

Supporting Information for

Ce-MIL-140: Expanding the synthesis routes for Cerium(IV) metal-organic frameworks

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1. Synthesis optimization

During the development of the new synthesis route the reaction time was varied between 30 min and 6 h for all title compounds and thereby a trend was observed. During the synthesis with the 2-chloro terephthalic acid (H₂BDC-Cl), products were observed at all tested reaction times, probably due to the high polarity and solubility of the linker. In contrast, with terephthalic acid (H₂BDC) and naphthalene dicarboxylic acid (H₂NDC), longer reaction times are necessary.

Table S 1: Results of the investigation of the influence of the reaction time on the product formation for Ce-MIL-140-BDC, Ce-MIL-140-BDC-Cl and Ce-MIL-140-NDC. All syntheses were carried out using the molar ratios given in the manuscript. The number reactions which were carried out at each reaction temperature are given in parentheses after the percent value.

Reaction time [min]	Successful synthesis of Ce-MIL-140-BDC [%]	Successful synthesis of Ce-MIL-140-BDC-Cl [%]	Successful synthesis of Ce-MIL-140-NDC [%]
30	0 (6)	100 (6)	0 (6)
60	0 (6)	100 (6)	0 (6)
120	58 (12)	100 (6)	0 (12)
180	46 (11)	100 (6)	0 (9)
210	83 (6)	100 (6)	33 (6)
240	100 (6)	100 (6)	83 (6)
300	100 (6)	100 (6)	100 (6)
400	100 (6)	100 (6)	100 (6)

2. Purification

2.1. Powder X-ray diffraction (PXRD)

PXRD patterns of as synthesized, purified MOFs and the linker molecules are given in the following figures.

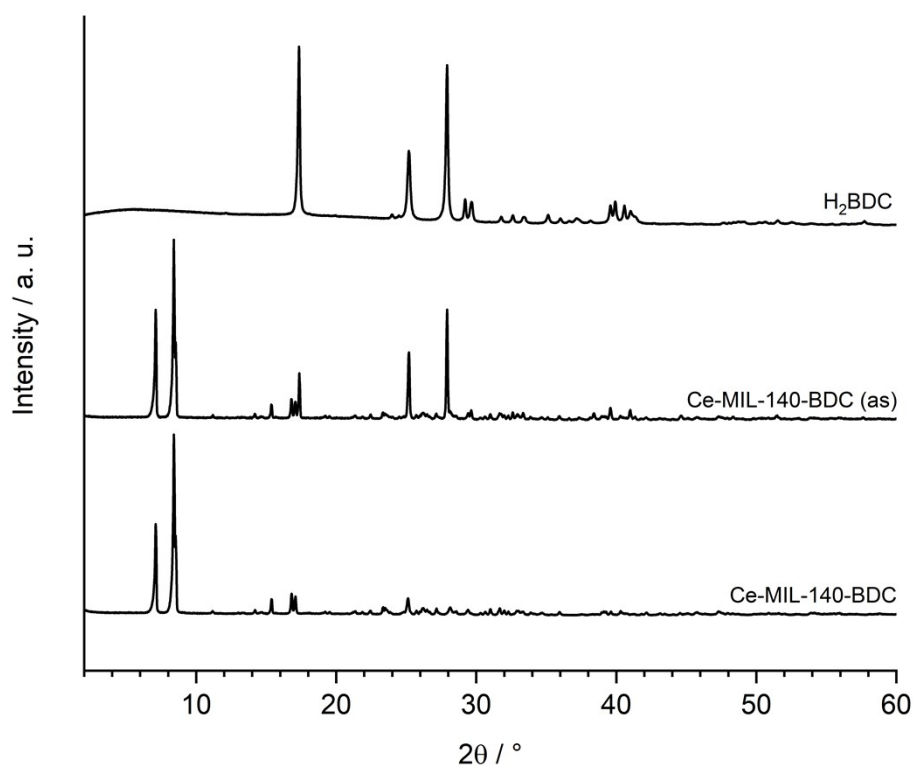


Figure S 1: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-BDC before and after the treatment and PXRD pattern of the linker molecule H₂BDC.

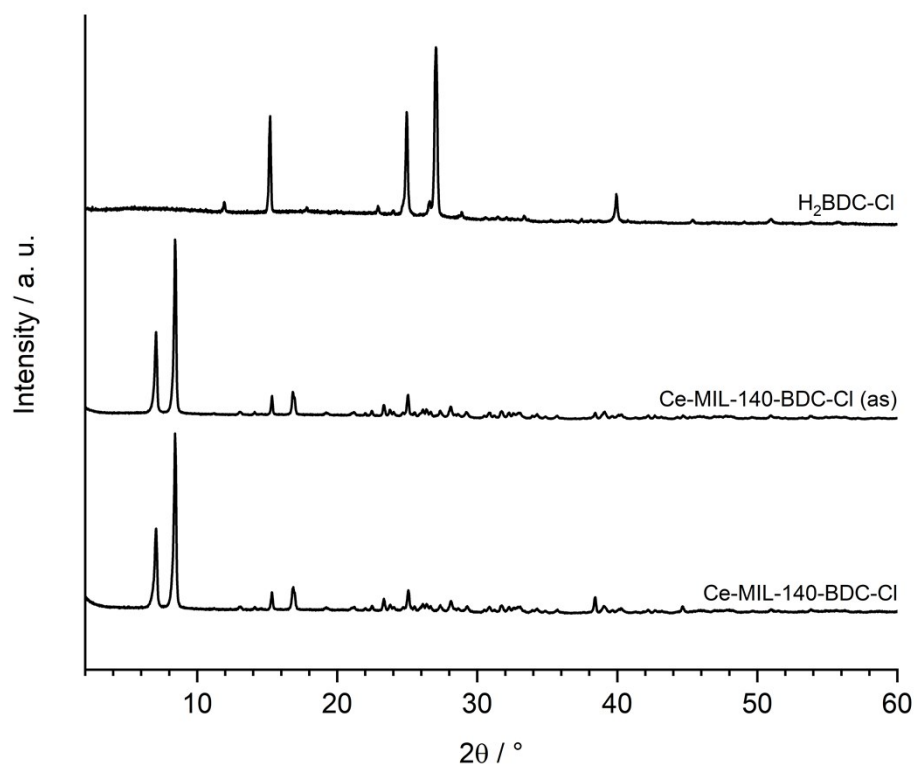


Figure S 2: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-BDC-Cl before and after the treatment process and PXRD pattern of the linker molecule $H_2BDC-Cl$.

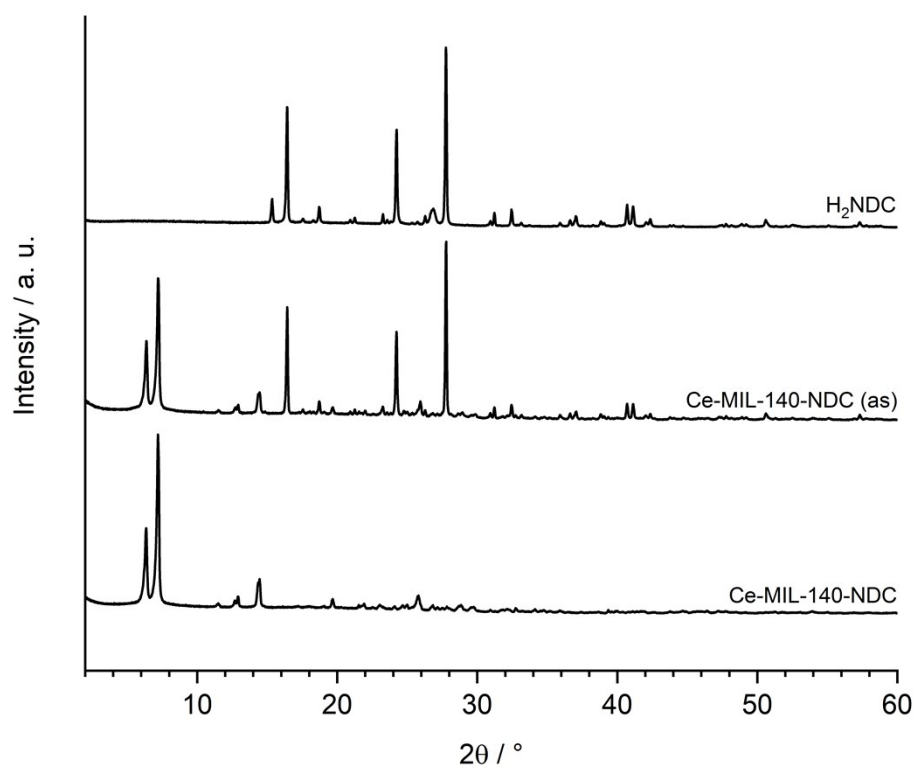


Figure S 3: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-NDC before and after the treatment process and PXRD pattern of the linker molecule H_2NDC .

2.2. ^1H -NMR spectroscopy

All ^1H -NMR spectra of the dissolved Ce(IV)-MOFs were recorded at 400 MHz and 300 K in a mixture of d_6 -DMSO and 10 % DCl (7:1). The signals of all detected solvents are labeled in each spectrum. In all spectra no acetone was detected which evaporated completely during the drying of the MOFs for 24 h at 70 °C. Only solvents with low volatility were detected in very small amounts.

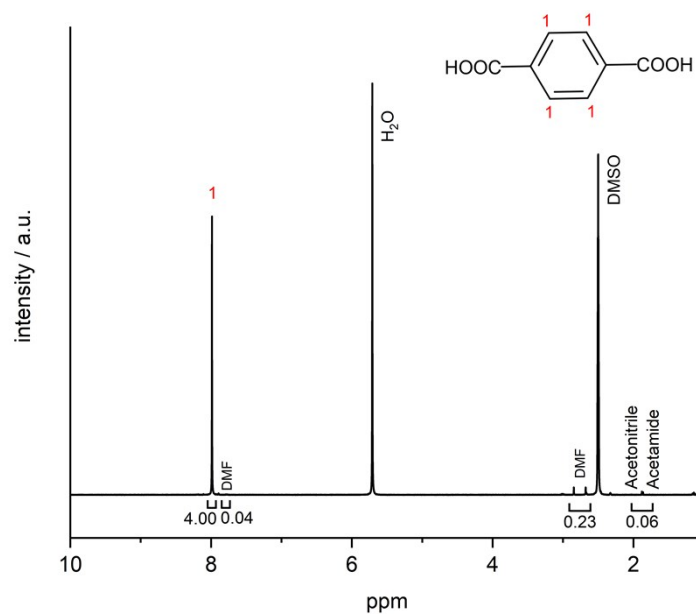


Figure S 4: ^1H -NMR of Ce-MIL-140-BDC dissolved in a mixture of d_6 -DMSO and 10 % DCl (7:1).

^1H -NMR (400 MHz, 300 K, $\text{DMSO-d}_6/\text{DCl}$): $\delta = 7.99$ (s, 4 H, H-1) ppm.

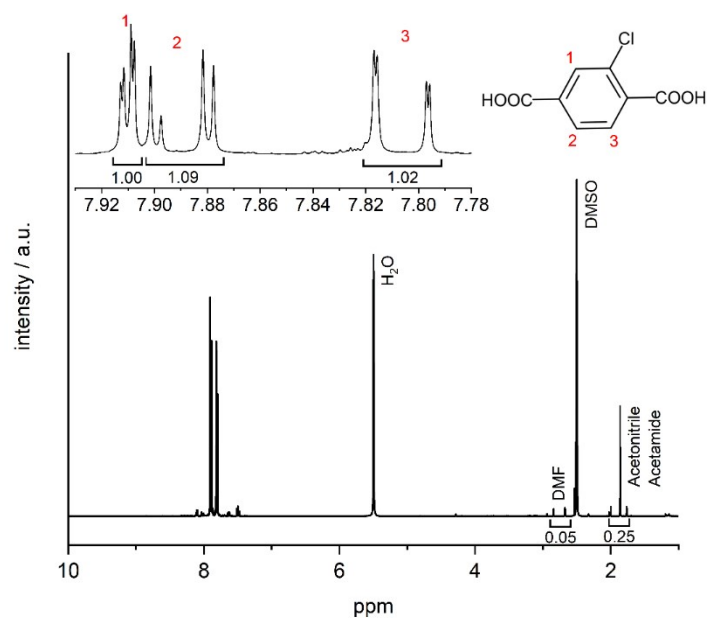


Figure S 5: $^1\text{H-NMR}$ of Ce-MIL-140-BDC-Cl dissolved in a mixture of d_6 -DMSO and 10 % DCl (7:1).

$^1\text{H-NMR}$ (400 MHz, 300 K, DMSO- d_6 / DCl): $\delta = 7.91$ (dd, 1H, H-1), 7.89 (dd, 1 H, H-2), 7.81 (dd, 1 H, H-3) ppm.

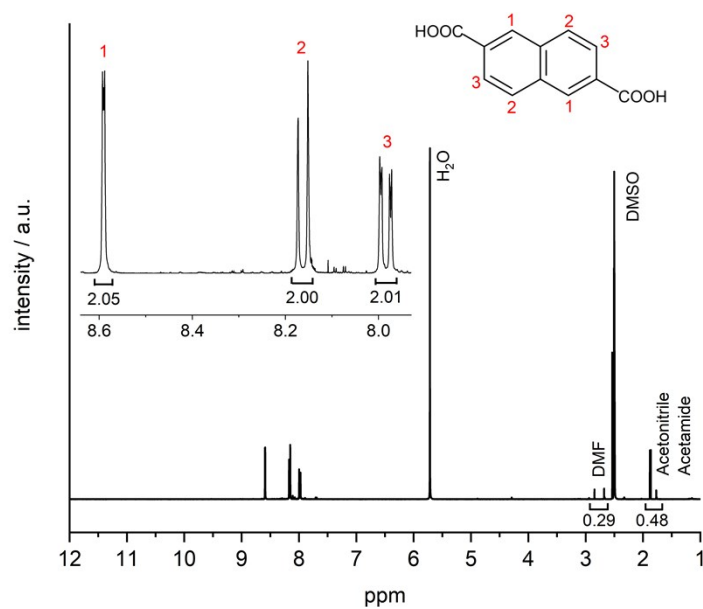


Figure S 6: $^1\text{H-NMR}$ of Ce-MIL-140-NDC dissolved in a mixture of d_6 -DMSO and 10 % DCl (7:1).

$^1\text{H-NMR}$ (400 MHz, 300 K, DMSO- d_6 / DCl): $\delta = 8.59$ (m, 2 H, H-1), 8.16 (m, 2 H, H-2), 7.98 (ddd, 2 H, H-3) ppm.

2.3. IR spectroscopy

IR spectra of purified reaction products are presented in Fig. S7. The observed bands are in line with the results of the other characterization methods. In all three IR spectra no bands were observed that can be linked to the presence of carboxylic acid (-COOH) groups, i.e. the presence of linker molecules in the pores.¹ Furthermore, the characteristic C≡N stretching vibration of the reaction solvent acetonitrile (2260 - 2230 cm⁻¹) as well as the C=O stretching vibration of the solvent acetone (1725 - 1705 cm⁻¹) or DMF (1670 - 1630 cm⁻¹) used in the purification are absent.¹ This is in line with the result of the ¹H-NMR spectroscopy where only minor amounts of solvent molecules were detected. Since none of these characteristic bands were detected, we assume that no impurities are present in larger amounts.

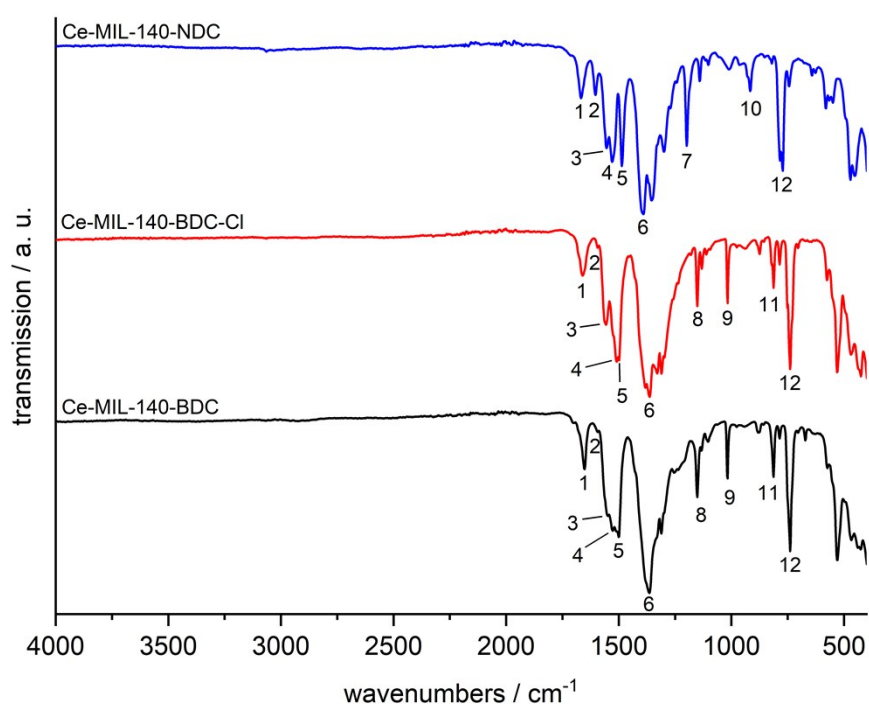


Figure S 7: IR spectra of Ce-MIL-140-BDC, Ce-MIL-140-BDC-Cl and Ce-MIL-140-NDC after purification. All labeled vibration bands were assigned in the following table and compared with literature values.¹

Table S 2: Assignment of bands in the IR spectra of the three different MOFs Ce-MIL-140-BDC, Ce-MIL-140-BDC-Cl and Ce-MIL-140-NDC.¹

Label	Kind of Vibration	Theoretical region ¹ [cm ⁻¹]	IR Bands [cm ⁻¹]		
			Ce-MIL-140-BDC	Ce-MIL-140-BDC-Cl	Ce-MIL-140-NDC
1	ν_{asym} (COO ⁻)	1695-1540	1653	1663	1672
2	$\nu_{aromatic}$ (C=C)	1625-1430	1592	1594	1602
3	$\nu_{aromatic}$ (C=C)	1625-1430	1551	1557	1555
4	$\nu_{aromatic}$ (C=C)	1625-1430 ¹	1529	1510	1529
5	$\nu_{aromatic}$ (C=C)	1625-1430	1500	1498	1484
6	ν_{sym} (COO ⁻)	1440-1335	1365	1382	1396
7	$\sigma_{aromatic, in-plane}$ (C-H)	1290-990	-	-	1196
8	$\sigma_{aromatic, in-plane}$ (C-H)	1290-990	1149	1151	-
9	$\sigma_{aromatic, in-plane}$ (C-H)	1290-990	1016	1016	-
10	$\sigma_{aromatic, out of plane}$ (C-H)	900-650	-	-	916
11	$\sigma_{aromatic, out of plane}$ (C-H)	900-650	812	812	-
12	$\sigma_{aromatic, out of plane}$ (C-H)	900-650	739	739	773

2.4. TG analysis

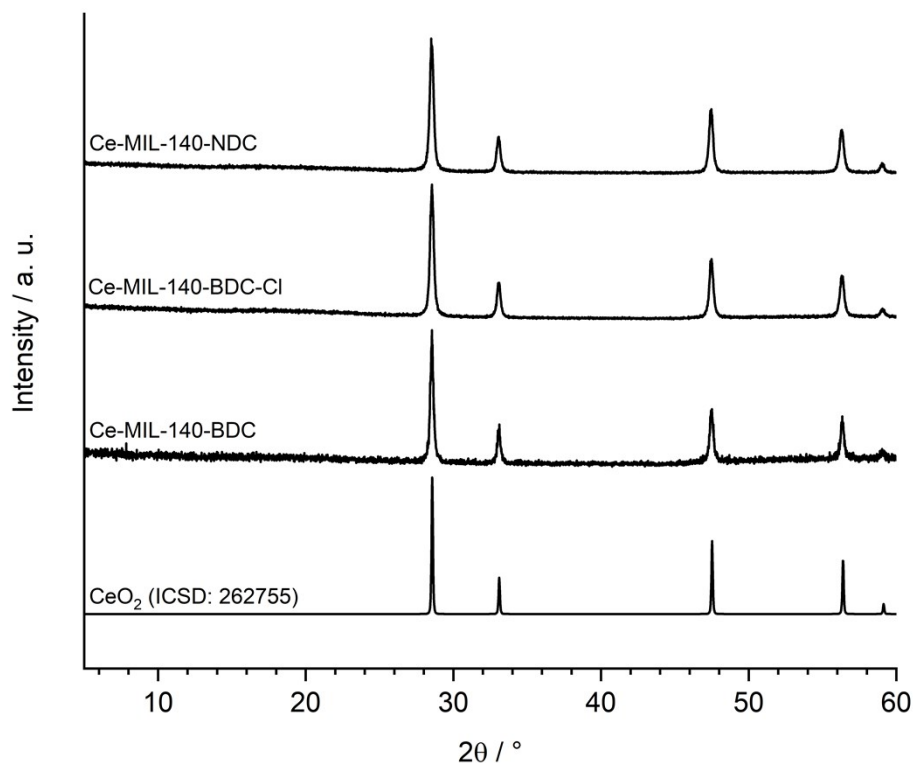


Figure S 8: Thermal decomposition products after TG analysis.

3. Powder X-ray diffraction (PXRD)

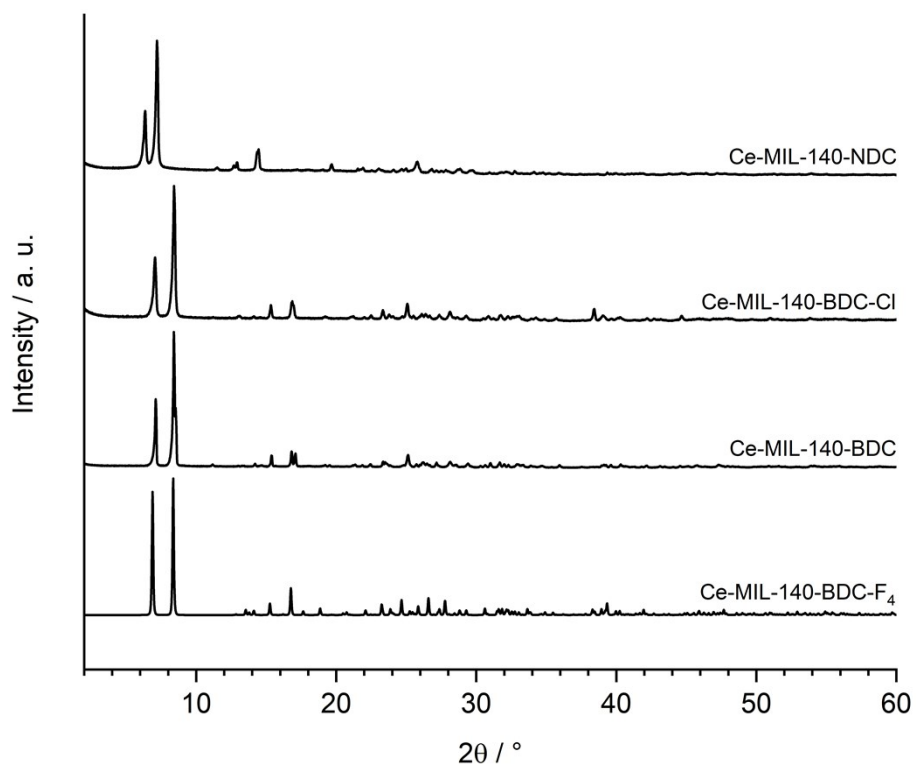


Figure S 9: Measured and calculated PXRD patterns of the three title compounds and Ce-MIL-140-BDC-F₄, respectively ($\lambda = 1.5401 \text{ \AA}$).²

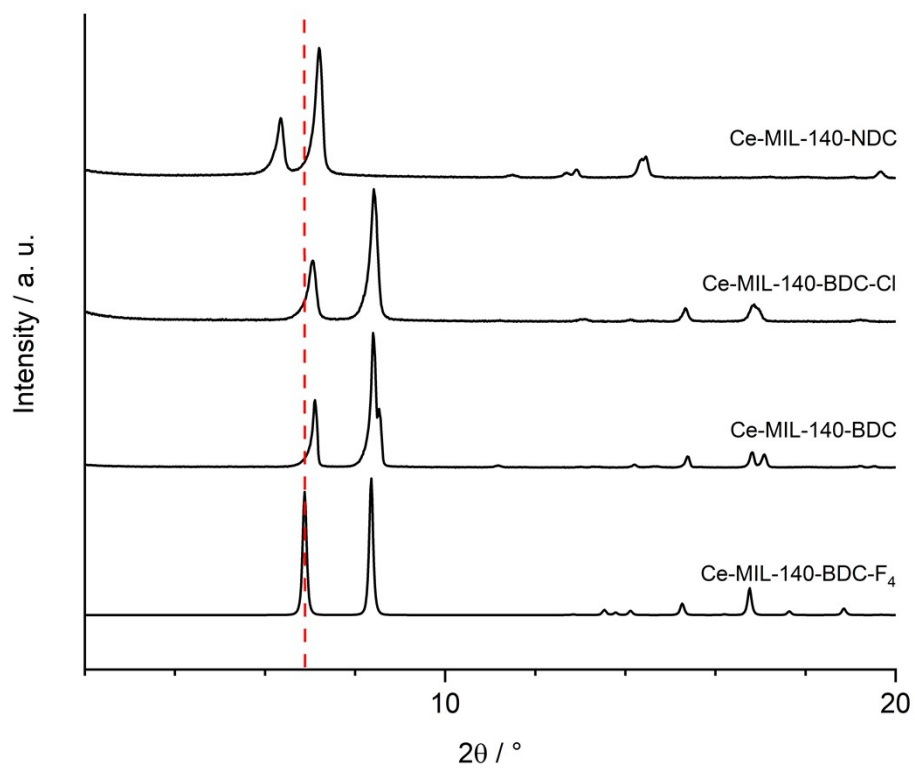


Figure S 10: Section of measured and calculated PXRD patterns of the three title compounds and Ce-MIL-140-BDC-F₄, ($\lambda = 1.5401 \text{ \AA}$) between 2 and 20° (2 Theta). The 200 peak of the latter is marked with a dashed red line.

4. Structure determination of Ce-MIL-140-BDC

The pattern of Ce-MIL-140-BDC could be indexed using TOPAS academics,³ suggesting a triclinic unit cell ($a = 8.165(2)$, $b = 11.547(2)$, $c = 13.983(2)$ Å, $\alpha = 113.06(1)$, $\beta = 102.25(1)$, $\gamma = 90.64(2)^\circ$). This unit cell can be related to the monoclinic *C*-centered cell of Zr-MIL-140 via supergroup-subgroup relationship. An initial model of the triclinic Ce-MIL-140 was generated by converting the structure of Zr-MIL-140A (space group *C2/c*) into a model with its subgroup symmetry *P*-1 using Powdercell.⁴ The indexed cell parameters were imposed and the structure was fully optimized by force-field calculations using Materials Studio⁵ and converted to its conventional setting using Platon.⁶ The thus obtained model could be successfully refined by Rietveld methods. The benzene rings (one on a general position and two on a center of inversion) had to be treated as rigid bodies, therefore no standard deviations are reported. All other atoms were freely refined using only distance restraints and element specific temperature factors. Residual electron density inside the channels was modeled using oxygen atoms with refinable occupancy which serve as dummy atoms for any kind of guest species. In addition, a slight preferred orientation along the *b*-axis was considered.

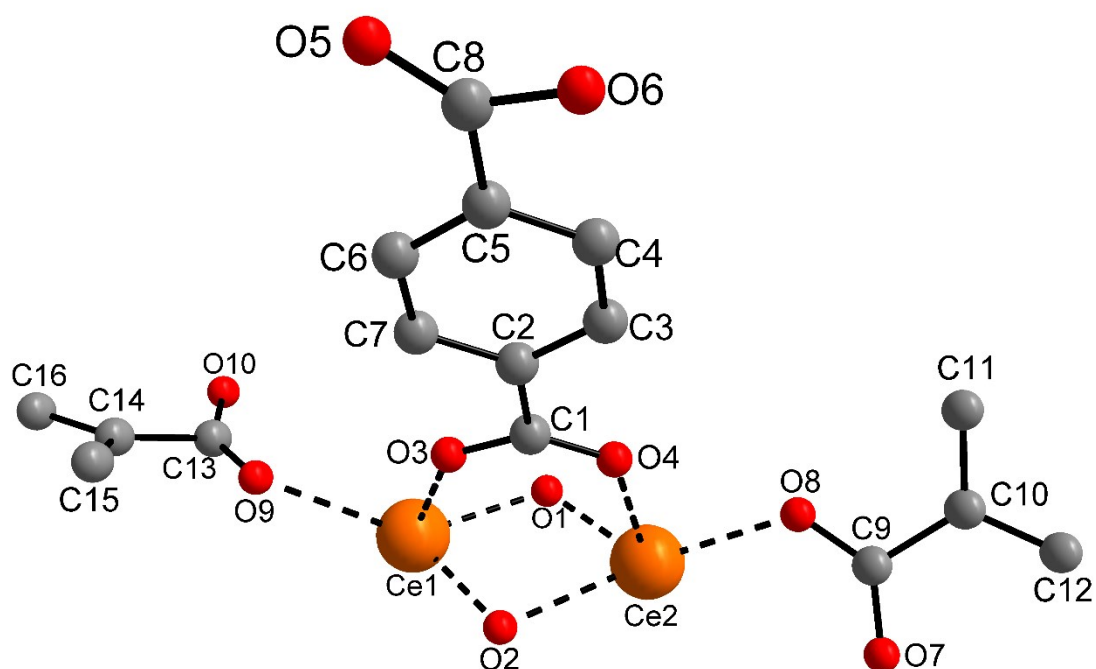


Figure S 11: Asymmetric unit of Ce-MIL-140-BDC obtained by Rietveld refinement. Solvent molecules are not shown.

Table S 3: Relevant bond distances observed in Ce-MIL-140-BDC.

Atom 1	Atom 2	Bond length [Å]	
Ce1	O1	2.29(4)	
	O2	2.12(4)	
	O3	2.43(3)	
	O5	2.20(3)	
	O7	2.39(3)	
Ce2	O9	2.66(3)	
	O1	2.11(4)	
	O2	2.50(5)	
	O4	2.46(3)	
	O6	2.65(3)	
	O8	2.44(3)	
	O10	2.21(2)	
	O3	C1	1.29(3)
	O4	C1	1.29(2)
	O5	C8	1.28(3)
O6	C8	1.31(3)	
O7	C9	1.28(3)	
O8	C9	1.27(3)	
O9	C13	1.26(3)	
O10	C13	1.25(2)	
C1	C2	1.482	
C2	C3	1.404	
	C7	1.408	
	C3	C4	1.398
	C4	C5	1.407
	C5	C6	1.405
		C8	1.481
C6		C7	1.396
C9		C10	1.529
C10		C11	1.411
		C12	1.418
	C11	C12	1.367
	C13	C14	1.557
	C14	C15	1.417
		C16	1.422
C15		C16	1.380

5. Le Bail-Fits

The cell parameters of Ce-MIL-140-BDC-Cl and Ce-MIL-140-NDC were refined starting from the crystallographic parameters of Zr-MIL-140-A and -B⁷ of the respective MOFs. Since for both Ce-MOFs no Rietveld refinement was possible, likely due to guest molecule and/or linker disorder, Le Bail fits were carried out (Figures. S11 and S12) to confirm phase purity and to determine the unit cell parameters.

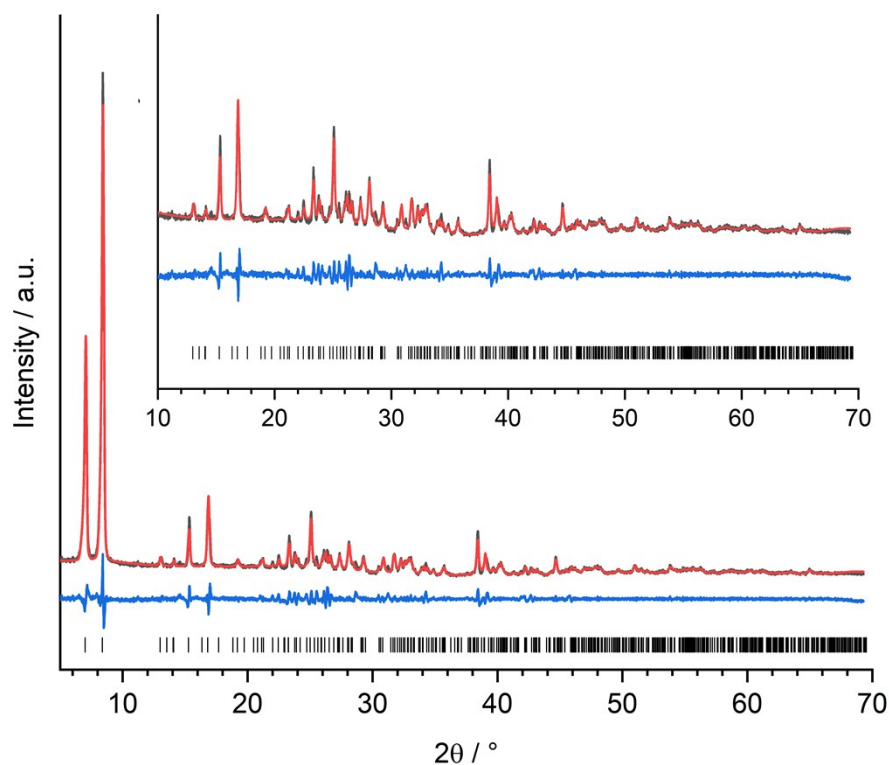


Figure S 12: Le Bail plot of Ce-MIL-140-BDC-Cl. The observed PXR pattern ($\lambda = 1.5401 \text{ \AA}$) (black), the calculated curve (red) and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks.

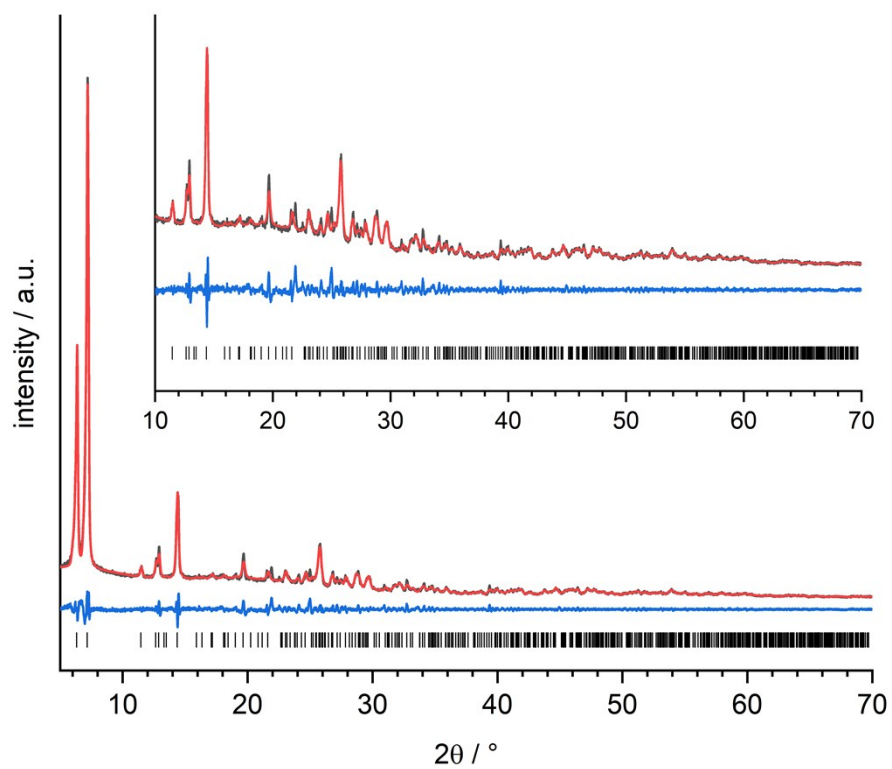


Figure S 13: Le Bail plot of Ce-MIL-140-NDC. The observed PXR pattern ($\lambda = 1.5401 \text{ \AA}$) (black), the calculated curve (red) and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks.

6. Sorption measurements

For all three title compounds type compounds different activation conditions were investigated. These results are summarized below (Table S4). The molar amount on N₂ uptake were determined based on the molar masses of pristine networks (Ce-MIL-140-BDC: 320.24 gmol⁻¹, Ce-MIL-140-BDC-Cl: 355.69 gmol⁻¹, Ce-MIL-140-NDC: 370.30 gmol⁻¹, Ce-MIL-140-BDC-F₄: 392.20 gmol⁻¹, Zr-MIL-140-A: 271.34 gmol⁻¹ and Zr-MIL-140-B: 321.40 gmol⁻¹). Additionally the theoretical micropore volume of Ce-MIL-140-BDC was determined ($V_{mic} = 0.135 \text{ cm}^3\text{g}^{-1}$) and the measured value is slightly lower ($V_{mic} = 0.103 \text{ cm}^3\text{g}^{-1}$).

Table S4: Results of the different investigated activation conditions for the N₂ sorption measurements. All activation procedures were carried out under reduced pressure ($\leq 10^{-2}$ kPa). If additional solvent treatments were performed, the compound was stirred for 24 h at room temperature in the named solvent and dried thereafter in air before activation. The results are compared with the reported values for Zr-MIL-140-A and-B as well as Ce-MIL-140-BDC-F₄.^{2,7}

Compound	Activation conditions [temperature, time, solvent treatment]	Specific surface area [m ² g ⁻¹]	Specific surface area [m ² mmol ⁻¹]
Ce-MIL-140-BDC	120°C, 16 h	78	24.9
	160°C, 16 h	88	28.2
	160°C, 16 h, MeOH	103	32.9
	160°C, 48 h	222	71.1
	220°C, 16 h	44	14.1
Ce-MIL-140-BDC-Cl	120°C, 16 h	18	6.4
	160°C, 16 h	14	4.9
	160°C, 16 h, MeOH	20	7.1
	160°C, 48 h	22	7.8
	220°C, 16 h	15	5.3
Ce-MIL-140-NDC	120°C, 16 h	124	45.9
	160°C, 16 h	114	42.2
	160°C, 16 h, MeOH	123	45.5
	160°C, 48 h	99	36.7
	220°C, 16 h	44	16.3
Zr-MIL-140-A ⁷	200, 16h	415	112.6
Zr-MIL-140-B ⁷	200, 16h	460	147.8
Ce-MIL-140-BDC-F ₄ ²	120, 16h	320	125.5

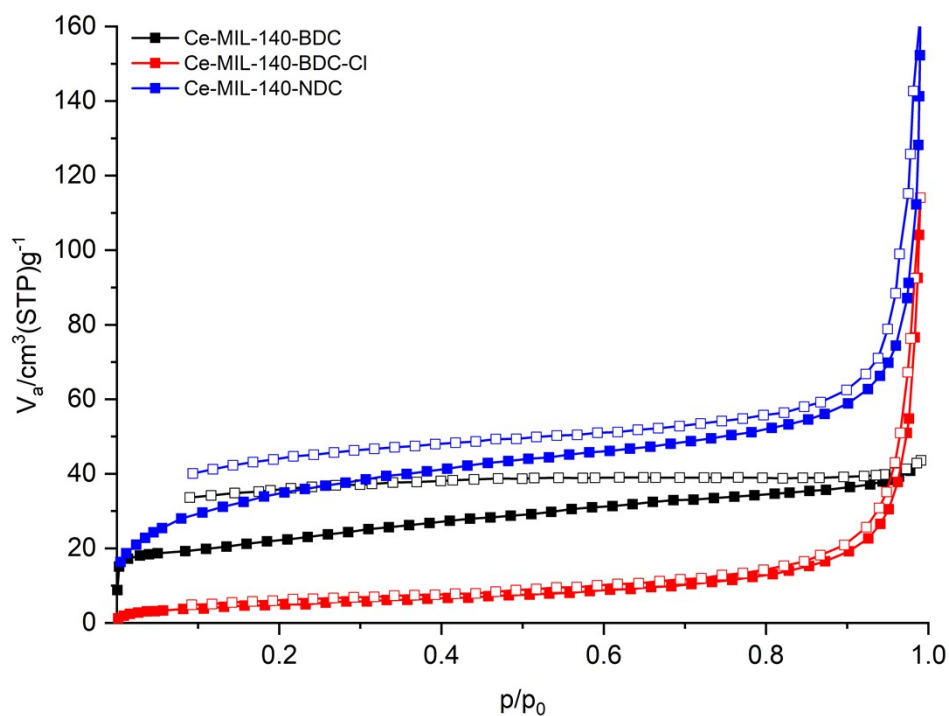


Figure S 14: N₂ isotherms of the activated (120 °C, 16 h, 10⁻² kPa) tile compounds measured at 77 K. The filled symbols mark the adsorption isotherm, the empty symbols mark the desorption isotherm.

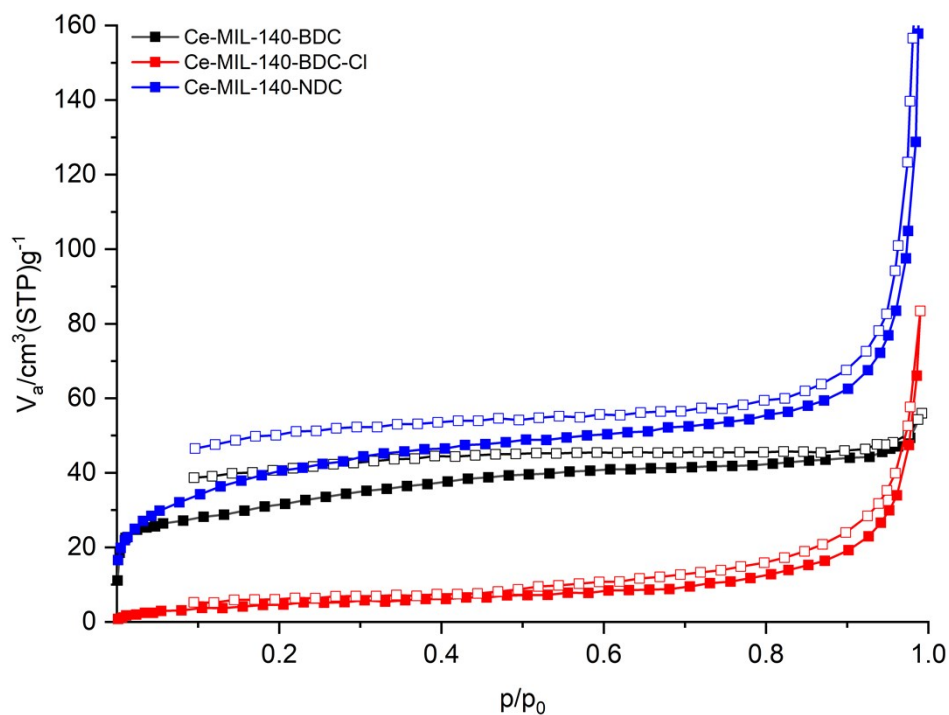


Figure S 15: N₂ isotherms of the activated (160 °C, 16 h, 10⁻² kPa) tile compounds measured at 77 K. The filled symbols mark the adsorption isotherm, the empty symbols mark the desorption isotherm.

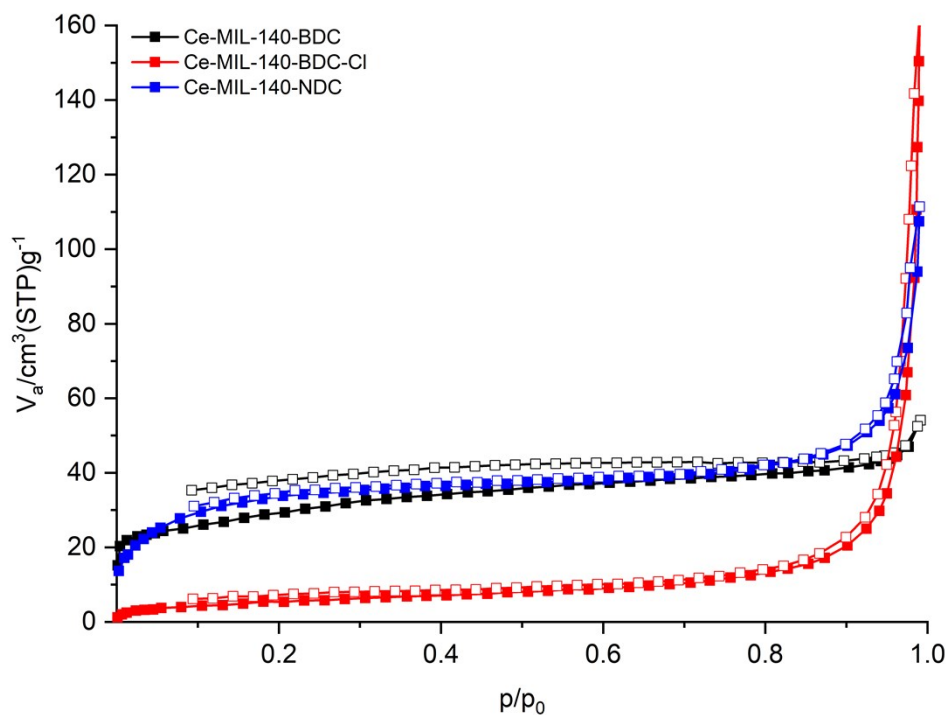


Figure S 16: N₂ sorption isotherms of the activated (24 h in stirring in MeOH, 160 °C, 16 h 10⁻² kPa) title compounds measured at 77 K. The filled symbols mark the adsorption isotherm, the empty symbols mark the desorption isotherm.

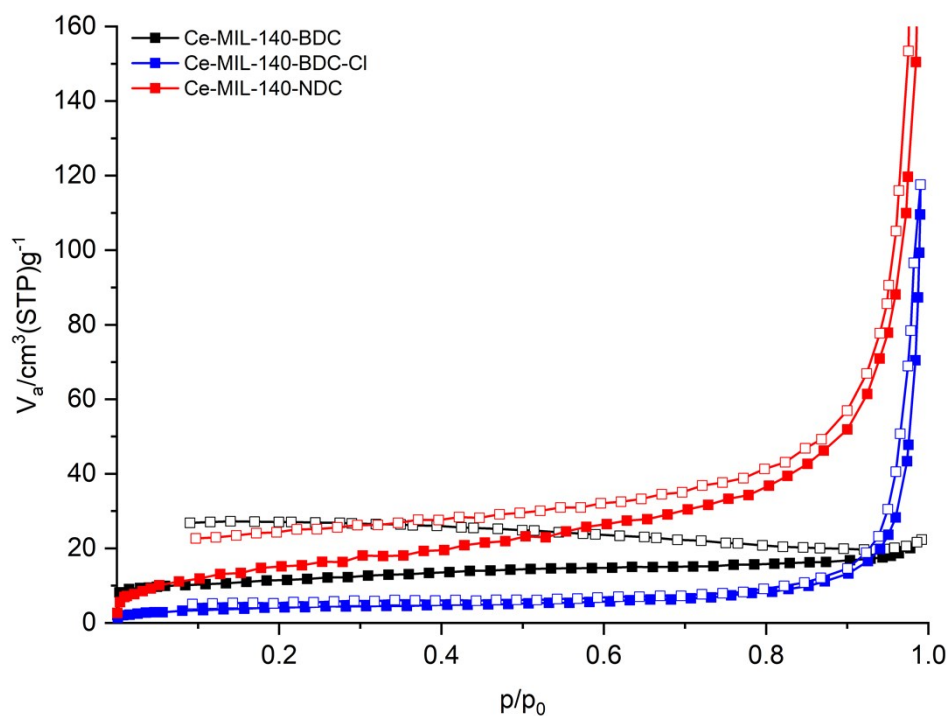


Figure S 17: N₂ sorption isotherms of the activated (220 °C, 16 h, 10⁻² kPa) title compounds measured at 77 K. The filled symbols mark the adsorption isotherm, the empty symbols mark the desorption isotherm.

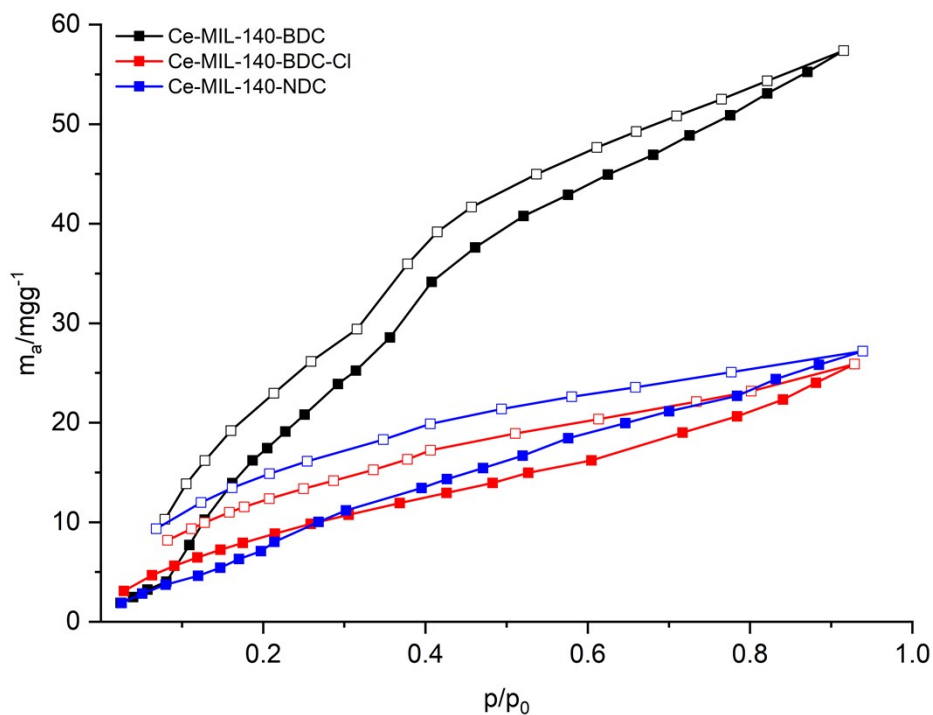


Figure S 18: Results of the H_2O sorption measurements at 25 °C of the activated (160 °C, 48 h, 10^{-2} kPa) title compounds. The filled symbols mark the adsorption isotherm, the empty symbols mark the desorption isotherm.

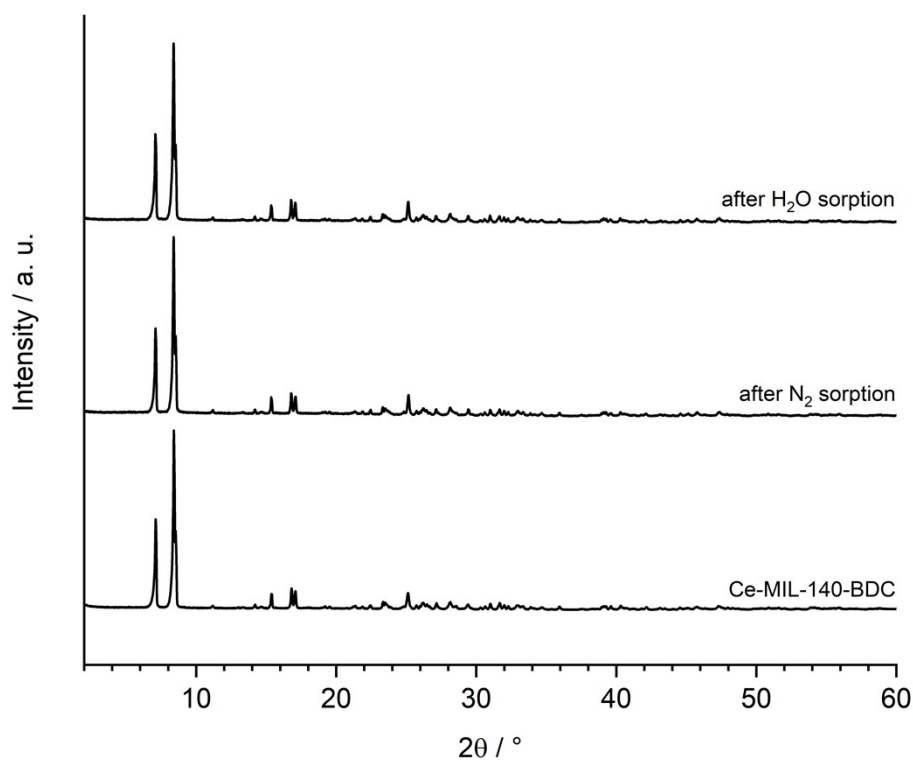


Figure S 19: PXRD ($\lambda = 1.5401 \text{ \AA}$) patterns of Ce-MIL-140-BDC before and after sorption measurements. Before the sorption measurements the compound was activated at 160 °C for 48 h under reduced pressure (10^{-2} kPa).

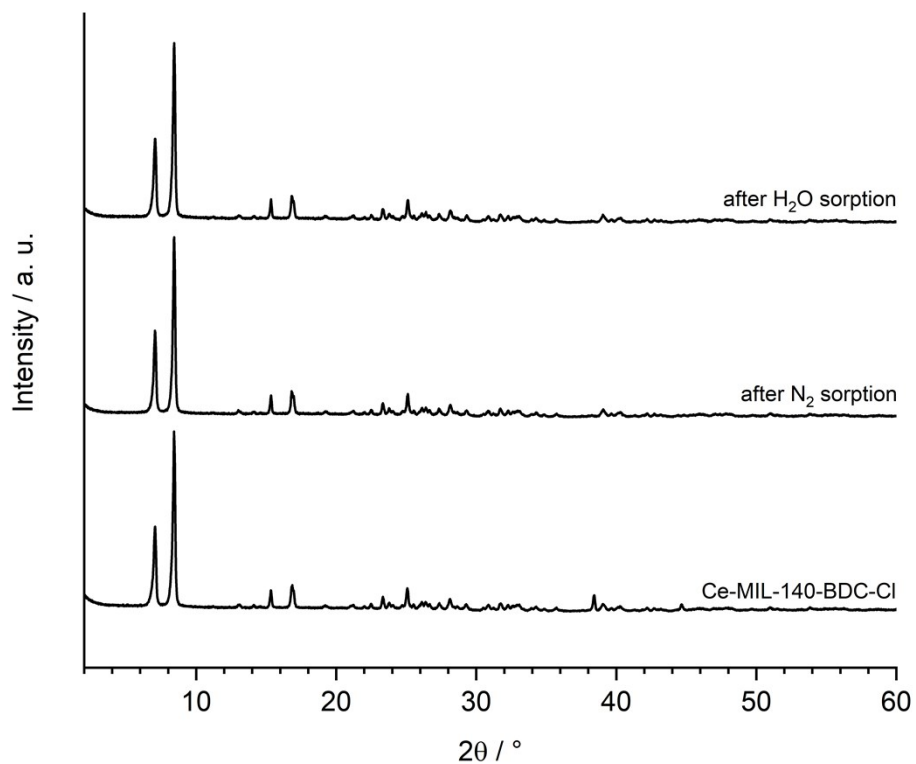


Figure S 20: PXRD ($\lambda = 1.5401 \text{ \AA}$) patterns of Ce-MIL-140-BDC-Cl before and after sorption measurements. Before the sorption measurements the compound at 160 °C for 48 h under reduced pressure (10^{-2} kPa).

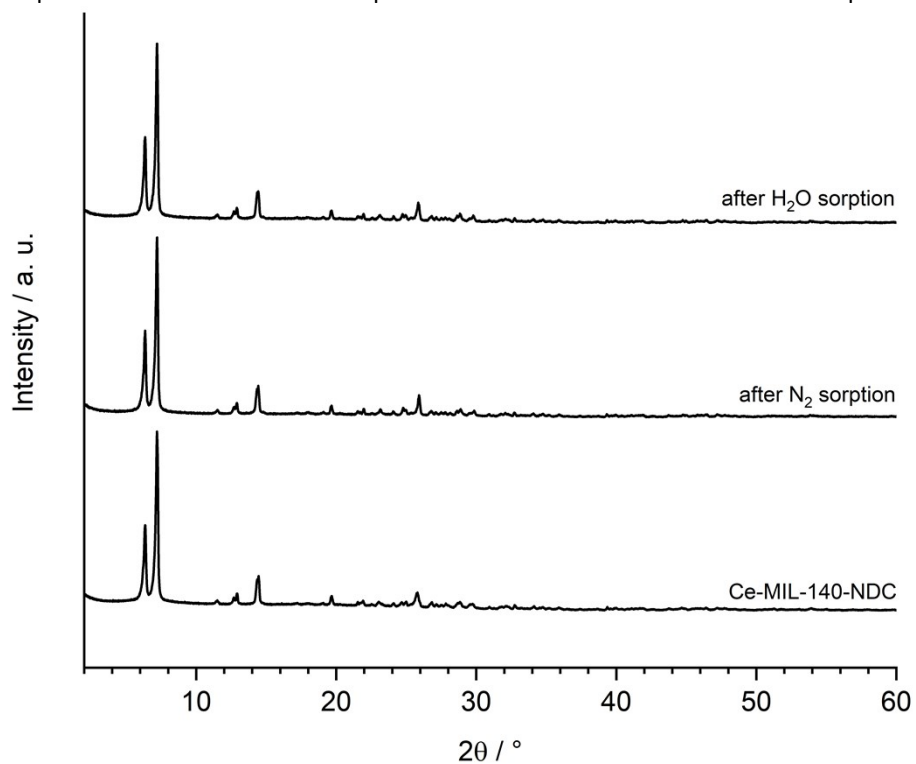


Figure S 21: PXRD ($\lambda = 1.5401 \text{ \AA}$) patterns of Ce-MIL-140-NDC before and after sorption measurements. Before the sorption measurements the compound at 160 °C for 48 h under reduced pressure (10^{-2} kPa).

7. Variable temperature (VT) PXRD

All title compounds were investigated by VT-PXRD to determine their thermal stability. Therefore, capillaries were prepared as described in the experimental section and heated up to 700 °C in steps of 10 °C.

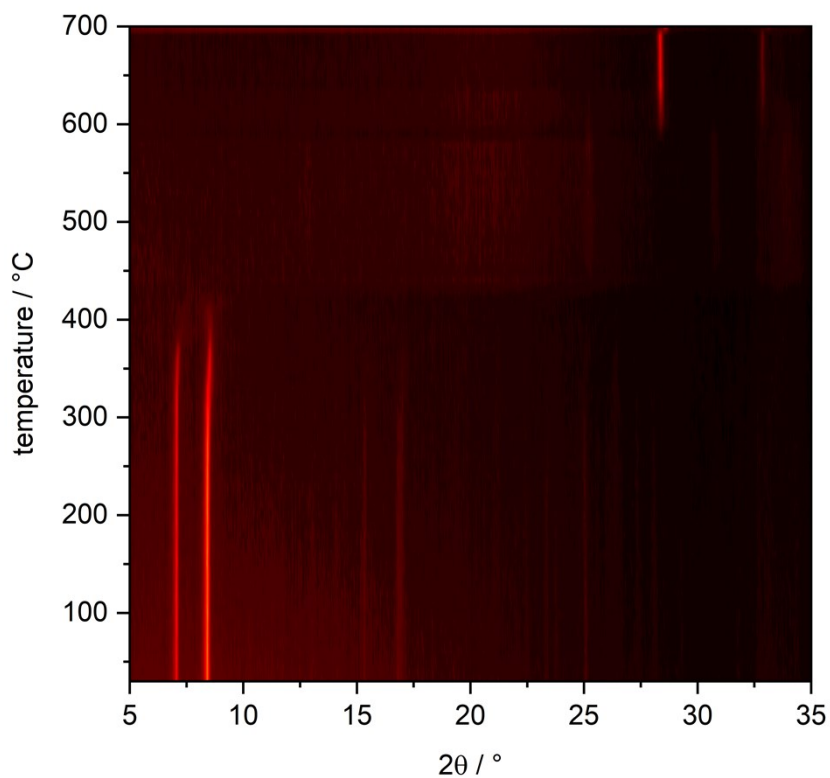


Figure S 22: Results of the VT-PXRD measurement of Ce-MIL-140-BDC.

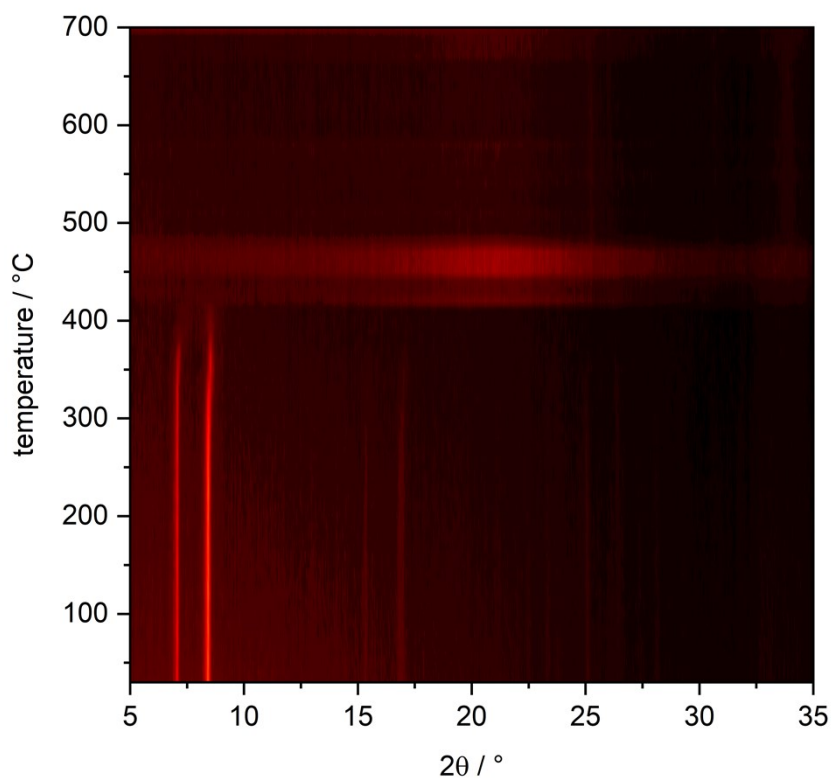


Figure S 23: Results of the VT-PXRD measurement of Ce-MIL-140-BDC-Cl.

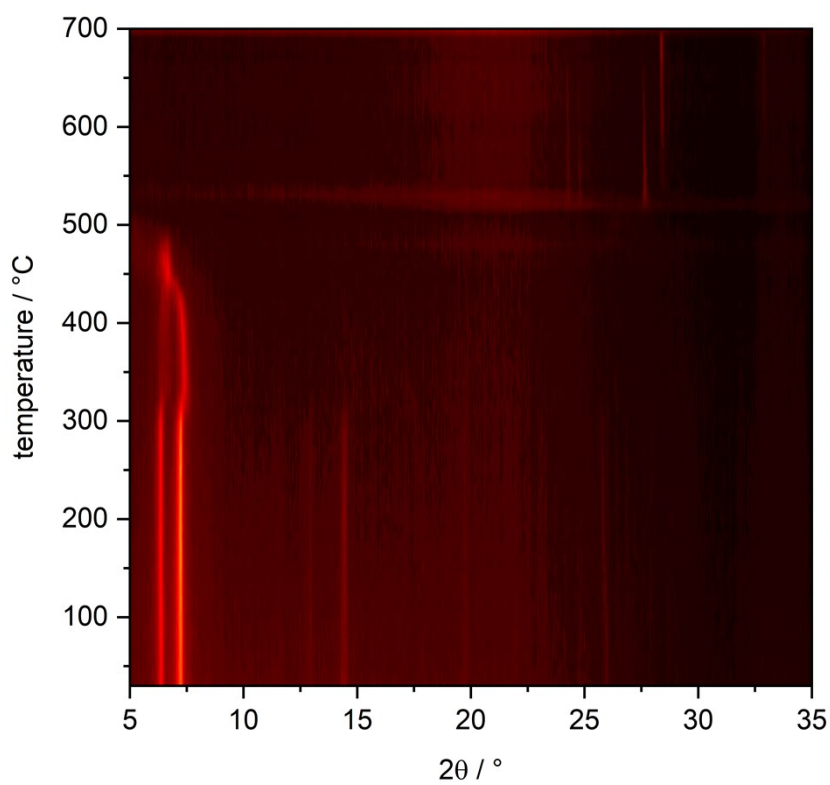


Figure S 24: Results of the VT-PXRD measurement of Ce-MIL-140-NDC.

8. Chemical stability

The chemical stability of all title compounds was investigated in different solvents. Therefore, around 5 mg of the MOF product were placed in a glass vial with stirring bar and 3 mL of the solvent was added. This mixture was stirred for 24 h and thereafter the crystallinity of the remaining solid was investigated by PXRD.

Table S 5: Summarized results of the stability tests of the three title compounds.

Solvent	Ce-MIL-140-BDC	Ce-MIL-140-BDC-Cl	Ce-MIL-140-NDC
water	Ⓜ	Ⓜ	Ⓜ
ethanol	Ⓜ	Ⓜ	Ⓜ
acetone	Ⓜ	Ⓜ	Ⓜ
DMF	Ⓜ	Ⓜ	Ⓜ
DMSO	Ⓜ	Ⓜ	Ⓜ
acetonitrile	Ⓜ	Ⓜ	Ⓜ
methanol	Ⓜ	Ⓜ	Ⓜ
2M NaOH	Ⓜ	Ⓜ	Ⓜ
2M HCl	Ⓜ	Ⓜ	Ⓜ

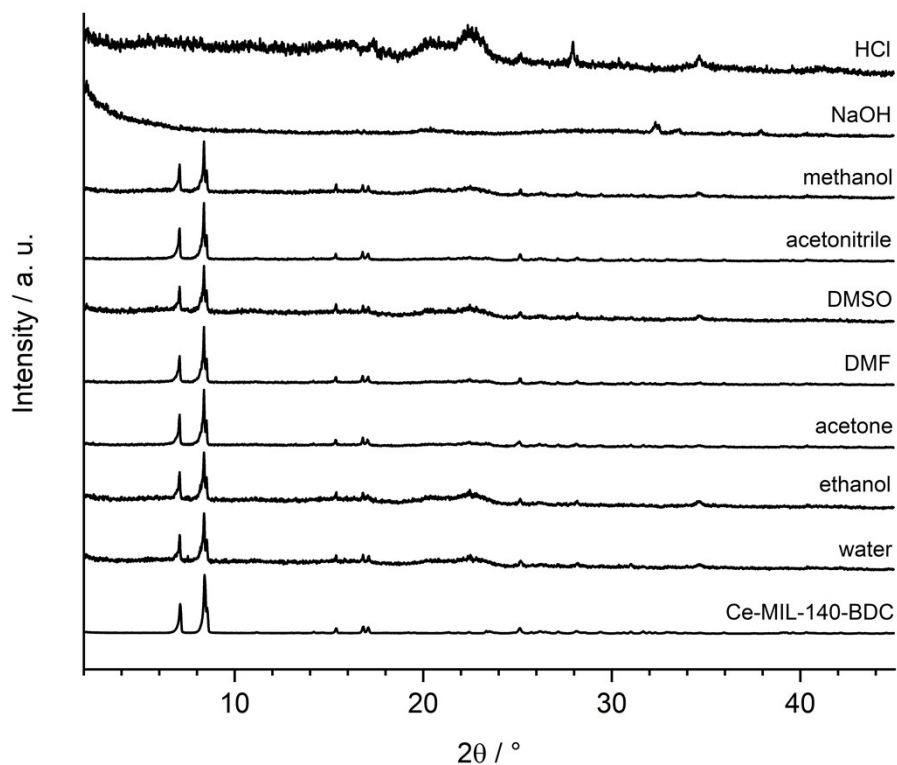


Figure S 25: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-BDC after stirring in different organic solvents, water, sodium hydroxide (2 mol/l) and hydrochloric acid(2 mol/l) for 24 h at room temperature.

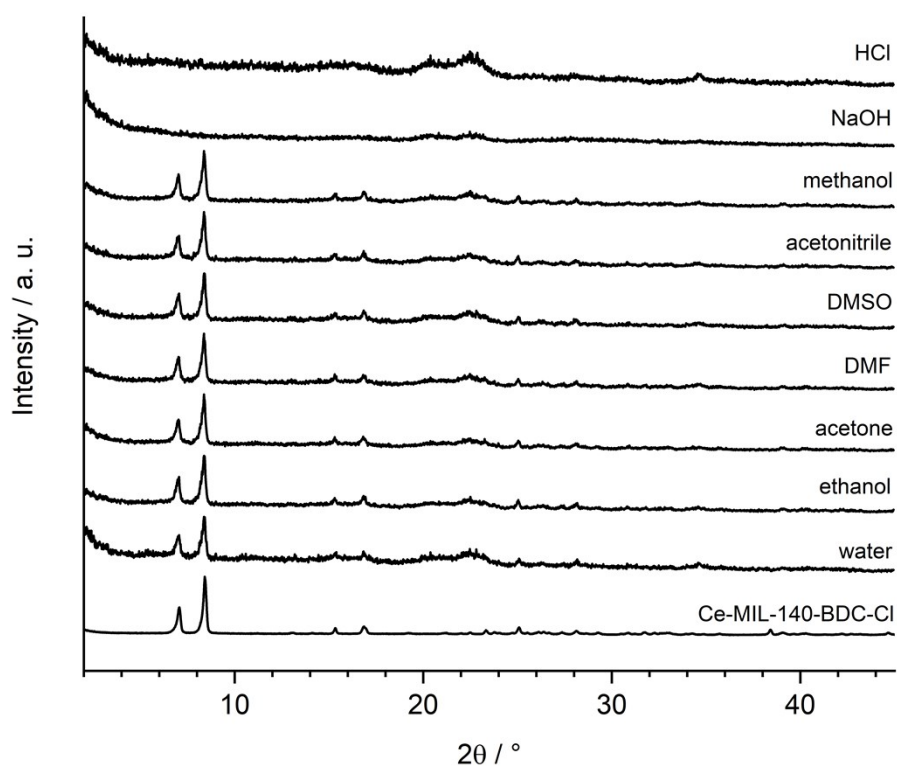


Figure S 26: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-BDC-Cl after stirring in different organic solvents, water, sodium hydroxide (2 mol/l) and hydrochloric acid (2 mol/l)for 24 h at room temperature.

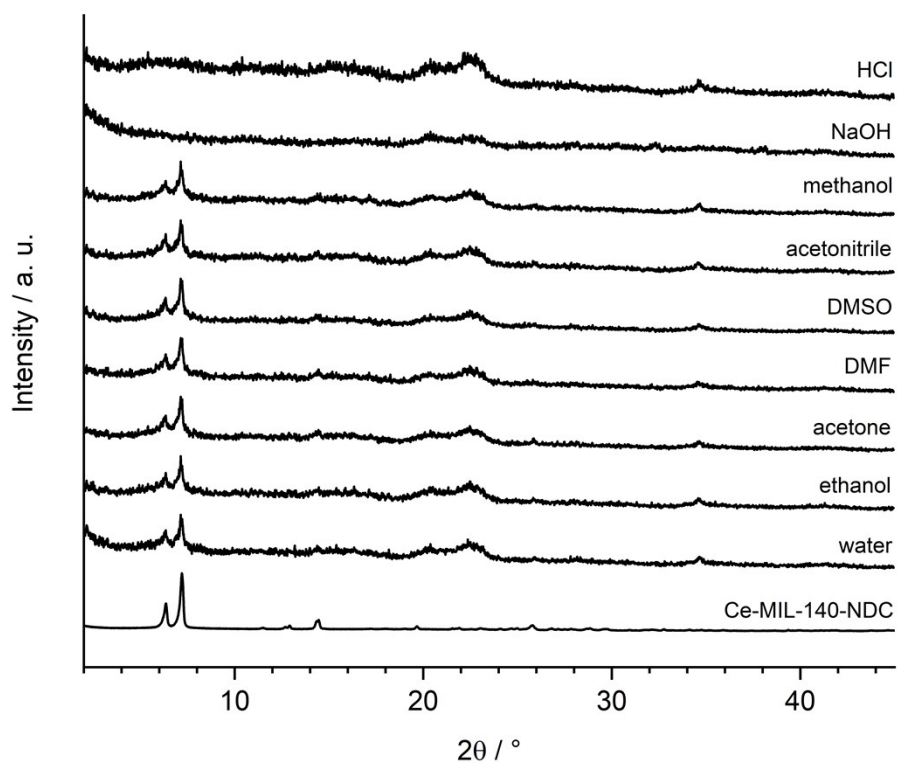


Figure S 27: PXRD patterns ($\lambda = 1.5401 \text{ \AA}$) of Ce-MIL-140-NDC after stirring in different organic solvents, water, sodium hydroxide (2 mol/l) and hydrochloric acid (2 mol/l) for 24 h at room temperature.

9. Literature

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