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Microporous Hyper-Crosslinked Aromatic Polymers Designed for Methane and Carbon Dioxide Adsorption


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Abstract

Friedel-Crafts reaction was used to obtain covalent aromatic networks with high surface area and microporosity suited for CO₂ and CH₄ adsorption, even at low pressures. Starting from tetraphenylmethane and formaldehyde dimethyl acetal in different concentrations, the reaction yields porous polymers which were characterized with a wealth of experimental and computational methods. Thermogravimetry, infrared spectroscopy and solid-state-NMR were used to study the materials structure; the pore distributions were measured by applying the NLDFT (non-local density functional theory) analysis to the adsorption isotherms of N₂ at 77 K and Ar at 87 K (the latter being more suited for pore width lower than 10 Å). Carbon dioxide and methane were adsorbed at 273 and 298 K to evaluate the performance of these systems in gas capture, separation and storage. A theoretical model of the porous network was defined to describe the ordered fraction of the material, with particular attention to ultramicropores; Ar, CO₂ and CH₄ adsorption in this model material was simulated by Monte Carlo techniques with a purposely optimized force field.

Keywords: Microporous Materials, Friedel-Crafts reaction, CO₂ and CH₄ uptake, Hyper-crosslinked Aromatic Frameworks, NLDFT pore distribution, Monte Carlo simulations
Introduction

In recent years, the increase in world demand for energy has placed considerable strain on conventional energy supply like oil and coal. The need for alternative energy sources is also prompted by concerns about climate change arising from high greenhouse gas emissions associated with the use of conventional fossil fuels. Among the strategies developed to tackle both energy supply and the environmental impact issue, the use of methane as low CO\(_2\) emission fuel is very appealing, but it requires the development of new highly efficient storage solutions. To this end, there is a strong interest in new porous materials characterized by high surface areas and nanometer pore size not only to achieve optimal gas storage \(^1,2\), but also for capture and storage of anthropogenic CO\(_2\). High surface areas materials have attracted great interest also for the variety of applications in many areas such as molecular separations \(^3,4\) and catalysis \(^5,6\).

Along with well-established traditional adsorbents such as crystalline inorganic frameworks (e.g., zeolites) or amorphous network structures (e.g., silicas, activated carbons), the last decade has seen major advances in the preparation of a broad variety of organic or organic/inorganic hybrid microporous structures either crystalline or amorphous. Metal Organic Frameworks (MOFs) are highly crystalline structures consisting of metal ions or clusters coordinated to rigid organic molecules to form one-, two-, or three-dimensional structures with nanometer-sized pores \(^7\). The large specific surface area (up to 6240 m\(^2\)/g for MOF-210) and high porosity enable MOFs to adsorb large amounts of gases \(^8\). The pores are adjustable in terms of size and polarity, to be fine-tuned for specific applications. However, most MOFs suffer from low thermal and hydrothermal stability, which limit their industrial applications \(^9,10\), with some relevant exceptions in catalysis \(^11\), gas storage \(^12\) and drug delivery \(^13\). Increasing research efforts have been focused on the generation of stable microporous, covalent, purely organic materials characterized by the replacement of the coordination bonds present in MOFs with stronger covalent bonds which provide increased thermal and chemical stabilities \(^14\). Several porous organic polymers have been reported to date, including Covalent Organic Frameworks (COFs)\(^{15}\), Conjugated Microporous Polymers (CMPs) \(^{16,17}\), Polymers of Intrinsic Microporosity (PIMs) \(^{18,19}\), Hyper-Crosslinked Polymers (HCPs) \(^{20,22}\), Porous Polymer Networks (PPNs) \(^{23}\) and Porous Aromatic Frameworks (PAFs) \(^{24,25}\). These microporous materials have been proposed for H\(_2\), CH\(_4\) and CO\(_2\) capture/adsorption and often exhibit high uptake capacities \(^{26}\). Other materials, specifically addressed to gas capture and storage are based on mixed matrix membranes, combining both zeolite and polymers \(^{27}\), or MOFs and polymers \(^{28}\). Hyper-Crosslinked Polymers (HCPs) are a class of low cost porous organic networks easily prepared by Friedel–Crafts reaction. The permanent porosity in HCPs is a result of extensive crosslinking reactions of aromatic residues which prevents the polymer chains from collapsing into a dense, nonporous state \(^{29}\). The extensive crosslinked nature of the materials confers them high thermal stability that is not
commonly expected for organic polymers. This stability, combined with high surface areas and simple, cost-effective and easy to scale-up preparation, make HCPs highly promising materials for fuel gas storage (methane and hydrogen) and carbon dioxide capture applications.

The following strategies for HCP preparation have been reported: 1) intermolecular and intramolecular crosslinking of preformed polymer chains (either linear chains or lightly cross-linked gels), 2) self-condensation of chloromethyl- or hydroxymethylaromatics in the presence of FeCl₃, and 3) knitting aromatic compounds using crosslinking agents. Recently, a new method for preparing microporous polymers by using formaldehyde dimethyl acetal (FDA) as crosslinking agent to polymerize various aromatic monomers has been reported. This approach is particularly convenient since it requires mild conditions without the use of expensive reagents, allowing the synthesis of a variety of porous polymers. During their extensive research on organic materials, Cooper and coworkers applied this approach to the polymerization of the rigid aromatic structure of tetraphenylmethane (TPM) obtaining materials with good CO₂ storage properties.

In this paper we explore the polymerization based on the Friedel-Crafts TPM/FDA reaction, with the aim to produce good adsorbents also for other gases, mainly methane and hydrogen (here we consider CO₂ and CH₄ adsorption, deferring the study of H₂ to a further work). The synthesis conditions were optimized by investigating how the porosity and the surface area of the final material depend on the reagent stoichiometry, varying the aromatic monomer/crosslinking agent ratio. The aim was to increase especially the microporous volume, and in particular the fraction of smallest pores, below 10 Å width, which are expected to lead to high gas uptake also at low pressures.

As mentioned above, in ref. 34 the same reaction was used to obtain a series of different porous materials tested for CO₂ adsorption: among them, the compound indicated with E is analogous to the materials presented here. Very recently, the same approach led to the synthesis of a material called PAF-32, tested for CO₂ adsorption as well. As for the naming, the acronym PAF (porous aromatic framework) is suited for this kind of systems, though it was originally proposed for materials obtained by a different route and, more important, with wider pores. To emphasize the role of smaller pores, as pointed out above, we use throughout this article the name mPAF-1/n (as microporous aromatic framework, with the explicit indication of the TPM/FDA ratio used in the synthesis, see below).
Experimental section

Chemicals. All chemicals were purchased either from Sigma Aldrich Co. or Alfa Aesar GmbH & Co and were used without further purification unless otherwise stated.

Characterization methodologies. N$_2$ physisorption measurements were carried out at 77 K in the relative pressure range from 1 x 10$^{-6}$ to 1 P/P$_0$ by using Micromeritics instrument ASAP 2020 HD. Ar physisorption measurement at 87K of a selected sample was performed in the relative pressure range from 1 x 10$^{-7}$ to 1 P/P$_0$ by using an Autosorb iQ/ASiQwin instrument (Quantachrome instrument). Prior to the analysis, the samples were outgassed at 150 °C for 16 h (residual pressure lower than 10$^{-6}$ Torr). Specific surface areas were determined using the Brunauer–Emmett–Teller (BET) equation, in the relative pressure range from 0.05 to 0.15 P/P$_0$. Pore size distributions were obtained by applying the NLDFT (non-local density functional theory) method and using a silica model with cylindrical pore. The true (skeletal) density of the samples was measured by Helium pycnometry at room temperature: the apparent density was computed by combining the true density and the porous volume provided by NLDFT.

The Infrared spectra of materials in KBr pellets were collected using a Bruker Equinox 55 spectrometer equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm$^{-1}$.

All solid state NMR (SS-NMR) spectra were acquired on a Bruker Advance III 500 spectrometer and a wide bore 11.7 Tesla magnet with operational frequencies for $^{13}$C of 125.77 MHz. A 4 mm triple resonance probe with MAS was employed in all the experiments. The samples were packed on a zirconia rotor and spun at a MAS rate of 15 kHz. For the $^{13}$C($^1$H) CPMAS experiments, the magnetic fields $\nu_H$ of 55 and 28 kHz were used for initial excitation and decoupling, respectively. During the CP period the $^1$H RF field $\nu_H$ was ramped using 100 increments, whereas the $^{13}$C RF field $\nu_C$ was maintained at a constant level. During the acquisition, the protons are decoupled from the carbons by using a TPPM decoupling scheme. A moderate ramped RF field of $^1$H of 62 kHz was used for spin locking, while the carbon RF field $\nu_C$ was matched to obtain optimal signal and the CP contact time of 2 ms was used. The relaxation delay between accumulations was 1 s and all chemical shifts are reported using δ scale and are externally referenced to TMS at 0 ppm.

The X-ray diffraction (XRD) was recorded on unoriented ground powders with a Thermo ARL ‘XTRA-048 diffractometer with a Cu Ka (k = 1.54 Å) radiation.

The Thermogravimetric analyses were performed on a Setaram SETSYS Evolution instrument under argon (gas flow 20 mL/ min), heating the samples up to 1173 K with a rate of 5 K/min.
The gas adsorption–desorption isotherms were measured on a Micromeritics instrument ASAP 2050. Methane and carbon dioxide adsorption–desorption measurements were carried out between 0 and 10 bar at 273K and 298 K and up to 1 bar at 195K. Ultra-high-purity grade (99.99%) N$_2$, CH$_4$, and CO$_2$ gases were used for all adsorption measurements. In order to evaluate the selectivity of CO$_2$/N$_2$, a binary mixtures of 15:85 was used from the single-component isotherms with the ideal adsorbed solution theory (IAST), which has been successfully used to calculate gas mixture separation by porous materials. Elemental analysis were carried out with a EA3000 CHN Elemental Analyser (EuroVector, Milano, Italy). Acetanilide, purchased by EuroVector (Milano, Italy) was used as calibration standard (C % = 71.089, H % = 6.711, N % = 10.363).

**Standard procedure for the synthesis of mPAF materials.** In a typical procedure Ferric chloride (0.16 mol), and tetraphenylmethane (TPM 0.01 mol) were suspended in dichloroethane (DCE, 240 mL). The resulting mixture was stirred vigorously at room temperature to obtain a homogeneous solution. Then, formaldehyde dimethylacetal (FDA 0.16 mol) was added dropwise. The resulting thick gel was stirred at room temperature for 4h and then heated under reflux overnight. During the polymerization, the networks precipitated from solution as a brown solid. After cooling to room temperature the gel was washed in soxhlet by refluxing overnight first in methanol, then in water, and finally dried in oven at 100 °C overnight. In addition, the reaction was carried out changing the ratio between TPM and FDA (1:3, 1:9 and 1:30). At higher TPM:FDA ratio, macroscopic gelation of solutions was observed immediately after reagent addition then evolving quickly in extremely thick phase. All mPAF-1/n (n ranges 3 to 30, as stated above) materials are totally insoluble in all solvents tested (water and common organic solvents) and exhibited good chemical stability to strongly acidic and basic conditions (37% HCl, saturated aqueous NH$_4$OH). The elemental analysis is reported in Table S1 (Supporting Information, SI).

**Theoretical modeling.** To support the characterization of mPAF materials, a periodic molecular model was defined as a network of tetraphenylmethane moieties connected by methylene bridges in para position. The model was actually built by starting from the polyaromatic network PAF-301 described in refs. 36, 37 (i.e. a diamond structure where each C-C bond has been substituted by one phenyl group), and replacing two aromatic rings with H in every second sp$^3$ carbon. The resulting structure was optimized at the Density Functional Theory (DFT) level with the plane-wave code PWSCF, using the Perdew-Burke-Ernzerhof (PBE) functional and 120 Ry energy cutoff: the periodic lattice is triclinic with P1 symmetry (i.e. no point group symmetry is imposed, to leave the largest flexibility to the atoms inside the unit cell). The optimized structure is available in CIF (Crystallographic Information File) format as Supporting Information.

The adsorption isotherms of Ar at 87 K, CH$_4$ and CO$_2$ at 273 and 298 K were simulated with Monte Carlo techniques in this model material, and compared to the corresponding experimental isotherms. The
simulations were performed with a purposely adapted force field; for the adsorption of methane and carbon
dioxide we used previously optimized force fields, as reported in refs. 36 and 37, respectively: these force
fields were obtained for PAF networks, but they can be used safely for mPAF too, since the kind of atoms and
the expected interactions are the same in the two classes of materials. For Ar we used an adapted version of
PCFF force field \(^{39}\): Argon parameters were slightly modified to reproduce the free gas density \(^{40}\) at 87 K in the
0-1 bar pressure range (with the results shown in Figure 1d). On the other hand, the standard PCFF
parameters for carbon and hydrogen were employed, since we verified that they provide a good agreement
with high level quantum mechanical calculations, at MP2 level with 6-311+G(2d,2p) basis set, for different
energy scans of Ar-benzene and Ar-diphenylmethane complexes, as shown in Figure 1a-c. The optimized
Lennard-Jones parameters for Ar are 0.1864 kcal/mol and 3.980 Å.

![Figure 1](image_url)

Figure 1. (a)-(c): Interaction energy (kcal/mol) of Argon atom with aromatic residues in the indicated configurations. Red
circles: modified PCFF; black squares: MP2. (d): Density (mg/cm\(^3\)) of Argon gas at 87 K. Red circles: Monte Carlo
simulation; black squares: experimental density.
Results and discussion

Material synthesis and characterization.

A series of porous organic materials were prepared by polymerization of tetraphenyl methane (TPM) by means of Friedel-Crafts reaction (employing formaldehyde dimethylacetal as electrophile and FeCl₃ as catalyst) modifying a reported procedure (Figure 2) 34,38. Since Friedel-Crafts alkylation is unselective under the conditions employed, substitution on the aromatic rings cannot be easily controlled. However, at the outset of this research we considered that, by changing the amount of electrophile, some degree of control over polymerization rate and crosslinking extent could be achieved. We focused our study on understanding how different synthetic conditions and reagents ratio can influence the microscopic structure of the materials modulating both porosity and surface area that are the main features controlling gas loading by physisorption on a porous structure. Reaction conditions, which in principle could modulate the substitution of the aromatic residues from partial to extensive substitution, were explored by keeping all reaction parameters constant except the amount of electrophile employed as crosslinking agent. We rationalized that ideal reaction conditions should exist to grant regular and extended polymerization giving narrow pore size and large surface areas. Therefore, at a first stage, the reaction was performed with a TPM:FDA ratio (1:3), lower than that needed for a full cross-linking polymerization, to get the first material (mPAF-1/3). Then, an intermediate crosslinking was explored by synthesizing a polymer with a TPM:FDA ratio 1:9 (mPAF-1/9). This is the material that was supposed to be more similar to that reported by Cooper et al. (ratio TPM:FDA 1:8). A TPM:FDA ratio 1:16 was also used to yield the (supposedly) fully cross-linked material mPAF-1/16. Indeed, under these conditions the electrophile is over-stoichiometric allowing for fast polymerization. Finally, “forced” crosslinking conditions were also explored, synthesizing a polymer with a TPM:FDA ratio 1:30 (mPAF-1/30). Elemental analysis (Table S1) showed that the materials contain 10-15% of elements other than the expected C and H, as also reported in the literature for analogous polymeric systems 29, 41. EDX data report that small amounts of chlorine, oxygen and iron are present in the material probably due to side reactions and residues of catalyst. We hypothesized that, as polyalkylation of the aromatic rings occurs in excess of FDA, the formation of chloromethyl or hydroxymethyl groups would arise in presence of chloride ions or traces of water when there is no possibility to cross-link with another TPM unit.
The different polymeric materials mPAF-1/n were characterized using various spectroscopic techniques. In particular, FT-IR spectroscopy permits to determine some structural features and the connectivity of the hyper-crosslinked polymers (Figure 3). In the high frequency region both the precursor (curve a) and materials (curves b-e) are characterized by bands with medium intensity at 3100 and 3000 cm$^{-1}$, attributed to aromatic C-H groups stretching modes. After polymerization a new group of bands appears in the region 3000-2800 cm$^{-1}$ due to the stretching of aliphatic C-H, related to methylene linkers between the aromatic rings and, in minor extent, to chloro-methylene residues. The low frequency region of FTIR spectra shows the presence of bands characteristic of substituted aromatic rings: the spectrum of mPAF-1/3 (Figure 3b) shows bands at 1600 cm$^{-1}$ and 808 cm$^{-1}$, indicating a predominant 1,4-substitution. Increasing the relative concentration of FDA during the synthesis (mPAF-1/9, mPAF-1/16 and mPAF-1/30) increases crosslinking and multiple substitution of aromatic ring in different positions, as demonstrated by the increase of signals in the region 1650-1850 cm$^{-1}$.

All the materials prepared present characteristic band at 1441 cm$^{-1}$ due to CH$_2$ bending mode of the methylene linker along with bands at 1414 cm$^{-1}$ and 1269 cm$^{-1}$ due to CH$_2$ bending and wagging modes respectively of the chloro-methylene groups.
Figure 3. FTIR spectra of the precursor tetraphenyl methane (a), mPAF-1/3 (b), mPAF-1/9 (c), mPAF-1/16 (d), mPAF-1/30 (e) recorded as KBr pellets in the 3800-500 cm\(^{-1}\) frequency range.

Standard CP MAS conditions at room temperature were used to acquire the \(^{13}\text{C}[^1\text{H}]\) CPMAS NMR spectra on the different mPAF materials with short contact time of 2 ms (Figure 4). In accordance to previous reports from the literature \(^{29}\), all spectra show five peaks at about 37, 64, 128, 136 and 144 ppm. In the aliphatic carbon region, the methylene linking groups generate the peak at 37 ppm and quaternary carbon of TPM units at 64 ppm. The aromatic carbons signals are assigned as the following: 128 ppm for the aromatic C-H, 136 ppm for the methylene substituted aromatic quaternary carbons and 144 ppm for the quaternary carbon linked to the central tetrahedral carbon atom. Interestingly, the resolution of the peaks related to the aromatic carbons is reduced as the amount of FDA in the reaction increases, which confirms a greater substitution according to the FTIR spectra. Additional resonance is visible in the spectra at 43 ppm that can be assigned to CH\(_2\)Cl substitution, while only for the sample mPAF-1/30 the spectrum shows a peak at 71 ppm probably due to CH\(_2\)OH groups \(^{43}\). However, in quantitative \(^{13}\text{C}\) solid state MAS NMR spectra (Figure S2) this signal is under the limit of detectability: the chloromethyl carbon peak is found at very low intensity confirming that a small amount of these groups is formed during side reactions. Noteworthy, the resonances due to methylene carbons are broadened either due to the non-averaging of \(^{13}\text{C}-35,37\text{Cl}\) residual dipolar couplings (as in –CH\(_2\)Cl) or due to the heterogeneous broadening associated with an extensive distribution of chemical shifts (as in Ph-CH\(_2\)-Ph) \(^{29}\).
Figure 4. $^{13}$C solid state CPMAS NMR spectra of mPAF51/3 (a), mPAF51/9 (b), mPAF51/16 (c) and mPAF51/30 (d). A cross polarization contact time of 2 ms and a MAS spin rate of 15 kHz were used in all the experiments. * denotes spinning sidebands.

Powder X-ray diffraction (Figure S3) confirms the formation of amorphous materials, as expected for cross-linked polymers, with only two broad signals at 2$\Theta$ ~15° - 20° and 43°, related to direct ring-ring interactions, which are favored by the intrinsic flexibility of the polymeric structure. Small ordered, crystal-like domains embedded in the amorphous matrix cannot be excluded, though, as suggested by the pore distribution discussed below.

Thermogravimetric analysis (TGA), and its derivative curves (DTG), showed that all the polymers exhibit great thermal stability (Figure S4). All the materials are characterized by a weight loss of 8-15% between 250 and 450 °C, which can be correlated to the removal of the chloromethyl or hydroxymethyl groups derived by side reactions, in agreement with the elemental analysis (vide supra). As the post-synthesis treatments described above are likely to remove the adsorbed organic species from the network, this weight loss is probably due to covalently bound groups. The degradation of the framework is found at temperatures higher than 450 °C.
**Pore distribution.**

The polymer porosity was analysed by adsorbing gases at low temperature. First, N\textsubscript{2} adsorption/desorption isotherms were collected for all the mPAF materials at 77 K (Figure 5a); then, the experiment was repeated with Ar at 87 K for the material showing the highest surface area (Figure 6a), for a better description of pores below 10 Å width.

The isotherms can be classified as type I, with large quantities of gas (> 200 cm\textsuperscript{3}/g) adsorbed at low relative pressures, as expected for microporous materials. All the samples display also a further gradual filling of mesopores at higher relative pressures in the range 0.45-1 P/P\textsubscript{0}. All the materials showed a H\textsubscript{2}-type hysteresis in the desorption branch, indicative of mesoporous phase. The apparent BET surface areas (Table 1) were calculated over a relative pressure range P/P\textsubscript{0} = 0.05-0.15.

N\textsubscript{2} isotherms show that increasing the FDA to TPM ratio leads to materials with a progressive increase of surface area from 948 m\textsuperscript{2}/g for mPAF-1/3 (FDA:TPM ratio 3:1) to 1063 m\textsuperscript{2}/g for mPAF-1/9 (ratio 9:1), and 1314 m\textsuperscript{2}/g for mPAF-1/16 (ratio 16:1). A further increase in FDA:TPM ratio to 30:1 corresponds to a lower surface area (1162 m\textsuperscript{2}/g) measured for mPAF-1/30 sample. The pore size distribution was assessed by NLDFT approach (Figure 5b-d): the mPAF materials show several families of pores, namely micropores at 8 and 13.5 Å, and mesopores broadly distributed around 25 Å. In the series, the increase in surface area and pore volume (Table 1) can be related to enhanced polymerization degree, associated to higher crosslinking.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Langmuir surface area (m\textsuperscript{2}/g)</th>
<th>Total Pore Volume (cc/g)</th>
<th>Micropore Volume (cc/g)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPAF-1/3</td>
<td>948</td>
<td>1254</td>
<td>0.64</td>
<td>0.099</td>
<td>0.08</td>
</tr>
<tr>
<td>mPAF-1/9</td>
<td>1063</td>
<td>1512</td>
<td>0.71</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>mPAF-1/16</td>
<td>1314</td>
<td>1827</td>
<td>0.83</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>mPAF-1/30</td>
<td>1162</td>
<td>1655</td>
<td>0.83</td>
<td>0.097</td>
<td>0.095</td>
</tr>
</tbody>
</table>
Figure 5. (a) N\textsubscript{2} physisorption isotherms at 77K; (b) pore size distribution; (c) cumulative pore volume; (d) cumulative pore volume in the micropore region (5-20 Å). Pore size analysis performed with NLDFT method for silica cylindrical pores in the adsorption branch. Green spheres: mPAF-1/3; magenta stars: mPAF-1/9; red squares: mPAF-1/16; blue triangles: mPAF-1/30

It is known that ultramicropores, below 7 Å width, are better described by Ar physisorption\textsuperscript{15}: since this fraction of the porous volume is particularly important for gas uptake at low pressure, we refined the analysis for the mPAF-1/16 sample, which shows the largest surface area after N\textsubscript{2} adsorption. In Figure 6 the Ar adsorption/desorption isotherms in mPAF-1/16 at 87 K are presented along with the results of NLDFT analysis, performed at the same conditions as above: as expected, though the isotherms for Ar and N\textsubscript{2} are qualitatively very similar, the pore distribution analysis differs in the micropore region.
Figure 6. Ar physisorption isotherm at 87 K (a) and pore size distribution with the cumulative pore volume calculated using NLDFT method for silica cylindrical pores in the adsorption branch (b) of the sample mPAF-1/16

A narrow peak is observed in the pore distribution curve (Figure 6b), corresponding to 5.82 Å wide ultramicropores, with a much smaller peak around 15 Å: the total microporous volume due to these pore families is 0.30 cm³/g. A very broad signal is observed above 20 Å, attributed to several kinds of mesopores: the total porous volume results 0.89 cm³/g. These findings compare well with NLDFT data on N₂ adsorption isotherms, except that the ultramicropores are found at a smaller width: as said above, the analysis of Ar isotherms provides more reliable results for such small pores. The presence of a narrow distribution of ultramicropores suggests that a part of the material is regularly polymerized, indicating the presence of ordered islands surrounded by less regular and amorphous regions. This picture is strongly supported by the comparison with the theoretical models presented below.

The skeletal density of mPAF-1/16 was estimated ca. 1.22 g/cm³ by helium adsorption at room temperature: this result, along with the porous volume reported above, lead to an apparent density of 0.6 g/cm³ for this sample.

**Crystal structure from modeling.**

An ideal crystal structure for mPAF was optimized as described in the Experimental section: the unit cell is reported in Figure 7, along with a 2x2x1 supercell where van der Waals atomic spheres are used to sketch the porous free volume. In this model the unit cell formula is C₁₀₈H₆₀ and the cell volume 3100 Å³, with a resulting
density of 0.738 g/cm³. This value agrees well with the apparent density measured for mPAF-1/16 (0.6 g/cm³), considering that the fraction of mesoporous volume in the actual sample is expected to lower the density.

Figure 7. Optimized periodic structure of model mPAF; (a) unit cell, showing the sp3 carbon atoms belonging to TPM (red) and FDA (green); (b) 2x2x1 supercell, showing the van der Waals surface obtained with radii: 1.7 Å for C, 1.2 Å for H; (c) 2x2x6 supercell to highlight the 3D channel structure. Hydrogen atoms not shown.

In Figure 8a the Ar adsorption isotherm at 87 K, simulated with Monte Carlo technique and the force field described above, is compared to the adsorption isotherm of mPAF-1/16, which showed the largest specific surface area among the experimental samples. One can see that at very low pressure the two curves are in very good agreement (Figure 8a, inset), indicating a similar intensity of the host-guest interactions when the gas is preferentially adsorbed in the smallest micropores. At slightly higher pressures (10⁻⁵ to 10⁻³ bar), the simulated adsorption is larger than in the experiment, since all the specific volume in the model material is microporous (unlike in the experimental samples). On the other hand, at pressures around 1 mbar the model pores are saturated, while the experimental isotherm keeps growing as the gas fills larger and larger pores. We recall that the model is an idealized picture of the mPAF crystal, with no defects and perfectly regular crosslinking in para position: as a result, only one family of micropores is expected in the model.
Figure 8. (a) Simulated and experimental Ar adsorption isotherms at 87 K. Inset: logarithmic plot of the low pressure region. (b) Pore size distribution calculated with NLDFT method for silica cylindrical pores on simulated and experimental (magnified x3) adsorption isotherms. Black squares: theoretical model; red circles: mPAF-1/16 sample.

The NLDFT procedure was applied to the simulated isotherm, in the same conditions as for the experimental curve: the results are reported in Figure 8b and also in Figure S5, along with the cumulative pore volume.

As shown in Figure 8b, the agreement between the simulated and experimental pore distributions is very good in the region of ultramicropores: in fact, a narrow micropore distribution around 5.52 Å width is found, in very good agreement with the smallest pores found for the experimental sample (that is 5.82 Å). The second, much lower peak at 15 Å visible for the simulated distribution in Figures 8b and S5 is likely due to an artifact of NLDFT, related to the noisy trend of Monte Carlo simulations around 0.1 bar (Figure 8a). In the mesoporous region, between 20 and 60 Å, the experimental pore distribution lies above the simulated curve, as expected.

Note that the total porous volume in the model is 0.80 cm$^3$/g (entirely microporous, as remarked above), while for mPAF-1/16 the NLDFT analysis indicated 0.89 and 0.30 cm$^3$/g for total and microporous volume, respectively.

The plausibility of this pore size estimate can be qualitatively appreciated by considering a sphere embedded in the van der Waals surface reported in Figure 7b: as shown in Figure S6 a sphere with 5.8 Å diameter fits in the model pore quite well, whereas a 8 Å sphere, as indicated by the less reliable N$_2$ isotherm, would clearly be too wide for this model.
In conclusion, on the basis of the discussion above we believe that the most regular and ordered fraction of mPAF materials is well described by this model structure, which can be used to predict the gas uptake in the ultramicroporous volume.

**Experimental uptake of CH$_4$ and CO$_2$.**

The suitable pore size, large surface area and stability against moisture make these porous materials good candidates for gas storage and separation. CH$_4$ and CO$_2$ sorption isotherms were measured volumetrically up to 10 bar at 273 K (Figure 9a) and 298 K (Figure 9b) for all samples. The CH$_4$ and CO$_2$ isotherms show a Langmuir profile, although at both temperatures and at 10 bar the saturation values have not yet been reached. The adsorption isotherms at 195 K and 1 bar were also collected (Figures S7, S8), to evaluate the maximum uptake for CO$_2$ and to calculate the isosteric heat for methane.

![Figure 9. CH$_4$ adsorption isotherms up to 10 bar at 273K (a) and 298K (b), CO$_2$/N$_2$ selectivity (c) and heat of adsorption of CO$_2$ and CH$_4$ (d) of the mPAF polymers: mPAF-1/3 (green spheres), mPAF-1/9 (magenta stars), mPAF-1/16 (red squares) and mPAF-1/30 (blue triangles).](image-url)
In Table 2 the excess gas uptake capacity of the four materials at different temperatures and pressures are reported: mPAF-1/16 shows the highest adsorption for both CH₄ and CO₂ gas, in good agreement with the highest apparent BET surface and microporous volume with respect to the other mPAF samples. The desorption isotherms are reported in the Supporting Information (Figure S9 and S10): the limited hysteresis loops can be attributed to the desorption from micro and mesopores.

The series of mPAF materials is particularly efficient under mild conditions (1 bar), where mPAF-1/16 adsorbs 64 cm³(STP)/g (2.82 mmol/g) of CO₂ at 273 K (Figure 9a). In the same conditions, mPAF-1/3, mPAF-1/9 and mPAF-1/30 CO₂ uptakes are about 46, 51 and 60 cm³(STP)/g (2.03, 2.25 and 2.64 mmol/g), respectively. These uptake values are comparable to PAFs (2.05 – 3.48 mmol/g)⁴⁶, COFs (1.21 – 3.84 mmol/g)⁴⁷, and other HCPs polymers (1.11 – 3.96 mmol/g)³², ³⁴, ⁴⁸. In particular the CO₂ uptake measured in the present work is very close to the value (2.95 mmol/g) reported in ref. 3⁴ for an analogous material with a slightly higher BET surface area. High CO₂ uptakes have also been measured in activated porous carbons, ranging from 2 to 7.4 mmol/g for materials with BET SSA up to 3400 m²/g ⁴⁹, ⁵⁰.

The good performance of mPAF materials can be attributed to the abundance of ultramicropores (centered around 0.58 nm): in fact, very high CO₂ uptakes at low pressure are expected in porous materials with a high fraction of pores below 1 nm, as observed for instance in the case of KOH carbonization of PAF⁵¹. This behaviour has also been related to the presence of pores commensurated with the kinetic diameter of carbon dioxide⁵².

Table 2. Experimental excess uptake of methane and carbon dioxide and nitrogen at 298, 273 K up to 10 bar and methane and carbon dioxide at 195 K up to 1 bar into mPAF networks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH₄(cm³/g)</th>
<th>CO₂(cm³/g)</th>
<th>N₂(cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>195 K 1 bar</td>
<td>273 K 10 bar</td>
<td>298 K 10 bar</td>
</tr>
<tr>
<td>mPAF-1/3</td>
<td>86</td>
<td>65</td>
<td>46</td>
</tr>
<tr>
<td>mPAF-1/9</td>
<td>84</td>
<td>57</td>
<td>52</td>
</tr>
<tr>
<td>mPAF-1/16</td>
<td>106</td>
<td>84</td>
<td>64</td>
</tr>
<tr>
<td>mPAF-1/30</td>
<td>91</td>
<td>70</td>
<td>50</td>
</tr>
</tbody>
</table>

The isosteric heat of adsorption (Qₛₑ) computed from the excess isotherms at 273 and 298 K is reported in Figure 9d for all samples: at low coverage (< 10 cm³/g) Qₛₑ varies between 24.5 and 26 kJ/mol, demonstrating the occurrence of favorable interactions of CO₂ with the aromatic network; these values agree with the
isosteric heats measured in refs. 34 and 38, tending to 26 kJ/mol at very low CO₂ uptakes. Remarkably, Q_{st} for CO₂ in mPAF materials exceeds that measured in PAF-302 (15 kJ/mol, ref. 24, where it is referred to as PAF-1), which contains the same chemical moieties but has markedly wider pores, confirming the role of ultramicroporosity in the adsorption process.

Nitrogen uptake (Figure 9a,b) is quite low even at pressures as high as 10 bar, indicating a low affinity for the absorbent. This result can be exploited favorably for selective adsorption of CO₂/N₂ mixtures in actual industrial applications. At low pressure and 273 K, the mPAF hyper-crosslinked networks show high CO₂/N₂ selectivity between 20 and 23 (Figure 9c), which is comparable to most microporous organic polymers³⁴.

The uptake capacities of all samples for methane were also studied; mPAF-1/16 showed a CH₄ uptake of 84 and 64 cm³(STP)/g at 10 bar and 273 and 298 K, respectively (Figure 8a,b), while the maximum uptake measured at 195 K, amounts to 106 cm³(STP)/g (Figure S8). On the other hand, mPAF-1/3, mPAF-1/9 and mPAF-1/30 samples exhibited lower CH₄ uptakes, according to their lower surface areas. Isosteric heats of adsorption were measured from the excess isotherms at 195, 273 and 298 K, with the results shown in Figure 9d at low coverage methane Q_{st} is in the range 17.5-19.5 kJ/mol. As already observed for CO₂, methane isosteric heats in mPAF are significantly higher than that measured for PAF-302 (slightly below 15 kJ/mol in ref. 24); a similar value of 15 kJ/mol was estimated theoretically for a methane molecule interacting with a single ditolyl-methane molecule, resembling the local environment in porous aromatic frameworks⁵³. Also in this case, the higher interactions experienced in mPAF can be attributed to the ultramicroporosity, which enhances the adsorption capacity at low pressures.

At low pressure the CH₄ uptake in mPAF exceeds that in PAF, recently presented and considered very promising for methane storage applications: as shown in Table 3, despite the lower specific surface area, the gravimetric adsorption in mPAF-1/16 is about 20% higher than in PAF-302 at 1 bar and 273 K. Due to mPAF higher density, such difference is even more evident in volumetric adsorption (Table 3, last column), which is often more relevant from the application point of view. It is worth noting that this behaviour is typical of materials with a high affinity for the adsorbate and in conditions far from the saturation: in this case, very small pores enhance the gas/solid interactions and lead to higher uptakes, while a larger SSA allows to adsorb more gas at saturation.
Table 3. Comparison of gravimetric and volumetric CH$_4$ uptake in mPAF-1/16 and PAF-302 (ref. 25) at low pressure.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SSA (m$^2$/g)</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>cm$^3$/g</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPAF-1/16 (d= 0.6 g/mL)</td>
<td>1321</td>
<td>273</td>
<td>1</td>
<td>21.7</td>
<td>9.2</td>
</tr>
<tr>
<td>PAF-302 (d= 0.3 g/mL)</td>
<td>5460</td>
<td>273</td>
<td>1</td>
<td>18</td>
<td>3.8</td>
</tr>
</tbody>
</table>

**Simulated uptake of CH$_4$ and CO$_2$.**

Monte Carlo simulations were performed to study methane and carbon dioxide adsorption in the mPAF model structure described above: in Figure 10 the theoretical excess isotherms at 298 K are compared to the corresponding experimental curves (referred to the mPAF-1/16 sample). As expected, the simulated excess adsorptions are systematically larger than the measured ones: at 1 bar the CH$_4$ adsorptions in the model and in mPAF-1/16 are 27 and 8 cm$^3$(STP)/g, respectively, while at 10 bar the two values are 98 and 64 cm$^3$(STP)/g. The CO$_2$ adsorptions in the model and in the real sample are 125 and 38 cm$^3$(STP)/g at 1 bar, and 210 and 136 cm$^3$(STP)/g at 10 bar.

![Figure 10. Simulated (empty symbols) and experimental (filled symbols, mPAF-1/16 sample) excess adsorption isotherms at 298 K. Blue triangles: carbon dioxide adsorption; red circles: methane adsorption.](image-url)
One can see that at 1 bar the ratio of the adsorbed amounts is quite close to the ratio of microporous volume in the model and in mPAF-1/16 (0.83 and 0.21 cm$^3$/g, respectively, as seen above), thus indicating that in these conditions the adsorption occurs mainly in the microporous fraction of the material. At higher pressure, however, also the mesoporous volume of the real sample makes an important contribution to the total adsorption, and the simulated and experimental curves get closer, also because the model isotherms are approaching the saturation plateau. The semi-logarithmic isotherms at very low pressures (Figure S11 in the Supporting Information) show that the trends of simulated and experimental uptakes coincide when the pressure tends to zero. The isosteric heats of adsorption were computed from the simulated excess isotherms as well, and the results at low coverage are in very good agreement with the measured values: 24 kJ/mol for CO$_2$ and 18 kJ/mol for CH$_4$.

The simulations confirm that this kind of material is expected to perform well in the gas uptake, especially at low pressures: in particular, the model highlights the central role of microporous and ultramicroporous volume to achieve such results, thus indicating the way to improve the uptake even further.

Conclusions.

Hyper-crosslinked aromatic polymers were produced by Friedel-Crafts reaction between TPM and FDA, providing an easy and low-cost route towards efficient adsorbents for carbon dioxide and methane. The TPM:FDA ratio was varied in the 1:3 – 1:30 range, to optimize the synthesis conditions, yielding four materials called mPAF-1/n (microPorous Aromatic Frameworks, with explicit indication of the reagents ratio).

The mPAF structure was studied by thermogravimetric, IR and SS-NMR techniques, showing the extent of polymerization and the low contamination by unreacted species or by-products; X-ray diffraction analysis indicated that amorphous materials are formed, though the pore distribution analysis and the comparison with theoretical models show the presence of regular domains. The porosity of the samples was carefully investigated, first by adsorbing N$_2$ at 77 K, then refining the analysis with Ar adsorbed at 87 K (since the latter is known to describe with greater accuracy the ultramicropores below 7 Å width). The NLDFT analysis showed that the porous volume of the four samples varies from 0.64 to 0.83 cm$^3$/g, with microporous (below 2 nm wide) volume from 0.16 to 0.21 cm$^3$/g. Correspondingly, the BET surface area was measured in the range 948-1314 m$^2$/g. The best material (with the highest volume, microporous volume and surface area) was mPAF-1/16, obtained with a fair excess of FDA in the reaction mixture. Based on Ar adsorption isotherms, the pore distribution in this sample exhibits a narrow peak at 5.82 Å, a smaller peak around 15 Å and a broad family of mesopores centered at 20 Å.
A theoretical model was developed to reproduce the most regular and ordered fraction of mPAF, with TPM units connected in a diamond arrangement by methylene groups in para position. The Ar adsorption isotherm at 87 K was simulated in this model by Monte Carlo technique, with a force field specifically optimized: the NLDFT analysis on the simulated isotherm showed a porous volume of 80 cm³/g with a narrow ultramicropore family at 5.52 Å in excellent agreement with the experimental value.

Carbon dioxide and methane were adsorbed in mPAFs at 273 and 298 K, proving that these materials are very good candidates for gas storage, even at low pressures. In particular, the CO₂ uptake in mPAF-1/16 in mild conditions (1 bar, 273 K) is as high as 2.82 mmol/g, comparing very well with other porous materials recently described. The crystalline model showed higher uptakes than the experimental measures, but the simulated and experimental isotherms were in good agreement for very low pressures, confirming the good description of the mPAF microporous fraction by the model.

Methane adsorption at 1 bar and 273 K reached very interesting values, outperforming similar materials (PAF) thanks to the ultramicroporous volume present in mPAF.

Acknowledgement.

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Supporting Information description.

Experimental and computational characterization of mPAF materials: 1. Elemental analysis and EDX; 2. ¹³C solid state MAS NMR; 3. X-Ray powder pattern; 4. Thermogravimetric analysis; 5. Pore distribution size calculated with NLDFT method in the simulated adsorption isotherm of Ar in the model mPAF at 87 K; 6. Spheres of 5.8 Å diameter embedded in the mPAF model structure; 7. Experimental CO₂ adsorption isotherms at 195K and up to 1 bar; 8. Experimental CH₄ adsorption isotherms at 195K and up to 1 bar; 9. Experimental CO₂, CH₄ and N₂ adsorption and desorption isotherms up to 10 bar at 298K; 10. Experimental CO₂, CH₄ and N₂ adsorption and desorption isotherms up to 10 bar at 273K; 11. Semi-logarithmic plots of the simulated...
(empty symbols) and experimental (filled symbols, mPAF-1/16 sample) excess adsorption isotherms at 298 K: (a) methane adsorption; (B) carbon dioxide adsorption. This information is available free of charge via the Internet at http://pubs.acs.org

Crystal Information File (CIF) with the optimized structure of mPAF model.

References.


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