Supporting Information

Synthesis of Porous Aromatic Framework with Tuning Porosity via Ionothermal Reaction

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1. Instruments

The X-ray Photoelectron Spectroscopy (XPS) was performed using a Thermo ESCALAB250. The thermogravimetric analysis (TGA) was performed using a Netzch Sta 449c thermal analyzer system at the heating rate of 10 ^{o}C/min in air or N_2 atmosphere. The Inductive Coupled Plasma (ICP) analysis was measured using a Perkin Elmer Optima 3300DV. The Elemental analysis (for C, H, N) were measured using a Perkin Elmer 2400 Series II CHNS/O Analyzer. The FTIR spectra were measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. The nitrogen adsorption isotherms were measured on a Quanta Autosorb-1c analyzer. The XRD was performed by a Rigaku D/max 2500 diffractometer using CuKα radiation, 40 kV, 200 mA with scanning rate of 0.3° min^{-1} (2θ). Scanning electron microscopy (SEM) was recorded using a JEOL JEM 6700. Transmission electron microscopy (TEM) was recorded using a JEOL JEM 3010. The solid–state ^{13}C NMR was performed by a Bruker Avance 400MHz Solid-State NMR Spectrometer.

2. Materials

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. The anhydrous $ZnCl_2$ was purchased from Aldrich and used in glove box. The Tetrakis (4-cyanophenyl) silican was prepared according to the previously reported method.[1]

3. Synthetic Procedures

Synthesis of PAF-16: General synthesis procedure: The monomer and the metal salt were transferred into a Pyrex ampoule (3*4 cm) in the glove box. The ampoule was evacuated, sealed and heated to 400 °C (PAF-16-1, PAF-16-2, PAF-16-3) and 600 ^{o}C (PAF-16-4) for 40 h (**table 1**). When the ampoule was cooled down to room temperature, the ampoule was opened carefully. The black block was stirred in the fresh water for 48 h three times to remove $ZnCl_2$. Further stirring in diluted HCl for 24 h was performed to purify the product. PAF-16 was isolated as a black rock in 76% yield.

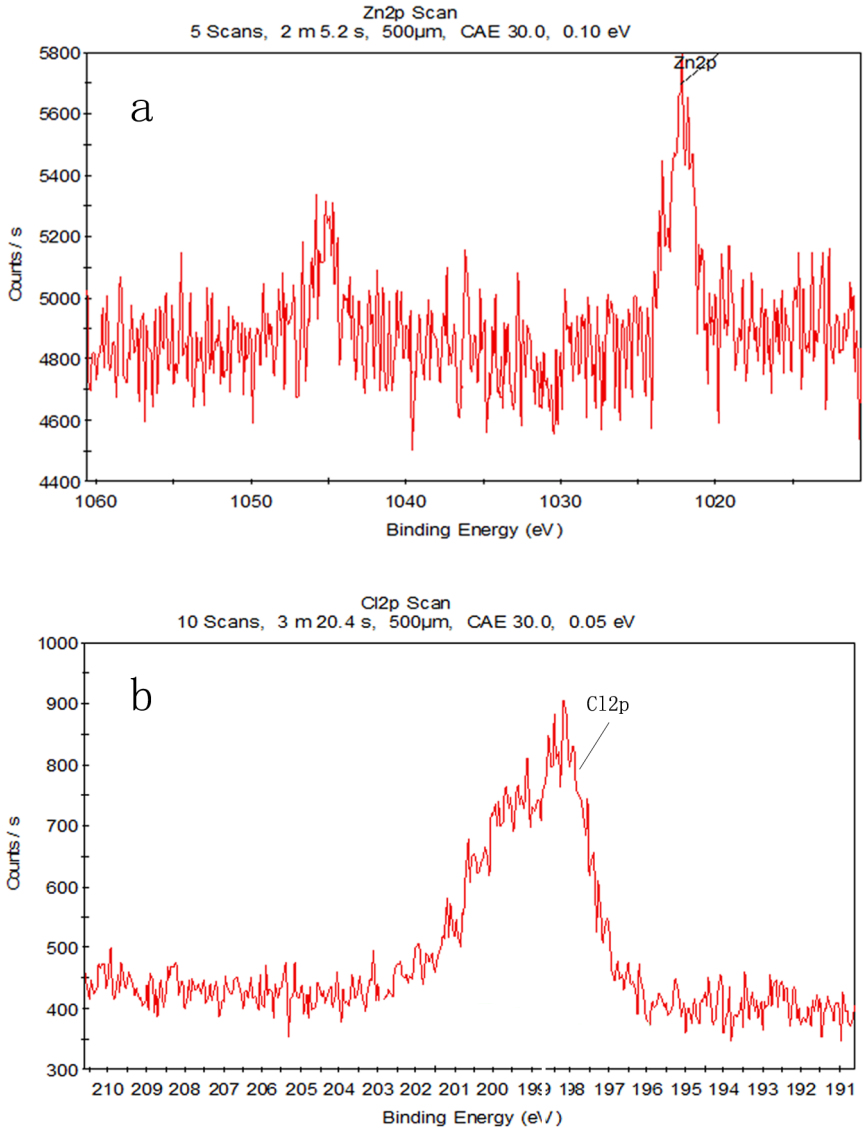

Figure S1. Zn XPS pattern (a) and Cl XPS pattern (b) of PAF-16-3.

Table S1 Elemental analysis of the PAF-16. Si and Zn contents were determined by ICP.

	C (wt %)	H (wt %)	N (wt %)	Si (wt %)	Zn (wt %)
PAF-16-1	63.15	3.56	4.96	1.51	8.56
PAF-16-2	64.74	3.08	5.30	2.17	10.24
PAF-16-3	65.0	3.94	3.74	1.8	16.45
PAF-16-4	77.23	2.27	5.46	2.63	0.21
Theoretical value	79.24	0.94	13.2	6.65	-

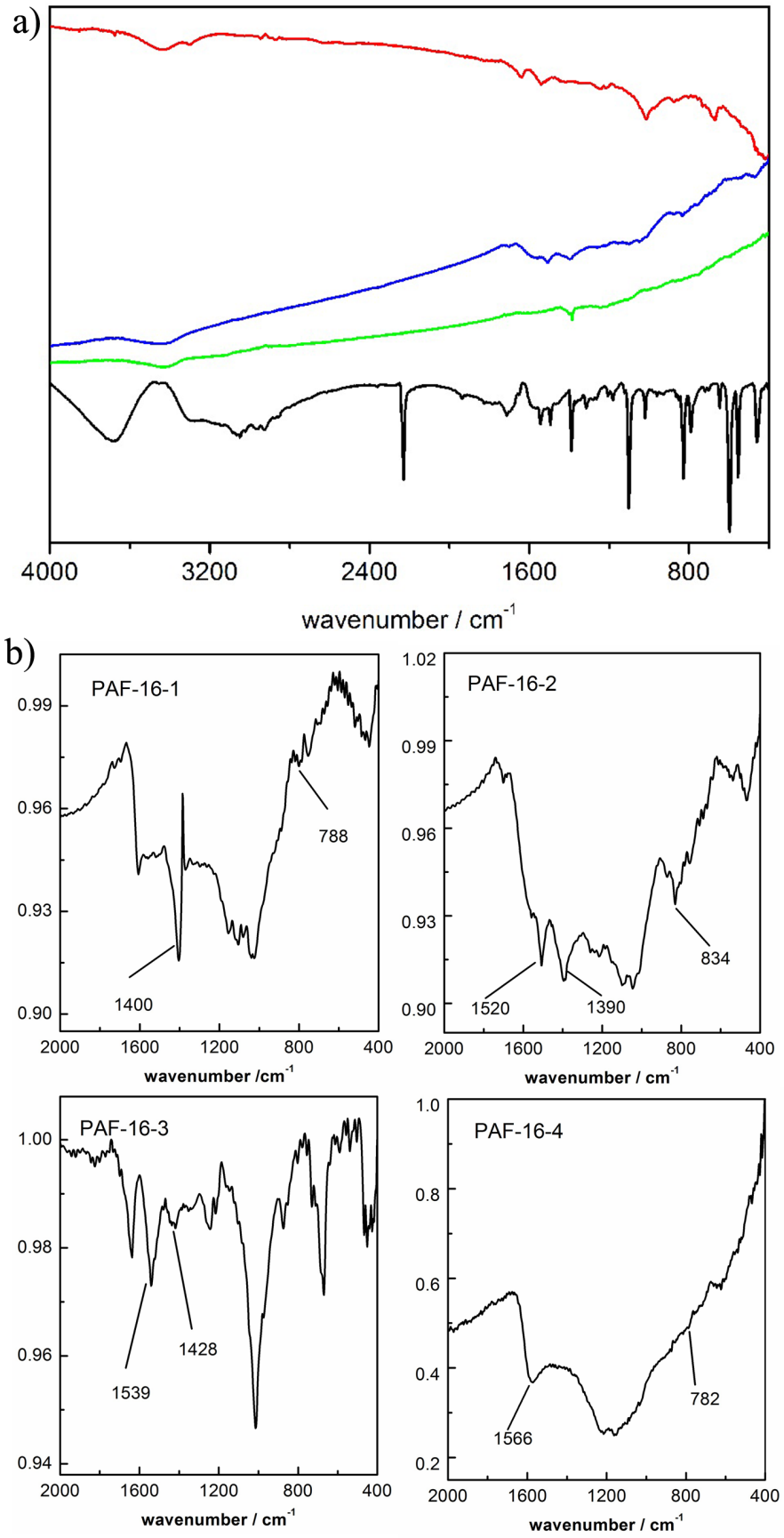

Figure S2. a) FTIR spectra of TCPSi (black), PAF-16-1 (red), PAF-16-2 (blue), and PAF-16-4 (green). b) Details of PAF-16-1, PAF-16-2, PAF-16-3, and PAF-16-4.

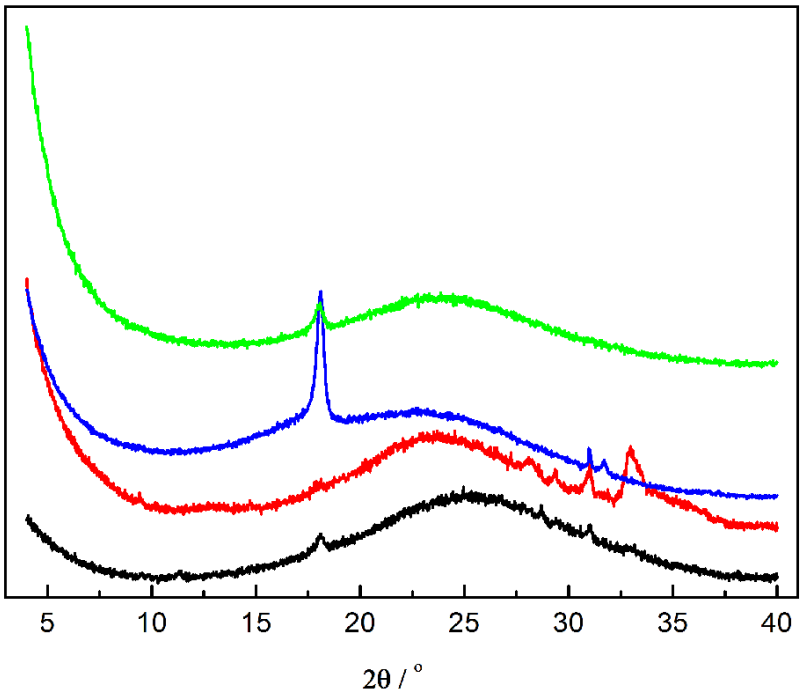

Figure S3 The PXRD patterns of synthesized PAF-16-1 (red), PAF-16-2 (blue), and PAF-16-4 (green).

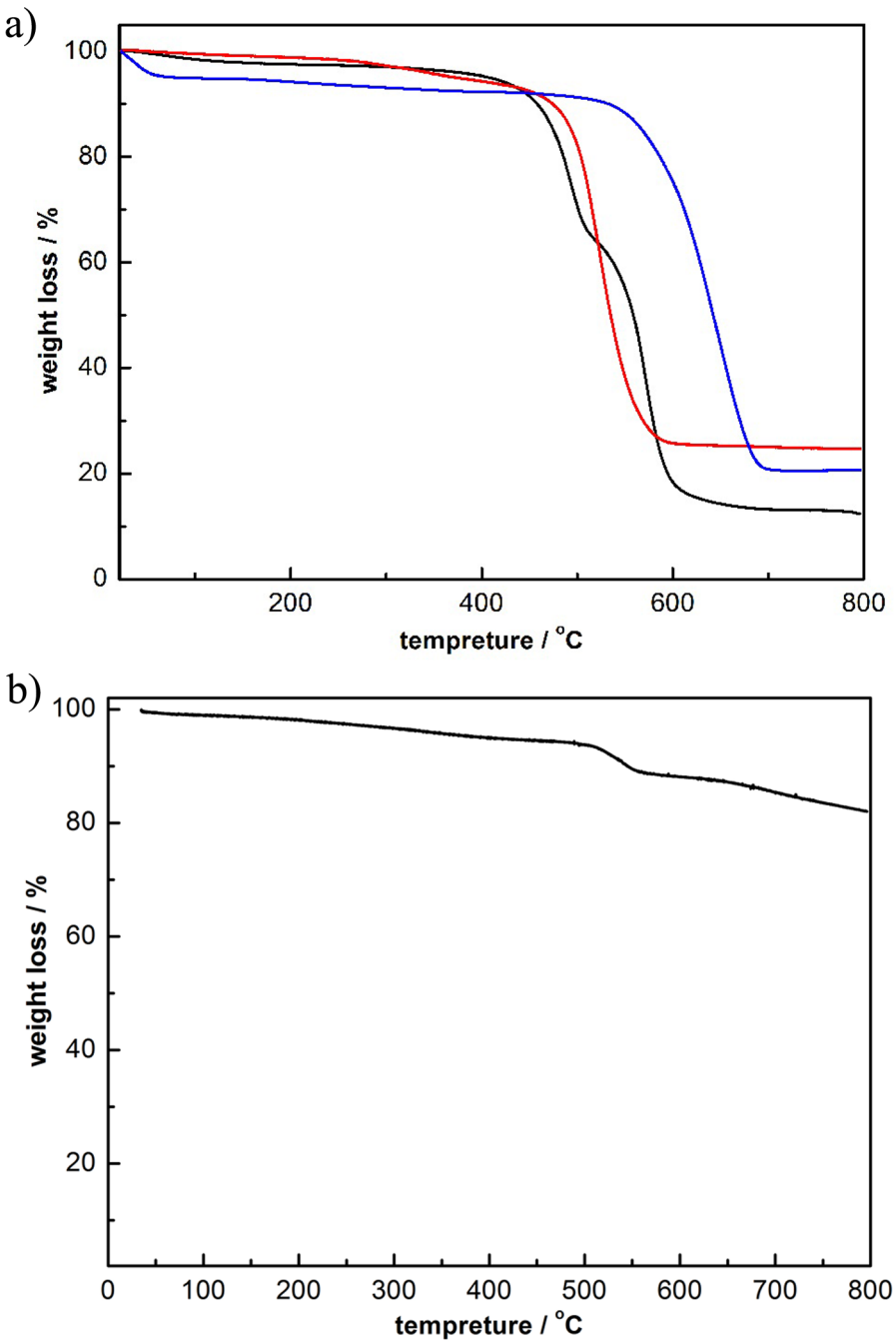

Figure S4. a) TGA plots of PAF-16-1 (black), PAF-16-2 (red), and PAF-16-4 (blue) under air atmosphere; b) TGA plot of PAF-16-4 under N_2 atmosphere.

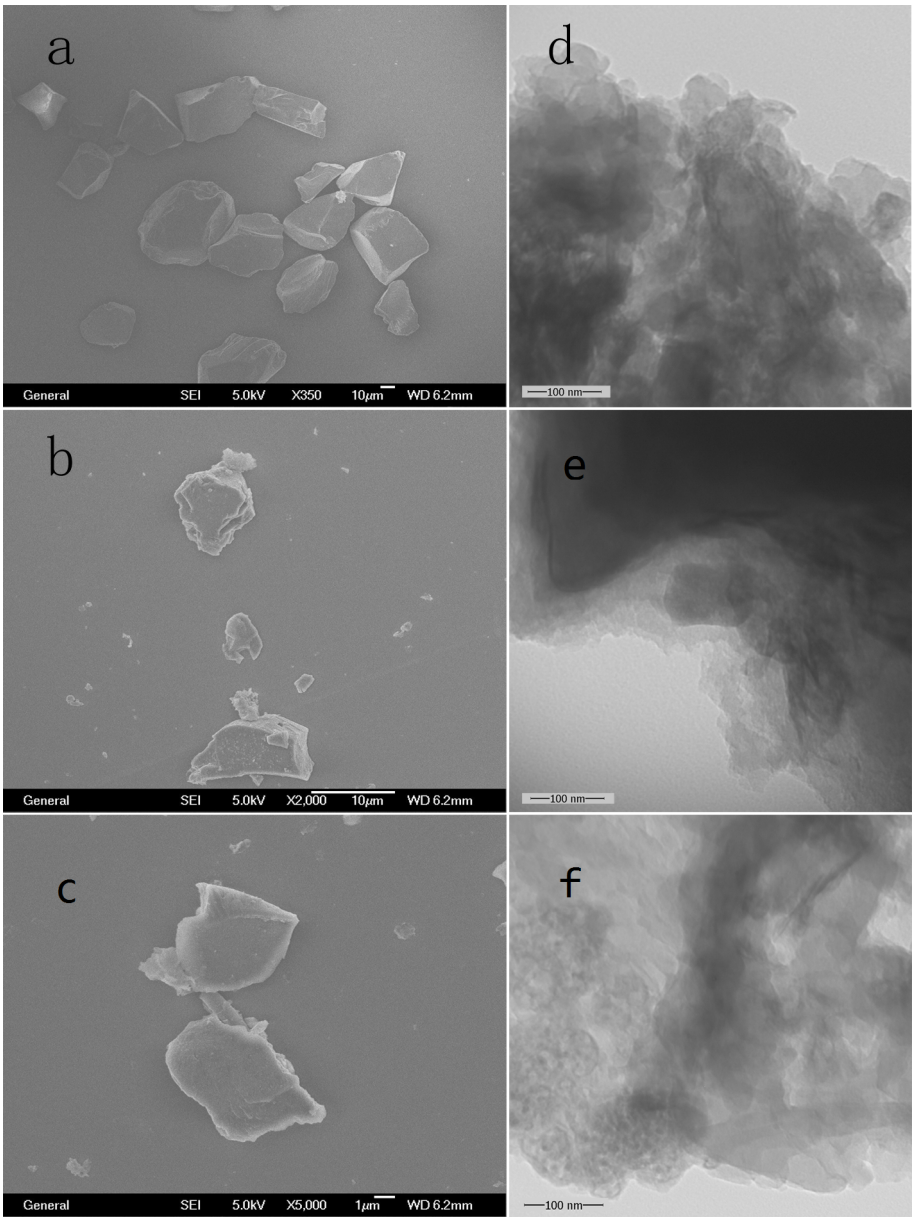

Figure S5. SEM images of PAF-16-1 (a), PAF-16-2 (b), and PAF-16-4(c); TEM images of PAF-16-1 (d), PAF-16-2 (e), and PAF-16-4(f).

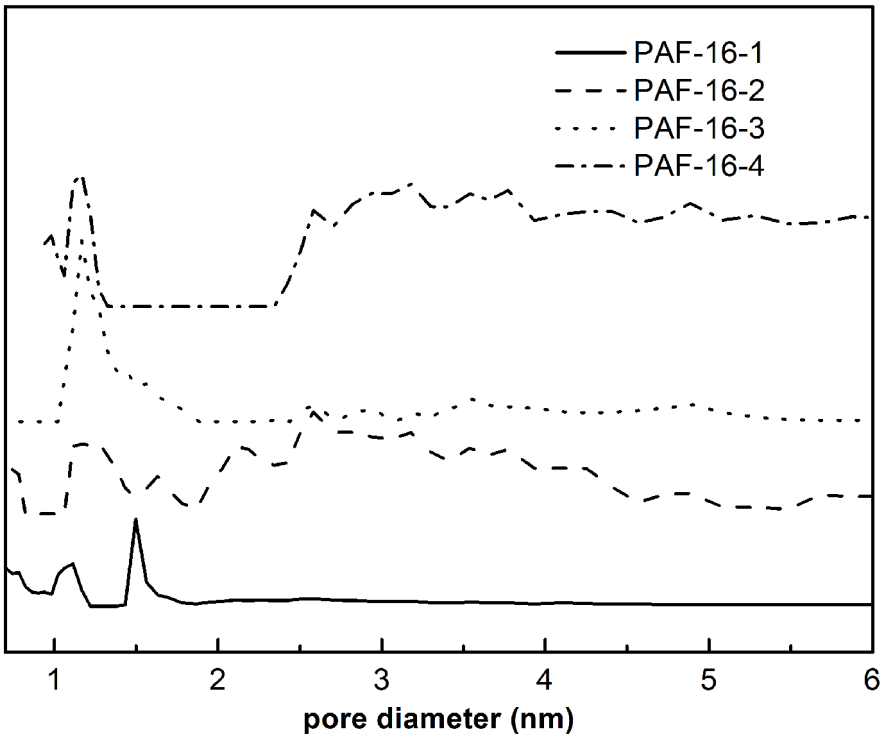

Figure S6. NL-DFT pore size distributions of the PAF-16 materials.

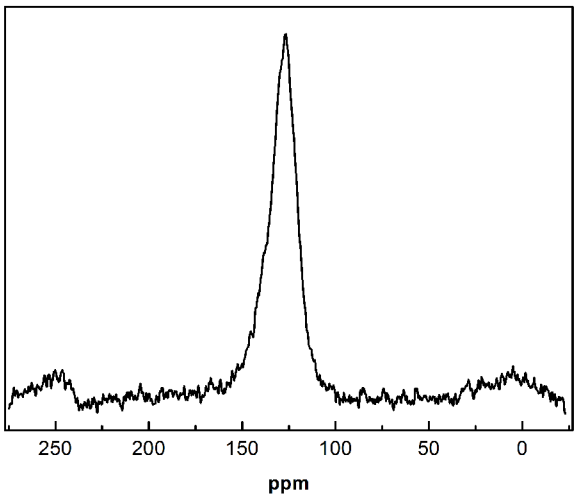

Figure S7. Solid–state ^{13}C NMR of PAF-16-2.

Reference:

1 F. Q. Liu, T. D. Tilley. *Inorg. Chem*., 1997, **36**, 5090-5096.