

Well-Defined Nitro-Functionalized Aromatic Frameworks (NO₂-PAF-1): A Synthesis by Copper-Mediated Ullmann Homo-Coupling Polymerization on Nitro-Containing Monomer and Its High CO₂ Adsorption

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Experimental Section

Chemicals

Tetrakis(4-bromophenyl)methane (TBPM) was synthesized through the method reported by Zhu group¹, fuming nitric acid and copper were purchased from Sinopharm Chemical Regent Co. DMF was purchased from Sigma Aldrich, sulphuric acid and methanol were purchased from Beijing Tongguang Fine Chemical Company.

Apparatus

Infrared spectra were recorded on a Nicolet 8700 Fourier transform spectrometer. NMR spectra were measured on a Bruker AV400 or Varian INOVA-400M (¹H at 400 MHz, ¹³C at 100 MHz) magnetic resonance spectrometer. High-resolution EI mass spectra (HR-EI-MS) were recorded on an GCT CA127 Micronass UK mass spectrometer. Thermogravimetric analysis (TGA) was performed in a TGA analyzer (TGA/DSC1SF/417-2, Mettler Toledo) at heating rates of 20 °C/min from room temperature to 1000 °C in a nitrogen atmosphere (40 mL/min). Polymer surface areas were screened using a Micromeritics ASAP 2020 volumetric adsorption analyser with a 9-point BET measurement between the pressure range of 0.005-0.20 P/P₀. Polymer pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the nonlocal density functional theory (NL-DFT) pore model for pillared clay with cylindrical pore geometry. Samples were degassed at 150 °C for

12 h under vacuum before analysis. Carbon dioxide isotherms were measured at 273 K using a Micromeritics ASAP 2020 volumetric adsorption analyser, Nitrogen isotherms were also measured under this condition to give the CO₂/N₂ selectivity data.

Synthesis of the tetrakis(4-bromo-3-nitrophenyl)methane

To a ice-bathed flask was added sulfuric acid (10 mL, 187 mmol, 120 eq), fuming nitric acid (10 mL, 241 mmol, 154 eq), the mixture was stirred for 5 min, then treated with BTM (1) (1.00 g, 1.56 mmol, 1 eq) portionwise. The reaction mixture was allowed to warm to r.t. After 24 hours, the reaction mixture was poured onto ice, then the solid was filtered and washed by water and alcohol in that order. The solid was dried under vacuum to give pure NBTPM (2) as pink power (0.77 g, yield 61%).

R_f = 0.42 [V (EtOAc)/V (Petroleum Ether) = 1/4].

m.p. : 342-343 °C.

IR (KBr, cm⁻¹): 3076 (w), 1540 (s), 1352 (m), 1037 (m), 846 (w), 728 (w), 512 (w).

¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 7.59 (dd, J = 2.4 Hz, J = 8.8 Hz, 4H), 7.89 (d, J = 8.8 Hz, 4H), 8.05 (d, J = 2.0 Hz, 4H)

¹³C NMR (125 MHz, DMSO-d₆) δ (ppm): 172.1, 135.9, 131.5, 127.4, 126.1, 122.1, 121.8, 119.7, 109.3, 105.51, 76.9, 46.6, 31.7, 30.0, 29.8, 29.4, 29.3, 29.2, 29.0, 26.7, 22.5, 13.9.

HR-MS (EI): m/z 811.7400 [M]⁺ (found C₂₅H₁₂N₄O₈Br₄⁺, required 811.7389).

Synthesis of PAF-NO₂-1 by traditional heating

To a heat-dried flask was added activated copper powder (30 mg, 0.47mmol, 1.9 eq, activated with 12 N HCl then washed by water and ethanol). Then the system was sealed and heated by a heatgun under vacuum to remove water and air. A solution of TBNPM (100 mg, 0.123 mmol, 1 eq) in DMF (10 mL) was injected into the system under nitrogen atmosphere. The reaction mixture was then heated to 175 °C (oil bath) under stirring. After 48 hours, the reaction mixture was allowed to cool down to room temperature. The solid was filtered off, washed with DMF and water three times respectively. Then the solid was immersed in diluted nitric acid (25 wt%, 100 mL) for 6 hours in order to remove excess copper. After washed by water and ethanol three

times respectively, the product was dried by using super critical CO₂ to give the product as brown power (52 mg, yield 78%).

Synthesis of PAF-NO₂-1 assisted by microwave

To a heat-dried microwave tube was added activated copper powder (1.0 g, 15.6 mmol, 6 eq). Then the system was sealed and heated by a heat gun under vacuum to remove water and air. A solution of TBNPM (1.0 g, 1.23 mmol, 1 eq) in DMF (25 mL) was injected into the system under nitrogen atmosphere. The reaction mixture was heated by microwave irradiation of 150 W under stirring for 30 mins. When cooled down, the solid was filtered off, washed with DMF and water three times respectively. Then the solid was immersed in diluted nitric acid (25 wt%, 200 mL) for 6 hours in order to remove excess copper. After washed by water and ethanol three times respectively, the product was dried at 150 °C under vacuum for 12 hours to give a brown power (0.60 g, yield 90%).

IR (KBr, cm⁻¹): 3073 (w), 1532 (s), 1346 (s), 1105 (m), 1006 (m), 852 (w), 704 (w).

¹³C CP/MAS NMR(125 MHz): δ (ppm): 64.11, 121.35, 131.46, 146.91.

Elemental analysis: C 58.64%, H 2.864%, N 9.695%.

Characterization

NMR tests were performed with Bruker AV-300, AV-500 and Varian 400, IR were performed with Nicolet 380, MS was carried out with LCMS2010, SEM using Nova NANOSEM 450 and TGA using NETZSCH DSC204. All the gas adsorption was performed with Micromeritics ASAP 2020.

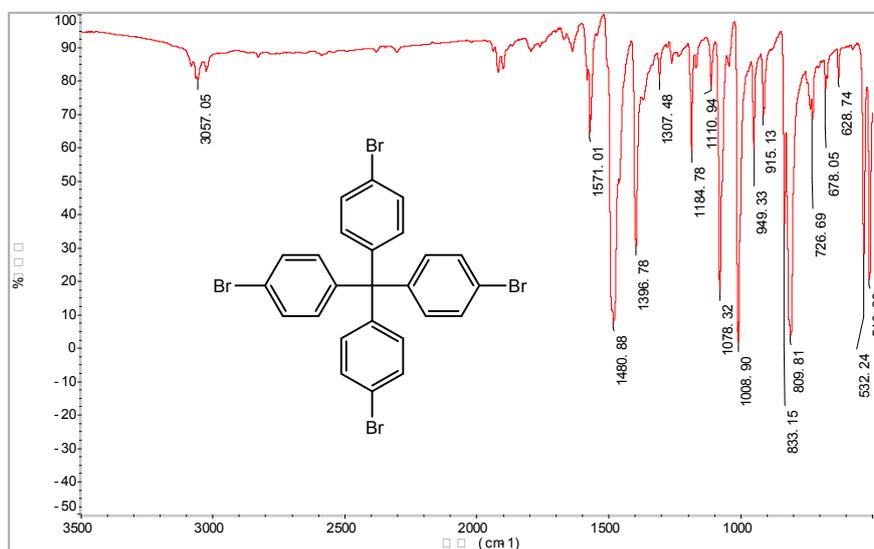


Figure S1 IR of tetra(bromophenyl)methane

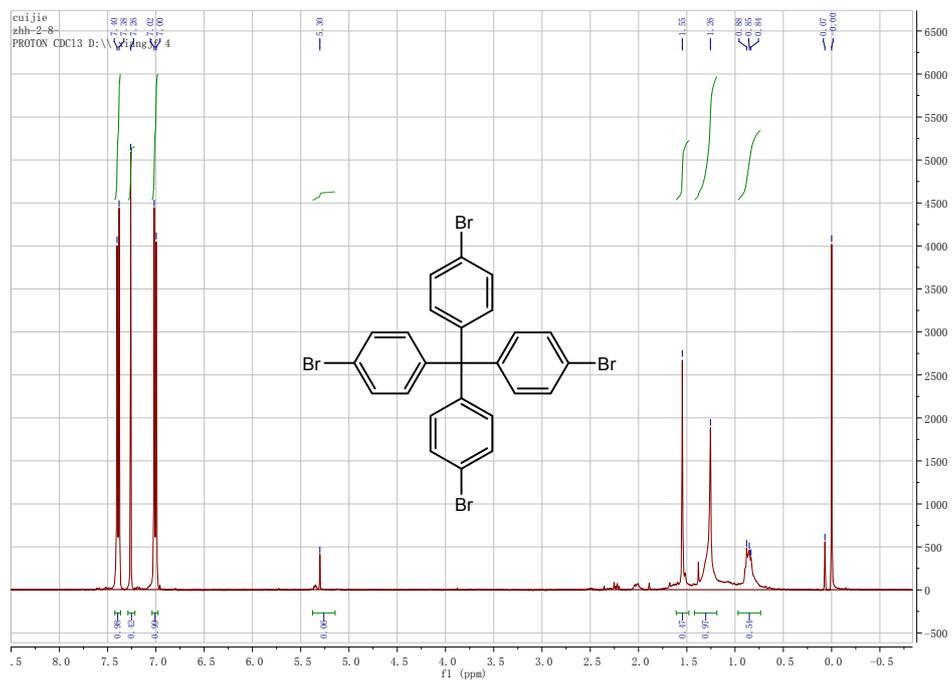


Figure S2 ¹H-NMR of tetra(bromophenyl)methane in CDCl₃

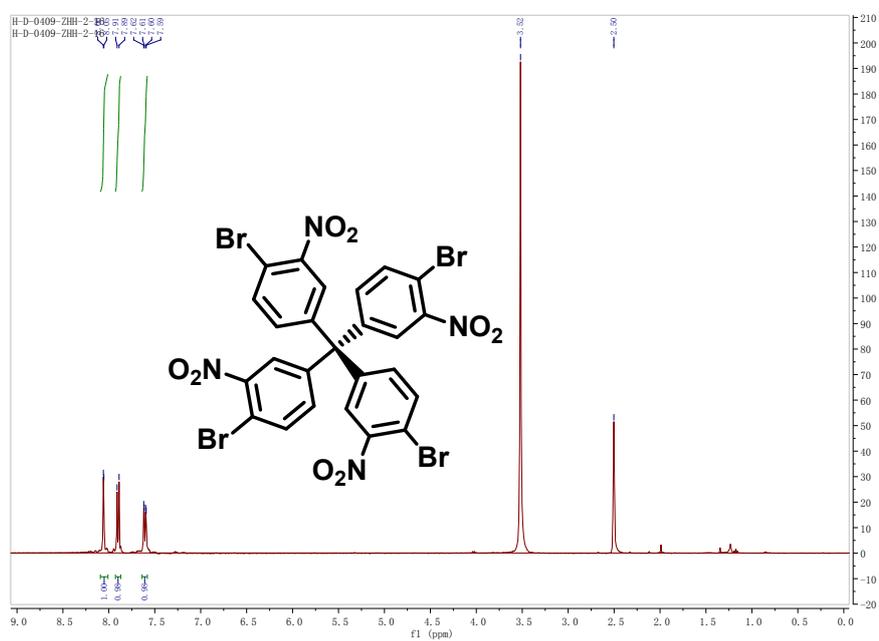


Figure S3 ¹H-NMR of TBNPM (2) in DMSO-d₆

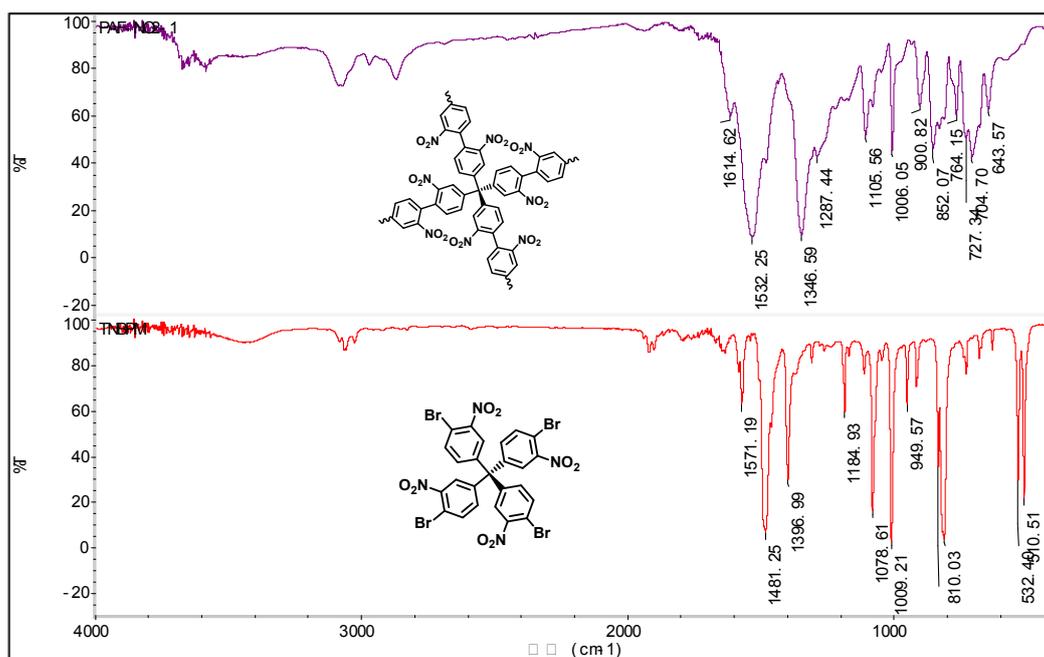


Figure S4 IR of TBNMP (2) and NO₂-PAF-1

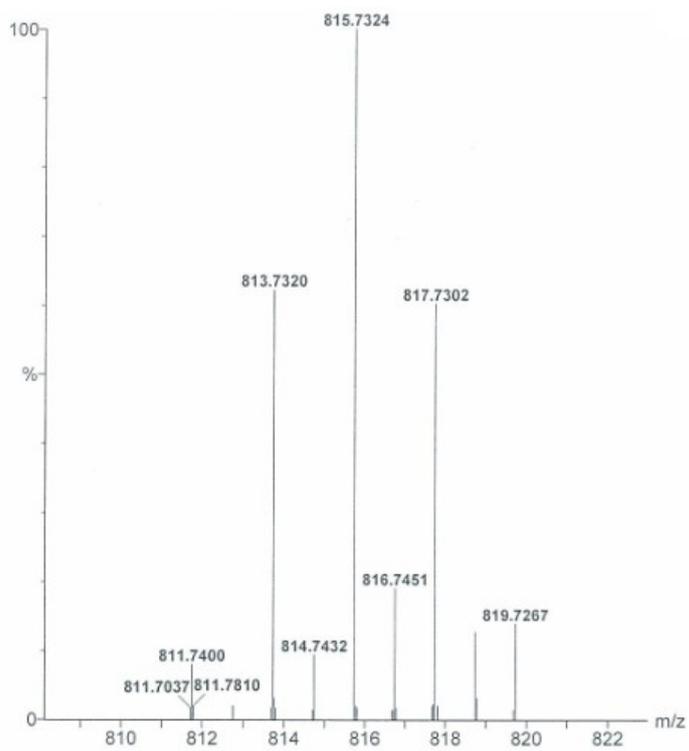


Figure S5 HR-MS (EI) of TBNMP (2)

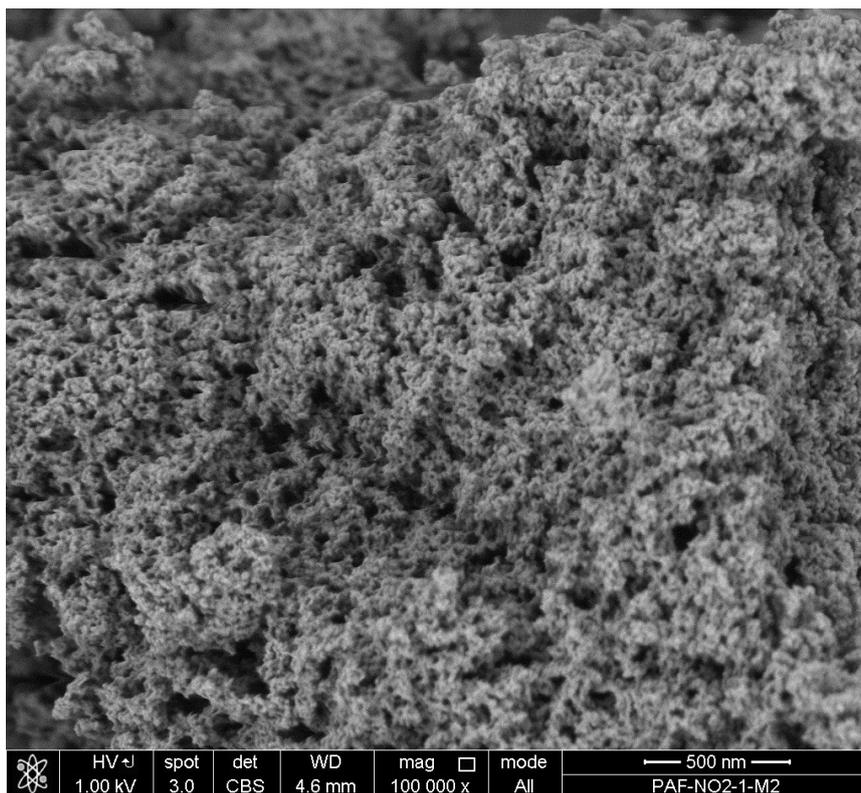


Figure S6 SEM picture of NO₂-PAF-1

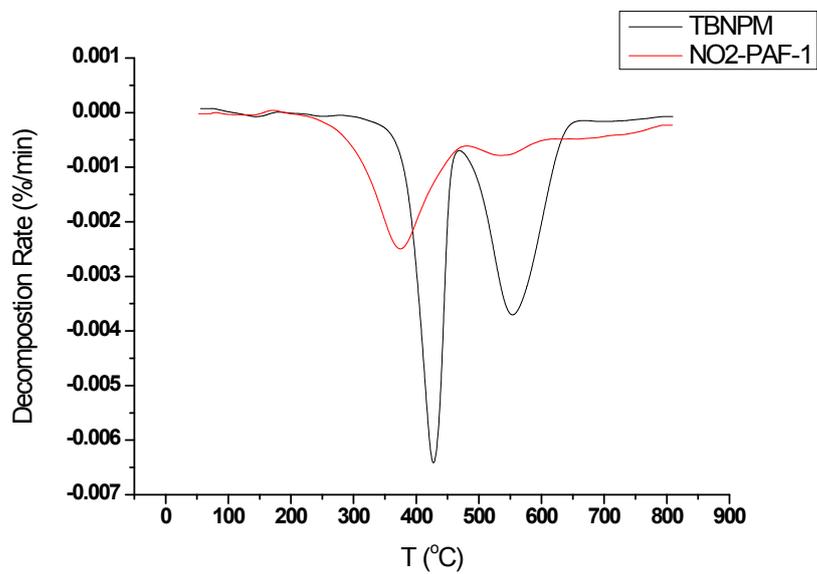


Figure S7 DTGA of TBNPM and NO₂-PAF-1

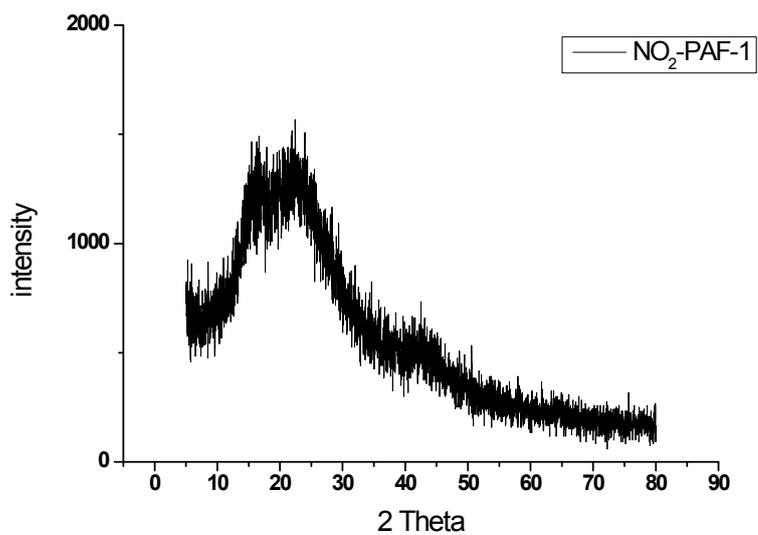


Figure S8 Powder X-Ray of NO₂-PAF-1

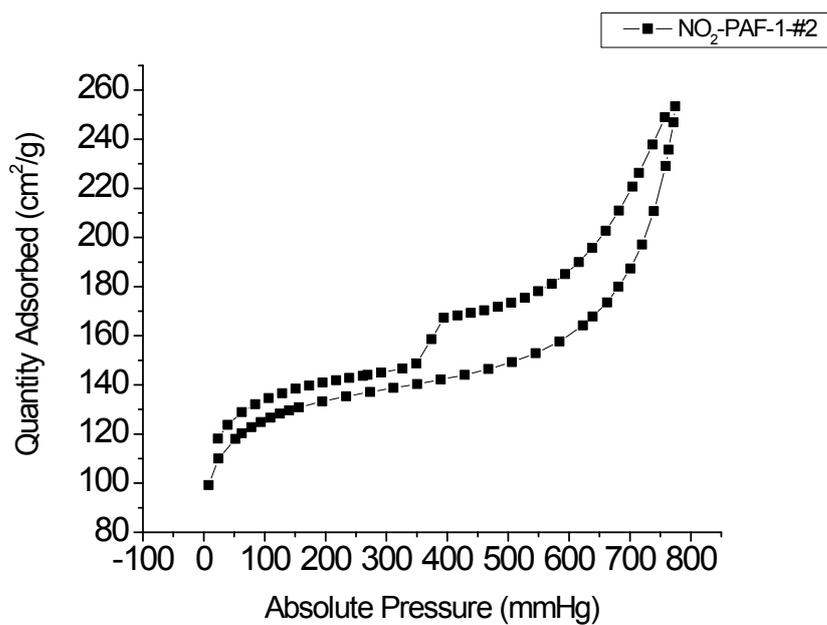


Figure S9 Nitrogen sorption-desorption isotherms of NO₂-PAF-1-#2

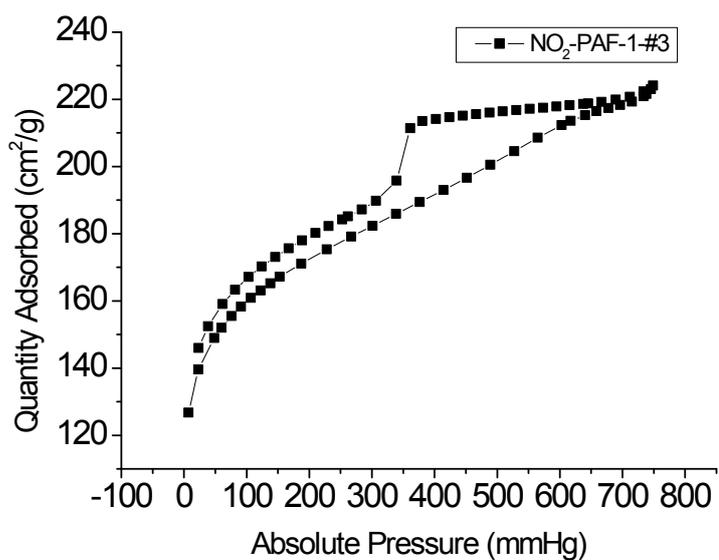


Figure S10 Nitrogen sorption-desorption isotherms of NO₂-PAF-1-#3

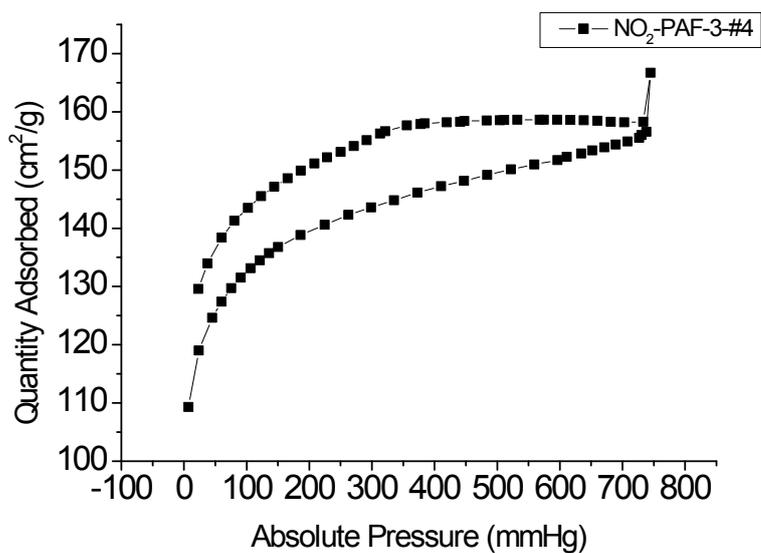


Figure S11 Nitrogen sorption-desorption isotherms of NO₂-PAF-1-#4

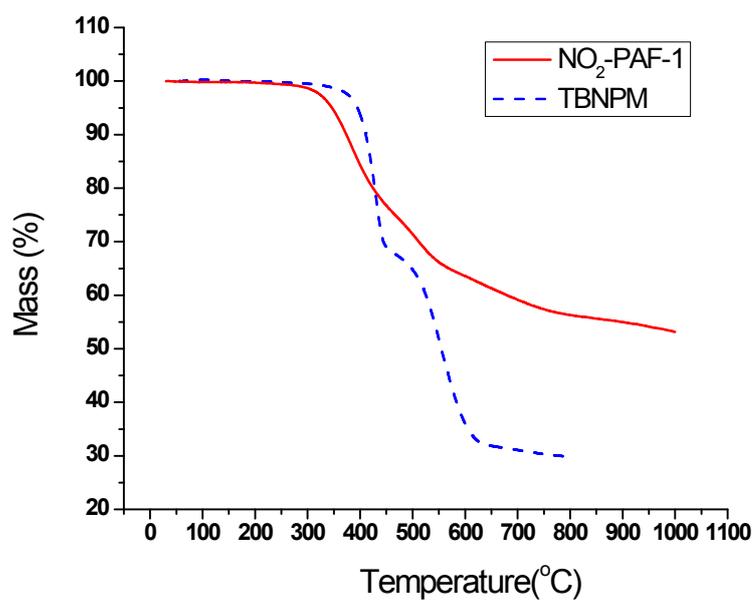


Figure S12 Thermo gravity analyses (TGA) of NO₂-PAF-1

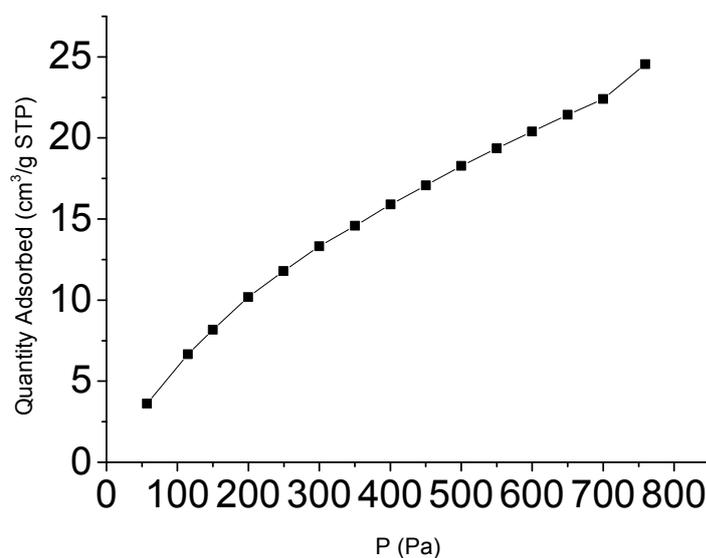
Table S1 The influence of work-up conditions on BET surface area of NO₂-PAF-1

Entry	Work-up method ^a	S _{BET} ^c /m ² ·g ⁻¹	Pore volume cm ³ /g ^d	Micropore volume cm ³ /g ^e	Micropore percentage ^f
1	Dried with Super critical CO ₂	610	0.93	0.10	11%
2	Ethanol ^a , vacuum @200 °C	468	0.39	0.13	32%
3	Ethanol ^a , vacuum @150 °C ^b	593	0.35	0.15	42%
4	Acetone ^a , vacuum@150 °C ^b	480	0.26	0.14	56%

a, materials were washed by DMF, water and solvents mentioned here. b, materials were dried at that temperature for 12 hours. c, Brunauer-Emmett-Teller specific surface area. d, single point adsorption total pore volume. e, t-Plot micropore volume. f, calculated with total pore volume and micropore volume.

Table S2 Heat of Adsorption data of NO₂-PAF-1 towards CO₂

Quantity Adsorbed (cm ³ /g STP)	Slope	Y-Intercept	Heat of Adsorption (kJ/mol)	Uncertainty (kJ/mol)
15.0000	-4623.2	21.409	38.439	0.000
16.0000	-4621.8	21.505	38.427	0.000
17.0000	-4631.8	21.638	38.511	0.000
18.0000	-4613.5	21.665	38.358	0.000
19.0000	-4606.4	21.728	38.299	0.000

**Figure S13** CO₂ adsorption isotherms of NO₂-PAF-1 @298K