Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

An aliphatic Hexene-Covalent Triazine Framework for Selective Acetylene/Methane and Ethylene/Methane Separation

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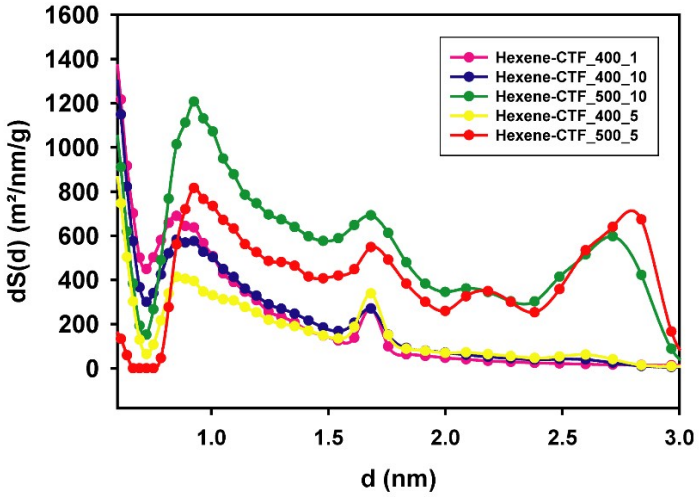


Figure S1: Pore size distribution of Hexene-CTF_400_10 and Hexene-CTF_500_10.

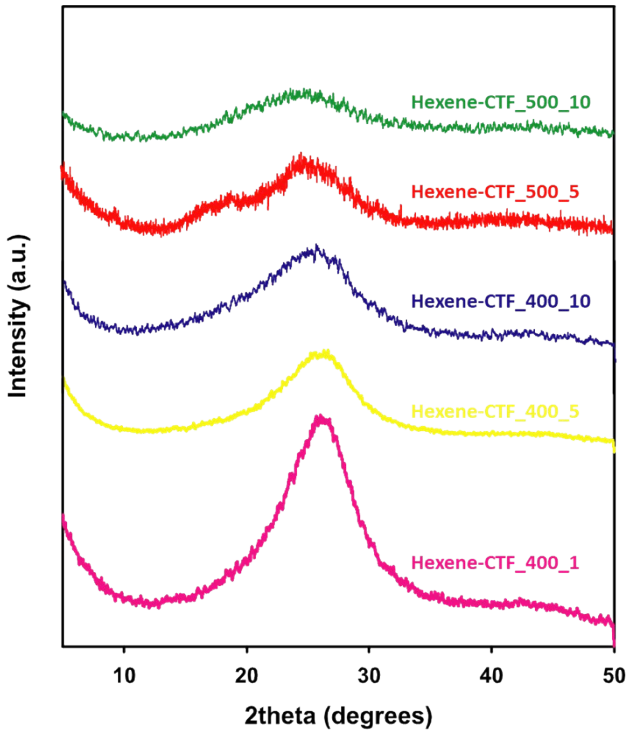


Figure S2: Powder X-Ray Diffraction (PXRD) patterns of all Hexene-CTFs.

Table S1: Porous properties of Hexene-CTFs

Material description	[a]S.A.$_{BET}$ ($m^2\ g^{-1}$)	[b]V_{micro} ($cm^3\ g^{-1}$)	[c]V_{tot} ($cm^3\ g^{-1}$)	V_{micro}/V_{tot} (%)
Hexene-CTF_400_10	499	0.2802	0.298	94.02
Hexene-CTF_400_5	579	0.3239	0.3413	94.90
Hexene-CTF_400_1	356	0.1965	0.2005	98.00
Hexene-CTF_500_10	1016	0.6437	0.6925	92.95
Hexene-CTF_500_5	1375	0.8293	0.8922	92.95

[a] BET surface area was calculated over the relative pressure range of 0.05−0.3 at 77 K. [b] V_{micro}, micropore volume was calculated by N_2 adsorption isotherms using the t-plot method. [c] V_{tot}, total pore volume was calculated at P/P0 = 0.98.

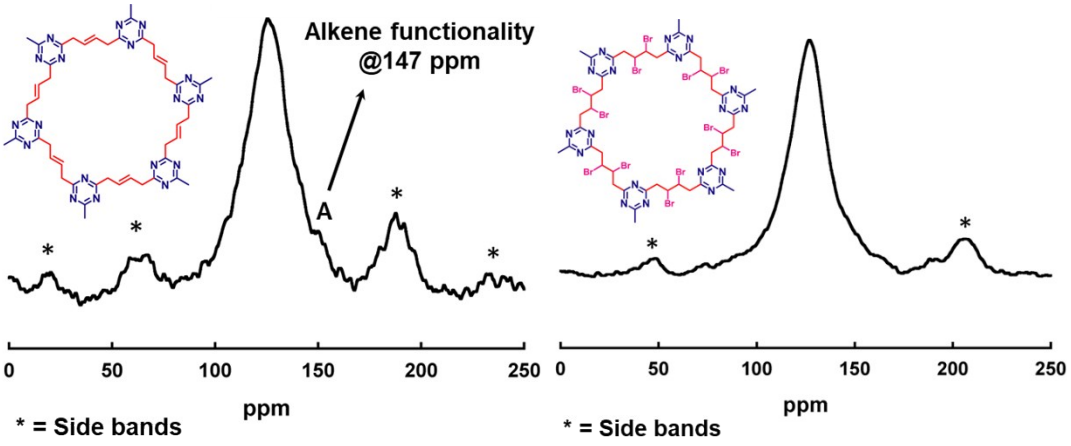


Figure S3: 13C CP-MAS NMR spectra of Hexene-CTF_400_5 (left) and Br-Hexene-CTF_400_5 (right).

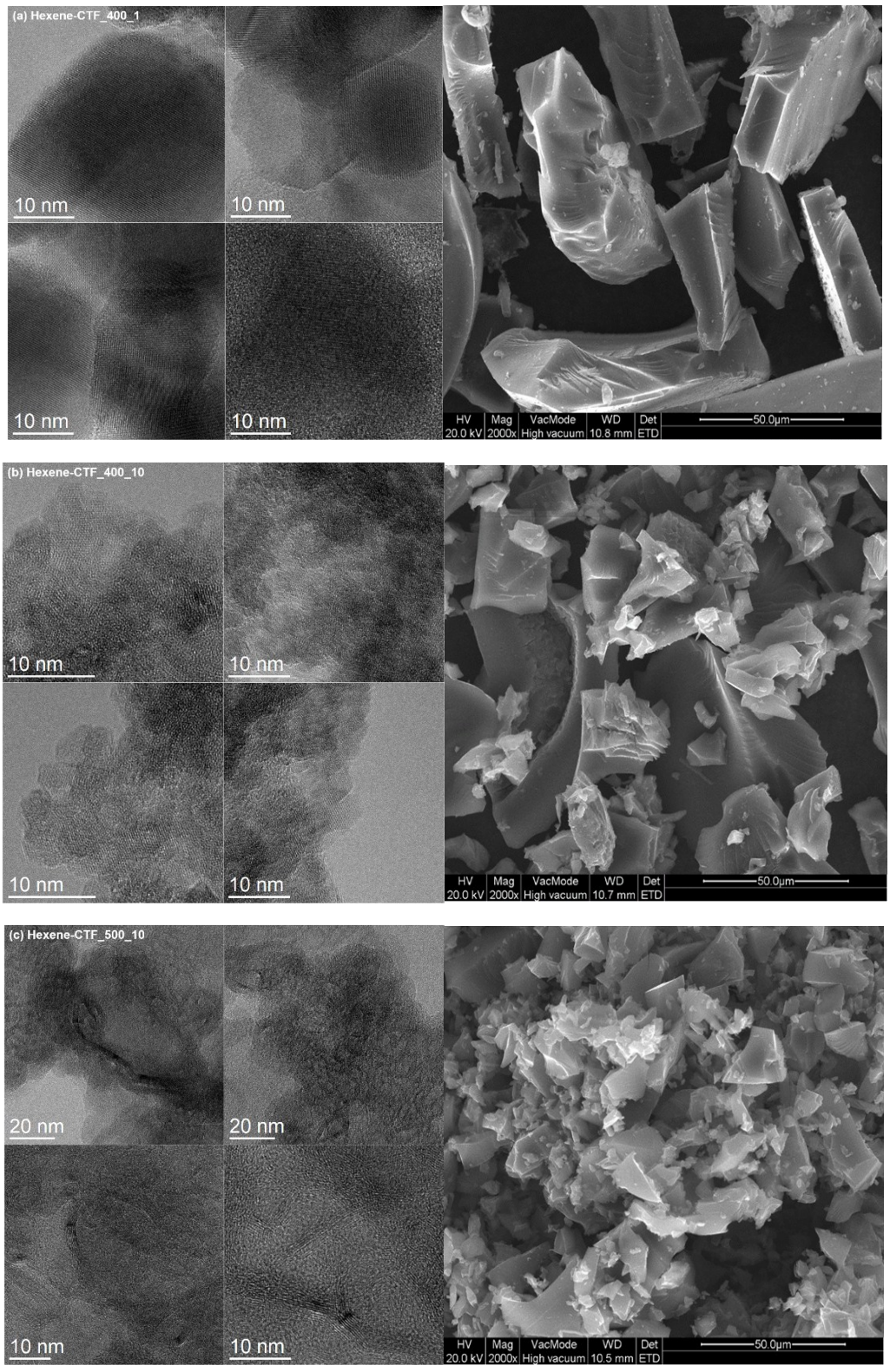


Figure S4: HR-TEM and SEM images of (a) Hexene-CTF_400_1, (b) Hexene-CTF_400_10 and (c) Hexene-CTF_500_10.

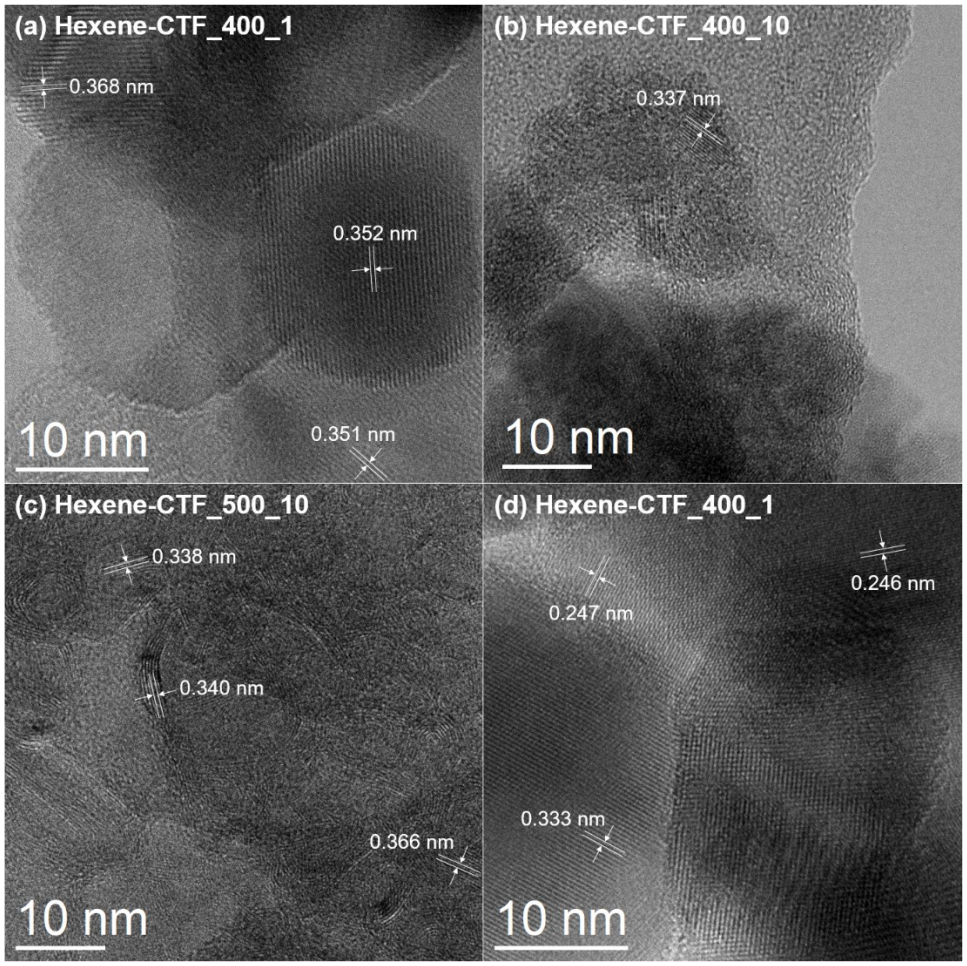


Figure S5: HR-TEM image of Hexene-CTF_400_1 showing two different plane-spacing.

Equation S1:

$$Degree\ of\ carbonization = \left\{\left[\frac{C\%}{(C\% + N\% + H\%)}\right] * 100\right\} - Theoretical\ C\%$$

Table S2: Elemental analysis (C/H/N) and Bromine number of all Hexene-CTFs.

Material description	C (wt. %)	H (wt. %)	N (wt. %)	Residue (wt. %)	Br number double bonds	C/N ratio	Excess carbon content (carbonization %)
Hexene-CTF_400_10	70.9	1.9	8.8	18.3	0.62 g/g (41%)	8.05	14.7
Hexene-CTF_400_5	68.9	2.6	9.5	19	0.67 g/g (44%)	7.25	17.2

Hexene-CTF_400_1	66.1	2.8	11.1	20	0.69 g/g (46%)	5.95	18.8
Hexene-CTF_500_10	73.7	1.5	8.4	16.4	0.59 g/g (39%)	8.77	19.5
Hexene-CTF_500_5	70.7	1.5	8.7	19.1	0.60 g/g (39.7%)	8.12	20.3
Theoretical	67.9	5.7	26.4	-	1.51 g/g (100%)	2.57	-

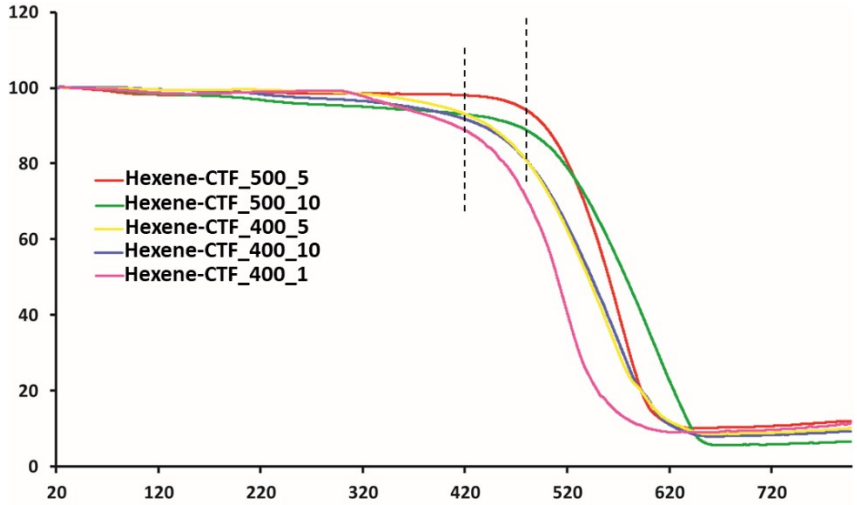


Figure S6: Thermogravimetric analysis (TGA) of all Hexene-CTFs.

Table S3: Zinc content in the CTF materials determined using ICP-OES analysis.

Material	Zn content (mg/g)
Hexene-CTF_400_1	24
Hexene-CTF_400_5	22.7
Hexene-CTF_400_10	26
Hexene-CTF_500_5	33.4
Hexene-CTF_500_10	22.2

Even after rigorous washing steps, Zn could not be removed completely. The amount of Zn was estimated from ICP-OES analysis (Table S3).

The rest of the residue could possibly be due to the excess chlorine from $ZnCl_2$. However, it was not possible to detect Cl content from ICP-OES due to instrumental limitations. In addition, certain unavoidable oxygen impurities (ZnO, surface OH, etc…) could account for the residue.

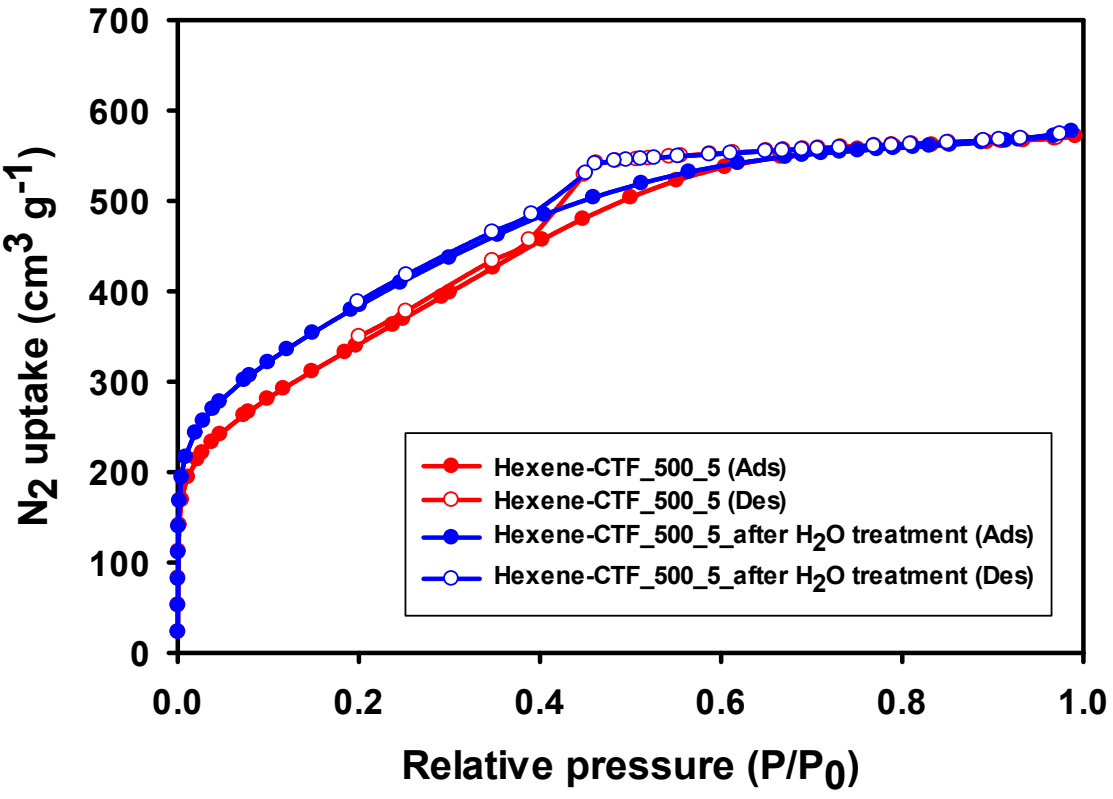
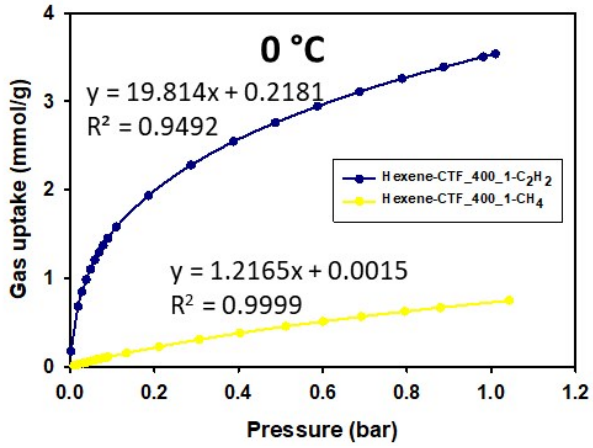


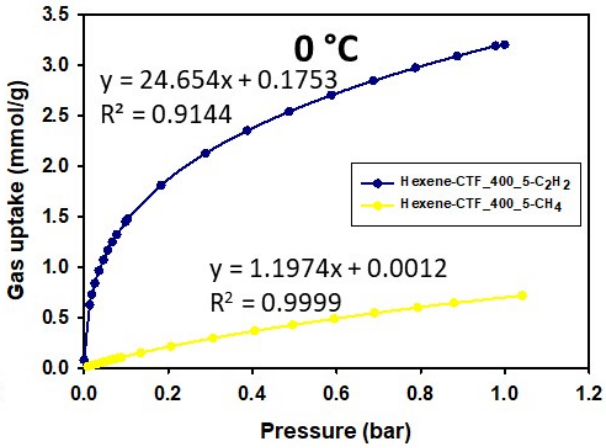
Figure S7: N_2 sorption isotherms of Hexene-CTF_500_5 before and after boiling water treatment.

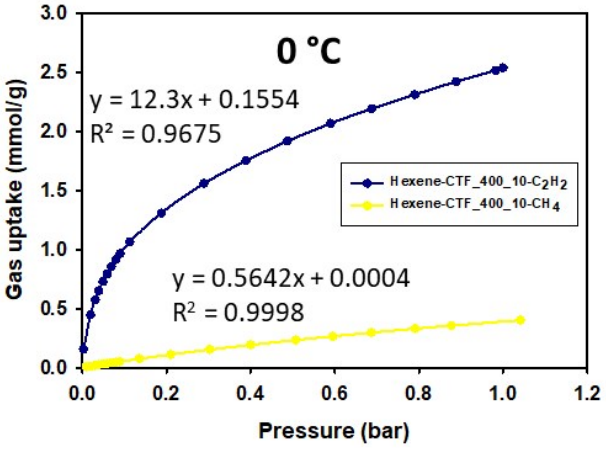
Table S4: CO_2, N_2, CH_4, C_2H_4 and C_2H_2 gas uptakes by Hexene-CTFs at 25°C and 0°C at 1 bar.

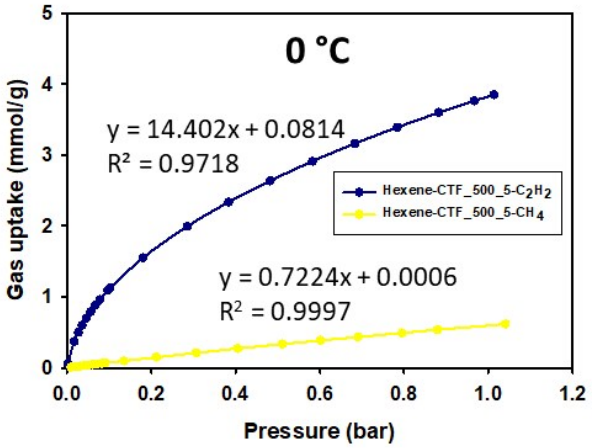
Material description	Temp (°C)	CO_2 (mmol/g)	N_2 (mmol/g)	CH_4 (mmol/g)	C_2H_4 (mmol/g)	C_2H_2 (mmol/g)
Hexene-CTF_400_10	25	1.02	0.048	0.25	1.12	1.69
	0	1.62	0.091	0.4	1.54	2.54
Hexene-CTF_400_5	25	1.63	0.13	0.45	1.75	2.24
	0	2.56	0.21	0.72	2.47	3.19
Hexene-CTF_400_1	25	1.72	0.13	0.46	1.89	2.28
	0	2.66	0.24	0.74	2.55	3.54
Hexene-CTF_500_10	25	1.18	0.09	0.28	1.48	2.08
	0	2.03	0.16	0.43	2.33	3.05

Hexene-CTF_500_5	25	1.27	0.11	0.36	1.76	2.45
	0	2.26	0.17	0.61	2.72	3.85









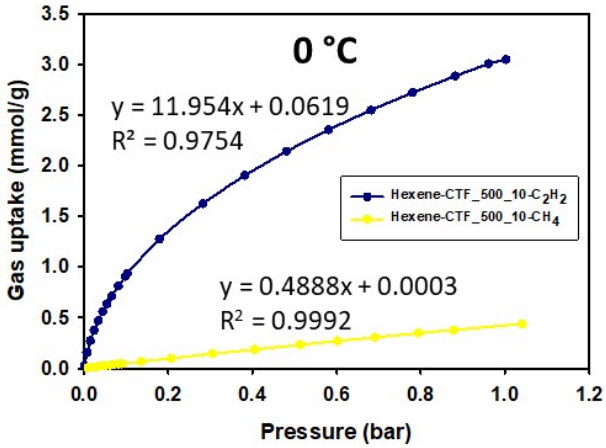


Figure S8: C_2H_2/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 0°C.

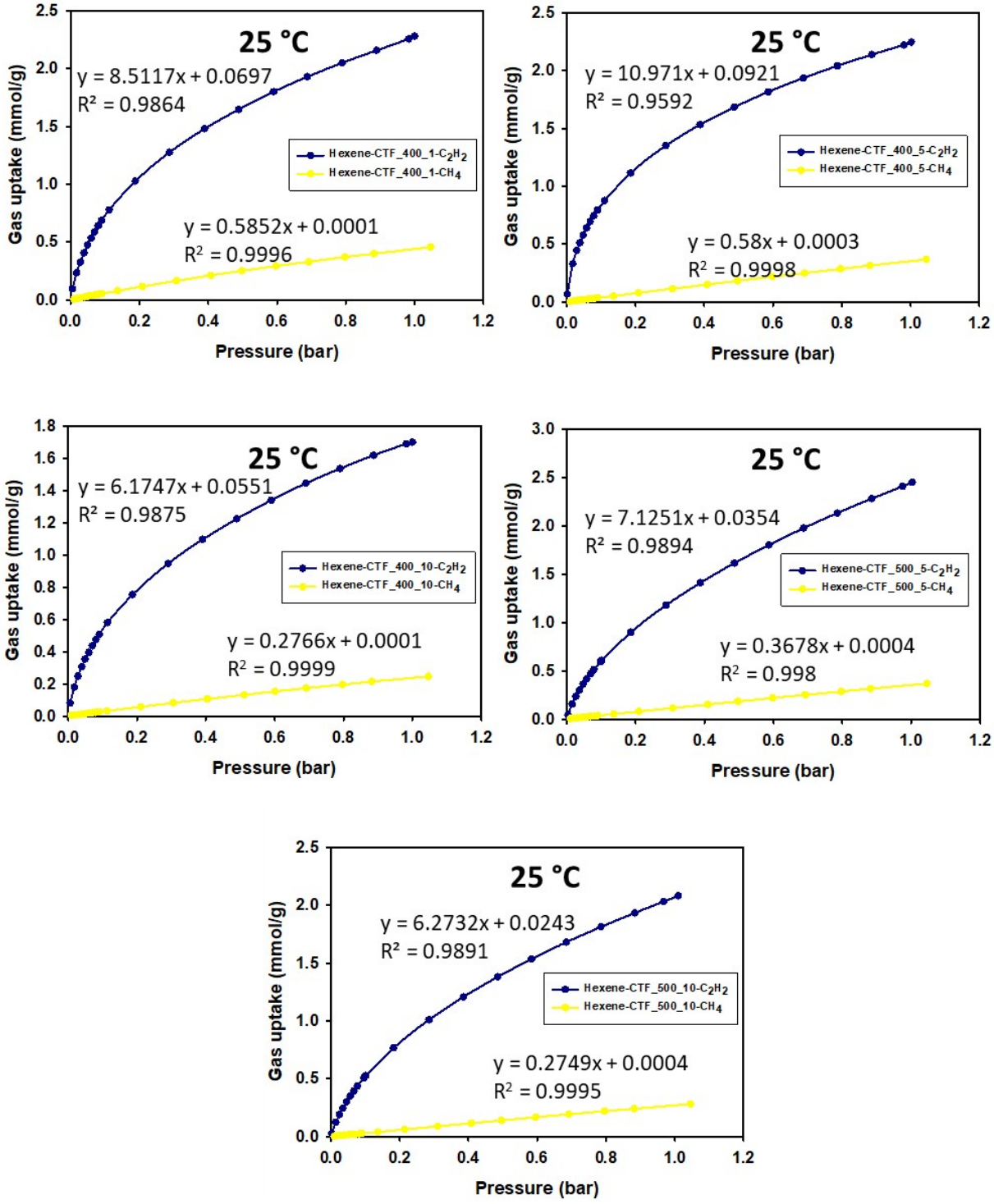


Figure S9: C_2H_2/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 25°C.

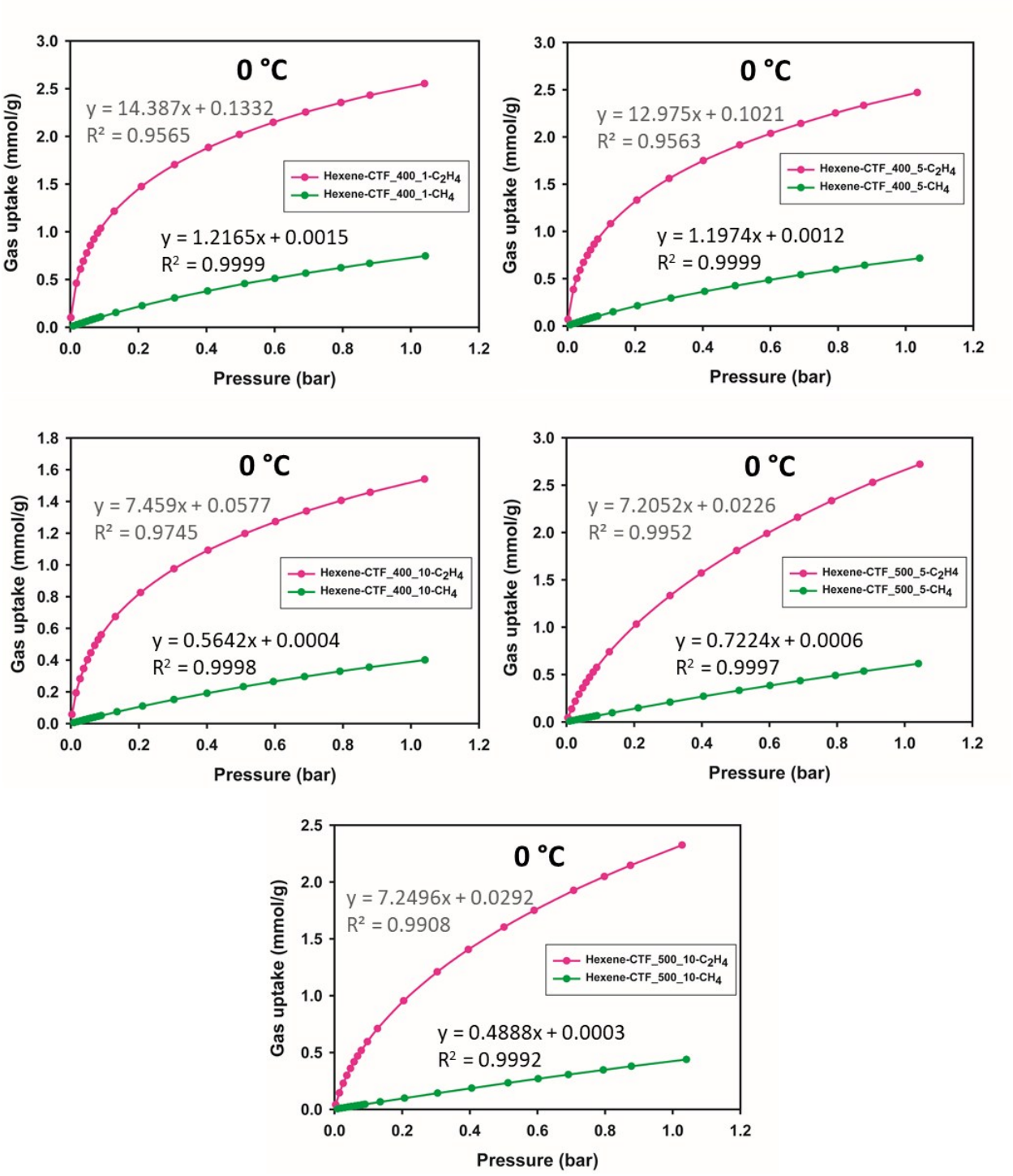


Figure S10: C_2H_4/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 0°C.

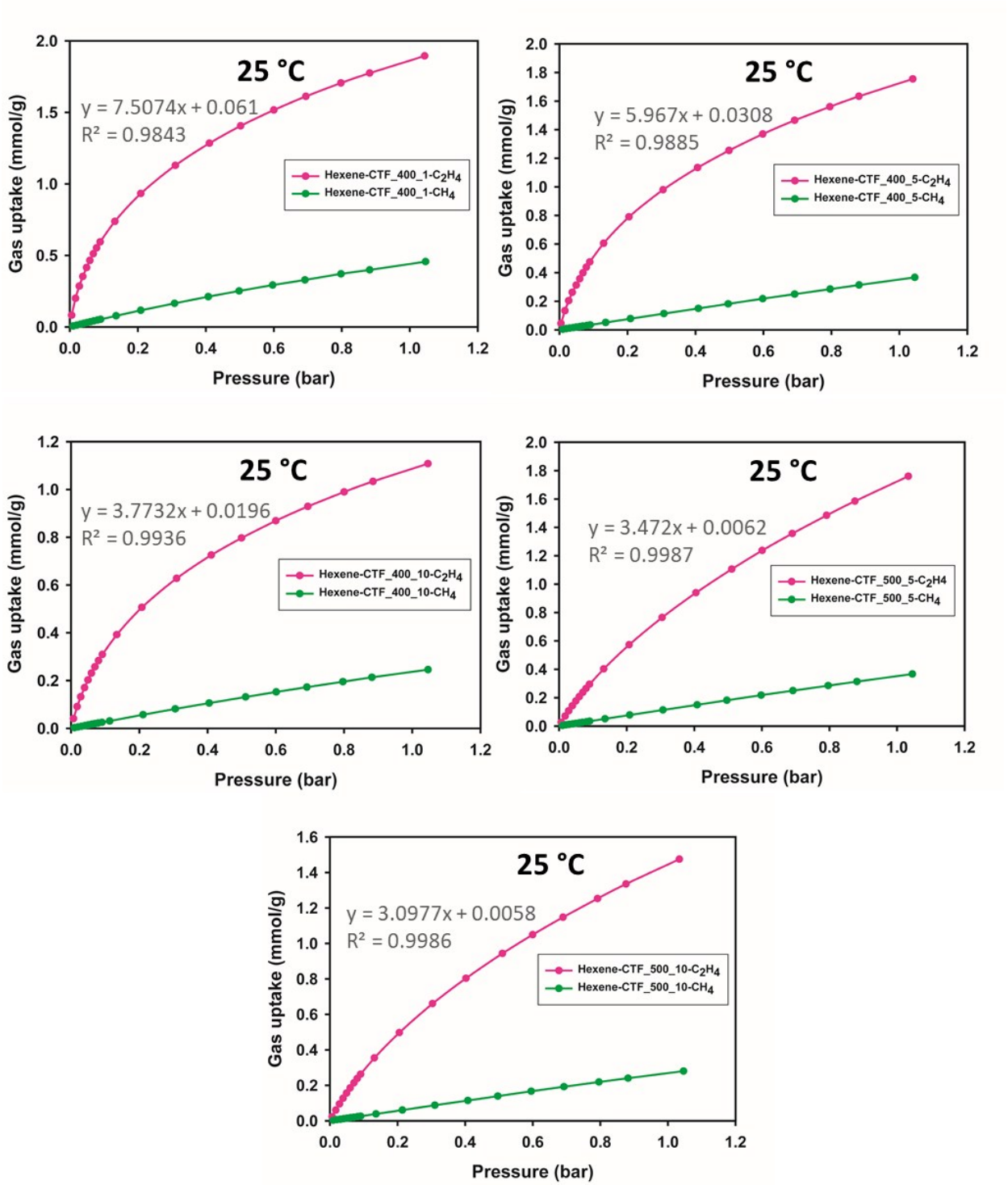


Figure S11: C_2H_4/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 25°C.

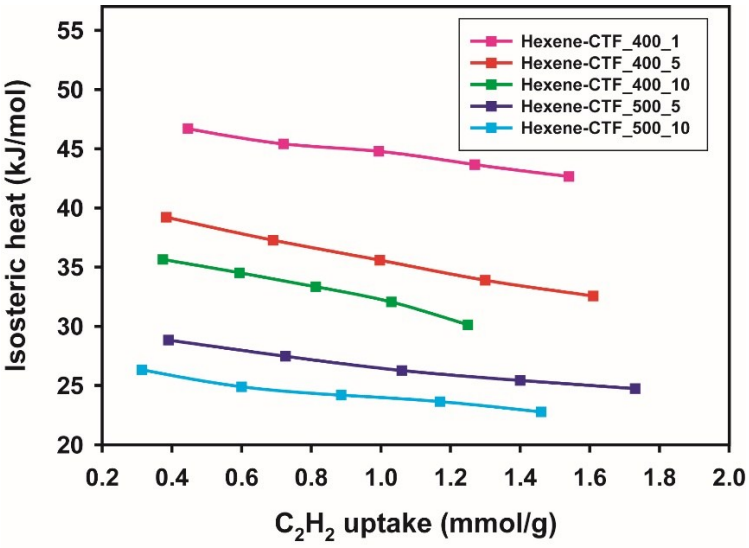


Figure S12: Isosteric heat of adsorption (Q_{st}) of C_2H_2 for all Hexene-CTFs.

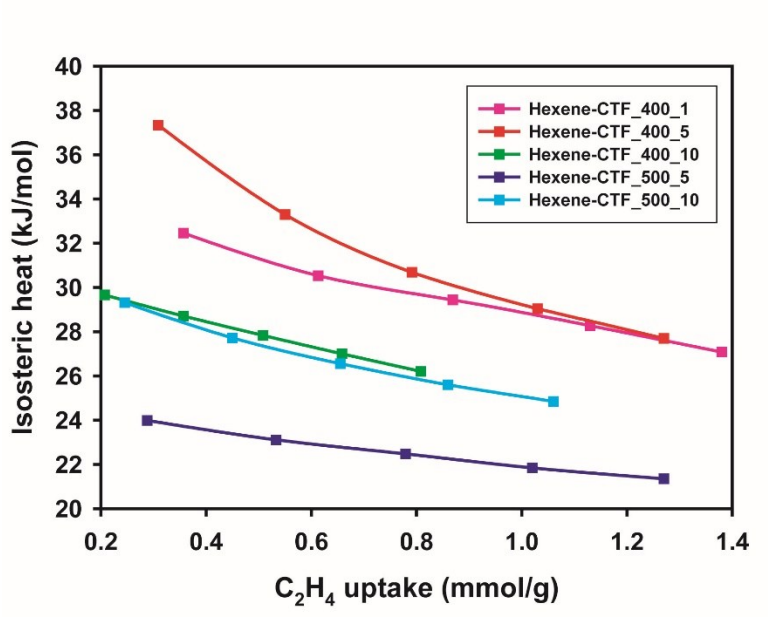


Figure S13: Isosteric heat of adsorption (Q_{st}) of C_2H_4 for all Hexene-CTFs.

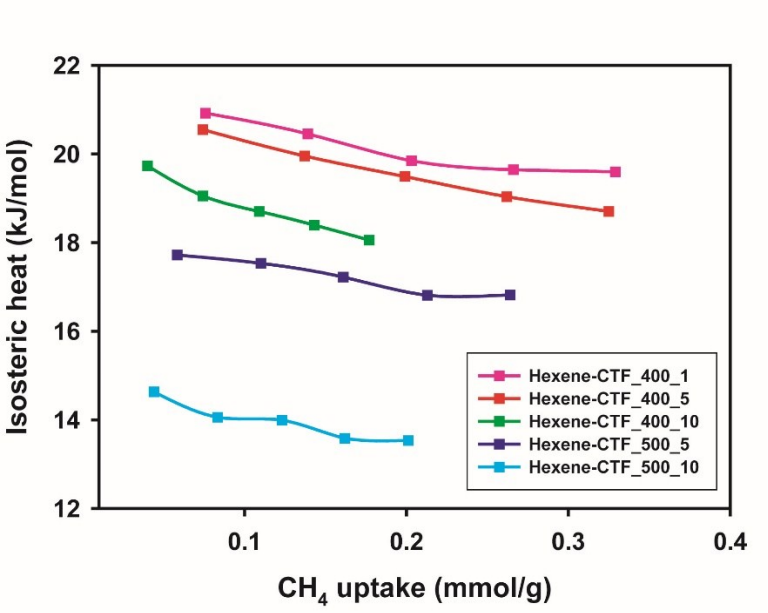
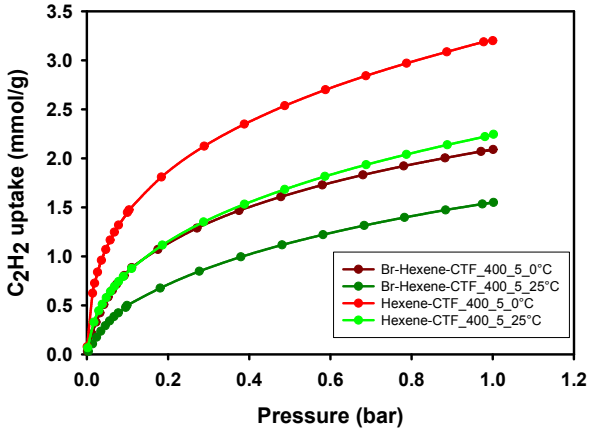


Figure S14: Isosteric heat of adsorption (Q_{st}) of CH_4 for all Hexene-CTFs.



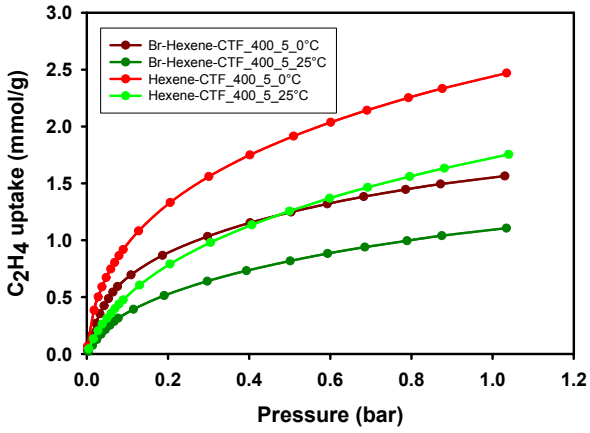


Figure S15: C_2H_2 (left) and C_2H_4 (right) uptake isotherms of Br-Hexene-CTF_400_5 and Hexene-CTF_400_5 at 0°C and 25°C. Note: The mass of Bromine is subtracted (according to the bromine number) in order to compare the pure CTFs by excluding the effect of overall increased mass due to Bromine.

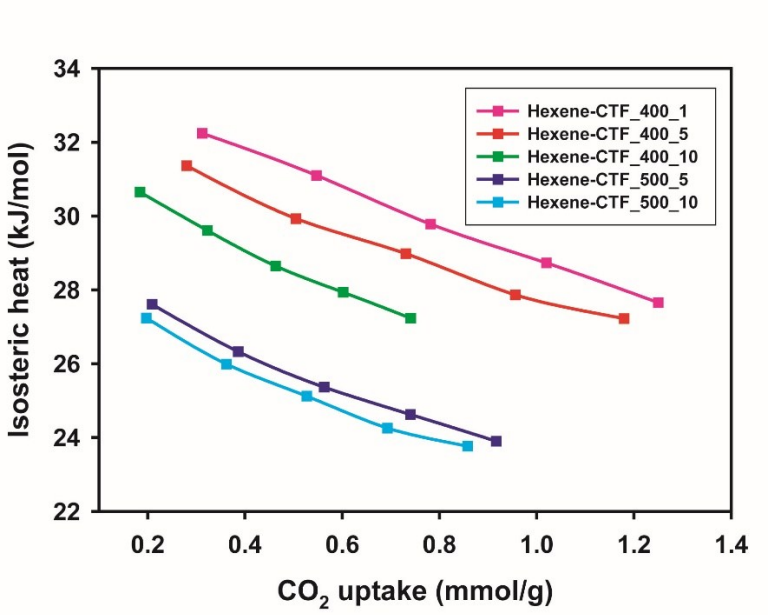


Figure S16: Isosteric heat of adsorption (Q_{st}) of CO_2 for all Hexene-CTFs.

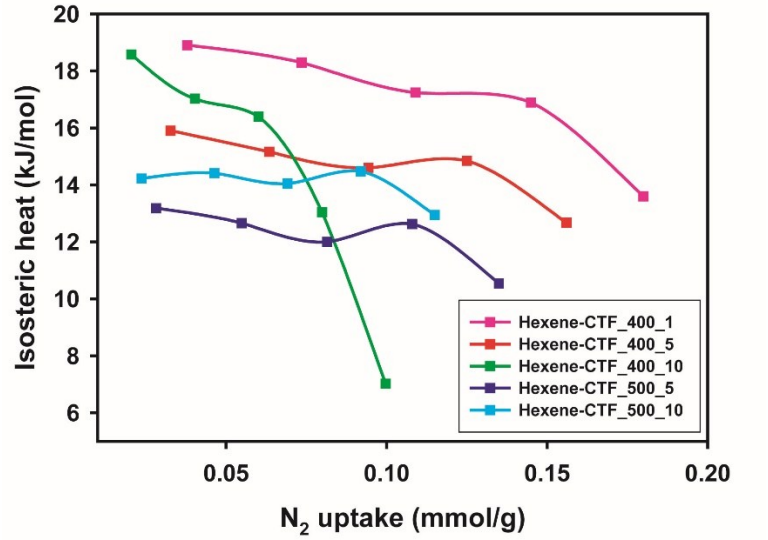


Figure S17: Isosteric heat of adsorption (Q_{st}) of N_2 for all Hexene-CTFs.

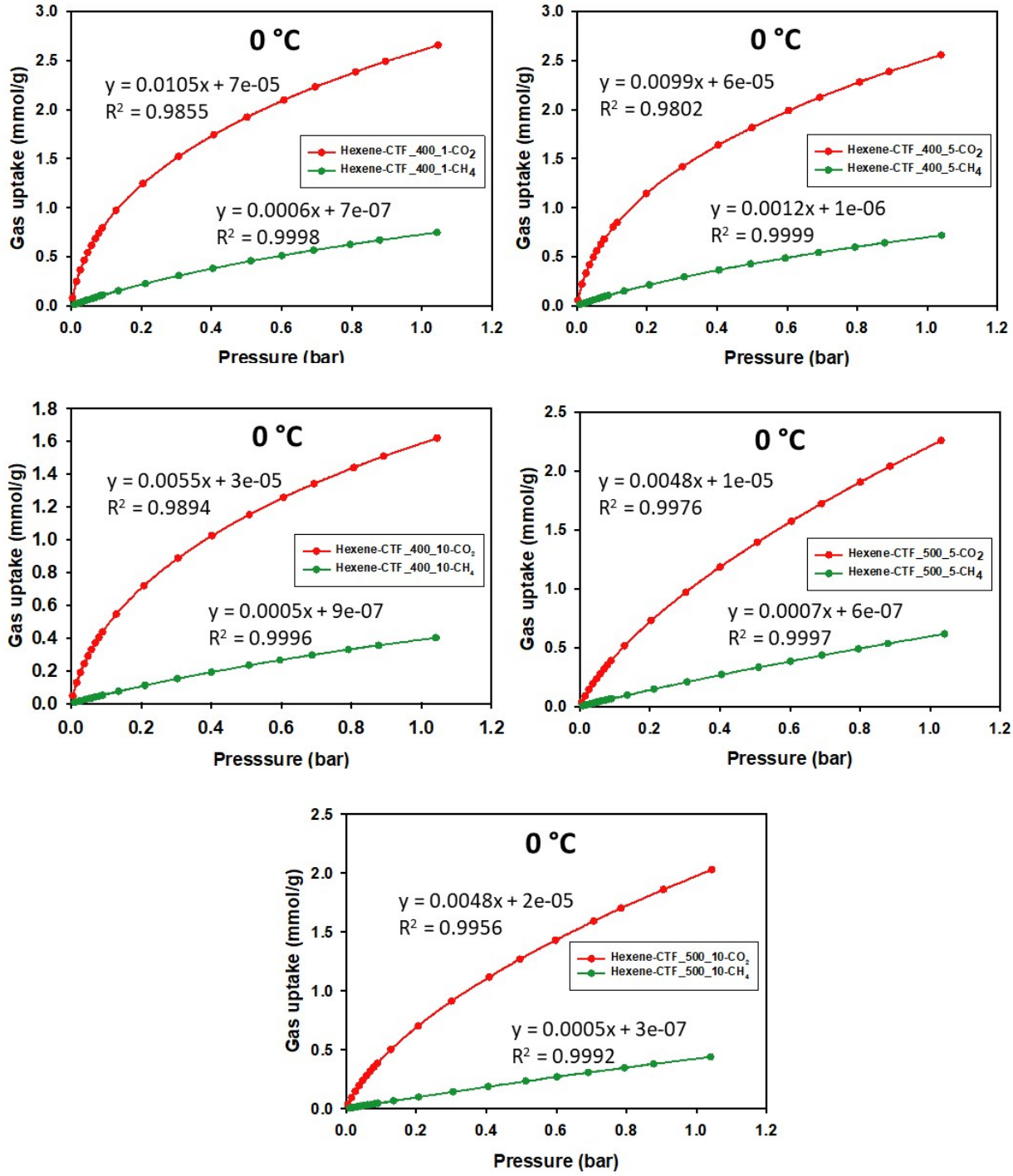


Figure S18: CO_2/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 0°C.

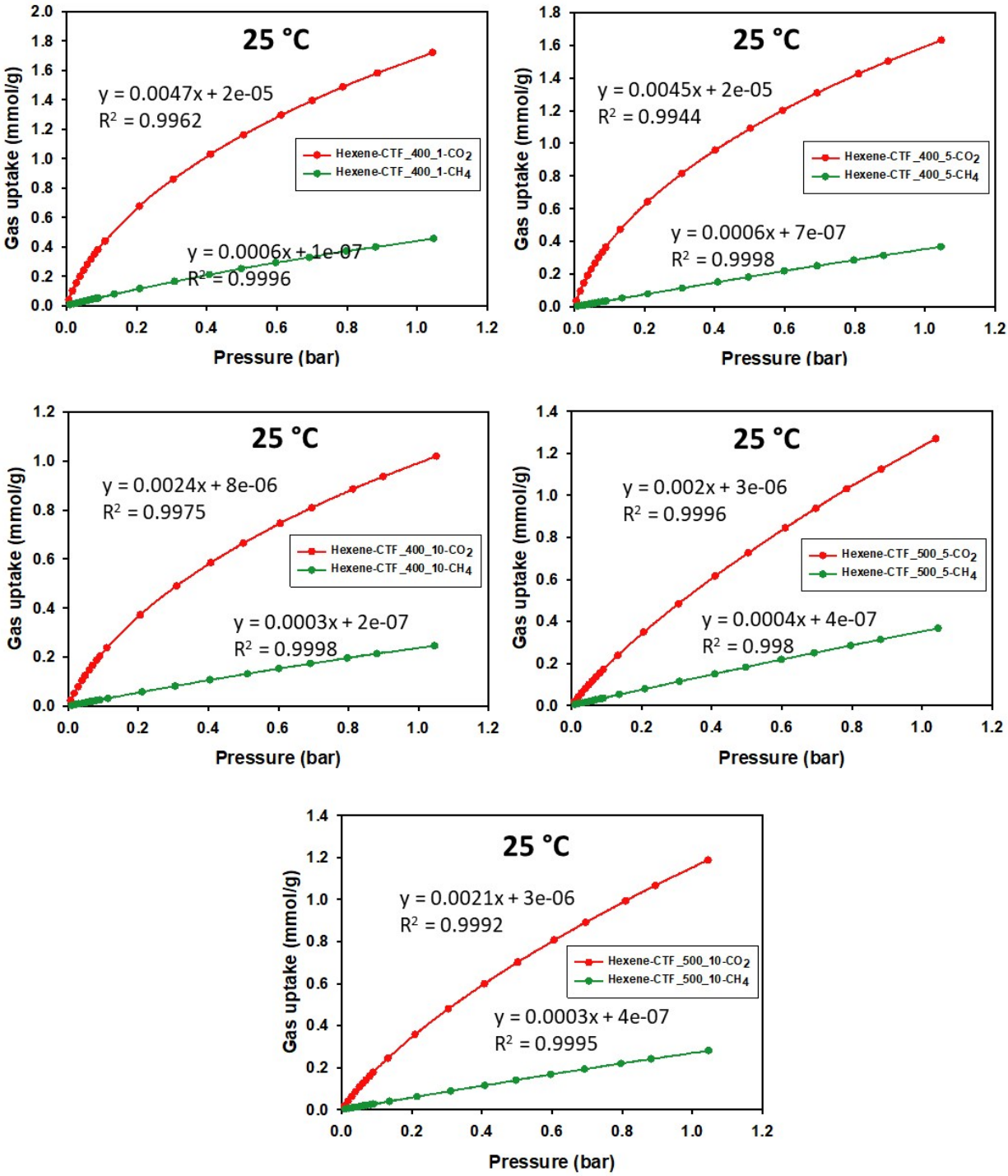


Figure S19: CO_2/CH_4 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 25°C.

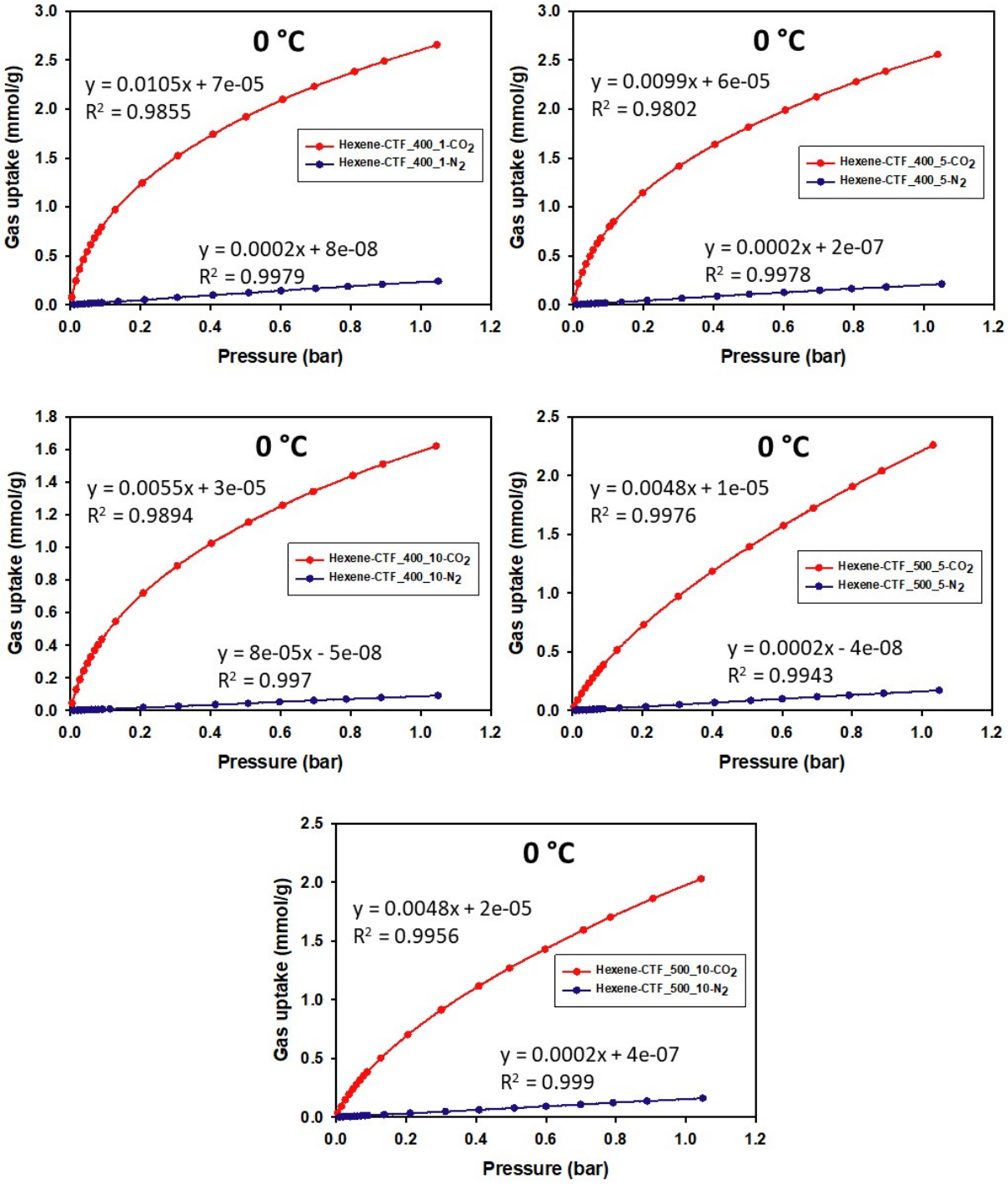


Figure S20: CO_2/N_2 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 0°C.

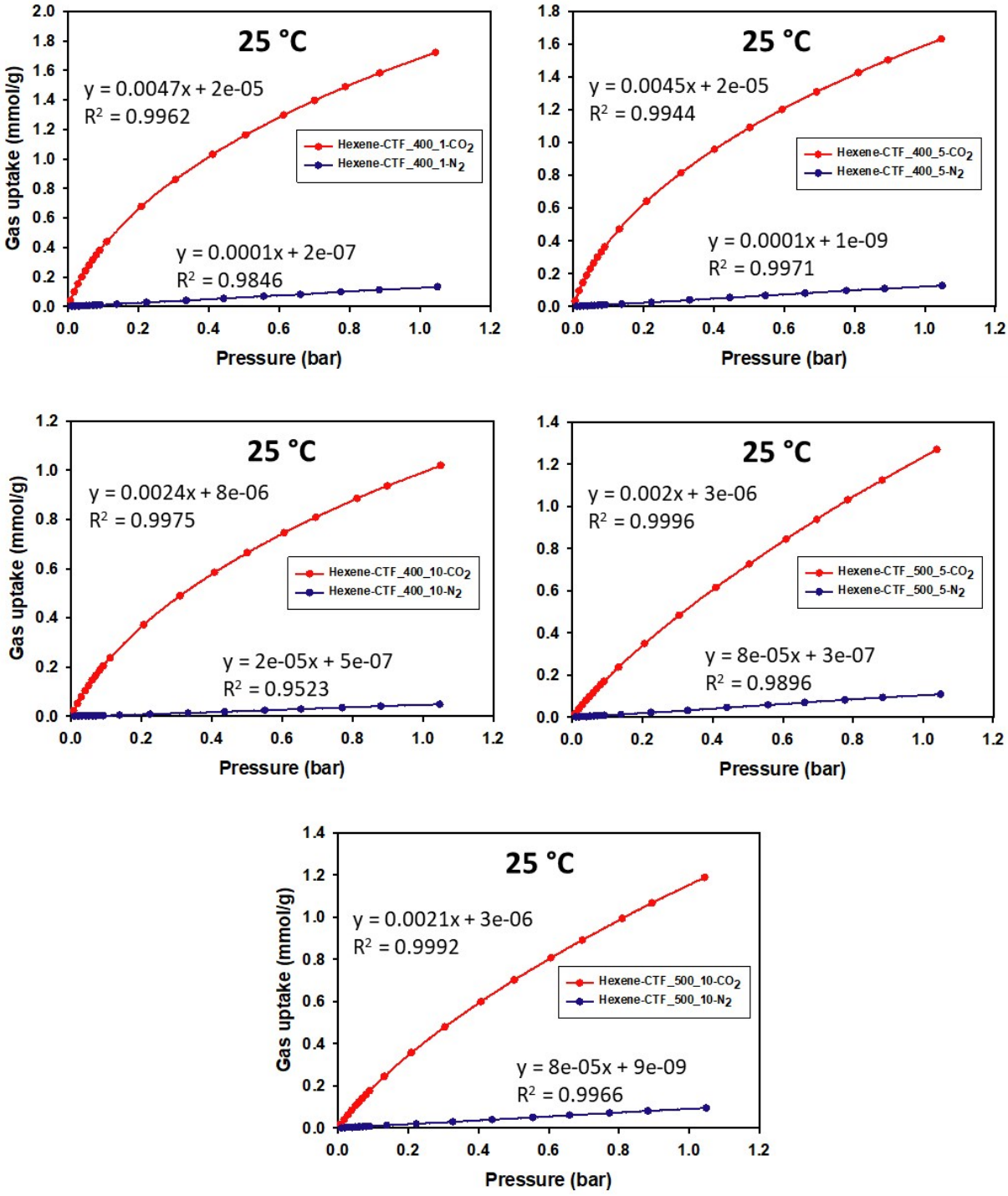


Figure S21: CO_2/N_2 selectivity estimated using the ratio of the initial slopes in the Henry regime of the adsorption isotherms at 25°C.