Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Tailoring open metal sites for high selectivity for CO_2 capture in isostructural metalloporphyrin porous organic networks

Hwa Seob Choi,[a] Hyung Joon Jeon,[b] Jung Hoon Choi,[b] Gyu-Heon Lee[b] and Jeung Ku Kang[a,b*]

[a] Graduate School of Energy, Environment, Water, and Sustainability (EEWS), Korea Advanced Institute of Science and Technology, 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea

[b] Department of Materials Science, Korea Advanced Institute of Science and Technology, 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea.

* Corresponding Author: Fax: +82-42-350-1710, E-mail: jeung@kaist.ac.kr.

Materials and methods

Bis(1,5-cyclooctadiene)nickel(0) was purchased from Across Organics. Chloroform, THF, methanol, ethanol, acetone and water were purchased from Duksan. The other chemicals were purchased from Sigma Aldrich. Also, the Liquid ^{1}H NMR spectra were recorded on a Agilent 400MHz 54mm NMR DD2 model. High Resolution Mass Spectrometer (HR-MS) were measured on a microTOF-QII of Bruker Daltonik(Germany). Model of UV-Visible spectrometer was cary 300 Conc from Varian. Scan range was from 800 nm to 200 nm with 1 nm interval, and scan speed was 600 nm/min. Elemental analysis (EA) was carried out using EA-1110-FISONS model of ThermoQuest. Solid ^{13}C NMR was done by Varian 600 MHz with CP/MAS technique. FT-IR-4100 from JASCO was used for FT-IR spectroscopy which scanned from 400 to 4000 cm^{-1} with ATR. TGA (Thermogravimetry analysis) was carried out by using TG209F3 of NETZSCH. Inductively coupled plasma optical emission spectroscopy (ICP-OES) were carried out by iCAP 6300 Duo model of Thermo Scientific Co. Field emission scanning electron microscopy was performed on a S-4800 model from HITACHI and the samples were coated with Pt sputtering before take images. Cs-corrected scanning transmission electron microscopy (STEM) was performed on JEM-ARM200F model of JEOL. The energy dispersive X-ray spectrometer (EDS) images were observed by using a BRUKER QUANTAX EDS. Powder x-ray diffractometer model was SmartLab from Rigaku. Scan was started from 2˚ to 60˚ which step size is 0.02˚, and IS was 2/3 degree, RS1 was 7 mm and RS2 was 13 mm. Used Cu Kα ray generated by 40 kV and 30 mA energy. Knife edge was used for remove incident beam at low angle, and non-reflection holder was used. All gas adsorption desorption isotherm analysis was carried out using Quadrasorp model of Quantachrome instruments. In addition, the adsorption points at the pressure of 0 to 0.025 atm were used to calculate the initial slopes for each adsorbate isotherm. Then, Henry‘s selectivity of CO_2/N_2 and CO_2/Ar were determined by dividing the slope of CO_2 with the slope of N_2 or Ar.

Synthesis

(1) Synthesis of 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphine (TBP).

Dissolve 3.7 g (0.02 mol) of 4-bromobenzaldehyde in 100ml of propionic acid and add 1.4 mL (0.01 mol) pyrrole. The reaction mixture was stirred at 150 °C in argon condition for 30 min, cooled to room temperature. The resulted violet precipitate was filtered and washed with methanol. The product was dissolved in chloroform and recrystallized by adding methanol twice for purification. Recrystallized product was filtered and dried in 80 ^{o}C vacuum oven. Resulted tetrakis(4'-bromophenyl)porphyrin was 1.832g which yield was 19.68%. 1H NMR (CDCl3, 400 MHz): δ (ppm) 8.17 (d, 8H, J = 8.3 Hz, aromatics), 8.43 (d, 8H, J = 8.3 Hz, aromatics), 8.56 (d, 8H, J=1.3 H-pyrrole). HRMS-ESI: *m*/*z* calcd for C44H26Br4N4 $[M + H]^+$ m/z = 930.89; found, 930.88. UV-visible spectrum in $CHCl_3$ shows peaks (λ; nm): 419. 515, 550, 590, 647. Elemental analysis found: C 56.75, N 6.11, H 2.76, calculated: C 56.81, N 6.02, H 2.82.

(2) Synthesis of cobalt 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphine (Co TBP).

600 mg (0.6449 mmol) of 5, 10, 15, 20-Tetrakis(4'-bromophenyl)porphine and 250.59mg (1.93 mmol) of $CoCl_2$ were placed into a 250 mL flask which dehydrated by making vacuum and blow hot air and recharged with argon gas. 60 mL of DMF was poured into flask and mixture was stirred at 150°C for 4 hours. After cooling to room temperature, equivalent amount (60 mL) of 4°C of DI water was added to precipitate product. The violet product was filtered with reduced pressure and dissolved in chloroform. Cobalt 5, 10, 15, 20-tetrakis(4'-bromophenyl)porphine solution in chloroform is recrystallized by adding methanol. Repeat recrystallization by twice and precipitated product is filtered with washing slightly with methanol and dried in 80°C vacuum oven overnight. Final product was 604 mg in 94.9% yield. 1H NMR (CDCl3, 400 MHz): δ (ppm) 8.17 (d, 8H, J = 8.3 Hz, aromatics),

8.43 (d, 8H, *J* = 8.3 Hz, aromatics), 8.56 (s, 8H, H-pyrrole). HRMS-ESI: *m*/*z* calcd for C44H24Br4N4Co $[M + Na]^+$ m/z = 1009.0; found, 1009.34. UV-visible spectrum in CHCl3 shows peaks (λ; nm): 409, 524. Elemental analysis found: C 53.84, N 5.61, H 2.66, calculated: C 53.93, N 5.59, H 2.72.

(3) Synthesis of nickel 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphine (Ni TBP).

600 mg (0.6449 mmol) of 5, 10, 15, 20-Tetrakis(4'-bromophenyl)porphine and 250.73mg (1.93 mmol) of $NiCl_2$ were placed into a 250 mL flask which dehydrated by making vacuum and blow hot air and recharged with argon gas. 60 mL of DMF was poured into flask and mixture was stirred at 150°C for 4 hours. After cooling to room temperature, equivalent amount (60 mL) of 4°C of DI water was added to precipitate product. The violet product was filtered with reduced pressure and dissolved in chloroform. Nickel 5, 10, 15, 20-tetrakis(4'-bromophenyl)porphine solution in chloroform is recrystallized by adding methanol. Repeat recrystallization by twice and precipitated product is filtered with washing slightly with methanol and dried in 80°C vacuum oven overnight. Final product was 604 mg in 94.9% yield. 1H NMR (CDCl3, 400 MHz): δ (ppm) 8.17 (d, 8H, *J* = 8.3 Hz, aromatics), 8.43 (d, 8H, *J* = 8.3 Hz, aromatics), 8.56 (s, 8H, H-pyrrole). HRMS-ESI: *m*/*z* calcd for C44H24Br4N4Ni $[M + Na]^+$ m/z = 1008.8; found, 1008.79. UV-visible spectrum in CHCl3 shows peaks (λ; nm): 415, 527. Elemental analysis found: C 53.72, N 5.68, H 2.45, calculated: C 53.54, N 5.68, H 2.45.

(4) Synthesis of copper 5, 10, 15, 20-Tetrakis (4'-bromophenyl)porphine (Cu TBP).

600 mg (0.6449 mmol) of 5, 10, 15, 20-Tetrakis(4'-bromophenyl)porphine and 260.12mg (1.93 mmol) of $CuCl_2$ were placed into a 250 mL flask which dehydrated by making vacuum and blow hot air and recharged with argon gas. 60 mL of DMF was poured into flask and mixture was stirred at 150°C for 4 hours. After cooling to room temperature, equivalent amount (60 mL) of 4°C of DI water was added to precipitate product. The violet product was filtered with reduced pressure and dissolved in chloroform. Copper 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphine solution in chloroform is recrystallized by adding

methanol. Repeat recrystallization by twice and precipitated product is filtered with washing slightly with methanol and dried in 80 °C vacuum oven overnight. Final product was 614 mg in 96.2% yield. 1H NMR (CDCl3, 400 MHz): δ (ppm) 8.17 (d, 8H, *J* = 8.3 Hz, aromatics), 8.43 (d, 8H, *J* = 8.3 Hz, aromatics), 8.56 (s, 8H, H-pyrrole). HRMS-ESI: *m/z* calcd for C44H24Br4N4Cu $[M + Na]^+$ m/z = 1013.80; found, 1013.78. UV-visible spectrum in CHCl3 shows peaks (λ; nm): 416, 539. Elemental analysis found: C 52.88, N 5.62, H 2.34, calculated: C 53.28, N 5.65, H 2.44.

(5) Synthesis of H_2P PON.

The reaction chamber was flame-dried and purged by argon gas. 0.213 g (1.36 mmol) of 2,2'-bipyridyl and 0.375 g (1.36 mmol) of bis(1,5-cyclooctadiene)nickel(0) were added to the flask. 0.175 mL (1.42 mmol) of 1,5-cyclooctadiene and 20 mL of anhydrous DMF were added. The mixture was stirred and heated at 80 °C for 1hour. Next, 243.3 mg (0.2616 mmol) of 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphyrin (TBP) was added and the mixture was stirred at the same temperature for 4 days to obtain a deep purple suspension. After cooling to room temperature, the concentrated 10 mL of HCl was added to the mixture and then stirred for 1 day. The product was filtered and washed by chloroform. The Soxhlet extractions have been carried out for 24 hours by each chloroform, THF, and water. The product was washed with HCl to remove the remaining catalyst and washed by water to remove HCl until the pH is neutralized. Finally, the product washed by acetone for solvent exchange and dried in the 150 °C vacuum oven for 3 days. The obtained amount of a final product was 97.7 mg with the 61.2 % yield. The elemental analysis shows the experimental values of C 74.36, N 7.99, and H 4.05, which are comparable to theoretical values of C 86.53, N 9.17, and H 4.29.

(6) Synthesis of CoP PON.

The reaction chamber was flame-dried and purged by argon gas. 0.213 g (1.36 mmol) of 2,2'-bipyridyl and 0.375 g (1.36 mmol) of bis(1,5-cyclooctadiene)nickel(0) were added to the flask. 0.175 mL (1.42 mmol) of 1,5-cyclooctadiene and 20 mL of anhydrous DMF were added. The mixture was stirred and heated at 80 °C for 1 hour. Then, 258.3 mg (0.2616 mmol) of cobalt 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphyrin (Co TBP) was added and the mixture was stirred at the same temperature for 4 days to obtain a deep purple suspension. After cooling to room temperature, the concentrated 10 mL of HCl was added to the mixture and then stirred for 1 day. The product was filtered and washed by chloroform. The Soxhlet extractions have been made for 24 hours with each chloroform, THF, and water. The product was washed with HCl to remove the remaining catalyst and washed by water to remove HCl until the pH is neutralized. Finally, the product washed by acetone for solvent exchange and dried in the 150 °C vacuum oven for 3 days. The final product was 113.7 mg in 65.14 % yield. The elemental analysis shows the experimental values of C 68.55, N 6.89, H 3.89, and Co 5.31 wt% (by ICP-OES), which are comparable to theoretical values of C 79.14, N 8.39, H 3.62, and Co 8.82 wt%.

(7) Synthesis of NiP PON.

The reaction chamber was flame-dried and purged by argon gas. 0.213 g (1.36 mmol) of 2,2'-bipyridyl and 0.375 g (1.36 mmol) of bis(1,5-cyclooctadiene)nickel(0) were added to the flask. 0.175 mL (1.42 mmol) of 1,5-cyclooctadiene and 20 mL of anhydrous DMF were added. The mixture was stirred and heated at 80 °C for 1 hour. Next, 258.5 mg of (0.2616 mmol) of nickel 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphyrin (Ni TBP) was added and the mixture was stirred at the same temperature for 4 days to obtain a deep purple suspension. After cooling to room temperature, the concentrated 10 mL of HCl was added to the mixture and then stirred for 1 day. The product was filtered and washed by chloroform. The Soxhlet extractions have been performed for 24 hours using each chloroform, THF, and water. The product was washed with HCl to remove the remaining catalyst and washed by water to remove HCl until pH is neutralized. Finally, the product washed by acetone for solvent exchange and dried in the 150 °C vacuum oven for 3 days. The final product was 111.8 mg in 64.03 % yield. The elemental analysis shows C 66.80, N 6.43, H 4.69, and Ni 5.81 wt% (by ICP-OES), comparable to theoretical values of C 79.19, N 8.39, H 3.62, and Ni 8.79 wt%.

(8) Synthesis of CuP PON.

The reaction chamber was flame-dried and purged by argon gas. 0.213 g (1.36 mmol) of 2,2'-bipyridyl and 0.375 g (1.36 mmol) of bis(1,5-cyclooctadiene)nickel(0) were added to the flask. 0.175 mL (1.42 mmol) of 1,5-cyclooctadiene and 20 mL of anhydrous DMF were added. The mixture was stirred and heated at 80 °C for 1hour. Next, 259.5 mg (0.2616 mmol) of copper 5, 10, 15, 20-tetrakis (4'-bromophenyl)porphyrin (Cu TBP) was added and the mixture was stirred at the same temperature for 4 days to obtain a deep purple suspension. After cooling to room temperature, the concentrated 10 mL of HCl was added to the mixture and then stirred for 1 day. The product was filtered and washed by chloroform. The Soxhlet extractions have been performed for 24 hours on each chloroform, THF, and water. The product was washed with HCl to remove the remaining catalyst and washed by water to remove HCl until the pH is neutralized. Finally, the product washed by acetone for solvent exchange and dried in the 150 °C vacuum oven for 3 days. The final product was 116.9 mg in the 66.47 % yield. The elemental analysis shows C 76.87, N 8.37, H 3.56, Cu 5.12 wt% (by ICP-OES), comparable to theoretical values of C 78.61, N 8.33, H 3.60, Cu 9.45 wt%.

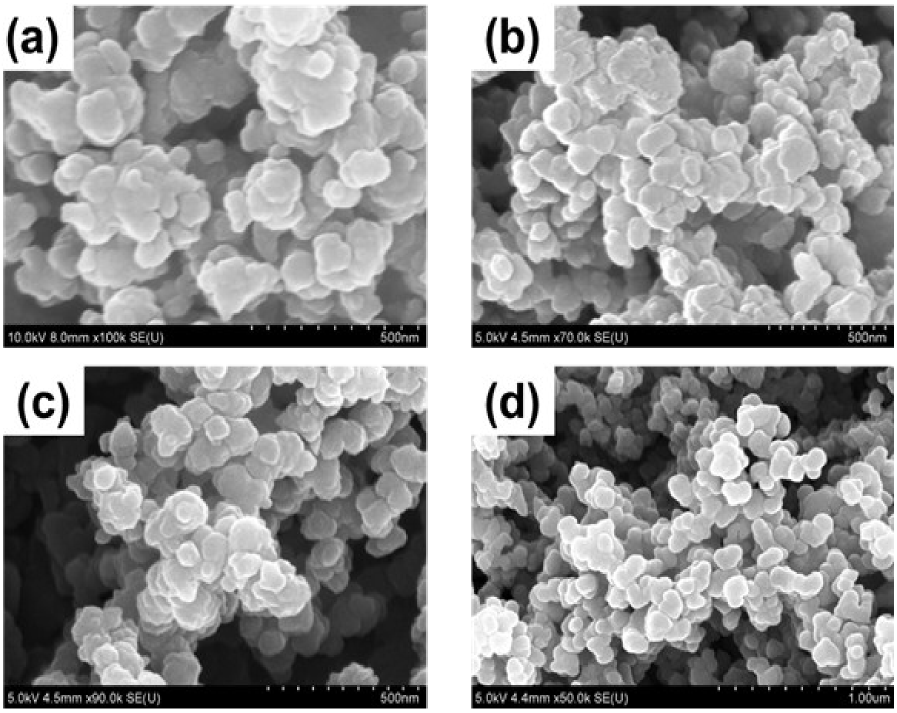

Fig. S1 SEM images of (a) H_2P PON, (b) CoP PON, (c) NiP PON, and (d) CuP PON.

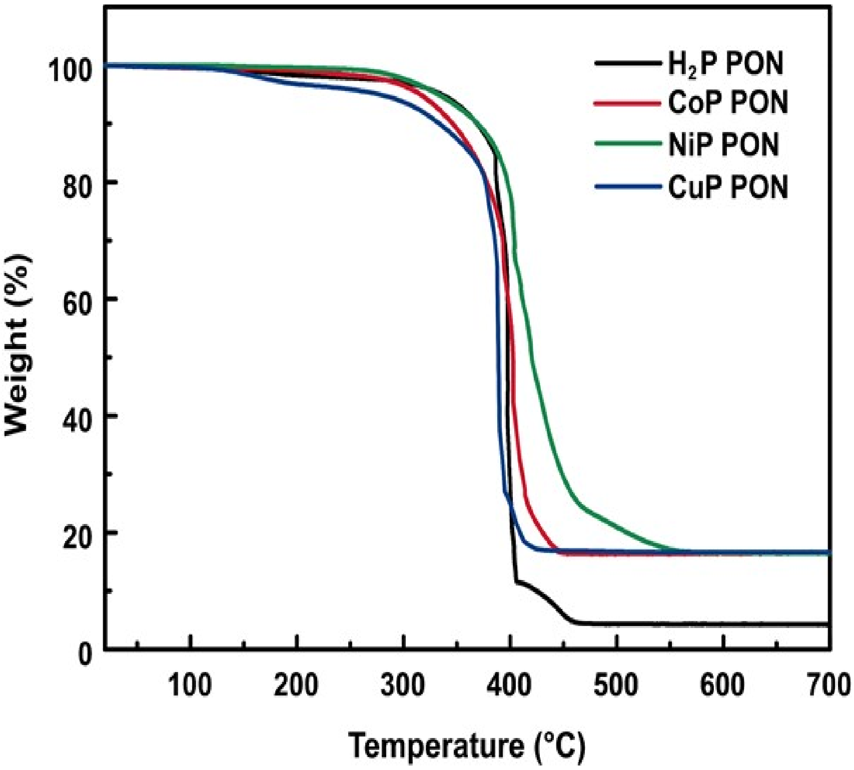

Fig. S2 Thermogravimetric analysis (TGA) plot of MP PONs in the air condition.

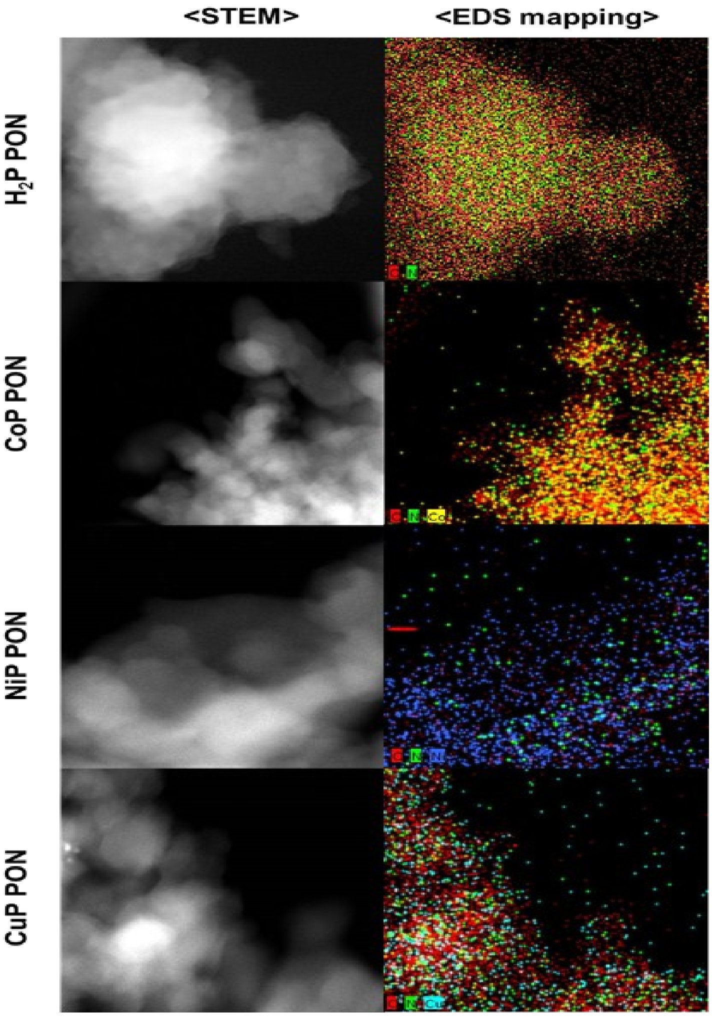

Fig. S3 STEM images and EDS mapping of MP PONs and H_2P PON

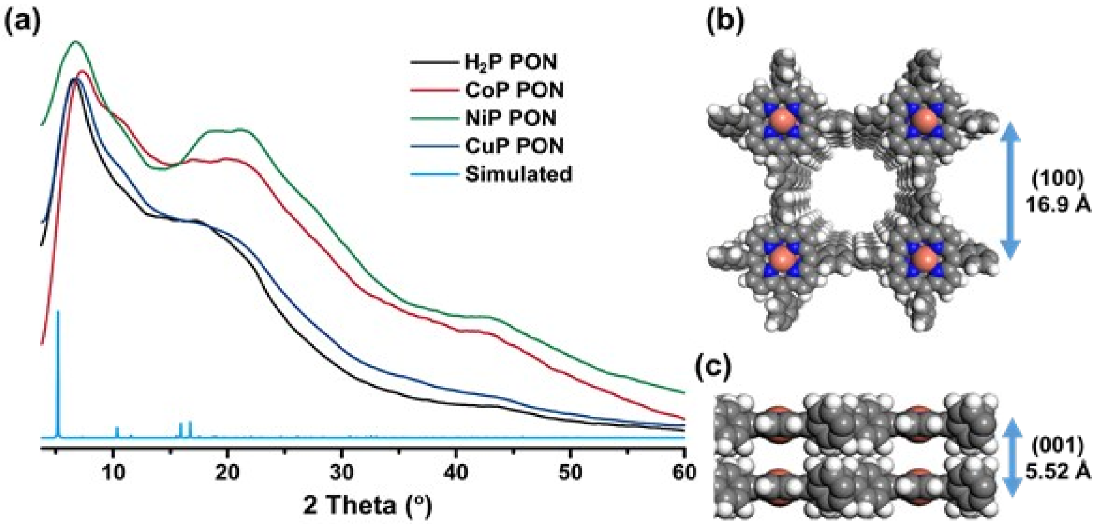

Fig. S4 (a) PXRD results of MP PONs and simulated XRD pattern. Simulated optimized structure of MP PONs in top view (b) and side view (c).

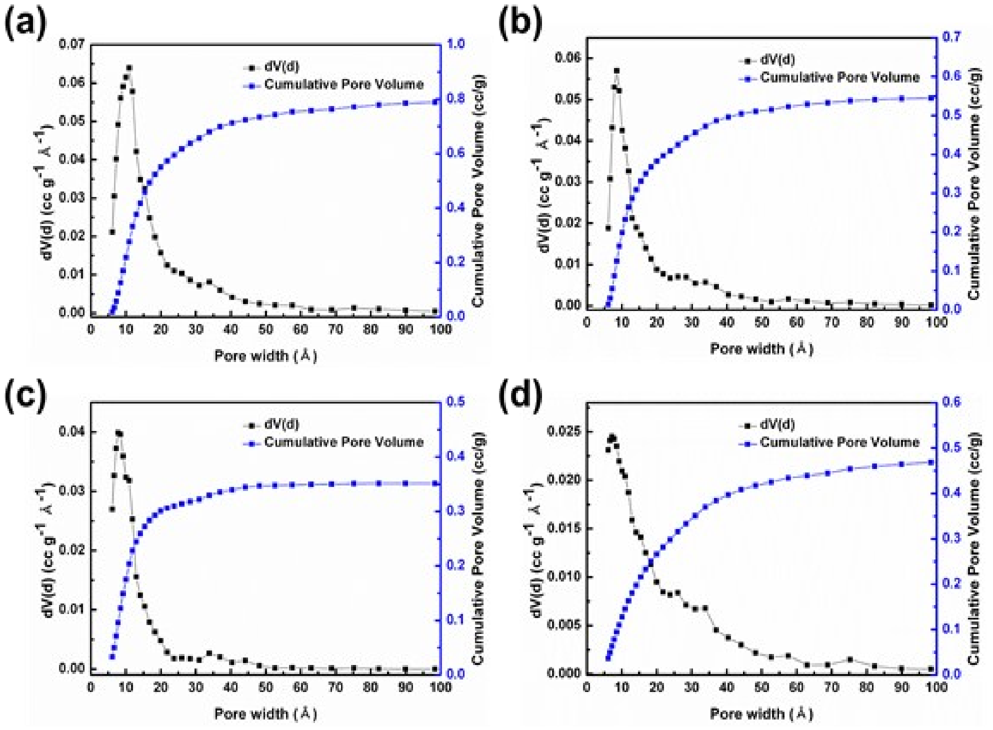

Fig. S5 Pore size distribution (black) and cumulative pore volume (blue) calculated by the QSDFT method for (a) H_2P PON, (b) CoP PON, (c) NiP PON, and (d) CuP PON.

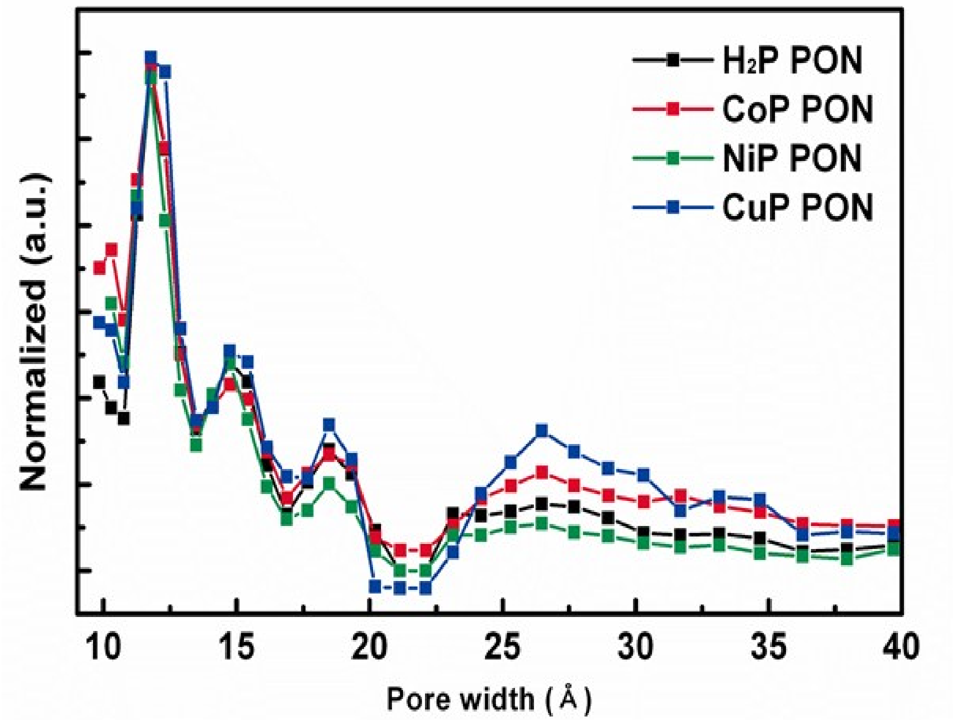

Fig. S6 Pore size distributions of MP PONs calculated by the NLDFT method.

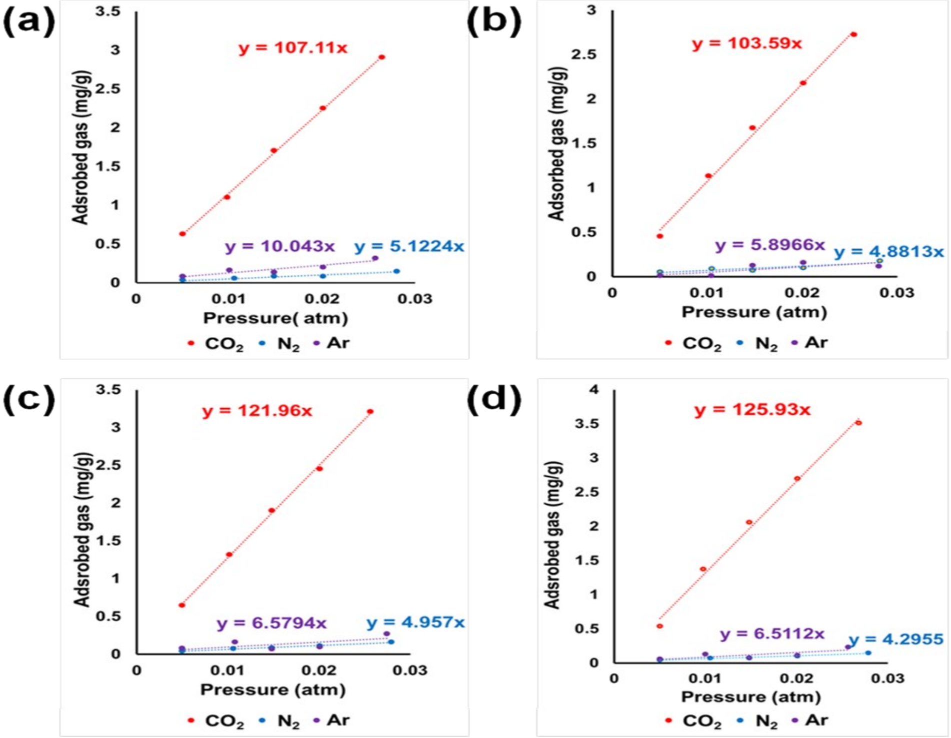

Fig. S7 Adsorption isotherms in the 0-0.025 atm range used to calculate the Henry's selectivty for CO_2, over N_2 and Ar for (a) H_2P, (b) CoP, (c) NiP, and (d) CuP PONs.

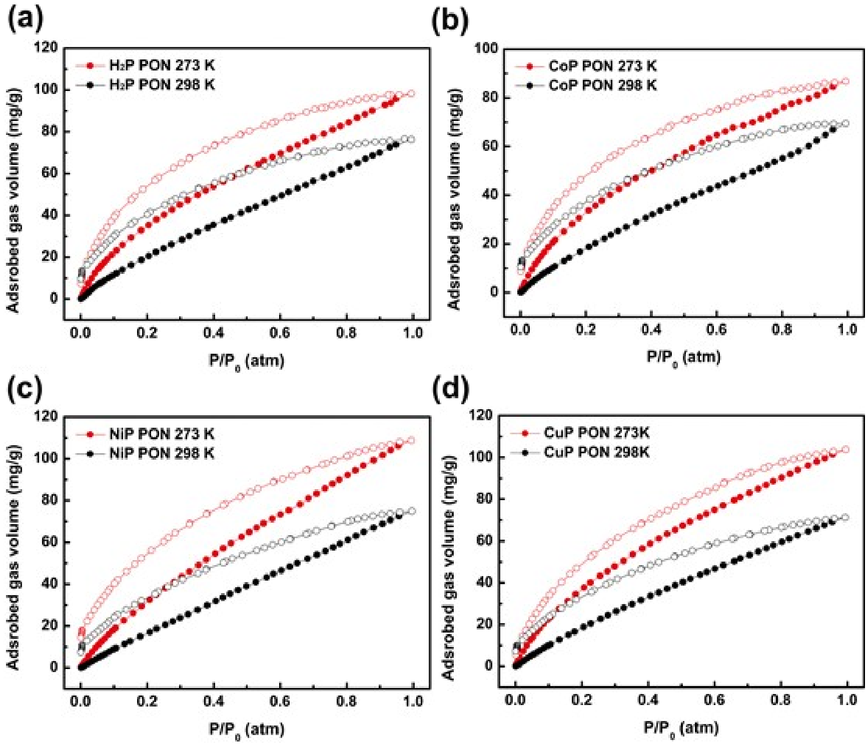

Fig. S8 CO_2 adsorption and desorption isotherms of (a) H_2P PON, (b) CoP PON, (c) NiP PON, and (d) CuP PON at 273 K and 298 K for heat of adsorption.