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Microporous Organic Polyimides for CO₂ and H₂O Capture and Separation from CH₄ and N₂ Mixtures – Interplay between Porosity and Chemical Function

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Porous polyimides have been considered to be a promising material class for gas capture and sequestration, leading to the synthesis of a substantial number of individual networks with noteworthy sorption properties. In spite of these efforts, the vision of a chemical control of adsorption and desorption of small molecules, in particular, for the competing uptake of technical relevant gas mixtures, is still hardly investigated. Here we present a systematic study of five new polyimide networks based on a set of linkers with chemical functionalities covering the full range from hydrophobic to hydrophilic interactions. The corresponding microporous organic polyimides (MOPI-I to -V) were synthesized successfully based on a condensation reaction between amino and anhydride linker molecules in *m*-cresol at high temperatures, resulting in crosslinking degrees beyond 95 % in all cases. Argon and carbon dioxide isotherms reveal surface areas up to 940 m^2/g with a ultramicroporosity, about 50 % microporosity and high thermal stabilities under air with decomposition temperatures up to 480 °C. Sorption screening for variable temperatures revealed remarkable uptakes for carbon dioxide up to 3.8 mmol/g and water vapor up to 19.5 mmol/g combined with a smooth gate opening around 0.25 p/p_0 for MOPI-IV. In contrast, for MOPI-V the water vapor uptake decreases down to 7 mmol/g. Interestingly, the trend of the selectivities calculated by IAST and Henry does not correlate with the uptake behavior. For instance, MOPI-I and MOPI-III exhibit with 78 and 13 the highest CO_2 over N_2 and CH_4 Henry selectivities, although their CO_2 uptake is around 3.0 mmol/g. In total, we attribute the sorption properties for this class of materials mainly to the void size and shape within the ultramicroporous region. The chemical environment of the surfaces seems to have little influence on the uptake and a stronger effect on the separation behavior.

Introduction

To satisfy the energy requirements of modern society, the combustion of fossil fuels is still one of the most important energy sources nowadays.1 This implicates the emission of large amounts of carbon dioxide rich gas mixtures, increasing the atmospheric carbon dioxide concentration and in turn intensifying global warming.² According to the World Meteorological Organization (WMO), CO, is the most important anthropogenic greenhouse gas, contributing 65 % to radiative forcing. However, the atmospheric CO₂ level still rises now reaching 145 % of the pre industrial status.³ Until environmentally more friendly techniques are developed, the capture and sequestration (CCS) of CO₂ is important to decrease the global carbon dioxide emission. In general, CCS techniques address two main fields, precombustion and postcombustion processes, which provide different demands on potential materials.⁴

The typical conditions for a postcombustional gas stream are nearly ambient pressures (~1 bar) and temperatures around 40-80 °C for typical coal-fired power plants.⁴ The high volume streams consist of 15-16 % CO₂, 70-75 % N₂, 5-7 % water vapor and other impurities like CO, N_xO_x and SO_x.^{2,5} Precombustion is usually further subdivided into natural gas sweetening and the purification of gas mixtures from gasification or water/gas-shift reactor processes.² The first one deals predominantly with CO_2 impurities (> 40%), whereas in the second CO₂/H₂ separation is of major interest. In both cases, elevated temperatures above 40 °C and high pressures around 30 bar have to be taken into account.^{2,4} Natural gas and precombustional gas for coal fire plants are usually contaminated with 5-20 % and 40-60 % of CO₂, respectively. CO₂ as main contaminant is not only an initiator for global warming, but has also corroding effects on the transporting pipeline systems due to its acidity. Additionally, captured CO2 could be used as reactant for the synthesis of various chemical compounds.⁶ This makes the CO₂ capture and sequestration important for both environmental and industrial interests. Considering the gigantic amount of annual CO₂ release, any solution has to be based on reversible processes.

Since 1930 CCS systems were predominantly based on wet amine solutions (e.g. MEA), which use chemisorptive interactions with carbon dioxide as filtration mechanism.⁷ Due to severe drawbacks, like high cost regeneration, instabilities towards impurities and equipment corrosion, this method is regarded to be highly inefficient.^{4,8-10} Some

of the main drawbacks are a substantial parasitic load of CO₂ capture about 25-30 % and a high energy demand for the regeneration step which mounts to 25 – 40 % of the power plants energy output.^{2,4,9,11} A more elegant solution could be provided by solid-state materials with high surface areas, which interact with the adsorptives via physisorption and, in succession, the advantage to facilitate their regeneration by changing physical parameters to unload incorporated molecules like in pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) techniques.⁴ Thus the possibility to modify both adsorbent properties and process designs strongly influences the effectiveness of a separation method.¹⁰ Additionally, new materials should provide further properties like low cost synthesis, recyclability and high selectivity values.

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59 60 In this respect microporous organic polymers^{11–13} (MOPs) exhibit outstanding physicochemical properties combined with high surface areas as well as chemically modifiable structures and are thus in line with other porous solid materials like carbons^{14–17}, zeolites^{18–21} and metal organic frameworks^{22–24}. In fact, many publications on MOPs have proven their high potential and established strategies for enhancing the CO₂ uptake like surface area modification, pore size engineering or isosteric heat of adsorption tuning.^{4,12,13,25–27} Simulations have shown, that CO₂ acting both as Lewis acid and Lewis base can bind to phenyl rings and polar functionalities inside of a porous network.¹³ Thus the incorporation of such moieties is a promising start to tune the CO₂ sorption behavior.

Applying these strategies led to the synthesis of promising materials like BILP-4, PPN-6-deta and ALP-1 with the remarkable CO₂ uptake values of 5.3, 4.3 and 5.4 mmol/g at 273 K and 1 bar ,respectively, which are among the best porous polymer networks up to date.^{9,28,29} Focusing on microporous polimides like PI-NO₂-1 uptakes up to 4.0 mmol/g at 273 K and 1 bar were reached.³⁰ Furthermore, excellent selectivities of CO₂ over N₂, like in TPI-2@IC³¹ (151) or STPI-2³² (107), and CH₄, e.g. PI-NO₂-2³⁰ (21) or NPI-1³³ (13), have been reported.

Similar or even better sorption properties were obtained for microporous, crystalline materials like metal-organicframeworks (MOFs). E.g. mmen-Mg₂(dobpdc) adsorbs up to 6.4 mmol/g at 298 K and 1 bar in combination with a CO₂ over N₂ selectivity over 96 %.^{34,35} The zeolitic imidazolate framework UTSA-49a shows a CO₂ uptake capacity of 4.8 mmol/g at 273 K and 1 bar in combination with a substantial CO₂ over CH₄ selectivity around 35.³⁶ Nevertheless, MOFs often suffer from a limited chemical and thermal stability underlining the competitiveness of MOPs.

Herein we report the synthesis of five new microporous polyimides (MOPIs) via a polycondensation polymerization process of amine and anhydride linker molecules. While the synthesis procedure is based on our previous work on TPIs,³⁷ here we focus on 3D networks with a central tetrahedral core based on tetrakis(4-aminophenyl)methane for all five MOPIs. The corresponding anhydrides are chosen to favor a more or less linear expansion of the network. Their individual electronic properties, additionally, allow to vary the chemical nature of the void surfaces in a systematic fashion among other things from hydrophilic to hydrophobic. After a thorough characterization of the polymers by IR-, ¹³C and ¹⁵N solid-state NMR spectroscopy, CHN and TG analysis as well as X-ray diffraction, the influence of surface areas, pore structures and different side groups on their gas sorption behavior will be discussed. In addition, the gas uptake and selectivity for N₂, CO₂ and CH₄, as well as the water vapor uptake into the networks is considered. All these properties are discussed in the context of the chemical nature of the inner surfaces.

Experimental Section

General Information

Argon and nitrogen sorption measurements were carried out on a Quantachrome Autosorb-1 pore analyzer at 87 K and 298 K, respectively. The data were analyzed using the ASIQ v 3.0 software package. Pore size distributions were calculated with methods of quasi stationary density functional theory (QSDFT). The isosteric heat of adsorption was calculated using the CO_2 adsorption isotherms at 273, 298 and 313 K. CO2 and CH4 adsorption isotherms were measured on a Quantachrome Nova surface analyzer at 273, 298 and 313 K, respectively. Selectivities and adsorption parameter were calculated using IAST and Henry methods according to the literature.^{38,39} Calculations of the specific surface area, pore volumes and pore size distributions measured with CO2 at 273 K were carried out using the nonlocal density functional theory (NLDFT) slit-pore model for carbon materials. For the Ar based isotherms, the choice of the QSDFT adsorption branch kernel for cylindrical pores in carbon based materials depended on the calculated fitting error. Water sorption isotherms were measured using a BEL JAPAN INC. Belsorpmax instrument. To avoid extremely long measuring times the desorption branch was aborted when the pressure equilibration exceeded 24 h. Thus for two networks (MOPI-I and MOPI-IV) the water isotherms are not fully closed. All polymers have been degassed under vacuum (10⁻² kPa) at 110 °C for 12 to 16 h before starting the adsorption experiments. ¹H and ¹³C liquid-NMR spectra of the linker molecules were carried out on a Bruker 500 MHz spectrometer using either CDCl₃ or DMSO as solvents. For infrared spectra (IR) a JASCO FT/IR-6100 fourier transform infrared spectrometer with attenuated total reflectance (ATR) unit was used. CHN analysis was carried out at a vario EL-III with acetanilide as standard (Meas.: C [71.09], H [6.71], N [10.36]; Calc.: C [71.09], H [6.71], N [10.36]). Mass spectrometry (MS) was performed at a Finnigan MAT-8500spectrometer with an ionization energy of 70 eV. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA851^e. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical X'Pert Pro diffractometer. Here, a region from 2-30° 2θ was measured with a 1/4 anti-scatter slit and Cu K_{α}-radiation (nickel

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filtered). All solid-state NMR spectra were acquired on a Bruker Avance-III HD spectrometer operating at a Bo field of 9.4 T. 13 C (δ = 100.6 MHz) and 15 N (δ = 40.6 MHz) MAS spectra were obtained with ramped cross-polarization (CP) experiments where the nutation frequency v_{nut} on the proton channel was varied linearly from 70 - 100 %. The samples were spun at 12.5 kHz ($^{13}\text{C})$ and 10.0 kHz ($^{15}\text{N})$ in a 4 mm MAS double resonance probe (Bruker). The corresponding v_{nut} on the ¹³C channel and the contact time were adjusted to 70 kHz and 3.0 ms, respectively. On the ¹⁵N channel the corresponding ν_{nut} and the contact time were adjusted to 35 kHz and 5.0 ms, respectively. Proton broadband decoupling with spinal-64 and v_{nut} = 12.5 kHz was applied during acquisition.⁴⁰ ¹³C spectra are referenced with respect to TMS (tetramethylsilane) using the secondary standard adamantane. ¹⁵N spectra are referenced with respect to CH₃NO₂ using the secondary standard glycine.

Synthesis

All chemicals were purchased at *Sigma-Aldrich Chemistry GmbH*, *VWR Chemicals*, *TCI* or *Grüssing GmbH* and were, if not mentioned otherwise, used without further purification (Table S1). *m*-Cresol was freshly distilled over CaH₂ and stored under Ar over a molecular sieve M4 prior to use. All polymerizations were carried out under Ar atmosphere.

Synthesis of the linker

Tetraphenylmethane⁴¹

15 g of trityl chloride (0.054 mol, 1 eq.) and 14.05 ml aniline (0.154 mol, 2.9 eq.) were heated up to 180 °C in a round flask with magnetic stirrer and condenser, until the reaction mixture turned into a violet solid. The heating process was extended for 10 more minutes. The solid was cooled down, crushed and suspended in 75 ml MeOH and 75 ml 2 *M* HCl. The suspension was refluxed for 30 min., filtered and washed with water. After suspending in ethanol the reaction mixture was cooled down to -30 °C and 15.75 ml sulfuric acid and 9.44 g of isopentylnitrite (0.081 mol, 1.5 eq.) were added under vigorous stirring. After stirring for 1 h at -10 °C, 26.9 ml of phosphinic acid (0.609 mol, 11 eq.) were added slowly and the reaction mixture was refluxed for 1.5 h. After cooling down, the solid was filtered, washed with DMF, H₂O and Ethanol and subsequently dried in vacuo to get a light brown powder. Yield: 16.1 g (0.05 mol, 93 %). ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 7.07-7.20 (m, 5H, Ar-H). ¹³C-NMR (500 MHz, CDCl₃): δ [ppm] = 146.8 (C-2), 131.2 (C-3), 127.5 (C-4), 125.9 (C-5), 65.0 (C-1). EA [%]: C [91.73], H [6.91], N [0.24]; Calc.: C [93.71], H [6.29], N [0.00]. MS [M/z] = 320, 243, 165. IR (ATR): $v [cm^{-1}] = 3050, 1589$, 1496, 1434, 1319, 1268, 1185, 1080, 1029, 987, 935, 899, 842, 749, 697, 635.

Tetrakis(4-nitrophenyl)methane42

14 ml of fuming nitric acid in a flask equipped with a magnetic stirrer, a thermometer and a gas funnel were cooled down to -10 °C, followed by the portioned addition of 2.5 g tetraphenylmethane (7.8·10⁻³ mol), 9 ml acetic acid and 4 ml acetic anhydride. The mixture was stirred at -10 °C for 1 h. The resulting yellow solid was filtered, washed with acetic acid and water and dried in an oven at 100 °C. Yield: 2.5 g (4.9·10⁻³ mol, 63 %). ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 8.2 (d, 2H, Ar–H), 7.3 (d, 2H, Ar–H). ¹³C-NMR (500 MHz, CDCl₃): δ [ppm] = 150.8 (C-2), 141.0 (C-5), 136.3 (C-3), 117.9 (C-4), 66.3 (C-1). EA [%]: C [59.67], H [3.25], N [10.67]; Calc.: C [60.00], H [3.22], N [11.20].MS [M/z] = 500. 278, 332, 302, 285, 239, 213, 163. IR (ATR): v [cm⁻¹] = 3095, 1590, 1510, 1407, 1339, 1222, 1182, 1106, 1011, 962, 917, 836, 746, 706.

Tetrakis(4-aminophenyl)methane43

0.75 g of tetrakis(4-nitrophenyl)methane (1.5·10⁻³ mol, 1 eq.) were suspended in 50 ml THF. 1 g of N₂H₄·H₂O (20·10⁻³ mol, 13 eq.) and ~5 g of Raney nickel were added and the mixture was refluxed for 3 h. After hot filtration and washing with THF the solvent was evaporated and the residue washed with DCM to give a white solid. Yield: 0.358 g (9·10⁻⁴ mol, 63 %). ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 6.9 (d, 1H, Ar-H), 6.5 (d, 1H, Ar-H), 3.5 (s, 2H, NH₂). ¹³C-NMR (500 MHz, CDCl₃): δ [ppm] = 146.1 (C-5), 136.3 (C-2), 131.6 (C-3), 113.1 (C-4), 61.5 (C-1). EA [%]: C [77.31], H [6.70], N [14.32]; Calc.: C [78.92], H [6.36], N [14.73]. MS [M/z] = 380, 288, 271, 195, 180. IR (ATR): v [cm⁻¹] = 3391, 3162, 1609, 1501, 1425, 1268, 1177, 1191, 1101, 1011, 955, 859, 809.

General polymerization procedure

Based on a former publication in the field of porous polyimides, all polymerization reactions were carried out under argon atmosphere in dry three-necked flasks equipped with a magnetic stirrer and a thermometer.³⁷ For all polymers, *m*-cresol was used as solvent. The molar ratio of tetrakis(4-aminophenyl)methane to the corresponding anhydride was set to 1:2 to provide equimolar amounts of amine and anhydride groups. The following, more detailed synthesis of MOPI-I is given as reference protocol for all polymerization reactions.

Synthesis of MOPI-I

68.9 mg tetrakis(4-aminophenyl)methane (0.181·10⁻³ mol, 1 eq.) and 130 mg 3,3',4,4'-diphenylsulfonetetracarboxyldianhydride (0.362·10⁻³ mol, 2 eq.) were added to 20 ml of *m*cresol under Ar atmosphere. The mixture was stirred for 24 h at 0 °C. Afterwards, a catalytic amount (\approx 1 mg) of isoquinoline was added and the mixture was again stirred for 12 h at room temperature. The polymerization reaction was carried out at 80 °C for 4 h, 120 °C for 4 h, 160 °C for 6 h, 190 °C for 18 h. After cooling down to room temperature,



Scheme 1: General polymerization reaction and simplified structures of the presented MOPI networks.

the resulting solid was filtered and washed with toluene, dichloromethane and methanol. Additional purification was achieved in a soxhlet apparatus with tetrahydrofuran over night. After drying in an oven at 100 °C, MOPI-I was obtained as brown powder. Yield: 56 mg (0.055 mmol, 28 %). ¹³C-NMR (CP-MAS, 12.5 kHz): δ [ppm] = 166 (C-6), 147 (C-2, C-9), 132 (C-3, C-7), 124 (C-4), 115 (C-8), 64 (C-1). EA [%]: C [61.12], H [3.66], N [5.11]; Calc.: C [67.18], H [2.72], N [5.40]. IR (ATR): ν [cm⁻¹] = 1784, 1721, 1603, 1507, 1420, 1367, 1317, 1223, 1184, 1150, 1094, 1057, 1023, 916, 820, 740.

Synthesis of MOPI-II

81.9 mg tetrakis(4-aminophenyl)methane ($0.215 \cdot 10^{-3}$ mol, 1 eq.) and 134 mg 4,4'-oxydiphthalicdianhydride ($0.43 \cdot 10^{-3}$ mol, 2 eq.) were used as reactants. MOPI-II was obtained as light brown powder. Yield: 170 mg ($0.183 \cdot 10^{-3}$ mol, 85 %). ¹³C-NMR (CP-MAS, 12.5 kHz): δ [ppm] = 166 (C-6), 159 (C-9), 146 (C-2), 134 (C-5, C-7), 130 (C-3), 126 (C-4), 117 (C-8`), 108 (C-8), 64 (C-1). EA [%]: C [70.45], H [3.43], N [5.72]; Calc.: C [74.04], H [3.00], N [5.95]. IR(ATR): v [cm⁻¹] = 1780, 1717, 1603, 1507, 1474, 1430, 1360, 1273, 1234, 1080, 1020, 956, 806, 744.

Synthesis of MOPI-III

100 mg of tetrakis(4-aminophenyl)methane (0.262·10⁻³ mol, 1 eq.) and 169 mg of 3,3',4,4'-benzophenontetracarboxylic-dianhydride (0.525·10⁻³ mol, 2 eq.) were used as reactants. MOPI-III was obtained as ocher colored solid. Yield: 168 mg (0.176·10⁻³ mol, 67 %). ¹³C-NMR (CP-MAS, 12.5 kHz): δ [ppm] = 193 (C-10), 166 (C-6), 144 (C-2, C-9), 134 (C-5, C-3), 131 (C-4), 124 (C-8), 64 (C-1).EA [%]: C [69.59], H [3.48], N [5.29]; Calc.: C [74.59], H [2.92], N [5.81]. IR(ATR): v [cm⁻¹]

= 1780, 1710, 1615, 1497, 1411, 1365, 1294, 1255, 1208, 1161, 1082, 1019, 972, 918, 854, 815, 714.

Synthesis of MOPI-IV

118 mg of tetrakis(4-aminophenyl)methane (0.311·10⁻³ mol, 1 eq.) and 0.154 mg of bicyclo[2,2,2]oct-7-en-2,3,5,6-tetracarboxylicdianhydride (0.621·10⁻³ mol, 2 eq.) were used as reactants. MOPI-IV was obtained as brown solid. Yield: 132 mg (0.164·10⁻³ mol, 53 %). ¹³C-NMR (CP-MAS, 12.5 kHz): δ [ppm] = 177 (C-6), 147 (C-2, C-9), 131 (C-3, C-5), 127 (C-4), 65 (C-1), 42 (C-7), 35 (C-8). EA [%]: C [69.61], H [4.20], N [6.26]; Calc.: C [73.52], H [3.95], N [6.86]. IR(ATR): v [cm⁻¹] = 1782, 1714, 1663, 1679, 1495, 1444, 1368, 1334, 1241, 1182, 1123, 1022, 979, 819, 751.

Synthesis of MOPI-V

80 mg of tetrakis(4-aminophenyl)methane (0.209·10⁻³ mol, 1 eq.) and 186 mg 4,4[•]-(hexafluoroisopropyliden)diphthalic anhydride (0.418·10⁻³ mol, 2 eq.). MOPI-V was obtained as brown solid. Yield: 167 mg (0.140·10⁻³ mol, 67 %). ¹³C-NMR (CP-MAS, 12.5 kHz): δ [ppm] = 166 (C-6), 146 (C-2), 139 (C-9), 132 (C-7, C-5), 124 (C-3, C-8), 117 (C-11), 64 (C-1), 61 (C-10). EA [%]: C [62.02], H [2.93], N [4.65]; Calc.: C [63.59], H [2.33], N [4.63]. IR(ATR): v [cm⁻¹] = 1785, 1729, 1617, 1503, 1435, 1366, 1298, 1252, 1206, 1145, 1092, 1023, 986, 916, 886, 856, 818, 741, 711.

Results and discussion

Synthesis

Tetrakis(4-aminophenyl)methane was synthesized by a well established procedure, starting with the coupling of triphenylchloromethane and aniline.⁴¹ After nitration of

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58 59 60 the resulting tetraphenylmethane the nitro group was reduced to tetrakis(4-aminophenyl)methane using Raney nickel and hydrazine in an overall yield of 37 %.^{42,43} For the polymerization reaction, tetrakis(4-nitrophenyl)methane and the correspondent anhydride were used in a molar ratio of 1:2, following a procedure established by Liebl et al.³⁷ The choice of *m*-cresol as solvent is essential due to its high boiling point (202 °C), which turned out to be optimal for this kind of polymerization reactions.³⁷ After dissolving the reactants (Scheme 1) isoquinoline was added as catalyst due to its basic and hygroscopic properties.^{5,44} The reaction was carried out using a five step temperature program, starting at room temperature, followed by several heating periods including 80 °C for 4 h, 120 °C for 4 h, 160 °C for 6 h and 190 °C for 18 h. This induces a slow polymerization process and simultaneously circumvent an early precipitation of oligomers.^{37,45} At the final heating step the precipitation of the polymer was observed. All polymers were obtained with good yields between 50 and 85 %. Only for MOPI-I the yield was considerably lower (28 %).

Characterization

The resulting polymers were characterized by combining solid-state NMR and IR spectroscopy as well as elemental analysis. Further information about physicochemical properties were derived from PXRD (Figure S16) and TG experiments (Figure S17) carried out in air and All five MOPIs share a tetrakis(phenyl)methane core and imide linkages as a result of the crosslinking. The most characteristic peaks in the ¹³C and ¹⁵N MAS spectra (Figure 1, Table S2) for both units are 64 ppm assigned to the tetrahedral carbon atoms (1) as well as 165 ppm for the imide carbon atoms (6). The corresponding imide nitrogen atoms resonate at -209 ppm in the ¹⁵N NMR spectra. Furthermore, the absence of the ¹⁵N amine resonance around -315 ppm (Figure 1) as well as of the two characteristic anhydride bands around 1830 cm⁻¹ and 1750 cm⁻¹ and of the NH₂ stretching vibration around 3500 cm⁻¹ (Figure S4) ensure an almost complete crosslinking with an exception being MOPI-V, where a small amount of unreacted amine end groups remains.¹⁸

This is in agreement with the results of the CHN analysis which show only small deviations (< 1 % for H, N and < 5 % for C) from the calculated data (Table 1). In the case of **MOPI-IV** the resonances for both the imide carbons (6) and nitrogens are low field shifted to 177 ppm and -188 ppm due to the aliphatic character of the corresponding core of the linker (Figure 1, Table S2). The imide functional groups were also observed in the infrared spectra of the polymers at 1778 cm⁻¹ where the typical imide carbonyl band of cyclic five membered rings resonates at 740 cm⁻¹, which is due to N-H wagging (Figure S4).

Further distinct but individual ¹³C NMR and IR spectroscopic features are observed in the case of **MOPI-I** at 145 ppm, typical for the α -carbon of a sulfone group (9) (Figure 1). The IR-bands of the sulfone group appear at 1177, 1320 and 1058 cm⁻¹ (Figure S7). For **MOPI-II** the α -carbon of the ether group (9) resonates at 159 ppm. The corresponding CO stretching vibration for the aryl ether was found at 1273 cm⁻¹ (Figure 2, Figure S9). In the case of **MOPI-III** the α -keto-carbon signal (10) appears at 194 ppm and the aryl ketone band was observed at 1211 cm⁻¹ (Figure S11). For **MOPI-IV** the aliphatic β -carbon atom (7) next to the imide group is assigned to 42 ppm (Figure 1). The β -carbon atoms of the bicyclooctene group (8) resonate at 35 ppm. In the IR spectra the C=C stretching vibration of the bicyclooctene unit is prominent at 1663 cm⁻¹ (Figure S13). The structure of **MOPI-V** is furthermore validated by a signal at 61 ppm, assigned to the quaternary carbon atoms (10) next to the CF₃ moieties (11) expected around 113 ppm (Figure 1). Due to strong ¹³C¹⁹F dipole interactions the signal is broadened. The corresponding -CF₃ stretching vibration was observed at 1255 and 1191 cm⁻¹ (Figure S15).

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Figure 1: Solid-state ${}^{13}C$ (a) and ${}^{15}N$ (b) MAS NMR spectra of **MOPI I-V** measured with cross polarization and spinning speeds of 12.5 kHz and 16 kHz, respectively. Assignment correlates with Scheme 1. The asterisks mark spinning side bands.

Table 1: CHN-analysis (wt%) of MOPIs ((upper values) ar	nd decomposition	temperatures	measured	under air
(lower values) (SInfo. 3.2, Figure S16).					

CHN-Analysis	MOPI-I [%]	MOPI-II [%]	MOPI-III [%]	MOPI-IV [%]	MOPI-V [%]		
C (Exp./Calc.) ^a	61.12 (66.12)	70.45 (73.71)	69.59 (74.37)	69.61 (73.14)	62.02 (63.22)		
H (Exp./Calc.) ^a	3.66 (2.75)	3.43 (3.94)	3.48 (2.97)	4.20 (4.01)	2.92 (2.36)		
N (Exp./Calc.) ^a	5.11 (6.26)	5.72 (6.03)	5.29 (5.88)	6.26 (6.96)	4.65 (5.62)		
TGA-Analysis ^b	[°C]	[°C]	[°C]	[°C]	[°C]		
Decomposition	421	440	390	350	475		

"Repeating units used to derive calculated weight percentages are TG measurements carried out in air reveal first indications for structural decomposition between 350 °C for **MOPI-IV** and 475 °C for **MOPI-V** reflecting the thermal persistence of the core units (Table 1, Figure S16). For **MOPI-I** additionally, a weight loss of about 10% was observed at 160 °C due to desorption of water. PXRD measurements as well as SEM micrographs confirm the amorphous nature of all polymers (Figure S15/S35).

Surface area and porosity

The porosity of all MOPIs was determined from Ar adsorption isotherms measured at 87 K (Figure 2, SInfo 4.1). Ar, as monoatomic gas, is in comparison to the often used N₂ engaged in fewer interactions with surfaces, especially of polar compounds and due to its higher boiling point, equilibrium processes are significantly shortened. The isotherms show high Ar uptakes at low relative pressures, typical for microporous materials. The shapes of the isotherms resemble IUPAC Type I(b) isotherms, indicating broader pore size distributions including wider micropores and narrow mesopores.⁴⁶ For all polymers a hysteresis was observed, which is generally associated with capillary condensation, a phenomenon linked with mesoporosity.⁴⁶ The extension of the hysteresis into the low pressure region, nevertheless, favors swelling of the networks.

MOPI-I shows, the lowest BET and DFT surface areas around 220 m²/g, which is probably due to the high flexibility of the sulfone bridge leading to a more compact packing of the network. The highest surface area was observed for **MOPI-V** with roughly 930 m²/g. For the other polyimides specific surface areas in between (480 and 730 m²/g) are found.

For **MOPI-I** and –**III** the ratio V_{mic}/V_{tot} is around 30 %, indicating a large percentage of mesopores, which correlates with their lower surface areas in comparison with the other polyimides (Table 2). This in line with the pore size distributions given in Figure 2 revealing a broad distribution of mesopores up to 6 nm. **MOPI-II** and **MOPI-V** developed higher values of microporosity around 50 % with only small mesopores around 2 nm (Figure 2). The highest microporosity is observed for **MOPI-IV** (68 %) (Table 2). All five polyimide networks exhibit a narrow pore size distribution in the microporous region with a center of gravity between 1.0 nm for **MOPI-II** and 1.4 nm for **MOPI-I** (Figure 2). To probe potential ultramicropores CO₂ isotherms

^aRepeating units used to derive calculated weight percentages are given in SInfo 3.2. ^bFull decomposition curves are shown in Figure S17. TG measurements carried out in air reveal first indications for structural decomposition between 350 °C for **MOPI-IV** to detect pores between 0.3 and 1.5 nm.



Figure 2: Ar isotherms measured at 87 K (a) and normalized pore size distributions (b) calculated by QSDFT adsorption branch kernel for cylindrical pores in carbon based materials. Full symbols characterize adsorption isotherms, hollow symbols the corresponding desorption curve.

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Table 2: Surface areas determined from Ar and CO_2 isotherms and calculated by BET and DFT methods. Pore volumes calculated by DFT methods from Ar and CO_2 isotherms.

Polymer	$Ar/87.3 K^{a}$	Ar/87.3 K ^b	$CO_2/273 K^{c}$	V _{tot.,Ar,DFT}	V _{mic.,Ar,DFT}	V _{mic.} /V _{tot.}	V _{tot.,CO2,DFT}	
	[m²/g]	[m²/g]	[m²/g]	[cm ³ /g]	[cm ² /g]	Ar, DFT	[cm ² /g]	
MOPI-I	206	231	777	0.16	0.05	0.31	0.24	
MOPI-II	644	739	676	0.32	0.17	0.53	0.19	
MOPI-III	443	468	712	0.27	0.09	0.33	0.22	
MOPI-IV	660	735	896	0.28	0.19	0.68	0.27	
MOPI-V	921	939	690	0.44	0.23	0.52	0.23	

^aCalculated based on the BET equation. ^bCalculated using QSDFT for cylindrical pores in carbon based materials for the adsorption branch only. ^cCalculated based on NLDFT with a slit-pore model for carbon materials.

The pore size distributions for all polymers (Figure S18), calculated from the CO₂ isotherms show a broad distribution of pore sizes between 0.3 to 1 nm, which indicates an undirected pore formation due to the amorphous character of the networks. For MOPI-I, -III,-V the surface areas derived from the CO₂ isotherms are markedly higher compared to the Ar surfaces, in particular for MOPI-I $(777 \text{ m}^2/\text{g})$ vs. 231 m²/g), demonstrating a high degree of ultramicropores (Table 2). In contrast, the surface areas of MOPI-II und MOPI-V decrease towards 676 m^2/g and 690 m^2/g in comparison to Ar surface areas of 739 m²/g and 939 m^{2}/g , respectively. These values indicate a high amount of pore sizes beyond 1.5 nm for those networks (Table 2). In conclusion, MOPI-I, MOPI-III and MOPI-IV possess a higher ratio of ultramicropores than their related polymers, which is discussed in more detail together with the sorption behavior towards CO₂ and CH₄.

CO_2 , CH_4 and H_2O adsorption

The high surface areas and microporous structures render all MOPIs as suitable candidates for applications such as gas storage and separation. As mentioned before, the interaction of those materials with industrial relevant gas mixtures is of vital relevance. In particular, industrial flue gas mixtures contain high amounts of water (up to 7 %), which is a potential competitor for binding sites in filtering materials and would decrease the potential of an appropriate material. In return super hydrophilic materials could be favorable for alternative applications like water absorber or heat transformation. In this context, the uptake of water vapor at low pressures in materials like covalent organic frameworks and porous carbons for the application in atmospheric water capture (AWC), heat pumps or electric dehumidifiers has gained some interest in the literature.⁴⁷⁻⁴⁹ Recently Lotsch et al. synthesized the AB-COF for AWC application with a remarkable water uptake of 15 mmol/g at low relative pressure $(p/p_0 < 0.3)$, which shows the high potential of porous polymer networks in this field of application.49

With this in mind the behavior of the synthesized polymers towards CO_2 , CH_4 , N_2 and H_2O at various temperatures as well as their selectivity towards specific gas mixtures has been analyzed (Tables. 3 and 4). CO_2 adsorption

measurements at 273, 298 and 313 K, respectively, were performed to compare the uptake behavior of the polymers at 1 bar.



Figure 3: CO_2 uptake at 273 K (a) and isosteric heats of adsorption for CO_2 (b) calculated from adsorption isotherms at 273, 298 and 313 K. Full symbols characterize adsorption isotherms, hollow symbols the corresponding desorption curve.

the ones for N_2 and H_2O were extracted at $p/p_0 = 0.9$.									
		CO ₂	CO ₂	CO2	N ₂	CH4	CH ₄	CH ₄	H₂O
	Polymer	273 K	298 K	313K	298 K	273 K	298 K	313 K	298 K
		[mmol/g]	[mmol/g]	[mmol/g]	[mmol/g]	[mmol/g]	[mmol/g]	[mmol/g]	[mmol/g]
	MOPI-I	3.3	2.2	1.7	0.11	0.61	0.34	0.25	13.5
	MOPI-II	2.9	1.9	1.4	0.09	0.61	0.35	0.24	12.3
	MOPI-III	3.0	1.8	1.5	0.07	0.72	0.19	0.2	9.0
	MOPI-IV	3.8	2.3	1.6	0.10	0.83	0.4	0.3	19.5
	MOPI-V	2.9	1.6	1.3	0.04	0.49	0.5	0.17	7.0

Table 3: Uptakes taken from individual isotherms. The values for CO_2 and CH_4 were determined at p = 1 bar and the ones for N_2 and H_2O were extracted at $p/p_2 = 0.0$.

At 273 K MOPI-I, -II, -III and -V show CO, uptakes around 3 mmol/g which are already extraordinary high compared to literature values.^{5,30,32,33,50-56} The best CO₂ uptake, however, was obtained for MOPI-IV with 3.8 mmol/g at 273 K, which is actually the second best value for microporous polyimides next to the previous mentioned PI-NO₂-1 and exceeds all other polyimide networks where the uptake is not higher than 3.5 mmol/g.^{30-32,52} In accordance to the literature, we attribute the CO₂ uptake to the ultramicroporosity of the networks,⁴ for which we use the CO₂ surface areas as indicator. MOPI-IV has by far the largest ultramicroporous surface area, followed by MOPI-I, -III, -V and -II. This is in line with the CO₂ uptake given in Table 3 and explains e.g. why MOPI-V and -II exhibits lower CO, uptakes in spite of the comparably large microporous surfaces (determined with Ar). As expected, a decrease of the CO₂ uptake is observed with increasing temperature. Similar uptakes of around 1.5 mmol/g are found for all MOPIs at 313K (Table 3).

The isosteric heats of adsorption calculated from the CO₂ isotherms lead to values around 30 kJ/mol, which are typical for strong physisorptive interactions between guest molecules and the network (Figure 3). Here we observe the lowest Q_{st} near zero coverage (13 kJ/mol) for MOPI-V, which is expected to have the weakest interactions with CO_2 due to the presence of CF_3 groups. The highest Q_{st} value (39 kJ/mol) is observed for MOPI-I, which is caused by the stronger interactions of the CO₂ molecule with the highly polar sulfone groups. The values for MOPI-II, -III and -IV were found to be similar around 32 kJ/mol (Table 4). It is worth noting, that the trend for Q_{st} near zero coverage does not reflect the one for the CO₂ uptake. This suggests that the uptake at higher pressures is rather dominated by unselective interactions and not by preferred binding sites within the ultramicropores. The CH₄ uptake, determined from methane adsorption isotherms measured at 273, 298 and 313 K (SInfo. 4.3), is remarkably low for all polymers (around 0.5 to 0.7 mmol/g at 273 K) and decreases strongly with increasing temperature, caused by only weak interactions between the unpolar methane molecules and the polar network structures.

Water adsorption measurements at 298 K provide information about the behavior of the polymers in humid environments (Table 3). **MOPI-IV** shows the highest water uptake with 6.3 mmol/g at 0.3 p/p₀, which rises towards a total amount of 19.5 mmol/g at 0.9 p/p₀ (Figure 4). Recently published ultrahydrophilic covalent organic frameworks like AB-COF⁴⁹ (22.9 mmol/g), TpPA-1⁴⁸ (24.5 mmol/g) or porous carbons like PCC-1⁴⁷ (~22 mmol/g) give comparable results. This is surprising since for **MOPI-IV** the only polar groups are the imide linkages and it is thus considered to be less polar than e.g. **MOPI-I** with its sulfone bridges, reaching only 13.5 mmol/g at 0.9 p/p₀.

Thus the high water vapor uptake of **MOPI-IV** is more likely to correlate with its high CO_2 surface area which we take as a measure for the amount of ultramicropores (Table 2). For **MOPI-I**, -**II**, -**III** and -**V** the CO_2 surface areas are similar. Here the uptake values of 13.5, 12.3, 9.0 and 7 mmol/g correlate with the polarity of the bridging groups. Additionally, unlike **MOPI-IV** the other networks do not show an enhanced water uptake below 0.3 p/p₀.



Figure 4: Water vapor adsorption isotherm measured at 298 K. Full symbols characterize adsorption isotherms, hollow symbols the corresponding desorption curve.

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ld (d CO₂ isosteric heats of adsorption.								
	Sample	$CO_2/N_2^{a,(b)}$	$CO_2/CH_4^{c/d,(e)}$	$CO_2/CH_4^{c/d,(e)}$	$CO_2/CH_4^{c/d,(e)}$	H_2O/CO_2^{e}	Q_{st}^{f}		
		298 K	273 K	298 K	313 K	298 K	[kJ/mol]		
	MOPI-I	65.3 (78)	16/10 (11)	14/11 (9)	10/9(7)	92	39		
	MOPI-II	36.4 (51)	18/9 (8)	9/9(9)	10/12 (8)	63	32		
	MOPI-III	50.2 (50)	18/12 (13)	14/11 (10)	12/11 (10)	63	32		
	MOPI-IV	43.4 (52)	17/11 (10)	15/12 (9)	11/9 (10)	105	31		
	MOPI-V	26.4 (33)	9/7(7)	10/9 (9)	4/4 (5)	36	13		

Table 4: CO_2/N_2 , CO_2/CH_4 and CO_2/H_2O selectivities of all MOPIs calculated from the correspondent isotherms and CO_2 isosteric heats of adsorption.

^aCalculated by IAST for a mixture of 15 % CO₂ and 85 % N₂. ^bCalculated by initial slopes of pure-component sorption isotherms. ^cCalculated by IAST from a mixture of 5 % CO₂ and 95 % CH₄. ^dCalculated by IAST from a mixture of 15 % CO₂ and 85 % CH₄. ^eCalculated by initial slopes of pure-component sorption isotherms. ^fCalculated from CO₂ isotherms at 273, 298 and 313 K.

The introduction of CF_3 units in **MOPI-V** allowed to reduce the water uptake roughly by a factor of 2 and 3 compared to **MOPI-I** and **MOPI-IV**, while the CO_2 uptake is reduced only by 15 to 30 %, respectively. This trend was already reported for FPOP-2 by *Han et al.*⁵⁷ which exhibits uptakes as low as 1.5 mmol/g. In the case of **MOPI-V** the hydrophobicity of the CF_3 groups is probably counterbalanced by the imide linkages leading to significant higher values.

Selectivities towards CO₂, CH₄, N₂ and H₂O

Since flue gas is a complex mixture of diverse gases, potential filter materials should possess selective uptake proclivity towards specific molecules to ensure their effectiveness and efficiency. To estimate selectivities for the here presented networks, we applied ideal adsorbed solution theory (IAST) for the following industrial relevant gas mixtures CO_2/N_2 (15/85), CO_2/CH_4 (5/95 and 15/85) in comparison to initial slope calculations in the Henrys law region (< 0.1 bar) (SInfo. 5.1).^{38,39}

The highest CO₂ over N₂ IAST selectivities calculated at 298 K, are 65.3 and 50.2 obtained for **MOPI-I** and **MOPI**-IIII, respectively (Table 4). Especially, **MOPI-I** competes with materials in the top area of CO₂/N₂ selectivities, only surpassed by networks like modified PPN-6⁴ with values from 150 to 420 or IRMOF-1-4Li⁵⁸ with a selectivity of 395. We attribute these high values to their pronounced ultramicroporosity and the presence of keto/sulfone and imide groups, which provide Lewis acidic and basic preferred adsorption sites for CO₂. For **MOPI-IV**, **MOPI-II** and **MOPI-V** a further decrease of the selectivity to 43.4, 36.4 and 26.4 is observed, respectively.

This trend does not correlate solely to the CO₂ uptake and thus the ultramicroporosity (CO₂ surface areas). E.g. **MOPI-IV** exhibits the by far largest CO₂ surface area leading to a significant carbon dioxide uptake. Nevertheless, its CO₂/N₂ selectivity is with 43 markedly lower compared to **MOPI-I** (65) and -**III** (50). In contrast, the diene functionality of the corresponding linker within **MOPI-IV** is less polar compared to the sulfone and ketone groups for **MOPI-I** and -**III** and thus does not increase the affinity for CO_2 adsorption. Even lower but similar ultramicroporosities were obtained for **MOPI-II** and **MOPI-V** leading to a further decrease of the CO_2/N_2 selectivities. For this pair the CF_3 moieties within **MOPI-V** provide a much lower attraction for CO_2 (Table 4) compared to the ether units of **MOPI-II**, again accounting for the lower CO_2/N_2 selectivity of 26 in the case of **MOPI-V**. As consequence, in contrast to the CO_2 uptakes, the selectivities seem to be influenced by both the ultramicroporosity and the functionality of the networks in equal measures. Thus at least to a certain degree preferred binding sites are important to influence the separation properties.

The IAST selectivities for the corresponding CO₂/CH₄ mixtures, reveal similar trends, indicating that the same influencing effects discussed above are relevant. For MOPI-III, -IV, -I, -II and -V values of 12, 11, 10, 9 and 7 were found in order to their ultramicroporosity and decreasing affinity of their functional groups for CO₂ (Table. 4, SInfo. 5.2). Lowering the portion of CO₂ towards a ratio of 5:95 results in increasing selectivities for all networks with top values of 18 for MOPI-II and -III as well as towards 17 and 16 for MOPI-IV and -I, respectively. For MOPI-V only a minor CO₂ affinity improvement from 7 to 9 was observed (Table 4). The increase of the temperature leads towards significantly lowered CO2 affinities towards 12, 11, 10, 10 and 4 for MOPI-III, -IV, -I, -II and -V, respectively, for a 5:95 CO_2/CH_4 mixture. At higher CO_2 ratios (15:85) the temperature seems to have only a minor effect on the selectivities. Interestingly, in the case of MOPI-II even an increase from 9 to 12 was found hinting at a cooperative effect between CO_2 and CH_4 within the network (Table 4).

The calculation of H_2O/CO_2 selectivities by initial slopes of pure-component sorption isotherms, obtained high values of 105 and 92 for **MOPI-IV** and –I, respectively, indicating a major effect of the ultramicroporosity with respect to the chemical nature of the polymers. For **MOPI-II** and -III a lower selectivity of 63 was observed. Due to its hydrophopic -CF₃ moieties the selectivity for **MOPI-V** decreases to 36 (Table 4).

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Conclusion

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59 60 The condensation polymerization of amino- and anhydride-linker molecules in *m*-cresol, lead to five new microporous organic polyimides **MOPI-I** to -**V**. Compared to the recent literature, the here presented compounds are promising materials for gas capture and sequestration, as well as potential water vapor adsorber.^{9,28,29-32,55-57}

All polymers show high crosslinking degrees, confirmed by ¹³C-, ¹⁵N MAS NMR spectroscopy and elemental analysis. The polyimides exhibit moderate to high specific surface areas between $231 \text{ m}^2/\text{g}$ (MOPI-I) and $957 \text{ m}^2/\text{g}$ (MOPI-V) and a mainly micro- to ultramicroporous character. Their porosity in combination with different functional groups leads to remarkable CO₂ uptake values up to 3.8 mmol/g at 273 K and 1 bar in the case of MOPI-IV, which is among the highest values obtained for polyimides only surpassed by PI-NO₂-1 (4.03 mmol/g).³⁰ The polymers exhibit respectable IAST selectivity values towards N₂ (up to 65 for MOPI-I) and CH₄ (18 for MOPI-II, -III) and can compete with most polyimides $(CO_2/N_2 < 150 \text{ and } CO_2/CH_4 < 20)$.^{30,31,33,52} In addition, water sorption isotherms showed a surprisingly hydrophilic character for MOPI-IV, with uptakes of 6.3 mmol/g at 0.3 p/p₀ and 19.5 mmol/g at 0.9 p/p₀. For MOPI-I, -II, -III and -V a decrease of the water uptake in correlation with the polarity of their functional group down to 7 mmol/g at 0.9 p/po and 298 K for MOPI-V was observed.

Summarizing, the CO_2 and H_2O uptakes of all polyimides are dominated by the ultramicroporous character of the networks. Here, the chemical functionalities introduced by the individual linkers play only a secondary role indicating that size discrimination within the frameworks might be an essential part of the adsorption process. In contrast, for the selectivities both the porosity as well as the chemical functionality seem to be equally important. This in turn hints at the existence of preferred adsorption sites for CO_2 and H_2O .

Associated Content

Supporting information

Further spectra, isotherms and selectivity plots are provided in the supporting information.

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TOC-Graphic

