

Synthesis and Easy Functionalization of Highly Porous Networks through Exchangeable Fluorines for Target Specific Applications

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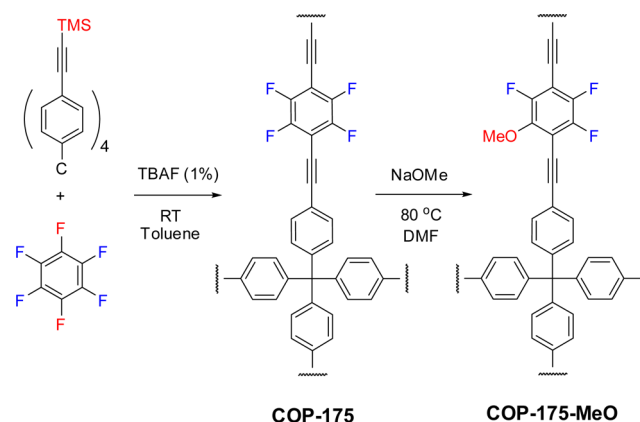
Supporting Information

Emerging porous materials like metal organic frameworks (MOFs),¹ covalent organic frameworks (COFs),² and porous polymers³ offer promise in applications such as gas capture,⁴ energy storage,⁵ or catalysis.⁶ Industrial processes that demand such materials prefer high chemical stability as well as scalable and affordable synthesis procedures. Porous polymers with robust C–C bonded networks such as porous aromatic frameworks (PAFs),⁷ porous polymer networks (PPNs),⁸ and conjugated microporous polymers (CMPs)^{3a,b} are chemically very stable and have been shown to reach high specific surface areas, leading to great interest in developing network (or highly cross-linked) polymers that feature permanent porosity.⁹ Despite the early achievements, the use of prohibitively expensive precious metal catalysts (e.g., Pd) and the less than ideal atom economy prevented a widespread use. In addition, the lack of reactive functional groups covalently tethered on the pore walls is now a great concern, since structures without inherent chemical functionality on the pore walls are behaving similarly to activated carbons or reduced graphene oxide. In order to introduce a suitably reactive functional group, one must resort to postmodification procedures, since high reactivity on a substituent brings chemical diversion in the network building toward extending from the substituent itself.¹⁰ This significantly prohibits chemical tunability (Scheme 1).

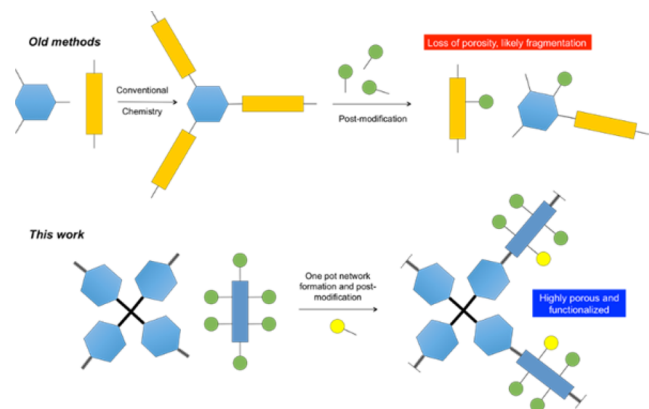
For covalently attaching target specific pendant functional groups, there are not many options because to do that one must alter the pore wall chemistry of the robust network with only C–H bonds to be substituted. So far, only undesirably

harsh postmodification methods succeeded.¹¹ We have been developing porous polymers for gas capture applications and always looked for catalyst-free, scalable synthesis conditions.¹² In this study, we designed a robust C–C bonded porous polymer, indexed as covalent organic polymer COP-175 (Scheme 2), using a unique synthetic methodology where

Scheme 2. One-Pot, Metal-Free Synthesis of a Highly Porous, Robust, Fluorinated Porous Network, COP-175, and Its Post-Functionalization with Methoxide



Scheme 1. Covalent Network Formation and Post-Modification Methods Are Best Combined To Preserve Porosity and Maximize Stability and Tunability



metal-free network formation also leads to easily exchangeable substituents, effectively solving two problems at once.^{13,14} The key for the success of this facile network building is the regioselective nucleophilic substitution. Unreacted, leftover fluorines provide grafting locations for the desired functionalities to be covalently tethered.

Fluorines in porous networks are mainly introduced for their well-known hydrophobicity.¹⁵ We, however, suggest that they can be especially useful because the fluorinated aromatics can undergo easy nucleophilic aromatic substitution,¹⁶ since the usual grafting options are limited to a couple of violent reactions, such as chloromethylation¹¹ and nitration,¹⁷ or very functional group specific additions such as the thiol–yne reaction.¹⁸ This strategy was never used, and there is no evidence for nucleophilic aromatic substitution-based post-modification methods. Previous nucleophilic substitutions have dealt with cross-linking or post-polymerization using ring

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opening of epoxides or Huisgen azide–alkyne 1,3-dipolar cycloadditions, but none were aromatic.^{19–21} Through the methodology described here, one can attach any reactive functional group to the pore walls of porous polymer networks.

COP-175 was synthesized through a metal-free, RT reaction between commercially available hexafluorobenzene and readily synthesized tetra(4-(2-(trimethylsilyl)ethynyl)phenyl)methane at constant stirring in toluene with a catalytic amount (1%) of tetrabutylammonium fluoride (TBAF) (Scheme 2). COP-175 was characterized by gas sorption, solid-state ¹⁹F and ¹³C NMR, FTIR, XRD, SEM, and TGA (full experimental details on analytical methods can be found in the Supporting Information). Solid-state ¹³C and ¹⁹F NMR were the primary confirmation for the chemistry of the network after synthesis and postmodification (Figure 1).

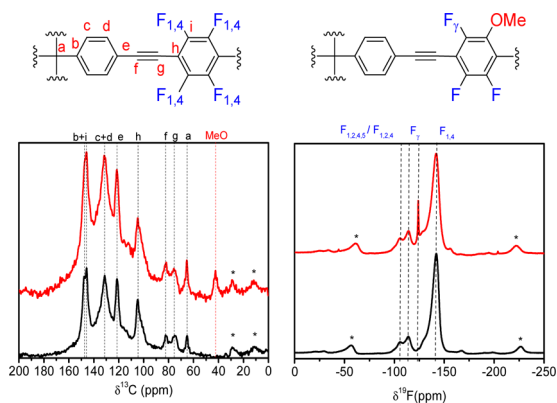


Figure 1. Assignment of ¹³C solid-state NMR spectra (left); ¹⁹F solid-state NMR spectra (right) of COP-175 (black) and COP-175-MeO (red). Asterisks denote spinning side bands.

The carbon NMR of COP-175 shows all expected peaks of the structure, which is not that common for insoluble amorphous network materials (in our experience) who tend to give broad signals.²² Clean peak distribution and assignment suggest that the structure is linked preferentially on the 1,4-position of the hexafluorobenzene moieties. Fluorine-NMR mainly confirms the presence of fluorines and their symmetry due to the regioselective reaction. It shows a main peak at −142 ppm integrating for 81% of all the present fluorine atoms (Figure 1). Two smaller peaks are at −106 ppm and −114 ppm and integrate for the rest of (16%) the fluorine content. A very small peak integrating for 3% can be found at −167 ppm. The chemical shifts and integrations are perfectly in line with the isolated compounds from a model reaction that Watson et al. performed between hexafluorobenzene and 1-phenyl-2-trimethylsilylacetylene in which they isolated all obtained products (Scheme S2). We also reproduced the same and confirmed the product distribution on model compounds.

Powder XRD of COP-175 gave a broad featureless spectrum, characteristic of an amorphous solid (Figure S1). Thermogravimetric analysis performed under nitrogen up to 800 °C gave thermal stabilities up to 400 °C for both COP-175 and COP-175-MeO due to the strong C—C bonded backbone (Figure S2). The FTIR spectrum of COP-175 shows the characteristic vibrations of the two building blocks, such as aromatic C=C and sp² C—H stretches at 3081, 3029, and 1484 cm^{−1}, alkyne stretch at 2214 cm^{−1}, and C—F stretch at 982 cm^{−1} (Figure S3).

Textural characterization of COP-175 was performed by argon sorption isotherms at 87 K (Figure 2). The isotherm

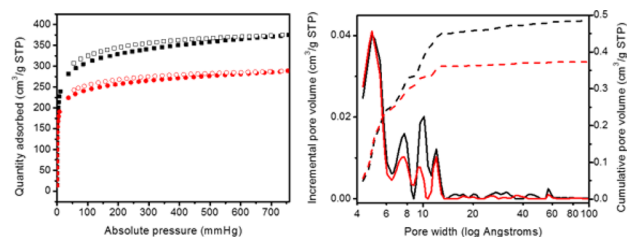


Figure 2. Argon adsorption (filled dots)–desorption (empty dots) isotherms at 87 K (left); pore size distribution (right) by NLDFT (argon 87 K, slit pores, aspect ratio 4) of COP-175 (black) and COP-175-MeO (red).

shows a clear *type I* behavior, reflecting the microporous nature of the network, with a calculated BET surface area of 1035 m²/g (with 74% microporous area) and a pore volume at $P/P_0 = 0.993$ of 0.487 cm³/g. The pore size distribution through an NLDFT calculation is narrow with four identifiable pore sizes from 5 to 12 Å, the main pores being located around 4.9 Å.

Structural confirmation and larger scale production of COP-175 allowed us to study the expected postmodification of the exchangeable fluorines. We performed a nucleophilic substitution reaction with sodium methoxide at 80 °C in dry DMF. The grafting efficiency was determined by solid-state NMR, FTIR, and argon sorption experiments, complementary to the parent network. The solid-state carbon NMR spectrum of COP-175-MeO shows a new signal at 42 ppm, characteristic of the grafted methoxide unit (Figure 1). In fluorine NMR, an additional sharp peak at −124 ppm is found, which confirms the substitution of fluorine atoms by methoxide units. Characteristic sp³ C—H stretching vibrations of methoxide units below 3000 cm^{−1} are found in the FTIR spectra of COP-175-MeO (Figure S3).

The BET surface area of the functionalized COP-175 was calculated from the argon sorption isotherms showing a decrease from 1035 to 829 m²/g (but with an increased 77% microporous area) while the pore volumes of the pores around 8 and 10 Å are also noticeably lowered (Figure 2). The filling of these pores confirms the presence of tethered functions inside the material. Particularly important is the largely preserved porosity, since it is well-known that postmodification routes tend to lead to significant losses in textural properties mainly because of the side reactions that compromise or at times fail the network structure.^{11,23}

In summary, we have successfully designed a metal free C—C bond formation reaction as a viable alternative to precious metal mediated coupling reactions (e.g., Sonogashira) to synthesize a perfluorinated porous network polymer. The obtained porous structure is highly microporous with a narrow pore size distribution. Thanks to the fluorinated aromatic backbone, a facile nucleophilic aromatic substitution of a porous network could be achieved. To the best of our knowledge this work reports the first nucleophilic aromatic substitution based postmodification, with great potential in making highly porous, stable, and versatile porous materials. Most of the surface area and pore size distribution is preserved after modification, allowing both properties from the network and grafted functionalities to be effectively used. We believe this synthetic approach will result in significant developments in

designing porous networks with specific functional groups without compromising structural integrity or giving up on scalability. We also expect aromatic nucleophilic substitution chemistry will be commonly visited for grafting purposes. In fact, we are already studying various functionalities such as thiols for heavy metal capture, amines for CO₂ capture, and hydrocarbons for gate opening effects in methane storage. We are also working on a number of new porous network structures by varying cores and linkers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.6b02152](https://doi.org/10.1021/acs.chemmater.6b02152).

Experimental procedures and characterization by TGA, XRD, SEM, and FTIR (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

COP, covalent organic polymer; TBAF, tetrabutylammonium fluoride; BET, Brunauer–Emmett–Teller; MeO, methoxide

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