Supporting Information

For

Ultramicroporous Polyimides with hierarchical morphology for carbon dioxide separation

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1 Chemicals

Table S 1: List of used chemicals, their purities and distributor.

Chemicals	Company	Purity
Isoquinoline	Sigma Aldrich	97 %
m-Cresol	abcr	99 %
Methanol	VWR Chemicals	100 %
Methylene chloride	VWR Chemicals	99.8 %
1,4,5,8-Naphthalenetetracarboxylic dianhydride	abcr	95 %
Pyromellitic dianhydride	Merck	97 %
Tetrahydrofuran	Bernd Kraft	99,5 %
Toluene	Sigma Aldrich	≥99.7 %
Tris(4-aminophenyl)methane	TCI	>97 %

2 Synthesis

2.1 Synthesis of MOPI-6_0

No product observable.

2.2 Synthesis of MOPI-6_0.3

MOPI 6_0.3 was observed as brown solid. Yield: 183.4 mg (0.326 mmol, 46 %). ^{13}C NMR (CP-MAS, 12.5 kHz): d [ppm] = 165 (C-6), 145 (C-2), 137 (C-7), 130 (C-3, C-4, C-5), 119 (C-8), 55 (C-1). ^{15}N NMR (CP-MAS, 5 kHz): d [ppm] = 207 (-CO-N-CO-), 247 (-CO-NH-), 327 (-NH_2). Anal. Found: C [71.12], H [3.97], N [7.38]. Calcd: C [72.60], H [2.87], N [7.47]. IR (ATR): ? [cm-1] = 1779, 1721, 1663, 1605, 1510, 1356, 1263, 723.

2.3 Synthesis of MOPI-6_0.5

MOPI-6_0.5 was obtained as dark purple powder. Yield: 321 mg (0.571 mmol, 64%). ^{13}C NMR (CP-MAS, 12.5 kHz): δ [ppm] = 165 (C-6), 144 (C-2), 137 (C-7), 129 (C-3, C-4, C-5), 119 (C-8), 56 (C-1). ^{15}N NMR (CP-MAS, 5 kHz): δ [ppm] = -207 (-CO-*N*-CO-), -326 (-*N*H_2). Anal. Found: C [69.41], H [3.53], N [7.45]. Calcd: C [72.60], H [2.87], N [7.47]. IR (ATR): ν [cm^{-1}] = 1781, 1725, 1512, 1362.

2.4 Synthesis of MOPI-6_0.7

MOPI-6_0.7 was observed as dark purple solid. Yield: 138 mg (0.245 mmol, 26 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 165 (C-6), 145 (C-2), 137 (C-7), 130 (C-3, C-4, C-5), 118 (C-8), 56 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -207 (-CO-*N*-CO-), -251 (-CO-*N*H-), -329 (-*N*H$_2$). Anal. Found: C [71.62], H [3.85], N [8.08]. Calcd: C [72.60], H [2.87], N [7.47]. IR (ATR): ν [cm^{-1}] = 1778, 1721, 1511, 1366.

2.5 Synthesis of MOPI-6_1

MOPI-6_1 was observed as pink solid. Yield: 125 mg (0.222 mmol, 25 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 166 (C-6), 144 (C-2), 137 (C-7), 130 (C-3, C-4, C-5), 120 (C-8), 55 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -207 (-CO-*N*-CO-), -246 (-CO-*N*H-), -327 (-*N*H$_2$). Anal. Found: C [63.99], H [3.91], N [7.33]. Calcd: C [72.60], H [2.87], N [7.47]. IR (ATR): ν [cm^{-1}] = 1778, 1721, 1666, 1606, 1510, 1372, 1269, 726.

2.6 Synthesis of MOPI-6_HP

MOPI-6_HP was obtained as dark purple powder. Yield: 279 mg (0.496 mmol, 67 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 165 (C-6), 144 (C-2), 137 (C-7), 130 (C-3, C-4, C-5), 119 (C-8), 55 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -206 (-CO-*N*-CO-). Anal. Found: C [68.65], H [3.49], N [7.39]. Calcd: C [72.60], H [2.87], N [7.47]. IR (ATR): ν [cm^{-1}] = 1778, 1723, 1511, 1363.

2.7 Synthesis of MOPI-7_0

MOPI-7_0 was observed as brown solid. Yield: 13 mg (0.021 mmol, 3 %). Anal. Found: C [75.12], H [5.18], N [5.05]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1716, 1671, 1505, 1246.

2.8 Synthesis of MOPI-7_0.3

MOPI-7_0.3 was observed as dark red solid. Yield: 455 mg (0.714 mmol, 91 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 163 (C-6), 145 (C-2), 128 (C-3, C-4, C-5, C-7, C-8, C-9), 56 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -196 (-CO-*N*-CO-), -329 (-*N*H$_2$). Anal. Found: C [72.57], H [3.56], N [6.66]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1711, 1668, 1504, 1244.

2.9 Synthesis of MOPI-7_0.5

MOPI-7_0.5 was observed as brown solid. Yield: 267 mg (0.419 mmol, 53 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 163 (C-6), 145 (C-2), 129 (C-3, C-4, C-5, C-7, C-8, C-9), 55 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -196 (-CO-*N*-CO-), -326 (-*N*H$_2$). Anal. Found:

C [72.10], H [3.37], N [6.60]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1713, 1671, 1508, 1340.

2.10 Synthesis of MOPI-7_0.7

MOPI-7_0.7 was observed as brown solid. Yield: 417 mg (0.654 mmol, 83 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 162 (C-6), 145 (C-2), 128 (C-3, C-4, C-5, C-7, C-8, C-9), 56 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -196 (-CO-*N*-CO-), -327 (-*N*H_2). Anal. Found: C [73.55], H [3.42], N [6.87]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1718, 1674, 1506, 1245.

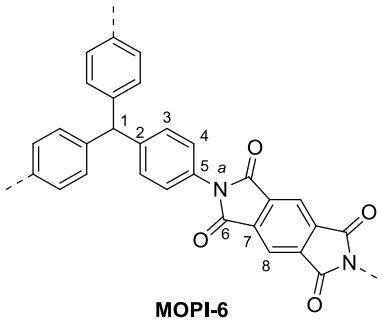
2.11 Synthesis of MOPI-7_1

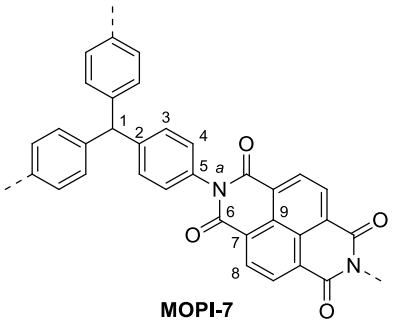
MOPI-7_1 was observed as dark purple solid. Yield: 269 mg (0.421 mmol, 54 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 163 (C-6), 145 (C-2), 130 (C-3, C-4, C-5, C-7, C-8, C-9), 56 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -196 (-CO-*N*-CO-), -328 (-*N*H_2). Anal. Found: C [71.64], H [3.69], N [7.06]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1714, 1667, 1504, 1246.

2.12 Synthesis of MOPI-7_HP

MOPI-7_0.1 was observed as dark purple solid. Yield: 184 mg (0.289 mmol, 39 %). ^{13}C NMR (CP MAS, 12.5 kHz): δ [ppm] = 163 (C-6), 145 (C-2), 129 (C-3, C-4, C-5, C-7, C-8, C-9), 56 (C-1). ^{15}N NMR (CP MAS, 5 kHz): δ [ppm] = -196 (-CO-*N*-CO-). Anal. Found: C [69.98], H [3.73], N [5.9]. Calcd: C [75.35], H [3.00], N [6.59]. IR (ATR): ν [cm^{-1}] = 1715, 1675, 1509, 1246.

3 Characterisation of Polymers





3.1 NMR- and IR-Spectra

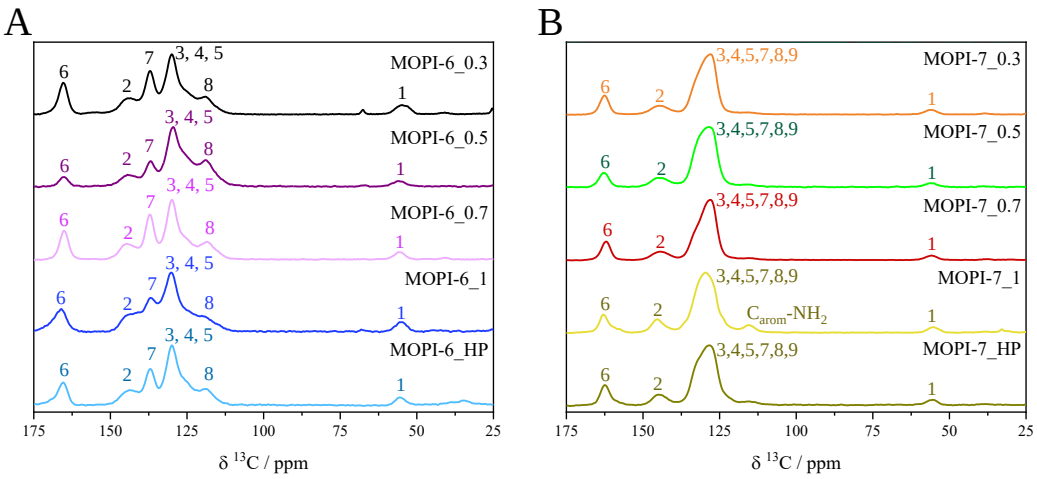


Figure S 1: ^{13}C CP MAS NMR spectra for the MOPI-6 (A) and MOPI-7 (B) synthesis series.

Table S 2: Assignment of ^{13}C and ^{15}N NMR shifts (All values are given in ppm).

Polymer	1	2	3	4	5	6	7	8	9	a	$-NH_2$	-NH-
MOPI-6_0.3	55	145	130	130	130	165	137	119	-	-207	-327	-247
MOPI-6_0.5	56	144	129	129	129	165	137	119	-	-207	-326	-
MOPI-6_0.7	56	145	130	130	130	165	137	118	-	-207	-329	-251
MOPI-6_1	55	144	130	130	130	166	137	120	-	-207	-327	-246
MOPI-6_HP	55	144	130	130	130	165	137	119	-	-206	-	-
MOPI-7_0.3	56	145	128	128	128	163	128	128	128	-196	-329	-
MOPI-7_0.5	55	145	129	129	129	163	129	129	129	-196	-326	-
MOPI-7_0.7	56	145	128	128	128	162	128	128	128	-196	-327	-
MOPI-7_1	56	145	130	130	130	163	130	130	130	-196	-328	-
MOPI-7_HP	56	145	129	129	129	163	129	129	129	-196	-	-

3.2 IR Spectroscopy

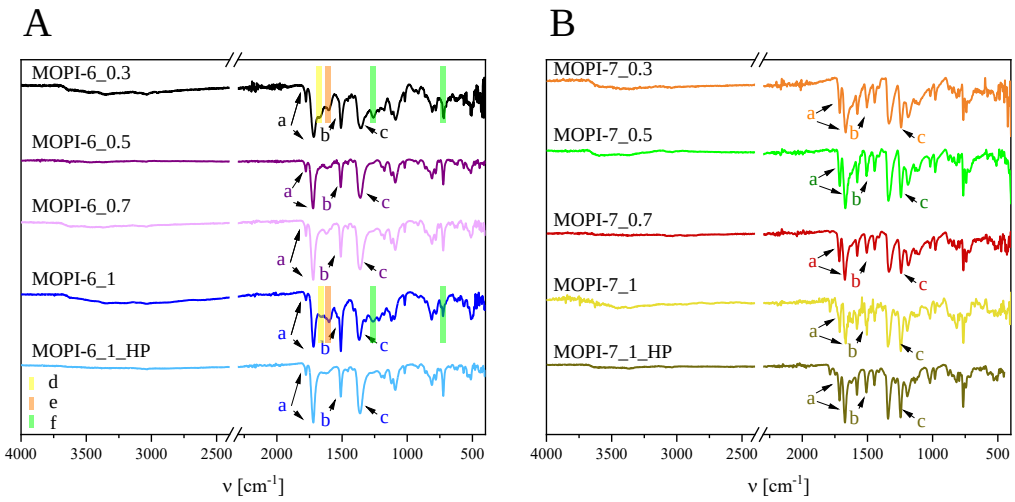


Figure S 2: FTIR spectra of the MOPI-6 series (A) and the MOPI-7 series (B) (450-4000 cm^{-1}). a: imide six- and five-membered ring, b: aromatic C=C stretching vibration, c: C-H tertiary C-atom, d: C=O stretching vibration of aromatic carboxylic acid, e: C=O stretching vibration of secondary amides, f: other secondary amide bands.

Table S 3: Assignment of IR signals (All values are given in cm^{-1}). a: imide six- and five-membered ring, b: aromatic C=C stretching vibration, c: C-H tertiary C-atom, d: C=O stretching vibration of aromatic carboxylic acid, e: C=O stretching vibration of secondary amides, f: other secondary amide bands.

Polymer	a		b	c	d	e	f	
MOPI-6_0.3	1779	1721	1510	1356	1663	1605	1263	723
MOPI-6_0.5	1781	1725	1512	1362	-	-	-	-
MOPI-6_0.7	1778	1721	1511	1366	-	-	-	-
MOPI-6_1	1778	1721	1510	1372	1666	1606	1269	726
MOPI-6_HP	1778	1723	1511	1363	-	-	-	-
MOPI-7_0	1716	1671	1505	1246	-	-	-	-
MOPI-7_0.3	1711	1668	1504	1244	-	-	-	-
MOPI-7_0.5	1713	1671	1508	1340	-	-	-	-
MOPI-7_0.7	1718	1674	1506	1245	-	-	-	-
MOPI-7_1	1714	1667	1504	1246	-	-	-	-
MOPI-7_HP	1715	1675	1509	1246	-	-	-	-

3.3 Elemental Analysis

Table S 4: Experimental data, theoretical data and the calculated deviation of CHN analysis.

	Exp.			Theo.			Deviation		
Polymer	C / %	H / %	N / %	C / %	H / %	N / %	C / %	H / %	N / %
MOPI-6_0.3	71.12	3.97	7.38	72.60	2.87	7.47	1.48	1.10	0.09
MOPI-6_0.5	69.41	3.53	7.45	72.60	2.87	7.47	3.19	0.66	0.02
MOPI-6_0.7	71.62	3.85	8.08	72.60	2.87	7.47	0.98	0.98	0.61
MOPI-6_1	63.99	3.92	7.33	72.60	2.87	7.47	8.61	1.05	0.14
MOPI-6_HP	68.65	3.49	7.39	72.60	2.87	7.47	3.95	0.62	0.08
MOPI-7_0.3	72.57	3.56	6.66	75.35	3.00	6.59	2.78	0.56	0.07
MOPI-7_0.5	72.10	3.37	6.60	75.35	3.00	6.59	3.25	0.37	0.01
MOPI-7_0.7	73.55	3.42	6.87	75.35	3.00	6.59	1.80	0.42	0.28
MOPI-7_1	71.64	3.69	7.06	75.35	3.00	6.59	3.71	0.69	0.47
MOPI-7_HP	70.51	3.62	6.33	75.35	3.00	6.59	4.84	0.62	0.26

3.4 Powder X-ray diffraction

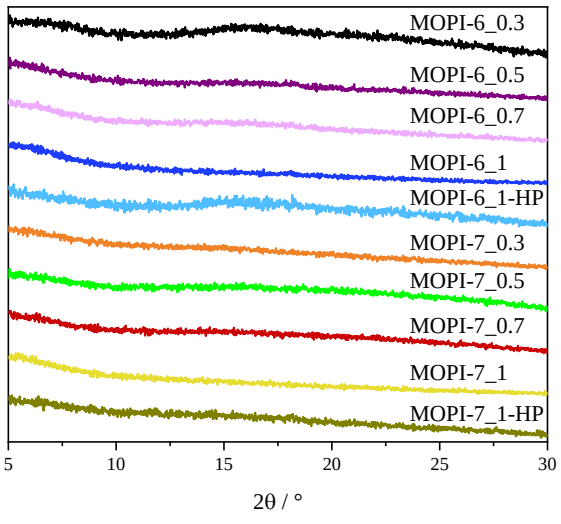


Figure S 3: Powder x-ray diffraction pattern of the MOPIs (5-30 °2θ, Cu-K_α).

3.5 TGA patterns

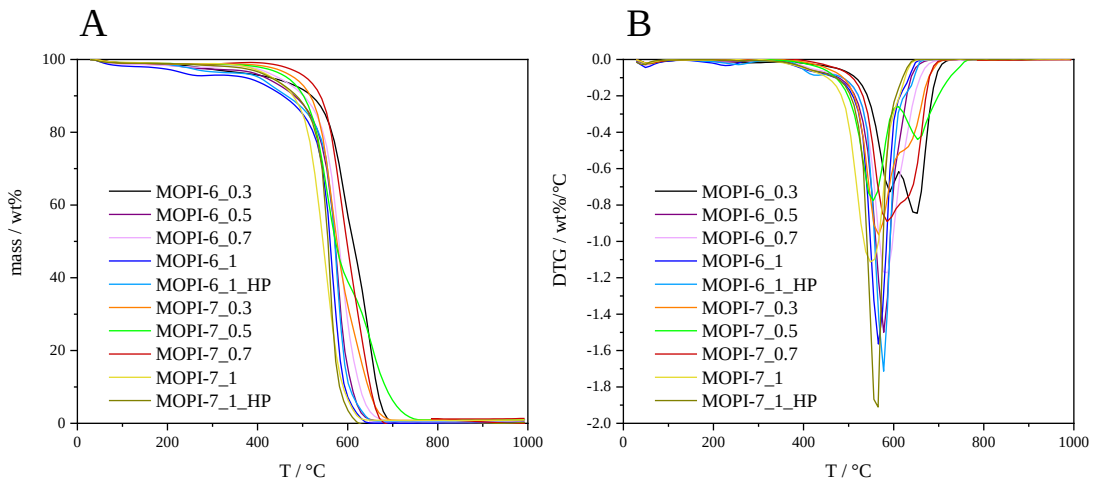


Figure S 4: Thermogravimetric analysis of the MOPI-6 and MOPI-7 series (A) (30-1000 °C, 10 °C/min, under air). Derivation of the thermogravimetric analysis according to temperature of the MOPI-6 and MOPI-7 series (B) (30-1000 °C, 10 °C/min, under air).

Table S 5: Temperature at which 5 wt% mass loss occurs detected from TGA for the MOPI-6 and the MOPI-7 series.

Polymer	$T_{-5wt\%}$ / °C
MOPI-6_0.3	458
MOPI-6_0.5	435
MOPI-6_0.7	464
MOPI-6_1	413
MOPI-6_HP	415
MOPI-7_0.3	492
MOPI-7_0.5	475
MOPI-7_0.7	517
MOPI-7_1	443
MOPI-7_HP	444

3.6 Physisorption argon isotherms

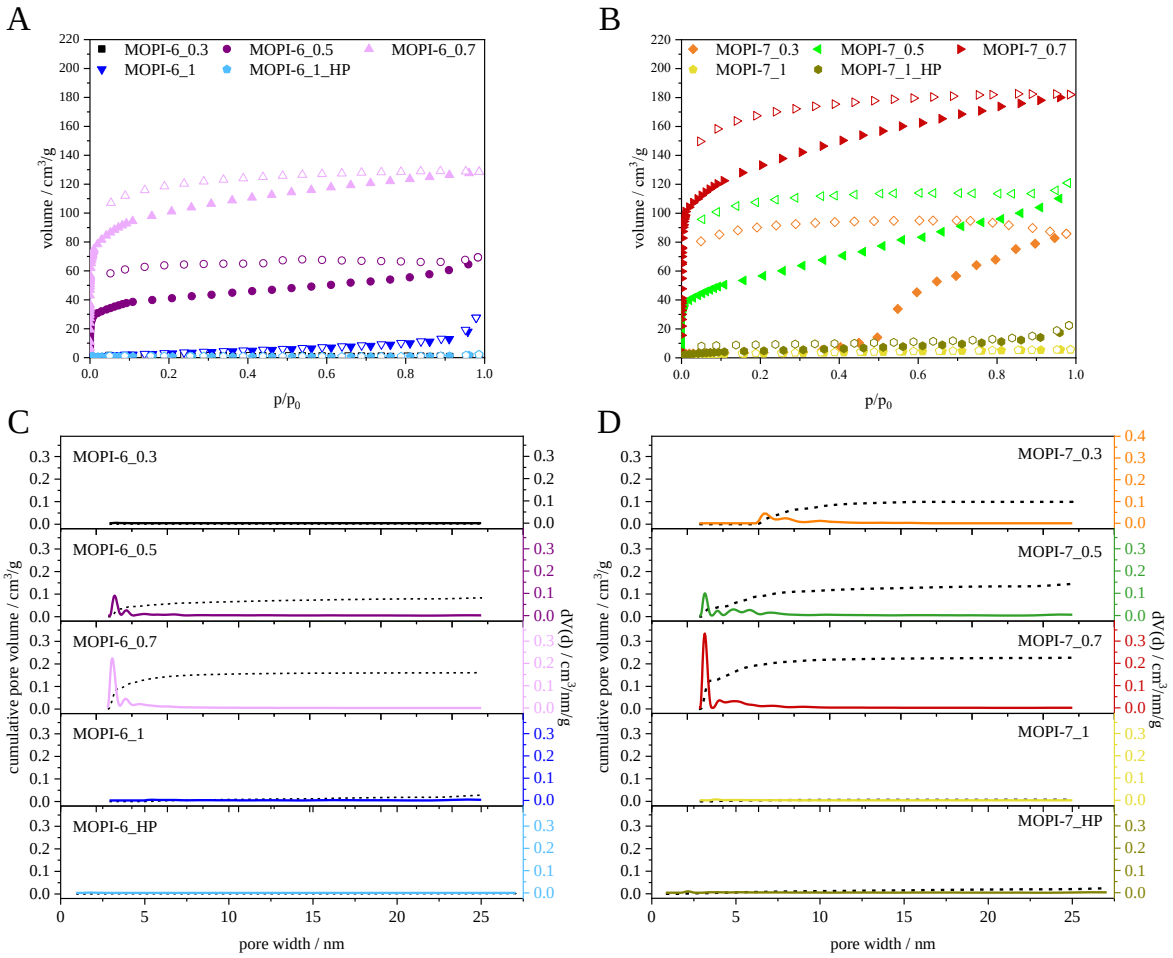


Figure S 5: Argon isotherms of the MOPI-6 (A) and MOPI-7 (B) series measured at 87 K and pore size distributions of the MOPI-6 (C) and MOPI-7 (D) series calculated by QSDFT adsorption branch kernel for cylindrical pores in carbon-based materials. Full symbols characterise adsorption isotherms, hollow symbols the corresponding desorption curve.

3.7 Physisorption CO_2 isotherms

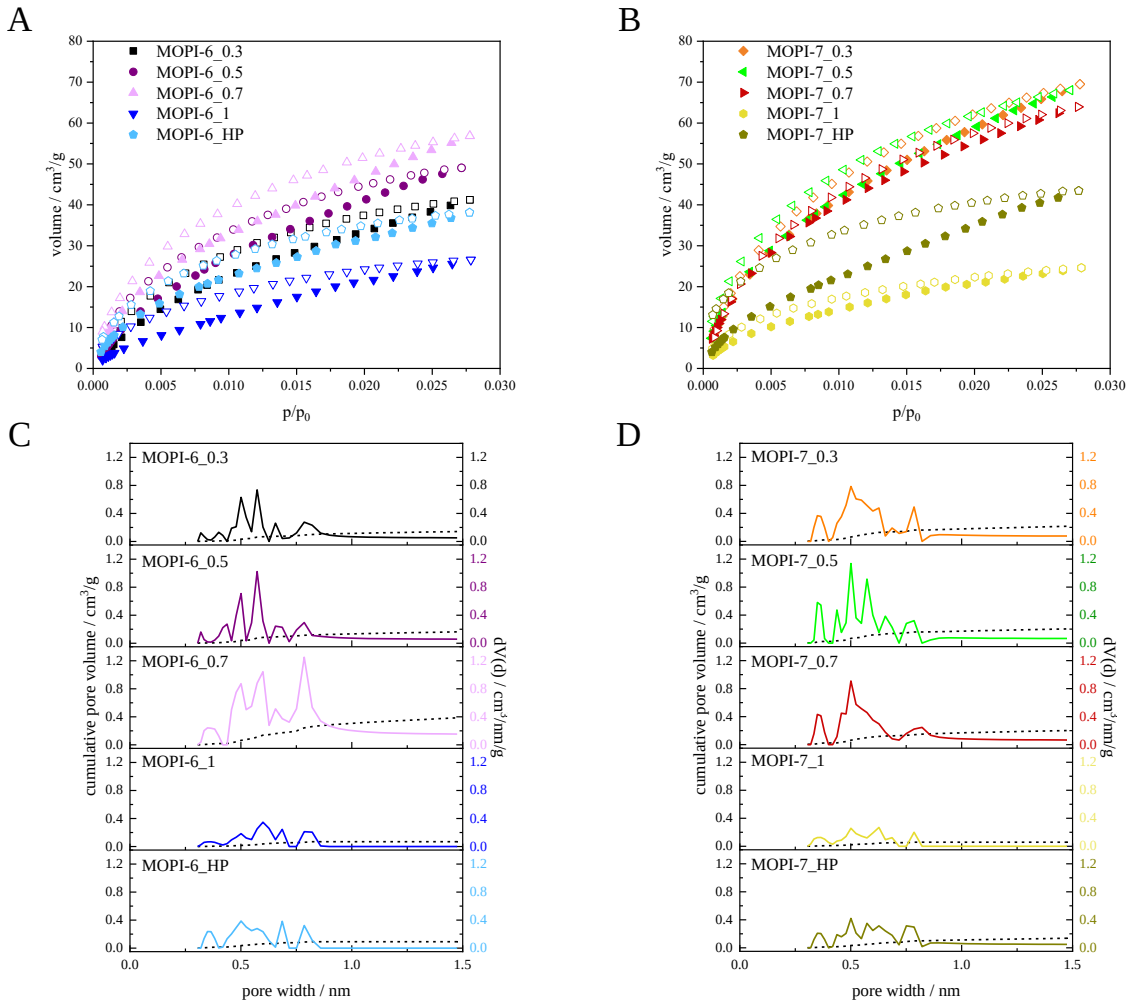


Figure S 6: CO_2 isotherms of the MOPI-6 (A) and MOPI-7 (B) series measured at 273 K and pore size distributions of the MOPI-6 (C) and MOPI-7 (D) series calculated by NLDFT adsorption branch kernel on carbon-based materials. Full symbols characterise adsorption isotherms, hollow symbols the corresponding desorption curve.

3.8 CO_2, N_2, CH_4 isotherms

Table S 6: Uptakes taken from individual Isotherms (the values were determined at p = 1 bar) and Isosteric Heats of Adsorption of CO_2 and CH_4.

MOPI-	CO_2 / mmol/g			Q_{CO2}	CH_4 / mmol/g			Q_{CH4}	N_2 / mmol/g		
	0 °C	25 °C	40 °C	/ kJ/mol	0 °C	25 °C	40 °C	/ kJ/mol	0 °C	25 °C	40 °C
6_0.3	1.8	1.2	1.1	25	0.3	0.2	0.1	45	0.02	-	0.01
6_0.5	2.2	1.5	1.3	25	0.3	0.2	0.2	21	0.06	0.03	0.01
6_0.7	2.5	1.9	1.5	37	0.5	0.3	0.1	39	0.07	0.05	-
6_1	1.2	0.7	0.6	32	0.2	0.1	-	-	0.03	0.01	-
6_HP	1.7	1.5	1.2	34	0.4	0.2	0.1	29	0.06	0.04	-
7_0.3	3.1	2.1	1.7	29	0.7	0.4	0.3	27	0.15	0.10	0.08
7_0.5	3.0	2.0	1.6	31	0.7	0.4	0.3	25	0.15	0.08	0.05
7_0.7	2.9	2.0	1.5	29	0.7	0.4	0.3	21	0.17	0.10	0.06
7_1	1.1	0.8	0.7	32	0.2	0.1	0.1	42	-	0.02	-
7_HP	1.9	1.5	1.4	32	0.4	0.2	0.2	30	0.06	0.03	-

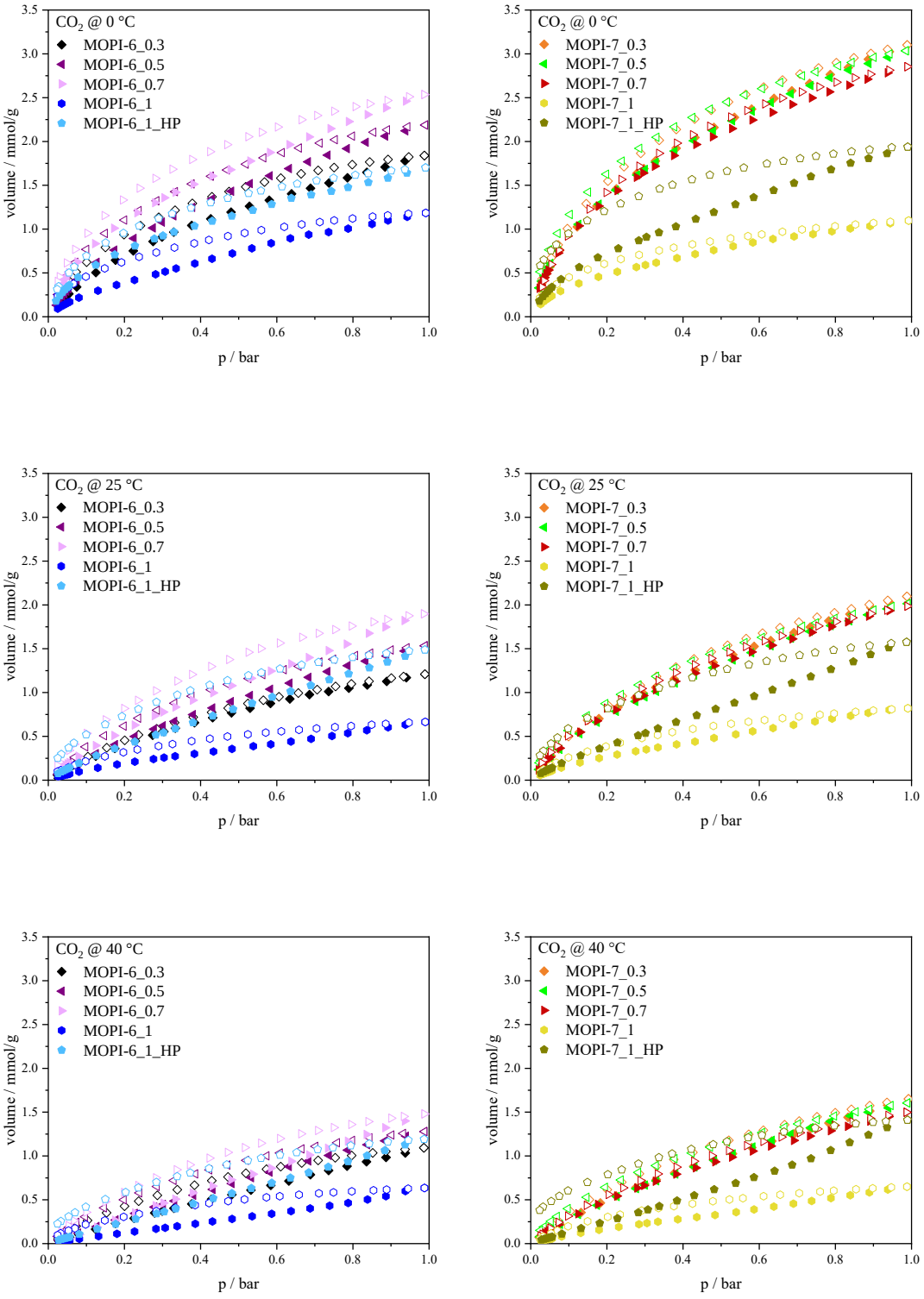


Figure S 7: CO_2 isotherms of the MOPI-6 (left) and MOPI-7 (right) series measured at 0 °C (top), 25 °C (middle) and 40 °C (bottom). Full symbols characterise adsorption isotherms, hollow symbols the corresponding desorption curve.

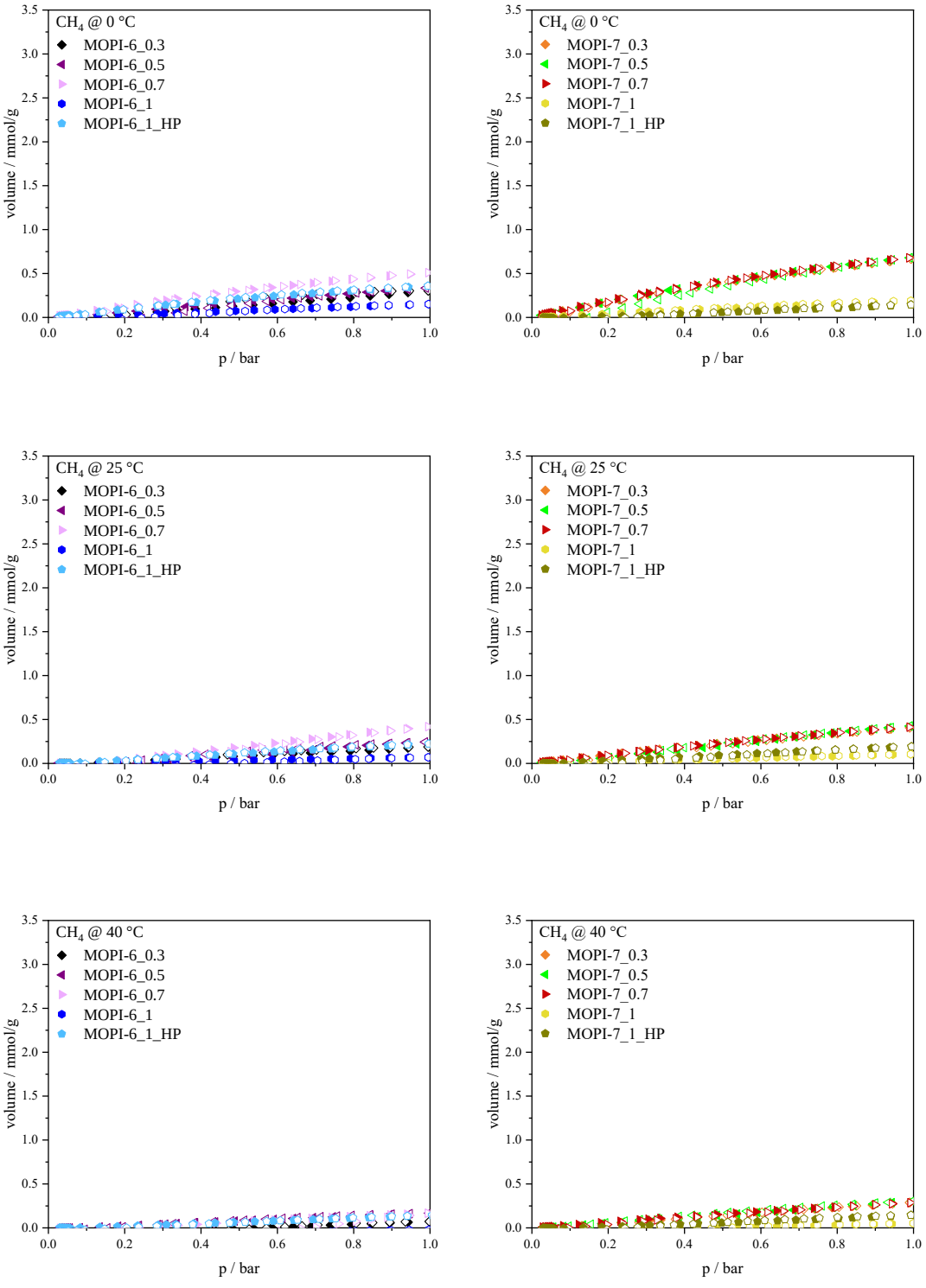


Figure S 8: CH_4 isotherms of the MOPI-6 (left) and MOPI-7 (right) series measured at 0 °C (top), 25 °C (middle) and 40 °C (bottom). Full symbols characterise adsorption isotherms, hollow symbols the corresponding desorption curve.

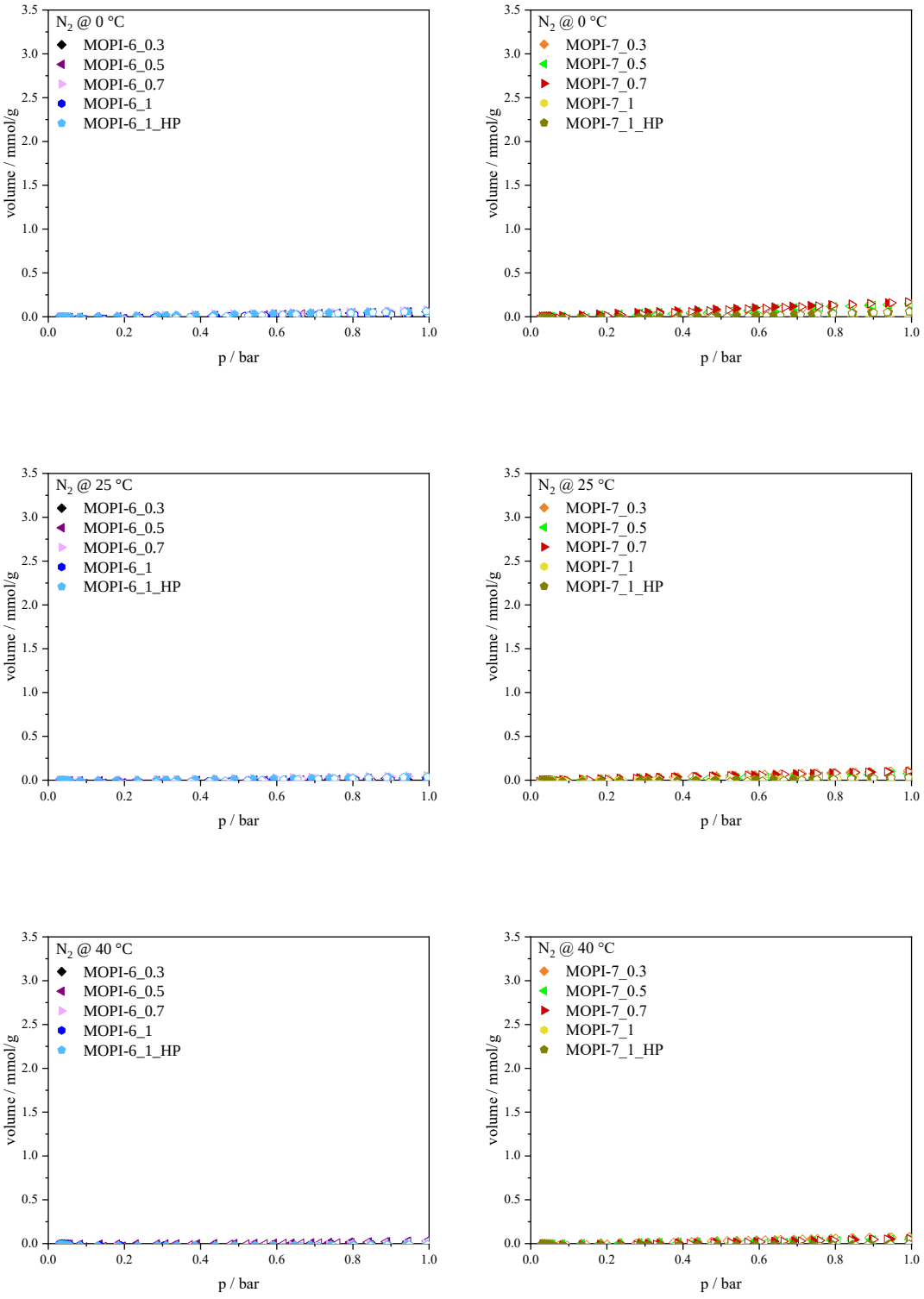


Figure S 9: N_2 isotherms of the MOPI-6 (left) and MOPI-7 (right) series measured at 0 °C (top), 25 °C (middle) and 40 °C (bottom). Full symbols characterise adsorption isotherms, hollow symbols the corresponding desorption curve.

3.9 Heats of adsorption

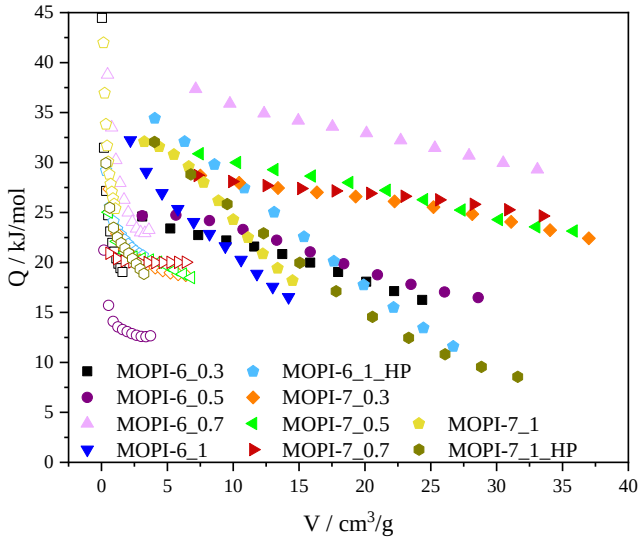


Figure S 10: Isosteric heats of adsorption for CO_2 (full symbols) and CH_4 (hollow symbols) calculated from adsorption isotherms at 273, 298, and 313 K.

3.10 Selectivities

Table S 7: CO_2/N_2 and CO_2/CH_4 selectivities at 1 bar calculated by IAST from the correspondent Isotherms.

MOPI-	CO_2/CH_4 5:95			CO_2/CH_4 50:50			CO_2/N_2 15:85		
	0 °C	25 °C	40 °C	0 °C	25 °C	40 °C	0 °C	25 °C	40 °C
6_0.3	17	14	14	7	15	4	1E+18	-	3E+7
6_0.5	18	16	11	19	72	24	-	-	1E+8
6_0.7	24	11	10	60	14	35	2069	3157	-
7_0.3	17	12	12	20	14	18	2013	68	112
7_0.5	18	14	10	23	26	9	577	2410	561
7_0.7	16	11	10	18	12	11	2655	67	2179

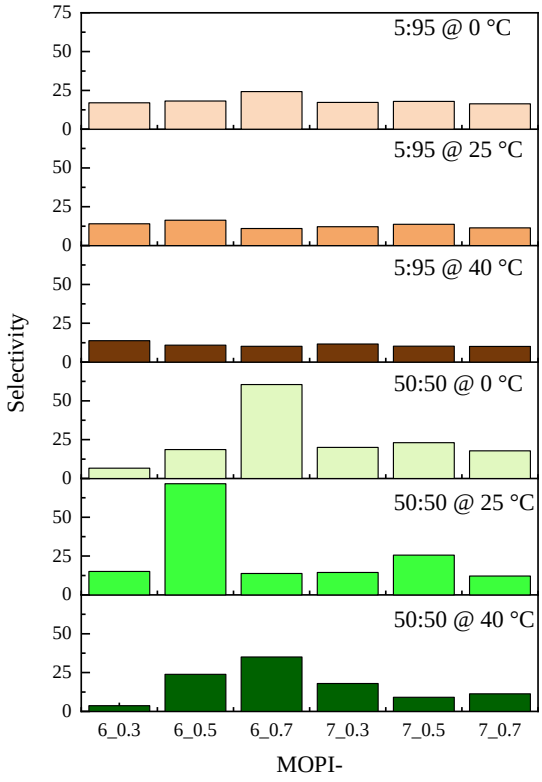


Figure S 11: CO_2/CH_4 selectivities at 1 bar calculated by IAST from the correspondent Isotherms.

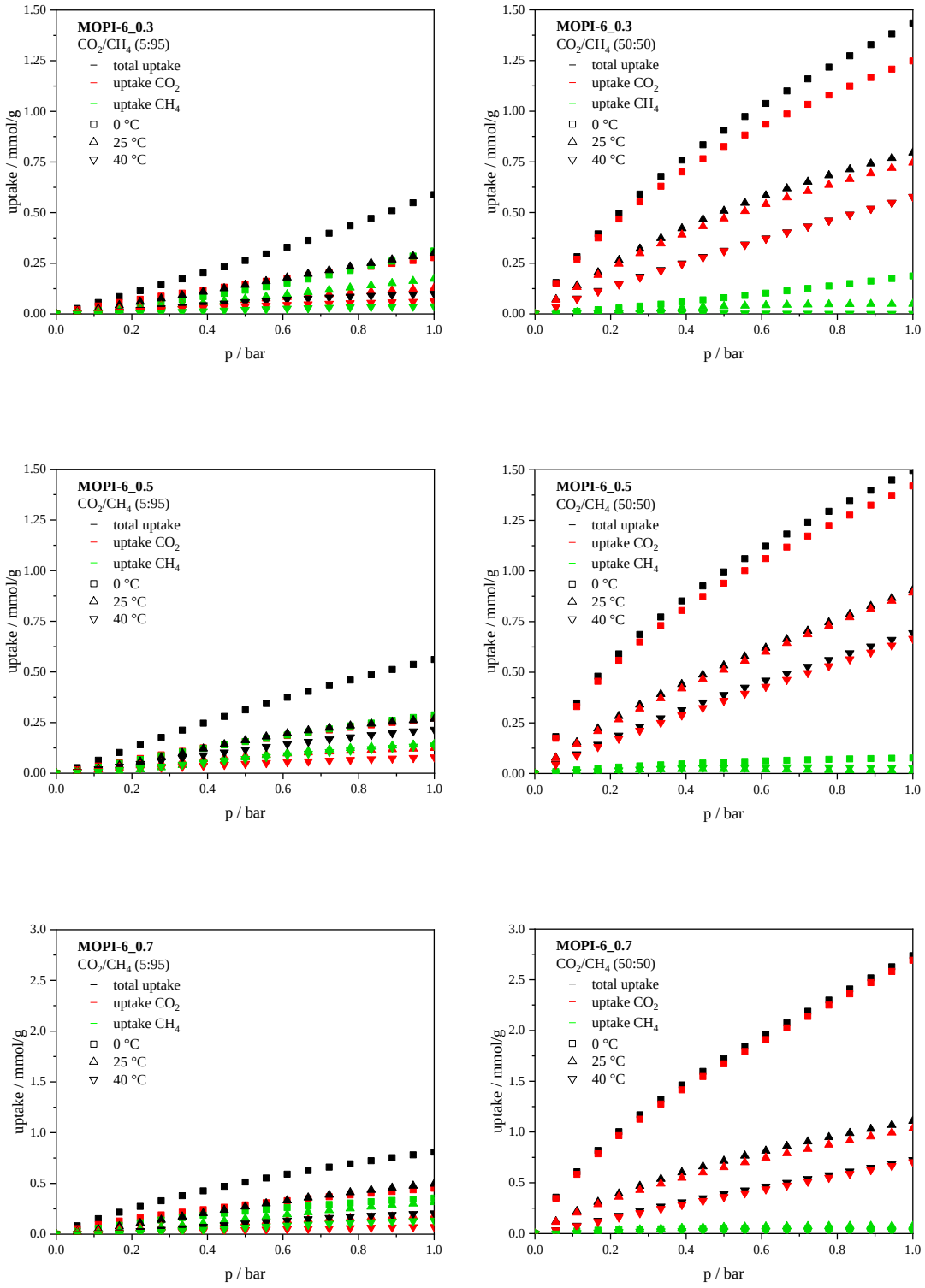


Figure S 12: Isotherms calculated by IAST for gas mixtures of 5:95 CO_2/CH_4 (left) and 50:50 CO_2/CH_4 (right) for the MOPI-6 series. Black indicates the total uptake, red the uptake of CO_2 and green the uptake of CH_4 in the mixture at 0 °C (square symbol), 25 °C (triangle with apex up) and 40 °C (triangle with apex down).

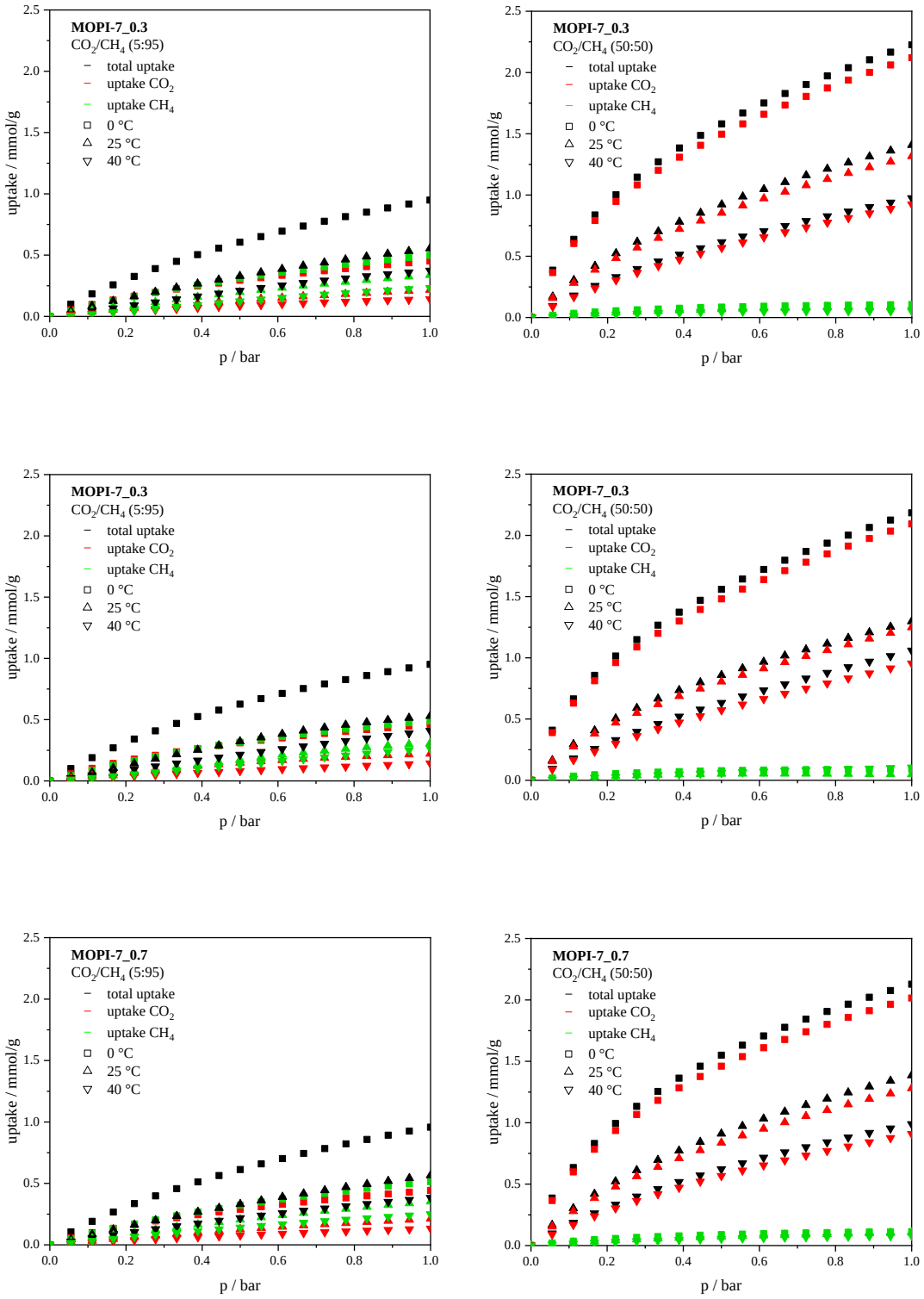


Figure S 13: Isotherms calculated by IAST for gas mixtures of 5:95 CO_2/CH_4 (left) and 50:50 CO_2/CH_4 (right) for the MOPI-7 series. Black indicates the total uptake, red the uptake of CO_2 and green the uptake of CH_4 in the mixture at 0 °C (square symbol), 25 °C (triangle with apex up) and 40 °C (triangle with apex down).

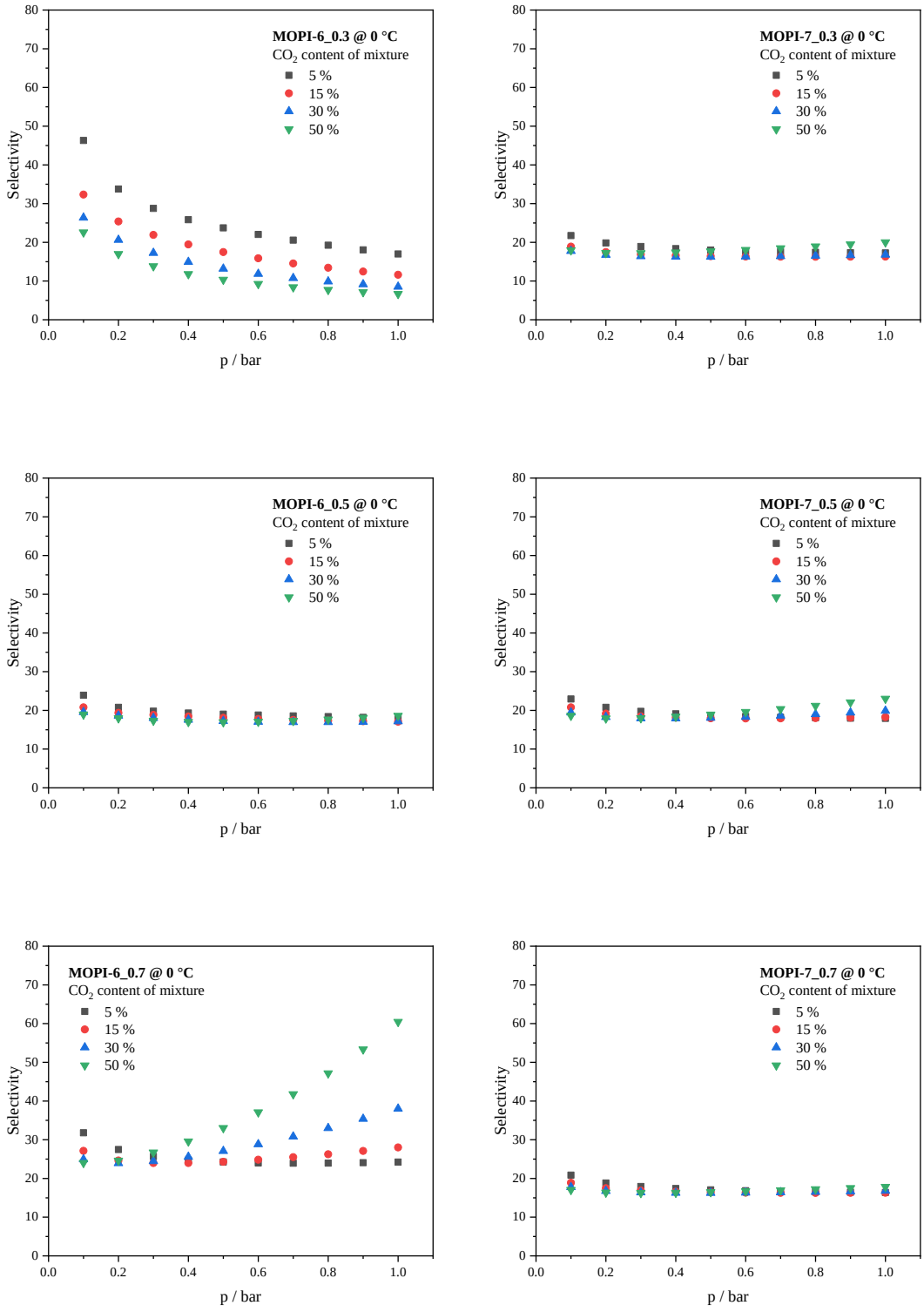


Figure S 14: Selectivities calculated by IAST with varying CO_2 content of the CO_2/CH_4 mixture for the MOPI-6 (left) and MOPI-7 (right) series as a function of pressure at 0 °C.

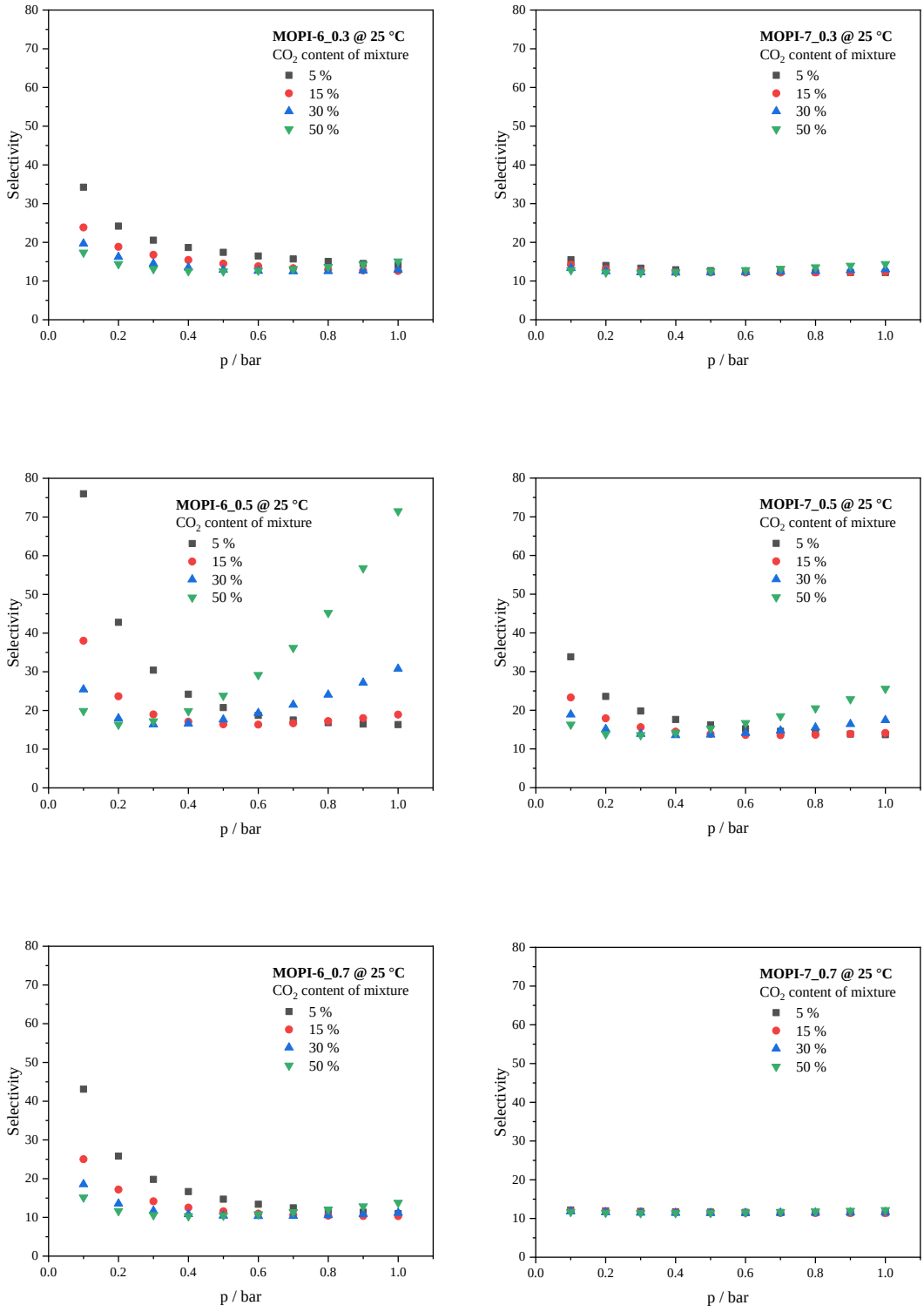


Figure S 15: Selectivities calculated by IAST with varying CO_2 content of the CO_2/CH_4 mixture for the MOPI-6 (left) and MOPI-7 (right) series as a function of pressure at 25 °C.

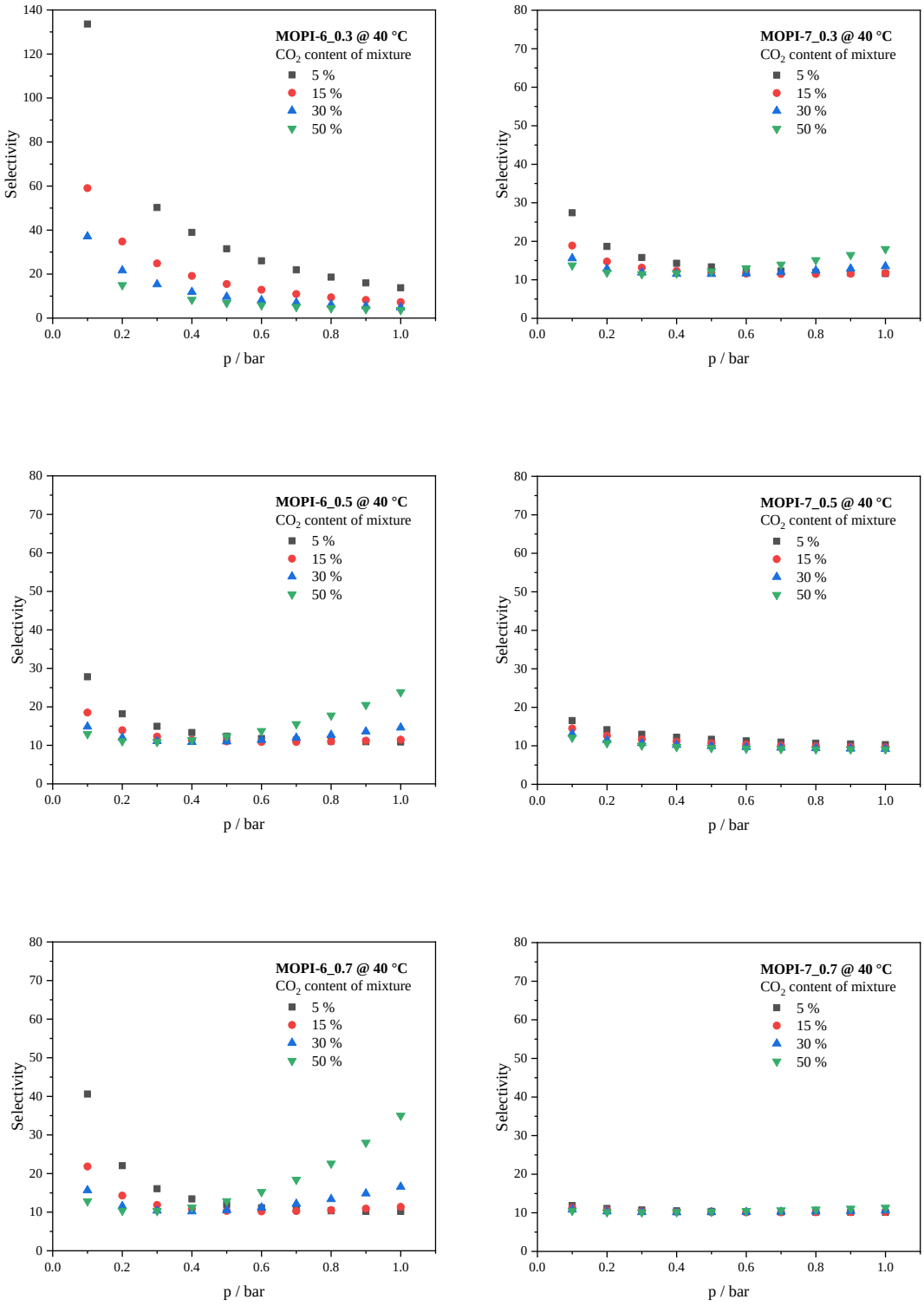


Figure S 16: Selectivities calculated by IAST with varying CO_2 content of the CO_2/CH_4 mixture for the MOPI-6 (left) and MOPI-7 (right) series as a function of pressure at 40 °C.

3.11 SEM images

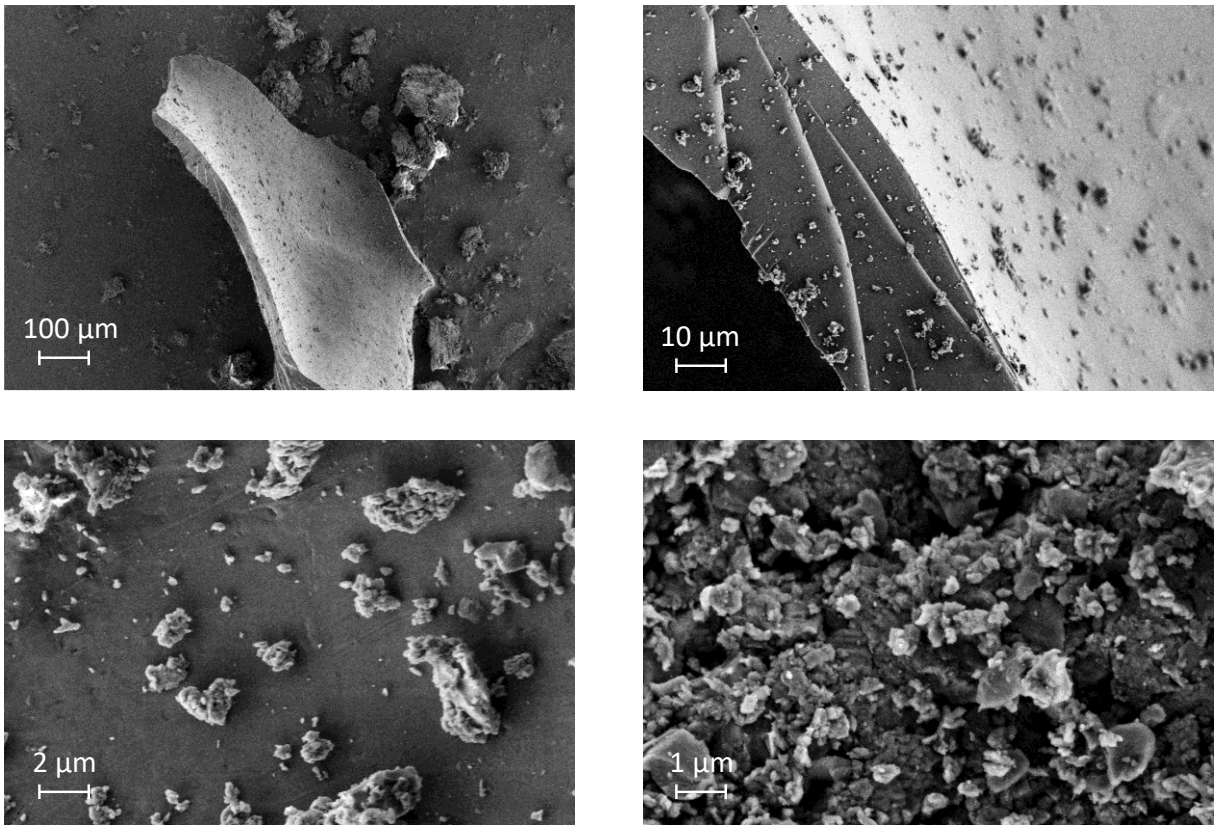


Figure S 17: SEM Images of MOPI-6_0.3.

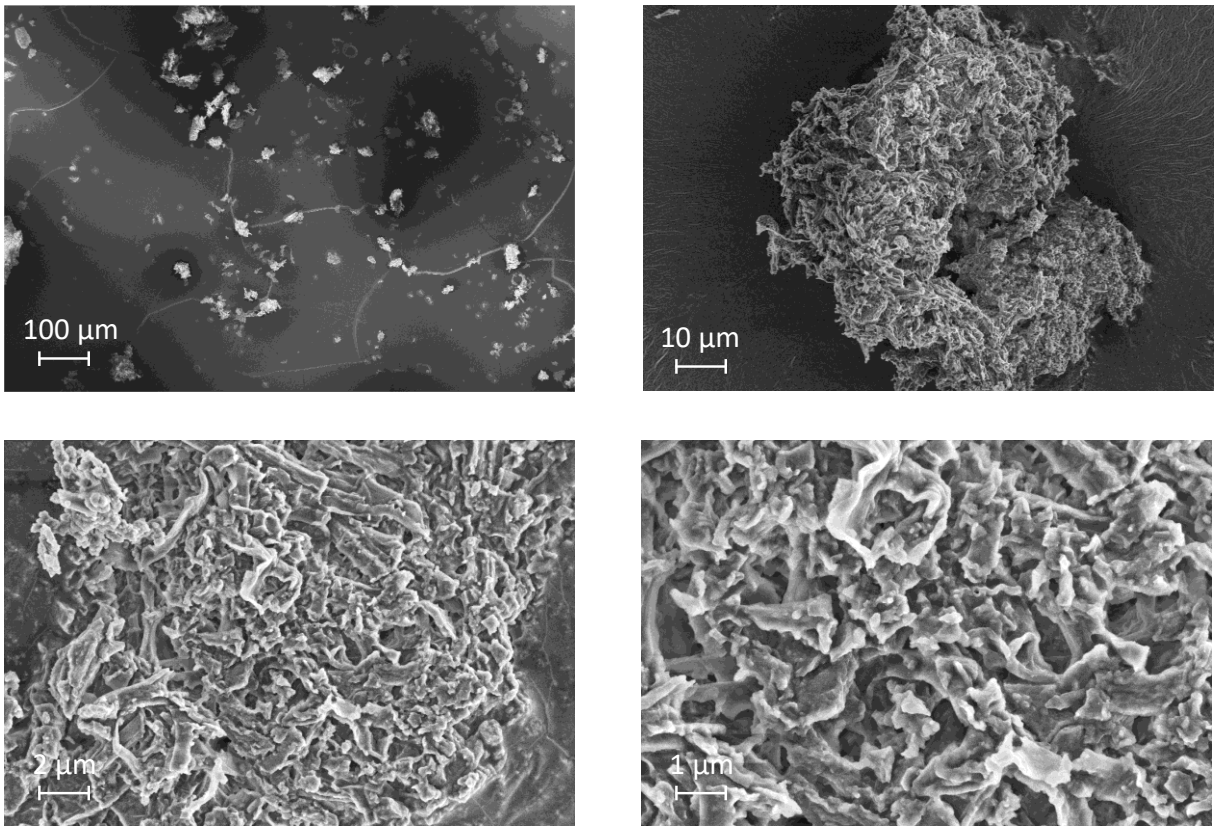


Figure S 18: SEM Images of MOPI-6_0.5.

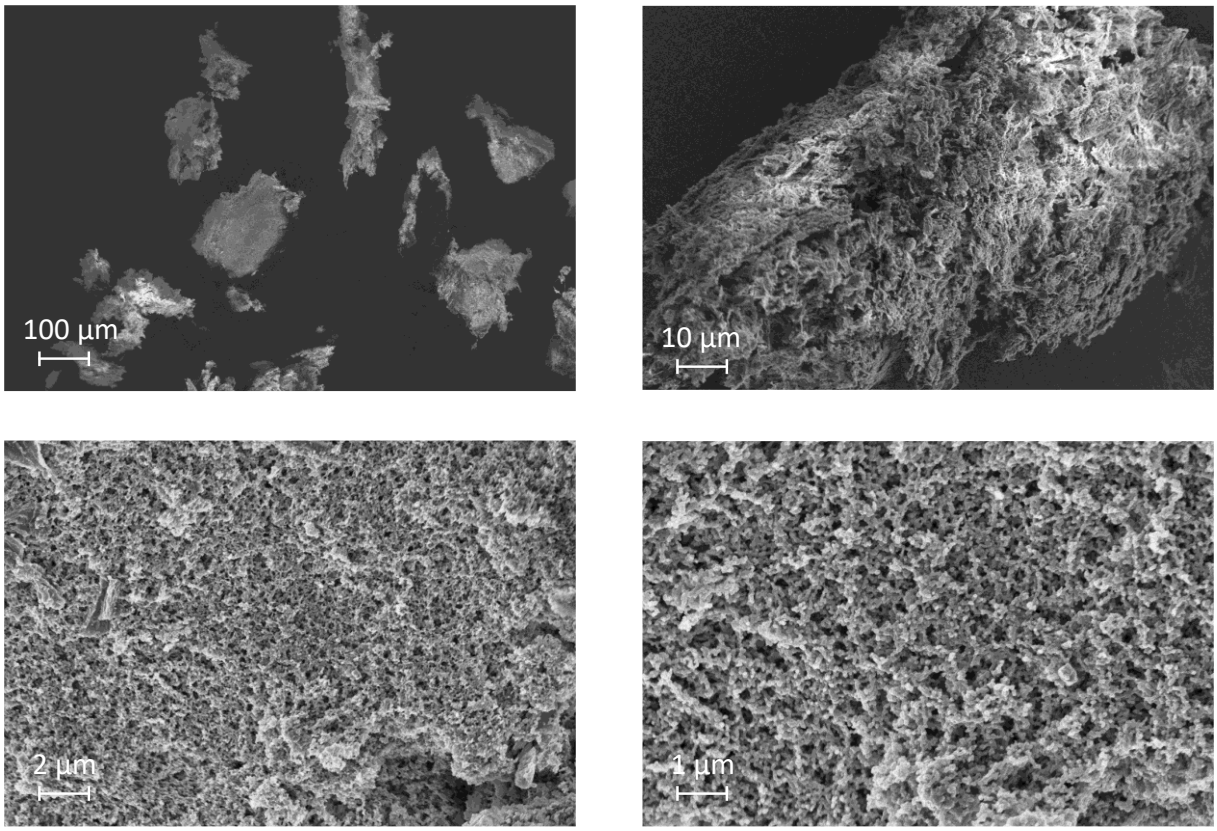


Figure S 19: SEM Images of MOPI-6_0.7.

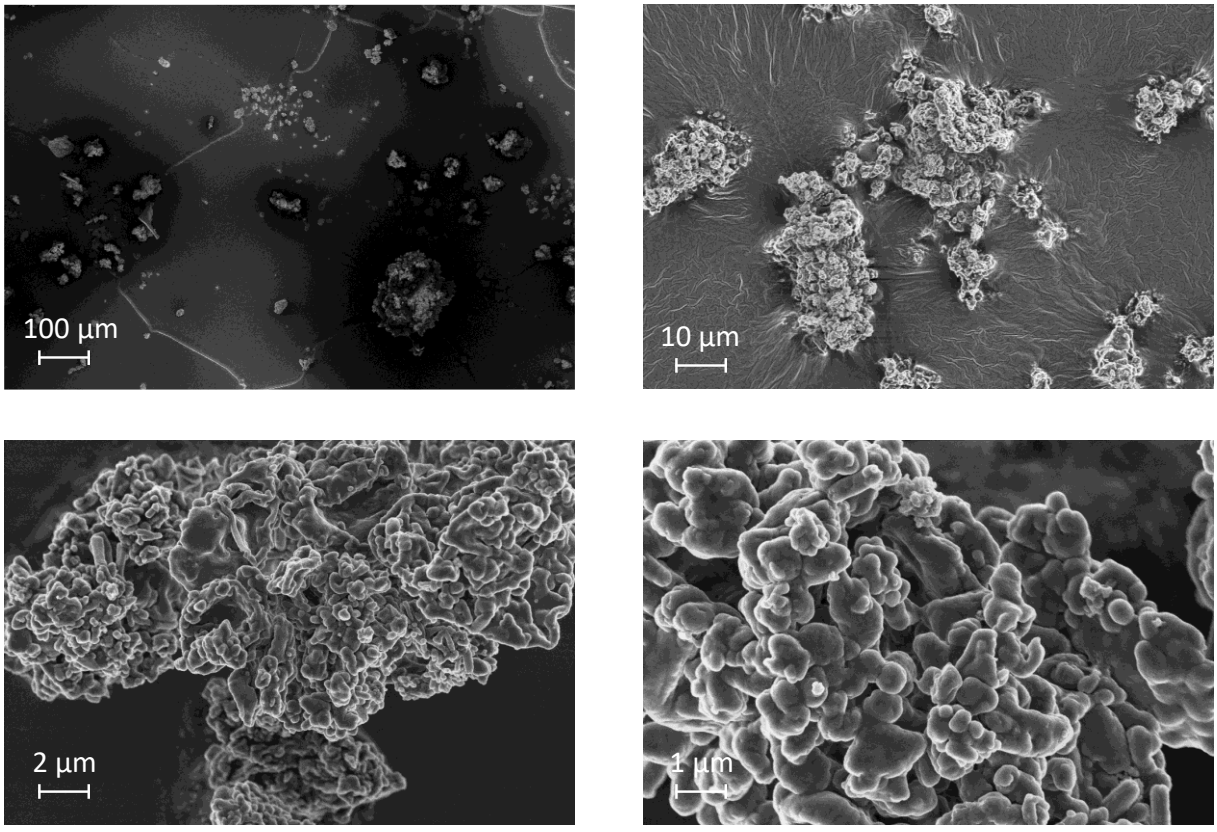


Figure S 20: SEM Images of MOPI-6_1.

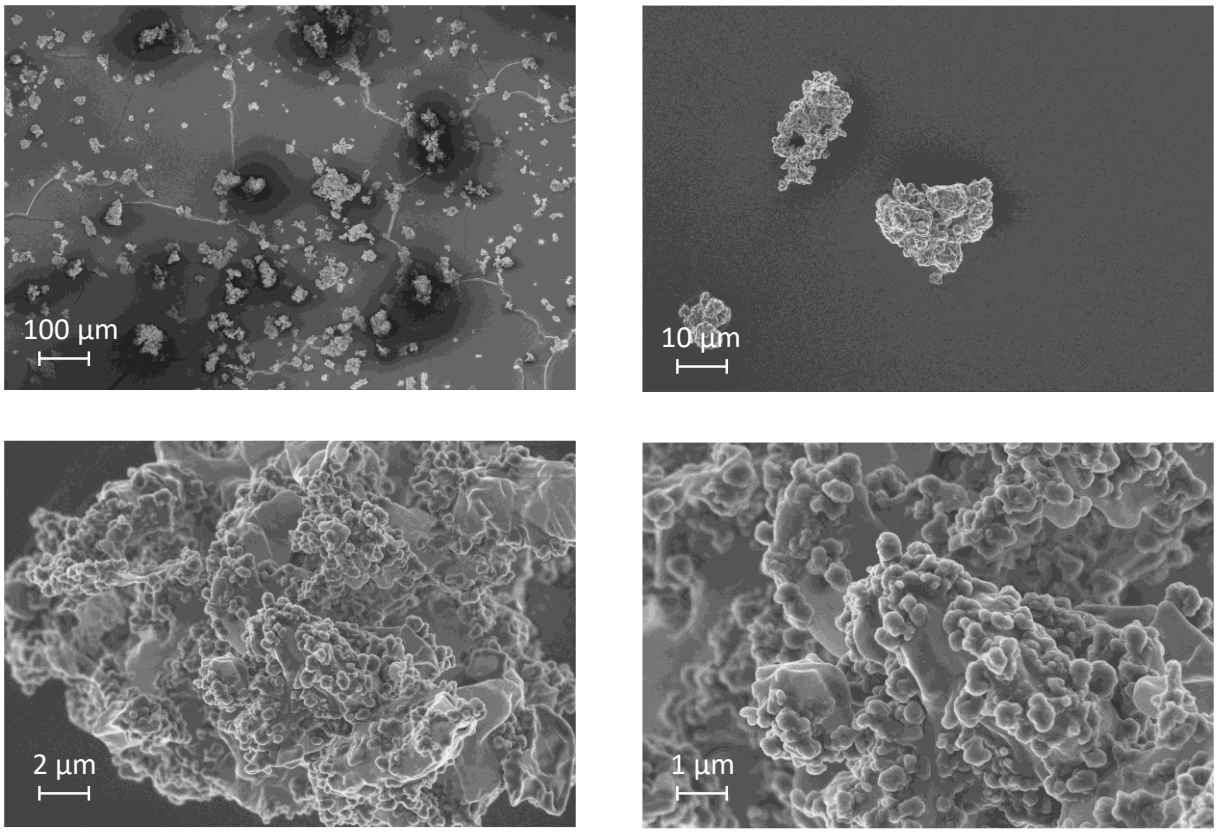


Figure S 21: SEM Images of MOPI-6_HP.

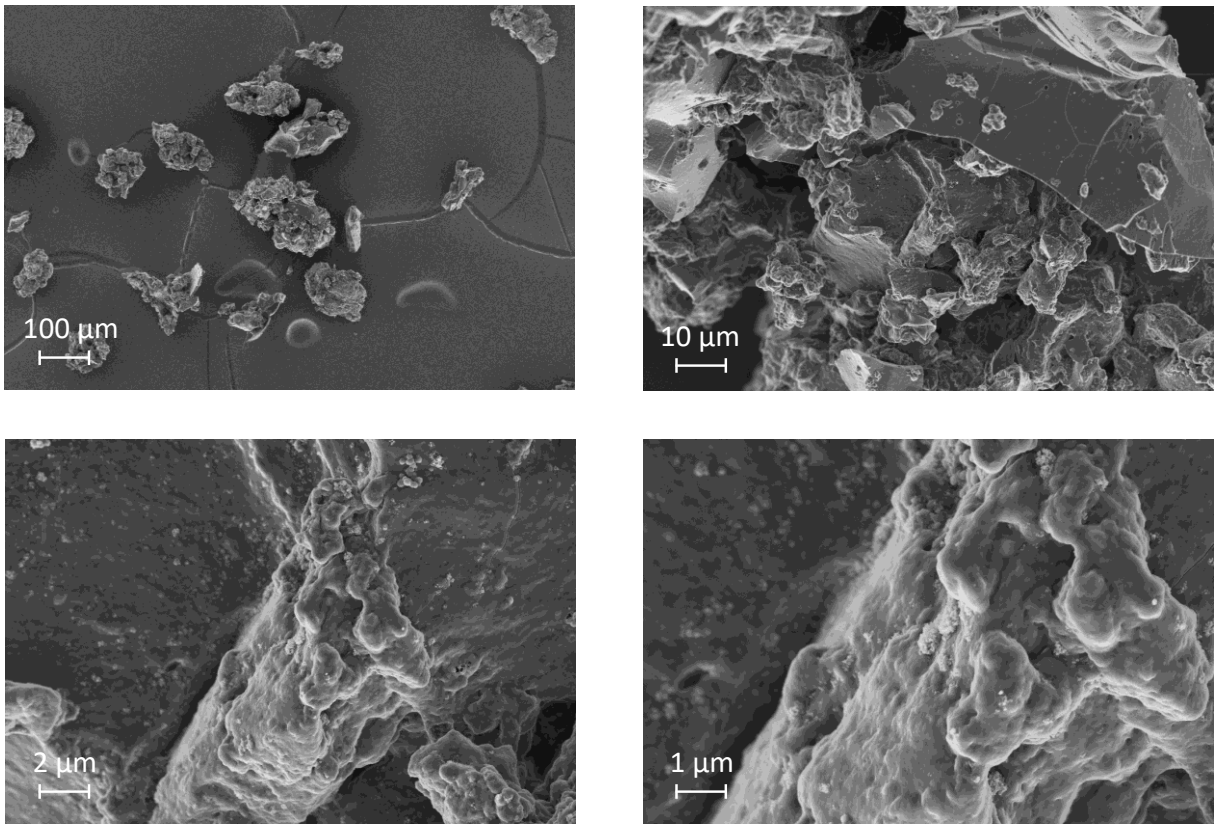


Figure S 22: SEM Images of MOPI-7_0.3.

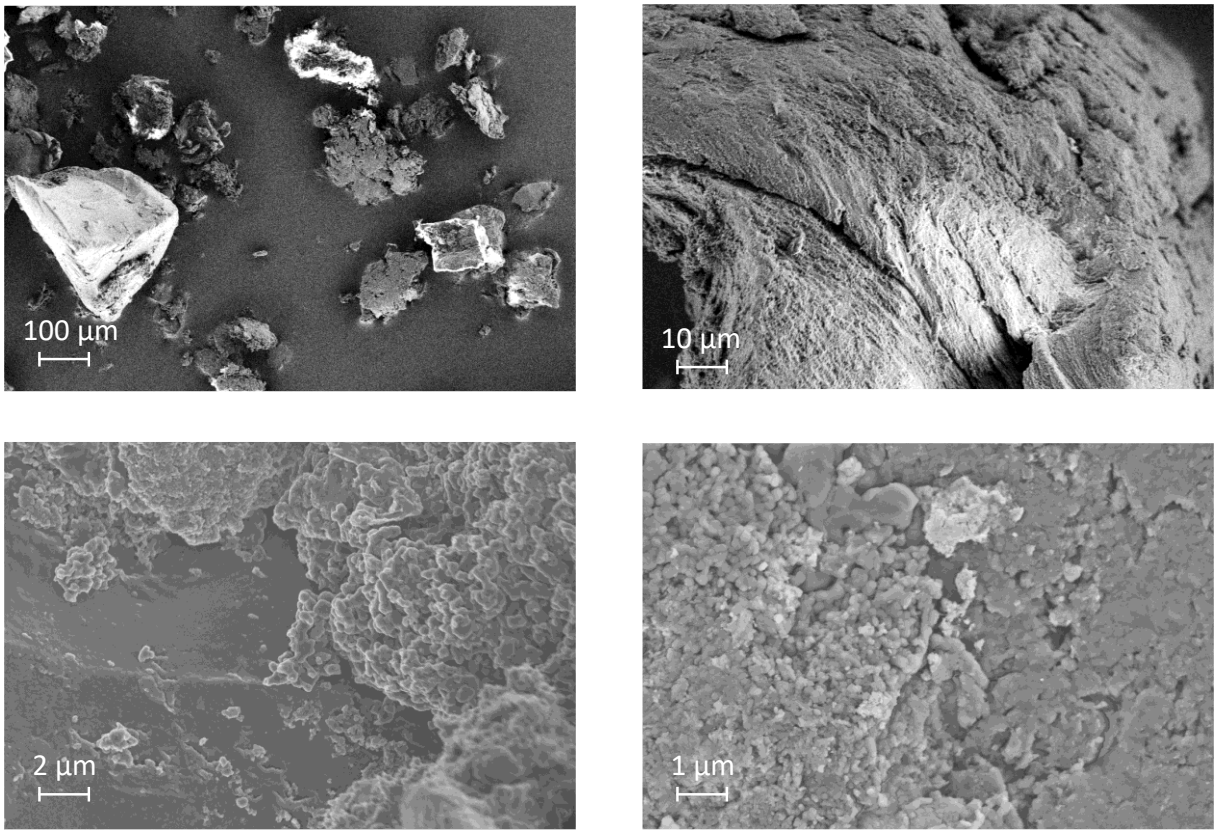


Figure S 23: SEM Images of MOPI-7_0.5.

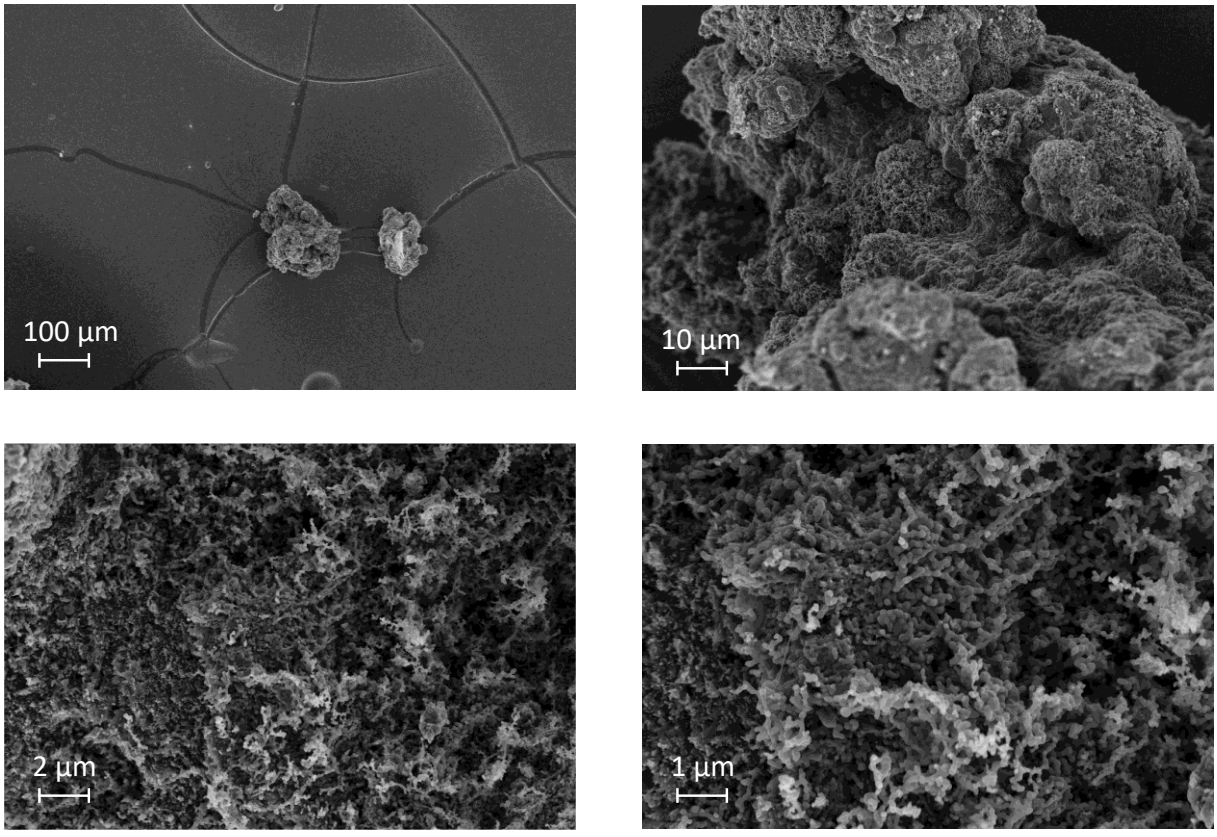


Figure S 24: SEM Images of MOPI-7_0.7.

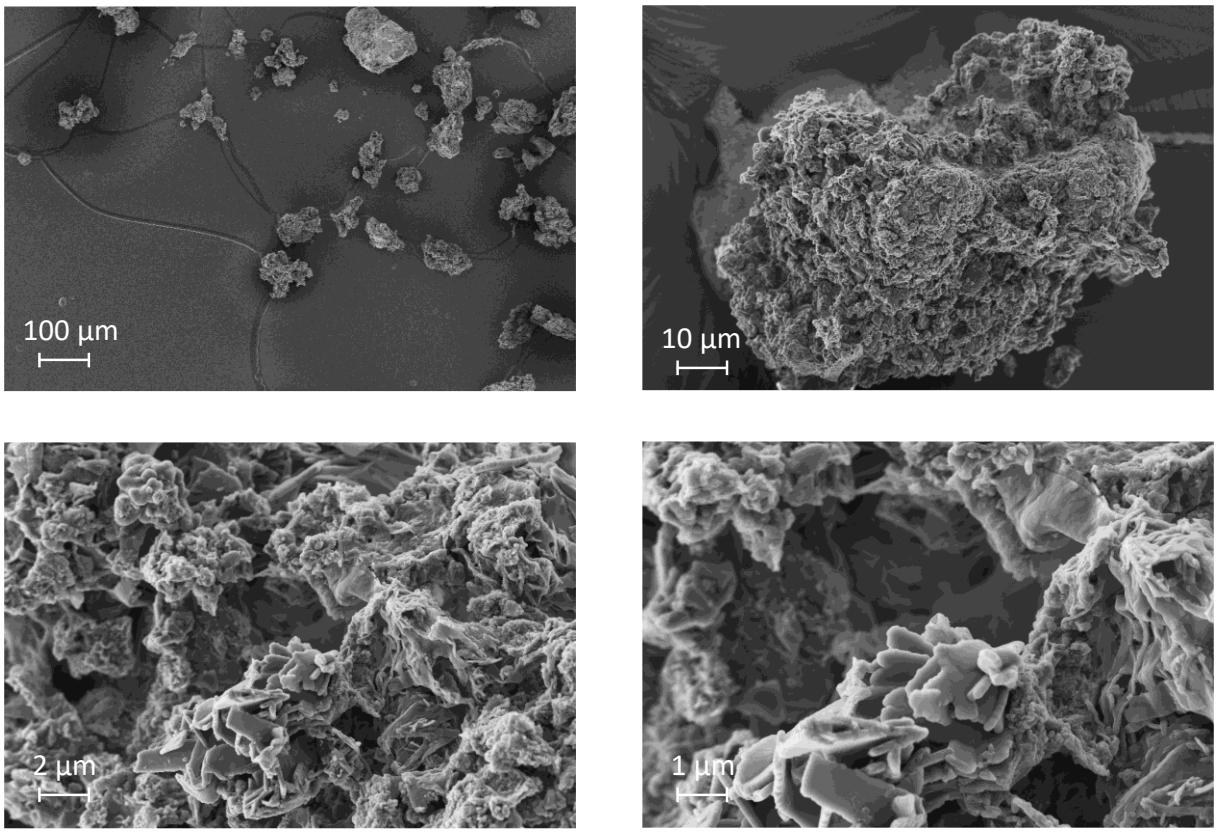


Figure S 25: SEM Images of MOPI-7_1.

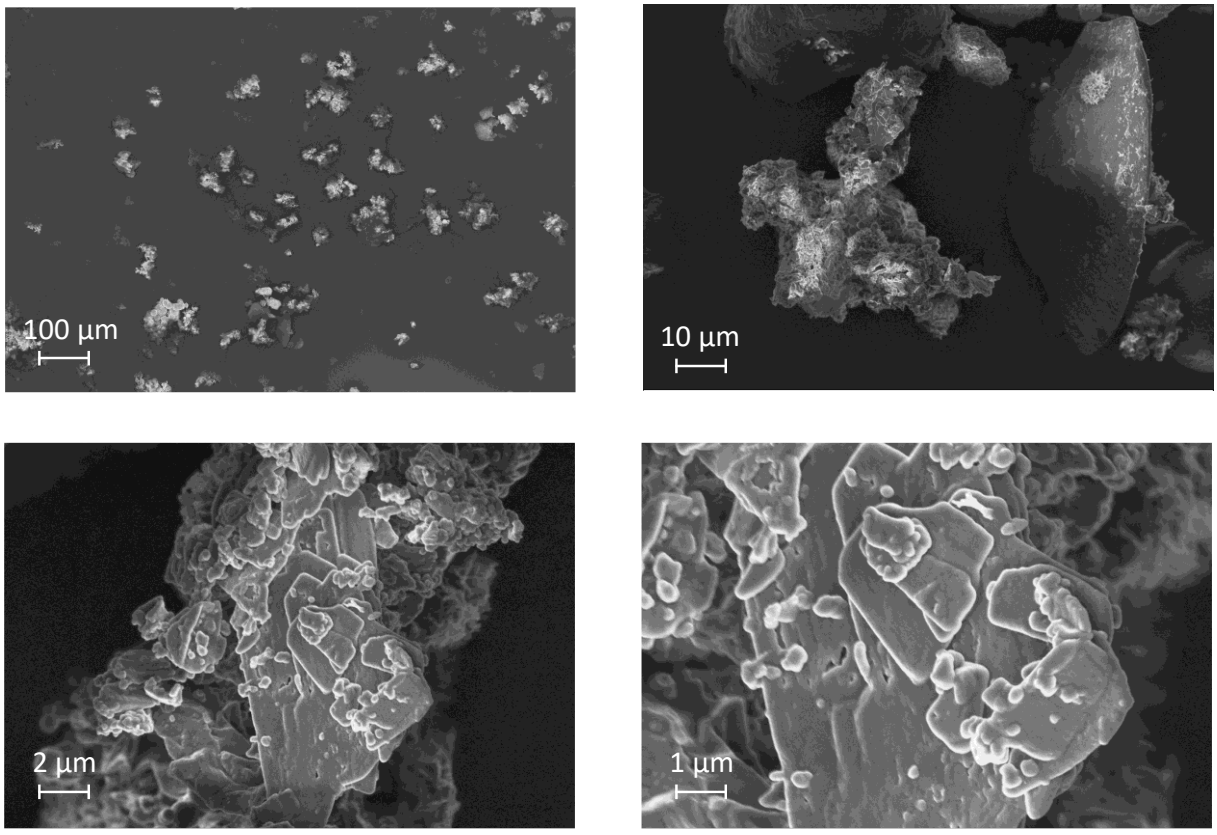


Figure S 26: SEM Images of MOPI-7_HP.