

Supplementary Information:

Targeted Synthesis of 3D Porous Aromatic Framework for selective sorption benzene

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1. Instruments

The elemental analysis was carried out on a Perkin-Elmer 240C elemental analyzer. The thermogravimetric analysis (TGA) was performed using a Netzsch Sta 449c thermal analyzer system at the heating rate of 10 °C/min in air atmosphere and nitrogen atmosphere. The FTIR spectra (KBr or film) were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The nitrogen adsorption isotherm was measured on a Micromeritics ASAP 2010M analyzer. The XRD was performed by a Rigaku D/MAX2550 diffractometer using CuK α radiation, 40 kV, 200 mA with scanning rate of 0.3° min⁻¹ (2 θ). Transmission electron microscopy (TEM) was recorded using a JEOL JEM 3010 with an acceleration voltage of 300 kV.

2. Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. The Tetrakis (4-cyanophenyl)methane, was prepared according to the previously reported method [1].

The anhydrous ZnCl₂ was purchased from Aldrich.

3. Synthetic Procedures

Polymerization of PAF-1 with ZnCl₂ Complex:

General synthesis procedure:

The monomer and the metal salt were transferred into a pyrex ampoule (3*4cm) in the glove box. The ampoule was evacuated, sealed and heated to 400°C for 48hs. When the ampoule cooled down to room temperature, opened the vacuum ampoule carefully. The black block was stirred in the fresh water for 48hs to remove most of the ZnCl₂. Further stirring in diluted HCl for 24 hs was performed to purify the

product. PAF-2 was isolated as a black powder in 80% yield.

4. Topology design of 3D Frameworks.

The 3D model of PAF-2 was obtained with the Materials Studio simulation environment [2] employing MS Visualizer. The structures were generated by beginning with the space group *I-43d* and *P-43m*. Laid the center carbon atom of the tetra-phenylmethane on the tetrahedron centroid, and replaced the C-N bonds with the phenyl rings. The vertices of the triangle were substituted with carbon atoms of the C_3N_3 rings and the nitrogen atoms were added between the carbon atoms. Then we performed energy minimization and geometry optimization calculations employing universal and COMPASS force-field to obtain reasonable structures.

5. Investigation of the Polymer

5.1 IR study of the PAF-2

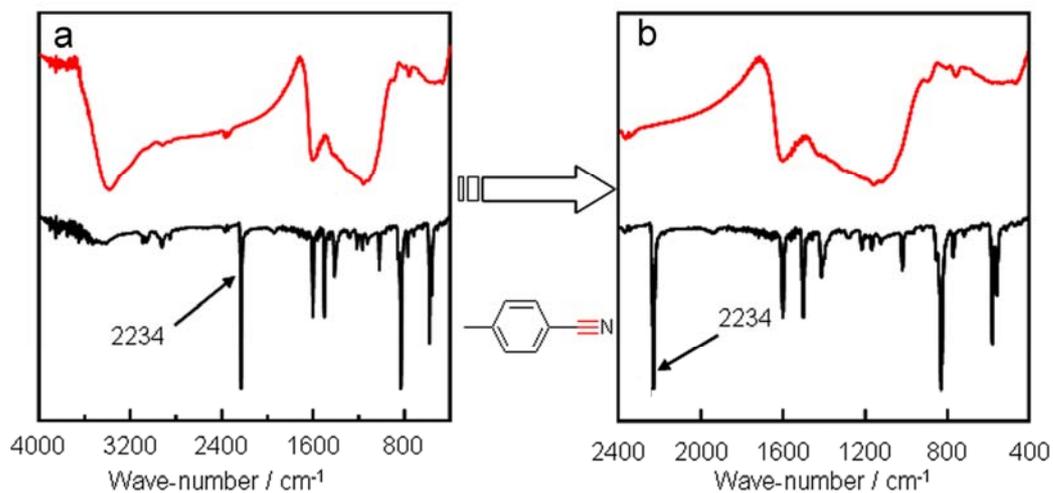


Figure s1. FTIR spectra of the monomer (black) and PAF-2 (red) from 400-2400 cm⁻¹(a) and 400-4000 cm⁻¹ (b). The characteristic absorption for carbonitrile is remarked.

5.2 XRD analysis of the PAF-2.

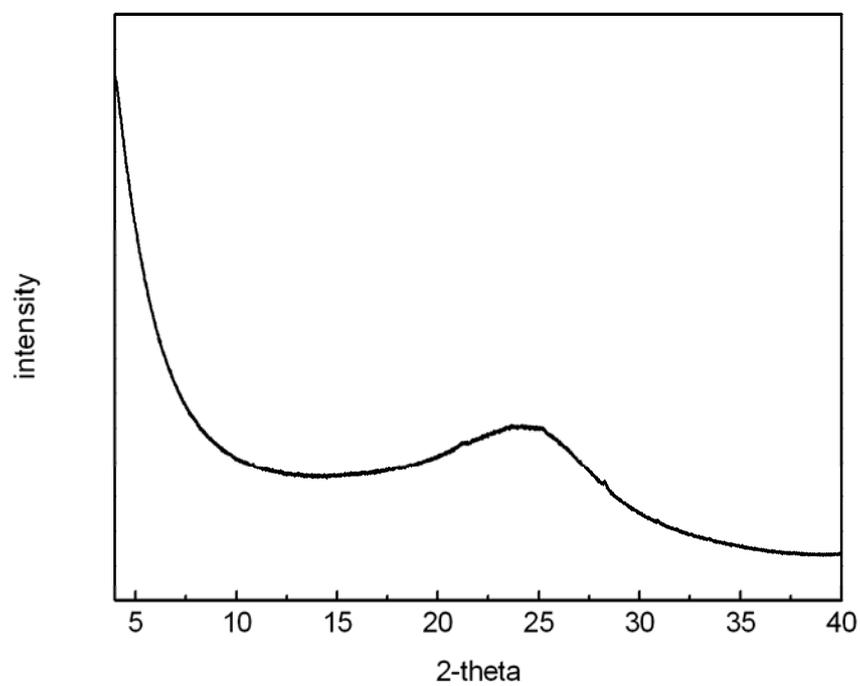


Figure s2. XRD pattern of the sample PAF-2.

5.3 TGA trace of the PAF-2.

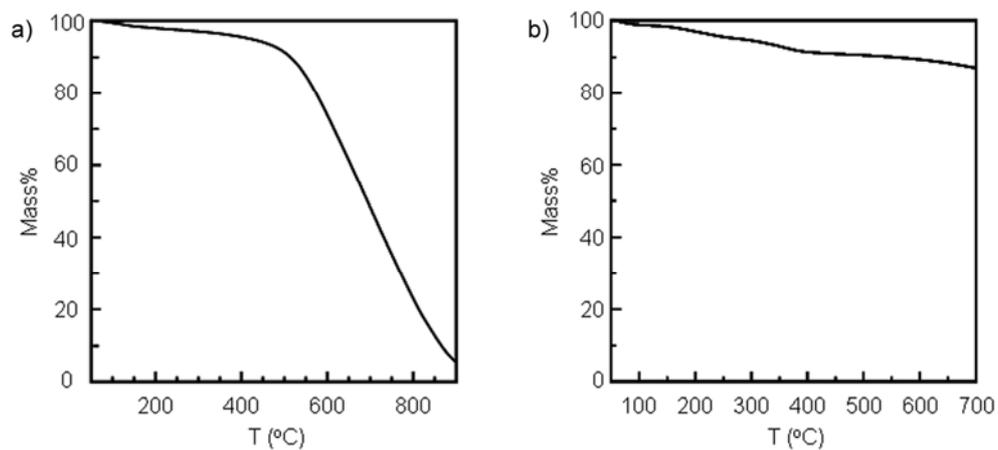


Figure s3. (a) TGA trace for an activated sample of PAF-2 under air atmosphere; (b) TGA trace for an activated sample of PAF-2 under N₂ atmosphere.

5.4 TEM image of the PAF-2.

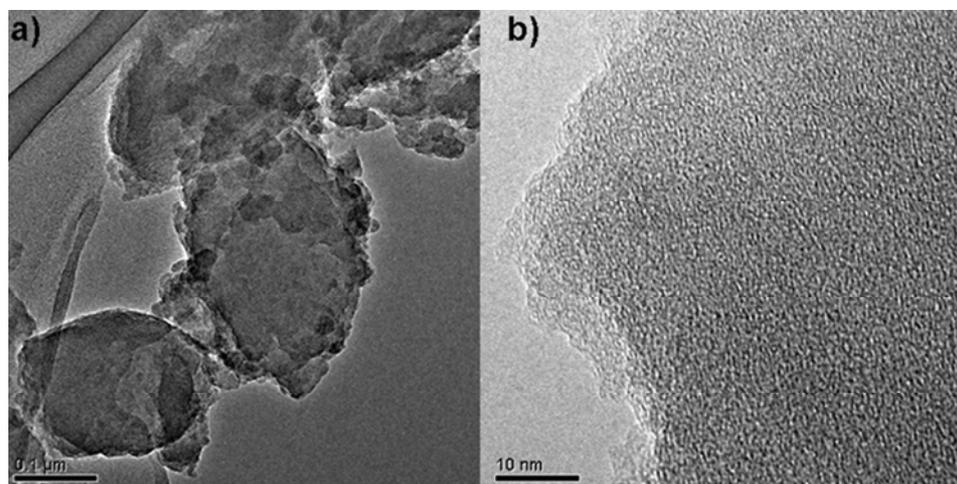


Figure s4. TEM image of the sample PAF-2 in large scale (a) and small scale (b).

5.5 The simulated nitrogen sorption.

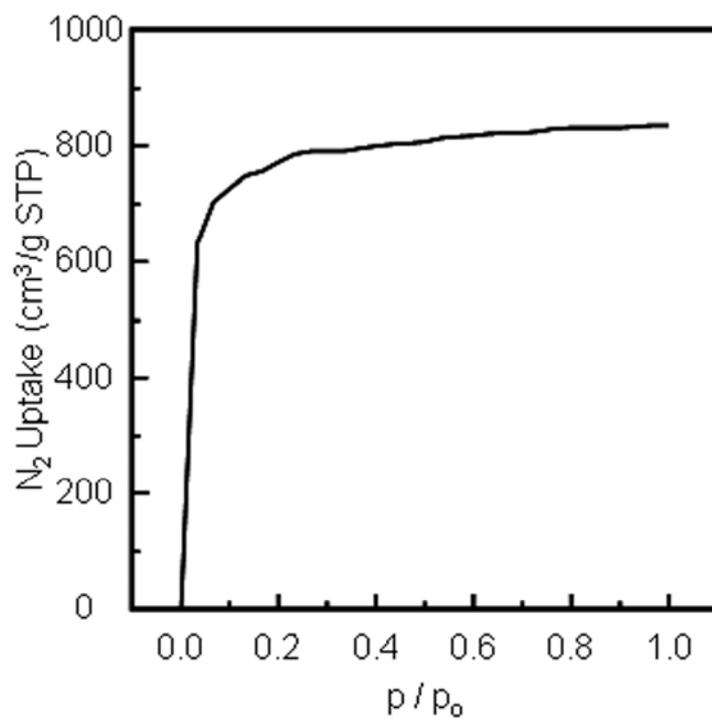


Figure s5 The nitrogen sorption simulated by Materials Studio software based on **ctn** net

Referenes:

1. Michael Grimm, Burkhard Kirste, and Harry Kurreck, *Angew. Chem. Int. Ed. Engl.* 1986, 25, 1097-1098
2. Materials Studio simulation environment, version 4.3. (Accelrys software Inc., San Diego, CA, USA)