Supporting Information

Mixed-linker MOFs with CAU-10 structure: synthesis and gas sorption characteristics

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S1: ^{1}H-NMR-spectra of dissolved CAU-10-X samples in solution

CAU-10-H/Br (**2**)

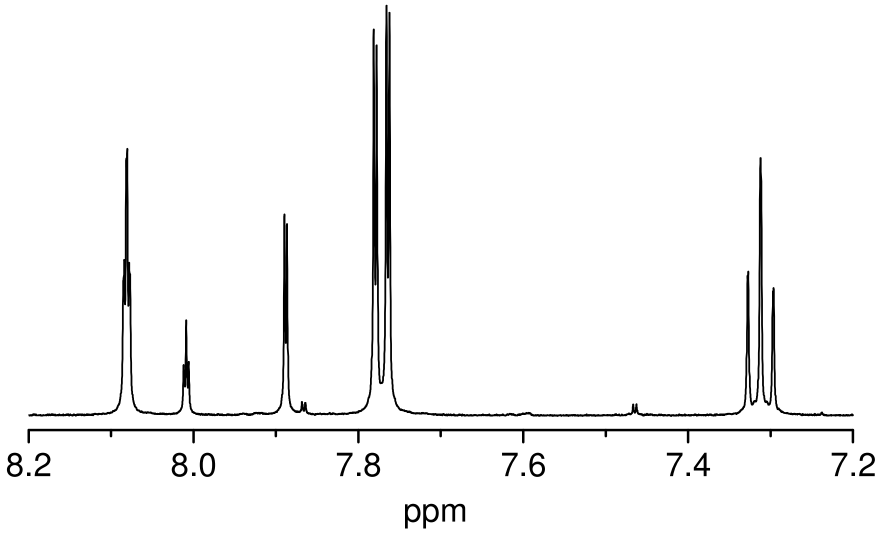


Figure S1: ^{1}H-NMR-spectrum of CAU-10-H/Br (**2**) after dissolution of the MOF in 5% NaOD in D_2O.

^{1}H-NMR spectrum of dissolved **2** (200 MHz, 5% NaOD in D_2O, 300 K, TMS): δ = 8.08 (m, BDC, 2-position), 8.01 (t, BDC-Br, 2-position), 7.89 (d, BDC-Br, 4,6-position), 7.77 (m, BDC, 4,6-position), 7.31 (t, BDC, 5-position) ppm.

CAU-10-NO_2/NH_2 (5)

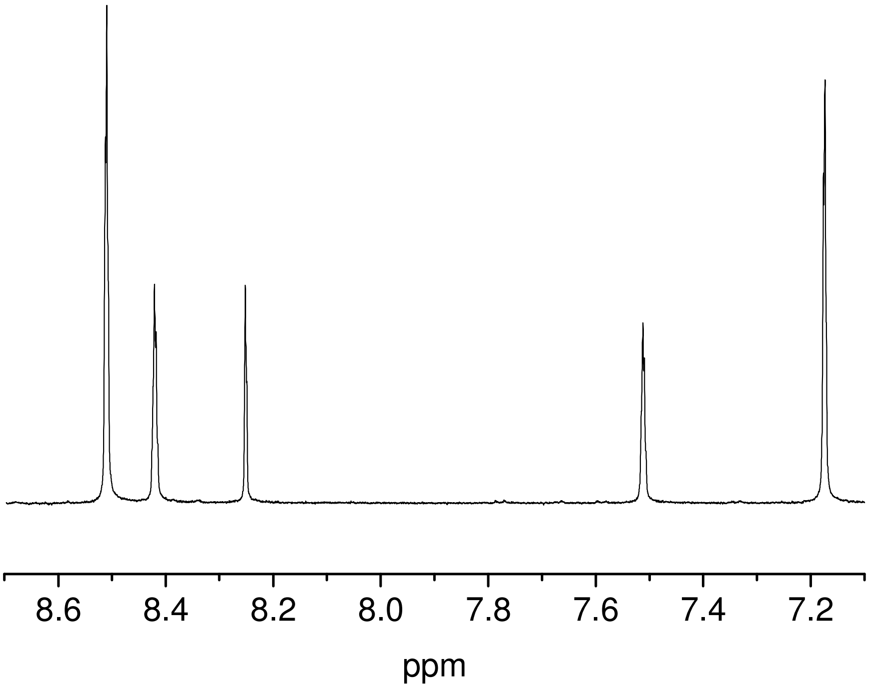


Figure S2: ^{1}H-NMR-spectrum of CAU-10-NO_2/NH_2 (**5**) after dissolution of the MOF in 5% NaOD in D_2O.

^{1}H-NMR spectrum of dissolved **5** (200 MHz, 5% NaOD in D_2O, 300 K, TMS): δ = 8.51 (d, BDC-NO_2, 4,6-position), 8.42 (t, BDC-NO_2, 2-position), 8.25 (s, formic acid), 7.51 (t, BDC-NH_2, 2-position), 7.17 (d, BDC-NH_2, 4,6-position) ppm. According to the integrals, the ratio BDC-NO_2 : BDC-NH_2 varies slightly between 5 : 4 and 4.7 : 4, thus the fraction of BDC-NH_2 is 44% to 46 %.

CAU-10-H/CH$_3$ (4)

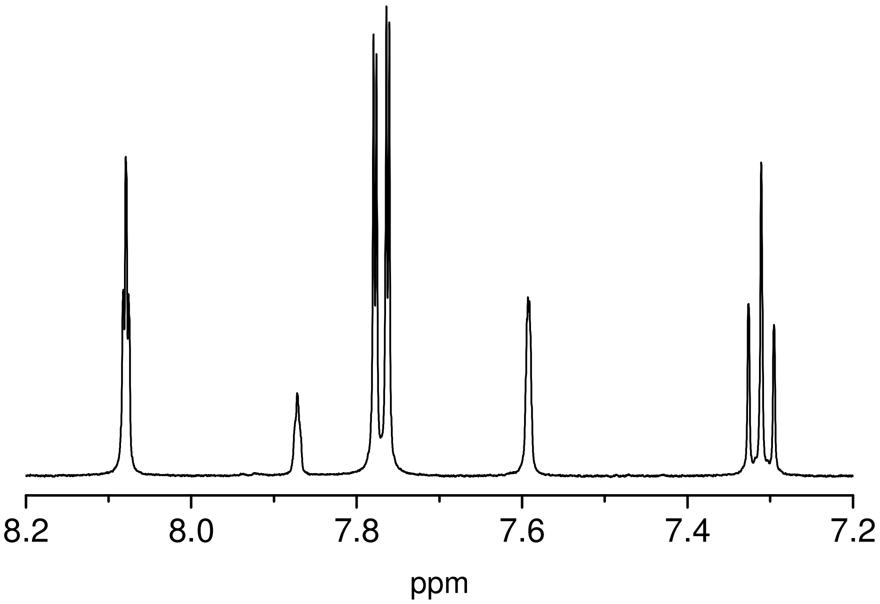


Figure S3: ^{1}H-NMR-spectrum of CAU-10-H/CH$_3$ (**4**) after dissolution of the MOF in 5% NaOD in D$_2$O.

^{1}H-NMR spectrum of dissolved **4** (200 MHz, 5% NaOD in D$_2$O, 300 K, TMS): δ = 8.08 (m, BDC, 2-position), 7.87 (s, BDC-CH$_3$, 2-position), 7.77 (m, BDC, 4,6-position), 7.59 (s, BDC-CH$_3$, 4,6-position), 7.31 (t, BDC, 5-position) ppm. According to the integrals, the ratio BDC : BDC-CH$_3$ varies between 3.6 : 1 and 3 : 1, thus the fraction of BDC-CH$_3$ is 21% to 25 %.

S2: Results of the Rietveld refinement of CAU-10-Br (1)

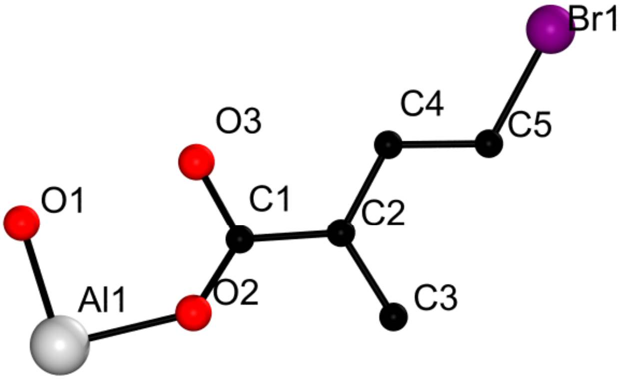


Figure S4: Assymetric unit of CAU-10-Br (**1**) with numbering scheme used in Tab. S1.

Table S1: Bond lengths in CAU-10-Br (1) in Å.

Al1	O1	1.83(2)
	O2	1.92(2)
	O3	1.95(2)
O2	C1	1.29(2)
O3	C1	1.29(2)
C1	C2	1.42(2)
C2	C3	1.39(1)
	C4	1.42(2)
C4	C5	1.41(1)
	C2	1.42(2)
C5	Br1	1.82(2)

S3: Additional XRPD-data for CAU-10-H/Br (2) and for CAU-10-H/CH$_3$ (4)

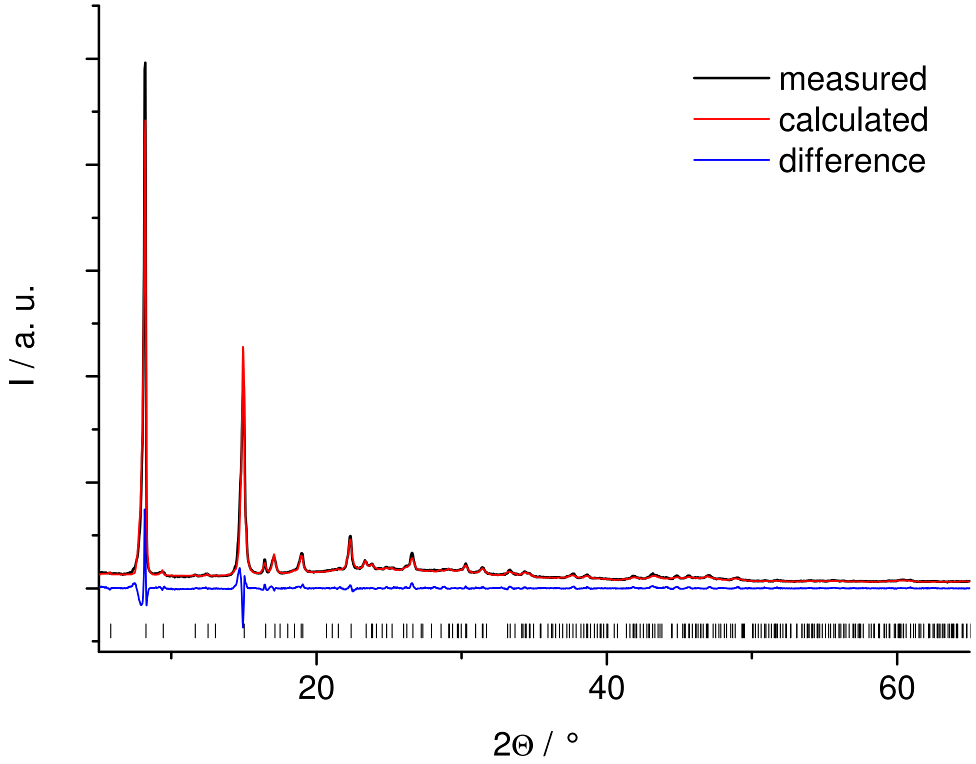


Figure S5: LeBail fit for CAU-10-H/Br (**2**) in the space group *I*4$_1$. The final R$_{WP}$ is 7.5 %, the refined cell parameters are *a* = *b* = 21.485(5) and *c* = 10.407(3) Å.

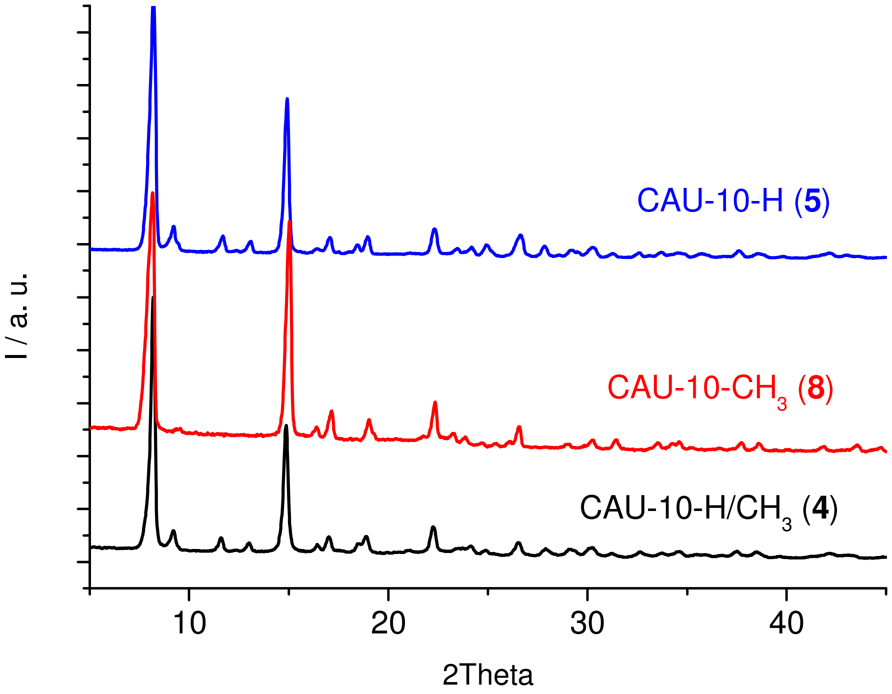


Figure S6: Comparison of the XRPD-patterns of CAU-10-H (**5**), CAU-10-CH$_3$ (**8**) and CAU-10-H/CH$_3$ (**4**), measured on a Stadi P Combi diffractometer equipped with an xy-stage with CuK$_{\alpha 1}$-radiation.

S4: Solid-state NMR spectroscopy

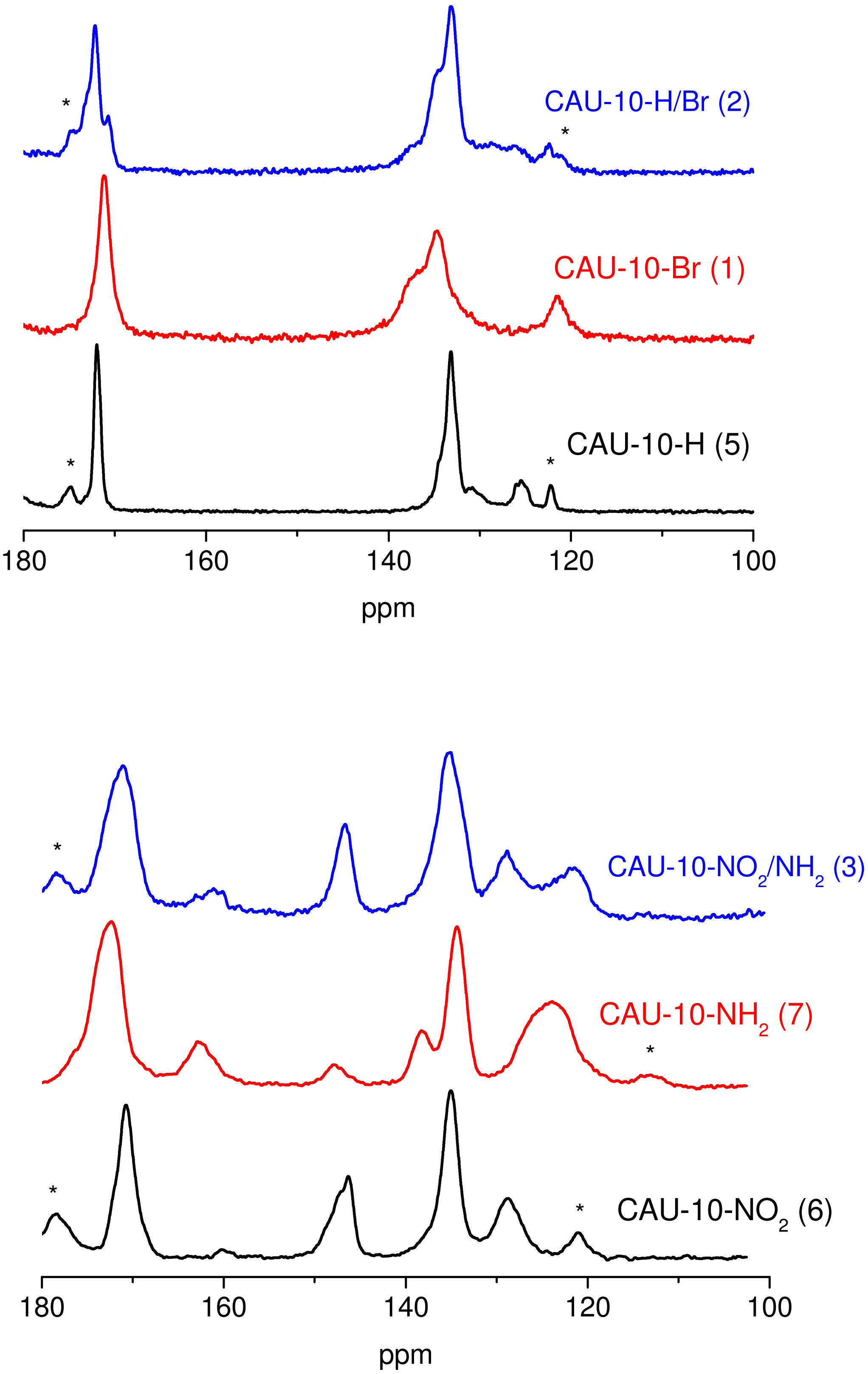
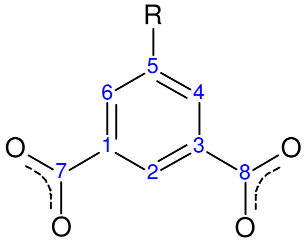


Figure S7: ^{13}C-CP-MAS-NMR spectra of **1**, **2**, **3, 5**, **6**, and **7**. The MOFs based on mixtures of linker molecules clearly show a spectrum that results from the combination of the pure-linker MOFs. Asterisks mark spinning side bands.

Table S2: Assignment of ^{13}C-NMR-signals (ppm).

C-atom	CAU-10-H	CAU-10-Br	CAU-10-NO_2	CAU-10-NH_2
7,8	172	171	171	172
1,3	133	134	135	134
2	131	134	135	124
4,6	135	138	129	124
5	125	121	146	148, 138
9				163



The ^{13}C-signals were assigned using data measured in solution.[1] Due to the limited resolution of the spectra, the signals for the mixed-linker MOFs are not assigned. The signal for atom 9 is caused by the partial formylation of the NH_2-group in **3** and **7** during the synthesis and thus belongs to the CHO-NH-aryl-group. This modification causes also two signals for the atom in 5-position of aminoisophthalate ions in these compounds. The signal at 148 ppm belongs to the formylated molecule, while the signal at 138 ppm is characteristic for the non-modified aminoisophthalate ion.

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[1] SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 20.8.2012)

S5: IR-spectroscopy

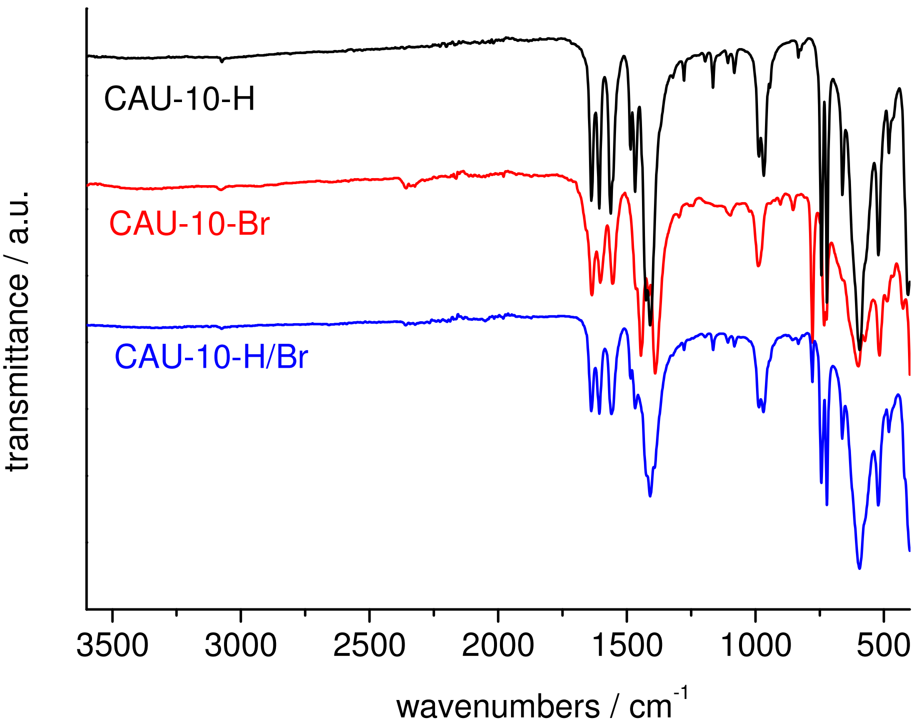
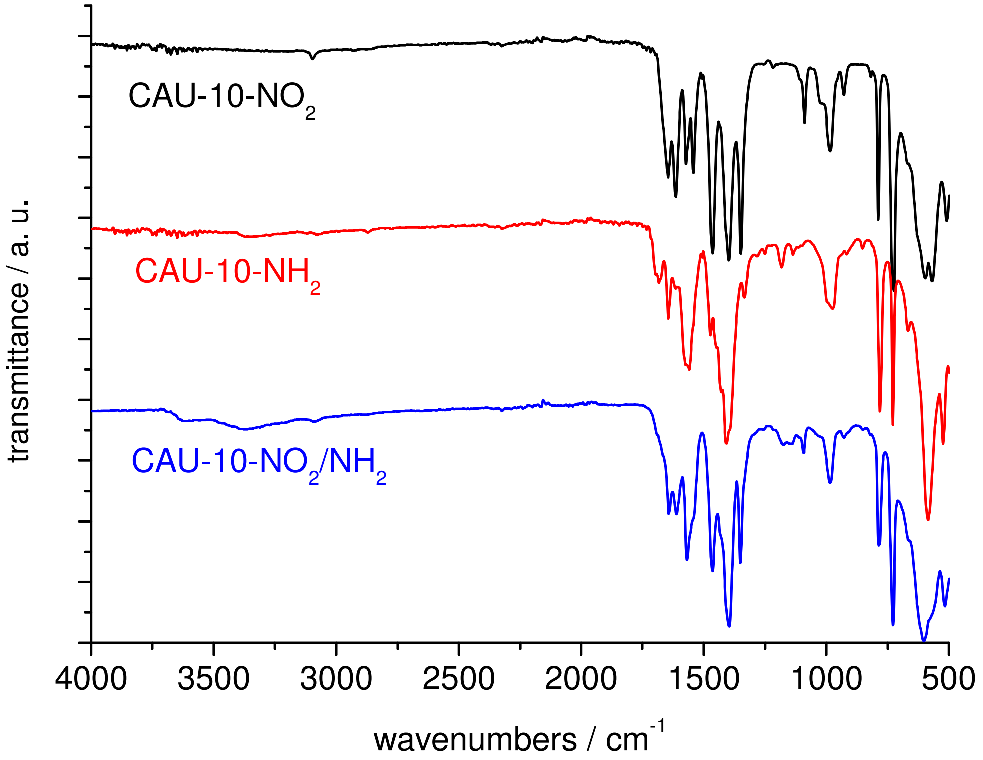


Figure S8: IR-spectra of CAU-10-H (**5**), CAU-10-Br (**1**) and CAU-10-H/Br (**2**).



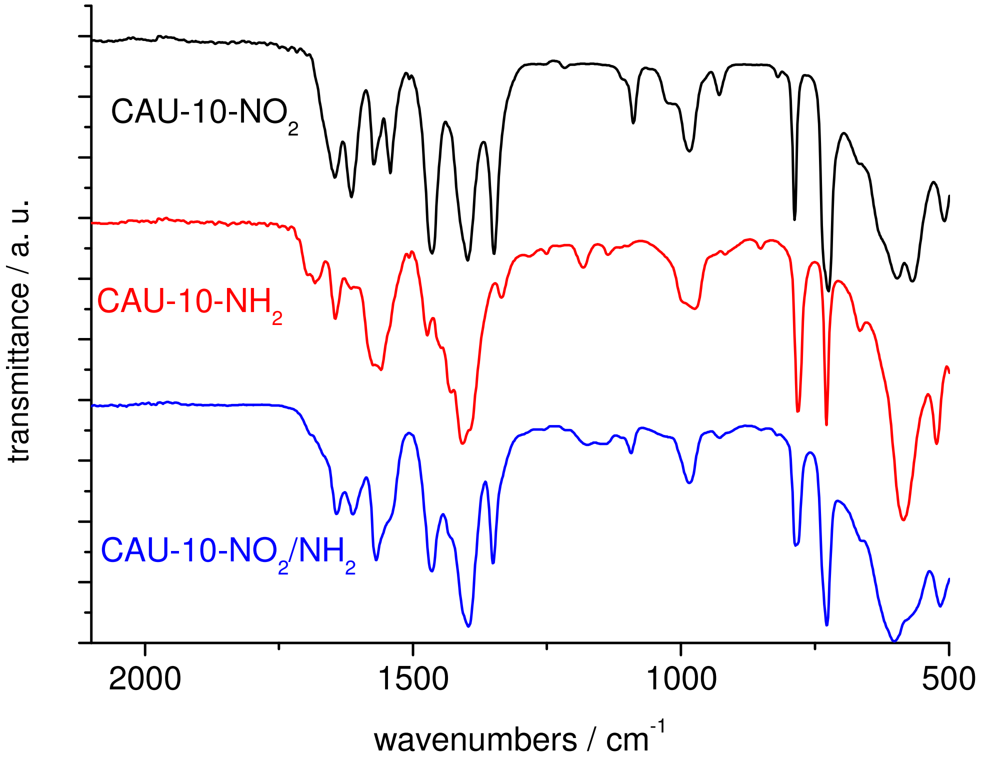
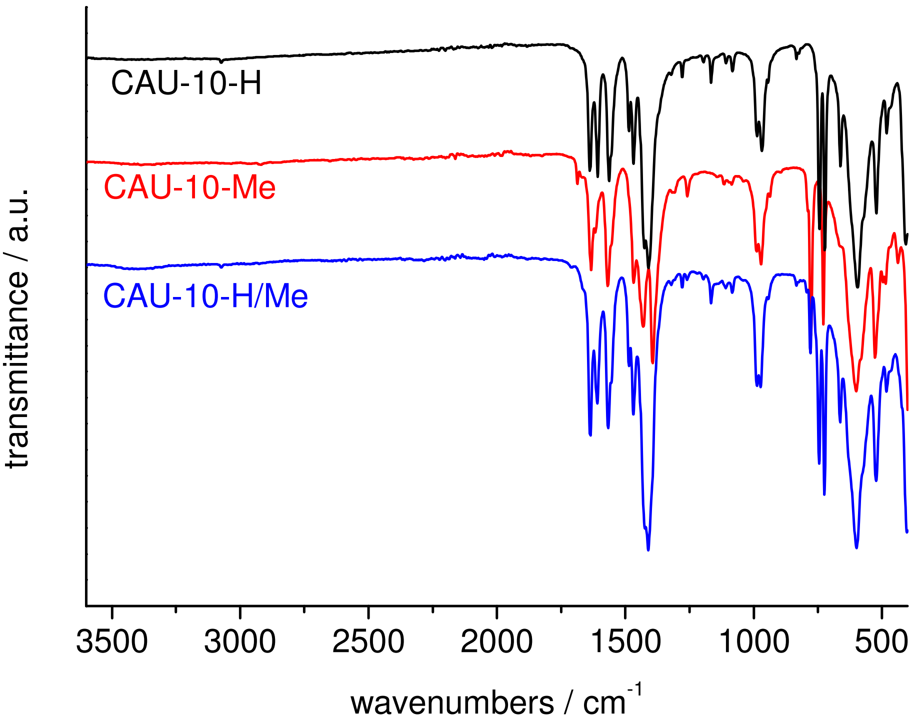


Figure S9: IR-spectra of CAU-10-NO$_2$ (**6**), CAU-10-NH$_2$ (**7**) and CAU-10-NO$_2$/NH$_2$ (**3**). Top: full spectra; bottom: region between 2100 and 500 cm^{-1}.



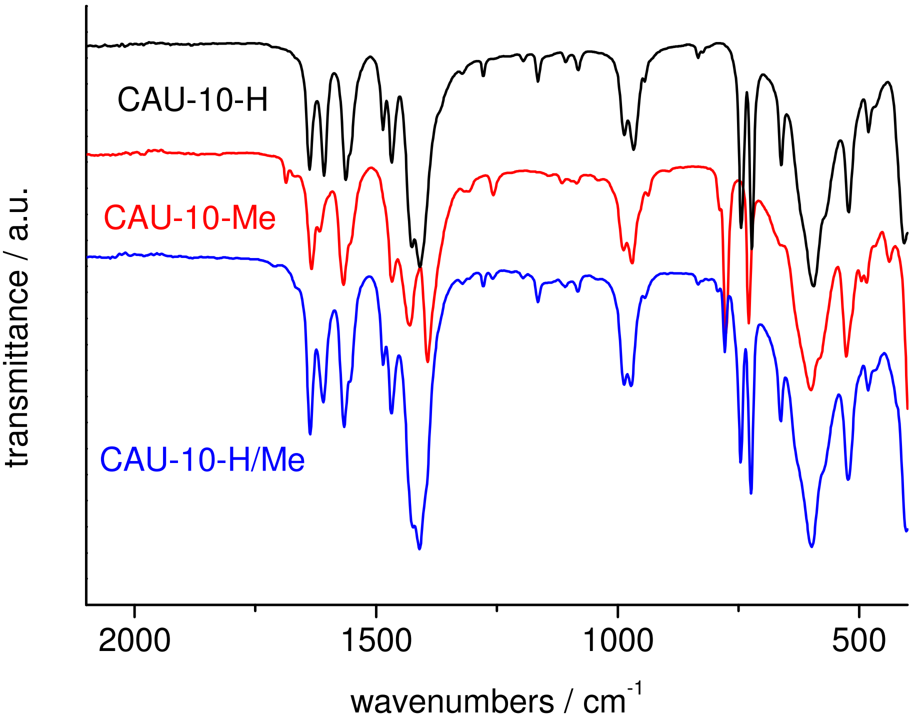


Figure S10: IR-spectra of CAU-10-H (**5**), CAU-10-CH_3 (**8**) and CAU-10-H/CH_3 (**4**). Top: full spectra; bottom: region between 2100 and 500 cm^{-1}.

S6: Scanning electron microscopy

Figure S11: SEM-micrograph of crystals of CAU-10-Br (**1**).

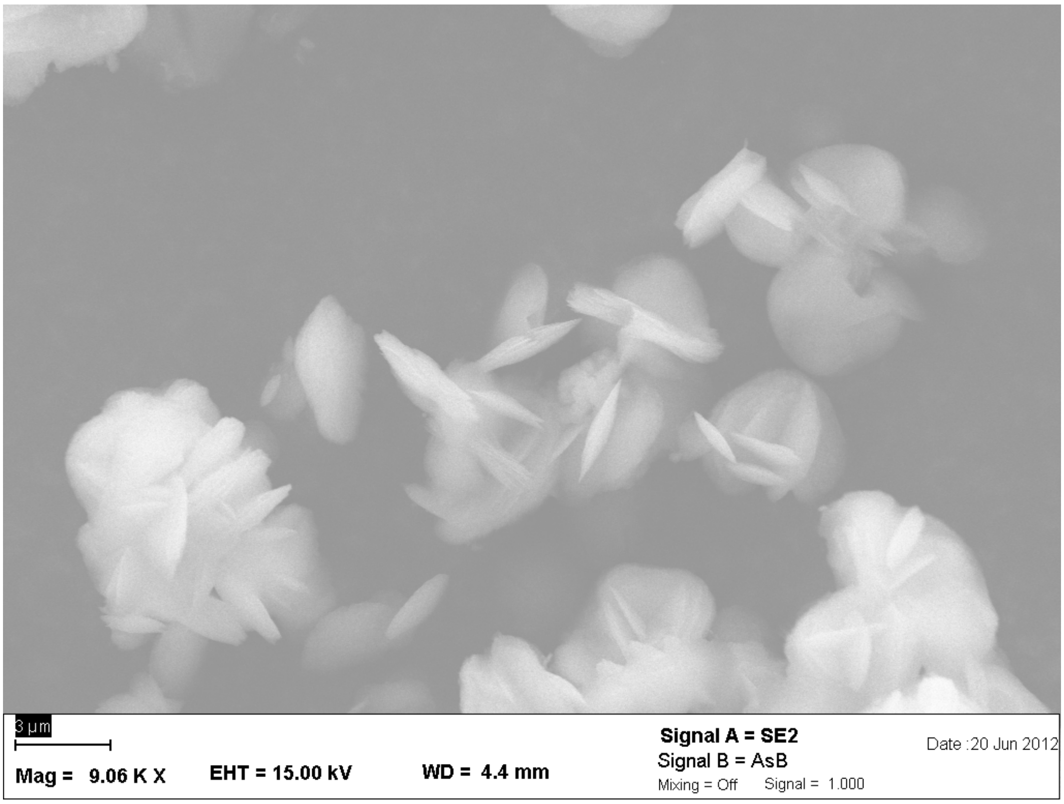


Figure S12: SEM-micrograph of crystals of CAU-10-H/Br (**2**)

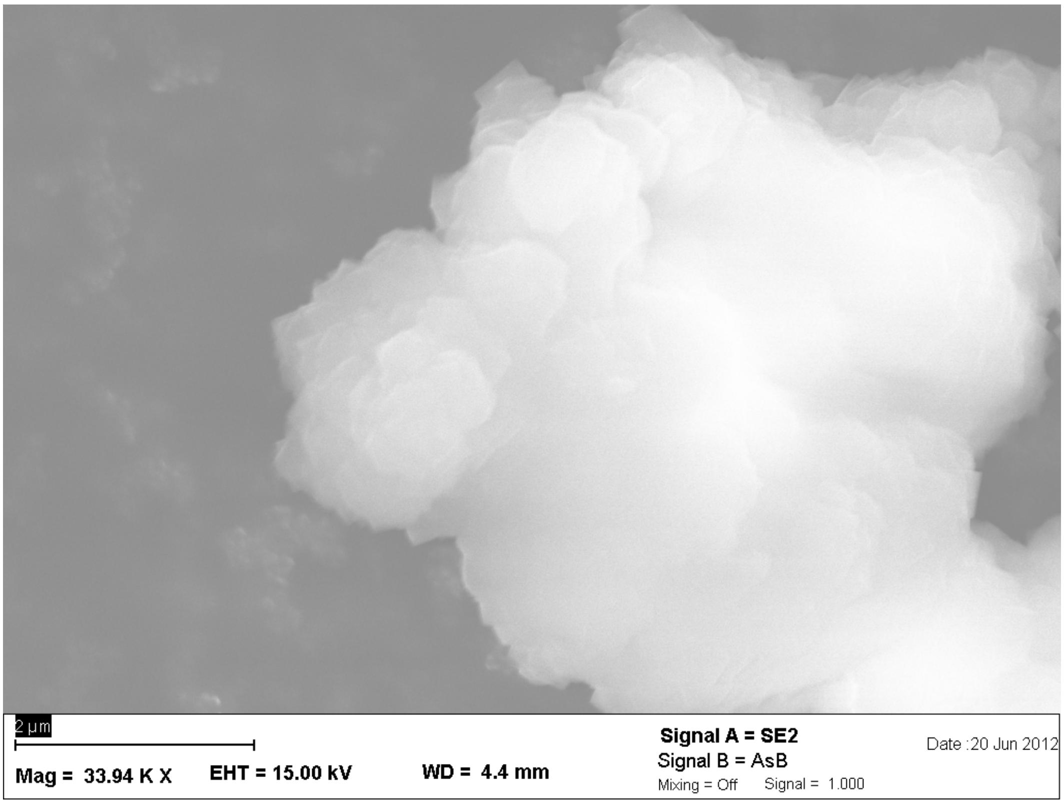


Figure S13: SEM-micrograph of crystals of CAU-10-NO_2/NH_2 (**3**).

S7: Additional Sorption Isotherms

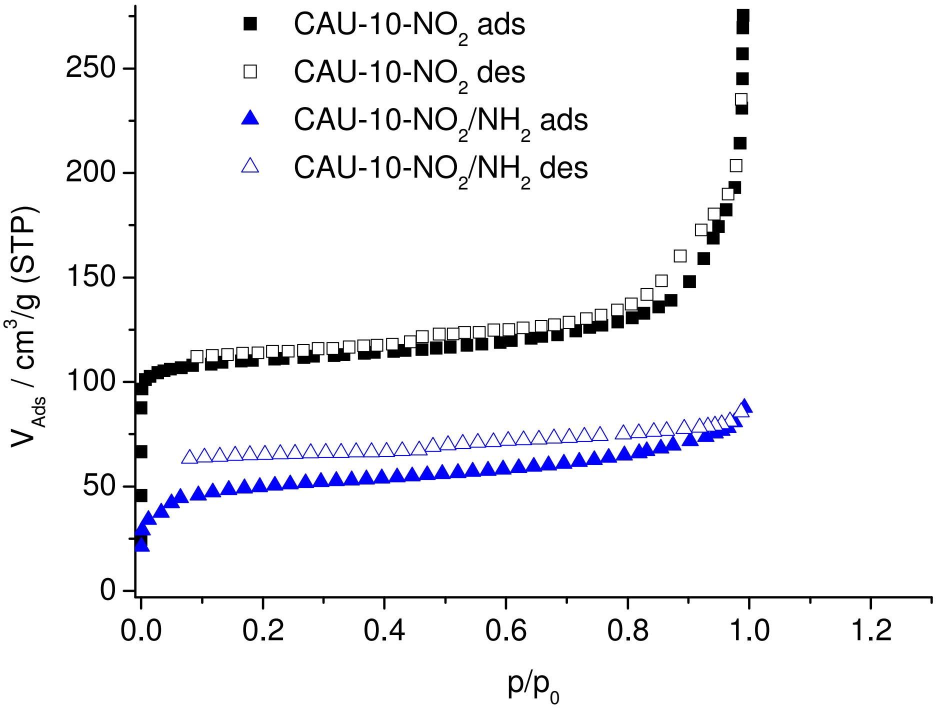


Figure S14: Nitrogen sorption isotherms for **6** and **3** measured at 77 K.

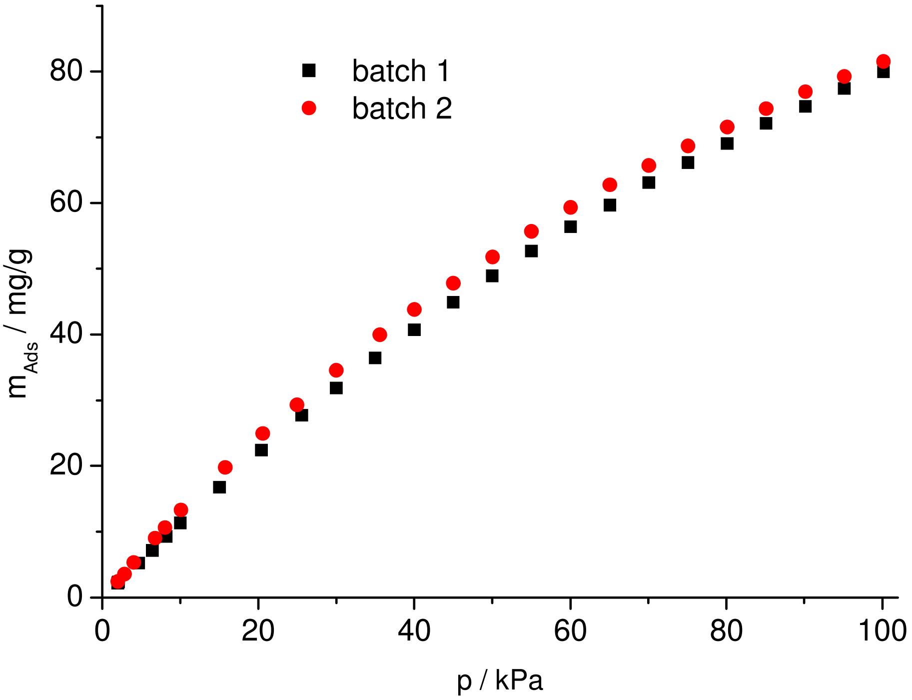


Figure S15: CO_2 adsorption isotherms for different batches of **2** measured at 298 K.

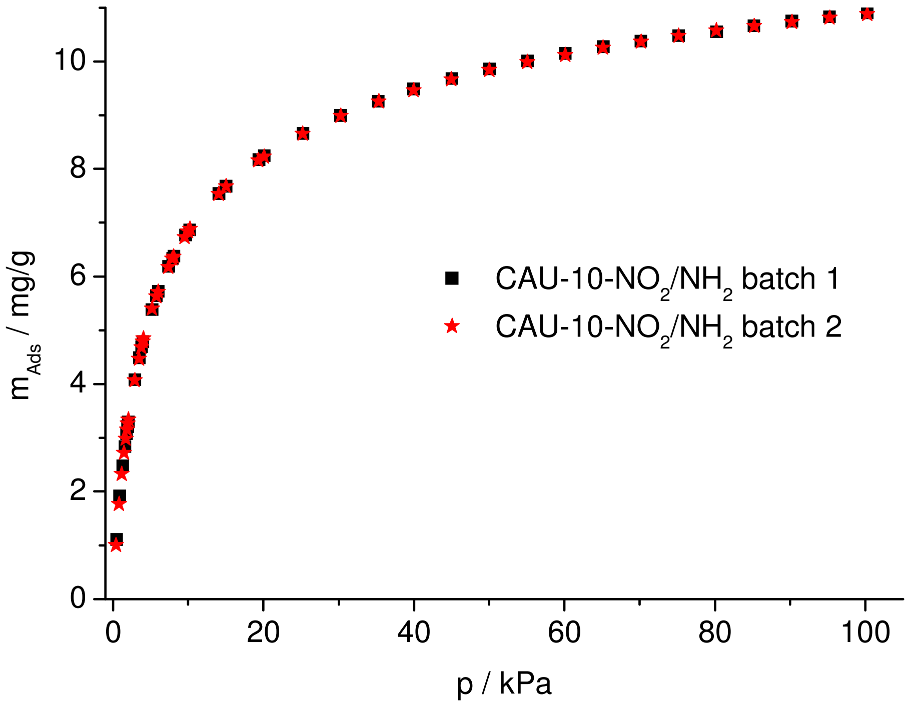


Figure S16: Hydrogen adsorption isotherms for different batches of **3** measured at 77 K.

S8: Crystallographic information file for CAU-10-Br

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_cell_length_b  21.5064(14)
_cell_length_c  10.1648(12)
_cell_angle_alpha 90
_cell_angle_beta  90
_cell_angle_gamma 90
_cell_volume 4701.48(80)
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loop_
_symmetry_equiv_pos_as_xyz
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       '-x, -y+1/2, z'
       '-x, y, z'
       '-x, y+1/2, -z'
       '-x+1/2, -y, z+1/2'
       '-x+1/2, -y+1/2, -z+1/2'
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       'x, y, z'
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       'x+1/2, y, -z+1/2'
       'x+1/2, y+1/2, z+1/2'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_B_iso_or_equiv
Al1 Al   0 0.31709(73) 0 0 1 0.20(65)
O1  O   0 0.25586(90) 0.00586(90) 0.125 1 0.6(13)
O2  O   0 0.38258(88) 0.00832(71) 0.1278(13) 1 0.20(61)
O3  O   0 0.33965(39) 0.07041(79) 0.2802(19) 1 0.20(77)
C1  C   0 0.38756(74) 0.04378(63) 0.2293(13) 1 1.2(14)
C2  C   0 0.44351(46) 0.0570(11) 0.2986(16) 1 0.2(13)
C3  C   0 0.5 0.0476(13) 0.2345(16) 1 0.2(16)
C4  C   0 0.44325(43) 0.0828(11) 0.4267(16) 1 0.2(14)
C5  C   0 0.5 0.0876(14) 0.4945(18) 1 0.2(18)
Br1 Br   0 0.5 0.11892(28) 0.66128(65) 1 3.11(39)
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S9: HT-experiment for mixed-linker MOFs

For the first synthesis of a mixed-linker-MOF we usually choose the same Al^{3+}-source as well as the same temperature program as for the synthesis of the parent-MOF. The molar ratios of Al^{3+} : linker molecules were varied slightly as well as the fraction of DMF and the absolute concentrations of the reactants (Tab. S2). Based on XRPD-measurements, we thus identified reaction conditions that lead to products with a high degree of mixing and sufficiently good crystallinity.

Table S3: Composition of the reaction mixtures in an archetypical HT-experiment.

linker 1 [%]	linker 2 [%]	linker 1 [mmol]	linker 2 [mmol]	Al^{3+} [mmol]	V H_2O [µL]	V DMF [µL]
87.5	12.5	0.11	0.02	0.12	400	100
75	25	0.09	0.03	0.12	400	100
50	50	0.06	0.06	0.12	400	100
87.5	12.5	0.11	0.02	0.12	350	150
75	25	0.09	0.03	0.12	350	150
50	50	0.06	0.06	0.12	350	150
87.5	12.5	0.21	0.03	0.24	400	100
75	25	0.18	0.06	0.24	400	100
50	50	0.12	0.12	0.24	400	100
87.5	12.5	0.21	0.03	0.24	350	150
75	25	0.18	0.06	0.24	350	150
50	50	0.12	0.12	0.24	350	150
87.5	12.5	0.11	0.02	0.24	400	100
75	25	0.09	0.03	0.24	400	100
50	50	0.06	0.06	0.24	400	100
87.5	12.5	0.11	0.02	0.24	350	150
75	25	0.09	0.03	0.24	350	150
50	50	0.06	0.06	0.24	350	150
87.5	12.5	0.21	0.03	0.48	400	100
75	25	0.18	0.06	0.48	400	100
50	50	0.12	0.12	0.48	400	100
87.5	12.5	0.21	0.03	0.48	350	150
75	25	0.18	0.06	0.48	350	150
50	50	0.12	0.12	0.48	350	150