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# Highly Efficient Carbon Dioxide Capture with a Porous Organic Polymer Impregnated with Polyethylenimine

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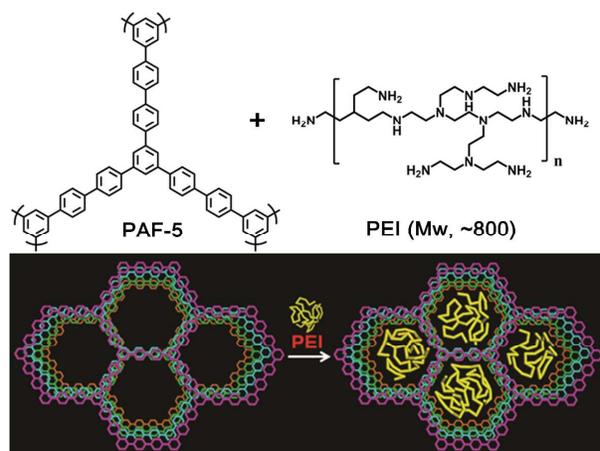
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Various amounts of a branched polyethylenimine are impregnated into a porous aromatic framework. PEI(40 wt%) ⊂ PAF-5 shows exceptionally high capacity and selectivity of CO<sub>2</sub> adsorption at 313 K. The material also displays fast adsorption/desorption kinetics and low energy penalty for regeneration in addition to water stability.

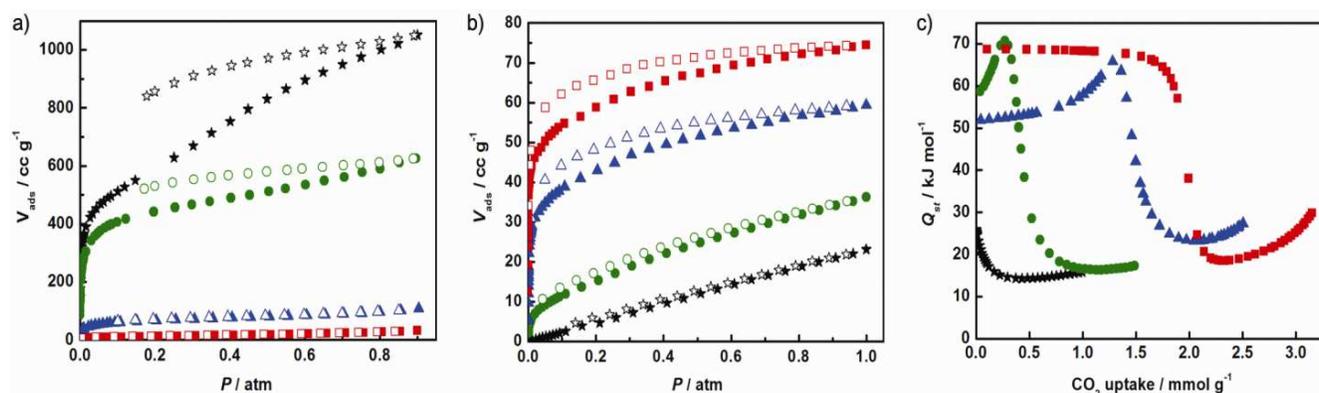
In order to mitigate the recent environmental crises such as global warming and ocean acidification, efficient carbon dioxide (CO<sub>2</sub>) capture technologies from flue gas or ambient air should be developed.<sup>1-4</sup> Typical post-combustion flue gas from a coal-fired power plant contains N<sub>2</sub> (73-77%), CO<sub>2</sub> (15-16%), H<sub>2</sub>O (5-7%), and other gases such as O<sub>2</sub> (3-4%), SO<sub>2</sub> (800 ppm), SO<sub>3</sub> (10 ppm), NO<sub>x</sub> (500 ppm), HCl (100 ppm), CO (20 ppm), and hydrocarbon (10 ppm), with the emission temperature of 313 ~ 343 K.<sup>1</sup> Therefore, CO<sub>2</sub> capture material for flue gas should have a high adsorption selectivity for CO<sub>2</sub> over N<sub>2</sub> at a low CO<sub>2</sub> partial pressure and outstanding water stability as well as a high CO<sub>2</sub> uptake capacity at elevated temperatures, fast adsorption and desorption kinetics, and regenerability.<sup>1</sup> As CO<sub>2</sub> capture materials, numerous solid adsorbents such as silica<sup>5</sup> and carbon materials,<sup>6</sup> metal-organic frameworks,<sup>7</sup> and porous organic polymers<sup>8-14</sup> have been developed. In particular, some porous organic polymers have attracted great attention due to their high surface areas, low density, and excellent thermal, chemical, and water stability.<sup>8-15</sup> Especially, the low density of porous organic polymers formed by the covalent bonds of only light elements such as C, N and H may lead to a high gas uptake per unit mass of the adsorbent.<sup>11,12</sup> In addition, the porous organic polymers display superior stability against water,<sup>13</sup> which is crucial for a post-combustion CO<sub>2</sub> capture material. Therefore, porous organic polymers must be an optimal class of CO<sub>2</sub> capture materials provided that their selectivity for CO<sub>2</sub> over N<sub>2</sub> is also high. Zhou and co-workers



**Scheme 1.** Schematic description of PAF-5 impregnated with branched PEI (Mw = ca. 800).

significantly improved CO<sub>2</sub> capture ability of a porous organic polymer, PPN-6, by tethering various polyamines or ammonium sulfonate to PPN-6.<sup>8(b),14</sup>

In this study, we impregnated various amounts of a branched PEI (Mw = ca. 800, water content ≤ 2%) into PAF-5 and investigated the CO<sub>2</sub> capture abilities of the materials. PAF-5 is a porous aromatic framework with a 2D layered hexagonal structure constructed from only phenyl rings. It displays a high surface area (BET: 1503 m<sup>2</sup> g<sup>-1</sup>) as well as a large pore width (1.66 nm) and pore volume (1.57 cm<sup>3</sup> g<sup>-1</sup>).<sup>16</sup> We expected that flexible polymer PEI would block the large windows of PAF-5 to interfere the N<sub>2</sub> adsorption while CO<sub>2</sub> can open up the windows and enter the pores due to its high polarizability and quadrupole moment.<sup>4</sup> Furthermore, numerous amine functional groups of PEI would strongly interact with CO<sub>2</sub>, which should increase the capacity and selectivity of CO<sub>2</sub>.



**Fig. 1.** Gas sorption properties of PAF-5 (★), PEI(10 wt%)⊂PAF-5 (●), PEI(30 wt%)⊂PAF-5 (▲), and PEI(40 wt%)⊂PAF-5 (■). a) N<sub>2</sub> at 77 K. b) CO<sub>2</sub> at 313 K. c) Isothermic heat of CO<sub>2</sub> adsorption. Filled shapes: adsorption process; Open shapes: desorption process.

adsorption. Although there have been a few reports on PEI incorporation in silica materials<sup>17-23</sup> and metal organic frameworks (MOF),<sup>24,25</sup> none of them has fully met the requirements for the aforementioned post-combustion CO<sub>2</sub> capture material. PEI-impregnated silica materials such as FS-PEI-50<sup>21</sup> and A-PEI/silica<sup>23</sup> showed high CO<sub>2</sub> uptake capacities at 298 K under the ambient air (1.71 and 2.26 mmol g<sup>-1</sup>, respectively), but the equilibrium adsorption time (420 min and 392 min, respectively) was too long for practical applications. In the case of PEI-impregnated MOFs, PEI-MIL-101-125, a high temperature (383 K) as well as a vacuum condition should be applied for an hour to regenerate the adsorbent, resulting in a high energy penalty.<sup>24,25</sup> To the best of our knowledge, incorporation of PEI into porous organic polymers for CO<sub>2</sub> capture is unprecedented. In the present work, PEI-impregnated PAF-5 shows a remarkable increase in the CO<sub>2</sub> uptake capacity and selectivity for CO<sub>2</sub> over N<sub>2</sub> under 0.15 atm of CO<sub>2</sub> at 298, 313, and 323 K. In particular, PEI(40 wt%)⊂PAF-5 showed the CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity of 2160 at 313 K, adsorbing 10.8 wt% of CO<sub>2</sub> under a stream of 15% (v/v) CO<sub>2</sub> in N<sub>2</sub> at 313 K within 20 min, and it was completely regenerated within 10 min at 343 K under a N<sub>2</sub> flow. Even after exposure to water vapor for 7 days at 313 K followed by reactivation, the material hardly loses its CO<sub>2</sub> adsorption capacity, demonstrating its superior water stability.

PAF-5 was prepared by a nickel(0)-catalyzed Yamamoto type Ullmann cross-coupling reaction of 1,3,5-tris-(4-bromophenyl)benzene,<sup>16</sup> and then a branched PEI (Mw = ca. 800, water content ≤ 2%) was impregnated into PAF-5 by using the conventional wet impregnation method.<sup>17</sup> To impregnate PEI in PAF-5, various amounts of PEI (1.0–3.0 g) were dissolved in methanol (25 mL), and the activated PAF-5 (ca. 0.2 g) was added to the solutions. After the solutions were stirred and sonicated for various time (1–6 h), the resulting slurry was filtered and washed with methanol (10 mL × 3) to remove extra PEI adsorbed on the surface of PAF-5. The PAF-5 impregnated with various amount of PEI was activated at 373 K under reduced pressure for 24 h. (Table S1, ESI†). The amount of impregnated PEI was determined by thermogravimetric analyses (TGA) and elemental analysis data

for the activated samples. In TGA, while dried PAF-5 is stable up to 873 K, PEI-impregnated PAF-5 samples show a sharp weight loss between 573 and 673 K, which is attributed to the thermal decomposition of impregnated PEI (Figure S1†). The weight percent of PEI in PAF-5 was determined by the weight loss in this stage. In the elemental analyses, the increase in weight percent of nitrogen was observed as more PEI was impregnated into PAF-5 (Table S2†). The activated samples show a broad peak at ca. 3300 cm<sup>-1</sup> in the IR spectrum, corresponding to the amine functional groups that form extensive hydrogen bonding (Figure S4†).

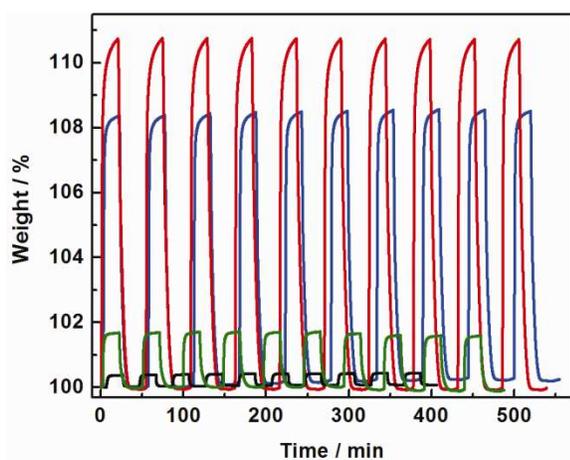
To investigate the porosity of PAF-5 and the PEI-impregnated PAF-5, the materials were activated at 373 K under vacuum for 24 h, and N<sub>2</sub> adsorption/desorption isotherms were measured. The N<sub>2</sub> adsorption isotherm measured at 77 K indicates that pristine PAF-5 has a BET surface area of 2070 m<sup>2</sup>g<sup>-1</sup>, and pore width of 2.11 nm and pore volume of 1.43 cc g<sup>-1</sup>, as calculated by non-local density functional theory (NLDFT) applying the model of carbon as an adsorbent and slit pore. These values are slightly higher than previously reported values of PAF-5.<sup>16</sup> For PEI(x wt%)⊂PAF-5, N<sub>2</sub> uptake at 77 K decreases gradually as the weight percent of loaded PEI increases as shown in Figure 1a) and Table 1, indicating that PEI are impregnated in the pores of PAF-5 instead of the solid surface. For PEI(40 wt%)⊂PAF-5, BET surface area and pore volume are reduced to less than 3% of those of PAF-5 (40.3 m<sup>2</sup> g<sup>-1</sup> and 0.046 cc g<sup>-1</sup>, respectively), indicating that PEI fills almost completely the channel spaces of PAF-5. It should be noted that impregnated PEI was not released even under the high vacuum condition, and this stability must be attributed to the C-H⋯π interactions between the ethylene groups of PEI and phenyl rings of PAF-5. N<sub>2</sub> adsorption and desorption isotherms of PAF-5 and its PEI-loaded samples were also measured at 298, 313, and 323 K up to 1 atm, and the data were used in the calculation of selectivity for CO<sub>2</sub>/N<sub>2</sub> adsorption (Figure S6†).

CO<sub>2</sub> adsorption/desorption isotherms were measured for PAF-5 and PEI-impregnated samples at 298, 313, and 323 K up to 1 atm. Pristine PAF-5 shows linearly increasing CO<sub>2</sub> adsorption isotherms under 298, 313, and 323 K, uptaking very

**Table 1.** Porosity and CO<sub>2</sub> gas sorption properties of PAF-5 and PEI(x wt%)@PAF-5 and comparisons with the properties of other materials.

Compound	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	CO <sub>2</sub> adsorption capacity		Selectivity <sup>d</sup>	Q <sub>st</sub> (kJ mol <sup>-1</sup> )	Ref
			Pure CO <sub>2</sub> (wt%) <sup>b</sup>	15% CO <sub>2</sub> (wt%) <sup>c</sup>			
PAF-5	2070 (2150)	1.43 (1.34)	1.2/0.8/0.7	0.4	9.3/9.7/15.6	26.0-14.3	This work
PEI(10 wt%)@PAF-5	1640	0.836	3.2/2.7/2.3	1.9	37.3/74.4/45.9	70.7-16.4	This work
PEI(30 wt%)@PAF-5	233	0.152	8.8/8.1/7.6	8.4	403/407/677	65.8-23.3	This work
PEI(40 wt%)@PAF-5	40.3	0.046	11.7/11.1/10.9	10.8	1200/2160/1750	68.7-18.5	This work
MC400/10PEI%83	6.16	0.016	-	18 <sup>e</sup>	-	-	5(a)
NPOF-4-NH <sub>2</sub>	554	0.28	4.8/2.3/-	-	81/29/- <sup>f</sup>	30.1	10
BILP-2	708	0.49	6.4/-/-	-	113/71/- <sup>g</sup>	28.6	12
PPN-6-CH <sub>2</sub> DETA	555	0.264	-/11.8 <sup>h</sup> /10.0	-	442 <sup>i</sup>	-	14
MCM-41-PEI-50	4.2	0.011	-/-/4.4 <sup>j</sup>	-	-	-	17
PEI/Zr11-SBA-15	230	0.613	-	6.9 <sup>k</sup>	-	-	20
PEI-MIL-101-125	182.9	0.095	16.9/-/17.4 <sup>l</sup>	-	770/-/1200 <sup>f</sup>	-	24

<sup>a</sup> Values are for the samples activated by heat-evacuation method, and those in the parentheses are for PAF-5 activated by supercritical CO<sub>2</sub> drying method. <sup>b</sup> Uptake under 0.15 atm of CO<sub>2</sub> in the gas adsorption isotherms measured at 298/313/323 K. <sup>c</sup> From the gas cycling data measured at 313 K under a stream of 15% (v/v) CO<sub>2</sub> in N<sub>2</sub>. <sup>d</sup> Calculated by using the molar ratio of the CO<sub>2</sub> uptake at 0.15 atm and the N<sub>2</sub> uptake at 0.85 atm at 298/313/323 K. <sup>e</sup> Measured under a flow of 20% CO<sub>2</sub> in N<sub>2</sub> at 348 K for 120 min using a TGA. <sup>f</sup> Calculated by using the molar ratio of the CO<sub>2</sub> uptake at 0.15 atm and the N<sub>2</sub> uptake at 0.75 atm at 298/323 K. <sup>g</sup> Calculated from Henry's law constants for single-component adsorption isotherms. <sup>h</sup> Measured at 295 K. <sup>i</sup> Calculated ideal adsorbed solution theory. <sup>j</sup> The weight change of the adsorbent was measured on a TGA analyzer under pure 1 atm CO<sub>2</sub> at 323 K. <sup>k</sup> Measured under a flow of 10% CO<sub>2</sub> in N<sub>2</sub> at 298 K for 12 hours using a TGA. <sup>l</sup> From the gas isotherm measured at 298 K and 323 K up to 0.15 atm. No desorption isotherm was reported.



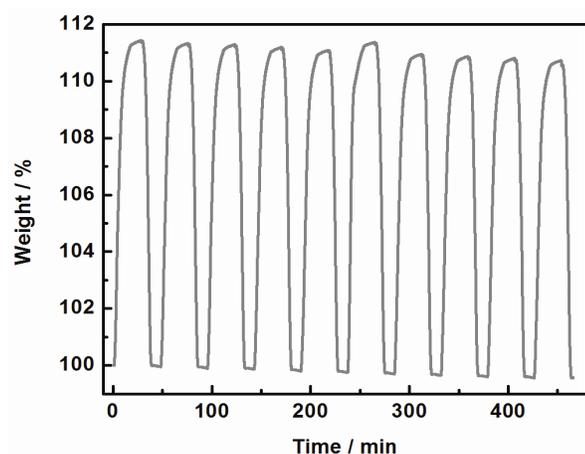
**Fig. 2.** Gas cycling data of PAF-5 (black), PEI(10 wt%)@PAF-5 (green), PEI(30 wt%)@PAF-5 (blue), and PEI(40 wt%)@PAF-5 (red) measured under the stream of 15% CO<sub>2</sub> (v/v) in N<sub>2</sub> at 313 K, followed by a pure N<sub>2</sub> stream at 323 K for PEI(10 wt%)@PAF-5, and at 343 K for PEI(30 wt%)@PAF-5 and PEI(40 wt%)@PAF-5. The adsorption and desorption time were given with 20 min in each process although the materials were completely regenerated in 10 min. The wt% in y axis refers to (observed weight/initial weight)×100.

small amount of CO<sub>2</sub> under 0.15 atm of CO<sub>2</sub> pressure, 1.2, 0.8, and 0.7 wt%, respectively (Figure 1b and Figure S7†). However, CO<sub>2</sub> adsorption isotherms of PEI-loaded adsorbents change to type-I curve at all three different temperatures, resulting in a drastic increase in CO<sub>2</sub> uptake capacities at 0.15 atm. In particular, PEI(40 wt%)@PAF-5 adsorbs 11.7 wt%, 11.1 wt%, and 10.9 wt% of CO<sub>2</sub> under 0.15 atm of CO<sub>2</sub> pressure at 298 K, 313 K, and 323 K, respectively, which are 10, 14, and 16 times greater than those of pristine PAF-5. The drastic increase in CO<sub>2</sub> uptake capacity at low CO<sub>2</sub> pressure stems from the strong interactions between the amine groups impregnated in PAF-5 and CO<sub>2</sub> molecules. Isothermic heat (Q<sub>st</sub>) of the CO<sub>2</sub> adsorption in PAF-5 and PEI-impregnated PAF-5 were calculated by using

Clausius-Clapeyron equation based on Dual-site Langmuir fit parameters obtained from the adsorption isotherms at 298, 313, and 323 K (Table 1, and Figure S8-S11†). As shown in Figure 1c, the plot of Q<sub>st</sub> values versus CO<sub>2</sub> uptake shows two distinctive regions. In particular, 30 wt% and 40 wt% PEI-loaded adsorbents display high Q<sub>st</sub> values (65.8 – 68.7 kJ mol<sup>-1</sup>) up to ca. 1.5 and 2.0 mmol g<sup>-1</sup> of CO<sub>2</sub> loading, respectively, which decrease to low Q<sub>st</sub> values (23.3 – 18.5 kJ mol<sup>-1</sup>) in the higher CO<sub>2</sub> loading. Interestingly, the first region of high Q<sub>st</sub> values covers broader ranges of CO<sub>2</sub> uptake capacity as more amount of PEI is impregnated in PAF-5. These clearly indicate that the first region corresponds to chemisorption of CO<sub>2</sub> on PEI and the second region to physisorption on the surface of PAF-5. The ratios of the adsorbed CO<sub>2</sub> amounts by chemi- and physisorption calculated for PEI(10 wt%)@PAF-5, PEI(30 wt%)@PAF-5, and PEI(40 wt%)@PAF-5 at 313 K, based on Figure 1, are 0.43, 1.49, and 1.72, respectively.

The CO<sub>2</sub> adsorption selectivity over N<sub>2</sub> based on IAST (Ideal Adsorbed Solution Theory) could not be calculated, since extremely low N<sub>2</sub> adsorption data for the PEI-impregnated adsorbents could not be reasonably fitted. Therefore, it was calculated by using the single component adsorption isotherms by using the molar ratio of the CO<sub>2</sub> uptake at 0.15 atm and the N<sub>2</sub> uptake at 0.85 atm at 298, 313, and 323 K. For the PEI-loaded adsorbents, a sharp increase in the CO<sub>2</sub> uptake at low CO<sub>2</sub> pressure together with the large decrease in the N<sub>2</sub> uptake synergistically enhances the CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity at 298, 313, and 323 K. As shown in Table 1, PEI(40 wt%)@PAF-5 shows the highest selectivity (2160) at 313 K. To the best of our knowledge, this selectivity is the highest value reported so far.

To test the possibility of practical application of PEI-impregnated PAF-5 in post-combustion CO<sub>2</sub> capture, a gas cycling experiment was conducted on a thermogravimetric



**Fig. 3.** Temperature swing adsorption (TSA) data of PEI(40 wt%)@PAF-5. A stream of 15% CO<sub>2</sub> (v/v) in N<sub>2</sub> was applied at 313 K for 10 min and then the temperature was increased to 413 K at a rate of 10 K/min under a stream of 1 atm CO<sub>2</sub>. For the complete regeneration of the sample, the temperature of 413 K was maintained for 10 min. The wt% in y axis refers to the observed weight/initial weight  $\times$  100.

(TG) apparatus. For the adsorption process, the adsorbents were exposed to a stream of 15% (v/v) CO<sub>2</sub> in N<sub>2</sub> at 313 K, which approximately mimics flue gas. After the adsorption process, a pure N<sub>2</sub> stream was applied to regenerate the adsorbents at the elevated temperatures, at 313 K for PAF-5, at 323 K for PEI(10 wt%)@PAF-5, and at 343 K for PEI(30 wt%)@PAF-5 and PEI(40 wt%)@PAF-5. As shown in Figure 2, PAF-5 and PEI(10 wt%)@PAF-5 reached an equilibrium of CO<sub>2</sub> adsorption quickly, within 20 min, at 313 K. They showed relatively low CO<sub>2</sub> uptake capacities, 0.4 wt% and 1.9 wt%, respectively, and they were regenerated in 10 min under a N<sub>2</sub> flow at 313 and 323 K, respectively. Contrary to these, PEI(30 wt%)@PAF-5 and PEI(40 wt%)@PAF-5 adsorbed 8.4 wt% and 10.8 wt% of CO<sub>2</sub>, respectively, at 313 K in 20 min, and they were completely regenerated in 10 min at 343 K, significantly low desorption temperature considering their very high  $Q_{st}$  values of the CO<sub>2</sub> adsorption. The 10.8 wt% weight increase of PEI(40 wt%)@PAF-5 in the gas cycling experiment is similar to 11.1 wt% CO<sub>2</sub> uptake at 0.15 atm in the CO<sub>2</sub> single component adsorption isotherm measured at 313 K. This 10.8 wt% of CO<sub>2</sub> uptake under a stream of 15% CO<sub>2</sub> in N<sub>2</sub> (v/v) at 313 K is one of the highest uptake capacities ever reported. Previously reported adsorbents such as PEI/Zr14-SBA-15<sup>20</sup>, 65PEI/monolith<sup>22</sup>, PEI-MIL-101-125<sup>24</sup>, and mmen-Mg<sub>2</sub>(dobpdc)<sup>26</sup> suffered from a slow adsorption (12 h)<sup>20</sup> or desorption process (*ca.* 100 min),<sup>22</sup> in addition to a high energy penalty derived from a high regeneration temperature.<sup>24,26</sup> However, PEI(40 wt%)@PAF-5 in this report adsorbs remarkably high amount of CO<sub>2</sub> and the material can be regenerated quickly at a slightly increased temperature (343 K). Furthermore, even after 10 cycles of adsorption/desorption, the adsorbent shows neither material decomposition nor decrease of CO<sub>2</sub> uptake capacity (Figure 2).

To exclude the possibility of cooperative N<sub>2</sub> adsorption<sup>27</sup> from a CO<sub>2</sub>/N<sub>2</sub> gas mixture and validate the highly selective

CO<sub>2</sub> adsorption in PEI(40 wt%)@PAF-5, similar gas cycling experiments were performed by using a CO<sub>2</sub>/He mixture, since He cannot be adsorbed by any adsorbents. In the gas cycling experiment under the CO<sub>2</sub>/He (15/85, v/v) gas mixture at 313 K, PEI(40 wt%)@PAF-5 increased its weight by 11.3 wt% within 20 min (Figure S13<sup>†</sup>), same as the weight increase under the CO<sub>2</sub>/N<sub>2</sub> (15/85, v/v) gas mixture, and the material was completely regenerated under a N<sub>2</sub> stream at 353 K within 30 min. The discrepancy of 0.5 wt% under two different gas mixtures may be originated from the slight difference in the CO<sub>2</sub> content, and the results suggest that the material adsorbs only CO<sub>2</sub> from the CO<sub>2</sub> and N<sub>2</sub> gas mixture.

Since industrial flue gas contains water vapor and other acidic impurities such as SO<sub>2</sub>, SO<sub>3</sub>, NO<sub>x</sub>, and HCl, CO<sub>2</sub> capture material should be highly stable against water vapor and the acidic impurities. To evaluate the water stability, PEI(40 wt%)@PAF-5 was exposed to water vapor in a closed bottle for 7 days at 313 K and then activated under reduced pressure at 373 K for 48 hours. The adsorbent showed the same weight changes in the gas cycling experiment carried out under the stream of 15% CO<sub>2</sub> in N<sub>2</sub> at 313 K followed by a pure N<sub>2</sub> gas stream at 343 K, indicating the robustness of the adsorbent against water (Figure S14<sup>†</sup>). Furthermore, water vapor adsorption and desorption isotherms were measured for PEI(40 wt%)@PAF-5 at 313 K (Figure S15<sup>†</sup>). The sample adsorbed 5.0 wt% of water vapor at  $P/P_0 = 0.68$ , which corresponds to 0.05 atm of water vapor pressure in the post-combustion flue gas. According to the previous report by Cooper *et al.*, POPs with hydrophilic functional groups showed reduced CO<sub>2</sub> uptake capacity after exposure to the ambient atmosphere ( $\sim$ 50% relative humidity conditions). In the present case also, water vapor might compete with CO<sub>2</sub> for adsorption on the polar PEI.<sup>28</sup> In addition, the acidic impurities in flue gas might react with PEI base that is impregnated in PAF-5, and the repetitive exposure of the material to the flue gas might gradually reduce the CO<sub>2</sub> capture ability, even though the concentrations of acidic impurities are extremely low and PAF-5 is stable even in concentrated HCl.<sup>12</sup>

Working capacity of PEI(40 wt%)@PAF-5 in a temperature swing adsorption (TSA) process was also estimated by using the equation,  $\Delta N = N^{ads} - N^{des}$ , where  $N^{ads}$  is the amount of CO<sub>2</sub> adsorbed in the adsorption condition, under a flow of 15% (v/v) CO<sub>2</sub> in N<sub>2</sub>, and  $N^{des}$  is the amount of CO<sub>2</sub> adsorbed in the regeneration condition, under a pure CO<sub>2</sub> stream at regeneration temperature.<sup>29</sup> As shown in Figure 3, under a stream of 15% (v/v) CO<sub>2</sub> in N<sub>2</sub>, PEI(40 wt%)@PAF-5 shows 11.1 wt% of CO<sub>2</sub> uptake at 313 K within 10 min. When the temperature was increased to 413 K at a rate of 10 K/min under a pure CO<sub>2</sub> stream, the sample began to lose its weight by releasing adsorbed CO<sub>2</sub> and was completely regenerated at 413 K. This reveals 11.1 wt% of working capacity on TSA process between 313 K and 413 K. The CO<sub>2</sub> uptake capacities slightly fluctuated during the 10 cycles of TSA, showing the highest amount of CO<sub>2</sub> (11.7 wt%) adsorption in the 6<sup>th</sup> cycle. However, the difference of the CO<sub>2</sub> uptake capacities between

the first and 10<sup>th</sup> cycle is only 0.23 wt% indicating the robustness of the material (Figure S16<sup>†</sup>).

## Conclusions

We have impregnated various amounts of PEI in PAF-5 and demonstrated that PEI(40 wt%) ⊂ PAF-5 is an effective material for CO<sub>2</sub> capture from the post-combustion flue gas. The material shows high CO<sub>2</sub> uptake capacity (11.1 wt% at 313 K under 0.15 atm of CO<sub>2</sub>), high selectivity for CO<sub>2</sub> adsorption over N<sub>2</sub> (2160 at 313 K), fast adsorption and desorption kinetics (within 10 min.), water stability, and yet low energy penalty for regeneration of the adsorbents (413 K with 11.1 wt% working capacity). For the practical application of this material in CO<sub>2</sub> capture from flue gas, however, we should solve several problems still left such as cost down of the material and development of large scale up methods, which might be challenging.

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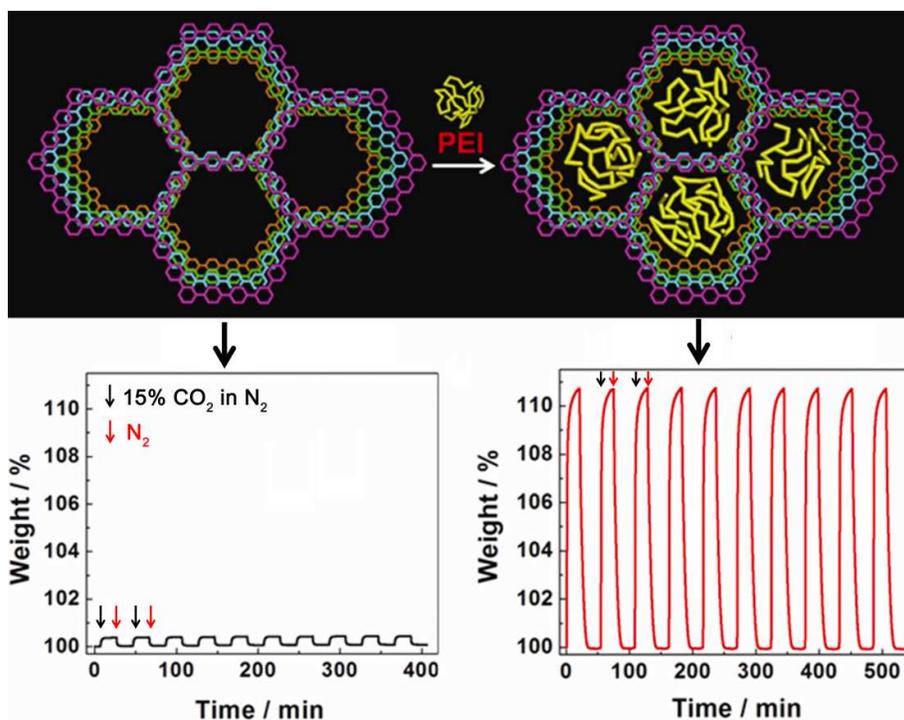
## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: [experimental details, TGA, pore size distribution, FT-IR, additional gas sorption isotherms, gas cycling experiments, and Tables for gas sorption isotherms]. See DOI: 10.1039/b000000x/

- 1 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781.
- 2 (a) H. J. Park and M. P. Suh, *Chem. Sci.*, 2013, **4**, 685-690; (b) H. He, W. Li, M. Zhong, D. Konkolewicz, D. Wu, K. Yaccato, T. Rappold, G. Sugar, N. E. David and Krzysztof Matyjaszewski, *Energy Environ. Sci.*, 2013, **6**, 488-493.
- 3 (a) D. H. Hong and M. P. Suh, *Chem. Commun.*, 2012, **48**, 9168-9170; (b) T. K. Kim and M. P. Suh, *Chem. Commun.*, 2011, **47**, 4258-4260.
- 4 H.-S. Choi and M. P. Suh, *Angew. Chem. Int. Ed.*, 2009, **48**, 6865-6869.
- 5 (a) G. Qi, Y. Wang, L. Estevez, X. Duan, N. Anako, A.-H. A. Park, W. Li, C. W. Jones, E. P. Giannelis, *Energy Environ. Sci.*, 2011, **4**, 444-452; (b) X. Wang, X. Ma, V. Schwartz, J. C. Clark, S. H. Overbury, S. Zhao, X. Xuza and C. Song, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1485-1492; (c) J. C. Hicks, J. H. Drese, D. J. Fauth, M. L. Gray, G. Qi and C. W. Jones, *J. Am. Chem. Soc.*, 2008, **130**, 2902-2903.
- 6 L. Wang and R. T. Yang, *J. Phys. Chem. C*, 2012, **116**, 1099-1106.
- 7 (a) W. R. Lee, S. Y. Hwang, D. W. Ryu, K. S. Lim, S. S. Han, D. Moon, J. Choi and C. S. Hong, *Energy Environ. Sci.*, 2014, **7**, 744-751; (b) N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, *Nat. Mater.*, 2011, **10**, 1485-793; (c) T. Li, J. E. Sullivan and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 9984-9987.
- 8 (a) V. Guillermin, L. J. Weselinski, M. Alkordi, M. I. H. Mohideen, Y. Belmabkhout, A. J. Cairns, M. Eddaoudi, *Chem. Commun.*, 2014, **50**, 1937-1940; (b) W. Lu, W. M. Verdegaa, J. Yu, P. B. Balbuena, H.-K. Jeong, H.-C. Zhou, *Energy Environ. Sci.*, 2013, **6**, 3559-3564; (c) S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548-568; (d) D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959-4015.
- 9 L.-H. Xie and M. P. Suh, *Chem. -Eur. J.*, 2013, **19**, 11590-11597.
- 10 T. Islamoglu, M. G. Rabbani and H. M. El-Kaderi, *J. Mater. Chem. A*, 2013, **1**, 10259-10266.
- 11 (a) H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, **4**, 1357; (b) R. Dawson, D. J. Adams, A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1173-1177. (c) R. Dawson, E. Stockel, J. R. Holst, D. J. Adams, A. I. Cooper, *Energy Environ. Sci.* 2011, **4**, 4239-4245.
- 12 M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, **24**, 1511-1517.
- 13 H. A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan and C. T. Yavuz, *Adv. Funct. Mater.*, 2013, **23**, 2270-2276.
- 14 W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 7480-7484.
- 15 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9457-9460.
- 16 H. Ren, T. Ben, F. Sun, M. Guo, X. Jing, H. Ma, K. Cai, S. Qiu and G. Zhu, *J. Mater. Chem.*, 2011, **21**, 10348-10353.
- 17 X. Xu, C. Song, J. M. Andresen, B. G. Miller and A. W. Scaroni, *Energy Fuels*, 2002, **16**, 1463-1469.
- 18 S. Kim, J. Ida, V. V. Gulians and J. Y. S. Lin, *J. Phys. Chem. B*, 2005, **109**, 6287-6293.
- 19 X. Ma, X. Wang and C. Song, *J. Am. Chem. Soc.*, 2009, **131**, 5777-5783.
- 20 Y. Kuwahara, D.-Y. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita and C. W. Jones, *J. Am. Chem. Soc.*, 2012, **134**, 10757-10760.
- 21 A. Goeppert, M. Czaun, R. B. May, G. K. S. Prakash, G. A. Olah and S. R. Narayanan, *J. Am. Chem. Soc.*, 2011, **133**, 20164-20167.
- 22 C. Chen, S.-T. Yang, W.-S. Ahn and R. Ryoo, *Chem. Commun.*, 2009, 3627-3629.
- 23 S. Choi, M. L. Gray and C. W. Jones, *ChemSusChem*, 2011, **4**, 628-635.
- 24 Y. Lin, Q. Yan, C. Kong and L. Chen, *Sci. Rep.* 2013, **3**, 1859.
- 25 Q. Yan, Y. Lin, C. Kong and L. Chen, *Chem. Commun.*, 2013, **49**, 6873-6875.
- 26 T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong and J. R. Long, *J. Am. Chem. Soc.*, 2012, **134**, 7056-7065.
- 27 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058-6082.
- 28 R. Dawson, L. A. Stevens, T. C. Drage, C. E. Snape, M. W. Smith, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2012, **134**, 10741-10744.
- 29 Y. S. Bae and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2011, **50**, 11586-11596.



A porous organic framework (PAF-5) impregnated with a polyethylenimine (PEI) displays excellent properties for post-combustion CO<sub>2</sub> capture.