[Supporting information to accompany *Chemical Science* manuscript SC-EDG-08-2014-002502] Hierarchically Porous Organic Polymers: Highly Enhanced Gas Uptake and Transport through Templated Synthesis

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S1. Materials and methods

Unless otherwise stated, all chemicals and solvents were purchased from Aldrich Chemicals Co. (Milwaukee, WI) and used without further purifications. Silbond H-5, a prehydrolysed ethyl polysilicate precursor was purchased from Silbond Corporation (Weston, MI). All gases used for the adsorption/desorption were ultra high purity grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL). POP1 was synthesized from 1,4-diethynylbenzene according to a literature procedure.^{S1}

Trace metal analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) conducted on a Varian Vista-MDX model ICP-OES spectrometer with simultaneous CCD detector (Varian, Inc., Walnut Creek, CA). POP samples (3-4 mg) were digested in conc. H_2SO_4 : H_2O_2 (30wt% in H_2O) (3:1 v/v) at 180 °C for 20 min using microwave irradiation. An aliquot of this clear acid solution was diluted to 8.0 vol% in ultrapure deionized H_2O (18.2 M Ω ·cm resistivity), which was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA). The instrument was calibrated using ultrapure deionized water and mixtures containing 0.5, 1, 5, 10, 15 and 20 ppm of Si that were prepared from commercially available ICP standard solutions.

All N₂ adsorption and desorption measurements for the POPs were performed on Autosorb 1-MP instrument (Quantachrome Instruments, Boynton Beach, FL). Between 20-80 mg of samples were employed in each measurement and the thermally activated samples were degassed at 150 °C prior to the measurements. N₂ adsorption and desorption isotherms were measured at 77 K. The specific surface areas for N₂ were calculated using the Brunauer-Emmet-Teller (BET) model in the range of $0.01 < P/P_0 < 0.1$. The pore size distributions of POP1 and hierarchical POPs were calculated from the adsorption-desorption isotherms by density functional theory (DFT) using the slit-pore N₂-DFT model.

All N₂ adsorption and desorption measurements for the silica aerogel templates were performed on a Micromeritics Tristar 3020 system (Micromeritics, Norcross, GA) and measured at 77 K. Between 50-100 mg of samples were employed in each measurement and the data were analyzed using the ASAP 2020 software (Micromeritics, Norcross, GA). Before measurements, samples were degassed for 12 h at 150 °C under high vacuum (< 10^{-4} bar). The specific surface areas for N₂ were calculated using the Brunauer-Emmet-Teller (BET) model in the range of $0.01 < P/P_0 < 0.3$. The pore size distributions were calculated from the adsorption-desorption

isotherms by density functional theory (DFT) in the range of $5.0 \times 10^{-5} < P/P_0 > 0.95$ using cylindrical-pore N₂-cylindrical pore model.

The micropore volumes, micropore surface areas, and external surface areas for all samples were determined using conventional t-plot methods^{\$2} from adsorption data. For all the POPs, the values were selected over the 3-5 Å t range by fitting the data to the Broekhoff-De Boer thickness equation. For all silica aerogel templates, the values were selected over a t range that is determined by fitting the data to the Harkins-Jura thickness equation over a data range that affords a physically sensible positive value for micropore volume while maintaining a correlation coefficient that is closest to 1. This process is recommended by Prof. A. W. Marczewski^{\$33} as well as the Micromeritics Instrument Corporation.^{\$4} For the parent aerogel that is used in this work, this range is 4.9-5.9 Å. For the TMS-modified aerogel that is used in this work, this range is 5.6-6.5 Å.

Scanning electron microscopy (SEM) images were obtained using a Hitachi SU8030 scanning electron microscope (Hitachi High Technologies America, Inc. Dallas, TX) with an acceleration voltage of 10 kV. The samples were finely grounded and dispersed onto a double sticky carbon tape (Ted Pella Inc., Redding, CA) attached to a flat aluminium sample holder. The samples were then coated with a gold-palladium film of thickness \sim 20 nm to facilitate conduction using a Denton III Desk sputter coater (Denton Vacuum, LLC, Moorestown, NJ) operating under argon atmosphere at 25 °C and \sim 30 mTorr.

Supercritical CO₂ drying was performed in a TousimisTMSamdri® PVT-30 critical point dryer (Tousimis, Rockville, MD) that has been retrofitted to fit 20 mL scintillation vial.

S2. Preparation of silica aerogels

Silica aerogel templates were synthesized inside a 20 mL scintillation vial following a previously reported procedure^{S5} except with the use of a commercially available Silbond H-5 pre-polymerized tetraethyl orthosilicate (TEOS) precursor. The use of this precursor, while more expensive than TEOS, consistently gave crack-free gel.

In a typical preparation, a silica solution was prepared by mixing Silbond H-5 (2.5 mL) with ethanol (5.5 mL). A catalyst solution containing a mixture of water (3.5 mL), ethanol (5.5 mL), and aqueous fluorinated ammonia (0.2 mL of a 3.3 M solution) was added slowly while stirring to form a sol. (The aqueous fluorinated ammonia solution was prepared by dissolving NH₄F (0.185 g, 4.99 mmol) into deionized water (10 mL) followed by the addition of 30% NH₄OH (2.29 mL)). Prior to the start of gelling (typically 5-7 min), the sol was divided into 2 mL portions and transferred into 20 mL scintillation vials, which were then capped. After the complete solidification of the sol inside the vials (~ 1 h), an aging solution (~ 3 × the volume of the gel) was added to each vial and the gels were aged at room temperature for 48 h to strengthen the gel network. (The aging solution contained an equal volume of ethanol and water along with 2 vol% of the aqueous fluorinated ammonia stock solution.) Following complete gelation, ethanol (~15 mL) was added to the resulting alcogels and the resulting mixture was left alone for 24 h to remove excess water. This solvent exchange procedure was repeated for 5-6 times more before the gel was dried with supercritical CO₂ to form the aerogel. Average mass of aerogel per vial is ~0.15 g.

S3. Preparation of hydrophobic silica aerogels

The free hydroxyl groups on the silica surface were capped with two different organosilane reagents namely trimethylchlorosilane (TMSCI) and phenyltriethoxysilane (PTES) according to literature procedures.^{S6} The ethanol-filled silica gel (alcogel) was prepared in a 20 mL scintillation vial following the procedure described above but was not processed with supercritical CO₂. Because ethanol will react with the organosilane reagents, the ethanol in the alcogel must be exchanged with the non-polar solvent hexanes before the gel can be surface modified. However, this process must be carried out in a gradient fashion to avoid any crack in the gel (sudden introduction of a non-polar solvent might form cracks in the monolith).^{S7}

The initial ethanol in the gel was replaced by exposing the alcogel monolith to mixtures of ethanol:hexanes with increasing proportion of hexanes ((3:1 v/v) then (1:1 v/v) and (1:3 v/v)) over a three-day period. Finally the solvent mixture was replaced with pure hexanes and the exchange process was carried out with pure hexanes for 5-6 more times, with each solvent exchange taking place over a 24 h period.

The surface modification was then carried out by adding hexanes solutions (~ 20 mL) containing 20 vol% of either TMSCl or PTES to the gel monolith in the vial (no special precaution was taken to exclude air and moisture from the vial). The vial was then capped, put into a 60 °C oil bath, and heated at 60 °C for 24 h. The vial was cooled down to room temperature, the mother liquor was then exchanged with fresh organosilane solution in hexanes (~ 20 mL), and the vial was capped and reheated at 60 °C again for 24 h. This surface modification process

was repeated for a total of 3 times before the organosilane solution was replaced with hexanes (~ 20 mL) and allowed to soak for 24 h to remove unreacted organosilane reagents. This soaking process was repeated four times (until the discarded solution does not show vigorous reaction between the left-over TMSCl and ethanol; PTES was assumed to have the same reactivity).

Before supercritical CO₂ processing, the hexanes-filled surface-modified gel must be converted back into the alcogel. For this, the hexanes-filled gel can be treated directly with ethanol and soaked for 24 h. This solvent exchanged was then repeated 5-6 times more, with each solvent exchange taking place over a 24 h period.

S4. General procedure for the synthesis of POP inside aerogel

In a nitrogen-filled glove box, a 2 dram vial equipped with a magnetic stir bar was charged with 1,4diethynylbenzene (0.15 g, 1.19 mmol) and anhydrous 1,4-dioxane (3 mL). Co₂(CO)₈ (0.06 g, 0.175 mmol) was added to the solution, which was allowed to stir for 1 h at room temperature. The reaction mixture was then transferred to the 20 mL vial containing the silica aerogel (~0.15 g) and a small amount of dioxane (1 mL) was added if necessary to bring the reaction mixture just to the top level of the aerogel. The vial was then capped, and kept inside the glove box overnight to facilitate equilibration of the reaction mixture and the complete diffusion of reactants into the pores of the gel. The vial was then removed from the glove box and placed in an oil bath at 120 °C where it was allowed to react for 24 h without stirring. After 24 h, the vial was removed from the oil bath, cooled to room temperature, filtered, and washed with methanol (~ 20 mL). The resulting solid was then sonicated in concentrated HCl (~12 mL) for 2 h before being filtered. The collected solid was placed in a beaker containing water (~50 mL) and stirred before being filtered. This collected solid was placed in a beaker containing methanol (~ 50 mL) and stirred before being filtered the third time and air-dried. The dried solid was then transferred into a plastic container followed by addition of 48% aqueous HF (~ 10 mL). The HF-added mixture was left for 6 h with occasional gentle sloshing but not with stirring. Then it was filtered through a plastic funnel and washed with copious amounts of water. The collected solid was activated at 150 °C under vacuum for 12 h followed by addition of 48% HF (~ 10 mL).

POP1_{|a}: a brown amorphous solid (0. 11 g). ICP-OES: Si = 0.001 wt% **POP1**_{|a-TMS}: a brown amorphous solid (0.12 g). ICP-OES: Si = 0.002 wt **POP1**_{|a-Ph}: a brown amorphous solid (0.12 g). ICP-OES : Si = 0.008 wt %

S5. General procedure for the synthesis of POP inside crushed powder aerogel (control experiment)

Silica aerogel monoliths were crushed into powder and transferred into two separate 20 mL scintillation vials: one vial contained twice as much of crushed silica aerogels as the other one (Figure S1) and taken into a nitrogenfilled glove box. Into each of two separate 2 dram vials was charged 1,4-diethynylbenzene (0.15 g, 1.19 mmol) and anhydrous 1.4-dioxane (3 mL). Co₂(CO)₈ (0.06 g, 0.175 mmol) was added to each of these solution and the mixtures were stirred for 1 h at room temperature before being transferred to each of the 20 mL scintillation vials containing crushed silica aerogels. To be consistent with the procedure described in section S4, a small amount of dioxane (1 mL) was added to each vial resulting in the reaction mixture being much higher than the top level of the crushed aerogel. The vials were then capped and kept inside the glove box over night to facilitate equilibration of the reaction mixture and the complete diffusion of reactants into the pores of the gel. Then they were removed from the glove box and heated in an oil bath at 120 °C for 24 h without stirring. The vials were then removed from the oil bath, cooled down, filtered, and washed with methanol (~ 20 mL). The solids were separately sonicated in concentrated HCl (~12 mL) for 2 h before being filtered. The collected solid were placed in separate beakers containing water (~50 mL) and stirred for 5 h before being filtered. These collected solids were placed in separate beakers containing methanol (~ 50 mL) and stirred for 5 h before being collected by filtration the third time and airdried. The dried solids were then transferred to two separate plastic containers followed by addition of 48% HF (~ 10 mL). The HF-added mixtures were left for 6 h with occasional gentle sloshing but not with stirring. Then they were filtered through plastic filter funnels and washed with copious amounts of water. The collected solids were activated at 150 °C under vacuum for 12 h to produce brown amorphous solids.

POP1 $|_{a-crushed 1\times}$: a brown amorphous solid (0.11 g). ICP-OES: Si = 0.002 wt%

POP1 $|_{a-crushed 2^{\times}}$: a brown amorphous solid (0.09 g). ICP-OES: Si = 0.004 wt%



Figure S1. Photographic images of crushed silica aerogels: left, 0.1 g; right, 0.19 g. The amount of the crushed silica aerogel in the right vial was chosen to be commensurate with the level of reaction mixture in our standard reactions, which were carried out in monolithic aerogel pieces. The amount of crushed silica aerogel in the left vial was the equivalent in weight of the monolithic aerogel piece in our standard reaction.

S6. General procedure for the preparation of hierarchical POPs by supercritical CO₂ processing

The hierarchically porous POPs were synthesized under the same protocol and scale as described in section S4 but worked up differently after the HF etching step. At this point, the HF-added mixture was filtered through a plastic funnel and rinsed thoroughly with water $(4 \times 20 \text{ mL})$ and methanol $(4 \times 20 \text{ mL})$, taking care to keep a layer of solvent over the solid (it is critical to never allow the polymer sample to dry in air as it will irreversibly shrink). The final polymer-methanol slush was transferred to a 20 mL scintillation vial and the methanol was exchanged with absolute ethanol by filling up the vial with the latter and waiting for 24 h before decanting and replacing with a fresh portion of absolute ethanol. This solvent exchange process was repeated for 5-6 times.

After the final exchange, the total volume of ethanol over the solid was kept to 1 mL and the vial was placed inside the supercritical dryer. The ethanol solvent was then exchanged with liquid CO_2 over a period of 10 h while maintaining the temperature between 0-10 °C. The liquid CO_2 and ethanol mixture were vented under positive pressure for 2-5 minutes at every 1 h interval, taking care to maintain the rate of venting below the rate of filling so that the drying chamber remained full. After 10 h, the temperature inside the sealed chamber was raised to 37 °C, which increased the pressure to above the critical point of CO_2 at 1400 psi. This pressure was maintained for 30 minutes; then the chamber was slowly vented over a period of 6 h while being kept at 37 °C. The final solid was then vacuum-dried for 6 h.

scp**POP1**_a: a brown amorphous solid (0.08 g). ICP-OES: Si = 0.002 wt%

scp**POP1**|_{a-TMS}: a brown amorphous solid (0.09 g). ICP-OES: Si = 0.005 wt%

 $^{scp}POP1|_{a-Ph}$: a brown amorphous solid (0.075 g). ICP-OES: Si = 0.002 wt%

S7. N₂ isotherms of the silica aerogel templates





Figure S2. The N₂ isotherms of silica aerogel (BET surface area = $600 \text{ m}^2\text{g}^{-1}$), TMS-modified silica aerogel (BET surface area = $650 \text{ m}^2\text{g}^{-1}$), and Ph-modified silica aerogel (BET surface area = $550 \text{ m}^2\text{g}^{-1}$) at 77 K. Closed symbols, adsorption; open symbols, desorption.





Figure S3. The pore size distribution based on DFT calculations (cylindrical pore model) for silica aerogel, TMSmodified silica aerogel, and Ph-modified silica aerogel.

Entry	Silica aerogels	BET surface area (m ² g ⁻¹)	Total pore volume	Micropore volume	Micropore surface area	External surface area
			$(cm^{3}g^{-1})^{b}$	(cm ³ g ⁻¹) ^{<i>a</i>}	$(m^2 g^{-1})^a$	$(m^2 g^{-1})^a$
1	Silica aerogel	600	1.00	0.0005	20	580
2	TMS-modified silica aerogel	650	1.07	0.0018	30	620
3	Ph-modified silica aerogel	550	0.88	0.0070	25	520

 Table S1.
 Pore and surface properties of silica aerogels

^{*a*}Obtained using t plot method (see Section S1). ^{*b*}Total pore volume is obtained from BET data up to $P/P_0 = 1$ and is defined as the sum of micropore volume and volumes of larger pores.

89. N₂ isotherms of POPs that were synthesized inside crushed aerogel



Figure S4. A) N₂ isotherms for the POP1 samples that were synthesized inside crushed aerogels (POP1|_{a-crushed 1×} and POP1|_{a-crushed 2×}) recorded at 77 K. Closed symbols: adsorption; open symbols:desorption. B) The pore size distribution based on DFT calculations (slit-pore model) for POP1|_{a-crushed 1×} and POP

Table S2. Pore and surface properties of the POP samples that were synthesized inside crushed aerogels.

Entry	РОР	BET surface area (m ² g ⁻¹)	Total pore volume	Micropore volume	Micropore surface area	External surface area
			(cm ³ g ⁻¹) ^b	$(cm^{3}g^{-1})^{a}$	$(m^2 g^{-1})^a$	$(m^2 g^{-1})^a$
0	POP1	800	0.42	0.23	547	253
1	POP1 a-crushed 1×	820	0.40	0.20	540	280
2	POP1 a-crushed 2×	790	0.40	0.18	515	275

^{*a*}Obtained using t plot method (see Section S1). ^{*b*}Total pore volume is obtained from BET data up to $P/P_0 = 1$ and is defined as the sum of micropore volume and volumes of larger pores.



S10. N₂ isotherms of thermally activated POPs (POP1|_{a-TMS} and POP1|_{a-Ph})

Figure S5. The N₂ isotherms of POP1|_{a-TMS} and POP1|_{a-Ph} recorded at 77 K. Closed symbols: adsorption; open symbols: desorption.

S11. N2 isotherms of supercritical CO2-activated POPs (scpPOP1|a-TMS, and scpPOP1|a-Ph)



Figure S6. The N₂ isotherms of sepPOP1|_{a-TMS}, and sepPOP1|_{a-Ph} recorded at 77 K. Closed symbols: adsorption; open symbols: desorption





Figure S7. The pore size distribution based on DFT calculations (slit-pore model) for ${}^{scp}POP1|_{a-TMS}$ and ${}^{scp}POP1|_{a-Ph}$.

S13. SEM images of hierarchically porous POPs and the parent silica aerogel templates

It is clear from comparing the panels in Figures S9, S10, and S11 (**POP1**|_a vs ^{scp}**POP1**|_a; **POP1**|_{a-TMS} vs ^{scp}**POP1**|_{a-TMS}; **POP1**|_{a-Ph} vs ^{scp}**POP1**|_{a-Ph} pairs, respectively) that the average size of the hierarchically porous POP particles in the supercritical CO₂-processed samples are smaller than those that have been thermally activated. (The thermally activated samples appear to comprise large chunks of aggregates where the individual particles are fused to each other.) This can be taken as an evidence that supercritical CO₂ processing is able to preserve the interstitial spaces between the particles and retain a higher portion of mesoporosity.



Figure S8. SEM images of POP1 (left) and thermally activated POP1|a (right).



Figure S9. SEM images of thermally activated POP1|_a (left) and ^{scp}POP1|_a (right).



Figure S10. SEM images of thermally activated POP1|_{a-TMS} (left) and ^{scp}POP1|_{a-TMS} (right).



Figure S11. SEM images of thermally activated POP1|a-Ph (left) and scpPOP1|a-Ph (right).



Figure S12. SEM images of silica aerogel (top left), TMS-modified silica aerogel (top right) and Ph-modified silica aerogel (bottom).

S14. Densities of POPs

The skeletal density of a porous material is the ratio of the mass to the volume occupied by the framework of the sample excluding the volume of any open pores. The bulk density is the ratio of the mass to the volume occupied by the whole sample, including all internal pore and interparticle void space (pore volume). Therefore, the bulk density can be calculated if the measured skeletal density and the total pore volume of each material are known (Eq S1).

$$\rho_{bulk} = 1/[(1/\rho_{skeletal}) + V_{total pore}]$$

Consistent with the increase in external surface areas and total pore volumes, the bulk densities of all the hierarchically porous POPs are lower than that for the parent POP1 (Table S3).

(S1)

Entry	РОР	Total NLDFT-derived pore volume (cm ³ g ⁻¹)	ρ _{skeletal} (g cm ³) ^a	ρ _{bulk} (g cm ³) ^b	
1	POP1	0.42	1.262	0.82	
2	POP1 _a	0.59	1.218	0.71	
3	POP1 _{a-TMS}	1.3	1.211	0.47	
4	POP1 _{a-Ph}	0.99	1.195	0.55	
5	^{scp} POP1 _a	1.7	1.266	0.40	
6	scpPOP1 a-TMS	1.9	1.216	0.36	
7	^{scp} POP1 _{a-Ph}	1.9	1.236	0.37	

Table S3. Densities of POPs

^{*a*}Derived from helium pycnometry. Data are averaged from ten measurements with standard deviations of less than 0.01. ^{*b*}The bulk densities calculated using the NLDFT-derived pore volumes from Eq S1.

S15. Measurement of adsorption equilibria and kinetics

The propane uptake measurements in all POP samples took place in a volumetric-type apparatus. The system is inside an environmental chamber to maintain constant room temperature (298 K). The inner volumes of the adsorption chambers were measured by He gas. The pressure change was collected in real time using an MKS Baratron transducer 627B (accuracy \pm 0.12 %) and LabVIEW software (version 7.1). Because the supercritical CO₂-processed samples were already activated by the supercritical CO₂-processing conditions, they were used directly. Other samples were heated at 80 °C for 4 h under vacuum prior to measurements. The system was subsequently vacuumed for at least 12 h. The adsorption data was calculated by the mass balance of the propane gas in the injection and sample chambers incorporated with the generalized virial-coefficient correlation.^{S8} More details about our procedure have been previously published.^{S9,10}

Diffusional time constants (D/r^2) were calculated by the short-time solution of the diffusion equation assuming a step change in the gas-phase concentration, clean beds initially, and micropore diffusion control:^{S11}

$$\frac{q_t}{q_{\infty}} = \frac{6}{\sqrt{\pi}} \bullet \sqrt{\frac{D \bullet t}{r^2}}$$
(S2)

where q_t is the adsorbed amount at time t, q_{α} is the adsorbed amount at equilibrium, r is the radius of the equivalent spherical particle (i.e., a spherical particle that has the same external surface to volume ratio as the POP particles), and D is the diffusivity.^{S10}

Table S4 reveals that the diffusional time constant values in the hierarchical POPs are 4-8 times greater than that in **POP1**. To rationalize this observed behavior, we looked at the mesopore volume fraction in each of the structures. We observe that 45% of the pore volume of **POP1** is due to mesoporosity. The next lowest fraction corresponds to **POP1**_a, with 63%. Such a 20% increase in the volume fraction due to mesoporosity augments the diffusional time constant ~ 4-fold. We also note that a higher volume fraction due to mesoporosity does not necessarily translate to a higher diffusional time constant. All of this data suggests there is a percolation transition at a porosity threshold between 45 and 63% mesopore volume fraction.

Entry	Mesopore volume fraction	$D/r^{2}[s^{-1}]$	$(D/r^2)/(D/r^2)_{POP1}$
POP1	0.45	8.9 x 10 ⁻⁵	1
POP1 _{a-TMS}	0.82	4.3 x 10 ⁻⁴	4.8
POP1 _{a-Ph}	0.79	7.8 x 10 ⁻⁴	8.7
scpPOP1 a	0.89	3.3 x 10 ⁻⁴	3.7
POP1 _a	0.63	3.3 x 10 ⁻⁴	3.7

Table S4. Diffusional time constants for propane uptake and mesopore volume fractions of POP samples





Figure S13. Time-dependent propane uptake profiles.

S17. Author contributions audit. S.C. and S.T.N. conceived the experiments presented herein except for the propane uptake and diffusional constant measurements, which were proposed by Y.J.C. and R.Q.S. S.C. carried out all the synthesis and characterizations of the POPs, including BET adsorption measurements. Y.J.C. performed the propane uptake measurements and the calculations of diffusional time constants. S.T.N. and R.Q.S. supervised the project. S.C. wrote the initial draft of the paper and received inputs and corrections from all co-authors. S.C. and S.T.N. finalized the manuscript.

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