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High CO₂-Capture Ability of a Porous Organic Polymer Bifunctionalized with Carboxy and Triazole Groups

Lin-Hua Xie and Myunghyun Paik Suh^{*[a]}

Abstract: A new porous organic polymer, SNU-C1, incorporating two different CO₂-attracting groups, namely, carboxy and triazole groups, has been synthesized. By activating SNU-C1 with two different methods, vacuum drying and supercritical-CO₂ treatment, the guest-free phases, SNU-C1-va and SNU-C1-sca, respectively, were obtained. Brunauer-Emmett-Teller (BET) surface areas of SNU-C1-va and **SNU-C1-sca** are 595 and 830 m^2g^{-1} , respectively, as estimated by the N₂-adsorption isotherms at 77 K. At 298 K and 1 atm, SNU-C1-va and SNU-C1-

show high CO_2 uptakes, sca 2.31 mmol g^{-1} and 3.14 mmol g^{-1} , respectively, the high level being due to the presence of abundant polar groups (carboxy and triazole) exposed on the pore surfaces. Five separation parameters for flue gas and landfill gas in vacuum-swing adsorption were calculated from single-component gas-sorption isotherms by using the ideal adsor-

Keywords: carbon dioxide capture • click reactions · porous organic polymers · vacuum-swing adsorption

bed solution theory (IAST). The data reveal excellent CO2-separation abilities of SNU-C1-va and SNU-C1-sca, namely high CO₂-uptake capacity, high selectivity, and high regenerability. The gas-cycling experiments for the materials and the water-treated samples, experiments that involved treating the samples with a CO₂-N₂ gas mixture (15:85, v/v) followed by a pure N₂ purge, further verified the high regenerability and water stability. The results suggest that these materials have great potential applications in CO₂ separation.

Introduction

The dramatic increase in the amount of greenhouse gases (GHGs), such as CO₂, CH₄, and N₂O, in atmosphere, an increase that began during the Industrial Revolution, is generally believed to be responsible for global warming and climate change. While all other GHGs with a mass similar to that of CO₂ have a much higher greenhouse effect than CO₂ itself, the concentration of CO_2 in the atmosphere is the highest among all the GHGs and is responsible for approximately 60% of the global-warming effect.^[1] The major source of anthropogenic CO₂ emissions is the combustion of fossil fuels, a process that will continue to be used in the coming decades. Therefore, carbon dioxide capture and storage (CCS) technologies need to be developed to reduce the concentration of CO₂ in the atmosphere.^[2] Although some technologies are already available for CO₂ capture, such as the use of amine scrubbers and cryogenic separation, the large energy penalties associated with these technologies limit their large-scale application.^[3] Alternative CO₂-capture materials are solid adsorbents such as activated-carbon materials,^[4] zeolites,^[5] metal-organic frameworks (MOFs),^[6,7]

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and porous organic materials,^[8-11] which physisorb CO₂ through relatively weak van der Waals forces. The weak interactions between CO_2 and the internal surface of the solid adsorbents make regeneration of the materials energy efficient. In addition, the sorption performance of the solid adsorbents can be optimized by tuning their overall structural topologies or local functionalities.

In developing solid adsorbents, current major research efforts are focused on improving CO₂-sorption capacity and selectivity of the materials at ambient temperature. One of the most extensively studied strategies is the introduction of alkylamine groups to the solid adsorbents.^[12-14] The introduction of alkylamine groups to the adsorbents results in increased CO₂-sorption capacities and excellent selectivity, despite the surface areas being lower than those of the parent materials. To fully regenerate the alkylamine-functionalized adsorbents, additional heating is necessary owing to the chemical reactions between the introduced alkylamines and CO₂. Temperature-swing adsorption (TSA) has been generally adapted to optimally use them. However, for practical applications, vacuum-swing adsorption (VSA) is preferred over TSA and pressure-swing adsorption (PSA) because TSA involves slow heating and cooling steps and PSA involves pressurizing the large feed stream, a process that is cost prohibitive.^[15] Therefore, there are drawbacks in introducing alkylamines and other highly CO₂-attracting functionalities to the solid adsorbents. It has been demonstrated that some polar functional moieties, such as -NO₂^[16] -OH,^[17,18] -COOH,^[19] -SO₃H,^[20] arylamines,^[21] and heterocyclic nitrogen atoms,^[22-24] incorporated into the porous mate-

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rials enhance CO₂ affinities because of the high quadrupole moment $(14.3 \times 10^{-4} \text{ Cm}^2)$ and polarizability $(26.3 \times$ 10^{-25} cm³) of CO₂.^[25] The adsorbents containing these moderately CO₂-attracting functionalities have their advantages in that they can be readily regenerated after CO₂ adsorption because no chemisorption is involved. Although MOF materials are some of the most intensively investigated solid adsorbents in recent years, they are often very unstable toward moisture. Therefore, porous organic polymers (POPs) have recently attracted attention.^[26-33] In general, POPs show good mechanical, thermal, and chemical stability because of



Scheme 1. Schematic representation of porous materials functionalized with a) highly CO2-attracting groups, b) moderately CO2-attracting groups, and c) densely distributed moderately CO₂-attracting groups.

the covalent bonding nature of the networks, and they are regarded as highly promising materials for practical CO₂capture applications.

With these considerations in mind, we planned to develop energy-efficient CO₂-capture materials by synthesizing POPs that contain moderately CO2-attracting groups covering the pore surfaces as densely as possible (Scheme 1). We have prepared a POP by using the copper-catalyzed 1,3-dipolar azide-alkyne cycloaddition (CuAAC) reaction, a popular type of click reaction (Scheme 2).)^[34,35] The POP contains two different types of moderately CO2-attracting groups, that is, carboxy and triazole groups. To our knowledge, all the POPs reported so far contain either none or, at most, only one type of moderately CO₂-attracting group. Single-component gas-sorption data, calculated separation parameters, and gas-cycling experiments suggest that this POP material has great potential applications in postcombustion CO2 capture and in landfill-gas separation. It was also shown that porosity and sorption performance of this POP are significantly affected by the activation method, either vacuum drying or supercritical-CO₂ treatment, similarly to the cases of metal–organic frameworks.^[36,37]

Results and Discussion

Synthesis, activation, and general characterization: The CuAAC click reaction between 3,5-diazidobenzoic acid (Hdab) and 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (tepa) afforded a porous polymer, SNU-C1 (caution: azides are potentially explosive). The guest solvent molecules of as-synthesized SNU-C1 were removed by two different activation methods, room-temperature vacuum drying and supercritical-CO₂ treatment. The color of vacuum activated



Scheme 2. Synthesis of SNU-C1.

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SNU-C1 (SNU-C1-va) was orange and that of supercritical-CO₂ activated SNU-C1 (SNU-C1-sca) was pale yellow (see Figure S1 in the Supporting Information). SNU-C1-va and SNU-C1-sca are insoluble in water and in all tested common organic solvents, thus suggesting that they have polymeric structures. Scanning electron microscopy (SEM) images showed that the size of the polymer particles was about 10-30 nm (see Figure S1 in the Supporting Information). The powder X-ray diffraction (PXRD) patterns revealed the amorphous nature of the samples. The infrared spectrum of the SNU-C1 samples showed bands at around 2115 cm^{-1} , which were assigned to unreacted azide groups and have also been reported for other reported POPs prepared using CuAAC click reactions (see Figure S2 in the Supporting Information).^[38-40] The presence of strong bands at 1710 cm^{-1} in the infrared spectra reveal that the carboxy groups remain intact during the reaction. Solid-state ¹³C CP MAS NMR spectra of SNU-C1-va and SNU-C1-sca showed broad peaks around 38, 125, 137, 148, and 165 ppm (see the Supporting Information, Figure S3), which are consistent with the structures. The POP is weakly acidic in water owing to the carboxy groups. When SNU-C1-va (0.132 g) was immersed in degassed water (20 mL) under an N2 atmosphere, the pH value of the suspension was 4.3. Thermogravimetric analysis revealed that SNU-C1-va and SNU-C1-sca lost water molecules adsorbed from air below 80°C (see Figure S4 in the Supporting Information). No apparent weight change was observed in the range 80-160°C. Continued weight loss at higher temperatures is assumed to be due to gradual decomposition of the porous polymer.

Gas sorption properties: To evaluate the porosity of SNU-C1-va and SNU-C1-sca, N₂-adsorption isotherms were measured at 77 K (Figure 1). The N₂-adsorption isotherm of SNU-C1-va indicated Brunauer—Emmett–Teller (BET) and Langmuir surface areas of 595 and 602 m^2g^{-1} , respectively. Dubinin–Radushkevich (DR) micropore analysis suggested



Figure 1. N_2 -adsorption isotherms at 77 K for **SNU-C1-va** and **SNU-C1-sca**. Filled circles: adsorption in **SNU-C1-va**; half-filled circles: adsorption in **SNU-C1-sca**; open circles: desorption.

FULL PAPER

a micropore volume of 0.24 cm3 g⁻¹ with an average micropore width of 12.9 Å. Pore-size distribution calculated by nonlocal density-functional theory (NLDFT)^[41] suggested the material contained 10–20 Å micropores that $(0.24 \text{ cm}^3 \text{g}^{-1})$, 23–43 Å mesopores $(0.05 \text{ cm}^3 \text{g}^{-1})$, and sparse macropores (0.04 cm³g⁻¹) (see Figure S8 in the Supporting Information). SNU-C1-sca showed much higher porosity than SNU-C1-va, having BET and Langmuir surface areas of 830 and 839 m^2g^{-1} , respectively, as estimated from its N₂adsorption isotherm at 77 K. DR micropore analysis suggested a micropore volume of 0.36 cm3 g-1 with an average micropore width of 16.5 Å. The results of NLDFT calculation suggested that SNU-C1-sca contained 10-19.5 Å micropores (0.31 cm³g⁻¹), 24–34 Å mesopores (0.18 cm³g⁻¹), and widespread macropore pores $(0.78 \text{ cm}^3 \text{g}^{-1})$ (see Figure S8 in the Supporting Information).

The N₂-adsorption results reveal that the activation method used significantly affects the pore features of the POP. The macropores in POPs are commonly believed to be interparticle cavities generated by aggregation of particles within the material.^[26,40] The large macropore volume of **SNU-C1-sca** implies that the supercritical-CO₂ treatment prevents dense aggregation of the polymer particles. Indeed, SEM images showed that particles of **SNU-C1-sca** were much less densely packed than those of **SNU-C1-va** (see Figure S1 in the Supporting Information). The different micropores and mesopores of **SNU-C1-va** and **SNU-C1-sca** suggest that the polymer framework responds differently, depending on the activation method used.

The CO₂-adsorption isotherms of **SNU-C1-va** and **SNU-C1-sca** were measured at 273, 285, and 298 K, and the data are summarized in Table 1. The isotherms show slight hysteresis on desorption (see Figure S10 in the Supporting Information). **SNU-C1-va** shows a CO₂ uptake of 2.31 mmolg⁻¹

Table 1. Gas adsorption data of SNU-C1-va, SNU-C1-sca, and some reported clicked POPs.

Clicked-POP	Gas	T Uptake ^[a]		BET	$Q_{ m st}{}^{[b]}$	
		[K]	$[\text{mmol } \text{g}^{-1}]$	$[m^2g^{-1}]$	$[kJ mol^{-1}]$	
SNU-C1-va	N_2	77	10.36	595	-	
		298	0.14	-	-	
	CO_2	273	3.49	-	34.9	
		285	2.77	-	-	
		298	2.31	-	-	
	CH_4	298	0.50	-	-	
SNU-C1-sca	N_2	77	39.07	830	_	
		298	0.32	-	-	
	CO_2	273	4.38	-	31.2	
		285	3.72	-	-	
		298	3.14	-	-	
	CH_4	298	0.67	-	-	
HCP-5 ^[c]	CO_2	298	1.25 ^[d]	494	28.5	
MOP-C ^[e]	CO_2	273	3.86	1470	33	
		298	2.20	_	_	

[a] At 1 atm. [b] Isosteric heat of the CO_2 adsorption at low coverage. [c] See ref. [40]. [d] Datum was obtained by digitalizing a high-pressure adsorption isotherm plot in the reference. [e] See ref. [8].

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 $(51.8 \text{ cm}^3 \text{g}^{-1})$ at 298 K and 1 atm (Figure 2a). The isosteric heat (Q_{st}) of the CO₂ adsorption at low coverage is 34.9 kJ mol⁻¹, as estimated using the Clausius–Clapeyron equation^[6] in conjunction with the Toth-equation fitting pa-



Figure 2. a) Adsorption isotherms of **SNU-C1-va** and **SNU-C1-sca** for CO_2 (squares), N_2 (circles), and CH_4 (triangles) gases at 298 K; desorption isotherms are not shown for clarity; b) isosteric heat of CO_2 adsorption in **SNU-C1-va** and **SNU-C1-sca**.

rameters obtained from the adsorption data measured at 273, 285, and 298 K (Figure 2b). At 1 atm and at all the measured temperatures, SNU-C1-sca shows higher (1.26-1.36 times) CO₂ uptake than SNU-C1-va (Table 1). It adsorbs 3.14 mmol g^{-1} (70.3 cm³g⁻¹) of CO₂ at 298 K and 1 atm. The low-coverage $Q_{\rm st}$ value of SNU-C1-sca is 31.2 kJ mol⁻¹, which is slightly lower than that of **SNU-C1**va. The data suggest strong physisorption $(<40 \text{ kJ mol}^{-1})^{[42]}$ rather than chemisorption of CO₂ in both SNU-C1-va and SNU-C1-sca. This is further supported by the fact that those materials could be fully reactivated under vacuum at room temperature after CO₂ adsorption and then subsequently being able to adsorb the same amount of gas (see Figure S14 in the Supporting Information). The low-coverage $Q_{\rm st}$ values of SNU-C1-va and SNU-C1-sca are quite high in comparison with that (15.6 kJ mol⁻¹) of **PAF-1**,^[43] which contains no additional functional group, and they are rather close to those of previously reported clicked POPs containing the triazole functional group, **HCP-5**^[40] and **MOP-C**^[8] (Table 1). Moreover, the CO₂ uptakes at 298 K and 1 atm of **SNU-C1-va** and **SNU-C1-sca** are significantly higher (1.85 and 2.51 times) than that of **HCP-5**, even when the higher (1.20 and 1.68 times) BET surface areas of **SNU-C1-va** and **SNU-C1-sca** are considered. Also, the CO₂ uptakes are even higher (1.05 and 1.43 times) than that of **MOP-C**, which has 2.47 and 1.77 times higher surface area than **SNU-C1-va** and **SNU-C1-sca**, respectively. Compared with those previously reported clicked POPs, the **SNU-C1** samples described herein contain carboxy groups in addition to the triazole groups on the pore surface. It is believed that enrichment of these moderately CO₂-attracting groups on the pore surface of **SNU-C1** enhances room-temperature CO₂ uptakes.

The CO₂-capture ability of SNU-C1-va and SNU-C1-sca: In general, uptake capacity and adsorption selectivity of CO₂ over other gases (for example, N₂, CH₄) have been regarded as two principle factors for evaluating CO₂-capture ability of materials. However, the regenerability of the material and the kinetics of separation cycles also need to be considered in real CO₂ capture and separation processes. Based on this consideration, Bae and Snurr have proposed five complementary parameters for better evaluating the CO₂-capture adsorbents in PSA and VSA applications.^[15] These parameters are: 1) CO₂ uptake under adsorption conditions, N_1^{ads} ; 2) working CO₂ capacity, $\Delta N_1 = N_1^{\text{ads}} - N_1^{\text{des}}$; 3) regenerability, $R = \Delta N_1 / N_1^{\text{ads}} \times 100$; 4) selectivity under adsorption conditions, $a_{12}^{ads} = (N_1^{ads} \times y_2)/(N_2^{ads} \times y_1)$; 5) sorbent selection parameter, $S = (a_{12}^{ads})^2 / a_{12}^{des} \times (\Delta N_1 / \Delta N_2)$, where subscripts 1 and 2 stand for CO_2 and the other gas (for example, N_2 and CH_4) in the gas mixture, respectively, superscripts ads and des indicate adsorption and desorption conditions, respectively, and y_i is the molar fraction of gas *i* in the gas mixture to be separated. It should be noted that the comprehensive parameter S takes into account the usually ignored α_{12}^{des} and ΔN_2 values, which contribute to purity of captured CO₂.

The abilities of SNU-C1-va and SNU-C1-sca for CO₂ separation from flue gas and landfill gas by the VSA method were evaluated by using the CO₂-, N₂-, and CH₄-adsorption data measured at 298 K (Table 1 and Figure 2). The five separation parameters of the two samples were calculated using the ideal adsorbed solution theory (IAST, see the Experimental Section),^[44] and they are presented in Table 2 together with the reported data of some promising adsorbents.^[15] For comparison, the gas mixture having the same compositions as flue gas and landfill gas (1:9 CO_2/N_2 and 1:1 CO_2/N_2 CH₄, respectively), and VSA conditions (temperature, 298 K; adsorption and desorption pressures, 1 and 0.1 atm) were adopted in the calculations. The data reveal that there is little difference between the regenerabilities of SNU-C1va and SNU-C1-sca. Overall, SNU-C1-sca shows higher working CO₂ capacities than SNU-C1-va. However, SNU-**C1-va** has higher selectivities and comprehensive S values than SNU-C1-sca. For flue-gas separation, although SNU-C1-va shows lower working CO₂ capacity than Zeolite-5A,

Table 2. VSA separation parameters of $SNU\text{-}C1\text{-}va,\ SNU\text{-}C1\text{-}sca,\ and some reported adsorbents for flue gas and landfill gas.^{[a]}$

Gas mixture	Adsorbent	N_1	ΔN_1	R	$lpha_{ m 12}^{ m ads}$	S
		$[\text{mmol } \text{g}^{-1}]$	$[\text{mmol}\text{g}^{-1}]$	[%]		
Flue gas ^[b]	SNU-C1-va	0.47	0.41	87.3	38.0	262
	SNU-C1-sca	0.58	0.51	88.5	17.0	88
	ZIF-78	0.60	0.58	96.3	34.5	396
	Zeolite-5A	3.50	2.36	67.4	61.8	163
	Zeolite-13X	2.49	1.35	54.2	86.2	128
	Ni-MOF-74	4.34	3.20	73.7	41.1	83.5
Landfill gas ^[c]	SNU-C1-va	1.51	1.21	80.6	9.7	84
	SNU-C1-sca	1.99	1.60	80.4	7.5	38
	CUK-1	2.76	2.33	84.4	14.0	359
	Mg-MOF-74	7.23	2.32	32.1	12.5	23.5
	HKUST-1	2.81	1.90	67.5	5.5	19.8
	Zeolite-13X	3.97	1.97	49.6	13.2	19.1

[a] See ref. [15]. [b] 1:9 CO_2/N_2 . [c] 1:1 CO_2/CH_4 ; for both cases, adsorption and desorption pressures are 1.0 and 0.1 atm, respectively; the VSA temperature is 298 K.

Zeolite-13X, and **Ni-MOF-74**, it has better regenerability and comprehensive *S* values (Table 2). It is also remarkable that the selectivity of **SNU-C1-va** is higher than **ZIF-78**, which shows the highest comprehensive *S* value among all the adsorbents. For landfill-gas separation, **SNU-C1-va** shows high regenerability, a large comprehensive *S* value, and moderate selectivity com-

pared with **Mg-MOF-74**, **HKUST-1**, and **Zeolite-13X**, although the top-performing adsorbent, **CUK-1**, has higher values. Compared with a recently reported POP, **BILP-10**, which has CO_2 selectivities of approximately 57 and 9 for flue gas and landfill gas separation, respectively, under similar conditions,^[45] the selectivity values of **SNU-C1-va** are a little bit lower than **BILP-10**.

Binary gas-cycling experiments: To test the CO₂-capture performance of SNU-C1-va and SNU-C1-sca from a gas mixture, gas-cycling experiments^[13,46] were performed at 30°C on a thermogravimetric analyzer by introducing a stream of a CO₂-N₂ mixture (15:85 v/v) followed by a pure N₂ purge. Before the experiment, the samples were dried at 60 °C with a pure N_2 stream for 5 hours to remove adsorbed moisture during the sample handling. For SNU-C1-va, in the first cycle, the weight was

increased by approximately 1.28 wt % under the gas mixture and the increase was almost fully reversed by the N2 purge (Figure 3a). Over 12 cycles, the weight changes were essentially identical, a behavior that reflects good regenerability and cyclability of the material. The steep slopes for weight increase and decrease during the cycles suggest rapid kinetics of gas adsorption and desorption. To test water stability of SNU-C1-va, the same gas-cycling experiments were performed after the material was soaked in water for 48 hours and subsequently dried at 60 °C under a pure N₂ stream for 5 hours. For the water-treated and activated sample, the weight increase caused by placing the sample under the gas mixture and the profile of the adsorption-desorption cycles were the same as those of the original sample. This result indicates that SNU-C1-va is highly stable in the presence of water (Figure 3a). For SNU-C1-sca, the weight increase (1.15%) under the stream of the gas mixture is slightly less than that of SNU-C1-va (Figure 3b), even though it shows higher CO₂ uptake than SNU-C1-va in the single-component gas adsorption at 1 atm. After being soaked in water for 48 hours followed by activation at 60 $^{\circ}$ C under a pure N₂ stream for 5 hours, SNU-C1-sca shows increased weight change under the gas mixture, and the value is close to that of SNU-C1-va (Figure 3b). It is believed that the network structure of SNU-C1-sca changes to that of SNU-C1-va



Figure 3. Gas-cycling experiments performed at 30 °C for a) **SNU-C1-va** and b) **SNU-C1-sca**. Data points for weight changes during the cycles of introduction of a CO_2/N_2 mixture (15:85 ν/ν) followed by a pure N_2 purge are shown as triangles. For comparison, similar experimental data for samples that were soaked in water for 48 h followed by activation with an N_2 purge at 60 °C for 5 h are shown as circles. For each cycle, the CO_2/N_2 mixture gas was introduced for 40 min and then pure N_2 gas for another 40 min. The relatively small buoyancy changes were not deduced from the data.

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 5

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 77



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during the water treatment and subsequent activation. This is also supported by the color change of SNU-C1-sca from pale yellow to orange, which is the color of SNU-C1-va, after activation of the water-treated sample. We assume that drying the water-adsorbed SNU-C1-sca sample under 60 °C induces a structural change to the one that vacuum drying of the as-synthesized SNU-C1 does.

Conclusion

We have synthesized a new porous organic polymer, SNU-C1, which contains two kinds of moderately CO₂-attracting functional moieties, carboxy and triazole groups. After SNU-C1 was activated by the conventional evacuation method and the supercritical-CO₂ drying method, respectively, the CO₂-capture ability of each guest-free material was evaluated by the experimental sorption studies as well as calculation of five VSA separation parameters, that is, CO₂-adsorption-capacity, working-capacity, regenerability, selectivity, and sorbent-selection parameters. The results reveal that porosity and CO₂-capture performance of the POP depend upon the activation method used. In addition, the POP described herein has high CO2-uptake capacity at room temperature, high selectivity, high regenerability, and good stability against water, and thus it has great potential application in CO₂ capture.

Experimental Section

Synthesis of SNU-C1: To a round-bottom flask (100 mL) containing 3,5diazidobenzoic acid (Hdab; 0.082 g, 0.4 mmol, 1.0 equiv), 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (tepa; 0.107 g, 0.2 mmol, 0.5 equiv), and a magnetic stirring bar, DMSO (20 mL) was added. The flask containing the resultant clear solution was placed in a preheated 90 °C oil bath and the solution was stirred. Then, an aqueous solution (0.5 mL) of CuSO₄·5H₂O (0.020 g, 0.08 mmol, 0.2 equiv) and L-ascorbic acid (0.028 g, 0.16 mmol, 0.4 equiv) was added dropwise to the solution, which immediately became cloudy. After addition, the flask was capped with a rubber septum and the heterogeneous mixture was stirred at 90 °C for 96 h. The reaction mixture was cooled to room temperature and filtered under reduced pressure. The solid product was washed with DMSO (100 mL) and MeOH (300 mL). This as-synthesized sample of SNU-C1 was immersed in MeOH for further activations, which are described below. Yield: 0.175 g (93% of weight sum of the two reactants). Elemental analysis calcd (%) for $C_{56}H_{40}N_{12}O_4$ ·3H₂O ([tepa][Hdab]₂·3H₂O): C 67.32, H 4.64, N 16.82; found: C 65.70, H 4.67, N 17.04 (for SNU-C1-va); C 65.83, H 4.55, N 16.94 (for SNU-C1-sca). The elemental-analysis data indicate that activated SNU-C1 samples adsorb water from air to various degrees during the sample handling.

Activation of SNU-C1: The guest solvent molecules included in SNU-C1 were removed by two different activation methods, namely, high dynamic vacuum activation at room temperature for 12 h, and supercritical-CO₂ treatment. Vacuum activation is a common method; supercritical-CO₂ treatment is described as follows. As-synthesized SNU-C1 was immersed in 30 mL MeOH for 3 h, during which time, the solution was replaced with fresh MeOH three times. The sample was then transferred to a supercritical dryer together with a small amount of MeOH. The temperature and pressure of the chamber were raised to 40 °C and 200 bar with CO₂ by using a CO₂ syringe pump, above the critical point (31°C, 73 atm) of CO₂. The supercritical CO₂ in the chamber was vented at a rate of 10 mLmin⁻¹ until pressurized CO₂ in the syringe pump was empty, which was then filled with CO2 again. The cycle of refilling with CO2, pressurizing, and venting was repeated over 8 h. Finally, the supercritical-CO2-activated sample of SNU-C1 was obtained as a pale yellow powder.

Gas-sorption experiments: The gas adsorption-desorption experiments were performed using an automated micropore gas analyzer, Autosorb-1 (Quantachrome Instruments). All the gases used were of 99.9999% purity. The N2-sorption isotherms were measured at 77 K and 298 K, CH₄-sorption isotherms were measured at 298 K, and CO₂-sorption isotherms were measured at 273 K, 285 K, and 298 K. The adsorption temperatures were achieved by using baths of liquid nitrogen (77 K), ice/ water (273 K), dry ice/dioxane (285 K), and water (298 K). N2-adsorption isotherms measured at 77 K were used for porosity analyses. Brunauer-Emmett-Teller (BET) and Langmuir surface areas were calculated from the adsorption data in the pressure range of 0.005-0.01 atm (see Figure S5 in the Supporting Information). Micropore analyses were performed by using the Dubinin-Radushkevich (DR) method^[47] in the pressure range of 0.005-0.01 atm (see Figure S6 in the Supporting Information). By using nonlocal density-functional theory^[41] (NLDFT), pore-sizedistribution calculations were performed with the adsorption data in the pressure range of 0.005-0.025 atm and with the desorption data in the pressure range of 0.025-0.95 atm. The NLDFT equilibrium model-N2 at 77 K on carbon (slit pore)-was used for the calculations because it provided the best fit (see Figure S7 in the Supporting Information).

Gas-cycling experiments: A sample (around 20 mg) introduced to a TA-Q50 thermogravimetric analyzer was heated at 60 °C for 5 h to remove adsorbed water under a pure N2 flow (99.9999%). After the temperature of the furnace was reduced and stabilized at 30°C, a CO₂/N₂ mixture (15:85 v/v) was introduced into the furnace for 40 min and then pure N₂ was introduced for another 40 min. This cycle was repeated 12 times. A flow rate of 60 mLmin⁻¹ was employed for both gases. The weights of the sample were recorded during the cycles.

Estimation of isosteric heat of CO₂ adsorption: Isosteric heat of CO₂ adsorption was estimated from the CO2-sorption data measured at 273, 285 and 298 K. Firstly, the Toth equation,^[48,49] Equation (1), was used for independent fittings of the isotherms (see Figure S9 in the Supporting Information), where N is the amount of adsorbed gas in cm^3g^{-1} , N_{sat} is the saturated adsorption amount, P is the pressure in atm, b and t are the equation constants. It is noteworthy that the Toth equation reduces to the Langmuir equation when t has the value of 1.

$$N = \frac{N_{\text{sat}}bP}{(1+bP^{\prime})^{\frac{1}{r}}}$$
(1)

Then, the expression for the pressure, P, in terms of the CO₂-adsorption amount, N, could be obtained by using Equation (2).

$$P = \frac{N}{\left(b^t N_{\text{sat}}^t - b N^t\right)^{\frac{1}{t}}} \tag{2}$$

Isosteric heats of the CO_2 adsorption (Q_{st}) were calculated with the Clausius–Clapeyron equation^[6,50] Equation (3), where T is the temperature, R is the universal gas constant, and C is a constant. The $Q_{\rm st}$ values at different CO₂ loading, N, were obtained from the slopes of the plots of $(\ln P)_N$ as a function of (1/T).

$$(\ln P)_N = -\frac{Q_{\rm st}}{R}\frac{1}{T} + C \tag{3}$$

Calculation of CO2-separation parameters: Ideal adsorbed solution theory (IAST)^[44] enables prediction of adsorption equilibriums of the binary gas mixtures from the related single-component isotherms. According to IAST:

$$y_1 + y_2 = 1$$
 (4)

$$x_1 + x_2 = 1 \tag{5}$$

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Chem. Eur. J. 0000, 00, 0-0

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$$p_{\rm mix}y_1 = p_1^{\rm o}x_1 \tag{6}$$

$$p_{\rm mix}y_2 = p_2^{\rm o}x_2\tag{7}$$

$$\pi_1^{\rm o} = \frac{RT}{A} \int_0^{p_1^{\rm o}} n_1(p) d\ln p \tag{8}$$

$$\pi_2^o = \frac{RT}{A} \int_0^{p_2^o} n_2(p) d\ln p \tag{9}$$

$$\pi = \pi_1^{\rm o} = \pi_2^{\rm o} \tag{10}$$

where y_i is the mole fraction of component *i* in the bulk gas mixture, x_i is the mole fraction of component i in adsorbed gas mixture, $p_{\rm mix}$ is the total pressure of the bulk gas mixture, p_i^{o} is the bulk pressure of pure component *i* that corresponds to the spreading pressure π of the binary mixture, R is the universal gas constant, T is adsorption temperature, A is surface area of the adsorbent, $n_i(p)$ is amount adsorbed at pressure p for pure component i.

Using Equations 4-10, the following equation can be obtained:

$$\int_{0}^{\frac{p_{\rm int}y_1}{n_1}} n_1(p) d\ln p = \int_{0}^{\frac{p_{\rm int}y_2}{1-n_1}} n_2(p) d\ln p \tag{11}$$

Total adsorbed amount of the gas mixture (n_{Λ}) is calculated by the following equation:

$$\frac{1}{n_{\Delta}} = \frac{1}{n_1(p_1^\circ)} + \frac{1}{n_2(p_2^\circ)}$$
(12)

where $n_1(p_1^{o})$ is the amount of component 1 adsorbed at spreading pressure π in the absence of component 2, and $n_2(p_2^{\circ})$ is the amount of component 2 adsorbed at spreading pressure π in the absence of component 1.

The adsorption amount for the component i (n^{Δ}) in the binary mixture adsorption is calculated using the following equation:

$$n_1^{\Delta} = n_{\Delta} x_1 \tag{13}$$

$$n_2^{\Delta} = n_{\Delta} x_2 \tag{14}$$

Adsorption selectivity of component 1 over component 2 (S_{12}) is calculated using the following equation:

$$S_{12} = \frac{x_1 y_2}{x_2 y_1} \tag{15}$$

For calculating the above-mentioned five CO₂ separation parameters for flue-gas separation by the VSA method, the gas-mixture composition is assumed to be 1:9 CO₂/N₂ and the adsorption and desorption pressures are assumed to be 1 and 0.1 atm, respectively; CO2 is component 1 and N_2 is component 2. For adsorption, p_{mix} is 1 atm, y_1 is 0.1, y_2 is 0.9, and the functions $n_i(p)$ can be obtained by fittings of the single-component adsorption isotherms with single-site Langmuir-Freundlich equation (see the Supporting Information, Figure S10–13). Value x_1 can be then obtained by solving Equation (11) by using MATLAB software.^[51] All other unknowns can be obtained from the value of x_1 . Value n_1^{Δ} , obtained from Equation (13), corresponds to the CO₂ uptake under adsorption conditions, value n_2^{Δ} , obtained from Equation (14), corresponds to the N₂ uptake under adsorption conditions, and value S_{12} , obtained from Equation (15), corresponds to the selectivity under adsorption conditions. For desorption, p_{mix} is 0.1 atm, y_1 is 0.1, y_2 is 0.9, and the functions $n_i(p)$ can be obtained by fittings of the single-component desorption isotherms with the single-site or dual-site Langmuir-Freundlich equation (see the Supporting Information, Figure S10–13). After solving the Equation (11), all other unknowns can be obtained. Value n_1^{Δ} , obtained from Equation (13), corresponds to CO₂ uptake under desorption conditions, value n_2^{Δ} , obtained from Equation (14), corresponds to N₂ uptake under desorption conditions, and value S_{12} , obtained from Equation (15), corresponds to selectivity under desorption conditions. The difference of the n_1^{Δ}

FULL PAPER

values, obtained under adsorption and desorption conditions, corresponds to the working CO₂ capacity. The regenerability can be obtained by the following expression: $(n_1^{\Delta^{ads}} - n_1^{\Delta^{des}})/n_1^{\Delta^{ads}} \times 100$, where the superscripts ads and des mean calculation under adsorption and under desorption conditions, respectively. The difference of the n_2^{Δ} values obtained under adsorption and desorption conditions corresponds to the working N2 capacity. The sorbent selection parameter can be obtained from the following expression: $(S_{12}^{ads})^2/S_{12}^{des}(n_1^{A^{ads}} - n_1^{A^{des}})/(n_2^{A^{ads}} - n_2^{A^{des}})$, where the superscripts ads and des mean calculation under adsorption and desorption conditions, respectively. Thus, all five parameters are obtained. The five CO2 separation parameters for landfill-gas separation by the VSA method can be obtained in the same way by using the gas-mixture composition, 1:1 CO₂/CH₄.

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Chem. Eur. J. 2013, 00, 0-0

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Porous organic polymer: The guestfree phases, **SNU-C1-va** and **SNU-C1sca**, of a porous organic polymer containing moderately CO₂-attracting carboxy and triazole groups (**SNU-C1**; see picture), obtained by vacuum drying and supercritical-CO₂ activation, respectively, show high CO₂ uptakes (2.31 mmol g⁻¹ and 3.14 mmol g⁻¹, respectively) at 298 K and 1 atm, high selectivity, a high ability to regenerate, and good water stability.



CO₂ Capture

L.-H. Xie, M. P. Suh*......

High CO₂-Capture Ability of a Porous Organic Polymer Bifunctionalized with Carboxy and Triazole Groups



Porous organic polymers.... functionalized with two types of moderately CO_2 -attracting groups, namely, carboxy and triazole groups, can be activated after preparation, by using either vacuum drying or supercritical- CO_2 treatment, to give waterstable phases that can reversibly and selectively adsorb CO_2 . For more details, see the Full Paper by M. P. Suh and L.-H. Xie on page \blacksquare ff.

Chem. Eur. J. 2013, 00, 0-0

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