Hierarchical porous materials via assembly of nitrogen-enriched polymer nanoparticles for efficient and selective CO_2 capture

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Materials. All chemicals were purchased from commercial sources (Sigma-Aldrich or Acros) and used without further purification unless otherwise stated. Pyrrole monomer was freshly distilled prior to use.

Characterization. The size distribution of the polymer nanoparticles was determined by dynamic light scattering (DLS) equipped with a Zetasizer Nano-ZS (He-Ne laser wavelength at 633nm). Field-emission scanning electron microscopy (FE-SEM) was performed on a FEI-MAGELLAN 400 FE-SEM operating at an accelerating voltage of 5.0 kV with energy dispersive X-ray spectrometer (EDS, Bruker, energy resolution of 123 eV). Specimens were mounted in aluminum stubs using carbon tapes and then coated with 3 nm Iridium. Transmission electron microscopy (TEM) measurements were performed on Titan 80–300 (FEI, 300 kV FEG TEM with point resolution 0.2 nm). Nitrogen absorption/desorption isotherms were recorded using Micromeritics ASAP 2020 static volumetric analyzer at -196 ^oC. The samples were degassed at 150 ^oC for 2 h prior to the measurements to ensure complete removal of residue moisture and gases. The specific surface area (S_{BET}) was calculated by Brunauer-Emmett-Teller method from adsorption data with partial pressure (P/P_0) range of 0.05-0.20. The total pore volume

(V_{total}) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.995. Micropore surface area (S_{micro}) and micropore volume (V_{micro}) were calculated *via* *t*-plot method. The pore size distribution was determined *via* non-local density functional theory (NLDFT) from nitrogen sorption data and assuming slit pore model. The CO_2 absorption isotherms were measured using Micromeritics ASAP 2020 static volumetric analyzer at 0 °C, 25 °C, and 45 °C. The CO_2 adsorption capacities were recorded as an adsorbed volume under standard temperature and pressure (STP). The Isosteric heat of adsorption (Q_{st}) values were calculated using the CO_2 adsorption isotherms measured at 0 °C, 25 °C, and 45 °C based on the Clausius-Clapeyron equation. X-ray photoelectron spectroscopy (XPS) was performed using PHI VersalProbe II equipped with monochromatic X-ray beam (Al Kα, 1486.6 eV). Fitting of XPS spectra was performed using Gaussian-Lorentzian peak shapes after Shirley-type background subtraction.[1] Elemental analysis was conducted by Midwest Microlab, LLC with triplicate measurements. Thermal gravimetric analysis (TGA) was performed using TGA/DSC-1 (Mettler Toledo) under N_2 flow at a heating rate of 10 °C/min

Synthesis of polypyrrole (PPy) *via* microemulsion polymerization. Sodium dodecylsulfate (SDS) (34.56 g, 0.135 mol), potassium persulfate (KPS) (12.12 g, 0.045 mol) and 1200 mL of DI water were added into 3 L three-necked round bottom flask equipped for stirring and the mixture solution was purged with N_2 for 30 min at 35 °C. After the mixture became clear, freshly distilled pyrrole (3.0 g, 0.045 mol) monomer was added into the reaction *via* syringe in one portion and the reaction color was turned to black within 5 min. After further stirring of the reaction for 1 h at 35 °C, the reaction was quenched by pouring 1 L of methanol into the reaction flask and the polymer was precipitated. The polymer was filtered using gravimetric filtration and washed with 1 L of methanol and 2 L of hot water. Upon the filtration, the polymer was transferred to 300 mL beaker before it is dried and the beaker was immersed into liquid nitrogen bath for 30 min followed by the sublimation of water using lyophilizer at -50 ^{o}C under high vacuum (0.03 mmHg) to ensure that the polymer preserves spherical shape after drying. The polymer was further purified by Soxhlet extractor using methanol for 24 h and dried under vacuum at 90 ^{o}C for overnight to yield 2.6 g of black powder.

KOH activation. The mixture of polymer and KOH (1:1, 1:2 and 1:4 ratios by weight) in deionized water was stirred for 30 min, transferred to combustion boat and dried at 90 ^{o}C for 4 h. The mixture was heated to target temperatures (500, 600 and 700 ^{o}C) with a rate of 3 ^{o}C/min and maintained at the temperature for 1 h under N_2 flow followed by natural cooling. The activated polymer was then rinsed with 1 M HCl followed by hot DI water until the neutral pH. The polymer was further dried under vacuum at 90 ^{o}C for 24 h.

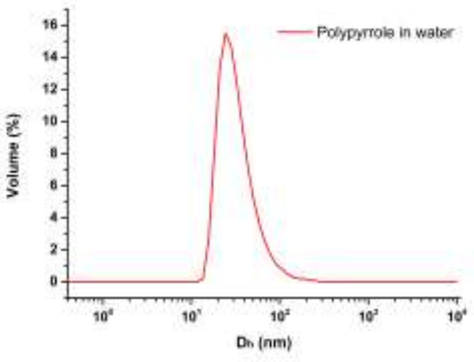


Figure S1. Hydrodynamic diameter (*D_h*) and size distribution of PPy nanoparticles in water determined by DLS.

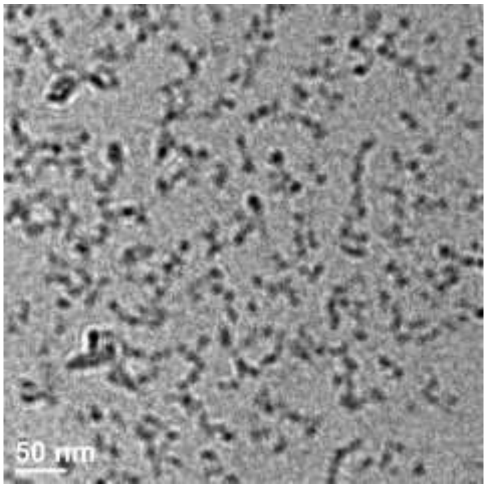


Figure S2. HR-TEM image of PPy nanoparticles.

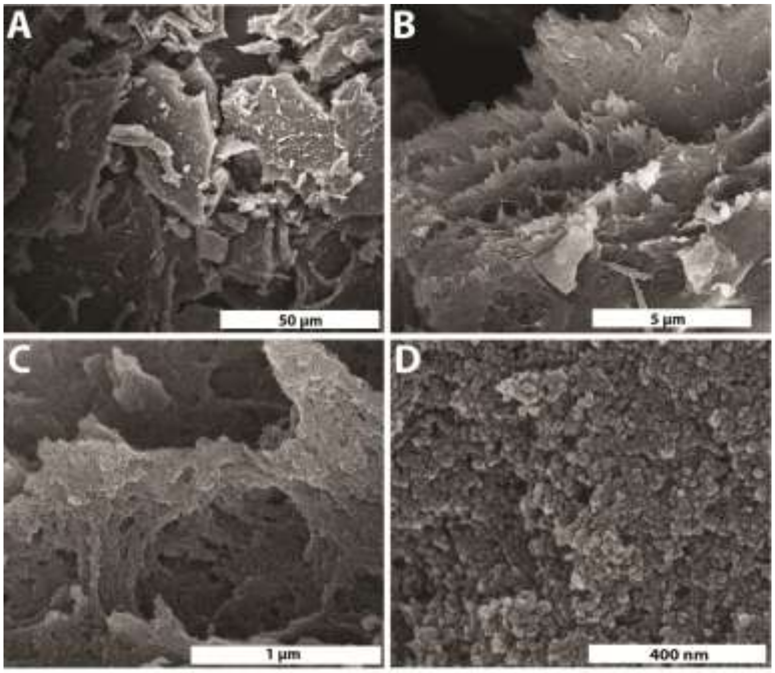


Figure S3. SEM images of PPy prepared *via* o/w microemulsion.

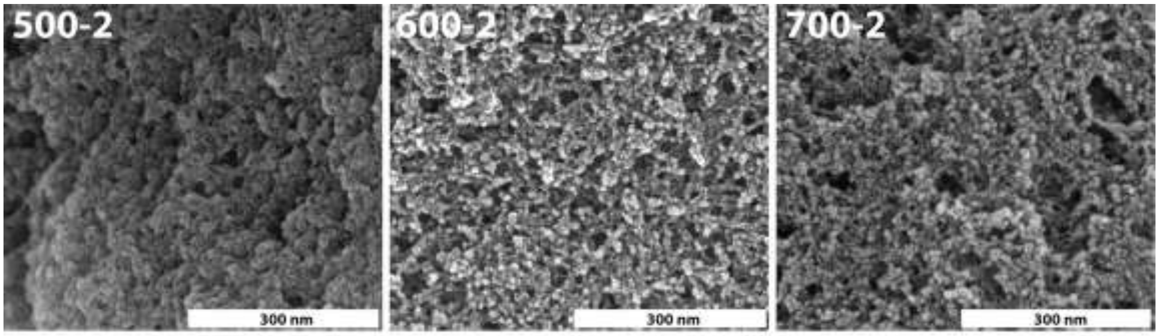


Figure S4. SEM images of PPy nanoparticle frameworks after chemical activation under various temperatures and constant weight ratio of KOH:PPy = 2.

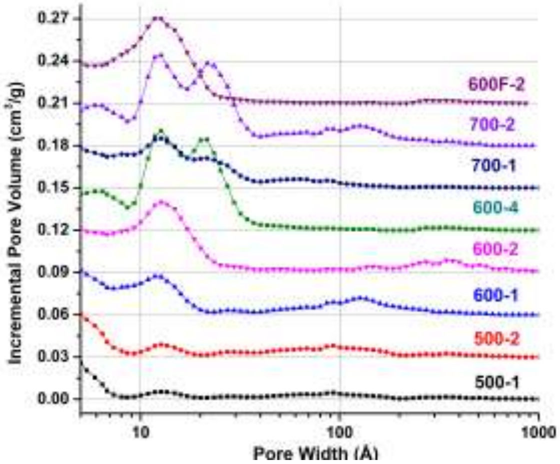


Figure S5. Pore size distribution of porous PPy materials obtained from NLDFT analysis; spectra were offset vertically by 0.03 cm^3/g for clarity.

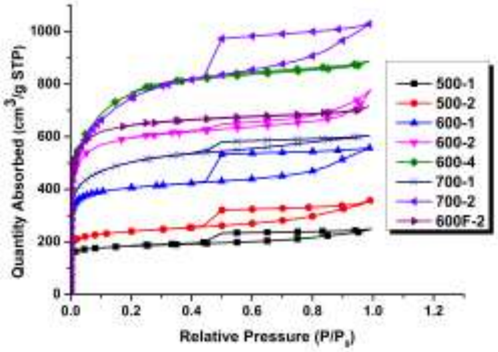


Figure S6. N_2 adsorption/desorption isotherms of activated porous materials at 77K.

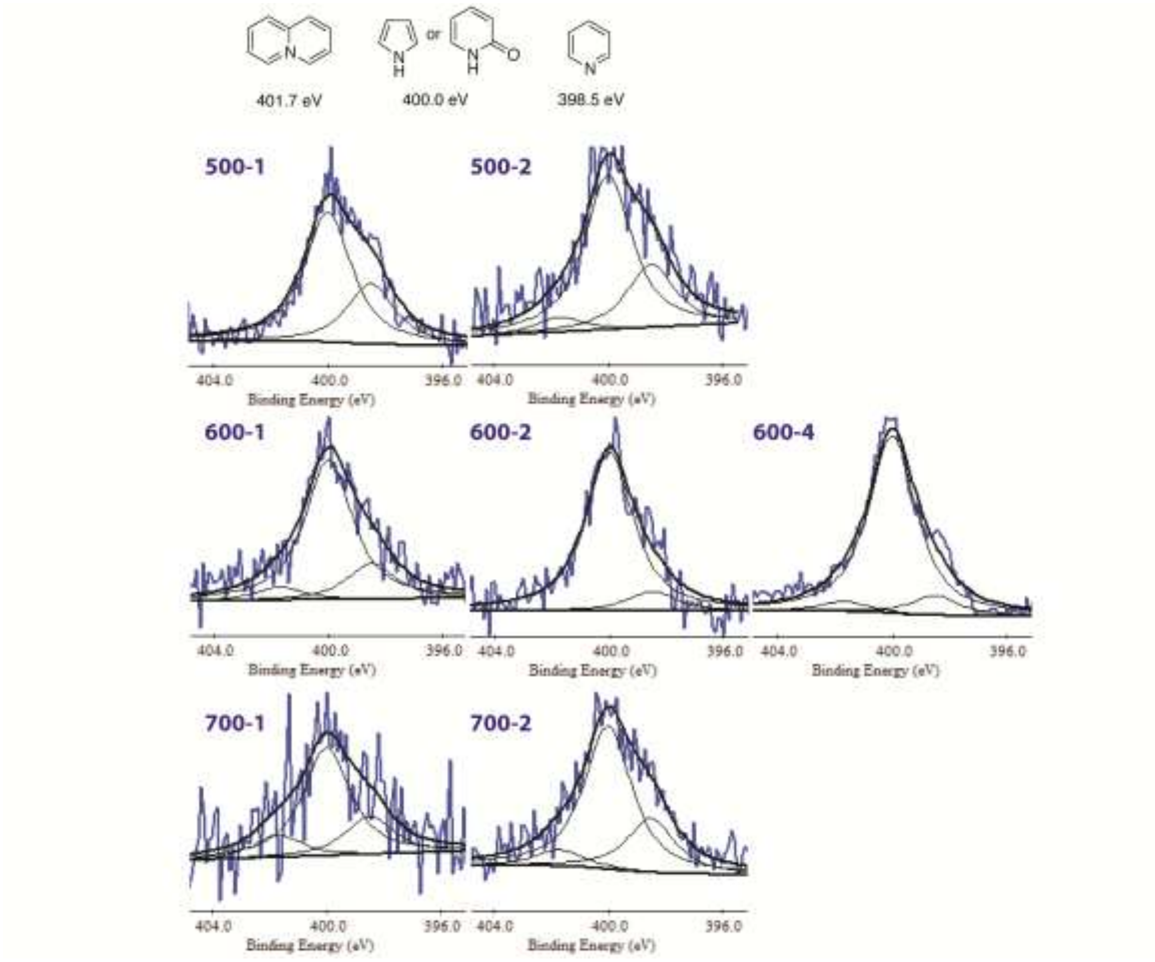


Figure S7. N 1s XPS spectra of activated porous PPy materials.

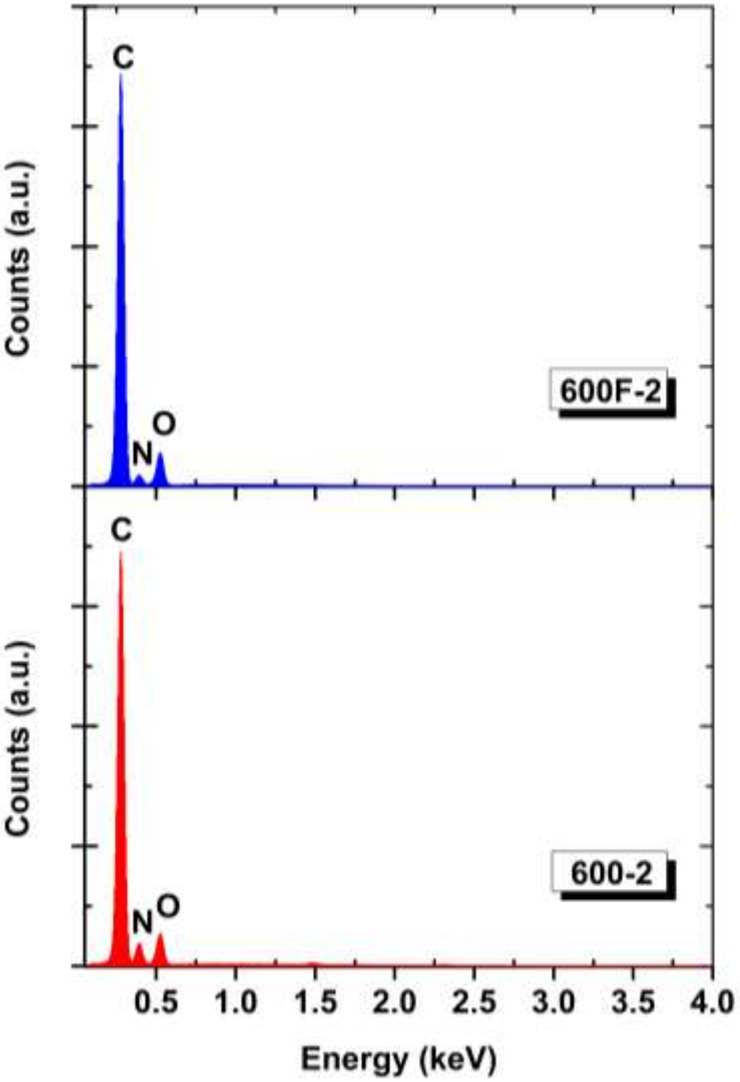


Figure S8. SEM-EDX spectra of 600-2 and 600F-2.

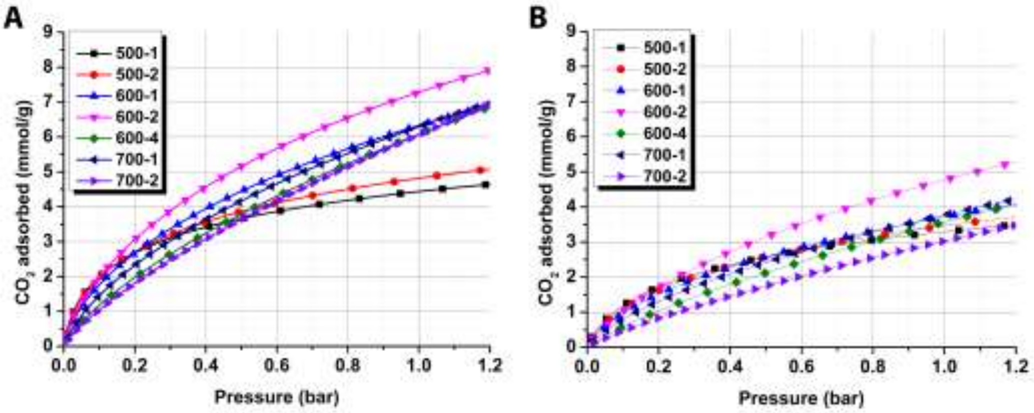


Figure S9. CO_2 adsorption isotherms of various activated porous materials at (A) 0 °C and (B) 25 °C.

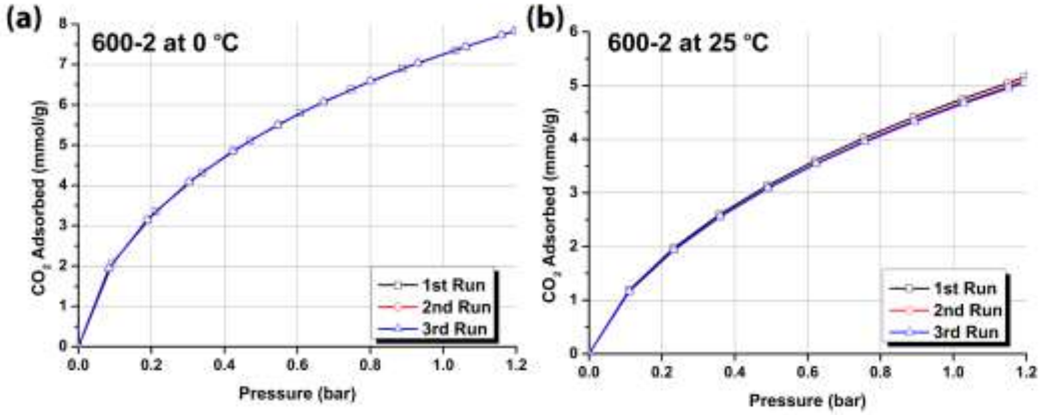


Figure S10. Three cycles of CO_2 adsorption isotherms for sample **600-2** at 0 °C and 25 °C.

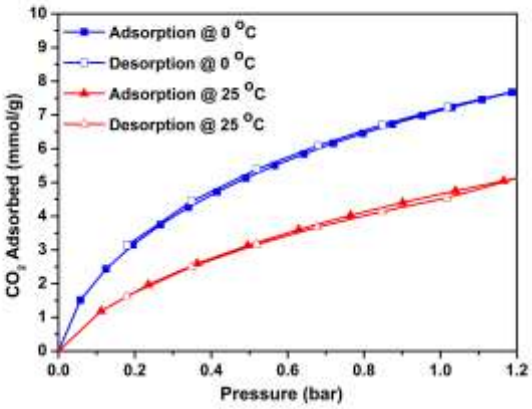


Figure S11. CO_2 adsorption and desorption isotherms of sample **600-2** at 0 °C and 25 °C.

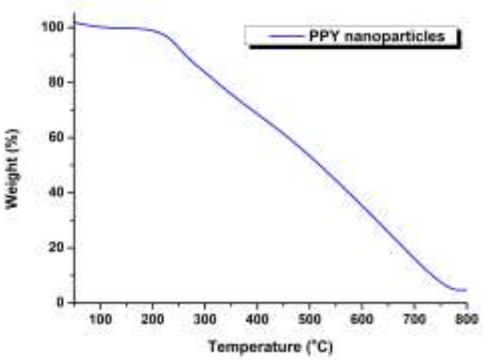
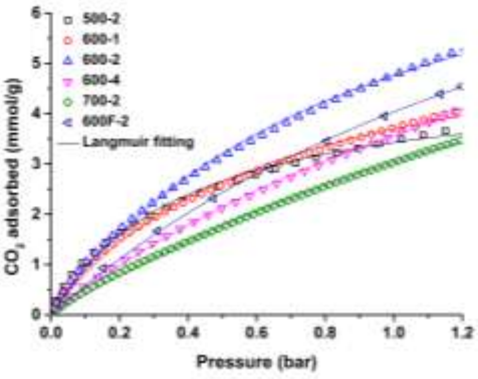
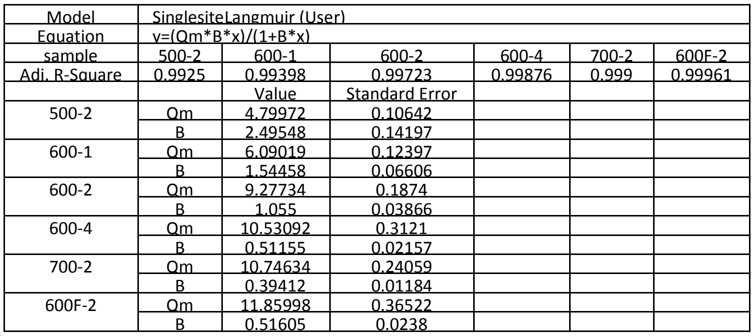


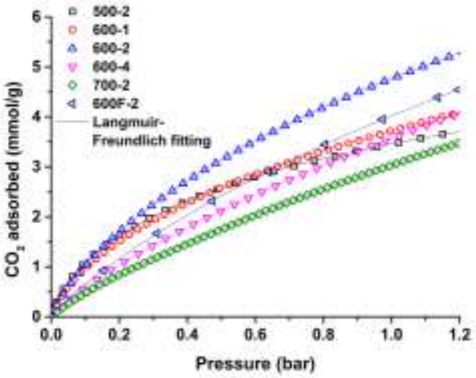
Figure S12. Thermo-gravimetric analysis (TGA) of PPy nanoparticle frameworks prepared *via* o/w microemulsion.

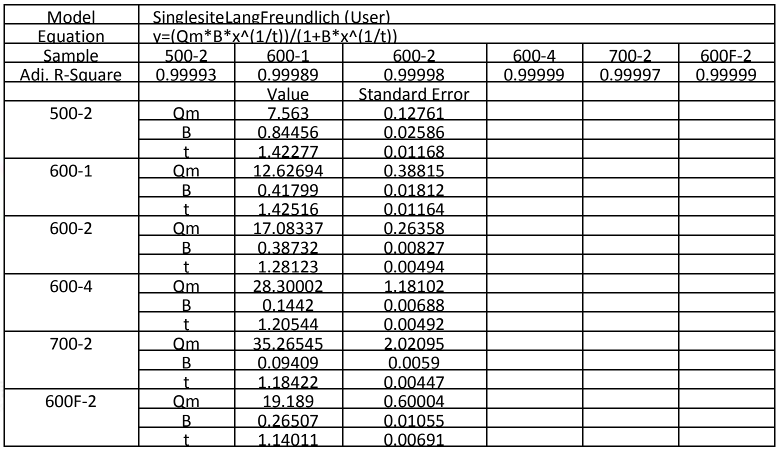




Model	SinglesiteLangmuir (User)					
Equation	y=(Qm*B*x)/(1+B*x)					
sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	0.9925	0.99398	0.99723	0.99876	0.999	0.99961
		Value	Standard Error			
500-2	Qm	4.79972	0.10642			
	B	2.49548	0.14197			
600-1	Qm	6.09019	0.12397			
	B	1.54458	0.06606			
600-2	Qm	9.27734	0.1874			
	B	1.055	0.03866			
600-4	Qm	10.53092	0.3121			
	B	0.51155	0.02157			
700-2	Qm	10.74634	0.24059			
	B	0.39412	0.01184			
600F-2	Qm	11.85998	0.36522			
	B	0.51605	0.0238			

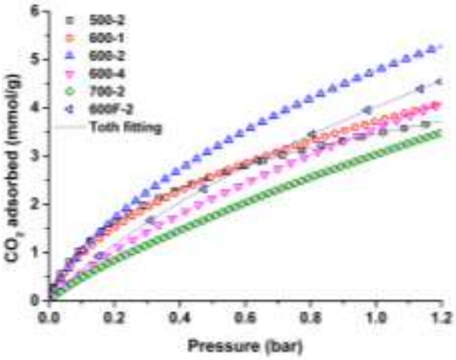
Figure S13. Langmuir fitting of CO_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.

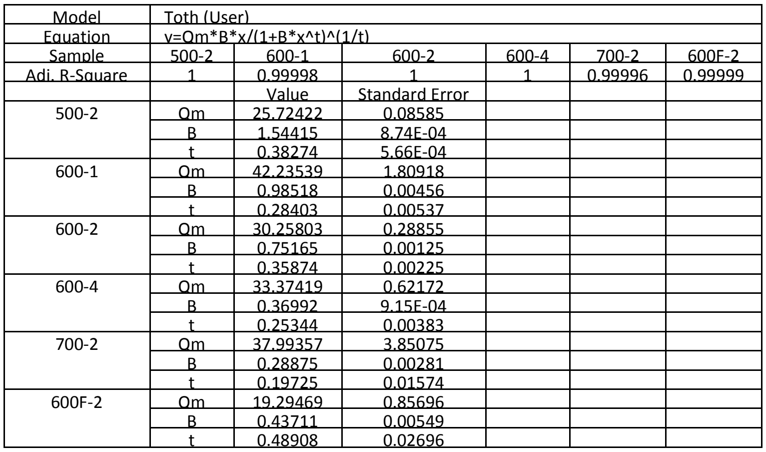




Model	SinglesiteLangFreundlich (User)					
Equation	y=(Qm*B*x^(1/t))/(1+B*x^(1/t))					
Sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	0.99993	0.99989	0.99998	0.99999	0.99997	0.99999
		Value	Standard Error			
500-2	Qm	7.563	0.12761			
	B	0.84456	0.02586			
	t	1.42277	0.01168			
600-1	Qm	12.62694	0.38815			
	B	0.41799	0.01812			
	t	1.42516	0.01164			
600-2	Qm	17.08337	0.26358			
	B	0.38732	0.00827			
	t	1.28123	0.00494			
600-4	Qm	28.30002	1.18102			
	B	0.1442	0.00688			
	t	1.20544	0.00492			
700-2	Qm	35.26545	2.02095			
	B	0.09409	0.0059			
	t	1.18422	0.00447			
600F-2	Qm	19.189	0.60004			
	B	0.26507	0.01055			
	t	1.14011	0.00691			

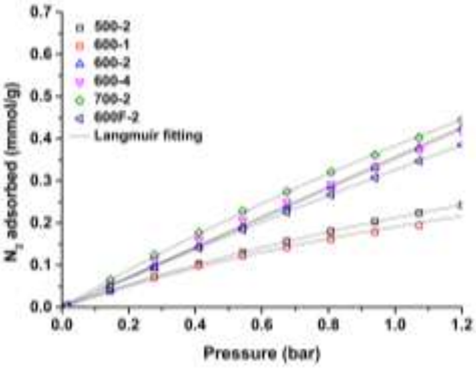
Figure S14. Langmuir-Freundlich fitting of CO_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.





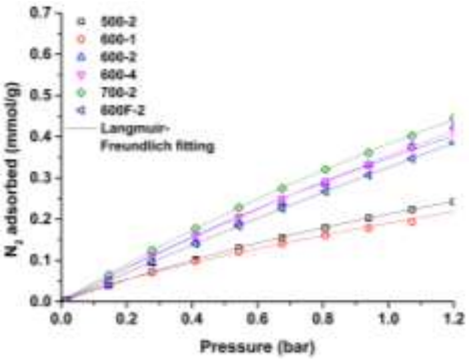
Model	Toth (User)					
Equation	y=Qm*B*x/(1+B*x^t)^(1/t)					
Sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	1	0.99998	1	1	0.99996	0.99999
		Value	Standard Error			
500-2	Qm	25.72422	0.08585			
	B	1.54415	8.74E-04			
	t	0.38274	5.66E-04			
600-1	Qm	42.23539	1.80918			
	B	0.98518	0.00456			
	t	0.28403	0.00537			
600-2	Qm	30.25803	0.28855			
	B	0.75165	0.00125			
	t	0.35874	0.00225			
600-4	Qm	33.37419	0.62172			
	B	0.36992	9.15E-04			
	t	0.25344	0.00383			
700-2	Qm	37.99357	3.85075			
	B	0.28875	0.00281			
	t	0.19725	0.01574			
600F-2	Qm	19.29469	0.85696			
	B	0.43711	0.00549			
	t	0.48908	0.02696			

Figure S15. Toth fitting of CO_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.



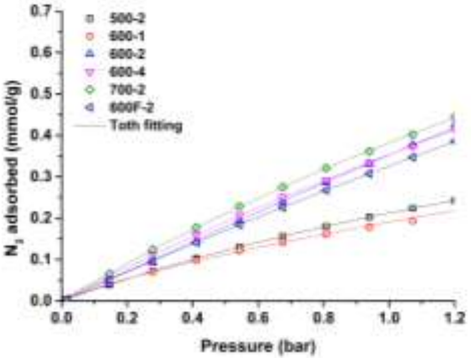
Model	SinglesiteLangmuir (User)					
Equation	y=(Qm*B*x)/(1+B*x)					
Sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	0.99999	0.99484	0.99991	0.9998	0.99967	0.99998
		Value	Standard Error			
500-2	Qm	0.84863	0.00717			
	B	0.33372	0.00366			
600-1	Qm	0.6324	0.08217			
	B	0.43301	0.07776			
600-2	Qm	3.36521	0.20125			
	B	0.1264	0.00845			
600-4	Qm	2.5076	0.1606			
	B	0.16435	0.01212			
700-2	Qm	2.01009	0.11915			
	B	0.23487	0.0169			
600F-2	Qm	4.05724	0.13619			
	B	0.08735	0.00317			

Figure S16. Langmuir fitting of N_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.



Model	SinglesiteLangFreundlich (User)					
Equation	y=(Qm*B*x^(1/t))/(1+B*x^(1/t))					
Sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	0.99997	0.99558	0.9999	0.99982	0.99961	0.99998
		Value	Standard Error			
500-2	Qm	0.83304	0.03658			
	B	0.34214	0.02022			
	t	1	0.01022			
600-1	Qm	2.6529	6.79504			
	B	0.07738	0.21374			
	t	1.2226	0.1756			
600-2	Qm	3.2998	0.78307			
	B	0.1292	0.03469			
	t	1	0.02181			
600-4	Qm	3.63549	1.33585			
	B	0.10776	0.04394			
	t	1.03687	0.02944			
700-2	Qm	1.95354	0.46532			
	B	0.24334	0.07227			
	t	1	0.04028			
600F-2	Qm	3.99709	0.56633			
	B	0.08878	0.01372			
	t	1	0.00908			

Figure S17. Langmuir-Freundlich fitting of N_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.



Model	Toth (User)					
Equation	y=Qm*B*x/(1+B*x^t)^(1/t)					
Sample	500-2	600-1	600-2	600-4	700-2	600F-2
Adj. R-Square	0.99999	0.9958	0.9999	0.99985	0.99963	0.99998
		Value	Standard Error			
500-2	Qm	0.84585	0.02359			
	B	0.33438	0.0066			
	t	1.00639	0.05176			
600-1	Qm	1.9304	4.34742			
	B	0.3269	0.08495			
	t	0.23615	0.447			
600-2	Qm	3.51913	0.48257			
	B	0.12237	0.01362			
	t	0.87689	0.31722			
600-4	Qm	3.11548	0.56204			
	B	0.14458	0.01533			
	t	0.55732	0.25091			
700-2	Qm	2.10873	0.36702			
	B	0.22787	0.02856			
	t	0.89662	0.3345			
600F-2	Qm	4.15857	0.28683			
	B	0.08567	0.00514			
	t	0.92213	0.18145			

Figure S18. Toth fitting of N_2 adsorption isotherms of porous materials at 25 ^{o}C and fitting parameters.

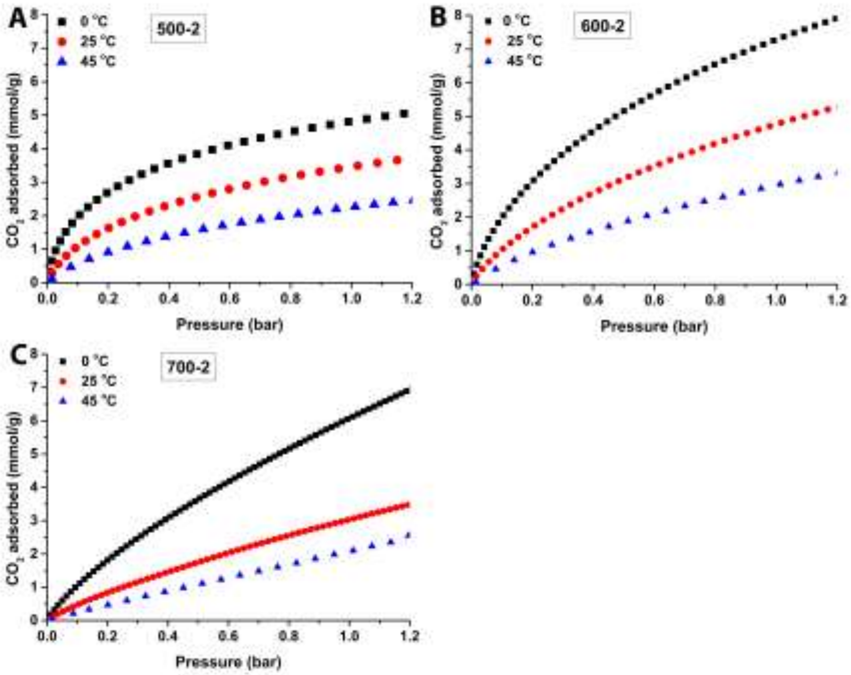


Figure S19. CO_2 adsorption isotherms of porous materials (A) 500-2, (B) 600-2, and (C) 700-2 at 0 °C, 25 °C, and 45 °C.

Table S1. Median pore width in the range of micropores determined by Horvath-Kawazoe method.

	500-1	500-2	600-1	600-2	600-4	700-1	700-2	700-4
Median pore width (nm)	0.62	0.60	0.70	0.67	0.79	0.75	0.84	0.90

Table S2. CO_2/N_2 selectivity of various porous PPy materials using ideal adsorbed solution theory (IAST) method[2] after fitting isotherms with Langmuir(L)[3], Langmuir-Freundlich(LF)[4], and Toth[4a] models.

	L[a]	LF[a]	Toth[a]
500-2	41.6	41.6	41.9
600-1	42.1	42.3	42.5
600-2	26.5	25.9	26.2
600-4	15.7	15.2	15.2
700-2	11.7	11.1	11.2
600F-2	18.6	18.6	18.5

a. S_{IAST} (selectivity of CO_2/N_2) = $(q_1/q_2)/(p_1/p_2)$, where q_1=CO_2 adsorbed amount at 0.15 bar at 25 °C, q_2= N_2 adsorbed amount at 0.85 bar at 25 °C, p_1=0.15 bar, p_2=0.85 bar.

Table S3. Elemental analysis data of typical porous PPy materials

	C %	N %	H %
1	58.97	15.08	4.40
500-1	56.30	11.78	2.40
500-2	55.92	11.46	2.67
600-1	66.67	9.75	0.85
600-2	71.54	8.95	1.17
600-4	73.11	7.27	1.05
700-1	58.41	4.81	1.59
700-2	81.43	3.87	0.70
F1	54.01	15.80	3.45
600F-2	76.18	6.11	1.09

References

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