Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Reaction Duration Dependent Formation of Two Cu(II)-MOFs with Selective Adsorption Property of C_3H_4 over C_3H_6

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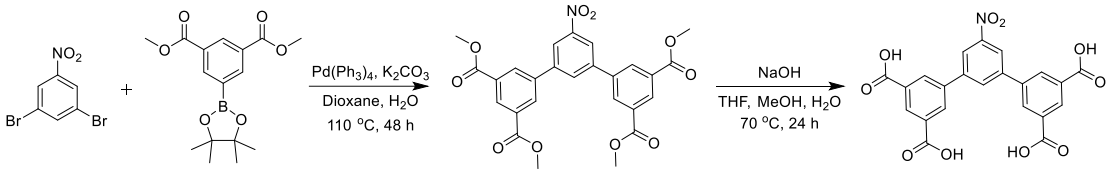
Section 1. Synthesis of H_4DDPN

H_4DDPN was synthesized by following procedures.



Scheme S1 Synthetic procedure of **H_4DDPN**.

(a) Tetramethyl 3,5-di(3,5-dicarboxylphenyl)nitrobenzene

A mixture of 1,3-dibromo-5-nitrobenzene (5.0 g, 17.8 mmol) and dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (17.1 g, 20.0 mmol) in dioxane (300 mL) and water (100 mL) was added K_2CO_3 (9.8 g, 71.2 mmol) and $Pd(PPh_3)_4$ (1.84 g, 1.8 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 48 h. After the starting materials were consumed, the organic solvent was removed and the residue was dissolved in $CHCl_3$ (400 mL), washed with water (400 mL × 2) and brine (300 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (SiO_2, $CHCl_3$) to give tetramethyl 3,5-di(3,5-dicarboxylphenyl)nitrobenzene (4.6 g, 59%) as a light yellow solid.

(b) 3,5-di(3,5-dicarboxylphenyl)nitrobenzene (H_4DDPN)

The solution of tetramethyl 3,5-di(3,5-dicarboxylphenyl)nitrobenzene (4.6 g, 9.1 mmol) in THF (100 mL), MeOH (100 mL) and 2 M NaOH aqueous solution (100 mL) was stirred at 70 °C for 24 h. The organic solvent was removed by rotary evaporation. The pH was adjusted to around 3 by progressively adding concentrated HCl. The suspension was filtered and washed with water (100 mL × 3). The solid was dried under vacuum at 60 °C to give 3,5-di(3,5-dicarboxylphenyl)nitrobenzene (3.2 g, 78%) as a light yellow solid.

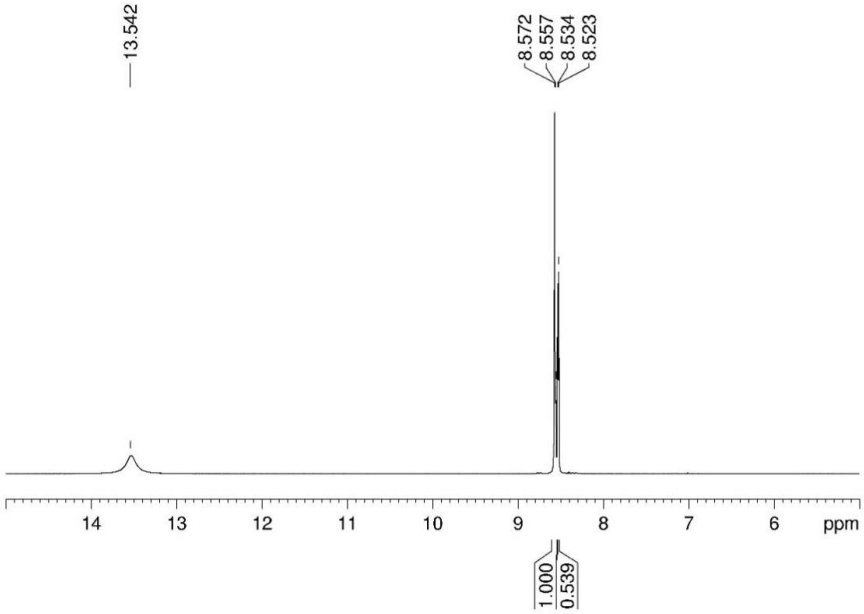


Fig. S1 ^{1}H NMR spectrum of **H_4DDPN**.

Section 2. Synthesis and General Characterizations of BUT-301 and BUT-302.

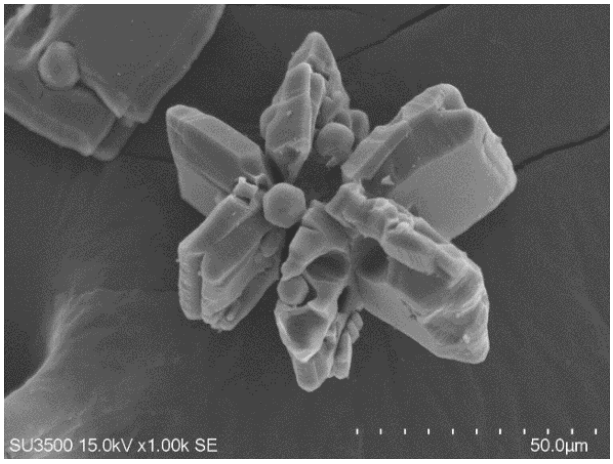


Fig. S2 SEM image of **BUT-301**.

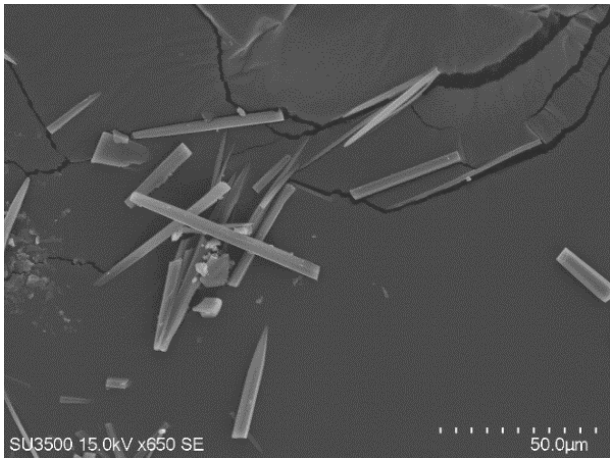


Fig. S3 SEM image of **BUT-302**.

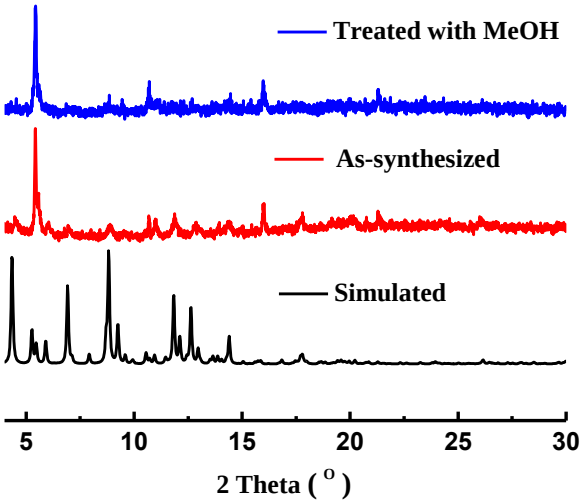


Fig. S4 PXRD patterns of as-synthesized sample of **BUT-301** and the samples of **BUT-301** after being treated with MeOH.

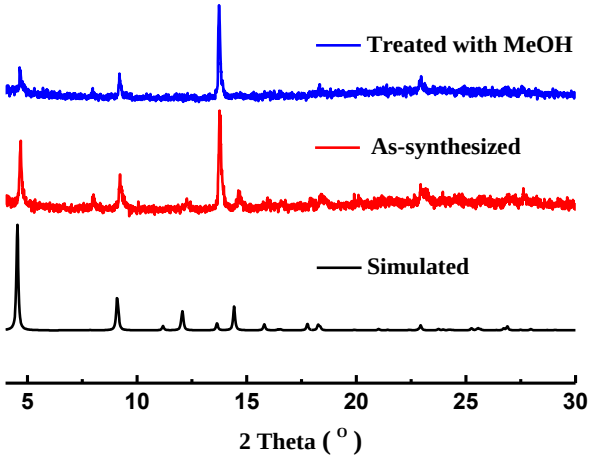


Fig. S5 PXRD patterns of as-synthesized sample of **BUT-302** and the samples of **BUT-302** after being treated with MeOH.

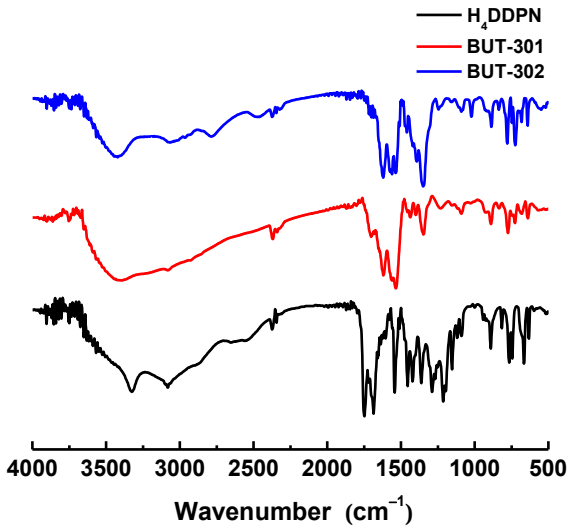


Fig. S6 FT-IR spectra of H_4DDPN, **BUT-301** and **BUT-302**.

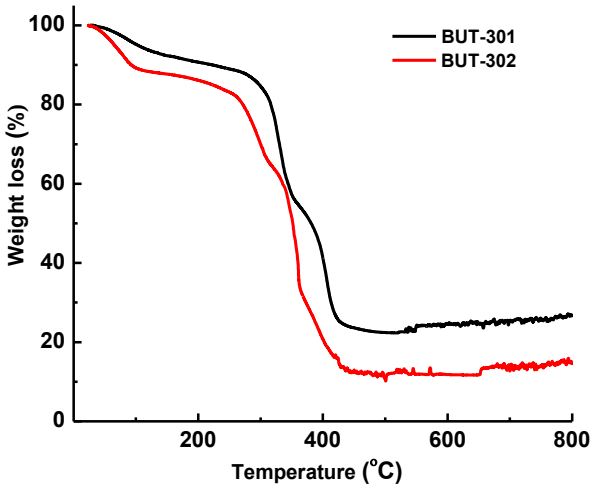


Fig. S7 TGA curves of **BUT-301** and **BUT-302**

Section 3. Structure of BUT-28 and Zr-abtc

Table S1 Crystal data and structure refinement parameters for **BUT-301** and **BUT-302**.

Compound	**BUT-301**	**BUT-302**
Formula	$C_{132}H_{54}N_6O_{70}ClCu_{12}$	$C_{22}H_9NO_{10}Cu$
Crystal system	orthorhombic	trigonal
Space group	*Pnnm*	$P3_221$
a (Å)	18.4362(7)	22.4612(9)
b (Å)	33.5056(10)	22.4612(9)
c (Å)	25.5225(9)	11.1324(6)
α (°)	90	90
β (°)	90	90
γ (°)	90	120
V (Å^3)	15765.7(9)	4863.9(5)
Z	4	3
D_c (g cm^{-3})	0.767	1.048
F (000)	3626.0	1548.0
Reflections collected	46526	12033
Unique reflections	13719	5501
Goof	0.918	1.012
R_1[a] [I > 2σ(*I*)]	0.0567	0.0680
wR_2[b] [I > 2σ(*I*)]	0.1324	0.1622

[a]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b]$wR_2 = |\Sigma w(|Fo|^2 - |Fc|^2)|/\Sigma|w(Fo)^2|^{1/2}$, where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$.

$P = (Fo^2 + 2Fc^2)/3$

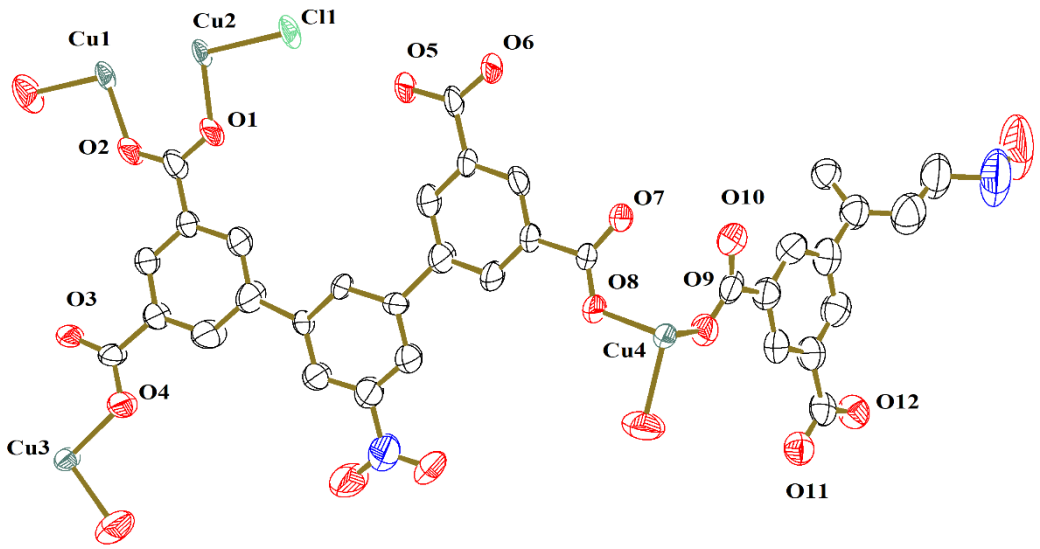


Fig. S8 Asymmetric unit of the compound **BUT-301** in ORTEP view (50% thermal ellipsoids).

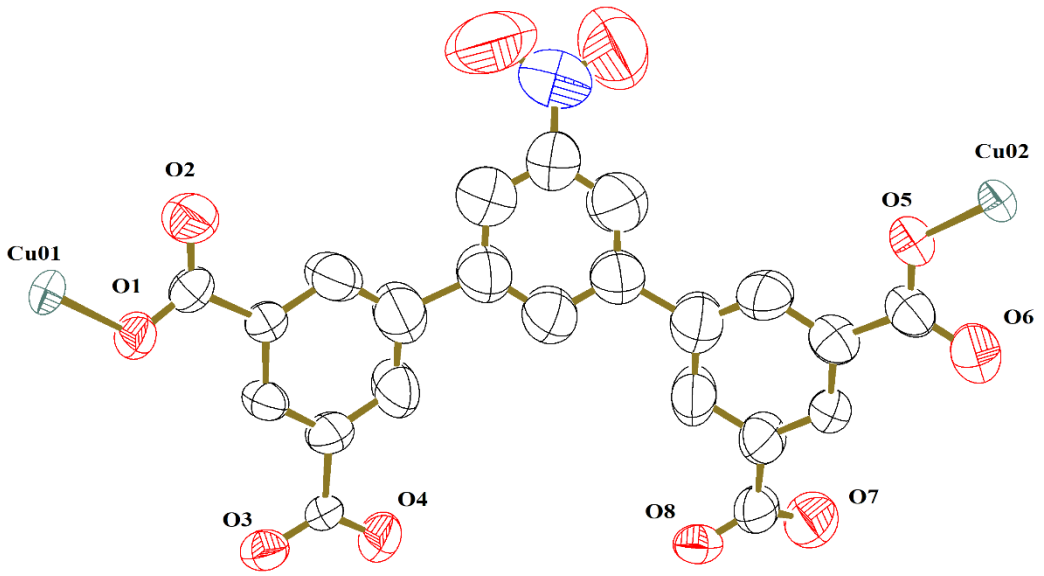


Fig. S9 Asymmetric unit of the compound **BUT-302** in ORTEP view (50% thermal ellipsoids).

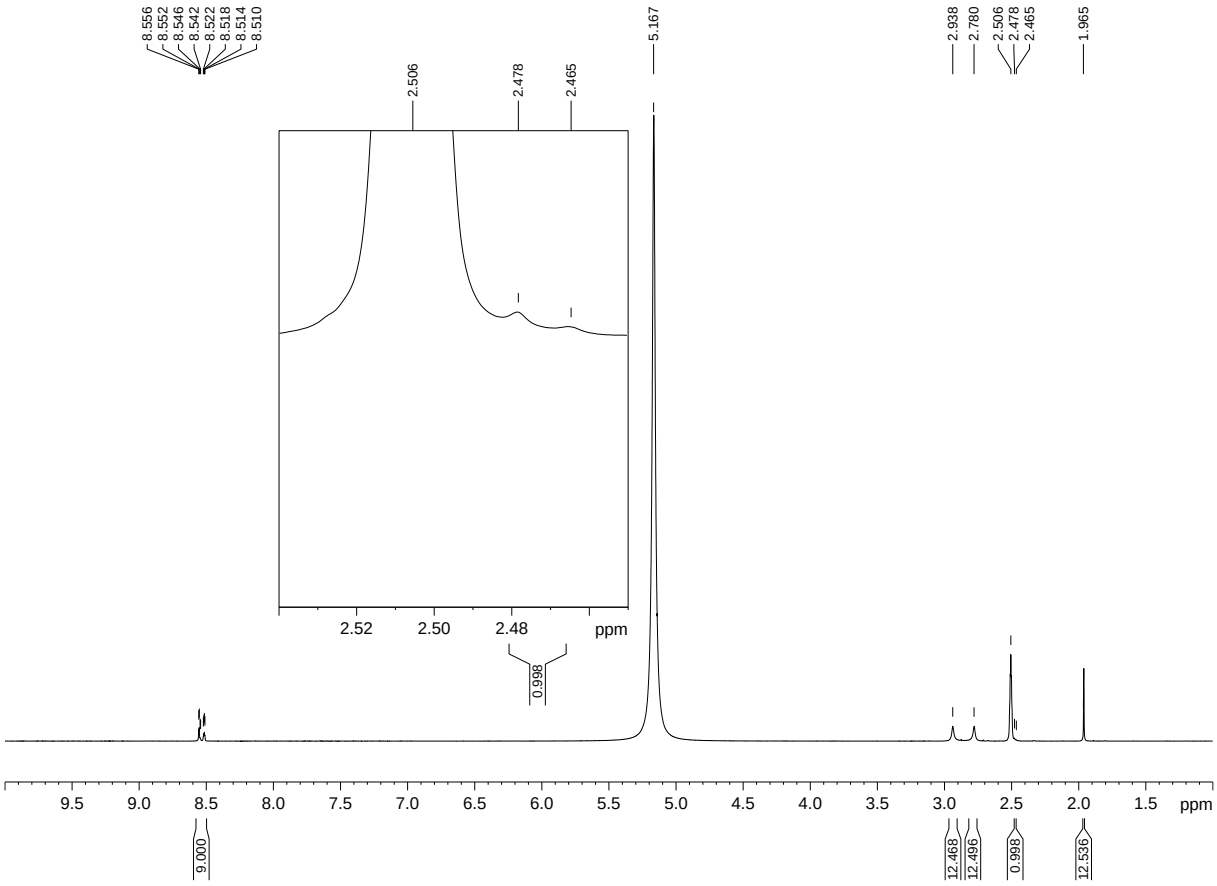


Fig. S10 ^{1}H NMR spectrum of digested **BUT-302** in deuterated DMSO (peaks for H_2O: 5.165 ppm, and DMSO: 2.506 ppm). Note that the triplet centered at 2.478 ppm corresponding to the methyl H atoms of dimethylammonium cations is partially overlapped with the peak centered at 2.506 ppm corresponding to methyl H atoms of DMSO, and one peak of the triplet could not be labelled (inset).

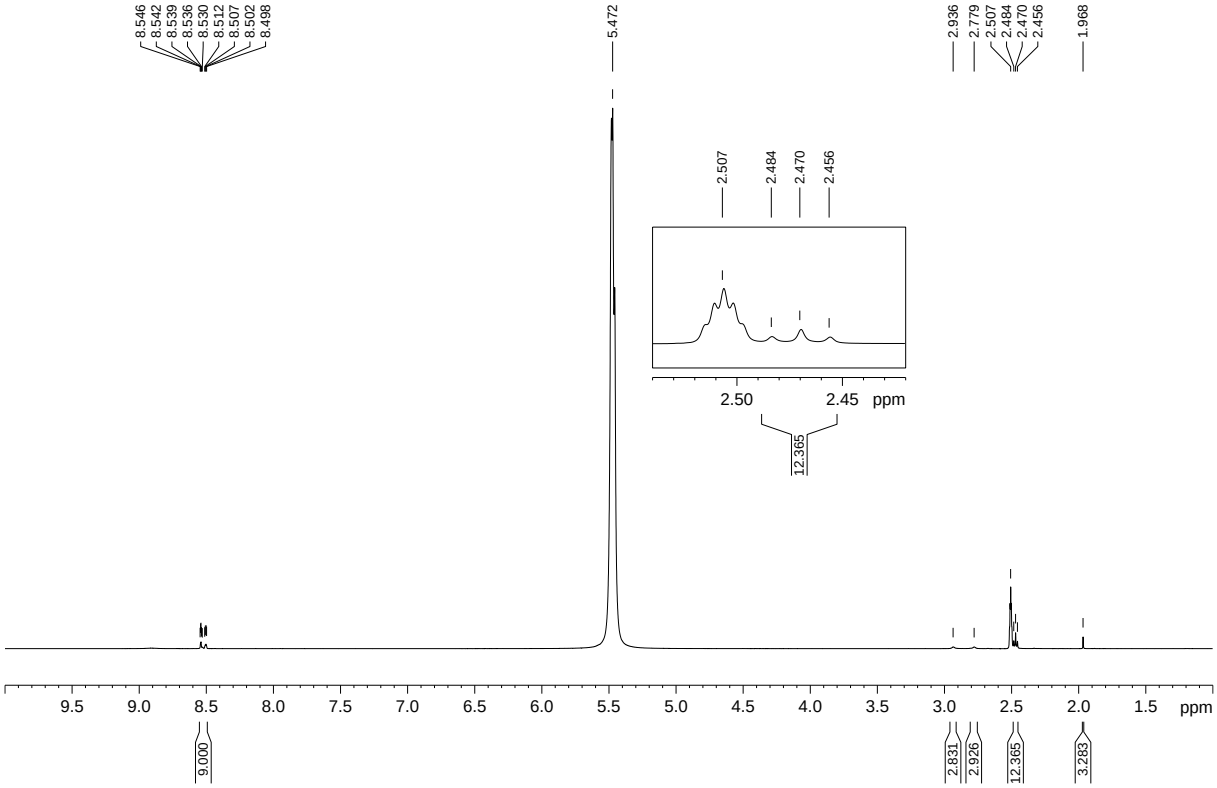


Fig. S11 ^{1}H NMR spectrum of digested **BUT-302** in deuterated DMSO (peaks for H_2O: 5.472 ppm, and DMSO: 2.507 ppm).

Section 4. Gas adsorption

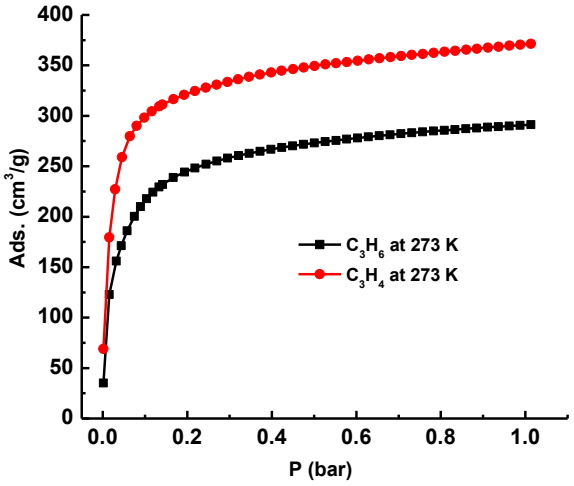


Fig. S12 C_3H_6 and C_3H_4 adsorption isotherms of **BUT-301** at 273 K

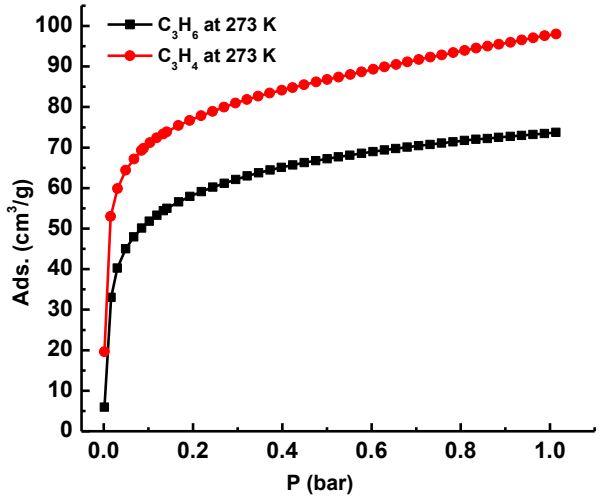


Fig. S13 C_3H_6 and C_3H_4 adsorption isotherms **BUT-302** at 273 K

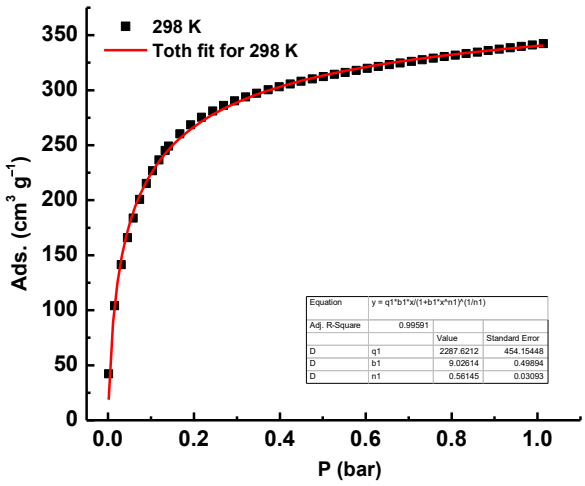


Fig. S14 The C_3H_4 adsorption isotherm of **BUT-301** measured at 298 K and its Toth fit.

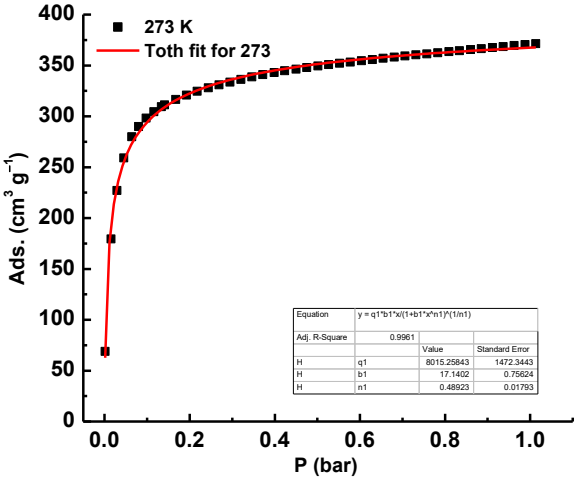


Fig. S15 The C_3H_4 adsorption isotherm of **BUT-301** measured at 273 K and its Toth fit.

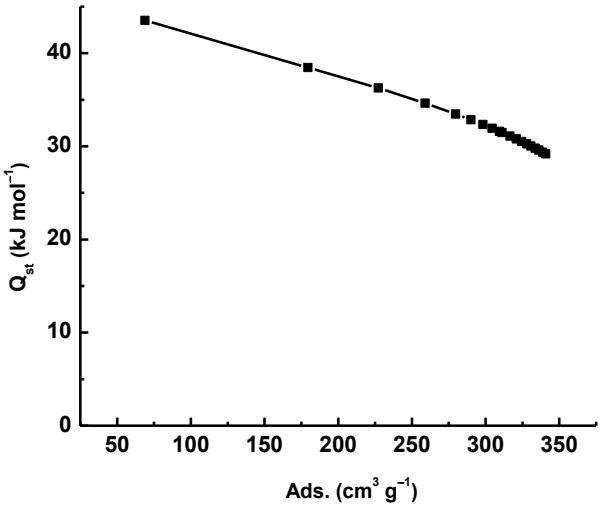


Fig. S16 The calculated isosteric heats (*Q*st) of C_3H_4 for **BUT-301**.

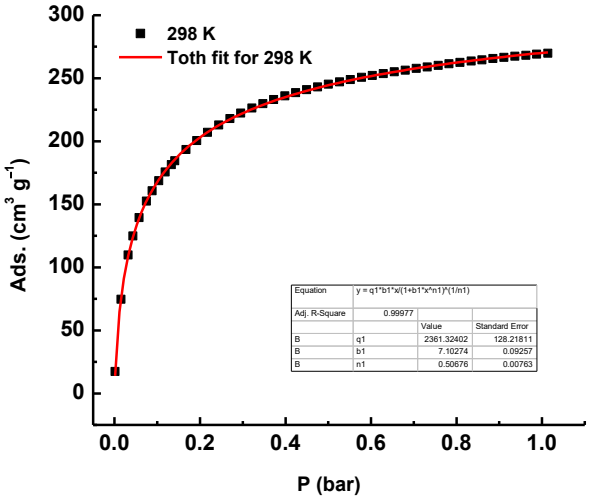


Fig. S17 The C_3H_6 adsorption isotherm of **BUT-301** measured at 298 K and its Toth fit.

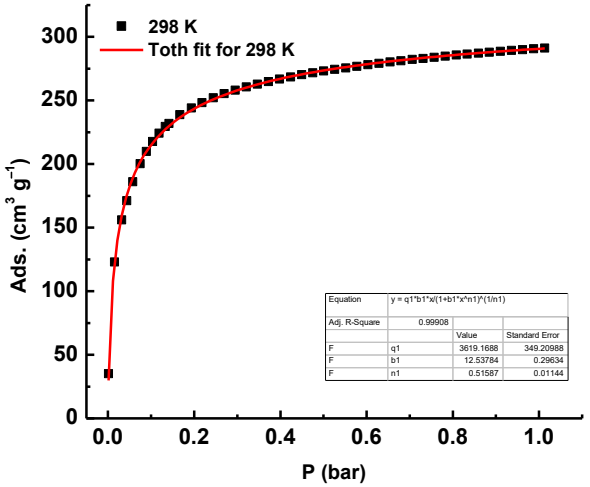


Fig. S18. The C_3H_6 adsorption isotherm of **BUT-301** measured at 273 K and its Toth fit.

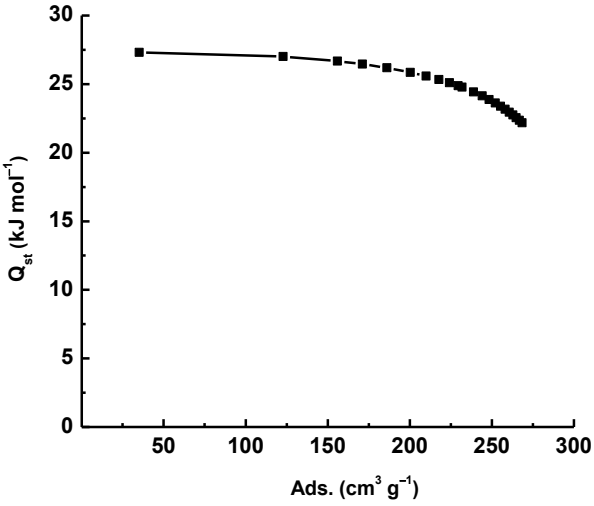


Fig. S19 The calculated isosteric heats (Qst) of C_3H_6 for **BUT-301**.

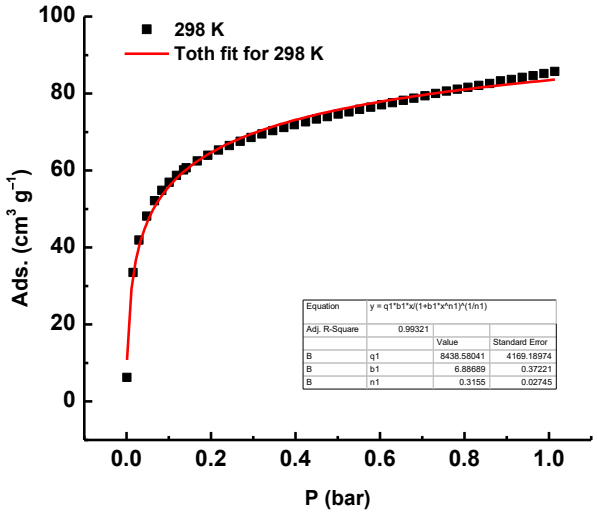


Fig. S20 The C_3H_4 adsorption isotherm of **BUT-302** measured at 298K and its Toth fit.

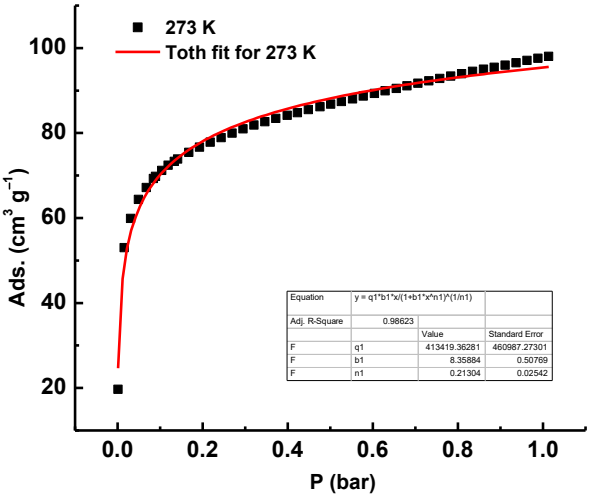


Fig. S21 The C_3H_4 adsorption isotherm of **BUT-302** measured at 273K and its Toth fit.

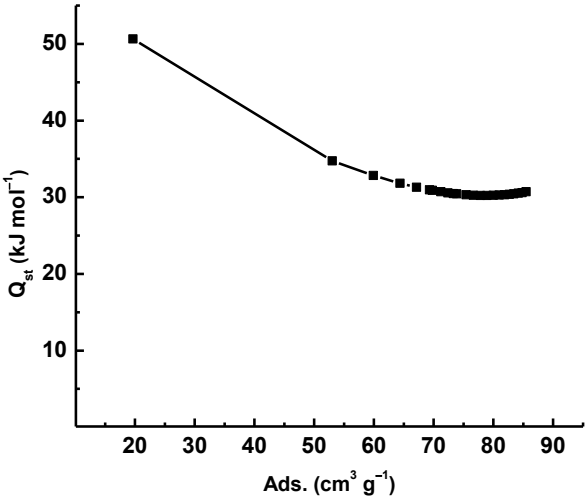


Fig. S22 The calculated isosteric heats (Qst) of C_3H_4 for **BUT-302**.

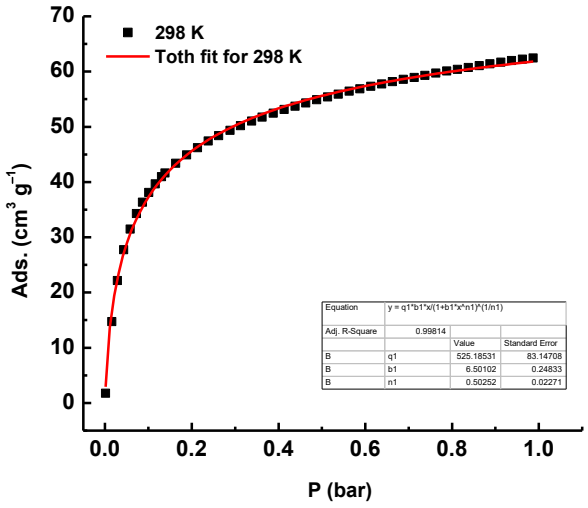


Fig. S23 The C_3H_6 adsorption isotherm of **BUT-302** measured at 298K and its Toth fit.

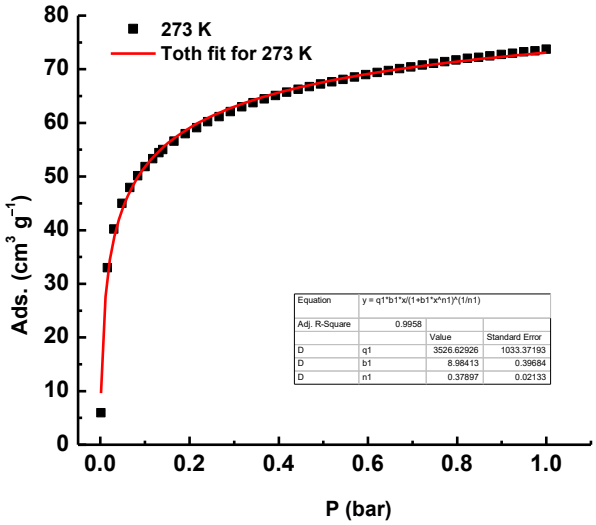


Fig. S24 The C_3H_6 adsorption isotherm of **BUT-302** measured at 273K and its Toth fit.

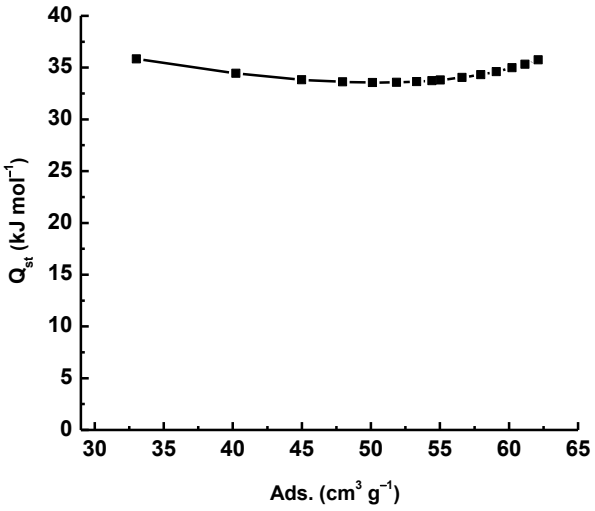


Fig. S25 The calculated isosteric heats (Qst) of C_3H_6 for **BUT-302**.

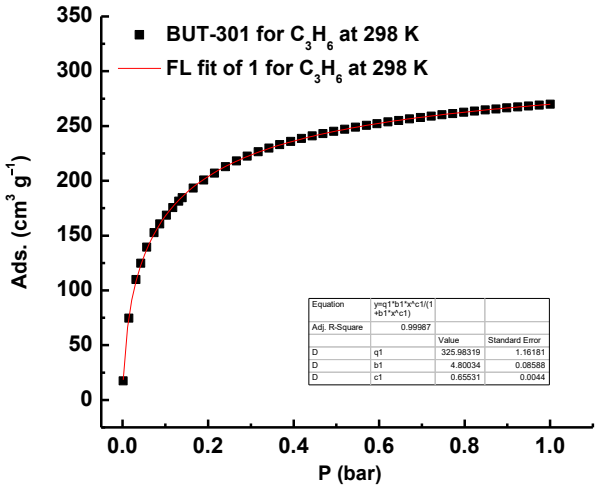


Fig. S26 The C_3H_6 adsorption isotherm of **BUT-301** measured at 298K and its single-site. Langmuir-Freundlich fit.

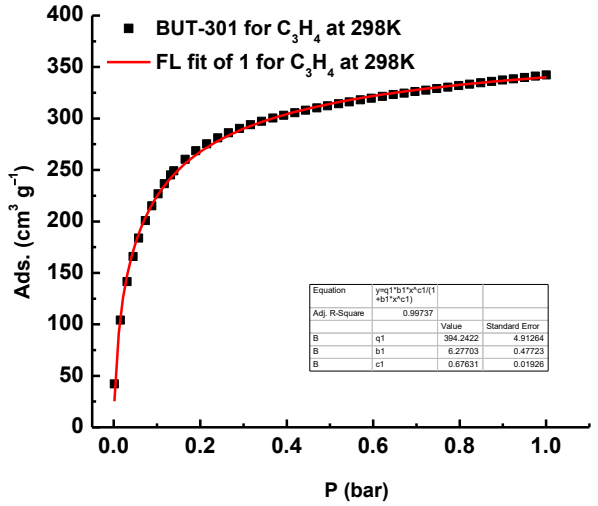


Fig. S27 The C_3H_4 adsorption isotherm of **BUT-301** measured at 298K and its single-site Langmuir-Freundlich fit.

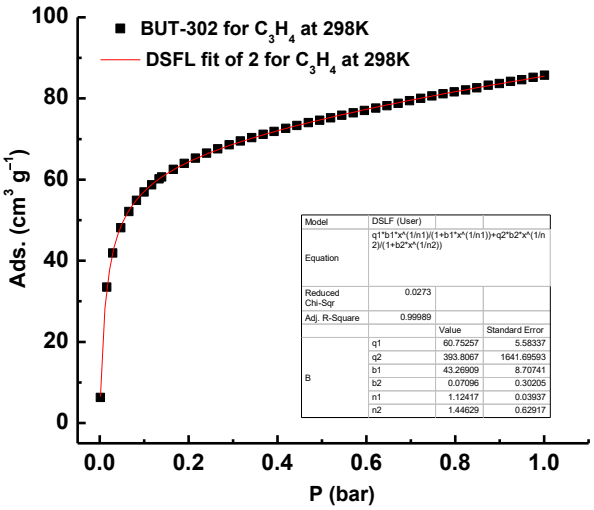


Fig. S28 The C_3H_6 adsorption isotherm of **BUT-302** measured at 298K and its double-site Langmuir-Freundlich fit.

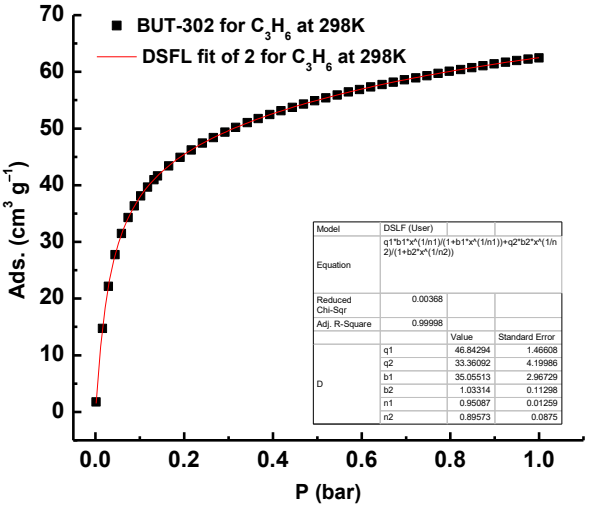


Fig. S29 The C_3H_4 adsorption isotherm of **BUT-302** measured at 298K and its double-site Langmuir-Freundlich fit.