Microporous Polyphenylenes with Tunable Pore Size for Hydrogen Storage

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Experimental Section

Materials. Chemicals were purchased from Aldrich, Alfa Asia, Oakwood and Strem, and were used without further purification unless otherwise noted. Tetrahydrofuran (THF) anhydrous solvent was distilled from commercial THF with sodium/benzophenone ketyl. Dioxane Et₂NH, Et₃N, and i-Pr₂NH anhydrous solvents were distilled from their respective mixture with CaH₂.

Equipment. ¹H and ¹³C NMR spectra were collected on a Bruker 400 or 500MHz FT NMR spectrometer. FTIR spectra were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc and Columbia Analytical Services, Inc. TGA data were obtained from a Shimadzu TGA-50 with a heating rate of 10 °C/min in an air atmosphere. BET surface area and pore structures were measured with a Micromeritics ASAP 2010 system using nitrogen as probing gas. The hydrogen adsorption isotherms were measured with a modified Sievert isotherm apparatus similar to that reported in the literature. In our study, typical polymer sample sizes ranged from 200 to 500 mg. Before each isotherm measurement, the sample was heated at 125 °C under vacuum to remove residual moisture or other trapped gases. Ultrahigh purity helium (99.9995%) was used to calibrate the free volume in the sample cell before each measurement. For H₂ uptake measurement, hydrogen with purity of 99.9995% was used. The ambient temperature was controlled through an isolated hood, 77 K, 87 K, 195 K

and 298 K measurements were conducted by immersing the sample cell into a dewar of liquid nitrogen, liquid argon, dry ice / acetone and temperature-stabilized circulating water, respectively. Hydrogen equilibrium pressure as high as 70 bar was applied for the measurement. A typical measurement error was $< \pm 10\%$ of the full hydrogen uptake capacity at high pressure limit. The error reduced to $< \pm 5\%$ at the low-pressure region. Commercial software, GASPAK, was used to accurately calculate the state equations of the hydrogen and helium under different pressures and temperatures.

Heat of adsorption calculation. Heats of adsorption were derived from the slope of $\ln P$ vs. 1/*T* at constant hydrogen loading using the Clausius-Clapeyron equation (1):

$$\Delta H = -R \left[\frac{\partial \ln P}{\partial (1/T)} \right]_{n^m} = -Rk \tag{1}$$

Where ΔH is the heat of adsorption, R is ideal gas constant, k is the slope of ln*P* vs. 1/*T* at constant hydrogen loading n^m .²

Synthesis of polymer POP-1: 1,4-diethynylbenzene (0.500 g, 3.97 mmol) was added to a dried round bottom flask under argon. Anhydrous dioxane (50 mL) was added via a syringe, and the mixture was stirred at room temperature until it became a clear solution. $Co_2(CO)_8$ (0.163 g, 0.477 mmol) was added under protection of argon, the mixture was stirred for about 20 min until no obvious solid suspension was observed. The flask was then placed into an oil bath that was pre-heated to 125 °C. After 1 h, the flask was lifted above the oil bath to cool to room temperature. The brown solid product was smashed to fine particles using a spatula, followed by the addition of 30 mL methanol. The solid product was collected by filtration. After air-drying for an hour, the solid was ground into fine powder and stirred into 40 mL 37% HCl solution. The mixture was sonicated for 2 h at room temperature and then filtered and washed with water and

methanol. Brown solid product (5.2 g, ~100% yield, contains some water and catalyst) was obtained after drying in vacuum oven at 100°C for 1 day. Elemental Analysis: Calculated for $[C_{10}H_6]_x$: C, 95.21; H, 4.79. Found: C, 75.92; H, 4.75; We speculate that the discrepancy was mainly resulted from water and air trapped in the sample which were not effectively removed by the outside analysis laboratory.

Synthesis of 4,4'-bis(trimethylsilylethynyl)biphenyl: 4,4'-dibromobiphenyl (10.0 g, 32.2 mmol), PdCl₂(PPh₃)₂ (0.27 g, 0.386 mmol) and CuI (0.037 g, 0.193 mmol) were placed in a 2-neck round bottom flask, anhydrous Et₂NH (70 mL) and trimethylsilyl acetylene (10.9 mL, 77.4 mmol) was added via a syringe. The reaction mixture was heated to 60 °C for 16 h, and then cooled down to room temperature. The mixture was filtered and washed with diethyl ether. The filtrate was concentrated in a rotary evaporator under vacuum and loaded to a silica gel column with CH₂Cl₂. Hexane/ CH₂Cl₂ (3:1 v/v) was used as an eluent, the major band was collected and white solid product (11.0 g, 99% yield) was obtained after removing the solvent. ¹H NMR: δ (ppm): 0.27 (s, 18H, CH₃), 7.53 (s, 8H, Ar-H).

Synthesis of 4,4'-diethynylbiphenyl: NaOH (4.62 g, 115.4 mmol) was dissolved in 40 mL methanol and added to a solution of 4,4'-bis(trimethylsilylethynyl)biphenyl (7.4 g, 21.4 mmol) in 50 mL CH₂Cl₂. The mixture was stirred for 12 h at room temperature. The organic solvent was then removed in a rotary evaporator under vacuum. 40 mL CH₂Cl₂ was added to the residue and the white insoluble solid was filtered away. The filtrate was then washed with brine (40 mL). Organic phase was separated using a separation funnel and dried over anhydrous Na₂SO₄. The solution was concentrated, and methanol was added to precipitate the desired white product (3.9 g, 90 % yield). ¹H NMR: δ (ppm): 3.15 (s, 2H, C=CH), 7.55 (m, 8H, Ar-H). ¹³ C NMR: δ (ppm): 78.23, 83.56, 121.65, 132.82, 140.71.

Synthesis of polymer POP-2: 4,4'-diethynylbiphenyl (0.487 g, 2.46 mmol) was added to a dried 2-neck round bottom flask, anhydrous dioxane (50 mL) was injected via a syringe, and the mixture was stirred until the solution became clear. $Co_2(CO)_8$ (0.100 g, 0.296 mmol) was added under protection of argon, and the mixture was stirred until there was no remaining visible bulk solid. The flask was placed into an oil bath that was pre-heated to 120 °C. The brown solution started to solidify after about 5 min. The reaction mixture was heated for another 55 min and allowed to cool to room temperature. The brown solid was smashed into fine particles using a spatula and collected by filtration and washed with methanol. After air-drying for an hour, the solid was ground into fine powder and stirred into 50mL 37% HCl solution and sonicated for 2 h at room temperature. The resulting mixture was filtered and washed with water and methanol. Brown solid product (0.53 g, ~100% yield) was obtained after drying in a vacuum oven at 100 °C for 1 day. Elemental Analysis: Calculated for [C₁₆H₁₀]_x: C, 95.02; H, 4.98. Found: C, 87.48; H, 4.86; Again, the discrepancy could be due to trapped water and air in the sample which were not effectively removed prior to analysis.

1,3,5-tris(trimethylsilylethynyl)benzene was prepared according to literature procedure.¹

Synthesis of 1,3,5-triethynylbenzene: NaOH (7.6 g, 190.6 mmol) was dissolved in 80 mL methanol and added to a solution of 1,3,5-tris(trimethylsilylethynyl)benzene (11.53 g, 31.45 mmol) in 100 mL CH₂Cl₂. The mixture was stirred for 12 h at room temperature. The organic solvent was then removed in a rotary evaporator under vacuum. 80 mL CH₂Cl₂ was added to the residue and the white insoluble solid was filtered away. The filtrate was then washed with brine (40 mL). The organic phase was separated using a separation funnel and dried over anhydrous Na₂SO₄. The organic solution was concentrated and passed through a short silica gel column to yield light brown product (4.3 g, 91 % yield). The product could be further purified by

crystallization from hexane. ¹H NMR: δ (ppm): 3.11 (s, 3H, C≡CH), 7.57 (s, 3H, Ar-H). ¹³ C NMR: δ (ppm): 78.87, 81.78, 123.09, 135.82.

Synthesis of polymer POP-3: 1,3,5-triethynylbenzene (0.4577 g, 3.05 mmol) was added to a dried round bottom flask, anhydrous dioxane (30 mL) was injected via a syringe, and the mixture was stirred until it became clear solution. $Co_2(CO)_8$ (0.188 g, 0.55 mmol) was added under protection of N₂; the mixture was stirred at room temperature until there was no remaining visible bulk solid, and then the flask was placed into an oil bath that was pre-heated to 125 °C. The brown solution started to solidify after about 5 minutes. Heating continued for 1 h. The flask was then lifted above the oil bath to cool to room temperature. The brown solid was smashed into fine particles using a spatula, followed by addition of about 50 mL dioxane. The mixture was filtered to collect the solid product. After air drying for an hour, the solid was ground into powder and stirred into 40mL 37% HCl solution and sonicated for 2 h at room temperature. The resulting mixture was filtered and washed with water and methanol. Brown solid product (0.60 g, ~100% yield) was obtained after drying in a vacuum oven at 100 °C for 1 day. Elemental Analysis: Calculated for [C₁₂H₆]_x: C, 95.97; H, 4.03. Found: C, 67.72; H, 4.22. The reason for discrepancy is discussed previously.

Synthesis of 1,2,4,5-tetra(trimethylsilylethynyl)benzene: 1,2,4,5-tetrabromobenzene (8.28 g, 94%, 20 mmol), PdCl₂(PPh₃)₂ (0.337 g, 0.48 mmol) and CuI (0.047 g, 0.24 mmol) were placed in a 2-neck round bottom flask. Anhydrous Et₂NH (100 mL) and trimethylsilyl acetylene (13.6 mL, 96 mmol) were added via a syringe. The reaction mixture was heated to 50 °C for 16 h and then cooled to room temperature. The mixture was filtered through a pad of celite and washed with diethyl ether. The filtrate was concentrated in a rotary evaporator under vacuum and loaded to a silica gel column. Hexane was used as an eluent, the major band was collected and white

solid product (9.17 g, 99% yield) was obtained after removing the solvent. ¹H NMR: δ (ppm): 0.28 (s, 36H, CH₃), 7.57 (s, 2H, Ar-H).

Synthesis of 1,2,4,5-tetraethynylbenzene: NaOH (2.6 g, 64.8 mmol) was dissolved in 40 mL methanol and added to a solution of 1,2,4,5-tetra(trimethylsilyethynyl)benzene (2.88 g, 6.22 mmol) in 50 mL CH₂Cl₂. The mixture was stirred for 7 h at room temperature; the organic solvent was removed in a rotary evaporator under vacuum, followed by addition of 100 mL CH₂Cl₂, and the white solid was filtered away. The filtrate was washed with brine (40 mL). The organic phase was separated using a separation funnel and dried over anhydrous Na₂SO₄. The solvent was removed and the crude product was purified by crystallization from a mixture of CHCl₃/methanol. Light yellow solid product (0.793 g, 73% yield) was obtained in its pure form. ¹H NMR: δ (ppm): 3.42 (s, 4H, C=CH), 7.64 (s, 2H, Ar-H). ¹³ C NMR: δ (ppm): 80.62, 83.63, 125.41, 136.71.

Synthesis of polymer POP-4: 1,2,4,5-tetraethynylbenzene (0.602 g, 3.45 mmol) was added to a dry round bottom flask, anhydrous dioxane (40 mL) was injected via a syringe and stirred to obtain a clear solution. $Co_2(CO)_8$ (0.283 g, 0.828 mmol) was added under protection of N₂, the mixture was stirred until no visible bulk solid remained, and then the flask was placed into an oil bath that was pre-heated to 125 °C. The brown solution started to solidify after about 5 min. Heating continued for 1 h, and the flask was lifted above the oil bath to cool to room temperature. The brown solid was smashed to fine particles using a spatula, followed by the addition of 50 mL dioxane. The mixture was filtered to collect the brown solid. After air-drying for an hour, the solid was ground into powder and stirred into 40 mL 37% HCl solution and sonicated for 2 h at room temperature. The mixture was filtered and washed with water and methanol. Brown solid product (0.831 g, ~100% yield, contains some cobalt catalyst and moisture) was obtained after drying in a vacuum oven at 90 °C for 1 day. Elemental Analysis: Calculated for $[C_{14}H_6]_x$: C, 96.53; H, 3.47. Found: C, 73.5; H, 3.81. The reason for discrepancy is discussed previously.

For POP-1 to -4 syntheses, all the samples have been extensively acid washed in HCl solution to remove cobalt carbonyl catalyst. It is conceivable that trace amounts of cobalt still present after acid treatment which could affect the measurement of isosteric heat of adsorption. To verify this, we conducted the elemental analysis of Co for POP-4 and found 0.75 wt %, or 0.012 mol Co/gram-adsorbent, in the washed sample. Since our lowest hydrogen coverage used for calculating adsorption energy starts at 0.05 mol-H₂/gram-adsorbent, the interference by residual Co carbonyl, if any, can be regarded as minimum to negligible.

Quantum chemical calculations: Quantum chemical calculations for M1, M3 and M4 interacting with hydrogen molecules were carried out using NWCHEM 5.1 computer code.³ Geometries was fully optimized at MP2/6-31+G* level of theory. The geometries are shown in Fig. S5. Single-point calculations were carried out at MP2/6-311++G (2d,2p) level of theory. Single-point calculations for H₂ between two monomers were performed using geometry of monomers obtained by adding an inversion of the geometry of an optimized single monomer with H₂ with respect to the H₂ center of mass. The binding energy for H₂ between two monomers with H₂ and the same without H₂.

Figures, Schemes, and Table



Fig. S1 FTIR spectrum of polymers **POP-1**, **POP-2**, **POP-3**, **POP-4**, and monomer **M4**, alkynyl C-H vibration band at 3275 cm-1 and C=C vibration band at 2112 cm-1 were noted with arrows.



Fig. S2 TGA graphs of polymers **POP-1**, **POP-2**, **POP-3**, and **POP-4**, note that continuous weight loss for POP-4 up to 200 °C suggesting slow release of adsorbed species via more tortuous frameworks.



Fig. S3 Pore size distribution based on HK calculation for **POP-1** (red square), **POP-2** (dark yellow diamond), **POP-3** (dark pink hexagon), and **POP-4** (dark cyan triangle).



Fig. S4 Hydrogen adsorption (solid symbols) / desorption (open symbols) isotherms for polymer **POP-1** (a), **POP-2** (b), and **POP-4** (c) at 77 K (black squares), 87 K (red circles), 195 K (green triangles), and 298 K (blue diamonds).



Fig. S5 Calculated geometries of H_2 adsorbed on (a) M1, (b) M3 and (c) M4 monomers. Distances are in Å.

| | H2 uptake@ 77 K ^a | H2 uptake@ 87 K ^a | H2 uptake@ 195 K ^a | H2 uptake@ 298 K ^a | |
|----------------------------|---------------------------------|---------------------------------|----------------------------------|----------------------------------|--|
| POP-1 | 2.78 | 2.31 | 0.36 | 0.22 | |
| POP-2 | 2.71 | 2.14 | 0.45 | 0.22 | |
| POP-3 | 3.07 | 2.51 | 0.43 | 0.20 | |
| POP-4 | 2.35 | 1.75 | 0.46 | 0.15 | |
| ^a Data at 60 ba | r in the unit of we | eight percentage (v | wt %) | | |

Table S1 Hydrogen adsorption capacities of the polymers



Scheme S1 Preparation of Polymers POP-2, POP-3, and POP-4

i) Co₂(CO)₈ (6 mol% relative to triple bonds), dioxane (dry), reflux at 125 °C, 1 h; ii) (2-trimethylsilyl) acetylene (1.2 eq), PdCl₂(PPh₃)₂ (0.6 mol%), Cul (0.3 mol%), Et₂NH (dry), 50 °C, 7 h (all reagent ratios are relative to bromide); iii) NaOH (2.5 eq of triple bonds) dissolved in CH₃OH /CH₂Cl₂, RT, 12h.

Notes and references

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