

Electronic Supplementary Information

A porous covalent porphyrin framework with exceptional uptake capacity of saturated hydrocarbons for oil spill cleanup

Xi-Sen Wang,^a Jian Liu,^b Jean M. Bonfont,^a Da-Qiang Yuan,^c Praveen K. Thallapally^b and
Shengqian Ma^{*a}

^a *Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620 USA. Fax: +1 813-974-3203; Tel: +1 813-974-5217; E-mail: sqma@usf.edu;*

^b *Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA.*

^c *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou, 350002, People's Republic of China*

General methods:

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieve. All reactions involving moisture sensitive reactants were performed under a nitrogen atmosphere using oven dried and/or flame dried glassware. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res. X-ray powder diffraction (XPD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 20 kV, 5 mA for CuK α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 60 s/step (0.05°/min) and a step size of 0.05° in 2 θ at room temperature. FTIR data were recorded on an IRAffinity-1 instrument. Scanning electron microscopy (SEM) images were taken on Hitachi Su-70. Solvent vapor adsorption isotherms were obtained using an intelligent gravimetric analyzer (IGA) supplied by Hiden Analytical Ltd., Warrington, U.K.

Synthesis PCPF-1:

A solution of 2,2'-bipyridyl (226 mg, 1.45 mmol), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂, 400.0 mg, 1.45 mmol), and 1,5-cyclooctadiene (COD, 0.18 mL, 1.46 mmol) in anhydrous DMF/1,4-dioxane (24.0 mL/36.0 mL) was added with 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (297.0 mg, 0.32 mmol), and the mixture was stirred at room temperature under nitrogen atmosphere overnight. Then, the mixture was cooled in ice bath followed by the addition of 6 mol/L HCl solution (20 mL), the resulting mixture was stirred for another 6 h. The precipitate was collected, washed with Chloroform (6 \times 10 mL), THF (6 \times 10 mL), methanol (6 \times 10 mL), water (6 \times 10 mL), and then dried under dynamic vacuum to afford PCPF-1 as dark red powder (163 mg, 0.26 mmol, 83%).

Gas Adsorption Experiments:

Gas adsorption isotherms of PCPF-1 were collected using the surface area analyzer ASAP-2020. Pore size distribution data were calculated from the Ar sorption isotherms based on the DFT model in the Micromeritics ASAP 2020 software package (assuming slit pore geometry). Before the measurements, the freshly prepared samples were activated at 120 °C for 10h. N₂ and Ar gas adsorption isotherm were measured at 77 K or 87K using a liquid N₂ or Ar bath.

Hydrocarbon Vapors Adsorption Measurements:

Hydrocarbon vapor adsorption isotherms were obtained using an intelligent gravimetric analyzer (IGA) supplied by Hiden Analytical Ltd., Warrington, U.K. Hydrocarbon vapors were generated at 50 °C and kept at that temperature to prevent any possible condensation before reaching the sample. The inter steps of the pressures were chosen based on the saturated vapor pressure of the solvent at 25 °C. The maximum equilibrium time for each data point is 160 min.

Hydrocarbon Liquids and Gasoline Adsorption measurements:

A weighted quantity of the PCPF-1 was immersed in various liquid hydrocarbons and gasoline (93#) at room temperature to reach the adsorption equilibrium. The wet samples were then separated from organic solvents or gasoline and weight measurements were done quickly to avoid evaporation of absorbed solvents or gasoline. Adsorptive capacity was estimated from the change in sample weight before and after adsorption of probing molecules.

The recyclability of PCPF-1 was examined in the context of adsorbing liquid-phase n-hexane. After each cycle, the PCPF-1 was re-activated 120 °C under dynamic vacuum to evacuate the adsorbed n-hexane, and then was immersed again in liquid n-hexane to measure the uptake capacity according to the above procedures.

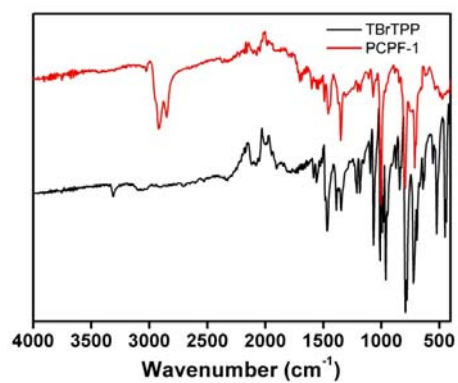


Fig. S1. FTIR spectra of 5,10,15,20-tetrakis(4-bromophenyl)porphyrin and PCPF-1.

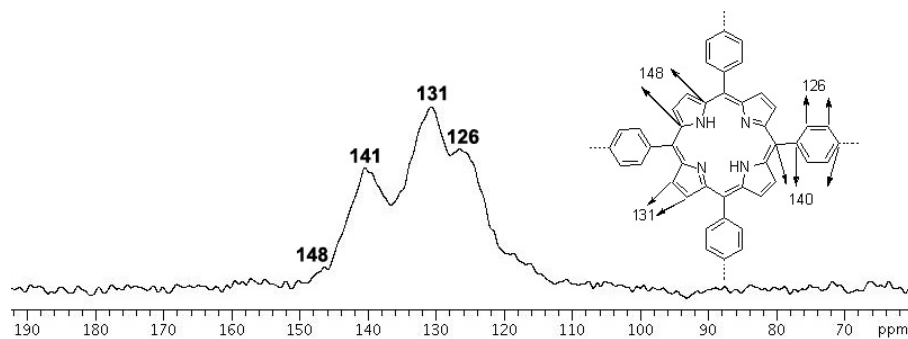


Fig. S2. Solid state ¹³C NMR spectra of PCPF-1.

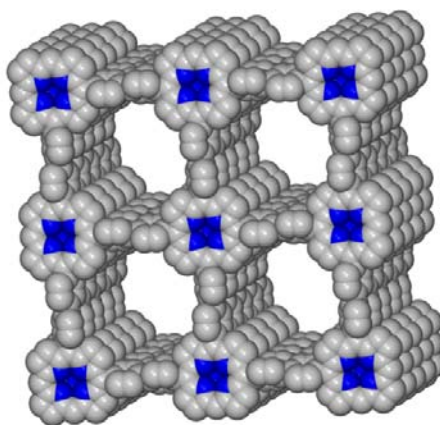


Fig. S3. Modeled structure of PCPF-1 showing 1D aligned tubular channels.

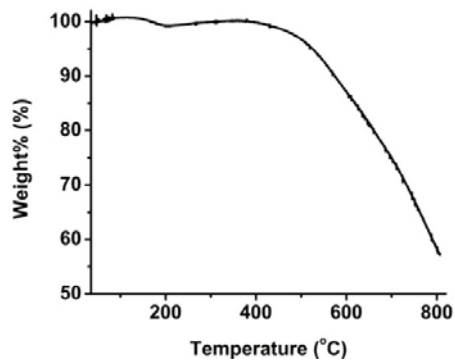


Fig. S4. TGA plot of PCPF-1.

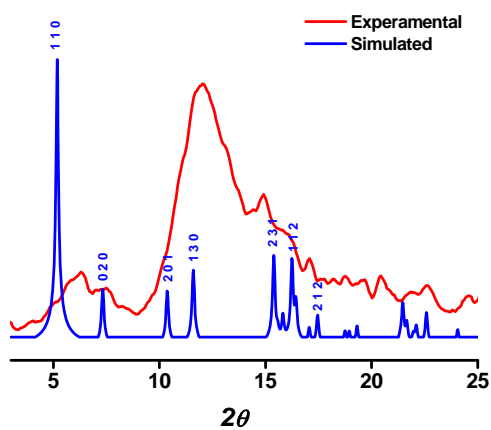


Fig. S5. PXRD patterns of PCPF-1.

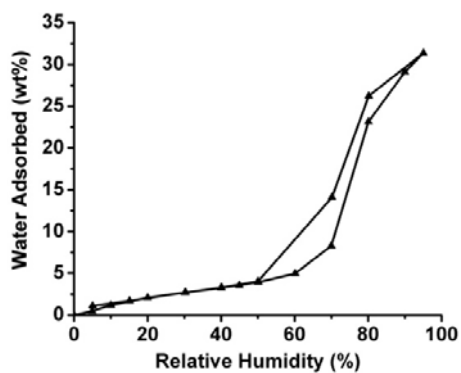


Fig. S6. Water vapor sorption isotherms of PCPF-1 at 298 K.

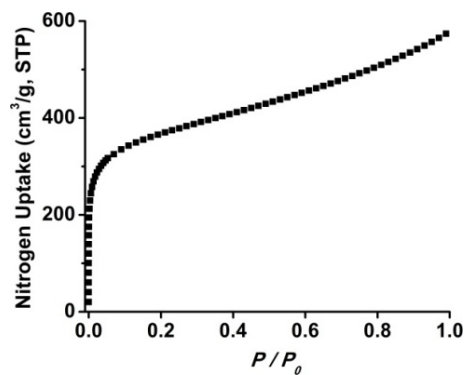


Fig. S7. N₂ adsorption isotherm of PCPF-1 at 77 K.

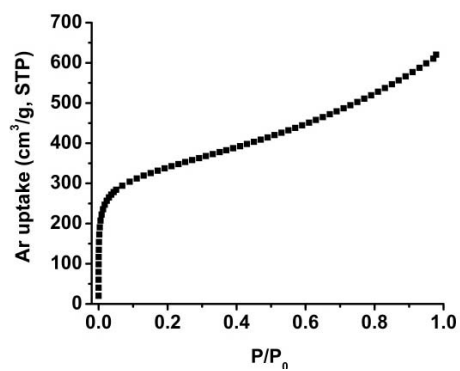


Fig. S8. Ar adsorption isotherm of PCPF-1 at 87K.

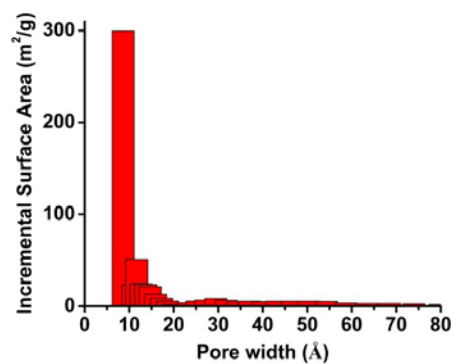


Fig. S9. Plots of pore size distribution for PCPF-1 calculated using DFT method.

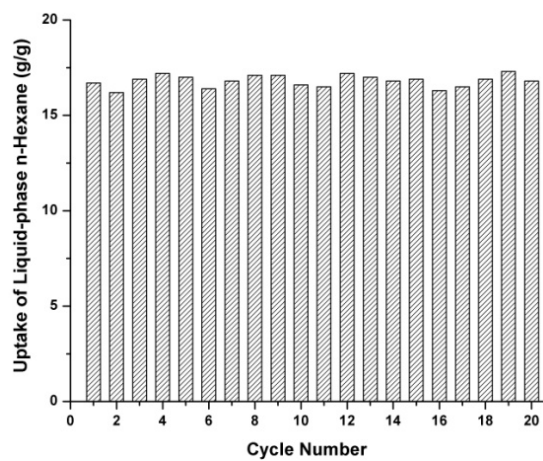


Fig. S10. Recycle of PCPF-1 in adsorbing liquid-phase n-hexane.

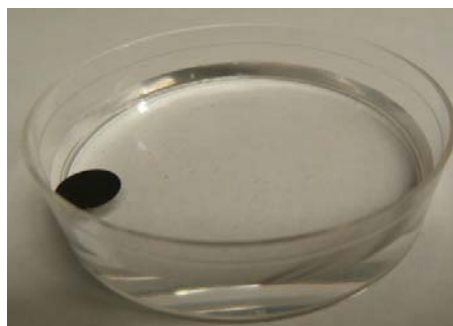


Fig. S11. Photo of PCPF-1 floating on the surface of water.

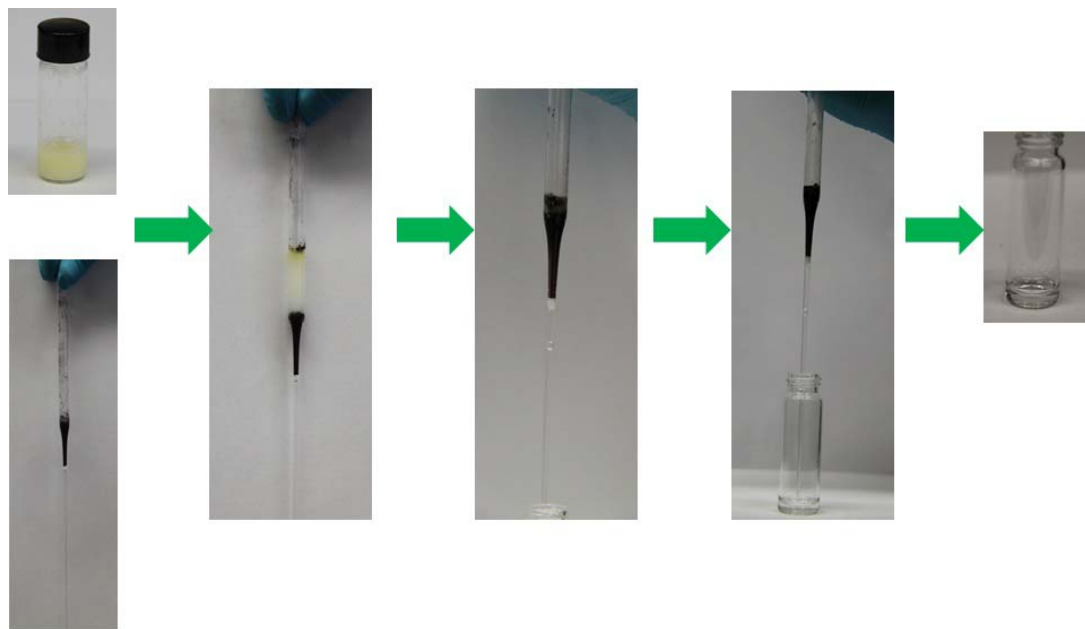


Fig. S12. Demonstration of using PCPF-1 to separate the mixed corn oil and water solution.