Supporting Information

Modulating the porosity of activated carbons via pre-mixed precursors for simultaneously enhanced gravimetric and volumetric methane uptake

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Table S1. Elemental composition and O/C atomic ratio of a range of activatable biomass precursors.

Biomass souce	C [%]	H [%]	O [%]	(O/C)[a]	Reference
Eucalyptus sawdust	46.4	5.8	47.8	0.773	35
Seaweed[b]	39.6	5.9	51.6	0.977	19
Camellia Japonica	46.2	5.4	48.4	0.786	25
Cellulose	44.4	6.2	49.4	0.830	35
ACDS carbon	78.5	4.0	16.3	0.156	This work
CNL carbon	77.7	3.1	19.2	0.185	This work
Polypyrrole[b]	55.5	2.7			This work

[a]Atomic ratio, [b]Seaweed contains 2.9 wt% N, [c]Polypyrrole contains 16 wt% N.

Table S2. Pore size distribution maxima of activated carbons derived from single precursors (Polypyrrole (PPY), CNL carbon and ACDS carbon) and pre-mixed mixtures of the precursors.

Sample	Pore size maxima (Å)
PPY4800	12/27
CNL4800	8/12/20
PPYCNL124	12/23
PPYCNL114	12/27
PPYCNL214	12/27
ACDS4800	6/12
PPYDS124	11/22
PPYDS114	12/25
PPYDS214	12/27

Table S3. Surface area and level of mesoporosity of activated carbons prepared from precursors with varying atomic O/C ratio. All the activated carbons were prepared at activation temperature of 800°C and KOH/precursor ratio of 4.

Sample	Precursor	O/C ratio	Surface area[a] (m^2 g^{-1})	Meso SA (%)
ACDS4800	ACDS carbon	0.156	2609 (1825)	30
CNL4800	CNL carbon	0.185	2134 (1819)	15
SD4800	Sawdust hydrochar	0.483	2783 (694)	75
ACGR-4800	Grass hydrochar	0.517	2957 (1578)	47
SD4800D	Raw sawdust	0.773	2980 (478)	84

The values in the parenthesis refer to: [a]micropore surface area.

Table S4. Total gravimetric methane uptake (expressed as g g^{-1}) of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY) and CNL4800 (CNL carbon) and from pre-mixed precursors containing PPY and CNL carbon at various weight ratios.

Sample	Total gravimetric methane uptake (g g^{-1})		
	35 bar	65 bar	100 bar
PPY4800	0.25	0.34	0.42
CNL4800	0.21	0.26	0.31
PPYCNL124	0.23	0.30	0.36
PPYCNL114	0.25	0.35	0.43
PPYCNL214	0.26	0.36	0.46
ACDS4800	0.20	0.25	0.29
PPYDS124	0.23	0.30	0.36
PPYDS114	0.24	0.32	0.39
PPYDS214	0.25	0.34	0.42

Table S5. Gravimetric and volumetric methane uptake at 25 ^{o}C and pressure of 35 bar for PPY4800, CNL4800, ACDS4800 and PPYCNL124 compared to the best performing carbons

Sample	Total uptake g g^{-1}	Total uptake cm^3 (STP) cm^{-3}	Reference
PPY4800	0.25	129	This work
ACDS4800	0.20	194	This work
CNL4800	0.21	194	This work
PPYCNL124	0.23	164	This work
DO00-3:1_700	0.18	184	10
LMA738	0.17	165	53
BEA-ZTC	0.16	148	54
BEA-ZTC-873	0.17	165	54
AX21	0.16	154	5

Table S6. Total volumetric methane uptake and working capacity of activated carbons derived from single precursor carbons (PPY4800, and CNL4800) and from pre-mixed precursors compared to $_{mono}$HKUST-1 and $_{mono}$UiO-66_D.

Sample	Total volumetric methane uptake[a] (cm^3 (STP) cm^{-3})		
	35 bar	65 bar	100 bar
PPY4800	129 (90)	176 (137)	215 (177)
CNL4800	194 (127)	249 (182)	291 (224)
PPYCNL124	164 (113)	217 (167)	260 (209)
PPYCNL114	138 (97)	189 (148)	232 (191)
PPYCNL214	132 (94)	183 (146)	229 (192)
ACDS4800	194 (122)	243 (171)	282 (209)
PPYDS124	150 (103)	199 (152)	240 (193)
PPYDS114	159 (110)	211 (162)	254 (205)
PPYDS214	141 (100)	192 (151)	234 (193)
$_{mono}$HKUST-1	224 (147)	261 (191)	275 (235)
$_{mono}$UiO-66_D	143 (100)	211 (172)	296 (261)

The values in parenthesis are the volumetric working capacity defined as the difference in uptake between the stated pressure (35, 65 or 100 bar) and 5 bar.

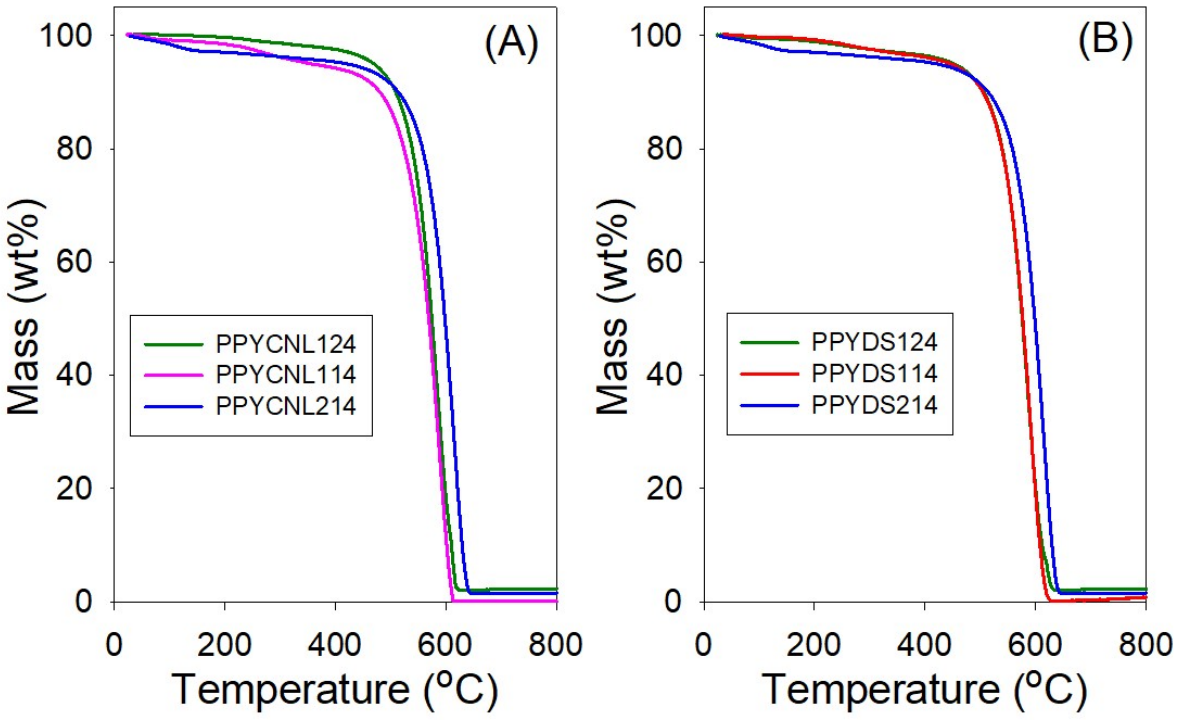

Figure S1. Thermogravimetric analysis (TGA) curves of activated carbons derived from pre-mixed mixtures of polypyrrole (PPY) and (A) CNL carbon or (B) ACDS carbon.

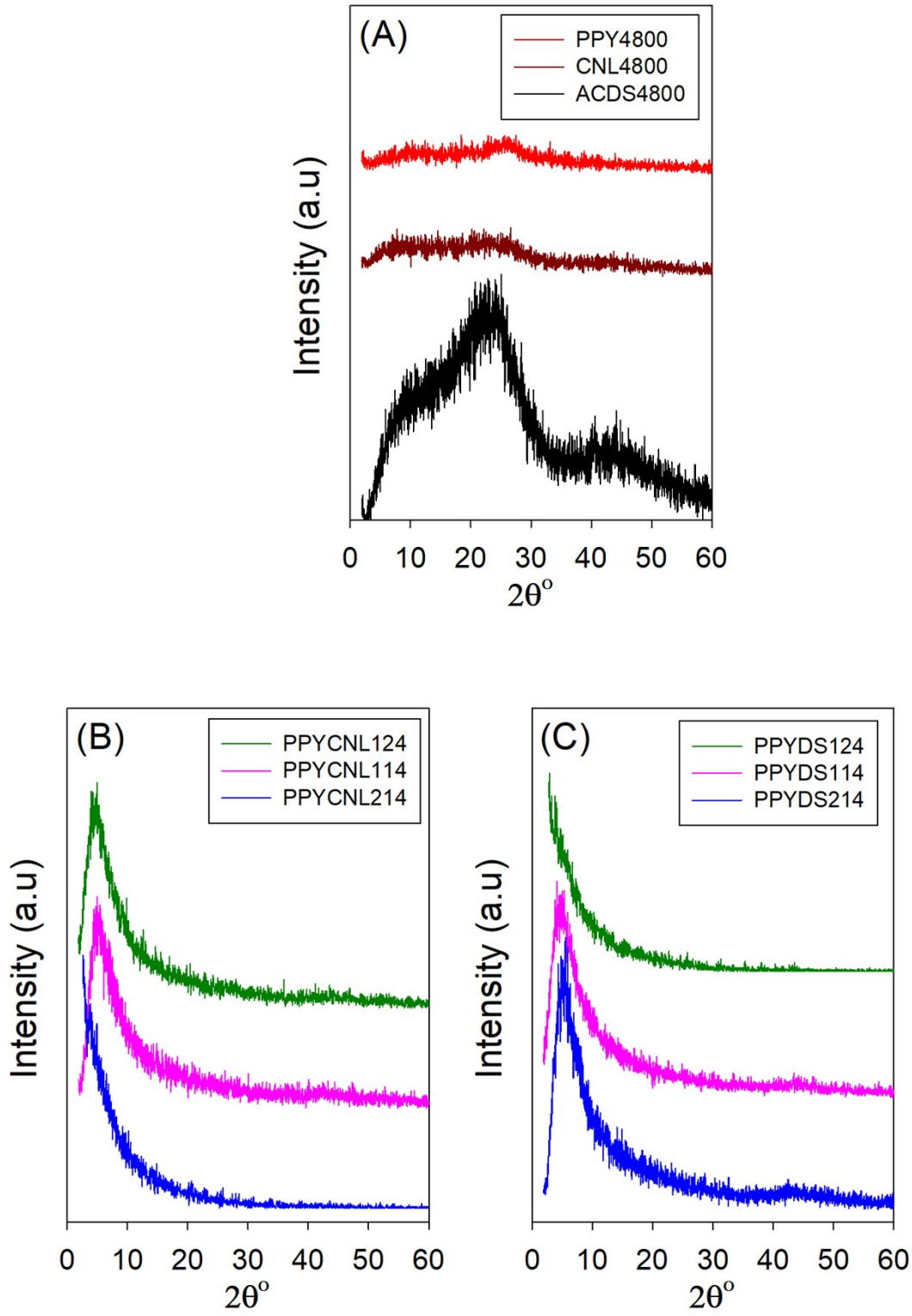

Figure S2. Powder XRD pattern of (A) Polypyrrole, CNL carbon and ACDS carbon precursor materials, and (bottom panels) of activated carbons derived from pre-mixed mixtures of polypyrrole (PPY) and (B) CNL carbon or (C) ACDS carbon.

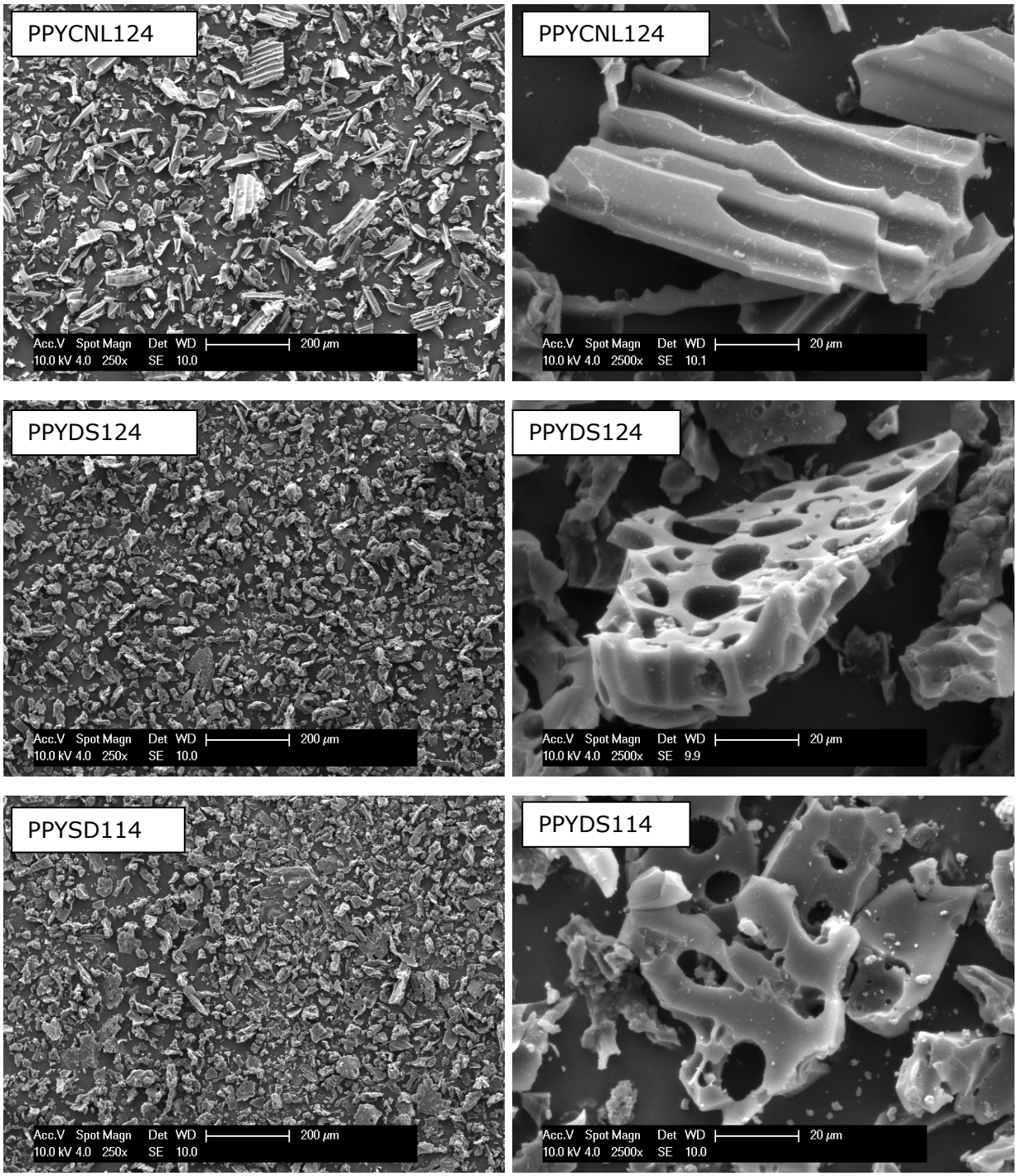

Figure S3. Representative SEM images of activated carbons derived from pre-mixed precursors.

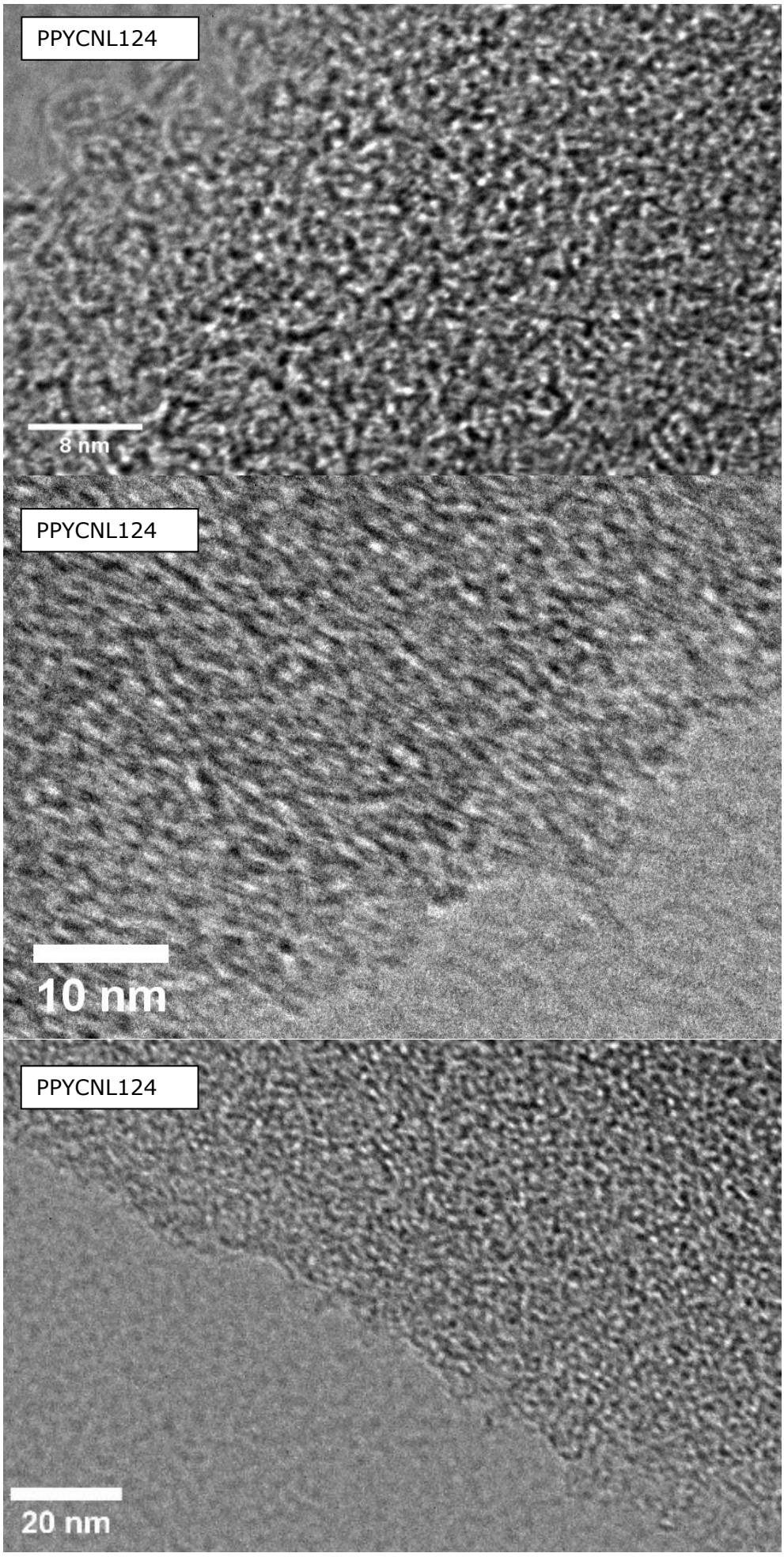

Figure S4A. TEM images of sample PPYCNL124.

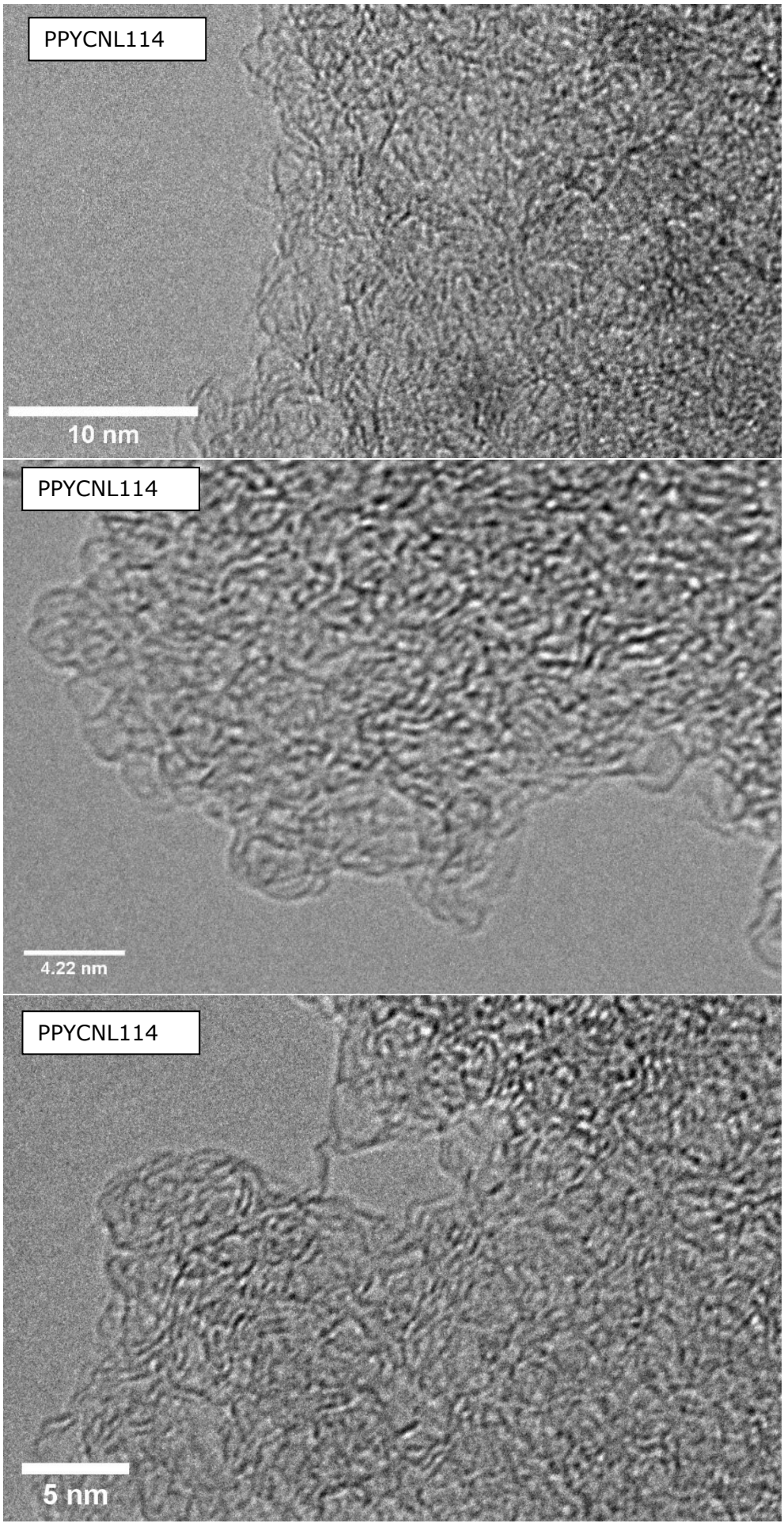

Figure S4B. TEM images of sample PPYCNL114.

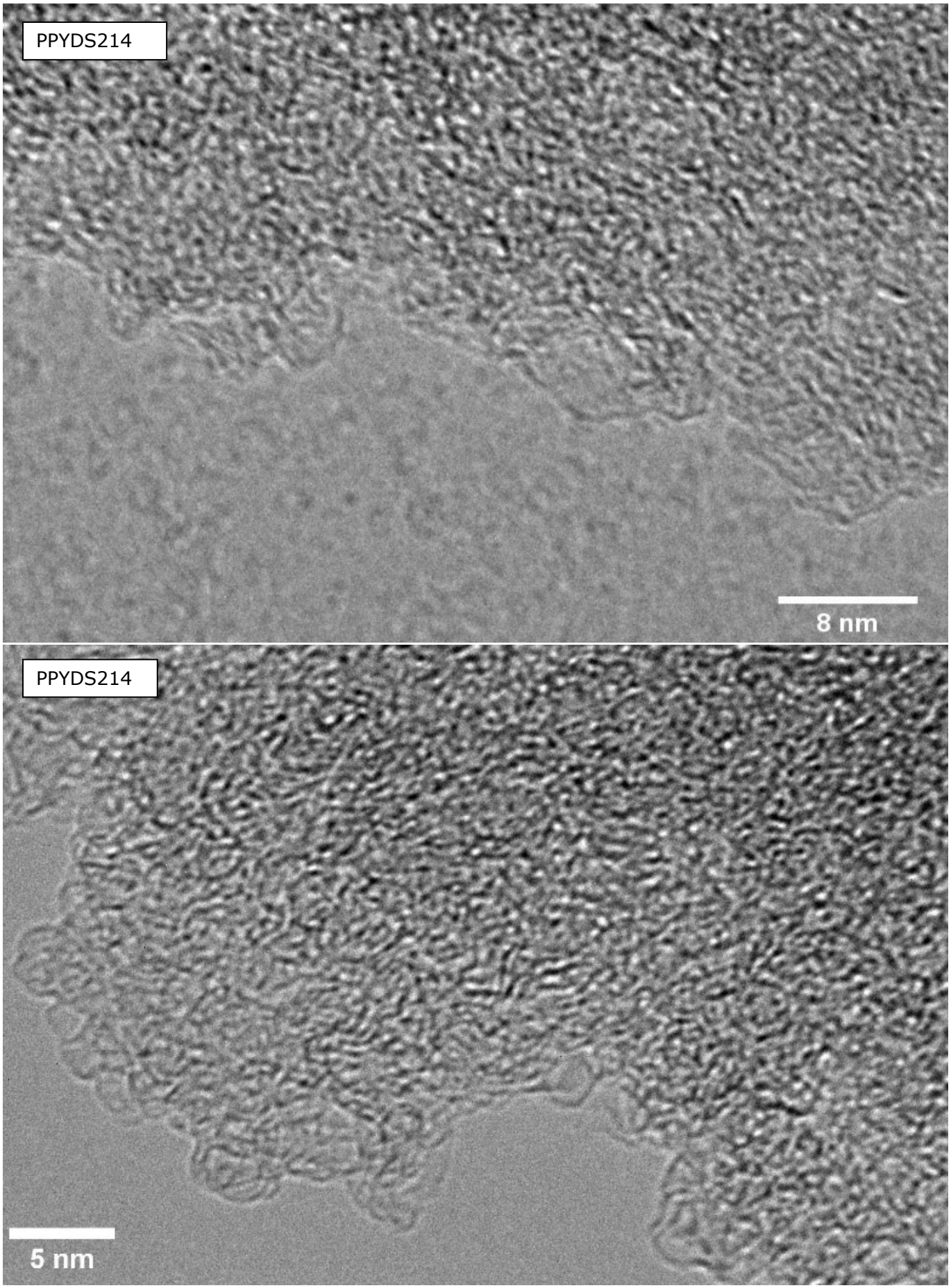

Figure S4C. TEM images of sample PPYDS214.

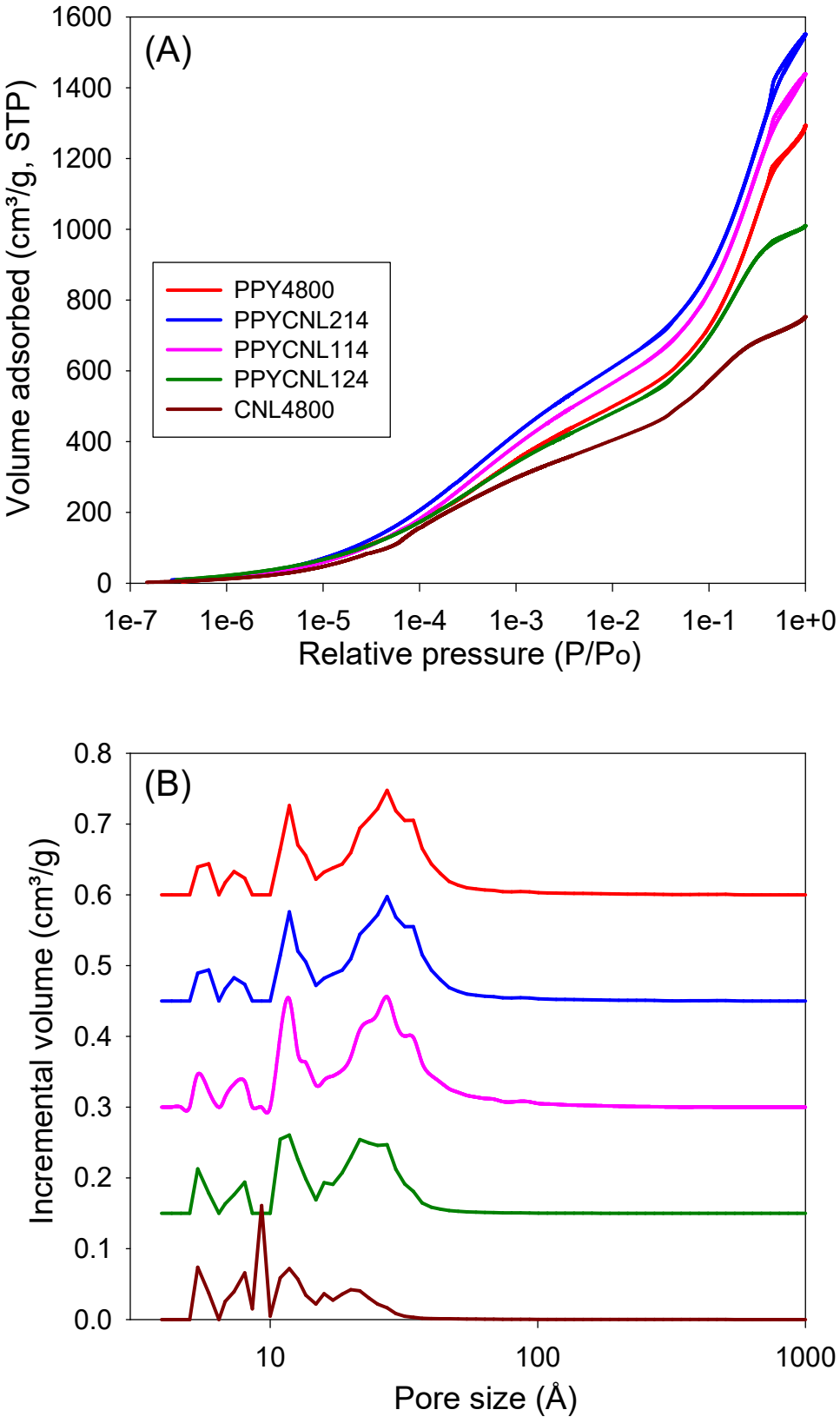

Figure S5A. Semi-log plots of (A) Nitrogen sorption isotherms and (B) pore size distribution curves of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY) and CNL4800 (CNL carbon) and from pre-mixed precursors containing PPY and CNL carbon at various weight ratios.

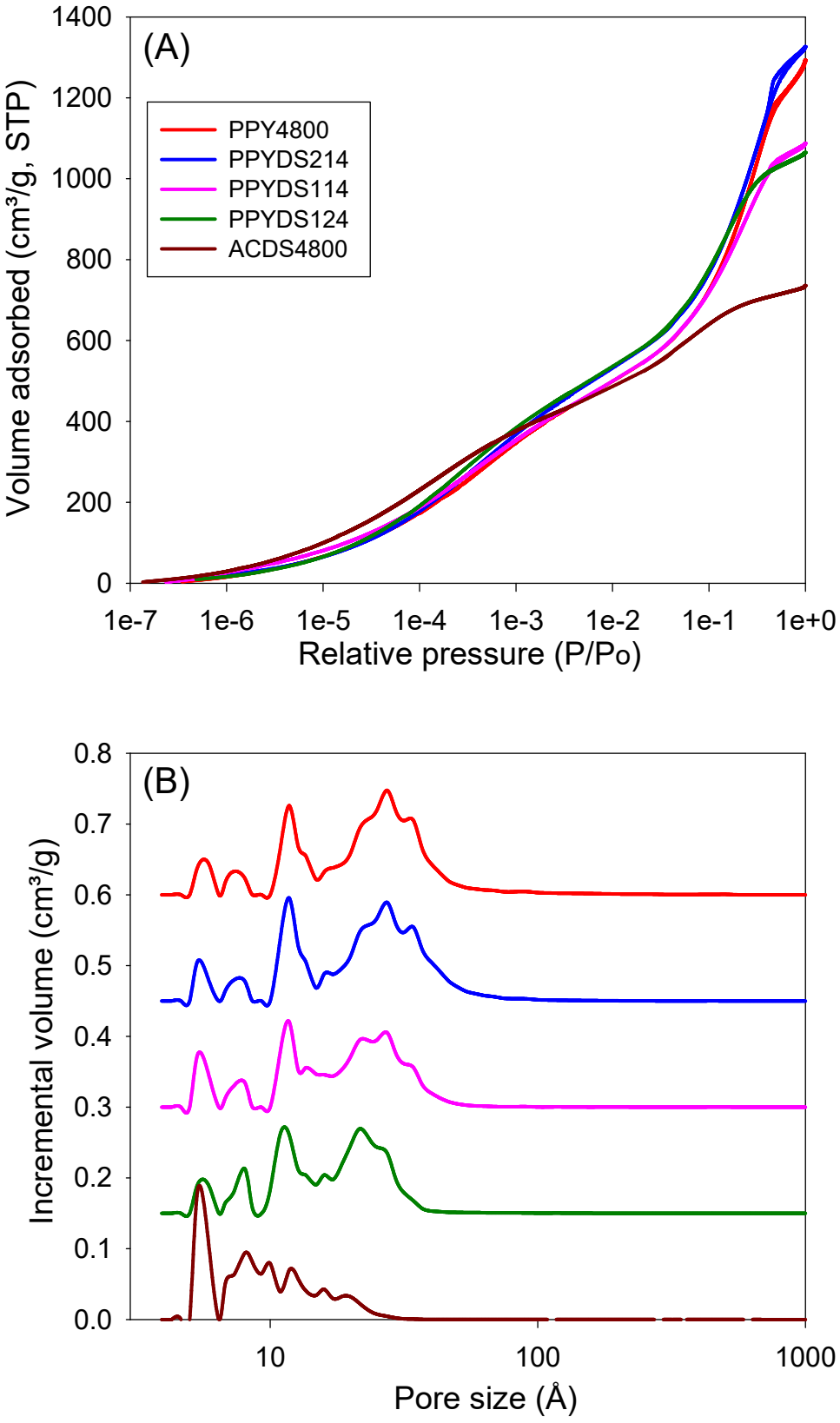

Figure S5B. Semi-log plots of (A) Nitrogen sorption isotherms and (B) pore size distribution curves of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY) and ACDS4800 (ACDS carbon) and from pre-mixed precursors containing PPY and ACDS carbon at various weight ratios.

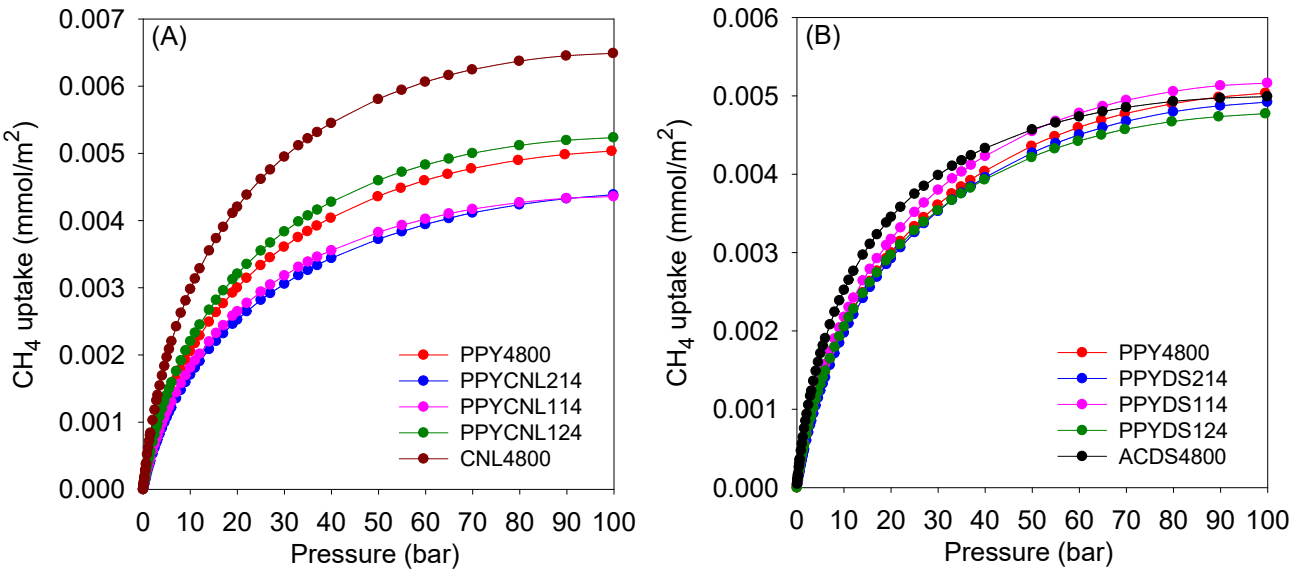

Figure S6. Excess gravimetric methane uptake density of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY), CNL4800 (CNL carbon) and ACDS4800 (ACDS carbon) and from pre-mixed precursors containing PPY and (A) CNL carbon or (B) ACDS carbon at various weight ratios.

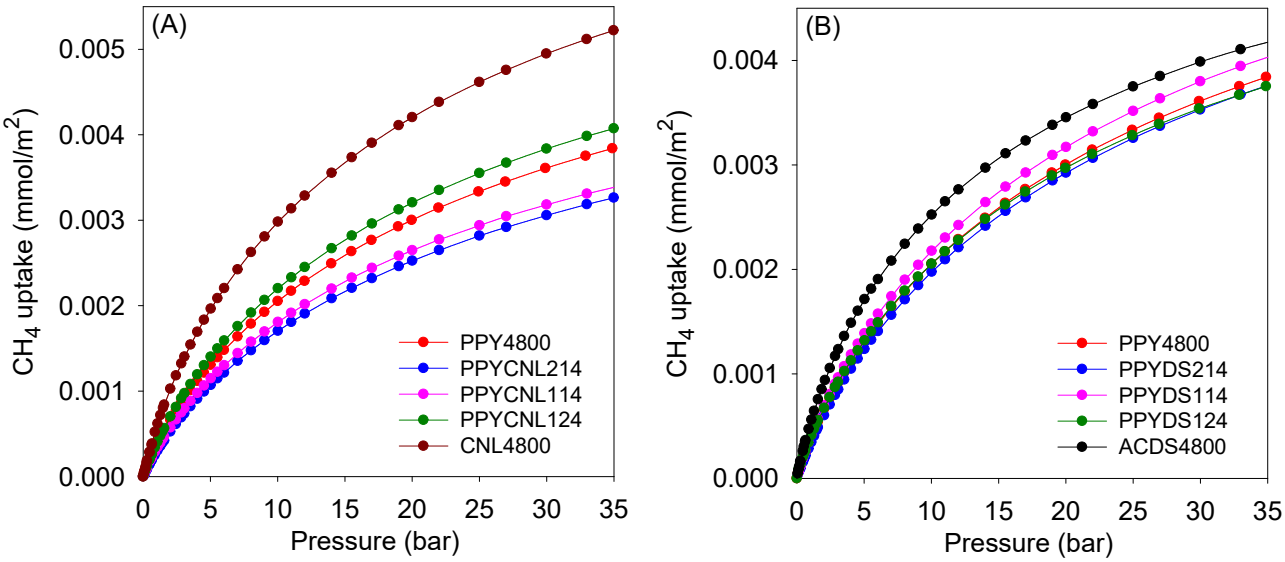

Figure S7. Excess gravimetric methane uptake density at low pressure (0 – 35 bar) of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY), CNL4800 (CNL carbon) and ACDS4800 (ACDS carbon) and from pre-mixed precursors containing PPY and (A) CNL carbon or (B) ACDS carbon at various weight ratios.

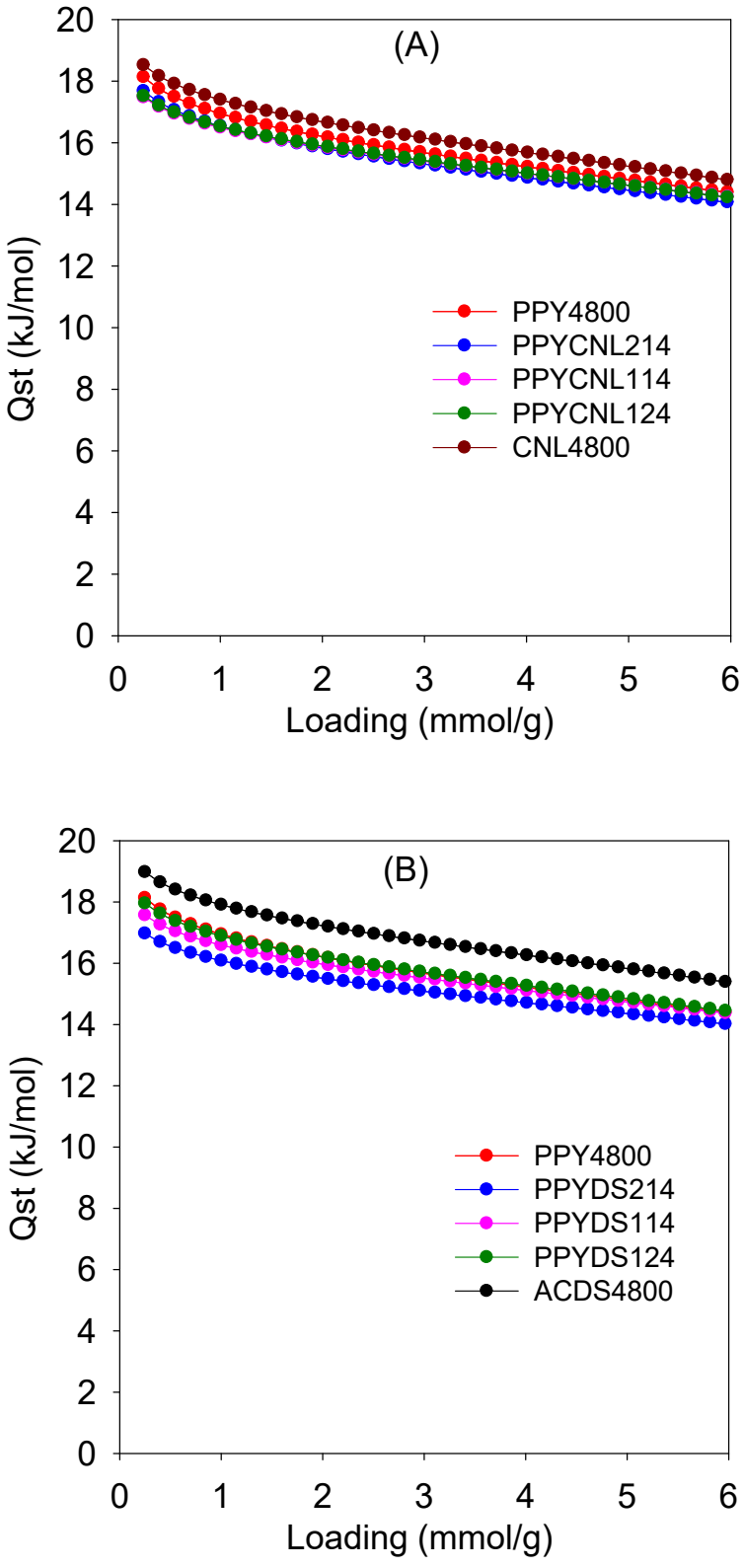

Figure S8. Isosteric heat of adsorption (Qst) as a function of methane loading of activated carbons derived from single precursor, PPY4800 (polypyrrole, PPY), CNL4800 (CNL carbon) and ACDS4800 (ACDS carbon) and from pre-mixed precursors containing PPY and (A) CNL carbon or (B) ACDS carbon at various weight ratios.

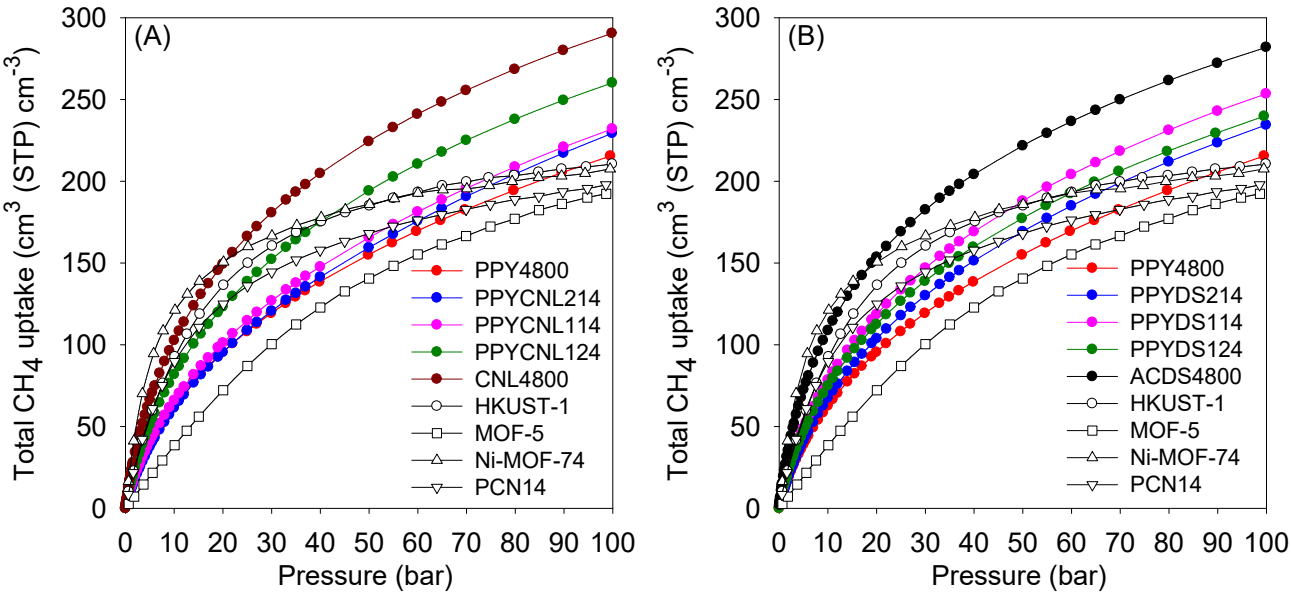

Figure S9. Total volumetric methane uptake of activated carbons derived from single precursors (PPY4800, CNL4800, ACDS4800) or (A) PPY/CNL or (B) PPY/DS pre-mixtures compared to benchmark MOF materials. The uptake of MOFs, allows for a 25% reduction of values calculated using crystallographic density.

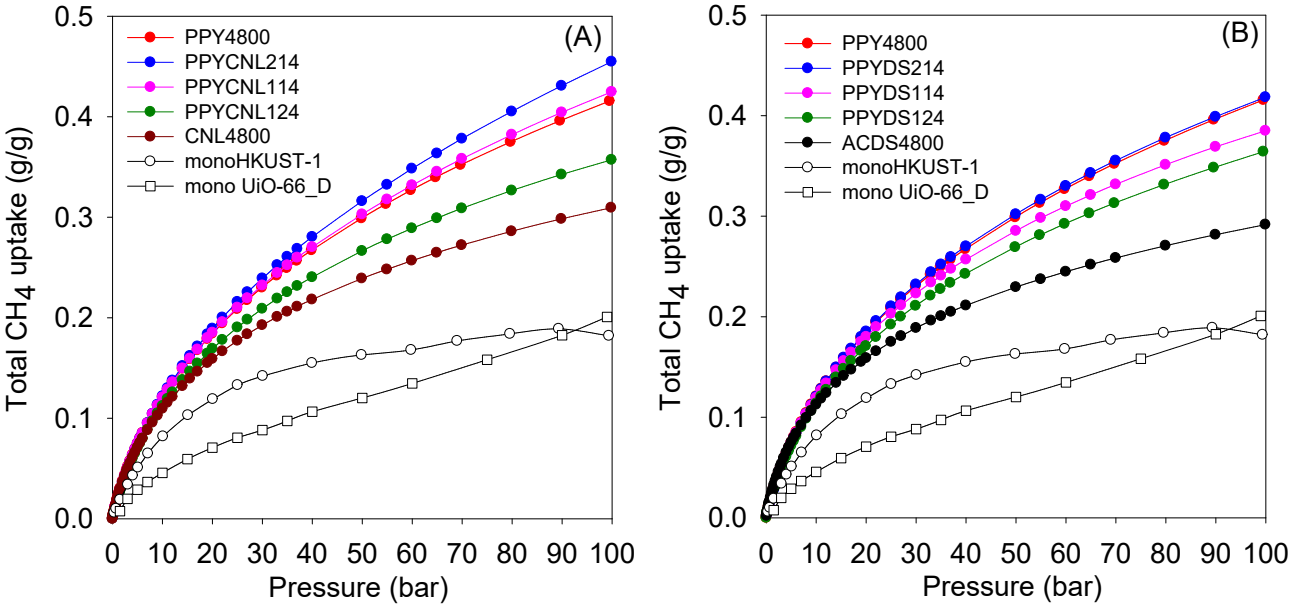

Figure S10. Total gravimetric methane uptake ($gCH_4\ g^{-1}$) of activated carbons derived from single precursors (PPY4800, CNL4800, ACDS4800) or (A) PPY/CNL pre-mixtures or (B) PPY/DS pre-mixtures compared to storage capacity of monolithic $_{mono}$HKUST-1 and $_{mono}$UiO-66_D.