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Benzimidazole functionalized Covalent Triazine Frameworks for CO₂ capture

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A series of covalent triazine frameworks containing benzimidazole segments (CTF-BIs) were designed and prepared by the dynamic trimerization under ionothermal conditions, based on the novel designed dicyano monomer of dicyano benzimidazole (DCBI). The CTF-BIs were all amorphous and exhibited BET surface areas as high as up to 1549 m² g⁻¹. The effect of reaction conditions including ratio of catalyst and temperature on the pore properties was discussed. Meanwhile, the capacity of CO₂ adsorption for all the CTF-BIs was studied and the CO₂ uptake capacity was as high as up to 21.68wt% at 273 K and 1.10 bar for CTF-BI-10. The CTF-BIs exhibited high selectivity of CO2 over N2 in the range of 31.3~88.5 at 273 K, and 29.0~102.7 at 303 K. respectively.

Introduction

Recently, due to the urgent need for strategies to reduce global atmospheric concentrations of greenhouse gases, the carbon capture and storage (CCS) has attracted significant interest. According to the International Energy Agency (IEA), appropriate capture and storage of post-combusted CO₂ has the potential of decreasing the emissions up to 20%.^{1, 2} Tremendous efforts have been made to the design and synthesis of microporous organic polymers (MOPs) for CO2 capture or selective adsorption because of their high physicochemical stability and excellent adsorption capacity.³⁻⁷ Therefore, various CO₂-philic moieties have been incorporated into MOPs to enhance the interactions between the MOPs' surfaces and CO₂ molecules. The CO₂-philic moieties usually contain heteroatoms (e.g. N, P) which have Lewis basic properties. They can simultaneously enhance CO₂ capture capacity and selectivity through Lewis acid-base interactions.⁸ ¹¹ Various kinds of nitrogen containing groups, including azos¹²⁻ ¹⁴ troger's base, ^{15, 16} benzimidazole, ¹⁷⁻²⁰ aminos, ²¹ carbazole, ²², ²³ and porphyrins,²⁴ have been incorporated into MOPs. Among them, benzimidazole linked polymers (BILPs) recently reported by H. M. El-Kaderi and co-workers showed promising performances for selectively CO₂ capture. These CO₂ uptakes are as high as 24wt% (BILP-4) among the highest values in all

reported BILPs were synthezed by the solution polycondensation reactions between aryl-o-diamine and arylaldehydes. The aryl-o-diamine monomers are easily oxidized and the stoichiometric should be strictly controlled. The benzimidazole groups are all generated during the polymerizations. While porous polymers derived from polymerization of benzimidazole containing monomers have been rarely researched.

porous organic polymers known to date.⁹ Till now, most of the

On the other hand, as a kind of nitrogen rich materials, covalent triazine-based frameworks (CTFs) were usually prepared by the ionothermal polymerization at high temperatures, where ZnCl₂ was used as both catalyst and solvents.²⁵⁻²⁸ The proper monomers were aromatic compounds with multiple cyanos. Under high temperature and the catalysis of molten ZnCl₂, the trimerization of cyano groups occurred. The molar ratio of monomer to ZnCl₂, the reaction temperature and time were the main factors which had important effect on the final results. Stoichiometric was not necessary because there was only one kind of monomer in the reaction system. Although with high nitrogen loadings in CTFs, the CO₂ adsorption abilities were not so high. Therefore, fluorine atoms²⁹ and fluorene groups³⁰ were introduced into CTFs respectively, which enhanced the CO₂ uptakes obviously. However, CTFs containing benzimidazole groups synthezed taking advantage of the ionothermal procedure mentioned above have not been reported so far.

In the present work, we prepared benzimidazole-linked CTFs (CTF-BIs) for the first time by use of benzimidazole containing monomers through the ionothermal polymerization. We first designed and synthesized a novel benzimidazole derived dicyano monomer, 2-(4-cyanophenyl)-1H-benzo[d]imidazole-5carbonitrile (DCBI), and then DCBI was polymerized to CTF-BIs under different conditions including molar ratio to the catalyst of ZnCl₂ and the reaction temperatures. We expected that the

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⁺ Electronic Supplementary Information (ESI) available: Structure characterization of DCBI and CTF-BIs; the nitrogen adsorption and desorption isotherms and pore size distributions of all CTF-BIs; the CO_2 adsorption isotherms, and the CO_2/N_2 selectivities of all CTF-BIs. See DOI: 10.1039/x0xx00000x

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 CO_2 -philic benzimidazoles would enhance the binding affinity between the CTFs and CO_2 , and thus increased the CO_2 adsorption of CTFs. The synthesis and characterization of the novel monomer DCBI, the synthesis and properties of the CTF-Bls, the effect of reaction conditions on the surface areas, pore volumes and distribution, CO_2 adsorption ability and the selectivity of CO_2 over N_2 , had been studied in detail.

Experimental

Materials

All chemicals including 3,4-diaminobenzonitrile, 4formylbenzonitrile, ceric ammonium nitrate (CAN), zinc chloride (ZnCl₂, anhydrous, 98%) and trifluorosulfonic acid (TFSA) were all purchased from J&K Scientific Ltd. (Beijing) and used without further purification. DCBI was synthesized in our laboratory according to the literature.³¹ ZnCl₂ was stored in a glove box and measured there.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer 782 Fourier transform spectrophotometer. The powder wide-angle X-ray diffraction (PXRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/K- α 1 radiation, operated at 40 kV and 200 mA. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were recorded on a Netzsch thermal analysis system (STA 449C), in nitrogen, at a heating rate of 10 °C/min. Elemental analysis was obtained with Vario EL analyser. FESEM images were obtained with a field emission scanning electron microscope (JSM-5600LV, JEOL, Japan). The powder samples were coated with gold by sputtering prior to observation. HR-TEM images were obtained with A JEM-2010 transmission electron microscopy, operating at an accelerating voltage of 200 KV. Nitrogen sorption experiments and micropore analysis were conducted at 77.3 K using Micromeritics ASAP 2020 HD88. Before sorption measurements, the samples were degassed in vacuum overnight at 150 °C. The surface areas were calculated from multipoint BET plot, and the pore volume was determined by nonlocal density functional theory (NLDFT). Carbon dioxide and nitrogen sorption isotherms at 273 K and 303 K were all obtained with a Micromeritics ASAP 2020 HD88 analyzer at the required temperature. The temperature during adsorption and desorption was kept constant using a circulator. Before the adsorption measurements, the samples were activated in situ by increasing the temperature at a heating rate of 10 °C/min up to 150 °C under vacuum and the temperature and vacuum were maintained for 5 hours before taking the sorption.

Table 1 Overview of the reaction conditions.

Polymer code	DCBI (mmol)	ZnCl ₂ (mmol)	Molar ratio of DCBI/ZnCl ₂	Reaction conditions	Yield (%)
CTF-BI-1	1.0	0.50	2:1	400 °C/40 hrs	92
CTF-BI-2	1.0	1.0	1:1	400 °C/40 hrs	90
CTF-BI-3	1.0	2.0	1:2	400 °C/40 hrs	90
CTF-BI-4	1.0	5.0	1:5	400 °C/40 hrs	94
CTF-BI-5	1.0	10.0	1:10	400 °C/40 hrs	94
CTF-BI-6	1.0	20.0	1:20	400 °C/40 hrs	94
CTF-BI-7	1.0	50.0	1:50	400 °C/40 hrs	94
CTF-BI-8	1.0	5.0	1:5	350 °C/40 hrs	84
CTF-BI-9	1.0	5.0	1:5	450 °C/40 hrs	81
CTF-BI-10	1.0	5.0	1:5	500 °C/40 hrs	81
CTF-BI-11	1.0	5.0	1:5	550 °C/40 hrs	76

Synthesis of 2-(4-cyanophenyl)-1H-benzo[d]imidazole-5carbonitrile (DCBI)

In a 250 mL three-necked flask with a magnetic stir and N₂ inlet, 2.623 g (20 mmol) 4-formylbenzonitrile and 2.663 g (20 mmol) 3,4-diaminobenzonitrile were dissolved in 70 mL acetonitrile. Then, H₂O₂ (30%, 80 mmol, 8.0 mL) and NH₄Ce(NO₃)₆ (2.0 mmol, 1.096 g) were added and the mixture was stirred at room temperature for 8 hours. After completion of the reaction, the reaction mixture was poured into icewater (400 mL). The pure solid product was filtered, washed with ice-water, and subsequently dried. The crude product was recrystallized in EtOH to give fine powder in light red-brown. (Yield, 4.32 g, 88%; mp: 322.9 °C by DSC in N₂, 10 °C/min). FT-IR (KBr pellets, cm⁻¹): 3276, 2232, 1609, 1421, 1320, 860. ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 13.75 (s, 1H); 8.38~8.36 (d,

2H); 8.29 (d, 1H); 8.09~8.07 (d, 2H); 7.90~7.88, (tetra, 1H); 7.68~7.66 (d, 1H).

Synthesis of the CTF-BIs

The CTF-BIs were synthesized according to a reported literature.²⁵ The synthesis of CTF-BI-4 was given as an example (Scheme 1). The DCBI monomer (244.3 mg, 1.0 mmol) and $ZnCl_2$ (682 mg, 5.0 mmol) were first mixed well in agate mortar in glove box and then transferred into a pyrex ampoule (3 × 18 cm, about 25 mL). The ampoules were evacuated to vacuum, sealed and heated to 400 °C and kept there for 40 hrs. The ampoule was then cooled down to room temperature and opened carefully. The black reaction mixture was subsequently grounded in an agate mortar and then washed thoroughly with diluted HCl to remove most of the ZnCl₂. Further purification including extracting in Soxhlet extractor by deioned water and THF for 24 hrs each and drying in vacuum at 150 °C. The yield

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was about 94%. The other CTF-BIs were synthesized in a similar procedure, while the reaction conditions, including the molar ratio of monomer to the catalyst and reaction temperatures, were set according to Table 1. For comparison, the polymerization was also carried in 1,2-dichloroethane solution by using TFSA as catalyst, according to a reported method.³²



Results and discussion

Synthesis and characterization of DCBI

The monomer DCBI was synthesized by the oxidative coupling of 3,4-diaminobenzonitrile and 4-formylbenzonitrile catalyzed by CAN at room temperature, with a good yield in a short reaction time (Scheme 1). The molecular structure was confirmed by FT-IR spectrometry and ¹H NMR spectrum. Fig. S1⁺ compared the FT-IR spectra of DCBI and the corresponding reactants. For 3,4-diaminobenzonitrile, the broad and strong absorption bands between 3100 cm⁻¹ and 3450 cm⁻¹ disappeared totally after coupling, indicating the amino had been consumed. At the same time, for 4-formylbenzonitrile, after coupling, the strong band of aldehyde at 1707 cm⁻¹ also disappeared. Accordingly, the characteristic bands of benzimidazole rings at 3276 cm⁻¹ appeared obviously, which can be attributed to the -NH- stretching vibration. The new bands appeared at 1609 cm^{-1} (C=N), and 1495 and 1435 cm^{-1} can be assigned to skeleton vibration of the benzimidazole ring.⁹ Meanwhile, the characteristic absorption bands of -CN groups can also be observed clearly at 2232 cm⁻¹. In the ¹H NMR spectrum shown in Fig. S2⁺, all protons could be assigned

clearly according to the integral values. The DSC curve of DCBI (Fig. S3⁺) showed the melting point at about 322.9 °C. In the TGA curve (Fig. S4⁺), the first/main weight loss started at about 350 °C indicated the decomposition of benzimidazole rings.

Synthesis and characterization of the CTF-BIs

The CTF-BIs were first synthesized by the procedure of ionothermal polymerization, which was first reported by A. Thomas et al.²⁵ In order to find the relationship between the reaction conditions and the porosity properties, a set of reaction conditions which were different in reaction temperatures and molar ratios was listed in Table 1. The molar ratio of DCBI to ZnCl₂ was set as 2:1, 1:1, 1:2, 1:5, 1:10, 1:20, and 1:50, respectively. The reaction temperature was set as 350 °C, 400 °C, 450 °C, 500 °C and 550 °C. All the reaction time was set as 40 hours. In all cases, after polymerization, the light brown powdery reactants turned black dust in the sealed tube. For CTF-BI-1 to CTF-BI-8, there were no positive pressures when the sealed tube was open. In comparison, for CTF-BI-9, CTF-BI-10 and CTF-BI-11 reacted at 450 °C, 500 °C, and 550 °C, there was obviously positive pressure, which should be paid more attention. All black dusts were rounded in agate mortar to get fine powders. The black powder were all immersed in deioned water and washed by diluted HCl and extracted by hot water, to remove most of the residual ZnCl₂. The final yields were in the range of 76%-94%, some of which were a little lower than the reported results due to the high reaction temperature. As the reaction temperature raised, the final yields decreased gradually maybe due to the partially decomposition of the triazine rings and/or the benzimidazole groups. For comparison, the polymerization catalyzed by TFSA in solution was also carried out at room temperature (CTF-BI-S). The formation of CTF-BIs was characterized by FT-IR, solidstate ¹³C NMR spectra, PXRD, and thermogravimetric analysis (TGA).



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Fig. 1 (a) and (b) FT-IR spectra of the monomer DCBI and CTF-BI-4 and CTF-BI-S obtained by KBr pellets, in the range of 4000 cm⁻¹~400 cm⁻¹ and 2000 cm⁻¹~400 cm⁻¹, respectively; (c) Solid-state ¹³C NMR spectra of DCBI, CTF-BI-4, and CTF-BI-11 (100 MHz); (d) PXRD patterns of CTF-BI-4 and CTF-BI-11; (e) FESEM image of CTF-BI-4; (f) HR-TEM of CTF-BI-4.

Representative FT-IR spectra of a CTF (CTF-BI-4, CTF-BI-S) and DCBI were shown in Fig. 1a and 1b. After polymerization, the cyano groups at about 2232 cm⁻¹ were almost totally disappeared for both CTF-BI-4 and CTF-BI-S, indicating the high degree of trimerization. The characterized peaks of triazine rings were not very strong, which were located at 1517 cm⁻¹ and 1353 cm^{-1} ,²⁵ maybe overlapped by nearby peaks. The other FT-IR spectra were all shown in Fig. S5⁺ and S6⁺. For CTF-BI-1 and CTF-BI-2, the cyano groups can still be observed clearly, indicating a low degree of trimerization. For the CTF-Bls obtained from higher reaction temperatures, the peaks of triazine rings were even weaker, maybe due to the partially decomposition or fragmentation.^{25, 33} In the solid-state ¹³C NMR spectra shown in Fig. 1c, the chemical signals located at 105.4 and 111.6 ppm should be assigned to the asymmetric nitrile carbons. After polymerization they almost disappeared totally, indicating the high reaction extent.^{30, 34} The signal located at 150.1 ppm in DCBI should be assigned to NC(Ph)N in benzimidazole units.^{30, 35} After polymerization at 400 °C, these signals can be still seen in CTF-BI-4 (152.6 ppm). However, for CTF-BI-11 obtained at 550 °C, the intensity attenuated obviously maybe due to the decomposition of benzimidazole

rings at higher temperatures, which in well accordance with the FT-IR results as mentioned above.

The CTF-BIs were also characterized by thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD). As shown in Fig. S7⁺, CTF-BI-11 exhibited remarkable thermal stability up to 600 °C in N2. The initial weight loss before 200 °C can be attributed to the absorbed water. The weight loss after 400 °C can be attributed to the degradation of organic frameworks. Therefore, they have similar thermal stability compared with the reported BILPs.^{8, 9} CTF-BI-11 showed high char yields higher than 70% at 800 °C. Due to the nature of their rigid structures, there was no observable glass transition temperature within the range of 30-500 °C (Fig. S8⁺), just like most of reported MOPs. The PXRD patterns of CTF-BI-4 and CTF-BI-11 shown in Fig. 1d indicated no long-range structures. They were amorphous with broad diffraction peaks at about 22.8 ° , which was in well accordance with the reported results.¹¹ The morphology was also characterized by FESEM as shown in Fig. 1e and S9⁺, which revealed aggregated particles of variable size of 1~10 µm. In the HR-TEM images shown in Fig. 1f and S10⁺, the alternating areas of light and dark contrast revealed their disordered porous structural natures.

Table 2 Porosity data for the CTF-BIs from N_2 isotherms collected at 77.3 K

Polymer code	$SA_{BET} [m^2 g^{-1}]^{(a)}$	$SA_{Lang} [m^2 g^{-1}]^{(b)}$	$SA_{micro} [m^2 g^{-1}]^{(c)}$	$SA_{ext} [m^2 g^{-1}]^{(d)}$	$V_{0.1} [m^3 g^{-1}]^{(e)}$	$V_{\rm tot} [m^3 g^{-1}]^{(f)}$	$V_{0.1}/V_{\rm tot}$
CTF-BI-1 ^(g)	0	0	0	0	0	0	-
CTF-BI-2 ^(g)	0	0	0	0	0	0	-
CTF-BI-3	677	992	531	146	0.33	0.36	0.92
CTF-BI-4	1025	1505	762	263	0.50	0.58	0.86
CTF-BI-5	836	1236	647	190	0.41	0.46	0.89
CTF-BI-6	759	1117	470	289	0.36	0.45	0.80
CTF-BI-7	642	938	358	284	0.30	0.38	0.79
CTF-BI-8	55	81	38	17	0.026	0.034	0.76
CTF-BI-9	885	1308	699	186	0.44	0.49	0.89
CTF-BI-10	1099	1641	669	431	0.51	0.59	0.86
CTF-BI-11	1549	2320	335	1214	0.64	0.88	0.73
CTF-BI-S	2	2.4	0.4	1	0.0007	0.0079	0.09

^(a) BET surface area calculated over the pressure range 0.05-0.30 P/P₀ at 77.3 K; ^(b) Langmuir specific surface area calculated from the nitrogen adsorption isotherm by application of the Langmuir equation; ^(c) Micropore surface area calculated from the nitrogen adsorption isotherm using the *t*-plot method; ^(d) The external surface areas calculated using the *t*-plot method based on the Halsey thickness equation; ^(e) $V_{0.1}$, pore volume at P/P₀ = 0.1 at 77.3 K; ^(f) V_{tot} , total pore volume calculated at P/P₀ = 0.9 at 77.3 K; ^(g) Not detected any reasonable data.

Porosity properties and gas uptake capacities of the CTF-BIs

The porous character of the CTF-BIs was studied by nitrogen adsorption-desorption experiments at 77.3 K. All samples were degassed at 150 °C overnight under vacuum prior to the measurement. As shown in Fig. 2a, 2d, S11⁺, S12⁺, and S14⁺, except CTF-BI-1, CTF-BI-2, CTF-BI-8, and CTF-BI-S, all the isotherms show a steep increase in adsorbed volume at low relative pressure, suggesting that these CTF-BIs were microporous materials. All the seven CTF-BIs showed type I N₂ sorption isotherms with Brunauer-Emmett-Teller (BET) surface areas ranging from 642 to 1549 m² g⁻¹ (Table 2). The Langmuir

surface area of CTF-BIs was varied from 938 to 2320 m² g⁻¹. None of them showed remarkable hysteresis at the low pressure region in the N₂ isotherms. Therefore, the dominating pores were micropores, which were in well accordance to the pore size distribution as shown in Fig 2b, 2e, S13⁺, and S15⁺. For CTF-BI-11, there was only a little mesopores (2.29 nm and 2.52 nm, Fig 2e), which can be ascribed to the partially decomposition of the polymeric frameworks under high temperature. For CTF-BI-S obtained in the solution polymerization, although the reaction extent was high according to the FT-IR spectra (Fig. 1a), the surface area was

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very small (Fig. S11⁺ and Table 2). The nonporous nature indicated the formation of oligomers with low molecular weights.

It was found that the physical properties such as BET surface area, Langmuir surface area, micropore surface area, micropore volume, and bulk density could be affected by adjusting the synthetic conditions.^{26, 28} Therefore, we investigated the influence of the amount of ZnCl₂, as well as reaction temperature on the properties of the CTFs and we set a series of reaction conditions (Table 1). First, the influence of the DCBI/ZnCl₂ ratio was investigated under standard conditions at 400 °C. The amount of ZnCl₂ used had obvious effect on the pore properties, because it was both catalyst and solvent in the reaction. When the amount was too little, *i.e.* the ratios of DCBI to ZnCl₂ were 2:1 and 1:1, the BET surface areas were too small to be detected and the materials were

nonporous, which probably because the low mass of ZnCl₂ was not sufficient in such a reaction mixture to fully dissolve the fluffy and powdery monomers and the produced oligomers.²⁵ There was still a large part of nitriles residue in the resultant mixture judging from FT-IR spectra (Fig. S5⁺). When the ratios of DCBI to ZnCl₂ increased from 1:2 to 1:50, the BET surface areas increased first and then decreased gradually, as shown in Fig 2c, which was in good agreement with that of dicyano bisphenyl (DCBP) under similar conditions.³⁶ For CTF-BI-4, where the ratio of DCBI to ZnCl₂ was 1:5, the BET surface area was as high as 1025 m²g⁻¹, which was a little lower than that of CTF-1 derived from 1,4-dicyanobenzene (DCB) under similar conditions (1123 m²g⁻¹). Further increase of ZnCl₂ amount lead to decrease in BET surface areas may be due to the dilutive effect of excess amount of solvents.



Fig. 2 Porosity properties of CTF-BIs. (a) Nitrogen adsorption and desorption isotherms at 77.3 K of CTF-BI-4; (b) Pore size distributions (PSD) for CTF-BI-4 calculated by the NLDFT method; (c) The influence of molar ratio (DCBI to ZnCl₂) on the surface areas; (d) Nitrogen adsorption and desorption isotherms at 77.3 K of CTF-BI-11; (e) Pore size distributions (PSD) for CTF-BI-12; (e) Pore size distributions (PSD) for CTF-BI-11; (e) Pore size distributions (PSD) for CTF-BI

As previously found for the polymerization of DCB,²⁵ higher reaction temperatures generated mesoporosity in addition to microporosity. Thus a series of temperatures from 350 °C to 550 °C was investigated. When reaction temperatures increased, the BET surface areas increased gradually, as shown in Fig. 2f. For CTF-BI-11 obtained at 550 °C, the BET surface area was as high as 1549 m²g⁻¹, much higher than that of CTF-BI-4, which can be ascribed to the appearance of mesoporosity in addition to microporosity. However, this value was much

lower than that of CTF-0 derived from 1,3,5-tricyanobenzen (TCB) under similar conditions $(2011 \text{ m}^2 \text{g}^{-1})$.²⁸ It can be partially ascribed to the relatively longer strut building block compared with TCB.³⁷ Furthermore, higher temperatures lead to some side reactions such as decompositions and ring fragmentations, as evidenced by FT-IR and solid-state ¹³C NMR analysis. In the present system, both the triazine rings and the benzimidazole rings could decompose under higher temperatures, leading to nitrogen doped porous carbons.

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Fig. 3 (a) CO₂ adsorption isotherms at 273 K of CTF-BIs; (b) CO₂ adsorption isotherms at 303 K of CTF-BIs; (c) The ratios of four N-configurations (N_(N)) in CTF-BIs; (d) Heat of adsorption for CTF-BI-4 and CTF-BI-11.

Once the porosity of CTF-BIs had been established, we considered their applications in gas storage. There were two kinds of CO₂-philic groups in the CTF-BIs obtained herein, e.g., the benzimidazole rings which contained secondary amine and the triazine groups. Therefore, it can be predicted that the CTF-BIs would have high CO2 adsorption ability. Generally speaking, with increasing specific surface areas and micropore volumes, the adsorption capacity for CO₂ increases. We tested the CO₂ adsorption properties at 273 K and a pressure up to 1.10 bar. The adsorption data at 1.10 bar were summarized in Table 3, from which we can see that all CTF-BIs showed moderate to high capacity of CO₂ adsorption, consistent with our expecting. The CO₂ adsorptions for all CTF-BIs ranged from 11.05wt% to 21.68wt% at 273 K and 1.10 bar. For CTF-BIs prepared at 400 °C, the CO₂ adsorption amount at 1.10 bar was in the order of CTF-BI-6 < CTF-BI-5 < CTF-BI-3 < CTF-BI-4, the same tendency with their BET surface areas. CTF-BI-4 and CTF-BI-11 had the highest CO₂ adsorption amount at 1.10 bar (about 21wt%). The adsorption amount was in the range of the highest values observed for CTFs under similar conditions. In fact, besides the recently reported FCTF-1 (20.55wt%-24.33wt%),²⁹ CTF-BI-4 and CTF-BI-11 show higher CO₂ adsorption than the reported values for all other CTFs such as

CTF-0 (18.57wt%) derived from TCB,²⁸ CTF-1 (10.87wt%-16.81wt%) based on DCB,²⁹ CTF-P1M-P6M (4.14wt%-18.48wt%) prepared by microwave method,³² MCTF300-500 (9.90wt%–13.90wt%) containing metalloporphyrin segments,³⁸ PCTF-1-7 (8.10wt%-14.21wt%) derived from tetranitrile containing tetraphenyl ethylene and adamantane segments,^{39,} 40 and TPI-1–7 (2.99wt%–10.78wt%) containing imide groups, 41 under similar conditions. This can be ascribed to the introduction of CO2-philic benzimidazole rings into the frameworks. Even compared with other kinds of porous organic polymers such as covalent organic frameworks (COFs: 7.92wt%-16.98wt%),42 microporous polyimides (MPIs: 9.90wt%-16.76wt%),43 and hyper-crosslinked organic polymers (HCPs; 8.46wt%-17.25wt%),44-47 CTF-BI-4 and CTF-BI-11 showed high advantage not only for the adsorption ability but also the preparation procedure which can be adapted to large scale. However, compared with benzimidazole-linked polymers (BILPs; 12.80wt%-23.50wt%), the present adsorption values were a little lower than the highest one (BILP-4).⁹ The main reason would be ascribed to the relatively high reaction temperatures which lead to partially decomposition and fragmentations of benzimidazole rings.

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Table 3 CO_2 and N_2 capture capacities, CO_2/N_2 selectivities for the CTF-BIs

Polymer Code ^(a)	$S_{BET}(m^2g^{-1})$	CO ₂ adsorption (cm ³ g ⁻¹)		N ₂ adsorption (cm ³ g ⁻¹)		CO ₂ /N ₂ ^(c)	
		273 K ^(b)	303 K	273 K	303 K	273 K	303 K
CTF-BI-3	676	77.5	49.7	1.4	1.3	88.5	52.4
CTF-BI-4	1025	108.7	61.1	7.1	4.0	44.0	102.7
CTF-BI-5	836	100.6	60.1	6.9	2.7	35.6	40.2
CTF-BI-6	759	75.2	44.2	6.3	3.1	34.5	41.0
CTF-BI-7	642	56.3	37.3	5.3	2.3	39.7	33.6
CTF-BI-9	885	96.1	52.9	5.4	3.1	67.4	29.0
CTF-BI-10	1099	99.9	57.8	9.0	4.6	31.3	39.1
CTF-BI-11	1549	110.5	58.9	9.6	5.0	34.3	34.9

^(a) The CO₂ adsorptions of CTF-BI-1, CTF-BI-2, and CTF-BI-8 were not measured due to the very low BET surface areas; ^(b) CO₂ adsorptions of CTF-BIs at 273 K and 1.10 bar; ^(c)Selectivity estimated using the ratios of the Henry law constant calculated from the initial slopes of the single-component gas adsorption isotherms at low pressure coverage (< 0.10 bar).

The reaction temperature played an important role to the CO₂ adsorption ability. For CTF-BI-4 (400 °C), CTF-BI-9 (450 °C), CTF-BI-10 (500 °C) and CTF-BI-11 (550 °C), higher reaction temperature lead to higher BET surface areas, but the CO₂ adsorption ability did not show a positive proportional relationship. CTF-BI-10 had a higher BET surface area than that of CTF-BI-4 (1099 m² g⁻¹ vs 1025 m² g⁻¹), but had a lower CO_2 adsorption amount (19.61wt% vs 21.34wt%). Furthermore, the BET surface area of CTF-BI-11 was much higher than that of CTF-BI-4 (1549 m² g⁻¹ vs 1025 m² g⁻¹), but the CO₂ adsorption amount was nearly in the same level with CTF-BI-4 (21.68wt% vs 21.34wt%). The main reason should be again ascribed to the partially decomposition and fragmentations of benzimidazole rings, as mentioned above. Table S1 showed the elemental analysis results of CTF-BI-8 (350 °C), CTF-BI-4 (400 °C), CTF-BI-9 (450 °C), CTF-BI-10 (500 °C), CTF-BI-11 (550 °C). As the reaction temperature increased from 350 °C to 550 °C, the loadings of N decreased gradually. It should be an evidence of the ring fragmentation. X-ray photoelectron spectroscopy (XPS) analyses of CTF-BIs were performed in order to further explore the origin of the effect of reaction temperatures on the CO₂ adsorption ability. The N1s XPS results of DCBI and CTF-BIs (Fig. S16⁺) reveal that about three to four distinct N configurations exist in the skeletons of CTF-BIs: pyridinic N (397.98-398.40 eV, N(1)), pyrrolic N (399.60–399.99 eV, N(2)), guaternary N(400.86-401.19 eV, N(3)), and N-oxide (402.65-403.94 eV, N(4)),^{27, 48-50} For CTF-BI-8 (350 °C), CTF-BI-4 (400 °C), and CTF-BI-9 (450 °C), there were three distinct N configurations while for CTF-BI-10 (500 °C) and CTF-BI-11 (550 °C), there were four, also indicated the decomposition or fragmentation reactions may occur under the high temperature conditions. The atomic ratios of the four N-configurations in CTF-BIs were further evaluated from the deconvolution of N1s peaks, and the

results are plotted as a function of synthesis temperature in Fig. 3c. In general, the ratio of N(2) tend to decrease when the synthesis temperature increases; while the ratios of N(3) and N(4) increase with increasing synthesis temperature. The high CO₂ uptakes by benzimidazole containing polymers were found to arise from strong interactions of the polarizable CO₂ molecules through hydrogen bonding and/or dipole-quadrupole interactions that utilize the protonated and proton-free nitrogen sites of imidazole rings, respectively.9, 17 The interactions between CO₂ and guaternary N and N-oxide were much weaker than those of pyridinic and pyrrolic N. Although CTF-BI-11 had a much higher BET surface area, the content of quaternary N and N-oxide were also much higher than that of CTF-BI-4 (31.3% vs 5.0%, Fig. S16⁺), thus leading to similar CO₂ uptakes.

To determine the binding affinity of CTF-BIs for CO₂, we calculated the isosteric heat of adsorption (Q_{st}) for CO₂ using the Clausius–Clapeyron equation, as shown in Fig 3d and S17⁺. The Q_{st} values of CTF-BIs were in the range of 31.7 kJ mol⁻¹ and 34.3 kJ mol⁻¹, which were well below the values expected for a chemisorption process (> 40 kJ mol⁻¹). Therefore, the high CO₂ affinity of the CTF-BIs was mainly attributed to the inherent microporosity and the enhanced dipole–quadrupole interactions between the quadrupole moment of the CO₂ molecules and the nitrogen-rich polar binding sites, both from benzimidazole and triazine rings.

In order to investigate the gas adsorption selectivity of CTF-BIs, CO_2 and N_2 sorption properties were measured by volumetric methods at the same conditions of 273 K and 303 K, respectively, and the selectivity was estimated according to a reported method,¹² in which the ratios of the Henry law constants calculated from the initial slopes of the single-component gas adsorption isotherms at low pressure coverage (0~100 mbar) were used (Fig. S18⁺ to Fig.

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S26⁺). For all CTF-BIs, the calculated CO₂/N₂ adsorption selectivities were in the range of 31.3~88.5 at 273 K, and 29.0~102.7 at 303 K, respectively (Table 3 and Fig. S26⁺). The selectivities were comparable to or better than the reported fluorinated CTF (TPC-1, selectivity of CO₂/N₂ at 273 K: 38),⁵¹ Cz-POFs (selectivity of CO₂/N₂ at 273 K: 19-37),²² and *fl*-CTFs (selectivity of CO₂/N₂ at 273 K: 13~35),³⁰ but lower than that of Azo-COPs (selectivity of CO₂/N₂: 73~124 at 273 K, 113~142 at 298 K) containing azo groups.¹²

Conclusions

In conclusion, a novel dicyano monomer containing benzimidazole groups (DCBI) was designed and synthezed by an oxidative coupling catalyzed by CAN at room temperature. A series of CTFs containing benzimidazoles (CTF-BIs) were prepared by the dynamic trimerization under ionothermal condition. The CTF-BIs exhibited BET surface areas as high as up to 1549 m² g⁻¹. The capacity of adsorption of CO₂ for all the CTF-BIs was studied and the CO₂ uptake capacity was as high as up to 21.68wt% at 273 K and 1.10 bar for CTF-BI-11. Some CTF-BIs exhibited high selectivity of CO₂ over N₂, which made these materials potential candidates for applications in CO₂ capture and storage technology.

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Combination of Covalent Triazine Framworks and Benzimidazoles

High BET surface area: up to 1500 m² g⁻¹

High CO_2 Adsorption: up to 21.7 wt% at 273 K

High selectivity at high temperature: CO_2/N_2 up to 102.7 at 303 K

102x59mm (300 x 300 DPI)