

## Supporting Information

### Preparation of Freestanding Conjugated Microporous Polymer Nanomembranes for Gas Separation

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**Chemicals:** All chemicals were purchased from commercial sources and used without any further purification if not indicated differently. Tetrahydrofuran (THF) was purchased from Acros Organics; tert-butyl nitrite was purchased from ABCR; toluene was purchased from Alfa Aesar and was used as received. Acetone, ethyl acetate and ethanol were purchased from Prolabo. Tetrakis-acetonitrile-copper(I) hexafluorophosphate and poly(methyl methacrylate) (PMMA) average  $M_w$  996,000 were purchased from Aldrich. Iodine and potassium iodide were purchased from Sigma-Aldrich. Tetrakis(4-azidophenyl)-methane (TPM-azide) and tetrakis(4-ethynylphenyl)methane (TPM-alkyne) were synthesized as described in literature.<sup>1</sup> The 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [BMIM][NTf2] ionic liquid was purchased from Io-li-tec (Ionic Liquid Technologies).

**Safety in the Handling of Sodium Azide and other Azides** Sodium azide is toxic ( $LD_{50}$  oral (rats)=27 mg kg<sup>-1</sup>) and can be absorbed through the skin. It decomposes explosively upon heating to above 275 °C). Some organic and other covalent azides are classified as toxic and highly explosive, and appropriate safety measures must be taken at all times.<sup>2</sup>

**Substrates:** As sacrificial substrate a 300 nm flame annealed gold film on mica was used. For analytical measurements the membrane was transferred to a Si(100) wafer coated with 5 nm titanium and 100 nm gold, this substrate was also used for growing CMP-films and for testing CMP on MOF. The substrates were obtained by Georg-Albert-PVD, Germany and were stored after preparation under argon and were rinsed with pure ethanol before use. The gas permeation tests were done on a supporting membrane consisting of a thin layer PDMS on a PAN membrane.<sup>3</sup>

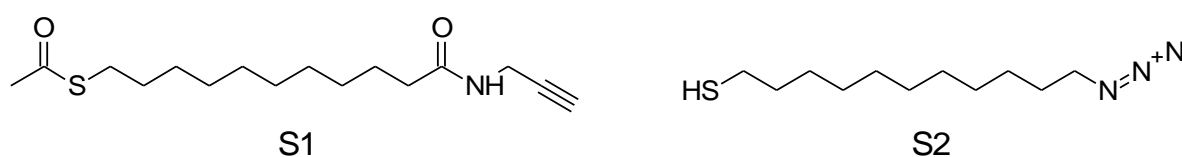
**Infrared reflection absorption spectroscopy (IRRAS):** The IRRAS-spectra were recorded on a Bruker Vertex 80 purged with dried air. The IRRAS accessory (A518) has a fixed angle of incidence of 80°. The data were collected on a narrow band liquid nitrogen cooled MCT detector. Perdeuterated

hexadecanethiol-SAMs on Au/Ti/Si were used for reference measurements. The absorption band positions are given in wave numbers  $\tilde{\nu}$  in  $\text{cm}^{-1}$ .

**Atomic force microscopy (AFM):** AFM-imaging was done using an Asylum Research Atomic Force Microscope, MFP-3D BIO. The AFM was operated at 25°C in an isolated chamber in alternating current mode (AC mode). AFM cantilevers were purchased from Ultrasharp<sup>tm</sup> MikroMasch. Three types of AFM-cantilevers were used, an NSC-35 (resonance frequency 315 kHz; spring constant 14 N/m), an NSC-36 (resonance frequency: 105 KHz; spring constant: 0.95 N/m) and an NSC-18 (resonance frequency: 75 kHz; spring constant: 3.5 N/m).

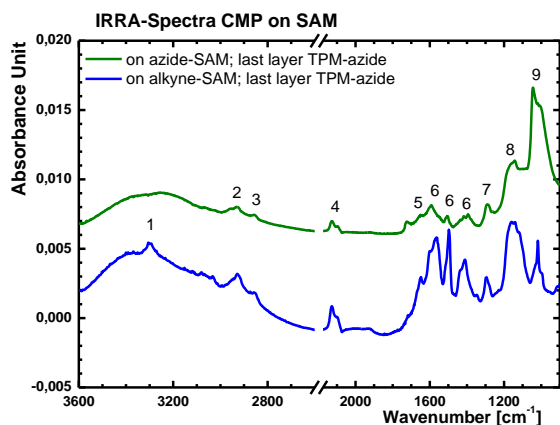
**Helium Ion Microscope (HIM):** Helium ion microscopy (HIM) was conducted with a Carl Zeiss Orion Plus<sup>®</sup> instrument.<sup>4</sup> The  $\text{He}^+$  beam was operated at 25.1 kV acceleration voltages at currents below 0.5 pA. Charging of insulating samples was compensated with an electron flood gun at 550 eV and a flood time of 1000  $\mu\text{s}$  in the line mode. The HIM images were recorded by an Everhardt-Thornley detector at 500 V grid voltages with 0.2  $\mu\text{s}$  dwell time to collect secondary electrons from the samples.<sup>5</sup>

**SAM-preparation:** For SAM formation a clean gold substrate was rinsed with pure ethanol and then immersed in a solution of 11-thioacetyl-undecane acid-propargyl amide (**S1**, Figure S1) and of 11-azidoundecanethiol (**S2**, Figure S1) (each with a concentration of 1 mmol/L) in ethanol for 18 h. Afterwards the substrate was taken out, rinsed thoroughly with ethanol and dried under nitrogen stream.<sup>6</sup>



**Figure S1:** Chemical structure for 11-thioacetyl-undecane acid-propargyl amide **S1** and 11-azidoundecanethiol **S2**.

**Preparation of CMP-films:** TPM-azide, TPM-alkyne and tetrakis(acetonitrile)copper(I) hexafluorophosphate were dissolved in water free THF ( $c = 2 \text{ mmol/L}$ ). The synthesis was carried out under inert conditions using a Schlenk line. TPM-azide and TPM-alkyne were alternately given to the substrate together with Cu(I)catalyst; after each step the substrate was rinsed with THF. The reaction time for the click-reaction was 30 minutes. After the desired amounts of cycles the coated substrate was taken out from the reaction solution, rinsed with THF, ethanol and dried with nitrogen. Figure S2 shows the IRRA spectra of CMP-films grown on azide terminated SAM-S2 (green) and alkyne terminated SAM-S1 (blue).

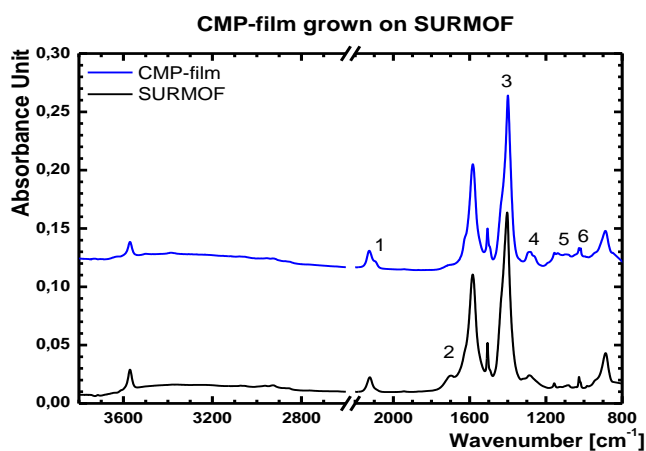


**Figure S2:** IRRA-Spectra from CMP-films grown on a) azide terminated SAM (**S2**) (green) and b) alkyne terminated SAM (**S1**) (blue).

**Table S1:** Assignment of the bands in the CMP-film spectra shown in Figure S2.

No.	Band (cm <sup>-1</sup> )	According vibrations/ functional group
1	3300	$\nu_s$ alkyne-H
2	2929	$\nu_{as}$ -CH <sub>2</sub>
3	2857	$\nu_s$ -CH <sub>2</sub>
4	2128, 2100	$\nu_{as}$ -N <sub>3</sub> , $\nu$ -C-C (alkyne group)
5	1646	$\nu$ C=C
6	1593, 1504, 1418	vibrations from the aromatic backbone
7	1288	$\nu_s$ -N <sub>3</sub> , $\omega$ CH (alkyne group)
8	1154	$\delta$ CH aromatic
9	1044	$\beta$ CH aromatic

**Preparation of CMP-films on SURMOF:** The SURMOFs were prepared as described in literature following a stepwise liquid-phase epitaxy procedure.<sup>7</sup> CMP-films were prepared on the SURMOF coatings as described above. The IRRA spectra are reported in Figure S3.



**Figure S3:** IRRA-Spectra from CMP-film grown on a SURMOF (in blue). As reference the SURMOF spectra (in black).

**Table S2:** Changed bands in the IRRA spectra (Figure S3) of CMP-film on SUR-MOF compared to the pure SURMOF.

No.	Band ( $\text{cm}^{-1}$ )	vibrations	change
1	2126	$\nu_{\text{as}} -\text{N}_3$	+ shoulder at $2093 \text{ cm}^{-1}$
2	1718	$\nu \text{ COOH}$	band is not seen in the CMP-film spectra
3	1399	$\nu_{\text{s}} \text{ COO}^-$	shifted $4 \text{ cm}^{-1}$ towards lower energy
4	1281	$\nu_{\text{s}} -\text{N}_3, \omega \text{ alkyne-H}$	broader band + shoulder at $1261 \text{ cm}^{-1}$
5	1138	$-\delta \text{ CH}_2$ in THF, cyclic ethers, $\text{COOH}$ v $\text{CO}$	new band, maybe remaining THF in pores
6	1017	$\delta \text{ Ar-H}$	new band

**Preparation of freestanding CMP-membranes:** CMP coated SURMOF samples were immersed in 10 mL ethanol/water 1/1 (volume) containing 1 mg ethylene diaminetetraacetic acid (EDTA). After a few seconds immersion at room temperature, the CMP-membrane started to detach from the substrate.

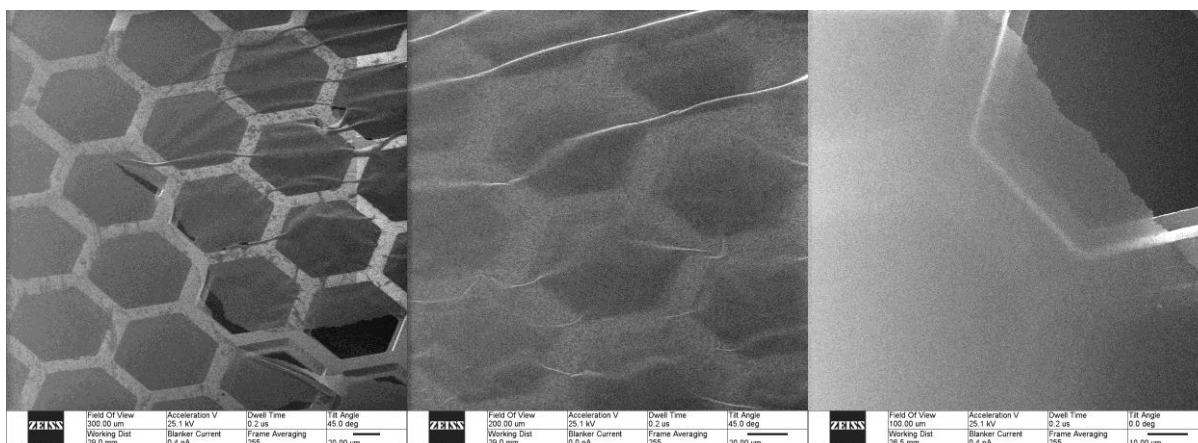


**Figure S4:** Optical microscope picture from a CMP-membrane after dissolving the SURMOF with EDTA.

**Preparation of the membrane from SAM on sacrificial substrate:** To obtain the membrane the CMP-film was grown on sacrificial substrate using above described method. The membrane was then obtained by following a procedure described in literature and shown in Figure S5.<sup>5</sup> First PMMA was spin coated as a supporting layer and afterwards the mica was removed by immersing in  $\text{I}_2/\text{KI}/\text{H}_2\text{O}$ ;  $\text{KI}/\text{H}_2\text{O}$  and in the last step  $\text{H}_2\text{O}$ . The retaining gold film was etched in a solution of  $\text{I}_2/\text{KI}/\text{H}_2\text{O}$ . The membrane was washed 3 times in water. Afterwards the membrane was transferred to the desired substrate as described by Beyer/Gölzhäuser.<sup>5</sup>

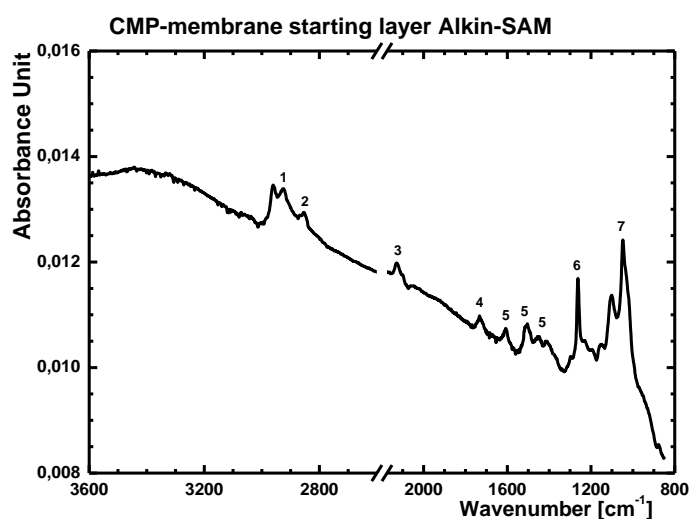


**Figure S5:** Schematic description of the transfer process of a CMP-membrane, starting with spin coating of PMMA on top of the CMP-film on Au-Mica. Afterwards the mica substrate was detached; the gold film was etched away and after several times washing, the PMMA/CMP-membrane was transferred to a new substrate. As last step the PMMA-layer was dissolved in acetone.



**Figure S6:** Helium-ion-microscopy (HIM) images of a CMP-membrane transferred to a TEM-grid.

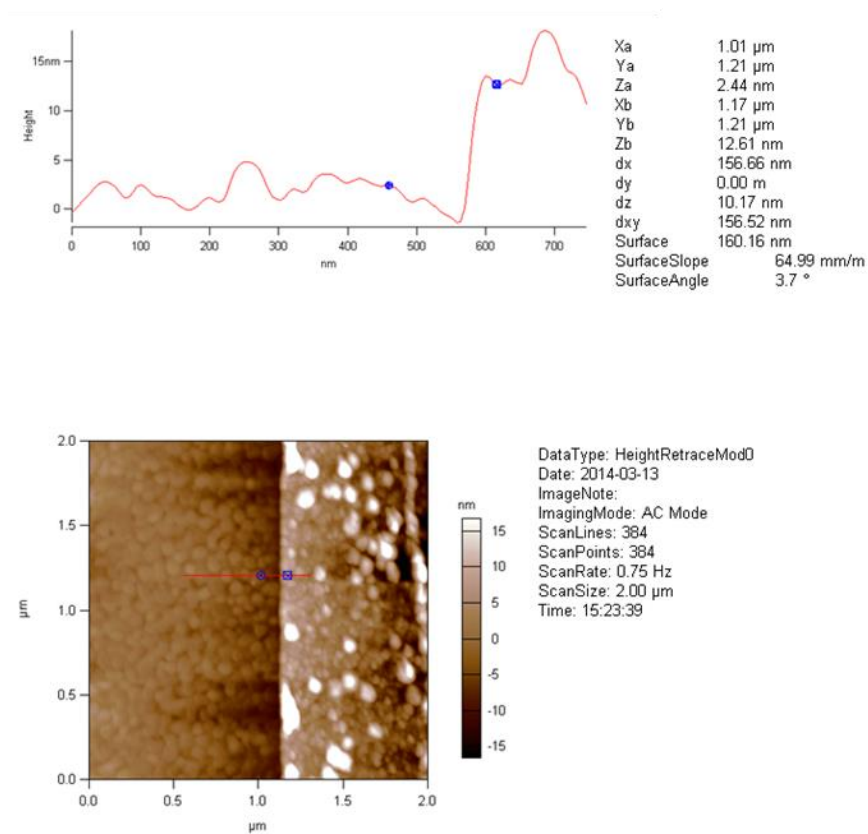
The IRRA spectra of the membrane transferred to a Au/Si substrate is shown in Figure S7.



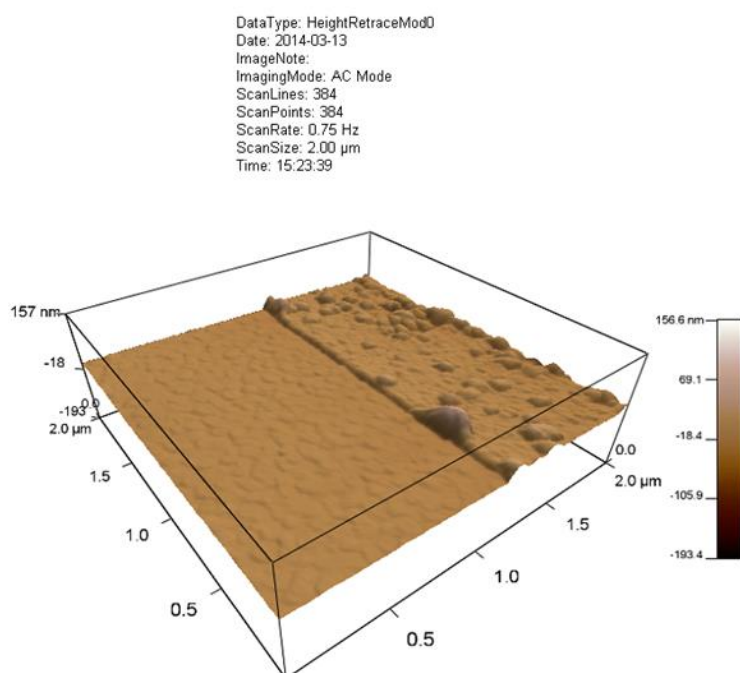
**Figure S7:** IRRA spectra of a 8 cycle CMP-membrane grown on alkyne terminated SAM and transferred to a gold wafer.

**Table S3:** Assignment of the bands in the CMP-membrane spectra shown in Figure S7.

No.	Band (cm <sup>-1</sup> )	According vibrations/ functional group
1	2925	$\nu_{as}-CH_2$
2	2853	$\nu_s-CH_2$
3	2128, 2100	$\nu_{as}-N_3$ , $\nu-C-C$ (alkyne group)
4	1733	$\nu-CO$ (CO group from SAM-molecule ( <b>S1</b> ))
5	1607, 1504, 1447	vibrations from the aromatic backbone
6	1262	$\nu_s-N_3$ , $\omega CH$ (alkyne group)
7	1048	B CH aromatic

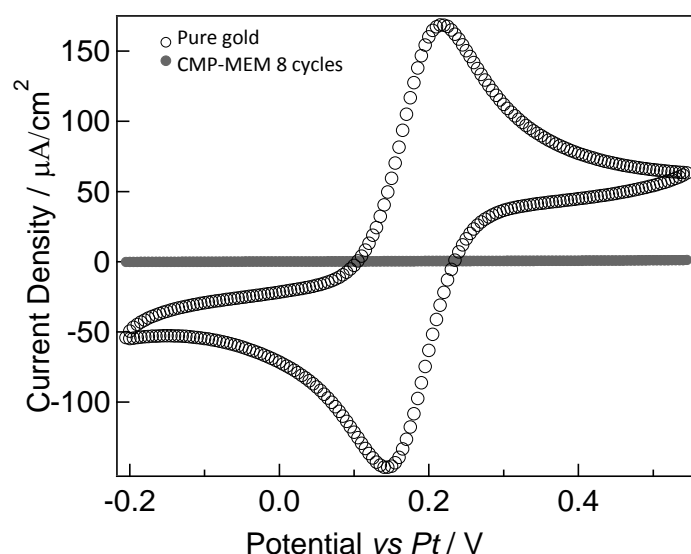


**Figure S8:** AFM measurement on membrane transferred to gold wafer. Height measurement shown on top was performed along the red line at the edge of the membrane in the image below.



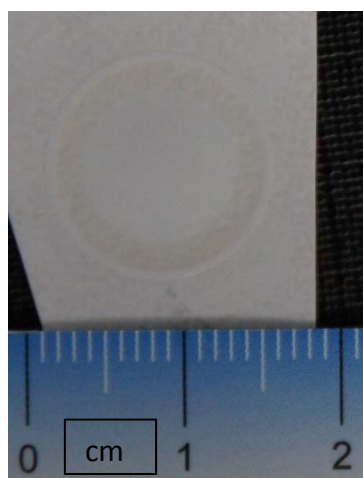
**Figure S9:** 3D image of a CMP-membrane transferred to a gold wafer and measured with AFM.

**Cyclic voltammetry:** The cyclic voltammogram was recorded using a PalmSens<sup>3</sup> potentiostat from Palmsens. In the home build electrochemical cell, the CMP substrate was used as working electrode, the ionic liquid [BMIM][NTf<sub>2</sub>] (with 4% ethanol) used as supporting electrolyte and ferrocene (2.85 mM) as electroactive species. Scan rate: 0.1 V/s. Platinum wires were used as reference and counter electrode.



**Figure S10:** Cyclic voltammograms of gold substrate before (empty black circles) and after (grey filled circles) the transfer of a CMP-nanomembrane.

**Gas transport measurements:** The permeances of  $\text{H}_2$ , He,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , Ar,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  for the CMP-PDMS/PAN samples were measured at feed pressures of 108 to 280 mbar and at a temperature of 30°C using a constant volume/variable pressure experimental setup, as described in details elsewhere.<sup>8,9</sup> The feed pressures were chosen to be sufficiently low to employ the ideal gas model in the data evaluation as well as sufficiently high to match the sensitivity of the measurement system. Each gas measurement was repeated four times and the result was considered as acceptable when the permeance values had a scattering below 5%. Figure S11 shows the CMP-membrane on top of supporting membrane after permeance measurement. The impress of the O-ring can be clearly seen. The measured area inside the O-ring is around 0.75  $\text{cm}^2$  big. Figures S12-S17 show the measured permeances for the different samples.



**Figure S11:** Photograph of the CMP-membrane on top of supporting membrane after permeance measurement.

Figures S12-S15: For these samples the CMP-nanomembranes were transferred to PDMS coated PAN support.

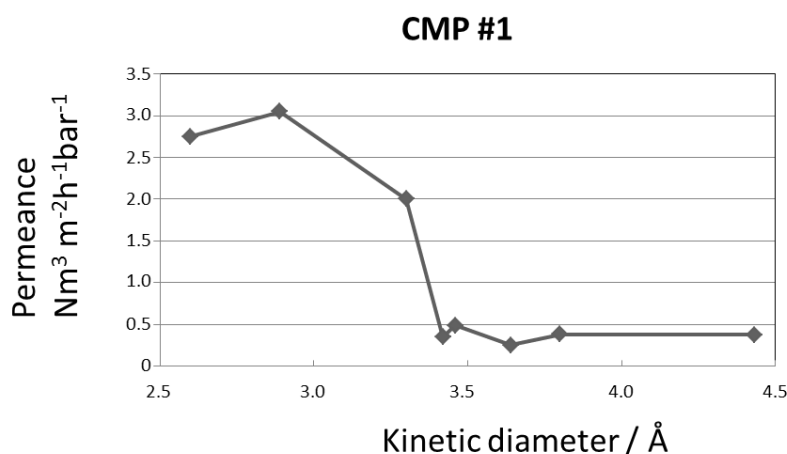
The values obtained by the permeance measurement ( $P_{\text{CMP-PDMS/PAN}}$ ) can be considered as combined values for the stacked system CMP-membrane ( $P_{\text{CMP}}$ ) and PDMS/PAN-membrane ( $P_{\text{PDMS/PAN}}$ ). The relationship between the permeances of the combined layers to the permeances of the individual layers is:

$$1/P_{\text{CMP-PDMS/PAN}} = 1/P_{\text{CMP}} + 1/P_{\text{PDMS/PAN}}$$

The tables below list the measured permeances (in  $\text{Nm}^3 \text{m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ) and the permeances of the CMP-nanomembrane alone (corrected). The calculation was performed as described in an earlier publication<sup>5</sup>.

The graphs show the corrected permeances against the kinetic diameter of the measured gases.

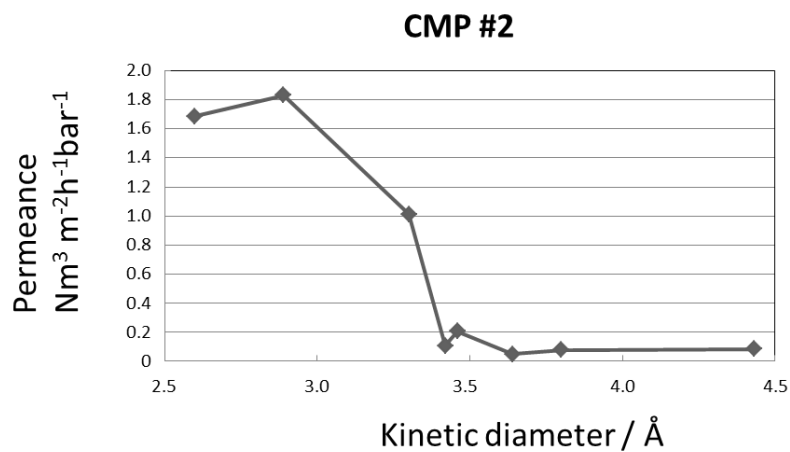
	He	H <sub>2</sub>	CO <sub>2</sub>	Ar	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	2.0414	2.4642	1.8673	0.3322	0.4639	0.2378	0.3679	0.3700
Corrected (considered coverage: 100%)	2.7499	3.0494	2.0004	0.3461	0.4912	0.2513	0.3798	0.3761



**Figure S12:** Permeance through CMP-membrane (sample 1) on PAN/PDMS support measured with eight different gases.

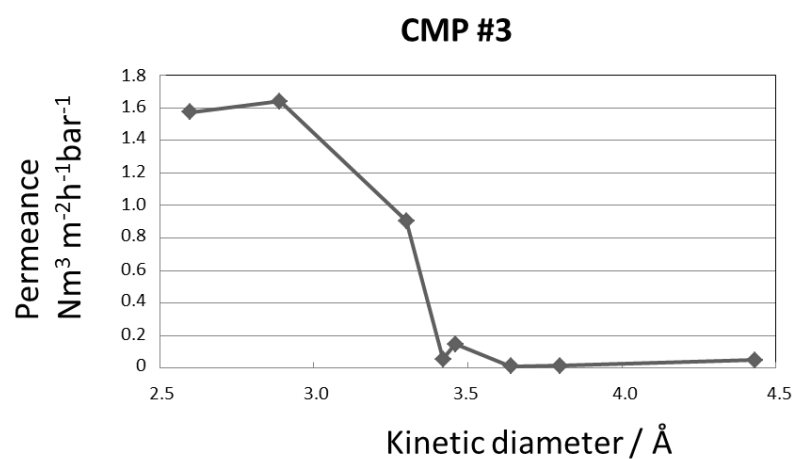


	He	H2	CO2	Ar	O2	N2	CH4	C2H6
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	1.3913	1.6031	0.9779	0.1050	0.1996	0.0469	0.0767	0.0845
Corrected (considered coverage: 100%)	1.6877	1.8318	1.0132	0.1064	0.2045	0.0474	0.0772	0.0848



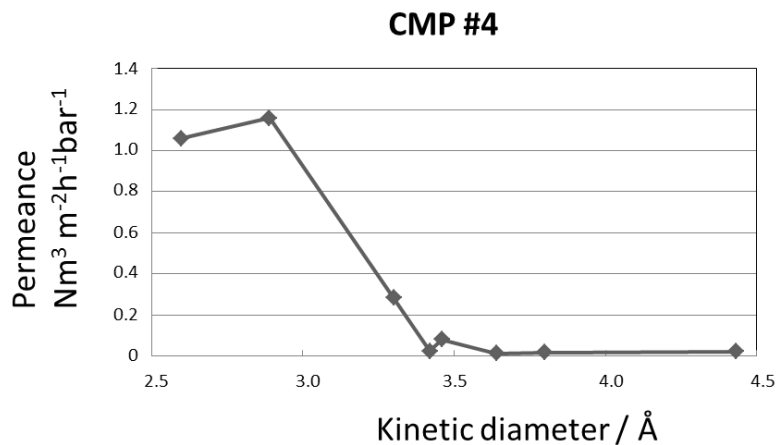
**Figure S13:** Permeance through CMP-membrane (sample 2) on PAN/PDMS support measured with eight different gases.

	He	H2	CO2	Ar	O2	N2	CH4	C2H6
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	1.5119	1.7959	1.6914	0.3007	0.3914	0.1444	0.3676	0.7315
Corrected (considered coverage: 97%)	1.5747	1.6400	0.9042	0.0551	0.1479	0.0118	0.0150	0.0490



**Figure S14:** Permeance through CMP-membrane (sample 3) on PAN/PDMS support measured with eight different gases.

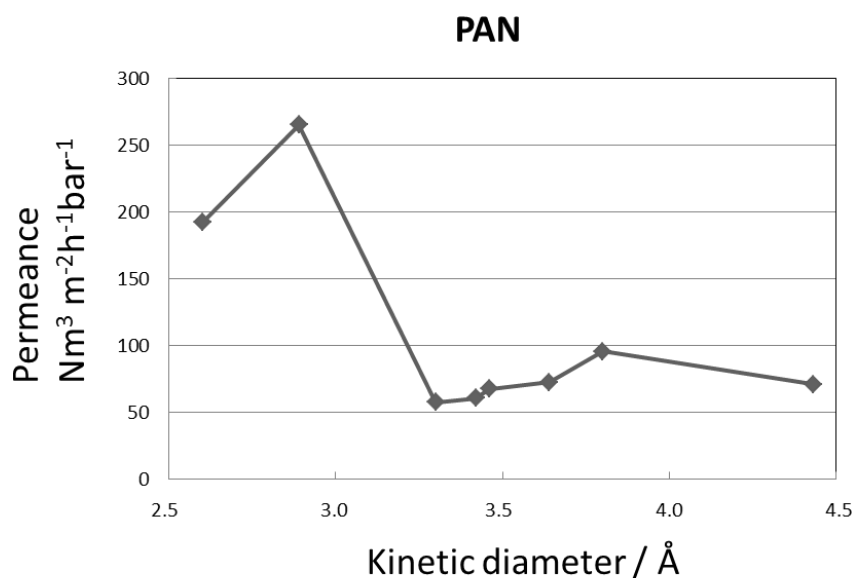
	He	H <sub>2</sub>	CO <sub>2</sub>	Ar	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	0.9356	1.0624	0.2799	0.0254	0.0792	0.0129	0.0170	0.0213
Corrected (considered coverage: 100%)	1.0609	1.1582	0.2827	0.0255	0.0800	0.0129	0.0170	0.0213



**Figure S15:** Permeance through CMP-membrane (sample 4) on PAN/PDMS support measured with eight different gases.

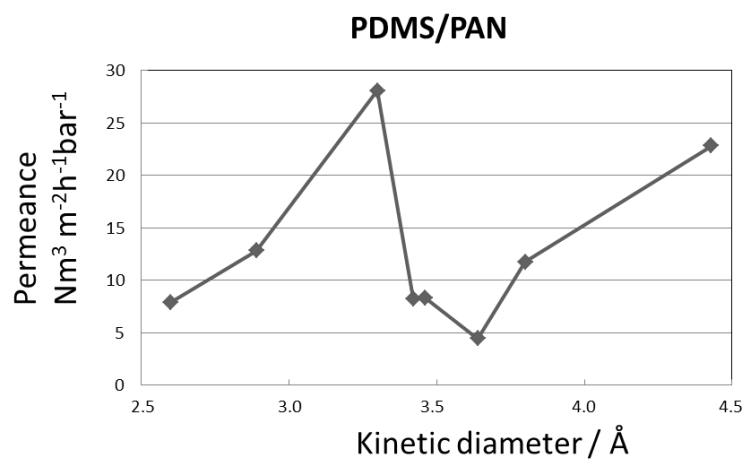
Figures S16 and S17 show the reference measurements for the bare PAN and PAN/PDMS substrates which were treated in the same way as the CMP coated samples.

	He	H <sub>2</sub>	CO <sub>2</sub>	Ar	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	192.0	265.3	57.4	60.4	67.5	72.4	95.5	71.1

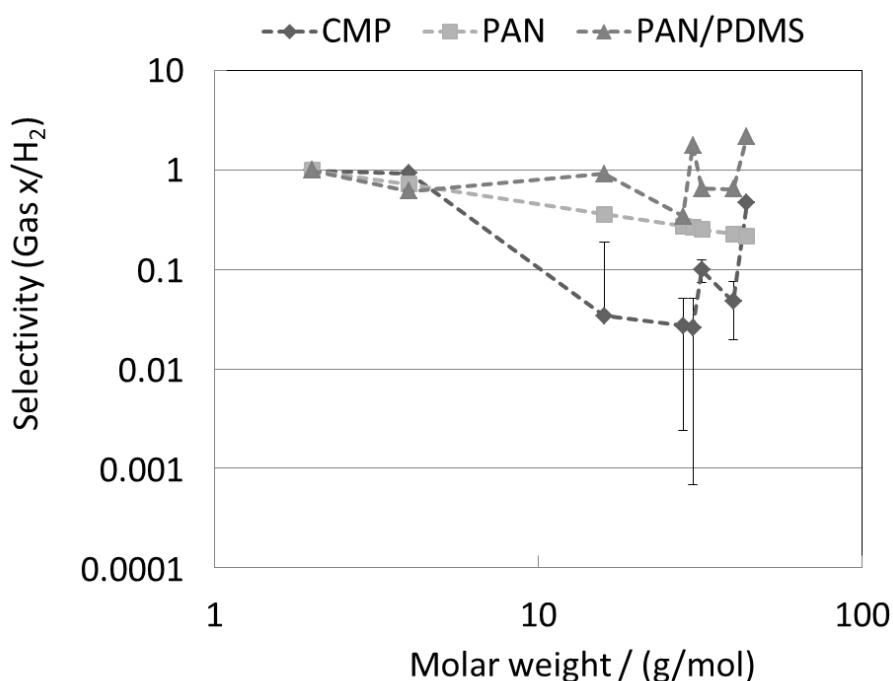


**Figure S16:** Permeance through pure PAN-substrate measured with eight different gases.

	He	H2	CO2	Ar	O2	N2	CH4	C2H6
kinetic diameter (Å)	2.6	2.89	3.3	3.42	3.46	3.64	3.8	4.43
MW (g/mol)	4	2	44	40	32	28	16	30
measured	7.9230	12.8412	28.0570	8.2551	8.3469	4.4315	11.7693	22.8019



**Figure S17:** Permeance through PAN/PDMS support measured with eight different gases.



**Figure S18:** Ideal selectivity of gas (x) versus  $H_2$  considered to the kinetic diameters of the gas molecules and calculated from the sole gas permeances.

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