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Supplementary Information

Synthesis and Sorption Properties of Hexa-(peri)-hexabenzocoronene-Based Porous Organic Polymers

Christina M. Thompson,[a] Fei Li,[a] and Ronald A. Smaldone[a]*

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[a]*Department of Chemistry and Biochemistry*
University of Texas, Dallas
800 W. Campbell Road, Richardson, Texas, 75080 (USA)

*** Correspondence Address**

Professor Ronald A. Smaldone
Department of Chemistry and Biochemistry
University of Texas, Dallas
800 W. Campbell Road
Richardson, Texas 75080
Tel: (+1)-972-883-6342
E-Mail: ronald.smaldone@utdallas.edu

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General Methods

All reagents were purchased from commercial suppliers (Sigma-Aldrich and Fisher Scientific) and used as received. **TPM**,[1] **1**[2] and **2**[3] were synthesized as previously reported. Fluorescence measurements were carried out on a Perkin-Elmer LS-50B Luminescence Spectrophotometer. FT-IR spectra were taken on a Nicolet 380 FT-IR with a SmartOrbit diamond attenuated total reflectance (ATR) cell. The thermogravimetric analyses were performed using a Mettler Toledo DSC/TGA 1 under nitrogen atmosphere with a heating rate of 10 °C h^{-1} from 25–800 °C. Low-pressure gas adsorption experiments (up to 760 torr) were carried out on a Micromeritics ASAP 2020 surface area analyzer. Ultrahigh-purity-grade N_2, H_2, CO_2, and He gases (obtained from Airgas Corporation) were used in all adsorption measurements. N_2 (77 K) and H_2 (77 K) isotherms were measured using a liquid nitrogen bath (77 K). CO_2 isotherms were measured using either a water ice bath (273 K) or in a room temperature water bath (296 K) whose temperature was measured prior to use for accuracy. The pore volume of each material was estimated from the DR model with the assumption that the adsorbate is in the liquid state and that the adsorption involves a pore-filling process. Pore size distributions were determined using an NLDFT carbon slit-pore model in the Micromeritics Software Package. Heats of adsorption values were computed by the Micromeritics ASAP software package using a variant of the Clausius-Claperyon equation. Powder X-ray diffraction of polymers **HBC-POP-1** and **HBC-POP-2** were carried out on a Bruker D8 Advance diffractometer with a sealed tube radiation source (Cu Kα, $\lambda = 1.54184$ Å), no background sample holder, and Lynxeye XE detector. Data were collected over a 2θ range of 5-50° in Bragg-Brentano geometry with a generator setting of 40 kV and 40 mA, step size of 0.02°, and exposure time per step of 2 s. Elemental analyses were performed by Micro-Analysis, Inc. 2038 Telegraph Rd, Wilmington, Delaware 19808. Iodine and bromine analysis was carried out by oxygen flask combustion; Pd and Cu concentrations were determined by mineral acid digestion followed by ICP-MS analysis.

Synthetic Procedures

HBC-POP 1: To a sealed tube containing **TPM** (43 mg, 0.103 mmol) in 3 mL toluene was added **1** (140 mg, 0.206 mmol), followed by 1 mL of Et_3N. This was degassed with nitrogen for 15 minutes before $Pd(PPh_3)_4$ (11 mg, 0.0103 mmol) and CuI (10 mg, 0.0206 mmol) were added and the tube was sealed. The reaction was then heated at 95 ºC for 20 hours. After that time the reaction was filtered, and the resulting brown solid was washed with 100 mL of CH_2Cl_2, followed by 100 mL of MeOH, 20 mL of concentrated HCl, and 100 mL of water before being sonicated in CH_2Cl_2 for 30 minutes and refiltered. The resulting solid was then dried at 150 ºC under high vacuum for 12 hours. 63 mg of a brown powder were recovered (42%). Elemental analysis (%) Calcd: C 96.67, H 3.33; Found: C 73.80, H 3.20, Br 6.55. ICP metal analysis Pd 11500 ppm, Cu 2200 ppm.

HBC-POP 2: To a sealed tube containing **TPM** (60 mg, 0.11 mmol) in 3 mL toluene was added **2** (125 mg, 0.14 mmol) followed by 1 mL Et_3N. This was degassed with nitrogen for 15 minutes before $Pd(PPh_3)_4$ (13 mg, 0.011 mmol) and CuI (3 mg, 0.011 mmol) were added and the tube was sealed. The reaction was then heated at 95 ºC for 20 hours. After that time the reaction was filtered, and the resulting light brown solid was washed with 100 mL of CH_2Cl_2, followed by 100 mL of MeOH, 20 mL of concentrated HCl, and 100 mL of water before being sonicated in CH_2Cl_2 for 30 minutes and refiltered. The resulting solid was then dried at 150 ºC under high vacuum for 12 hours. 65 mg of a light brown powder were obtained (54%). Elemental analysis (%) Calcd: C 96.67, H 3.33; Found: C 69.37, H 2.61, I 19.90. ICP metal analysis Pd 8500 ppm, Cu 1200 ppm.

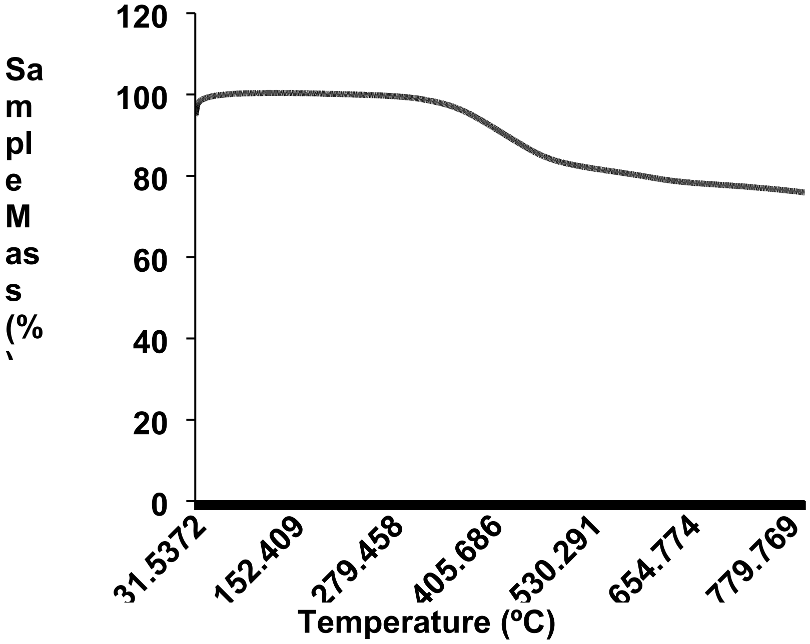
The elemental analyses are often reported to be different from the expected values as a result of incomplete combustion.[2,4-7] Molecular HBC halides have also been reported to display this limitation.[2] Pd and Cu values are similar to those in previously porous polymers synthesized with Sonogashira couplings.[7]

Summary of Surface Area Analysis for HBC-POPs

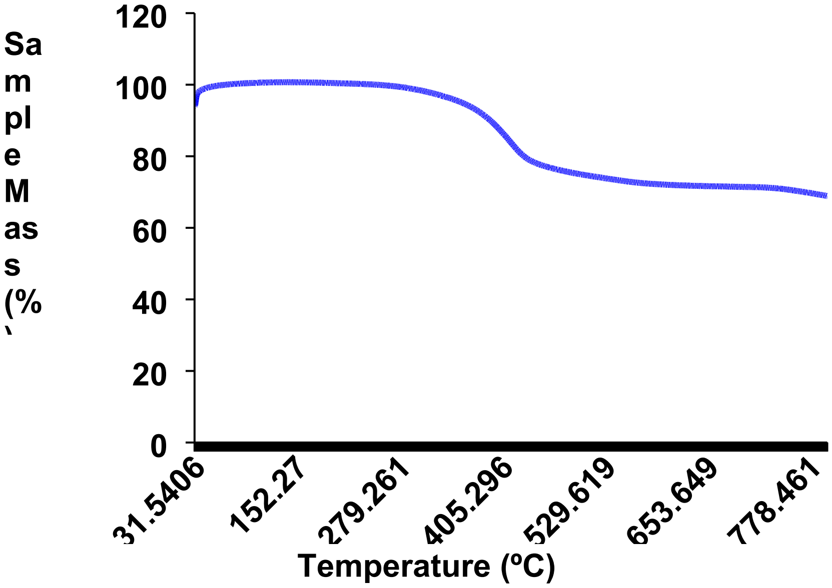
	BET Surface Area (m^2/g)	Langmuir Surface Area (m^2/g)	Pore Volume-Single Point (cm^3/g)	Pore Volume - Horvath-Kawazoe (cm^3/g)	Particle Size (Å)
HBC-POP-1	668.25	731.92	0.36	0.38	89.79
HBC-POP-2	457.53	501.73	0.32	0.35	131.14

Thermogravimetric analyses (TGA):

HBC-POP 1:

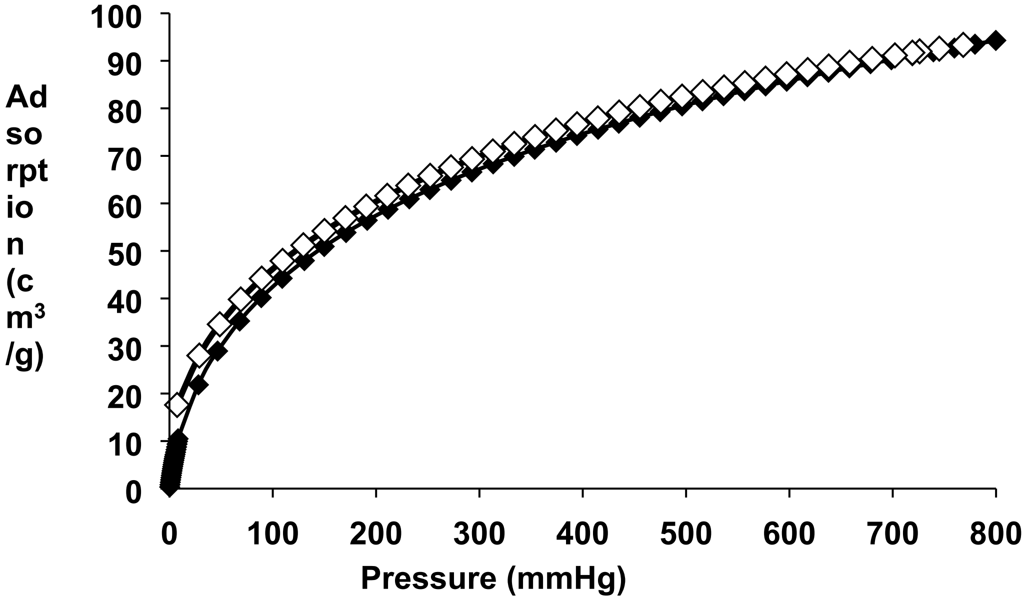


HBC-POP 2:

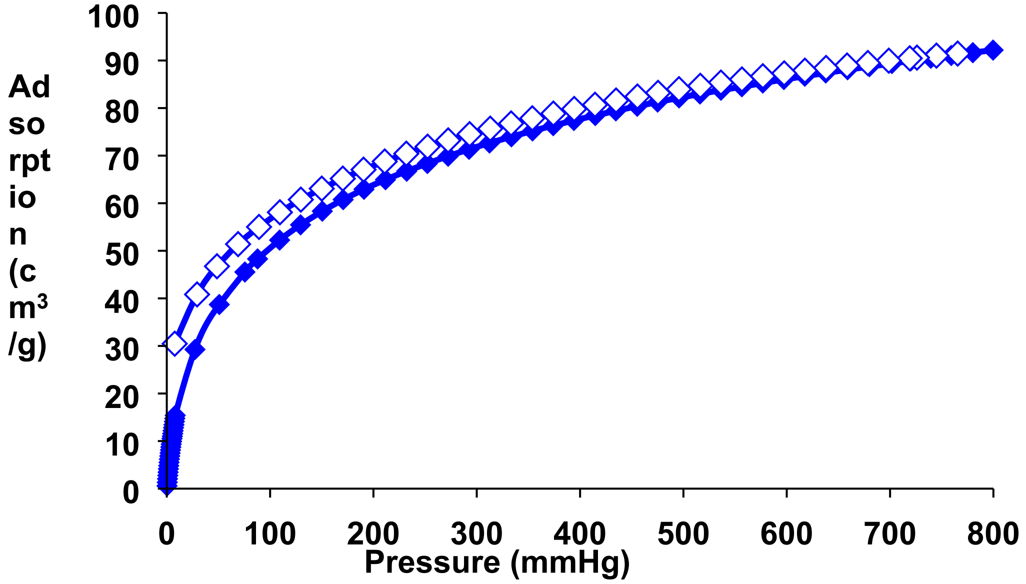


H_2 Isotherms

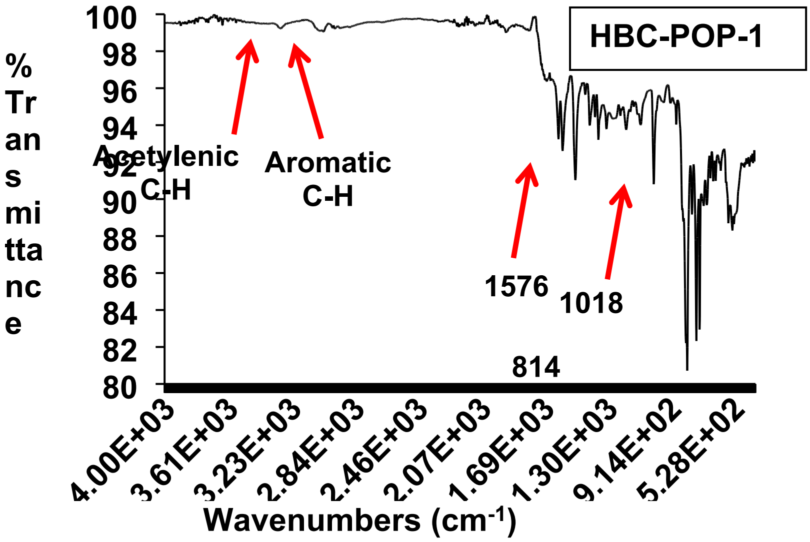
H_2 sorption isotherm for HBC POP-1. Filled diamonds represent the adsorption isotherm and the empty diamonds represent desorption.

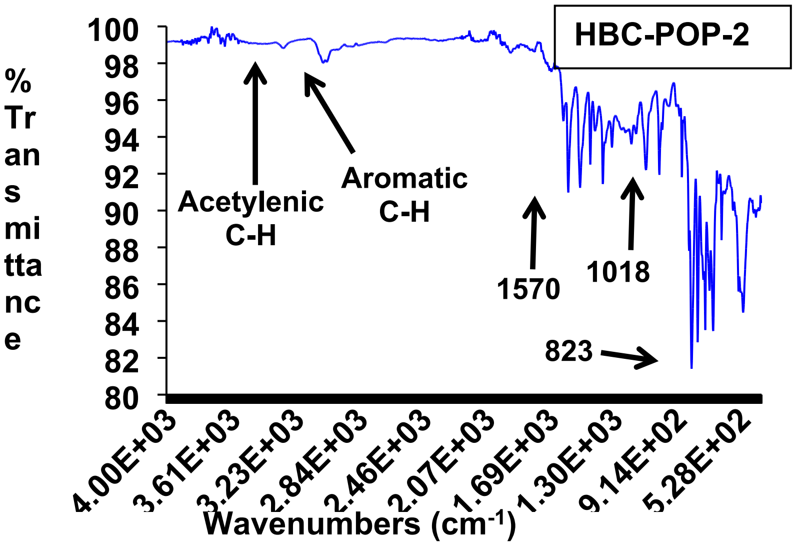


H_2 sorption isotherm for HBC POP-2. Filled diamonds represent the adsorption isotherm and the empty diamonds represent desorption.



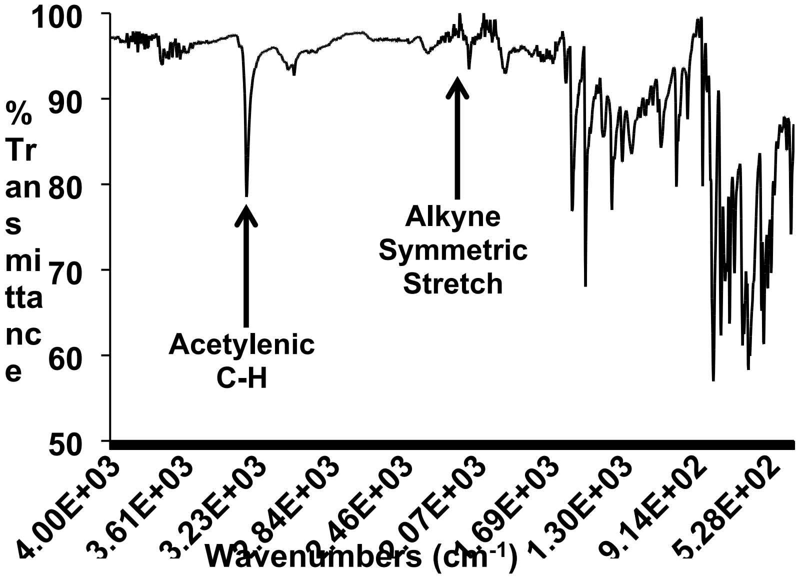
FT-IR Measurements



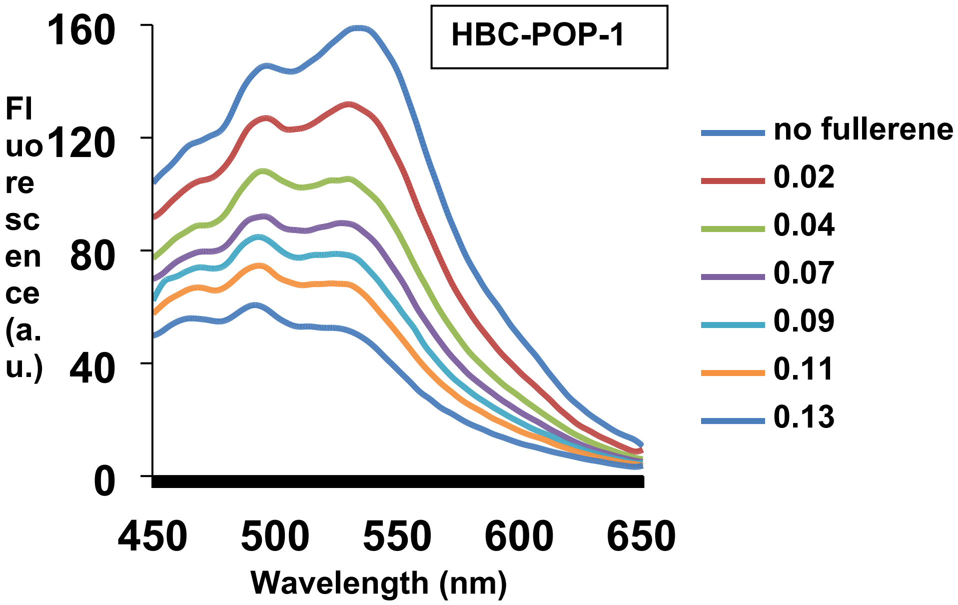


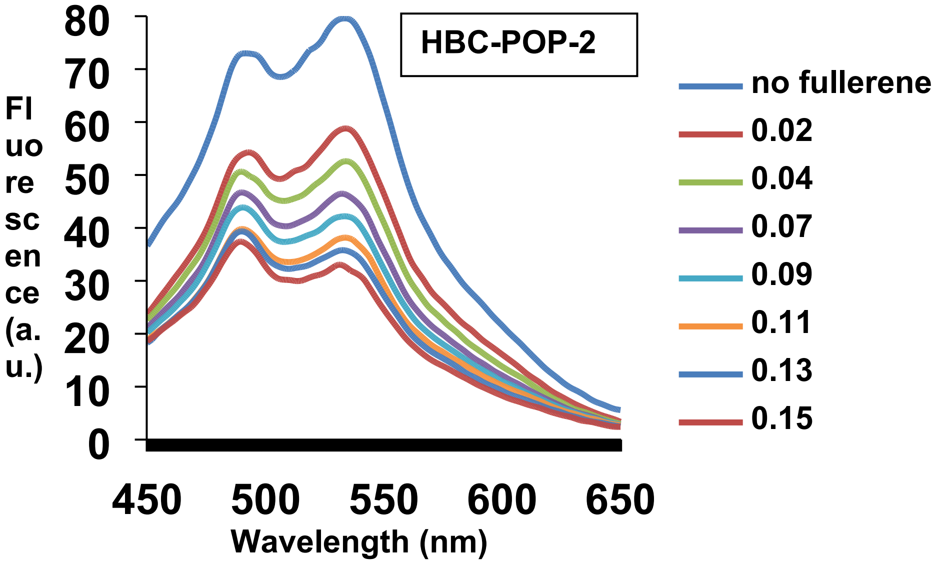
Each IR spectrum has been annotated to indicate the relevant peaks. Visible in the FT-IR spectra above are C-H bend and C=C ring vibrations which are consistent with previously reported IR spectra of HBC compounds.[2] Also visible are aromatic C-H stretching signals at ~3000 cm^{-1}. The small acetylenic C-H stretch peaks at ~3300 cm^{-1} indicate that there may be some incomplete coupling reactions between the HBC and TPM monomers.

Shown below is a stoichiometric, but unpolymerized mixture of **2** and **TPM**, which comprise the precursors for HBC-POP-2. This is shown as an example of the intensities of the TPM acetylene C-H peak and alkyne stretch, which are clearly visible in the pre-polymerized mixture, but are significantly reduced in the polymer IR. This indicates that there is little unreacted alkyne in the POP samples.



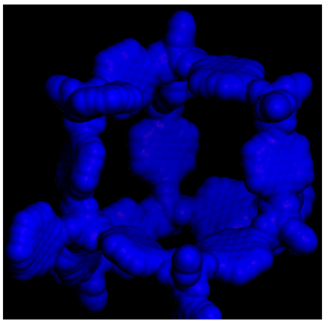
Fluorescence and Quenching Experiments



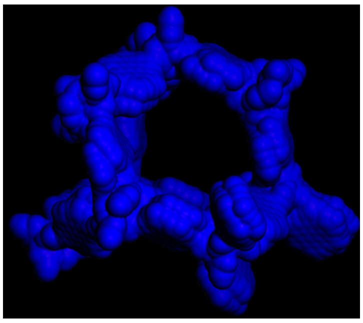


For each experiment the polymer (1.5 mg) was dispersed in toluene (3.0 mL). Aliquots (50 μL) of a C_{60} solution (1 mg/mL – 1.4 mM) in toluene were added sequentially to the polymer suspension and the fluorescence was measured after each addition. The units for the concentrations listed in the legends are in mM. The excitation wavelength used for both polymers was 365 nm. All of these experiments were carried out at room temperature (25 ºC).

Theoretical Surface Area Calculations



Diamondoid



**Diamondoid –
Singly Interpenetrated**

The surface area of a diamondoid net structure of HBC-POP-1 (left) was calculated to be 7980 m^2/g. This is vastly disparate from the observed surface area, and therefore we do not believe this accurately represents the structure. We also built an interpenetrated model (right image), which could explain the π-stacking observed by pXRD. The calculated surface area of this material was 4958 m^2/g indicating that it is unlikely a diamondoid structure of any kind is observed with these particular POPs.

Theoretical surface areas were calculated using Accelrys Materials Studio 7.0. The structures were minimized in the Forcite module using the Universal Force Field. Connolly surfaces were determined using a nitrogen probe with a radius of 1.86 Å. This procedure is adapted from one used in a previous report.[8]

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