Supporting information

Thiazole functionalized Covalent Triazine Frameworks for

C₂H₆/C₂H₄ Separation with Remarkable Ethane Uptake

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Experimental Section

Materials

4,7-Dibromo-2,1,3-benzothiodiazole (98.0%) was purchased from Shanghai Darui Fine Chemicals Co., Ltd. 4-cyanophenylboronic acid was obtained from Shanghai D&B Biological Science and Technology Co., Ltd. Zinc chloride (ZnCl₂, 98.0%) was supplied by Tianjin Damao Chemical Reagent Factory. Dichloromethane (DCM, \geq 99.5%), methanol (MeOH, \geq 99.5%), hydrochloric acid (HCl, 36.0–38.0%), and ethanol (EtOH, \geq 99.5%) were bought from Tianjin Bohai Chemical Reagent Co., Ltd. All the chemicals were used directly without further purification.

Preparation of monomer: 4,4'-(benzothiadiazole-4,7-diyl)dibenzonitrile (BT-Ph₂-CN₂).

All the chemicals and solvents were commercially available and used without further purification. 4,4'-(benzothiadiazole-4,7-diyl)dibenzonitrile was synthesized based on the previous reports¹⁻³.



4,7-Dibromo-2,1,3-benzothiodiazole (2.94 g, 10 mmol), 4-cyanophenylboronic acid (3.23 g, 22 mmol), K₂CO₃ (4.15 g, 30 mmol), tetrakis(triphenylphosphine)palladium (0.58 g, 0.5 mmol), toluene (60 mL), EtOH (30 mL), and H₂O (10 mL) were added to a 250mL Schlenk flask under a nitrogen atmosphere. After heating at 120 °C for 24 h, the reaction was quenched by addition of Milli Q water (60 ml). The formed solid was collected by filtration and washed thoroughly with Milli Q water, methanol and dichloromethane, respectively. The crude product was purified though silica column using dichloromethane as eluent. Finally, the titled product was obtained as light yellow powder after removal of the solvent (2.32 g, 75.2%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, 4H, ArH), δ 7.87 (d, 4H, ArH), δ 7.84 (s, 2H, ArH).

Preparation of CTF-BTs

CTF-BTs were synthesized by the ionothermal reaction. **BT-Ph₂-CN₂** (0.17 g, 0.5 mmol) and ZnCl₂ (0.68 g, 5 mmol) were put into a quartz ampule. The ampule was vacuumed and sealed with a flame. Then, the ampule was placed in a muffle furnace, heated to 400 °C, 500 °C and 600 °C in 2 h and held this target temperature for 40 h. The ampule was then cooled down to room temperature and opened carefully. The black reaction product was subsequently grounded and then stirred in 0.1 M HCl solution for 3 times to remove most of the ZnCl₂. Further, the sample was washed with water, MeOH, respectively. Finally, the resulting black powder was dried in an oven at 80 °C. The yields of CTF-BT-400, CTF-BT-500 and CTF-BT-600 are 81%, 75% and 67%, respectively.

Characterization

¹H nuclear magnetic resonance (NMR) spectrum was characterized using a Bruker AVANCE NEO 400 MHz instrument by dissolved the samples in CDCl₃. The solid-state ¹³C NMR was performed by a Bruker AVANCE 400 MHz Solid State NMR Spectrometer. Powder X-ray diffraction (PXRD)

measurements were performed on a Rigaku MiniFlex 600 instrument with Cu K α radiation. Fourier transform-infrared (FT-IR) spectra were obtained in TENSOR 37 spectrometer. Thermogravimetric analysis (TGA) curves were performed on a thermogravimetric analyzer TGA55 under N₂ flow, ramping at 10 °C min⁻¹ from room temperature to 800 °C. The morphology of sample was acquired from a JEOL JEM-2800 Transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Escalab 250 equipped with a hemispherical analyzer and using an aluminum anode as a source.

Gas adsorption measurement

 N_2 adsorption-desorption isotherms at 77 K, pore size distribution and the C_2H_6 and C_2H_4 adsorption isotherms at 298 and 273 K were obtained by a Micrometrics ASAP 2020 PLUS HD88 analyzer. The amount of adsorbent used for adsorption is about 0.15g. Before the measurement, the sample was degassed under vacuum at 423 K for 12h. The adsorption temperature was controlled by liquid nitrogen and ice-water bath, respectively.

Isosteric Heats of Adsorption (Q_{st})

A virial-type expression of comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for C_2H_6 and C_2H_4 in CTF-BT-400 and CTF-BT-500, which measured at two different temperatures 273K and 298K.

$$lnP = lnN + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

where P is pressure, N is the amount adsorbed (or uptake), T is temperature, and m and n determine the number of terms required to adequately describe the isotherm.

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

where R is the universal gas constant. The coverage dependencies of Q_{st} values were calculated from fitting the adsorption data (under the pressure range from 0-1 bar) at different temperatures for CTF-BTs.

IAST calculations of adsorption selectivity

To calculate the selectivity of C_2H_6/C_2H_4 for CTF-BTs at 298 K, the pure component isotherms were fitted by Langmuir-Freundlich model

$$q = q_{sat} \frac{bp^t}{1 + bp^t}$$

where *p* is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), *q* is the adsorbed amount per mass of adsorbent (mmol g^{-1}), q_{sat} is the saturation capacities of site (mmol g^{-1}), b is the affinity coefficients of site (1/kPa), and t represent the deviations from an ideal homogeneous surface.

$$S = \frac{q_A/q_B}{y_A/y_B}$$

where the q_A , and q_B represent the molar loadings within the CTF that is in equilibrium with a bulk fluid mixture with mole fractions y_A , and $y_B = 1-y_A$. IAST calculations were carried out assuming a

 C_2H_6/C_2H_4 (50/50 v/v %) gas mixtures.

Computational simulation studies of C₂H₆ and C₂H₄ adsorption

The GCMC simulations were carried out with the Sorption program (BIOVIA Material studio 8.0) to calculate C_2H_4 and C_2H_6 adsorption in CTF-BT-500. The simulation box was constructed by $1 \times 1 \times 8$ of CTF-BT-500 supercells (AA stacking) and the cutoff radius was set to 12.5 Å. The simulations started with a 1×10^7 -cycle of equilibration steps and were followed by 1×10^7 -cycle of production steps. The Lennard-Jones (LJ) parameters for framework atoms were obtained from Dreiding force field, while the LJ parameters for ethane and ethene are taken from literature.⁷⁻⁸ The dispersion corrected Density functional theory (DFT) calculations were performed to evaluate the binding energy for C_2H_4 and C_2H_6 in CTF-BT-500 by using DMol3 program in the Materials Studio. Initial locations of the gas molecules were obtained from GCMC simulations. Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation (GGA) were used for our calculations. All electron core treatment double numerical plus polarization (DNP) basis set were selected. And Grimme method was used for the dispersion-energy corrections. The tolerances for energy, force and displacement convergence were set to 1×10^{-5} hartree, 2×10^{-3} hartree/Å, and 5×10^{-3} Å, respectively. The static binding energy (at T = 0 K) was calculated by the following: $\Delta E = E_{(CTF)} + E_{(gas molecule)} - E_{(CTF + gas molecule)}$.

Breakthrough experiments

The breakthrough tests were conducted on a Multi-component Adsorption Breakthrough Curve Analyzer (BSD-MAB) under ambient conditions (298 K, 1atm) using a gas mixture of C_2H_6/C_2H_4 (1:1, v/v). In a typical breakthrough experiment test, about 0.4g active samples CTF-BT-500 were packed into a glass column (4 mm inner diameter, 123 mm length) and purged with He flow (10 mL/min) at 200°C for 2h. In the experiment, the C_2H_6/C_2H_4 mixture with He as the carrier gas (80%, vol%) were used to pass through the adsorption column with the rate of 5.0 mL/min. The outlet gas concentration was tracked and monitored by a mass spectrometry.

The purity (s) of C_2H_4 gas was calculated by the following equation.

$$s = \frac{q_{C_2H_4}}{q_{C_2H_4} + q_{C_2H_6}}$$

where q represent the amount of the gas.







Fig. S2 FTIR spectra of CTF-BTs.



Fig. S3 ¹³C CP/MAS NMR spectrum of CTF-BT-400 (a), CTF-BT-500 (b) CTF-BT-600 (c).



Fig. S4 C 1s XPS spectra of CTF-BTs. (The raw data is represented by gray dots; the peak summary is represented by solid purple line.)



Fig. S5 N 1s XPS spectra of CTF-BTs. (The raw data is represented by gray dots; the peak summary is represented by solid purple line.)



Fig. S6 TEM images and elemental mappings of CTF-BT-400 (a-f), CTF-BT-500 (g-l) and CTF-BT-600 (m-r).



Fig. S7 PXRD patterns of CTF-BT-400 (blue), CTF-BT-500 (red) and CTF-BT-600 (black).



Fig. S8 The pore size distributions of CTF-BTs.



Fig. S9 Single-component adsorption isotherms of C_2H_6 and C_2H_4 for CTF-BT-400 (a) and CTF-BT-600 (b) at 273 K and 298 K.



Fig. S10 Single-component adsorption isotherms of C_2H_6 for CTF-BT-500 and CTF-BT-TfOH catalyzed by CF_3SO_3H at low temperature.



Fig. S11 IAST selectivities of C_2H_6/C_2H_4 (1:1, v/v) mixtures for CTF-BTs at 298 K.



Fig. S12 TGA curves of CTF-BT-400, CTF-BT-500 and CTF-BT-600.



Fig. S13 FTIR spectra for CTF-BT-500 after the treatment of 6 M HCl and 6 M NaOH for 72h.



Fig. S14 C_2H_6 adsorption isotherms for CTF-BT-500 at 298 K after the treatment of 6 M HCl and 6 M NaOH for 72h.



Fig. S15 The regeneration experiments of CTF-BT-500.



Fig. S16 Q_{st} curves for CTF-BT-400 and CTF-BT-600.



Fig. S17 Experimental (solid lines with solid balls) and simulated (dotted lines with hollow balls) adsorption isothermsfor C₂H₆ (red), C₂H₄ (black) at 298 K and in CTF-BT-500.
 The difference between simulated C₂H₆/C₂H₄ uptakes and experimental results may be attributed to the existence of structural defects and poor crystallinity for real sample compared with ideal model of CTF-BT-500.



Fig. S18 Experimental breakthrough curves for CTF-BT-500 at 298 K and 1 bar. C_2H_6/C_2H_4 (1:1, v/v) mixtures with He as the carrier gas (80%, vol%).

Adsorbents	Pore size (Å)	C ₂ H ₆ uptake (mmol/g)	C ₂ H ₄ uptake (mmol/g)	Qst(C ₂ H ₆ /C ₂ H ₄) (KJ/mol)	IAST Selectivity	Reference	
CTF-BT-500	5.0,5.9,11.8,14.8	4.5	3.9	24.1/23.3	1.3	This work	
COF-1	9	2.4	1.9	22.5/22.2	1.92	[S4]	
COF-6	6.4	2.1	2.1	29.2/27.5	1.20	[S4]	
COF-8	18.7	1.6	1.5	27.5/25.1	1.21	[S4]	
COF-10	31.7	1.0	0.9	26.6/25.1	1.13	[S4]	
MCOF-1	6.4	3.3	2.8	30.0/27.5	1.73	[S4]	
COF-102	11.5	1.9	1.6	28.7/25.1	1.48	[S4]	
COF-300	7.8	4.1	3.1	26.9/25.0	1.57	[S4]	
COF-320	13.5×6.2	2.4	1.8	26.9/25.1	1.49	[S4]	
DBA-3D-COF-1	28	2.09	1.7	16.8/15.9	1.24	[S5]	
Ni-DBA-3D-COF	26	2.16	1.83	11.6/9.7	1.15	[S5]	
CTF-DCTC-400	7.3,11.8	1.82	1.68	22.7/22.0	1.04	[S6]	
CTF-DCTC-500	5.7,7.9,11.8	3.10	2.34	25.4/23.7	2.08	[S6]	
NKCOF-21	14	4.4	3.3	26.2/23.6	1.6	[S7]	
NKCOF-22	16	2.9	1.8	25.9/24.1	1.5	[S7]	
NKCOF-23	17	2.7	2.2	24.3/23.0	1.3	[S7]	

Table S1. Summary of the C_2H_6 adsorption data of CTFs at 298 K.

Table S2. The fitted parameters of the virial equation for CTF-BT-400.

Demonster	CTF-BT-400			
Parameter	C ₂ H ₆	C_2H_4		
a0	-2228.29481	-1657.11879		
al	10.29999	9.33894		
a2	-0.06586	-0.06953		
a3	2.30478E-4	3.10283E-4		
b0	7.61995	6.29355		
Adj. R-Square	0.99927	0.99493		

Dorrowston	CTF-BT-500			
Parameter	C ₂ H ₆	C_2H_4		
a0	-2993.19619	-2890.89795		
al	7.99182	8.47077		
a2	-0.04514	-0.05036		
a3	1.27059E-4	1.5065E-4		
b0	9.91525	9.88746		
Adj. R-Square	0.997	0.99913		

Table S3. The fitted parameters of the virial equation for CTF-BT-500.

Table S4. The fitted parameters of the virial equation for CTF-BT-600.

Dourous store	CTF-BT-600			
Parameter	C_2H_6	C_2H_4		
a0	-2593.19619	-2872.90451		
al	6.69794	12.01954		
a2	-0.03036	-0.10043		
a3	7.36936E-5	3.90894E-4		
b0	8.64392	10.60908		
Adj. R-Square	0.99991	0.99935		

Table S5. The fitted parameters for C_2H_4 and C_2H_6 adsorption isotherms of CTF-BT-400, CTF-
BT-500 and CTF-BT-600 at 298 K.

Material	Adsorbate	qı	b ₁	c	q ₂	b ₂	t	R ²
CTF-BT-400	C_2H_4	5.44721	0.00528	0.89951	2.0084	0.06419	0.78498	0.99999
	C ₂ H ₆	4.78658	0.00586	0.8896	2.7479	0.0689	0.73661	0.999999
CTF-BT-500	C ₂ H ₄	8.24303	0.0062	0.92775	1.7435	0.09756	0.79933	0.999999
	C ₂ H ₆	8.30347	0.0074	0.91927	2.10553	0.09922	0.77575	0.999999
CTF-BT-600	C ₂ H ₄	6.61194	0.00101	0.99821	3.50668	0.03342	0.39853	0.999999
	C ₂ H ₆	0.28481	0.16017	1.04108	5.53554	0.00655	0.99056	0.99997

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