Supplemental Information for

Nanoporous, hypercrosslinked polypyrroles: Effect of crosslinking moiety on pore size and selective gas adsorption

Jonathan Germain,[a] Jean M.J. Fréchet[a,b] and Frantisek Svec[b]*

[a] *College of Chemistry, University of California, Berkeley, CA 94720-1460 and*
[b] *The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8139*

Materials and Equipment. Polypyrrole (cat. *# 577030, conductivity 10-40 S/cm, contains proprietary organic sulfonic acid dopant)*, dimethylsulfoxide, cesium carbonate and diiodomethane were purchased from Aldrich (St. Louis, MO). Dimethylformamide and toluene were purified using a solvent purification system before use. All other solvents were of the best available quality and used without additional purification.

Hydrogen (99.999% purity) and nitrogen (99.9995% purity) adsorption measurements at pressures of up to 0.12 MPa were carried out on a Micromeritics ASAP 2020 (Norcross, GA) surface area and porosity analyzer as described elsewhere.[4,6] Degassing temperatures were determined by observing plateau pressures under vacuum. High pressure hydrogen adsorption measurements were carried out using a PCT Pro 2000 instrument (Hy-Energy, Newark, CA). Samples were first degassed on the ASAP 2020 instrument, then moved to a nitrogen filled glove box where they were transferred into the PCT Pro 2000 sample holder. To remove nitrogen from the system, the sample holder was flushed with helium several times before starting the measurements. Because the PCT Pro does not have a turbopump, an adapter was used to degas PCT Pro sample using the ASAP 2020. The Brunauer-Emmett-Teller (BET) equation was used to calculate specific surface areas based on nitrogen adsorption isotherms measured at 77 K and relative pressures approaching 1.0. The Langmuir equation was used to calculate specific surface areas based on hydrogen adsorption isotherms measured at 77 K and pressures of up to 0.12 MPa. Enthalpy of adsorption was calculated by applying the van’t Hoff equation to pairs of adsorption isotherms measured at 273 and 295 K or 77 K (liquid nitrogen) and 87 K (liquid argon).

Microwave-assisted reactions were carried out a Biotage Initiator 2.0 (Biotage, Inc., Uppsala, Sweden).

Elemental analyses were conducted by Quantitative Technologies, Inc. (Whitehouse, NJ).

Preparation of –CH_2- crosslinked polypyrrole using diiodomethane. A round bottomed flask was charged with 1.00 g of polypyrrole and 2.01 g of sodium *tert*-butoxide inside a nitrogen-filled glovebox and 15 mL of anhydrous dimethylsulfoxide was added to the mixture. With a nitrogen-purged reflux condenser cooled to -10 ^{o}C, the mixture in flask was brought to a temperature of 170 ^{o}C to dissolve the polymer . The flask was then removed from the heating bath and allowed to cool for a few minutes before 5.93 g of diiodomethane was added. The components reacted for 5 min before being placed back in the heating bath at 170 ^{o}C for 2 hours. The temperature was then reduced to 160 ^{o}C and the polymer allowed to react for additional 22 h. The resulting solid was rinsed with acetonitrile and extracted in a Soxhlet apparatus using acetonitrile under a nitrogen atmosphere. The solid was dried in vacuo. Before adsorption measurements, this polymer was degassed at a temperature of 105 ^{o}C.

Preparation of –CH- crosslinked polypyrrole using iodoform. A round bottomed flask was charged with 0.75 g of polypyrrole and 4.94 g of cesium carbonate inside a nitrogen-filled glovebox. Then, 1.74 g of iodoform was added and the flask purged with nitrogen. This was followed by addition of 9.5 mL of anhydrous dimethylsulfoxide. The contents were heated to 170 ^{o}C under a reflux condenser for 1 h. The temperature was then reduced to 160 C and the polymer allowed to react for an additional 23 h. The resulting solid was rinsed with water, dimethylformamide, and ether and then dried in vacuo. This polymer was degassed at a temperature of 250 ^{o}C.

Preparation of boron crosslinked polypyrrole. A dry microwave vial was charged with 0.25 g of polypyrrole and 1.25 g of cesium carbonate inside a nitrogen-filled glovebox and 3 mL of anhydrous toluene were added. Separately a 0.8 mol/L solution of boron triiodide was prepared in anhydrous toluene. After the polypyrrole had been dissolved, 1.6 mL of the BI_3 solution was added. Formation of precipitate was immediately visible. The mixture was allowed to react at room temperature for 15 min and then the temperature raised to 100 ^{o}C for 12 h in a microwave reactor. The resulting solid was extracted in an acetonitrile soxhlet under a nitrogen atmosphere and rinsed with a 1 M solution of sodium hydroxide, followed by water and acetonitrile. The solid was dried in vacuo, then rinsed with formamide and water, and extracted again in a Soxhlet apparatus using acetonitrile under a nitrogen atmosphere. Finally, the solid was dried in vacuo. This polymer was degassed at a temperature of 175 ^{o}C.