Supporting Information

Nitrogen-doped Ultrahigh Microporous Carbons Derived from Two Nitrogen-Containing Post-Cross-Linked Polymers for Efficient CO_2 Capture

Lishu Shao[a,b,*], Mingqiang Liu[b], Yafei Sang[b], Peng Zhan[a], Jienan Chen[a], Jianhan Huang[b,*]

[a] *Ministry of Forestry Bioethanol Research Center, School of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha, 410004, China*

[b] *College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China*

* Corresponding authors.

E-mail addresses: lishushao@csuft.edu.cn (L. Shao); jianhanhuang@csu.edu.cn (J. Huang).

S1. Materials

DVB, VP, and VIM were purchased from Xiya Chengdu Chemical Co. Ltd. DVB was purified with 5% NaOH and then dried by anhydrous magnesium sulfate. The initiator 2,2-azobis-(isobutyronitrile) (AIBN) was refined with ethanol. Poly(vinylalcohol) (PVA), toluene, benzyl alcohol (TA), and 1,2-dichloroethane (DCE) were analytical reagents and used as received. Potassium hydroxide (KOH) and anhydrous ferric (III) chloride ($FeCl_3$) was stored in a glove box.

S2. Characterization

Fourier transform infrared (FT-IR) spectra were tested on a Nicolet 6700 Fourier transform infrared spectrophotometer (Thermo Scientific Co., USA). Thermogravimetric analysis (TGA) was performed by a thermobalance (STA-499C, NETZSCH). The morphology was observed using a field emission scanning electron microscope (SEM, Nova Nano SEM 230) and high resolution transmission electron microscopy (HRTEM) (FEI Titan G2 60-300 microscope). The pore parameters was measured by N_2 adsorption-desorption isotherms at 77 K by Micromeritics ASAP 2020. Before the measurement, the samples (about 0.12 g) were degassed at 473 K under vacuum for 10 h to remove the impurities. The surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) model within the relative pressure range of P/P_0=0.05-0.30, the total pore volume (V_{total}) was calculated from the isotherms at P/P_0=0.99, the pore size distribution (PSD) and micropore volume (V_{micro}) were determined by the non-local density functional theory (NLDFT) method with the carbon slit-shaped pores. The Raman spectroscopy was accomplished by Renishaw Raman microscope with 532 nm and 50 mw laser excitation. The C, H, O, and N content were

obtained using CHNOS elemental analyzer (EA, Vario Micro Cube, Germany) and X-ray photoelectron spectroscopy (XPS) spectra (ESCALAB 250Xi using a monochromatized Al Ka X-ray source).

S3. Density functional theory (DFT) calculation

All of the first principle calculations were conducted on the basis of density functional theory (DFT) with the use of the DMol^3 code. The energy of the functional group and the interaction of carbon dioxide were calculated using the DFT calculation coupled with the van der Waals correct correction (DFT-D). Perdew, Burke, and Ernzerhof (PBE) within the generalized gradient approximation (GGA-PBE) were selected. The atomic orbit is described using double numeric polarization (DNP) basis set, which is comparable to 6-31G (d, p). The type of core processing is set up using a DFT half-core Pseudopots (DSPP) specifically designed for DMol^3 calculations. The real-space orbital global cutoff is 3.7 Å. The convergence threshold parameters for the optimization were 10^{-5} Hartree (energy), 2×10^{-3} Hartree (gradient), and 5×10^{-3} Hartree (displacement), respectively. Therefore, BSSE effects need not be taken into consideration for calculating the energies.

S4. The calculation for the isosteric heats of CO_2 adsorption

To further understand the interaction between CO_2 molecules and materials, the isosteric heats of CO_2 adsorption (Q_{st}) were calculated using the *Clausius-Clapeyron* equation from CO_2 adsorption isotherms at temperatures of 273 K and 298 K, Q_{st} is calculated according to Eq. 1.

$$Q_{\mathrm{st}} = \frac{RT_1T_2 \ln\left(P_2 / P_1\right)}{T_2 - T_1} \tag{1}$$

Where P_i represents the pressure from isotherm i, while T_i represents the corresponding

temperature of isotherm i. And R is the constant 8.314J K^{-1} mol^{-1}.

Here, the P_i was simulated with a virial-type expression (Eq. 2):

$$\ln(P) = \ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (2)$$

Where N is the amount adsorbed at pressure P, T is the temperature, a_i and b_i are temperature independent empirical parameters, and m and n determine the number of terms required to adequately describe the isotherm.

Table S1. The elemental analysis of polymers and porous carbons by EA and XPS

	C	N	H	O[a]
HPDV	89.60	0.60	7.90	1.90
PDVC1	63.68	0.48	3.06	32.78
PDVC2	69.50	0.58	2.51	27.41
PDVC3	77.40	0.09	3.20	19.31
HPDN	79.50	2.27	7.20	10.80
PDNC500	71.27	1.07	3.13	24.50
PDNC600	65.60	1.50	2.20	30.7
PDNC600[b]	79.92	2.38	/	17.70
PDNC700	54.23	0.67	3.41	41.69

[a] Calculated by the difference, O wt%=100%-C wt%- H wt%-N wt%, and the uncertainty of all elemental content ranged in 0.007 wt%-0.02 wt%.

[b] The elemental content was measured by XPS analysis, at.%, the uncertainty of the N content ranged in 0.005 at%-0.012 at%.

Table S2. Textural properties and the CO_2 uptake of various adsorbents

	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	CO_2 uptake at 273 K and 1 bar (mmol/g)	Selectivity		Reference
				Henry's law	IAST	
OMC	2255	/	3.00	/	12.8	52
TPC-1	1940	0.36	4.91	38	/	53
HCM-DAH-1-900-1	1392	/	4.90	17[a]	/	54
NPC-4-600	1518	0.54	4.70	16.6	34.5	27
NPC-2	1384	0.63	5.86	10.5	18.0	37
PC-2	1479	0.63	5.50	27.3	/	55
HCP2b-K700	2058	0.93	5.98	8.6	11.5	44
OTSS-2-550	2137	0.63	5.65	/	22.7	56
NPC-700-KOH	2616	1.14	5.45	11.2	14.2	43
SU-MAC-500	941	0.34	6.02	124	39	57
NDPC-20%	1923	0.92	6.16	9.0	11.9	36
NDPC-2-600	1211	0.55	6.79	18.4		58
SA-2-700	1759.5	0.66	6.82	/	23	59
R7-2T-10PEI	1190	0.42	6.80	115		48
NPC-2-600	1274	0.43	7.35	/	22.0	60
PC3-700	2110	0.78	7.82	/	/	61
AS-700-4-1	1643	0.63	8.00	/	/	62
PDVC3	1191	0.54	6.56	10.9	23.2	This work
PDNC600	978	0.44	6.34	11.7	34.3	This work

[a] The Henry selectivity is determined at 298 K.

Table S3. The Langmuir and Freundlich isotherm constants

T (K)	Sample	Langmuir model			Freundlich model		
		K_L (kPa^{-1})	Q_{max} (mmol/g)	R^2	1/n	K_F ((mmol/g)($kPa^{-1/n}$))	R^2
273	HPDV	0.3016	3.3471	0.9998	0.8583	0.7859	0.9997
	PDVC1	3.0019	6.1759	0.9945	0.4618	4.8723	0.9926
	PDVC2	2.4369	6.6857	0.9967	0.5005	4.9638	0.9925
	PDVC3	1.4373	10.9345	0.9983	0.6036	6.6940	0.9967
	HPDN	0.7065	2.0535	0.9981	0.7314	0.8705	0.9996
	PDNC500	3.0839	5.0392	0.9943	0.4529	3.9920	0.9909
	PDNC600	2.1173	9.0978	0.9963	0.5247	6.4468	0.9948
	PDNC700	1.3996	9.3352	0.9976	0.6051	5.6375	0.9973
298	HPDV	0.0482	8.4471	0.9999	0.9750	0.3897	0.9998
	PDVC1	1.2883	5.9876	0.9975	0.6206	3.4836	0.9979
	PDVC2	1.3561	5.9132	0.9981	0.6115	3.5207	0.9970
	PDVC3	0.7872	8.8461	0.9991	0.7136	3.9926	0.9987
	HPDN	0.3665	1.5179	0.9994	0.8325	0.4131	0.9996
	PDNC500	1.5658	4.4048	0.9976	0.5858	2.7988	0.9963
	PDNC600	1.1345	7.3941	0.9982	0.6429	4.0455	0.9979
	PDNC700	0.7735	7.6931	0.9989	0.7141	3.4318	0.9989

Table S4. CO_2 adsorption capacity and partition coefficient at different CO_2 partial pressure and 25 ^{0}C for carbonaceous materials

Sample	CO_2 adsorption capacity (mol kg^{-1})			Partition coefficient (mol kg^{-1} Pa^{-1})			Reference
	0.1 bar	0.5 bar	1 bar	0.1 bar	0.5 bar	1 bar	
PDVC3	0.75	2.49	3.98	0.000075	0.0000498	0.0000398	This work
N-doped carbon based on urea and petroleum coke	0.94	2.86	4.4	0.000094	0.0000572	0.000044	72
NPC-4-600	0.62	1.88	2.89	0.000062	0.0000376	0.0000289	27
NDPC-20%	0.64	2.16	3.68	0.000064	0.0000432	0.0000368	36
KOH-activated polymer-based carbon	0.81	2.69	4.0	0.000081	0.0000538	0.00004	73
NPC-2	0.60	2.06	3.34	0.00006	0.0000412	0.0000334	37
N-doped carbon fiber	N/A	N/A	3.5	N/A	N/A	0.000035	74
NPC-700-KOH	0.39	1.61	2.91	0.000039	0.0000322	0.0000291	43
HCP2b-K700	0.54	1.94	3.32	0.000054	0.0000388	0.0000332	44

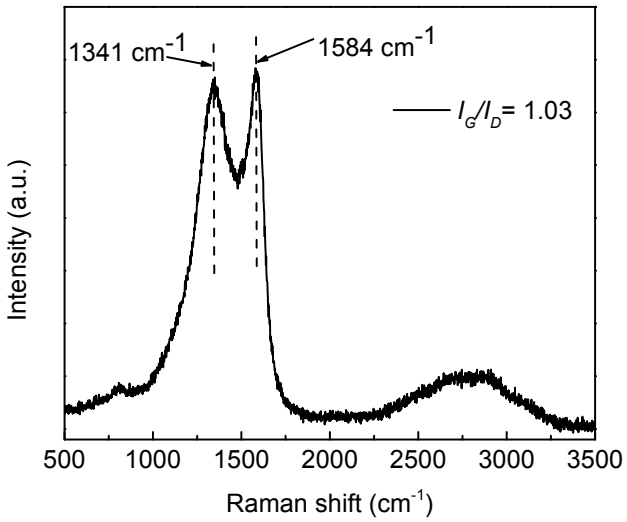


Figure S1. Raman spectra of PDVC3.

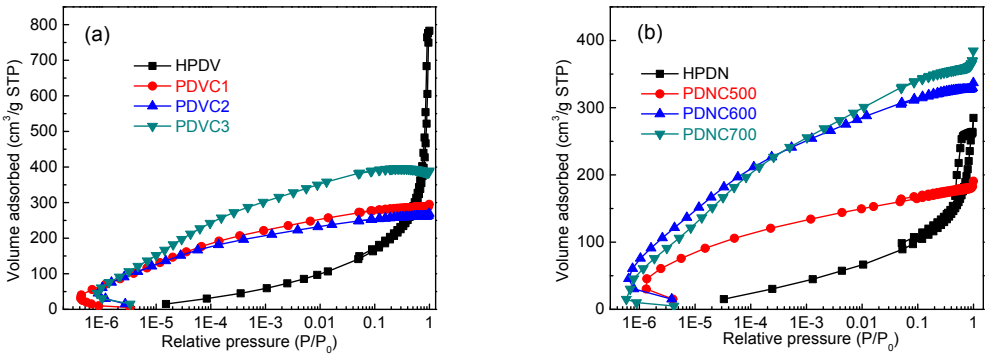


Figure S2. N_2 adsorption-desorption isotherms with semi-logarithmic form (a, b) of polymers and carbons.

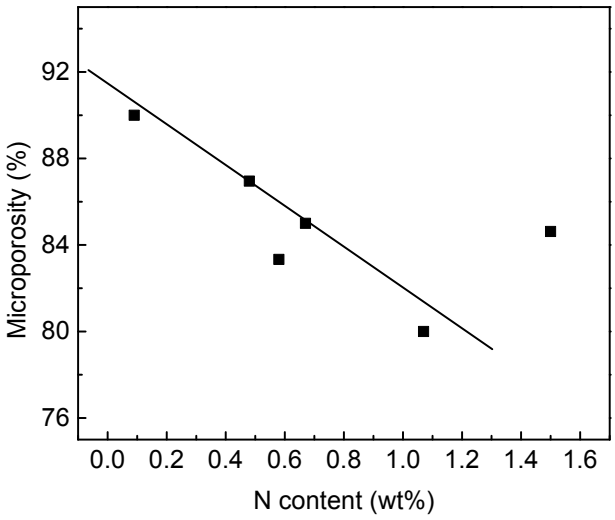


Figure S3. The relationship between microporosity and N content for carbon materials.

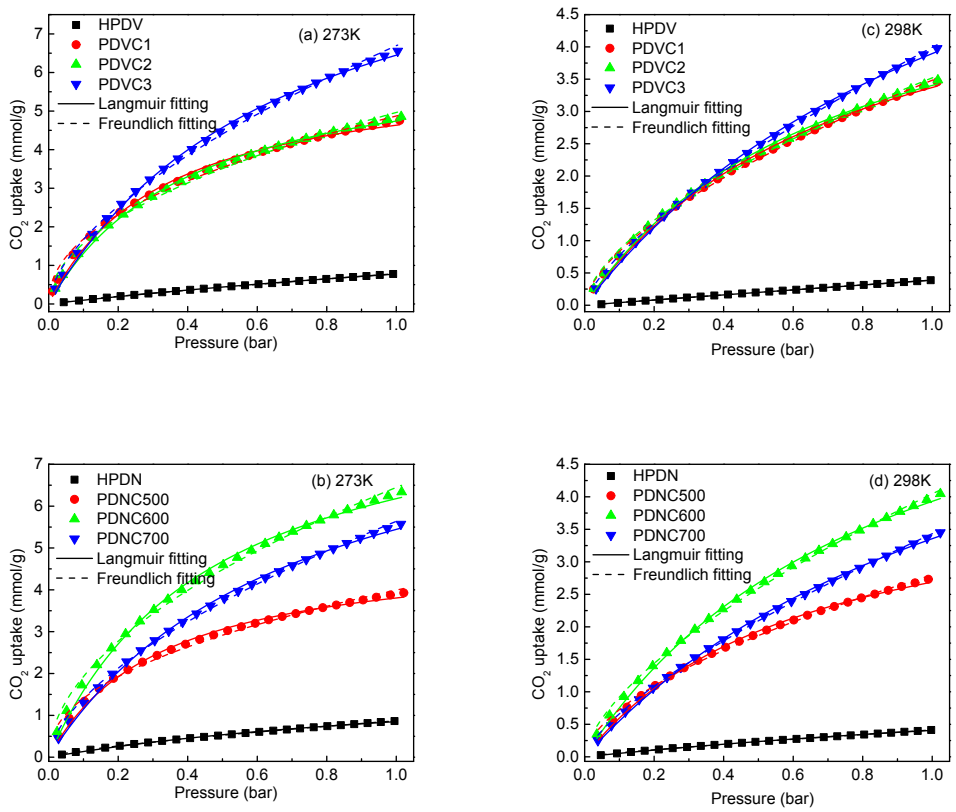


Figure S4. The Langmuir and Freundlich fitting of CO_2 adsorption isotherms on the polymers and porous carbons at 273 K (a, b) and 298 K (c, d).

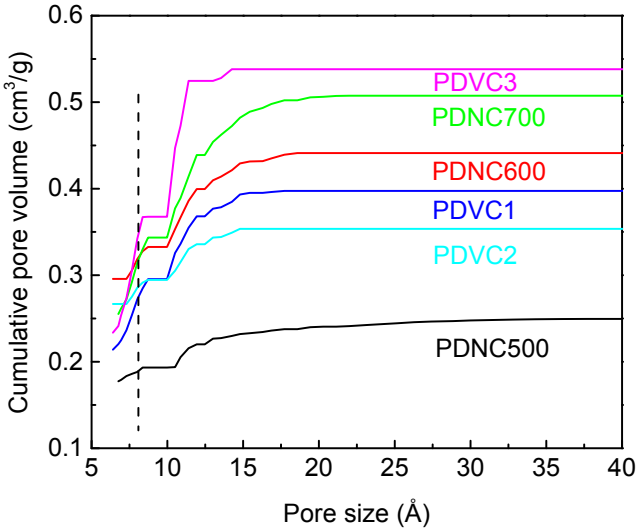


Figure S5. The cumulative pore volume of all carbons on different pore size.

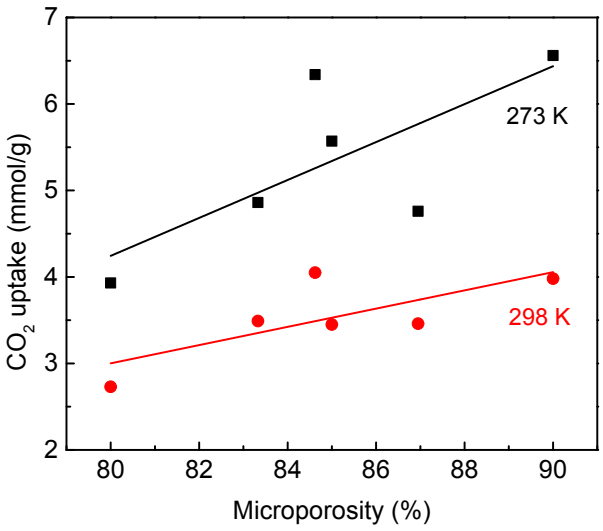


Figure S6. The relationship of CO_2 uptake with V_{micro}/V_{total} (microporosity) on the linear fitting for PDVCs and PDNCs porous carbons.

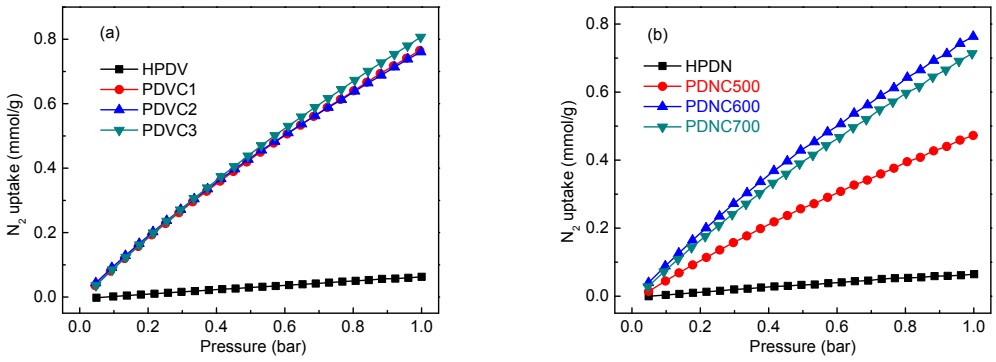
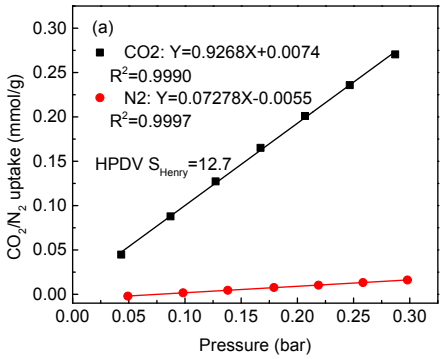
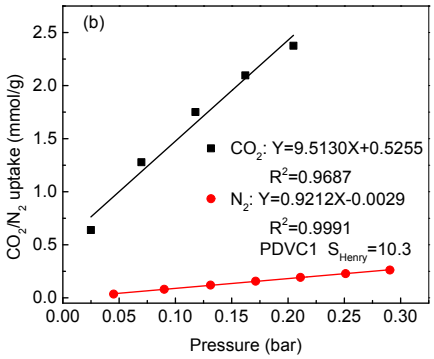
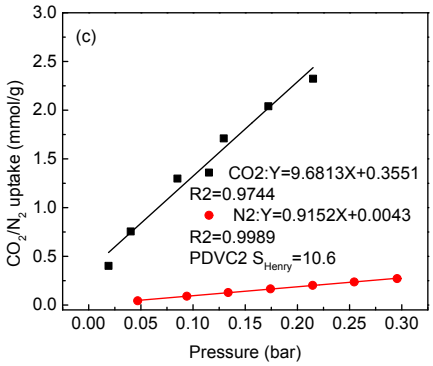
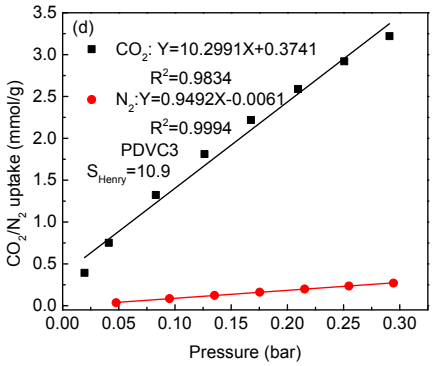


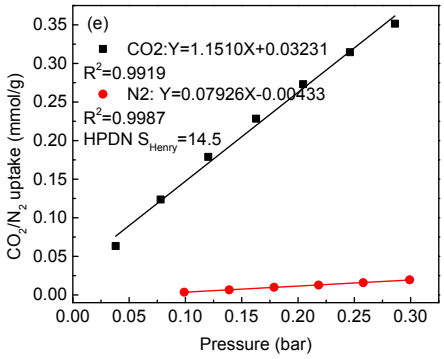
Figure S7. The N_2 adsorption isotherms of the polymers and porous carbons at 273 K and 0-1 bar (a) HPDV and PDVCs, and (b) HPDN and PDNCs.

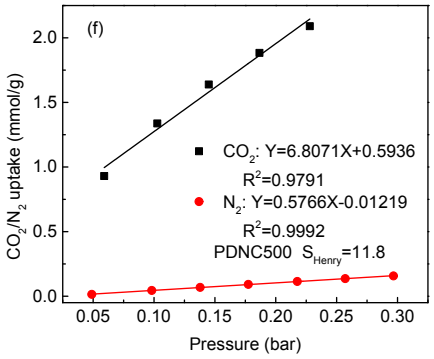

(a)
CO2: Y=0.9268X+0.0074
R2=0.9990
N2: Y=0.07278X-0.0055
R2=0.9997
HPDV S_Henry=12.7
CO2/N2 uptake (mmol/g)
Pressure (bar)


(b)
CO2: Y=9.5130X+0.5255
R2=0.9687
N2: Y=0.9212X-0.0029
R2=0.9991
PDVC1 S_Henry=10.3
CO2/N2 uptake (mmol/g)
Pressure (bar)


(c)
CO2:Y=9.6813X+0.3551
R2=0.9744
N2:Y=0.9152X+0.0043
R2=0.9989
PDVC2 S_Henry=10.6
CO2/N2 uptake (mmol/g)
Pressure (bar)


(d)
CO2: Y=10.2991X+0.3741
R2=0.9834
N2:Y=0.9492X-0.0061
R2=0.9994
PDVC3
S_Henry=10.9
CO2/N2 uptake (mmol/g)
Pressure (bar)


(e)
CO2:Y=1.1510X+0.03231
R2=0.9919
N2: Y=0.07926X-0.00433
R2=0.9987
HPDN S_Henry=14.5
CO2/N2 uptake (mmol/g)
Pressure (bar)


(f)
CO2: Y=6.8071X+0.5936
R2=0.9791
N2: Y=0.5766X-0.01219
R2=0.9992
PDNC500 S_Henry=11.8
CO2/N2 uptake (mmol/g)
Pressure (bar)

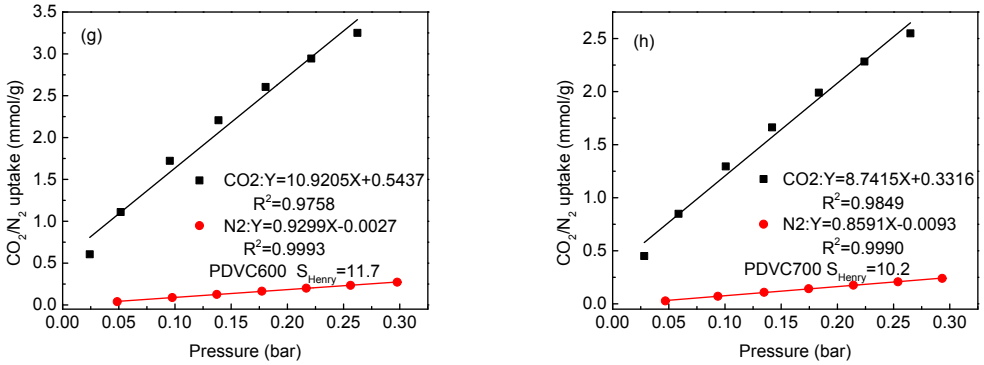


Figure S8. CO_2/N_2 selectivity based on Henry' law for the polymers and porous carbons.