0.37 ± 0.11	~100(*)	3900	**A** + **C**
0.1	325 ± 150	0.28 ± 0.03	60	4300	**A**
0.2	310 ± 120	0.30 ± 0.03	50	7000	**A**

* remaining ligand found prior activation due to poor $H_2BDC\text{-}NH_2$ solubility in water

Table S11. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$/HCl in water ([Fe] = 0.05 M, V H_2O = 4 mL, T= 100 °C, t= 5 min).

HCl (µL)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0	240 ± 100	0.35 ± 0.06	~100(*)	8500	**C** + **A**
50	480 ± 80	0.41 ± 0.05	~100(*)	8000	**C** + **A**
100	500 ± 100	0.50 ± 0.06	~100(*)	7500	**C** + **A**
150	590 ± 140	0.41 ± 0.06	~100(*)	7300	**A** + **C**
200	320 ± 110	0.39 ± 0.07	~100(*)	6500	**A**

* remaining ligand found prior activation due to poor $H_2BDC\text{-}NH_2$ solubility in water

Table S12. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 150 °C, t = 5 min).

[Fe] (M)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0.02	300 ± 80	0.28 ± 0.12	~100	2050	**B**
0.05	250 ± 140	0.29 ± 0.09	85	3100	**B**
0.1	250 ± 80	0.12 ± 0.03	45	3300	**B**
0.2	210 ± 70	0.10 ± 0.02	40	6200	**B**

Table S13. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 150 °C, t= 5 min, [Fe] = 0.2 M).

Ligand:Metal	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0.25:1	300 ± 85	0.15 ± 0.07	90	3200	**B**
0.5:1	290 ± 70	0.07 ± 0.05	60	4700	**B**
1:1	210 ± 70	0.10 ± 0.02	40	6200	**B**
1.5:1	270 ± 80	0.12 ± 0.06	35	5600	**B**

Table S14. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 100 °C, [Fe] = 0.1 M).

Time (min)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
5	220 ± 80	0.25 ± 0.05	95	16000	**B**
10	320± 80	0.34 ± 0.08	~100	10700	**B**
20	240 ± 80	0.28 ± 0.04	~100	6800	**C**
30	290 ± 70	0.20 ± 0.02	80	3500	**C**

Table S15. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, T = 150 °C, [Fe] = 0.1 M).

Time (min)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
5	250 ± 80	0.12 ± 0.03	40	3300	**B**
10	250 ± 100	0.16 ± 0.08	90	2600	**B**
20	250 ± 70	0.11 ± 0.01	60	2000	**B**
30	230 ± 60	0.07 ± 0.04	50	2100	**B**

Table S16. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in DMF (V DMF = 4 mL, T = 150 °C, ligand:metal = 1:1).

[Fe] (M)	Time (min)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
0.02	5	-	-	-	-	X
	30	300 ± 80	0.12 ± 0.09	70	600	**C**
0.05	5	250 ± 60	0.14 ± 0.09	40	1500	**C** + **B**
	30	270 ± 80	0.26 ± 0.09	70	400	**C** + **B**
0.1	5	270 ± 70	0.08 ± 0.01	50	3500	**B** + **C**
	30	490 ± 150	0.20 ± 0.02	70	2300	**B** + **C**
0.2	5	230 ± 80	0.2 ± 0.01	20	6000	**C** + **A**
	30			45	3800	**A** + **C**

Table S17. Particle size and reaction yield for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$/HCl in DMF (V DMF = 4 mL, T = 150 °C, t = 30 min, [Fe] = 0.05).

Ligand:Metal	HCl (µL)	Particle Size (Ø nm)	PdI	Yield (wt.%)	STY ($kg \cdot m^{-3} \cdot d^{-1}$)	Result
1:1	0	270 ± 80	0.26 ± 0.09	70	400	**C** + **B**
	100	293 ± 100	0.34 ± 0.06	90	500	**B**
1.5:1	0	500 ± 150	0.18 ± 0.02	70	450	**C** + **B**
	100	600 ± 130	0.20 ± 0.09	~100	600	**B**

4. TEM

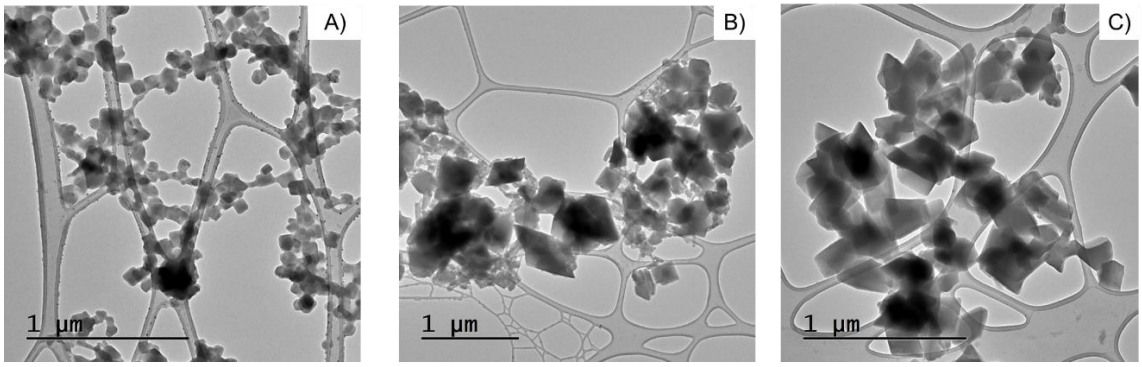

Figure S11. TEM micrographs for PXRD for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2/HCl$ in water (V H_2O = 4 mL, t = 5 min) after activation with EtOH: (**A**) T = 100 °C, HCl 0.1 M = 0 µL; (**B**) T = 100 °C, HCl 0.1 M = 100 µL; (**C**) T = 150 °C, HCl 0.1 M = 0 µL.

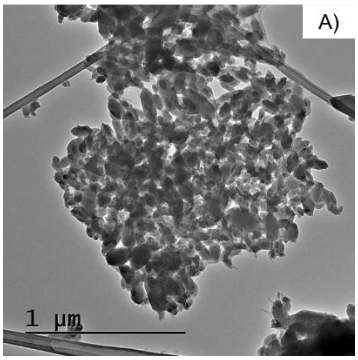

Figure S12. TEM micrographs for PXRD for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2$ in ethanol (V EtOH = 4 mL, t = 5 min T = 100 °C, [Fe] = 0.1 M) after activation with EtOH scale bar = 1 µm.

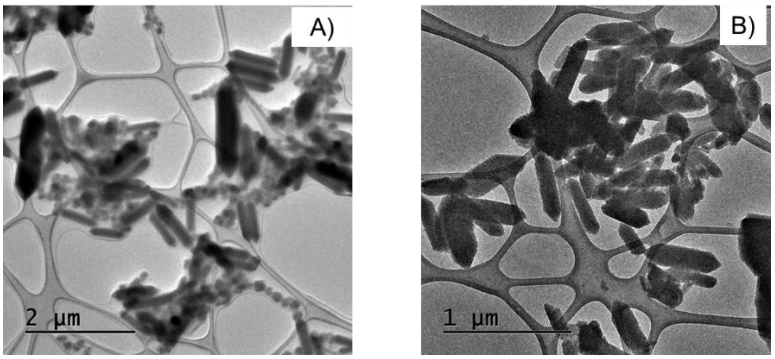

Figure S13. TEM micrographs for PXRD for the MW investigation of the system $FeCl_3 \cdot 6H_2O/H_2BDC\text{-}NH_2/HCl$ in DMF (V DMF = 4 mL, t = 30 min, T = 100 °C, ligand:metal = 1:1) after activation with EtOH: (**A**) HCl 0.1 M = 0 µL (scale bar = 2 µm); (**B**) HCl 0.1 M = 100 µL (scale bar = 1 µm).