

Supporting Information

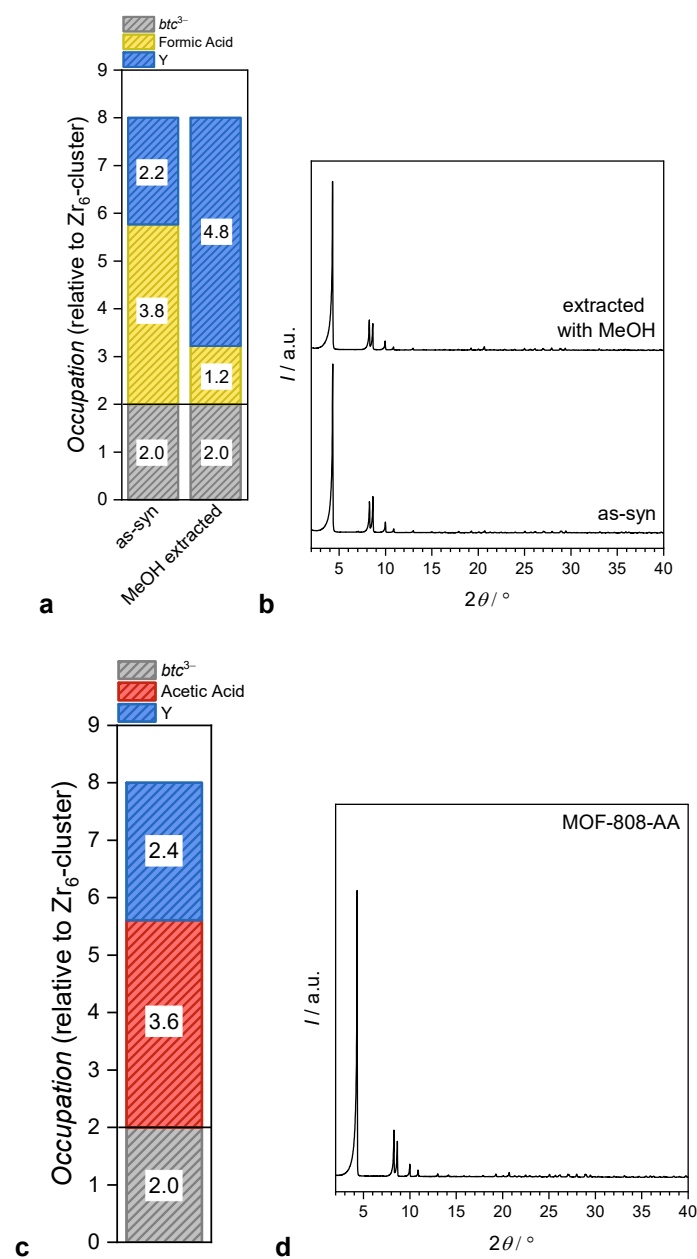


Figure S1: (a) Composition of MOF-808 synthesized using formic acid as modulator before and after MeOH extraction determined by $^1\text{H-NMR}$ spectroscopy (Y: H_2O , OH^- , Cl^-) and (b) the crystallinity of the materials after this procedure. (c) Composition of MOF-808 synthesized with acetic acid as modulator determined by $^1\text{H-NMR}$ spectroscopy and (d) the crystallinity of this material.

Table S1: EDXS data of Co-MOF-808 and Eu,Co-MOF-808 synthesized with different equivalents of cobalt(II) chloride salt.

Co-MOF-808							
added Co:Zr ₆	at% (Zr)	at% (Co)	at% (Eu)	at% (Cl)	Co:Zr ₆	Eu:Zr ₆	Cl:Zr ₆
0.5	2.57	0.30		0.81	0.70		1.89
1	1.32	0.27		0.53	1.23		2.41
2	0.86	0.17		0.41	1.19		2.86
3	0.52	0.12		0.21	1.38		2.42
4	7.79	1.94		2.6	1.49		2.00
5	0.96	0.22		0.48	1.38		3.00
6	2.24	0.54		1.23	1.45		3.29

Eu,Co-MOF-808							
added Co:Zr ₆	at% (Zr)	at% (Co)	at% (Eu)	at% (Cl)	Co:Zr ₆	Eu:Zr ₆	Cl:Zr ₆
0.5	1.73	0.04	0.37	0.24	0.14	1.28	0.83
1	2.02	0.12	0.45	0.32	0.36	1.34	0.95
2	4.86	0.31	1.05	0.75	0.38	1.30	0.93
3	0.81	0.06	0.19	0.13	0.44	1.41	0.96
4	0.86	0.07	0.21	0.15	0.49	1.47	1.05
5	3.89	5.54	0.47	1.2	0.51	1.21	1.30
6	2.05	0.20	0.45	0.47	0.59	1.32	1.38

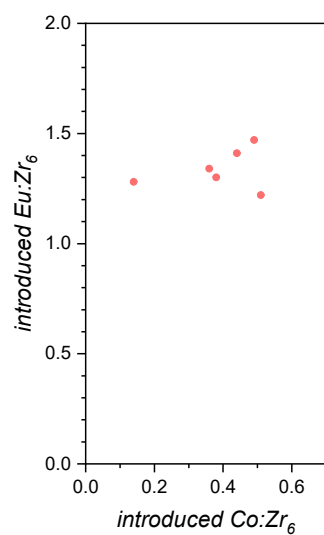


Figure S2: Amount of introduced europium cations in Eu,Co-MOF-808 depending on the introduced cobalt cations per Zr₆ cluster.

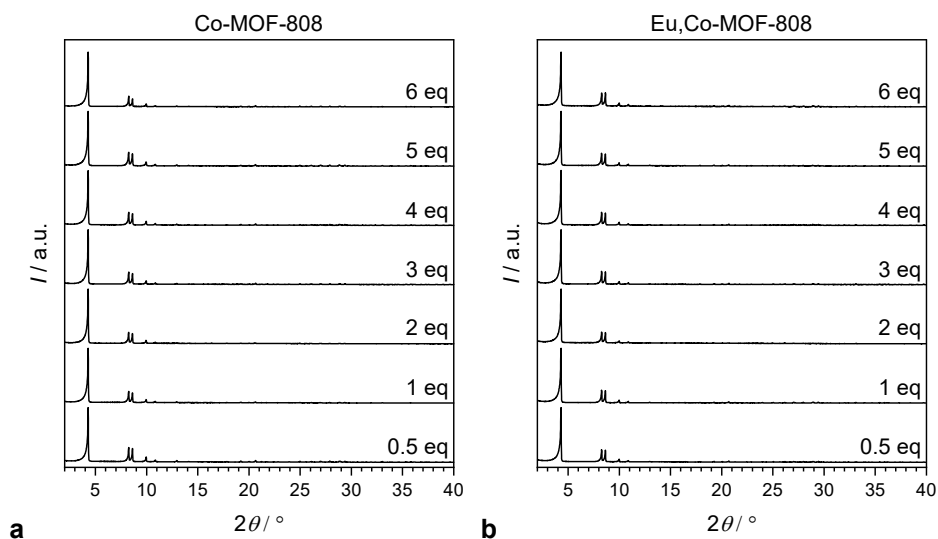


Figure S3: PXRDs of (a) Co-MOF-808 and (b) Eu,Co-MOF-808 synthesized with different equivalents of cobalt(II) chloride hexahydrate.

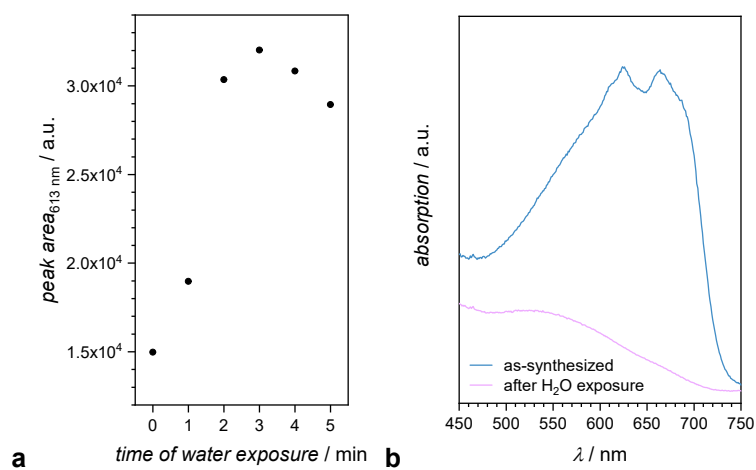


Figure S4: (a) Fluorescence intensity changes of Eu,Co-MOF-808 as a function of time of water exposure and UV-vis spectra before and after water exposure.

Table S2: EDXS data of Eu,Co-MOF-808 synthesized with 4 eq cobalt(II) chloride hexahydrate before and after water exposure.

	at% (Zr)	at% (Co)	at% (Eu)	at% (Cl)	Co:Zr ₆	Eu:Zr ₆	Cl:Zr ₆
as-synthesized	0.81	0.06	0.21	0.15	0.49	1.47	1.08
water exposed	0.86	0.07	0.27	0.20	0.49	1.46	1.05

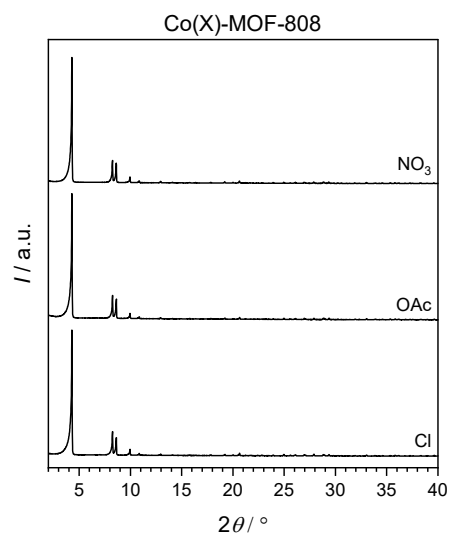


Figure S5: PXRDs of Co-MOF-808 synthesized with different cobalt salts: cobalt(II) chloride hexahydrate (bottom), cobalt(II) acetate tetrahydrate (mid) and cobalt(II) nitrate hexahydrate (top).

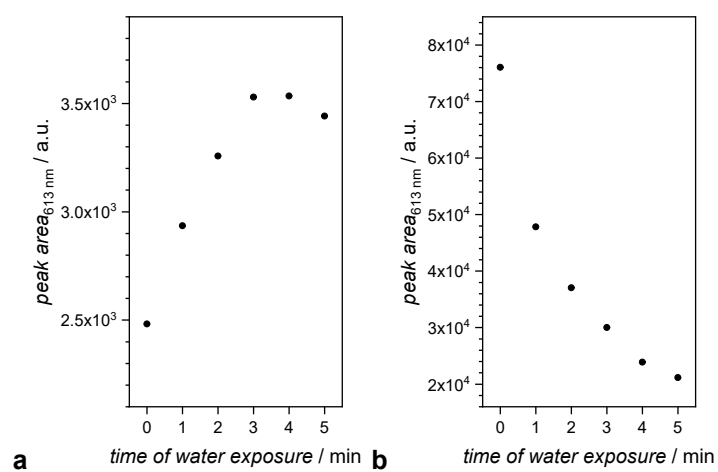


Figure S6: Changing fluorescence intensity of Eu,Co-MOF-808 synthesized with (a) cobalt(II) acetate tetrahydrate or (b) cobalt(II) nitrate hexahydrate depending on the time of water exposure.

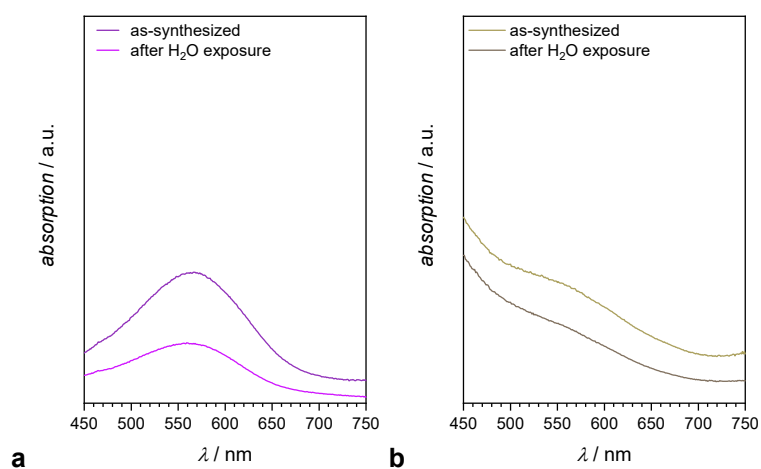


Figure S7: UV-vis spectra of Eu,Co-MOF-808 synthesized with (a) cobalt(II) acetate tetrahydrate or (b) cobalt(II) nitrate hexahydrate depending on the time of water exposure.

Table S3: EDXS data of Co-MOF-808-AA and Eu,Co-MOF-808-AA synthesized with different equivalents of cobalt(II) chloride salt.

Co-MOF-808-AA							
added Co:Zr ₆	at% (Zr)	at% (Co)	at% (Eu)	at% (Cl)	Co:Zr ₆	Eu:Zr ₆	Cl:Zr ₆
0.5	1.51	0.10		0.47	0.40		1.87
1	1.56	0.16		0.62	0.62		2.38
5	2.45	0.30		0.97	0.73		2.38
Eu,Co-MOF-808-AA							
added Co:Zr ₆	at% (Zr)	at% (Co)	at% (Eu)	at% (Cl)	Co:Zr ₆	Eu:Zr ₆	Cl:Zr ₆
0.5	2.58	0.10	0.22	0.54	0.23	0.51	1.26
1	2.29	0.15	0.15	0.62	0.39	0.39	1.62
5	2.01	0.15	0.12	0.58	0.45	0.36	1.73

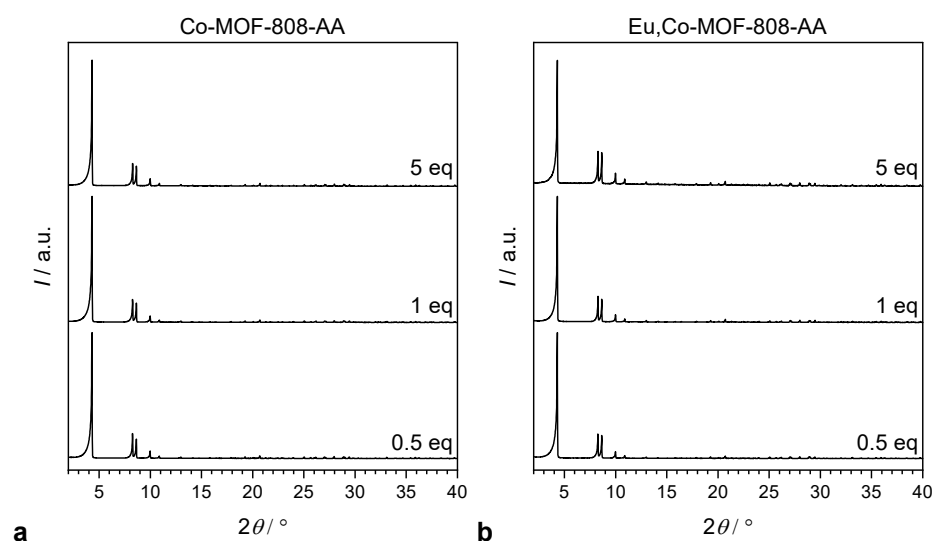


Figure S8: PXRDs of (a) Co-MOF-808-AA and (b) Eu,Co-MOF-808-AA synthesized with different equivalents of cobalt(II) chloride hexahydrate.

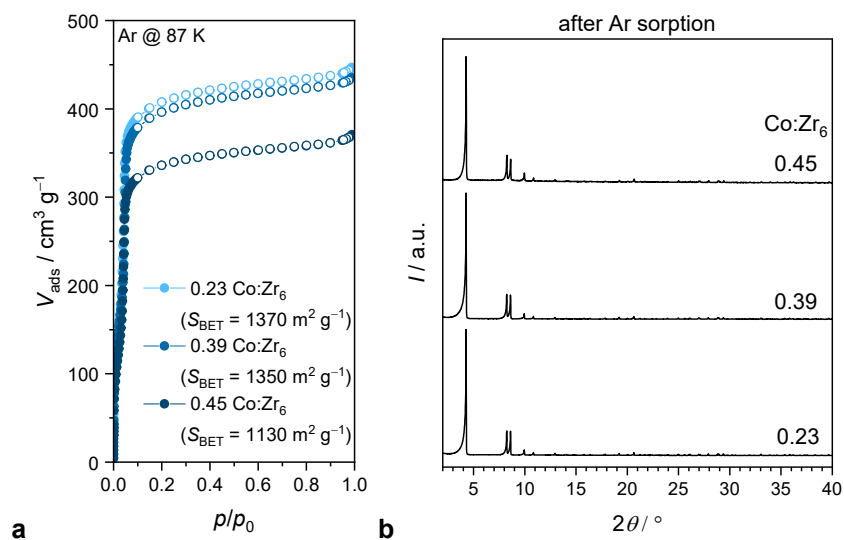


Figure S9: (a) Argon sorption isotherms of Eu,Co-MOF-808-AA containing 0.23, 0.39 and 0.45 Co:Zr₆ and (b) PXRDs of the materials after the measurements.

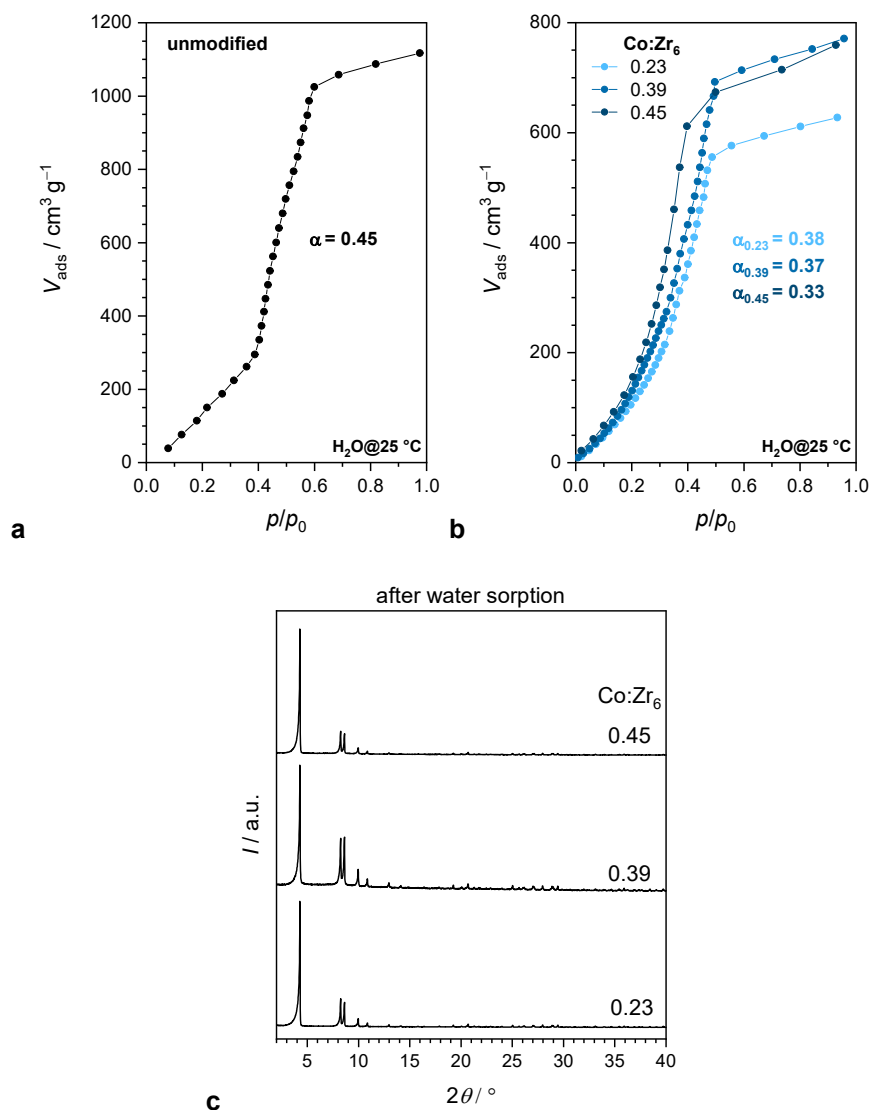


Figure S10: Water sorption isotherms at 25 °C of (a) unmodified and (b) europium- and cobalt-modified MOF-808-AA with different cobalt contents and the corresponding half-adsorption points α , which reflect the hydrophilicity of the material. (c) PXRDs after water sorption measurements.

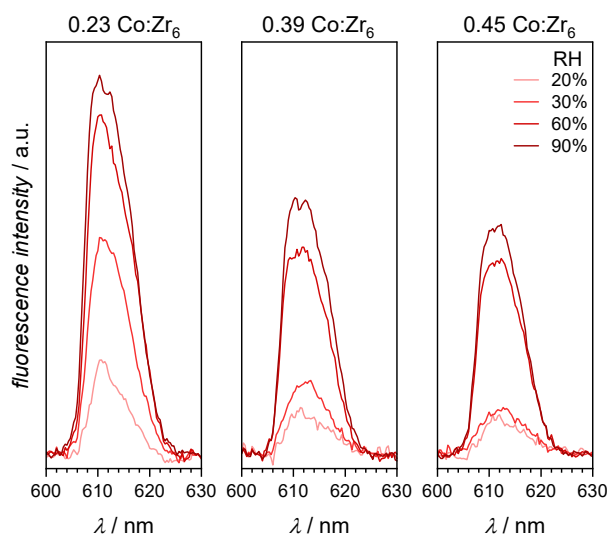


Figure S11: Fluorescence spectra of Eu,Co-MOF-808-AA (main peak at 613 nm) with different cobalt contents measured at relative humidities of 20%, 30%, 60% and 90% after 20 minutes exposure time.

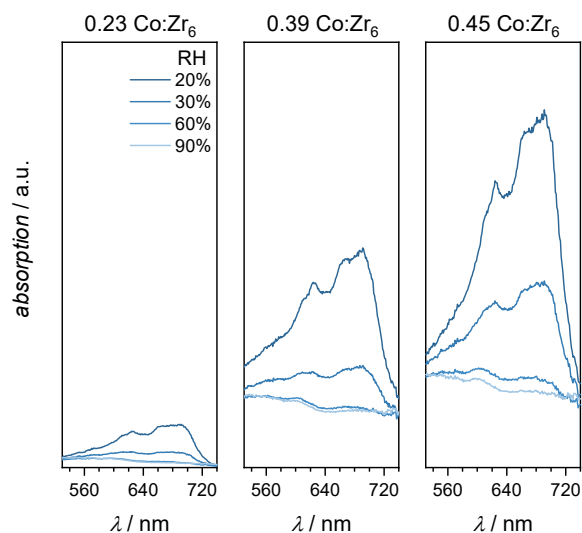


Figure S12: UV-vis spectra of Eu,Co-MOF-808-AA with different cobalt contents measured at relative humidities of 20%, 30%, 60% and 90% after 20 minutes exposure time.

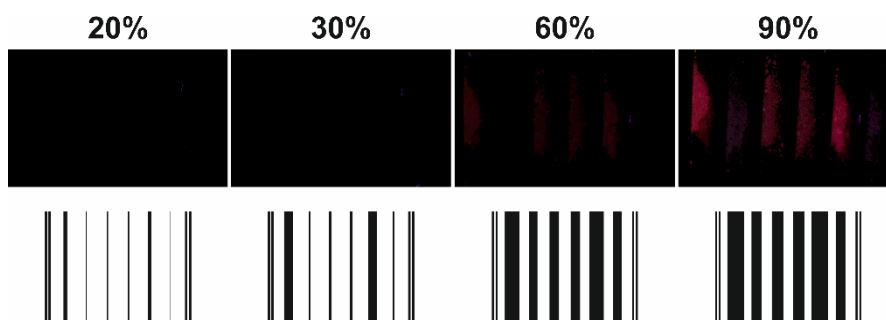


Figure S13: Pictures of Eu,Co-MOF-808-AA powders filled in the grooves of the barcode pattern in the row 0.23, 0.45, 0.39, 0.39, 0.23, 0.45 Co:Zr₆ at different relative humidities under the UV lamp (254 nm, top). The calculated peak areas from the measured fluorescence intensities of the main peak at 613 nm (see Figure 4a) were converted into bar widths (bottom), with the smallest width defined as 0.5 pt.

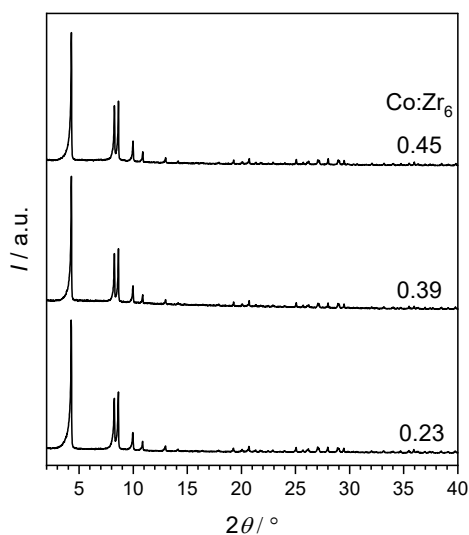


Figure S14: PXRDs of Eu,Co-MOF-808-AA including 0.23, 0.39 or 0.45 Co:Zr₆, respectively, after over three exposure cycles to relative humidities of 20, 30, 60 and 90% RH.

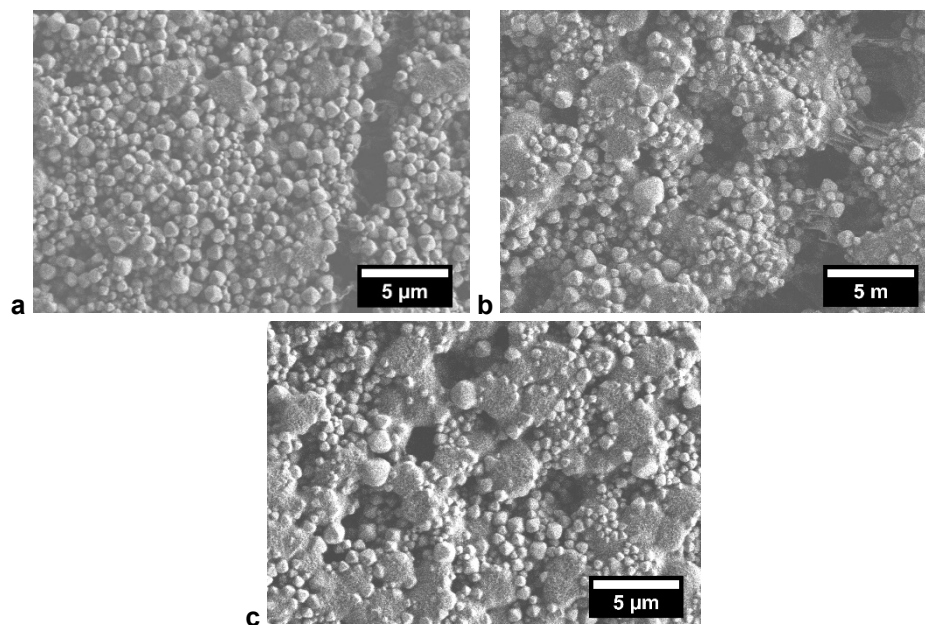


Figure S15: REM images of Eu,Co-MOF-808-AA@PVDF with different cobalt contents (modified with (a) 0.5 eq, (b) 1 eq and (c) 5 eq cobalt(II) chloride hexahydrate).

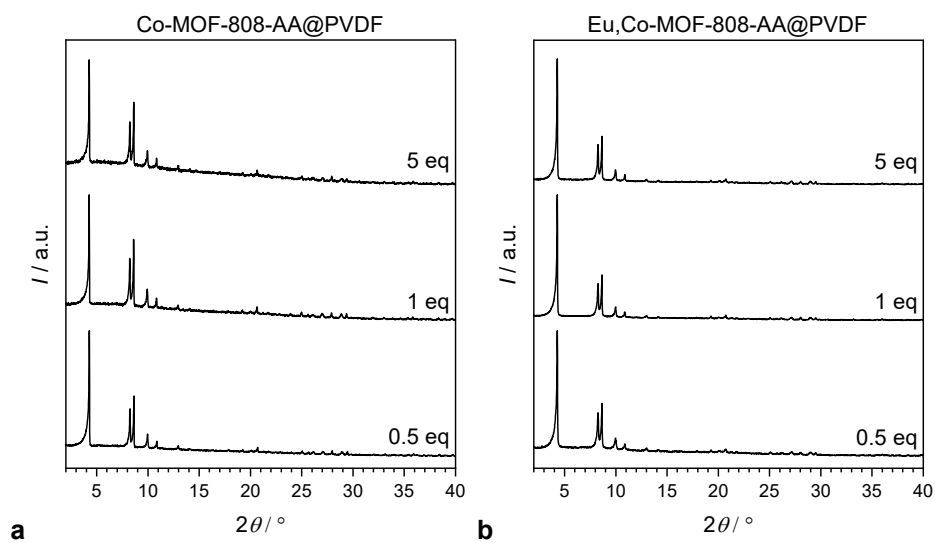


Figure S16: PXRDs of (a) Co-MOF-808-AA@PVDF and (b) Eu,Co-MOF-808-AA@PVDF synthesized with different equivalents of cobalt(II) chloride hexahydrate.

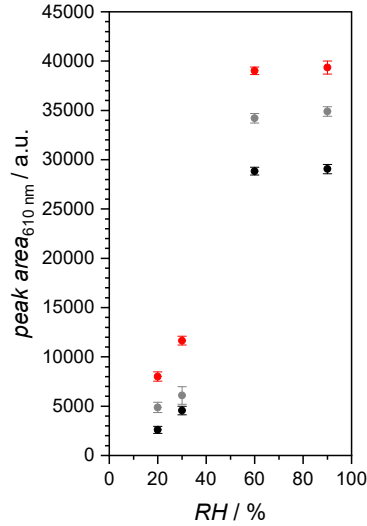


Figure S17: Average values of fluorescence read-out answers of Eu,Co-MOF-808-AA@PVDF with different cobalt contents at 610 nm calculated from the values detected from 15 minutes to 20 minutes after starting the exposure to the respective relative humidities.

Calculation of the bar widths of the barcode

The bar widths of the barcode shown in Figure 5c were calculated using the following formula

$$\text{bar width}_{x \text{ Co:Zr}_6} = \frac{\text{peak area}_{613 \text{ nm}, x \text{ Co:Zr}_6}(y\% \text{ RH})}{\text{peak area}_{613 \text{ nm}, 0.23 \text{ Co:Zr}_6}(20\% \text{ RH})} \cdot 0.5 \text{ pt} \quad (1)$$

with $x = 0.39$ or 0.45 and $y = 30\%$, 60% or 90% , as the smallest bar width is defined as 0.5 pt for the sample with the lowest peak areas at 613 nm :

$$\text{peak area}_{613 \text{ nm}, 0.23 \text{ Co:Zr}_6}(20\% \text{ RH}) = 996.31809 \text{ a.u.}$$

The exact bar widths of the barcode in Figure 5c are shown in Table S4 with the corresponding peak areas.

Table S4: Bar widths of the barcode at the respective relative humidity calculated from the fluorescence peak areas of the respective sample using formula (1).

RH / %	peak area _{613 nm} / a.u.			bar width / pt		
	0.23 Co:Zr ₆	0.39 Co:Zr ₆	0.45 Co:Zr ₆	0.23 Co:Zr ₆	0.39 Co:Zr ₆	0.45 Co:Zr ₆
20	5685.80	2353.49	996.32	2.9	1.2	0.5
30	13693.00	4276.30	2596.82	6.9	2.1	1.3
60	23156.27	14995.72	13016.27	11.6	7.5	6.5
90	26075.23	18152.55	15840.84	13.1	9.1	7.9