Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

A microporous yttrium metal-organic framework of an unusual *nia* topology for high adsorption selectivity of C_2H_2 and CO_2 from CH_4 at room temperature

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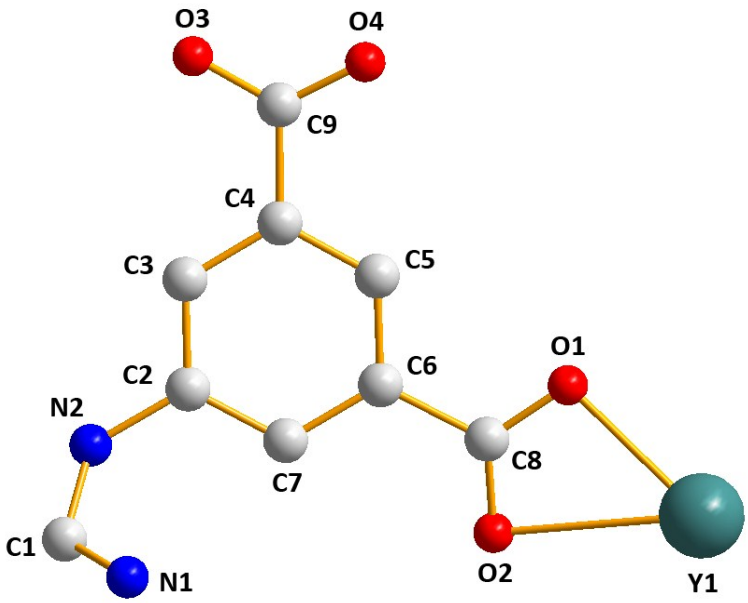

Figure S1. Asymmetric units of Y-H_3TDPAT (H atoms are omitted for clarity).

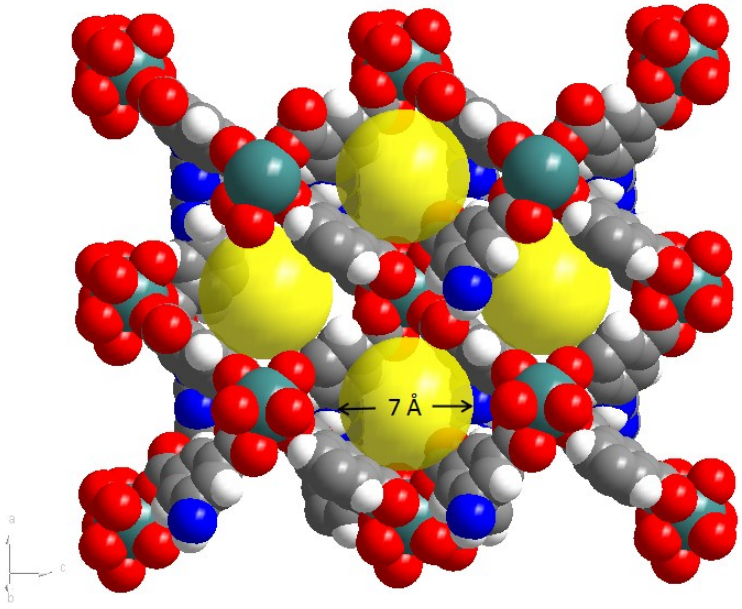

Figure S2. The space-filling view of the open channel along *b* axis in Y-H_3TDPAT.

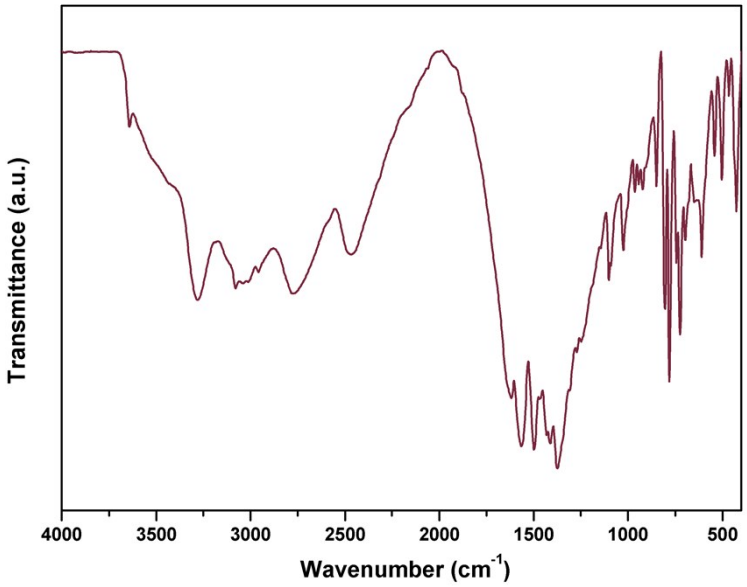

Figure S3. The infrared spectra for Y-H_3TDPAT.

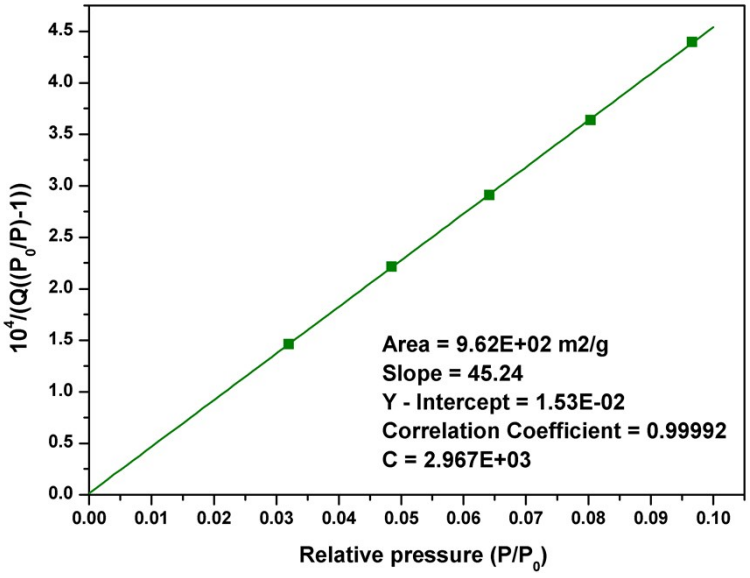

Figure S4. The BET surface area of Y-H_3TDPAT obtained from N_2 sorption isotherm at 77 K.

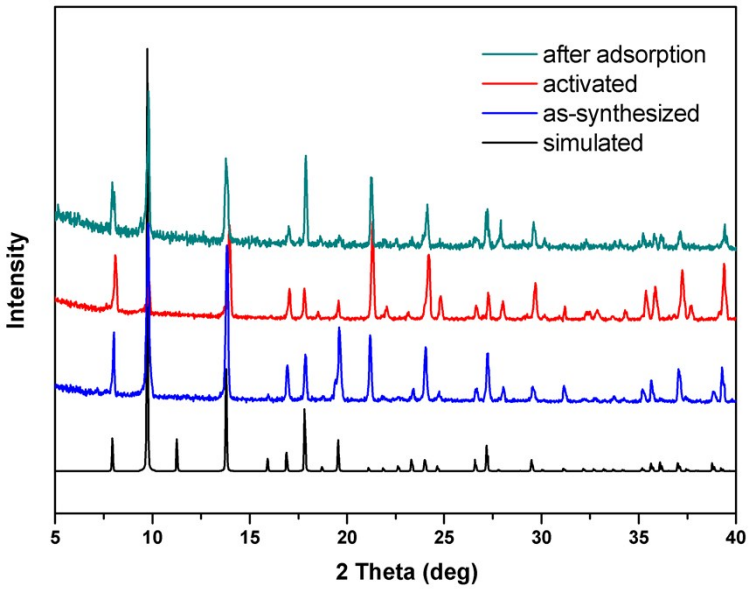

Figure S5. The PXRD data of Y-H_3TDPAT showing good agreement with simulated one for as-synthesized, activated and after adsorbed sample.

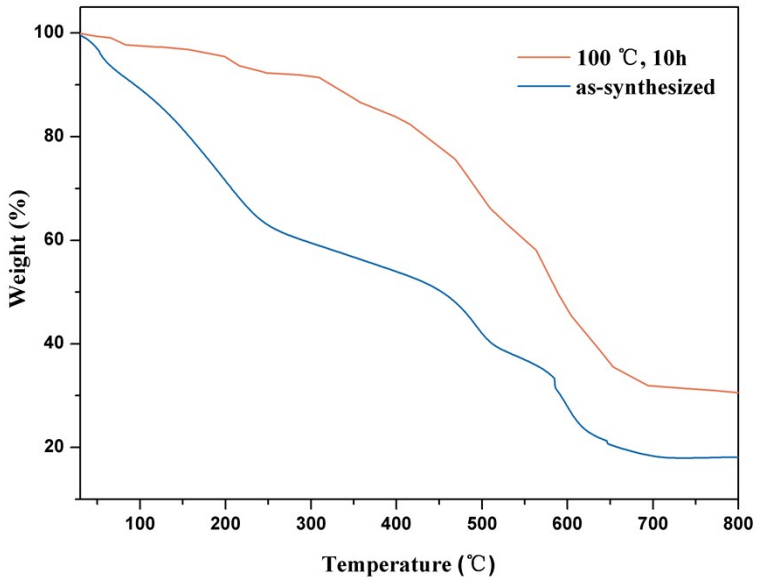

Figure S6. TGA plot of as-synthesised sample (blue) and guest-free sample (coral).

Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere with a heating rate of 20 °C/min using a Netzsch STA 449C apparatus. The amount of guest molecules in as-synthesized Y-H_3TDPAT is ~37 wt% according to the TG data.

Isosteric Heats of Gas Adsorption (Q_{st}). A virial-type[23] expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for , C_2H_2, CO_2 and CH_4 (at 273 and 298K) on Y-H_3TDPAT. In each case, the data were fitted using the equation: □□ □

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of varieties of gases sorption for Y-H_3TDPAT in this manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar, which is fitted by the virial-equation very well.

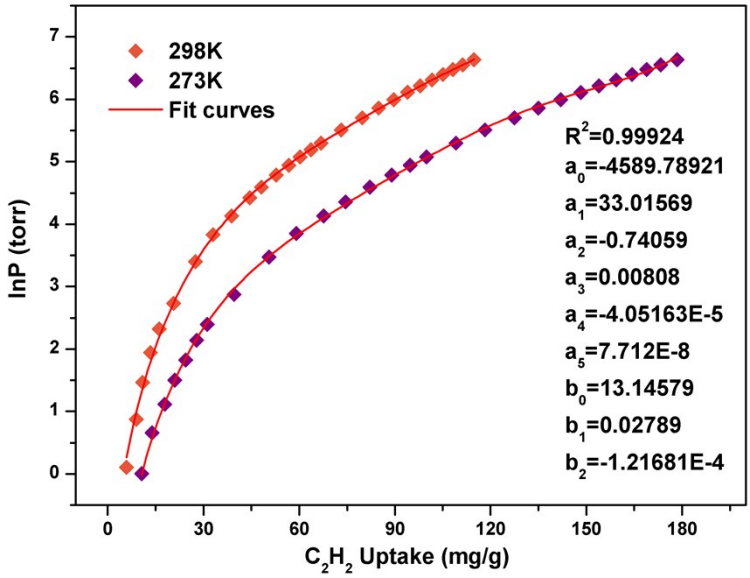

Figure S7. The details of virial equation (solid lines) fitting to the experimental C_2H_2 adsorption data (symbols) for Y-H_3TDPAT.

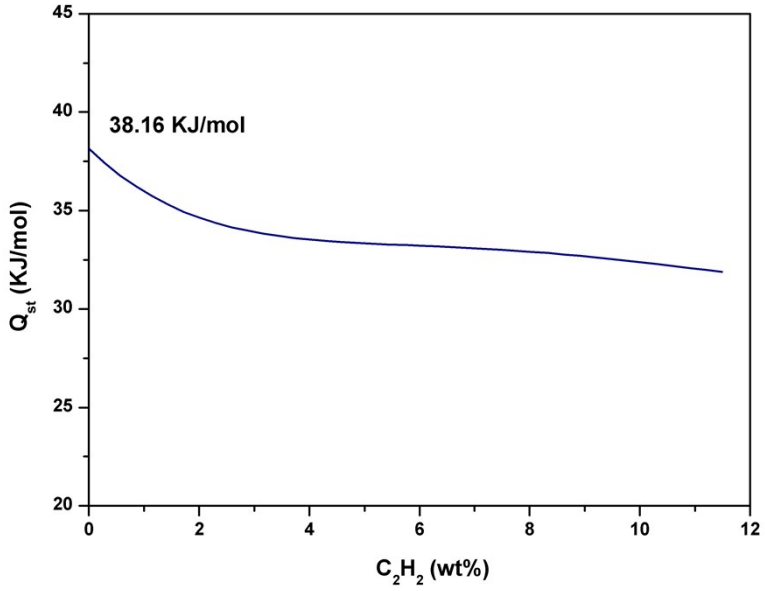

Figure S8. The C_2H_2 adsorption enthalpies of Y-H_3TDPAT.

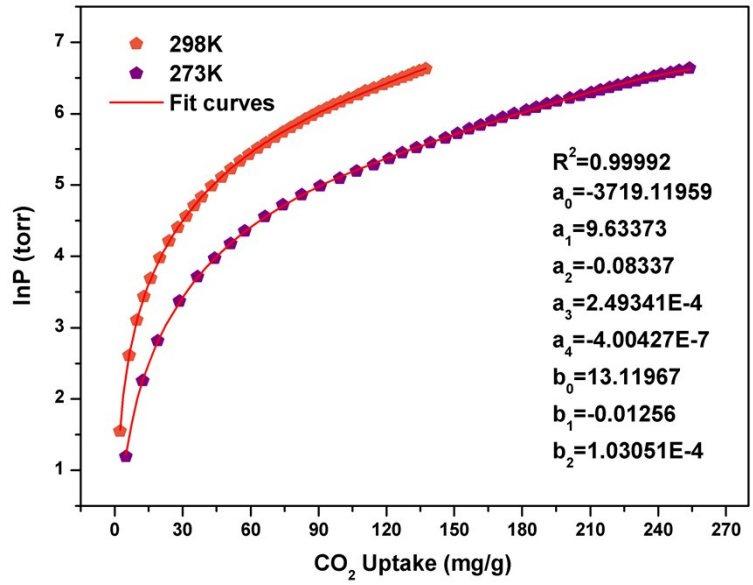

Figure S9. The details of virial equation (solid lines) fitting to the experimental CO_2 adsorption data (symbols) for Y-H_3TDPAT.

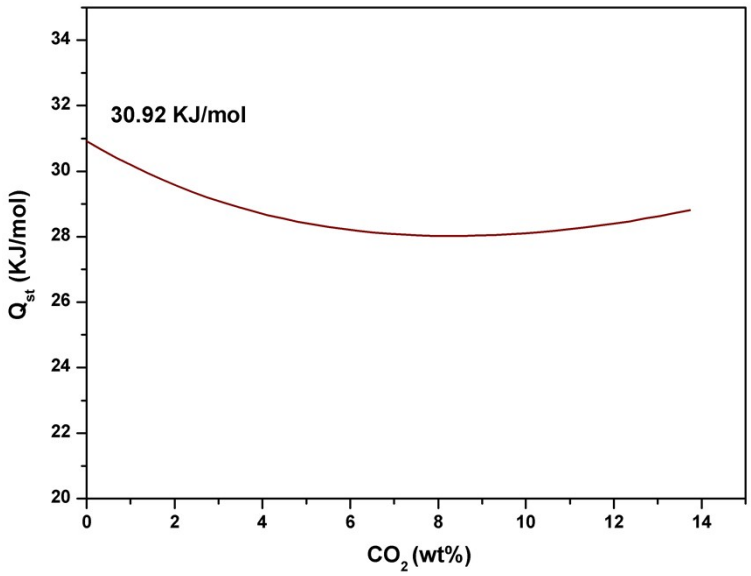

Figure S10. The CO_2 adsorption enthalpies of Y-H_3TDPAT.

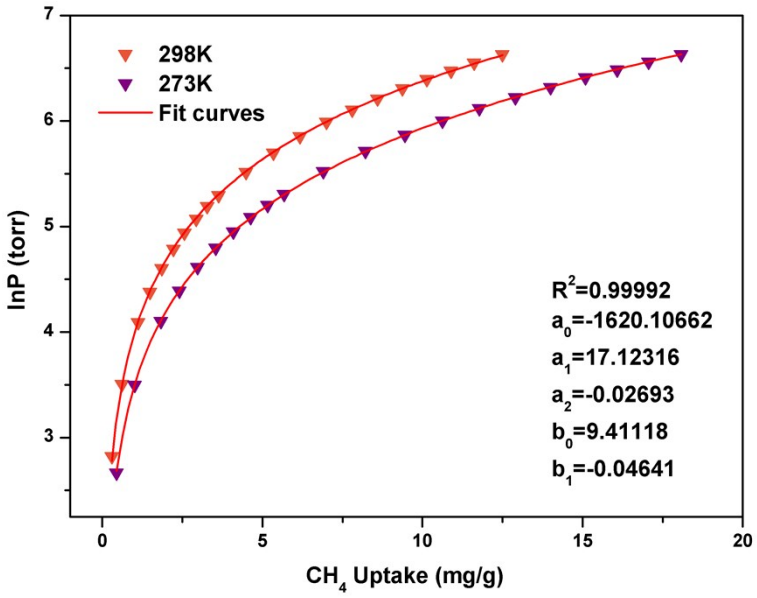

Figure S11. The details of virial equation (solid lines) fitting to the experimental CH_4 adsorption data (symbols) for Y-H_3TDPAT.

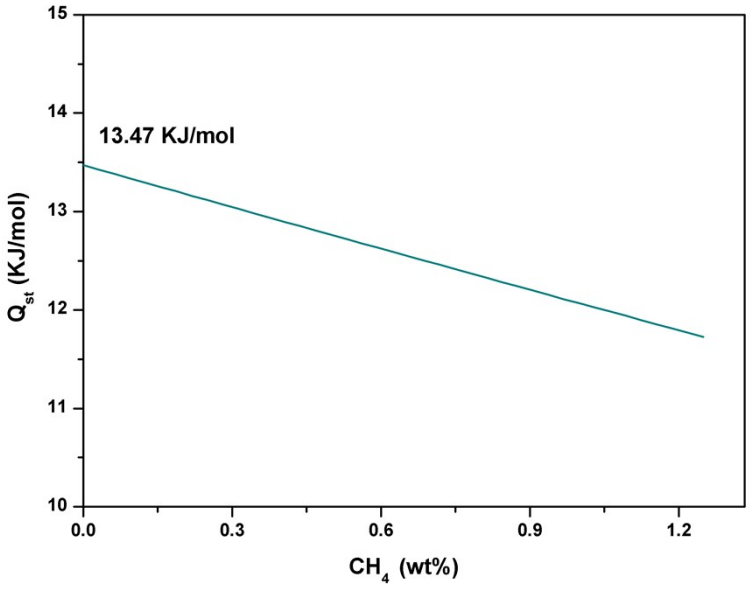

Figure S12. The CH_4 adsorption enthalpies of Y-H_3TDPAT.

Calculations of selectivity based on the Henry's Law.

The Henry's Law selectivity for gas component *i* over *j* at a specific temperature is calculated based on the following equation.

$$S_{ij} = K_{Hi} / K_{Hj}$$

The Henry's Law constants were calculated directly from the adsorption isotherms.

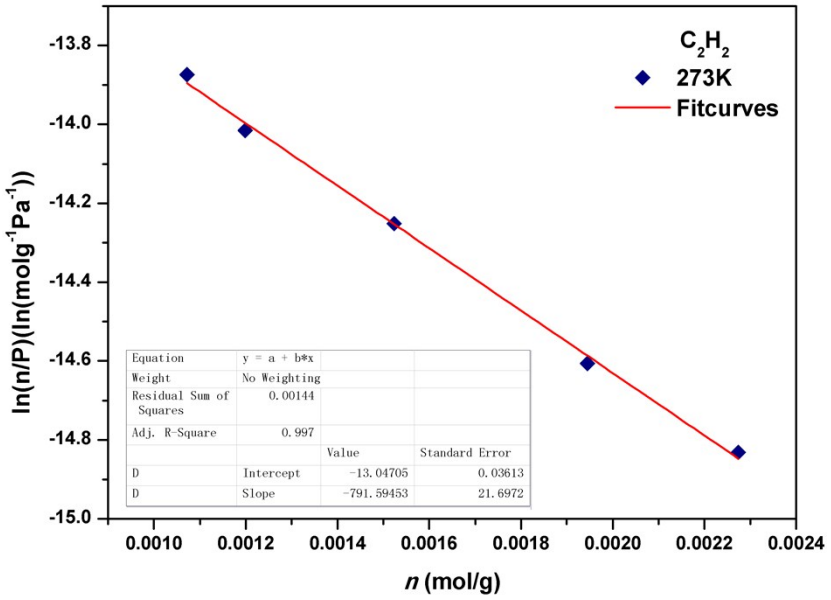

Figure S13. Virial analysis of the adsorption data for C_2H_2 on Y-H_3TDPAT at 273 K: Low pressure data.

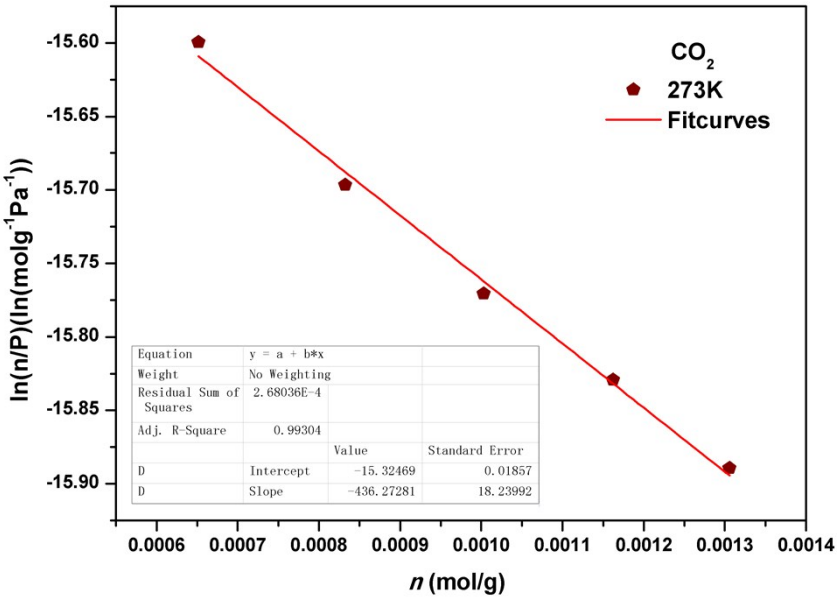

Figure S14. Virial analysis of the adsorption data for CO_2 on Y-H_3TDPAT at 273 K: Low pressure data.

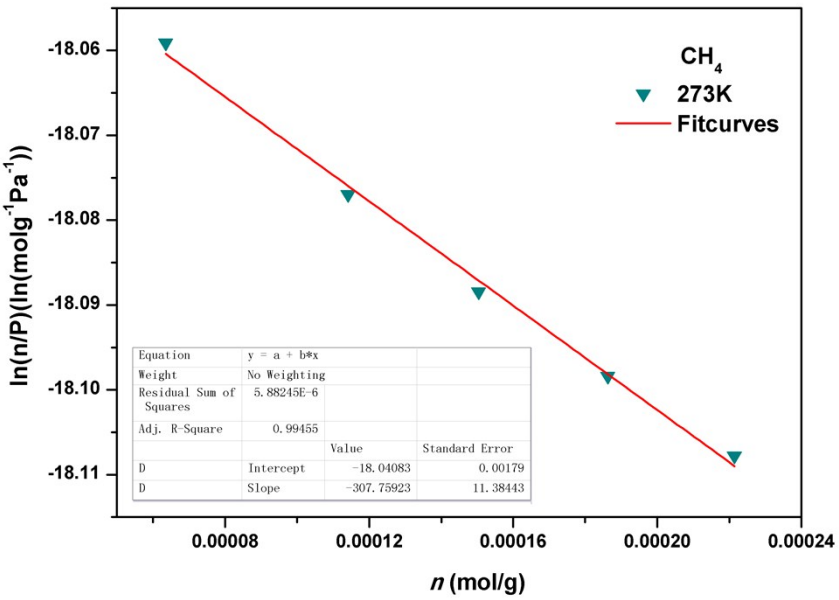

Figure S15. Virial analysis of the adsorption data for CH_4 on Y-H_3TDPAT at 273 K: Low pressure data.

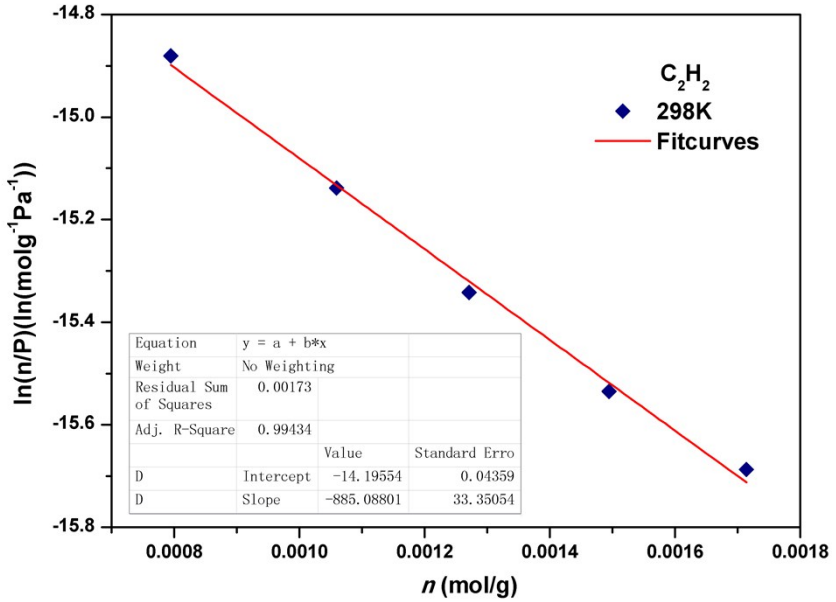

Figure S16. Virial analysis of the adsorption data for C_2H_2 on Y-H_3TDPAT at 298 K: Low pressure data.

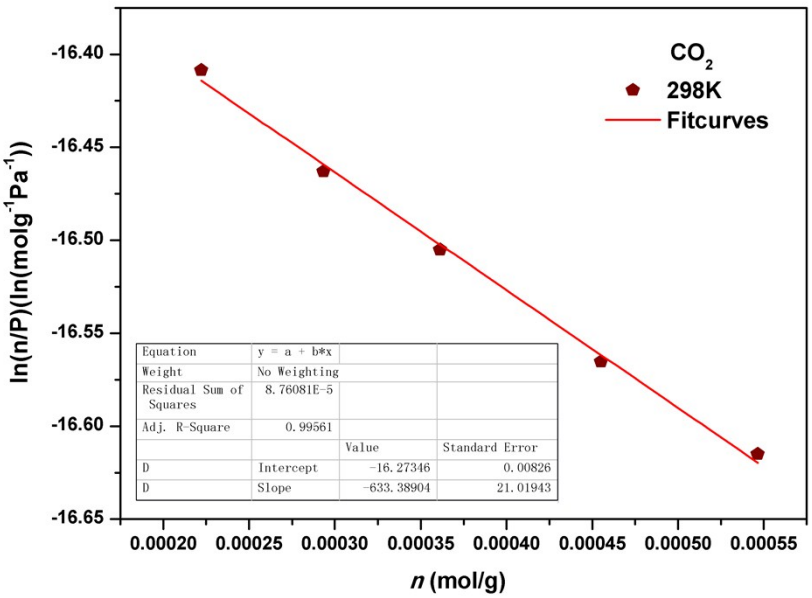

Figure S17. Virial analysis of the adsorption data for CO_2 on Y-H_3TDPAT at 298 K: Low pressure data.

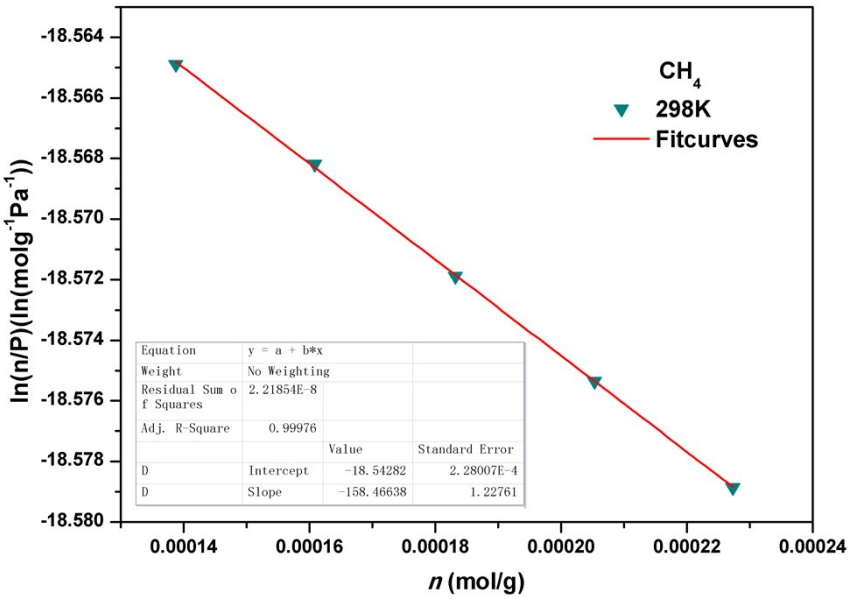

Figure S18. Virial analysis of the adsorption data for CH_4 on Y-H_3TDPAT at 298 K: Low pressure data.

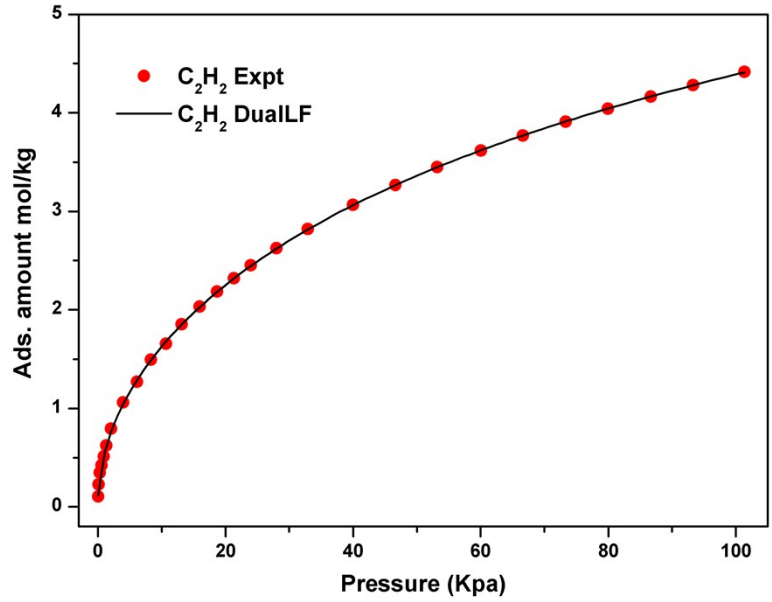

Figure S19. C_2H_2 adsorption isotherms at 298 K along with the Dualsite Langmuir Freundich (DSLF) fits.

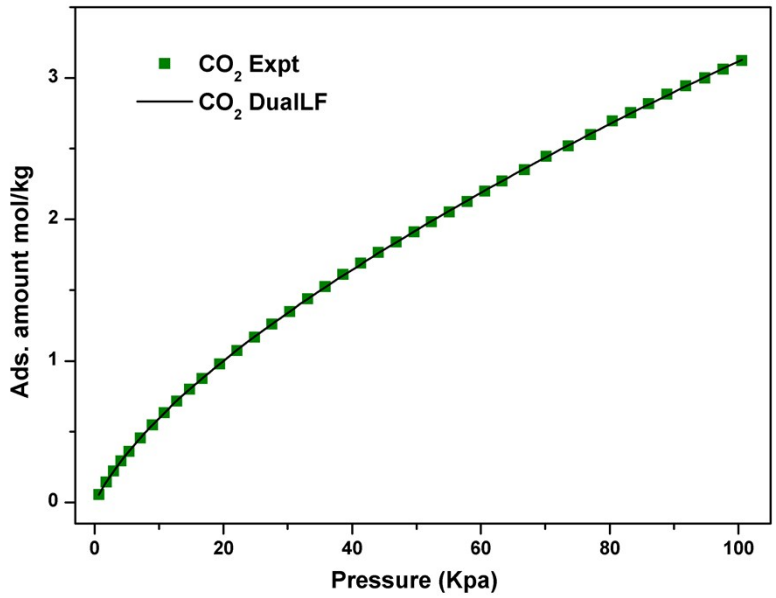

Figure S20. CO_2 adsorption isotherms at 298 K along with the Dualsite Langmuir Freundich (DSLF) fits.

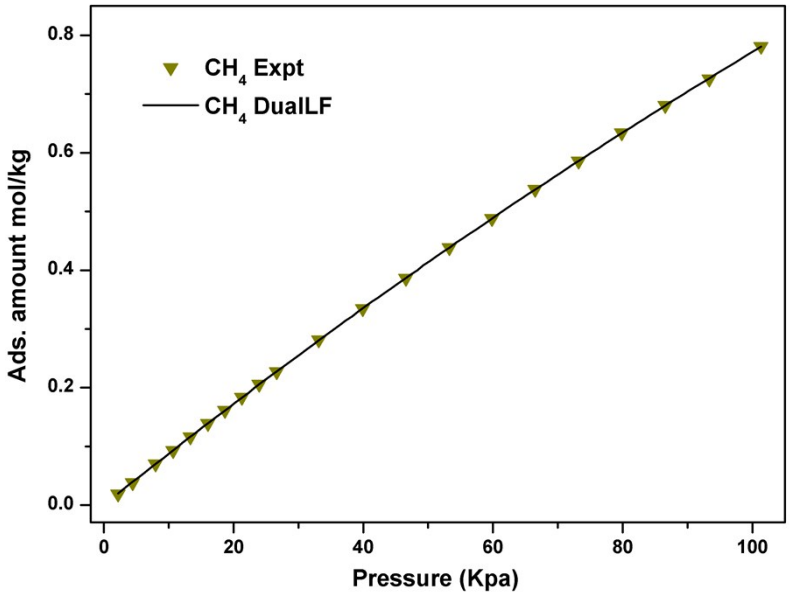

Figure S21. CH_4 adsorption isotherms at 298 K along with the Dualsite Langmuir Freundich (DSLF) fits.

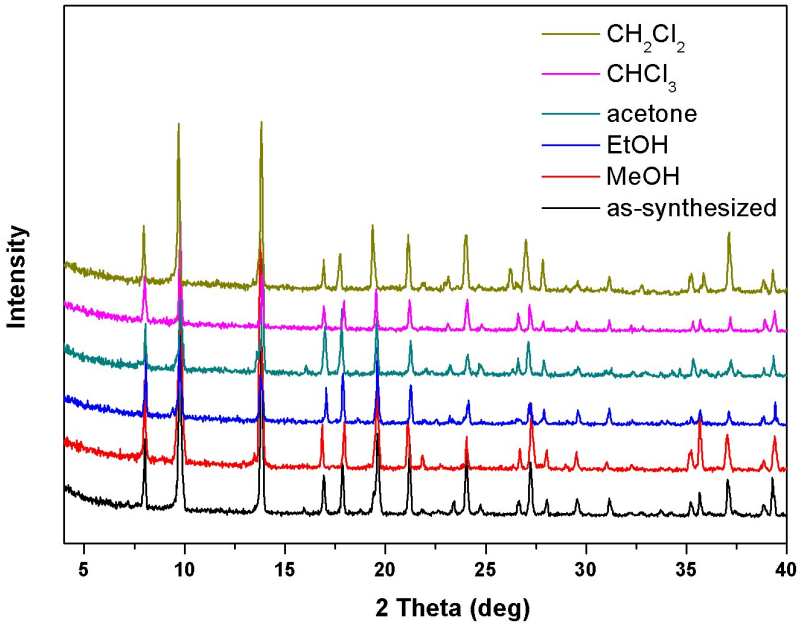

Figure S22. The PXRD data of Y-H_3TDPAT in several common organic solvents.

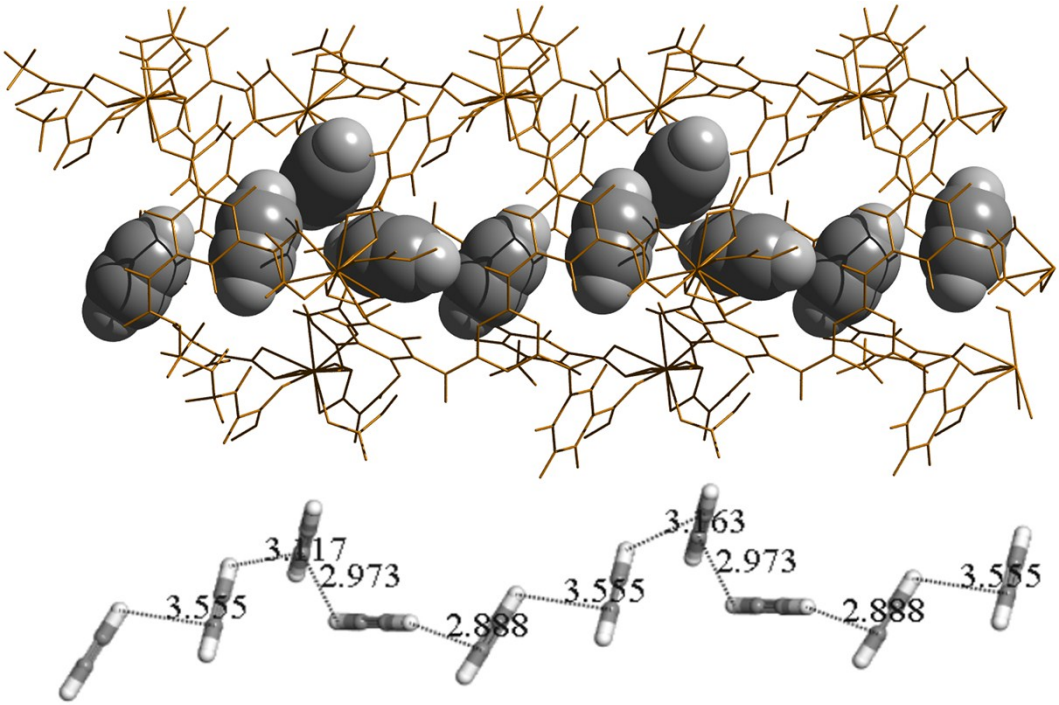

Figure S23. Wave type arrangement of C_2H_2 guests with C-H···π interactions.

Table S1. Acetylene adsorption on some porous MOFs at room temperature and atmospheric pressure.

Material	BET (Langmuir) SA [$m^2\ g^{-1}$]	C_2H_2 uptake [$cm^3\ g^{-1}$]	Q_{st} [kJ mol^{-1}]
HKUST-1	1401 (2095)	201	30.4
CoMOF-74	1018 (1504)	197	50.1
NOTT-101	(2930)	184	37.1
Cu-TDPAT	1938 (2608)	178	42.5
UTSA-20	(1894)	150	30.8
Y-H_3TDPAT	962	100	38.2
UTSA-5	462	60	30.8
$[Zn_4(dmf)(ur)_2(ndc)_4]$	1060	33	24.0
MOF-5	2381	26	16.5
ZIF-8	1112	25	13.3

Table S2. Crystal data and structure refinement for Y-H_3TDPAT.

	N_1^{max} [mmol/g]	b_1 [kPa^{-1}]	n_1	N_2^{max} [mmol/g]	b_2 [kPa^{-1}]	n_2	R^2
	Compound			Y-H_3TDPAT			
	Molecular formula			$C_{27}H_{15}N_6O_{12}Y$			
	fw			704.34			
	crystal system			Hexagonal			
	space group			*P*31*c*			
	a, Å			12.8501(18)			
	b, Å			12.8501(18)			
	c, Å			15.709(3)			
	V, Å^3			2246.4(6)			
	Z			6			
	Dcalc, g/cm^3			1.037			
	F(000)			702			
	final R indices [I > 2σ(I)]			R_1 = 0.0325, wR_2 = 0.0890			
	R indices (all data)			R_1 = 0.0345, wR_2 = 0.0897			

C_2H_2	1.38504	0.01491	0.98286	12.21666	0.04397	0.48779	0.999999
CO_2	0.86442	0.06945	1.09461	14.53642	0.00197	0.99843	0.999997
CH_4	2.42166	0.00043	1.03630	4.15031	0.00185	1.00292	1

Table S3. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of C_2H_2, CO_2 and CH_4 in Y-H_3TDPAT at 298K.