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The para-fluoro-thiol reaction: a versatile route for the production of functionalized nanoporous polymers for gas storage or separation

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ABSTRACT:

Hypercrosslinked polystyrene-like polymers (HCPs) exhibit great promise for numerous applications including environmental remediation processes, catalysis, gas storage and separation. They can be synthesized in a cost-effective way from readily available starting materials and have a good potential for scale-up. [1] Herein we demonstrate that the addition of pentafluorostyrene (PFS) to the classical vinylbenzyl chloride (VBC)-divinylbenzene (DVB) formulation of HCPs allows an efficient strategy to functionalize and influence the textural properties of HCPs. This fluorinated unit plays a double role, as a clickable unit and a hydrophobic/polar site. Together with an array of widely available thiol-containing compounds, PFS units offer a versatile way to tailor the properties of HCPs for specific sorption applications *via* the highly regioselective par-fluoro-thiol reaction which is performed at room temperature and in a few hours only, thus reducing the energy consumption associated with the process. The proportion of the three building blocks (i.e., DVB, VBC and PFS) in the polymer determines the number of available chemical sites but also the characteristics of the porous media. At a 4 mol% PFS composition, the resulting HCPs exhibit microporosity, irrespective of the incorporated functional groups (hexyl, alcohol, amine or sulfonate), with BET surface areas ranging from 760 m².g⁻¹ to 1700 m².g⁻¹. Consequently, it was possible to assess the eventual discrepancies brought to the various materials in terms of specific gas sorption properties. CO₂ adsorption at different loading pressures was accessed using a home-made manometric setup (adapted from [2]). At low pressure, under 10 bars, surface chemistry alongside textural properties significantly influences uptake capacity. In the pressure range of 10 to 25 bars, the uptake capacity correlates with porous volume. At higher pressure, the hexyl functionalized material surprisingly stood out with the best performance despite a lower porous volume than the non-functionalized material. (Fig.1)

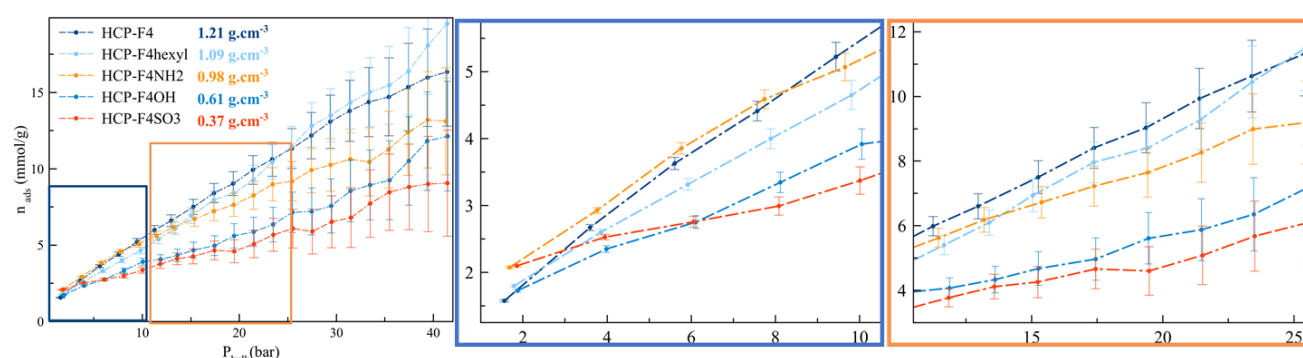


Fig. 1. The CO₂ adsorption isotherms of the 4 mol% PFS-containing materials at 30°C with low and mid pressure magnifications

[1] C. Li, W. Che, S. Y. Liu, G. Liao, *Mat. Today Chem.* **29**, 1–19 (2023).

[2] L. Perrier, F. Plantier, D. Grégoire, *Rev. Sci. Instrum.* **88**, 035104 (2017)