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Observation of the wrapping mechanism in amine carbon dioxide molecular interactions on heterogeneous sorbents†

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Liquid, solvated amine based carbon capture is the core of all commercial or planned CO_2 capture operations. Despite the intense research, few have looked systematically into the nature of amine molecules and their CO_2 interaction. Here, we report a systematic introduction of linear ethylene amines on the walls of highly porous Davankov type network structures through simple bromination intermediates. Surprisingly, isosteric heats of CO_2 adsorption show a clear linear trend with the increase in the length of the tethered amine pendant groups, leading to a concerted cooperative binding with additional H-bonding contributions from the unassociated secondary amines. CO_2 uptake capacities multiply with the nitrogen content, up to an unprecedented four to eight times of the starting porous network under flue gas conditions. The reported procedure can be generalized to all porous media with the robust hydrocarbon framework in order to convert them into effective CO_2 capture adsorbents.

Global warming is predominantly attributed to the greenhouse gases in the atmosphere, particularly carbon dioxide (CO_2) and that has made the research on effective gas capture and storage materials a major goal in academics and industry. Today's best CO_2 scrubbing method still relies mainly on the use of aqueous organic amine solutions like monoethanolamine (MEA), which has been developed in the early 1930s.[1,2] Despite the chemisorptive, high working capacity, the regeneration of an aqueous MEA solution requires a lot of heating because of the high heat capacity of water during desorption. This, in turn, leads to a parasitic energy, which unfortunately accounts for the 70–80% of the operating costs.[3,4] Porous solids have long been considered as viable alternatives, albeit without success, resulting in the development of a wide collection of porous materials as potential next generation CO_2 sorbents.[5–13]

Both the porosity and the chemistry of a porous solid have to be tuned for an ideal CO_2 capture.[14–17] The pore size, volume and surface area of a structure depend on the synthesis conditions and are mostly tuned by varying the experimental conditions. Chemically active sites for CO_2 binding, on the other hand, need to be installed by post-modification methods due to their reactivity and the deleterious interference in the network formation. This is why large polymeric amines are almost always loaded physically with or without the aid of a solvent.[18,19] Despite the few reports of successful post-modification routes, such as protection–deprotection of amines[20] and amidoxime formation from nitriles,[21] chemically modified sorbent surfaces largely negates porosity. In order to alleviate this inevitable consequence, one must first understand how much active material in which molecular form is needed. Solid amines such as polyethylenimines are not easy to study as their structures can take many conformations and hydrogen bonding is evident in nearly unlimited possibilities. For example, in a recent study, Jones showed that impregnated amines tend to interact with silica surfaces and cripple the CO_2 binding capabilities.[22] Understanding the molecular amine–CO_2 relationship may lead to predictable grafting procedures, a key design tool sorbent development research desperately is in need of.

In an attempt to better quantify the role of amines in porous solid sorbents for CO_2 capture, we, herein, chose a highly porous (around 750 m^2 g^{-1}), all hydrocarbon (without heteroatom), network polymer as the support base and developed a versatile grafting procedure through brominated intermediates. By varying only the length of the amine molecule (but not chain branching), we discovered that multiple amines cooperate together to enhance the binding strength, as evidenced by the increase of the heats of adsorption. Surprisingly, we found that the increase is directly proportional to the length of the amine molecule, a direct evidence and tool for designing ideal CO_2 binding functionalities. To the best of our knowledge, this marks the first study that systematically evaluates amine

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, FTIR spectra, elemental analysis, thermogravimetric analysis, textural properties, CO_2–N_2 adsorption–desorption isotherms, IAST calculations and SEM images. See DOI: 10.1039/c6cp01382a

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variation and we believe it will lead to many developments in durable CO_2 sorbents. The main challenge is that these studies are not normally trivial, even with the *in situ* techniques because of the structural irregularities (and beam penetration), stability issues, and overlapping signals from the free functional groups.

Porous polymers offer a nearly ideal platform for studying the effect of amine grafting on CO_2 adsorption since they do not contain metals, are mostly chemically inert, and inexpensive.[23,24] Among these, hypercrosslinked polymer networks are a well-studied class of materials since the first report by Davankov and Tsyurupa in 1971.[25,26] They are mostly identified by the three-dimensional, highly rigid, all hydrocarbon structure. The extensive crosslinking of the monomer units maintain the structure from collapsing and thus allow porous materials with high surface areas to be obtained.[27] These polymer networks are mainly synthesized by Friedel–Crafts alkylation reactions mediated by a Lewis acid such as iron(III) chloride, like in the self-condensation of *para*-xylylene dichloride or bis(chloromethyl) biphenyl.[27,28] As the starting materials for these network polymers are highly available and scalable,[29–33] the cost to make them in large quantities is not as much questionable, a particular necessity for carbon capture candidates. Two features of these structures are crucial for our study: (1) there are no nitrogens in the structures or the reagents; (2) the surfaces are hydrophobic, minimizing the amine surface interaction.

The polycondensation of the ideal biphenylic monomer, 4,4′-bis-(chloromethyl)-1,1′-biphenyl (BCMBP) with methanesulfonic acid gave a porous support (Covalent Organic Polymer, COP-115) that is suitable for varying length amine tethering (Scheme 1, see the ESI† for extensive details on synthesis and characterization). Attaching amines through post-modification of the porous polymer are not straightforward, as nucleophilic tethering requires the covalent displacement of the leaving group. Good leaving groups do not survive the harsh polymerization conditions or get involved in the framework building reactions, if they are introduced initially on the monomers. Post-modifications for leaving group placement usually end in

the loss of surface area by blocking the narrow pores that connect larger cavities of the porous structures.[34] Bromination, as we found, is one of the few exceptions that preserve most of the surface area of the porous polymer[35] and provide anchoring spots for amine grafting.[21]

As expected, after post-synthetic modification with amines, the surface areas of the polymer networks diminish linearly with the increase in the size of the amine, from 735 to 299 $m^2\ g^{-1}$ in the COP-115 series (Table 1). The reduced surface areas also confirm that the functionalized amines are mainly located inside the pores of the network. In the COP-115 series, all the functionalized networks show increased CO_2 adsorption capacities compared to the starting network, the highest being COP-115-D with an increase of 1.03 mmol g^{-1} at 0.15 bar and 0.81 mmol g^{-1} at 1 bar and 273 K (Table 1). These results reflect the higher amine loading observed in the characterization study (see Table S1, ESI†).

In order to assess the binding mode of CO_2 in the presented COP structures, *in situ* difference infrared spectra of adsorbed CO_2 were measured for COP-115-C (Fig. 1, see the ESI† for experimental details).

In amine containing systems under dry conditions, CO_2 can form ammonium carbamate ion pairs or carbamic acids.[36–39] The presence of characteristic vibrations for chemisorbed CO_2 can be found at 1680 cm^{-1} (amide I), 1523 cm^{-1} (amide II) and 1234 cm^{-1} (amide III) as well as at 3426 cm^{-1} (N–H stretching). The frequency of the amide I is low for a carbonyl unit, which points to the presence of strong H-bonding. This hydrogen bonding by NH groups can also be suggested by the broad region of 3300–3000 cm^{-1} as observed previously by Danon *et al.*[37] Previous studies on amine grafted materials have shown that close proximity of amine groups favors the formation of carbamates whereas long distance favors carbamic acid.[37–39] In COP-115-C, the grafted diethylenetriamine chains should favor the formation of carbamates which can be verified by the presence of characteristic bands of ionic $(NH)CO_2^-$. The symmetric stretching of CO_2^- can be found at 1436 cm^{-1} and 1396 cm^{-1}, the asymmetric stretching being overlapped with the amide II band. Several bands for ammonium moieties of ammonium carbamate can be found at 1488, 1604 cm^{-1}, around 2076 cm^{-1} and in the two broad regions around 3300–2800 and 2800–2500 cm^{-1}.[40] The most probable binding mode of CO_2 in COP-115-C seems to be through ammonium carbamate formation, rather than carbamic acid, even if an equilibrium between species cannot be completely excluded.

The isosteric heats of adsorption (Qst) were calculated from the adsorption data in order to quantify the strength of interaction between the COP networks and CO_2 (Table 1). To the best of our knowledge, no systematic attempts have been made towards the Qst variation based on the grafted amine molecules. We postulated that if we could build comparable substrates such as COP-115 networks with well-defined amine chain lengths (ideally with the same repeating unit) and morphology (linear not branched), we could understand some of the CO_2 capture mechanisms with amines. The Qst values with respect to the amine length are the best measurable parameter to show the binding motif. We have previously experimented on
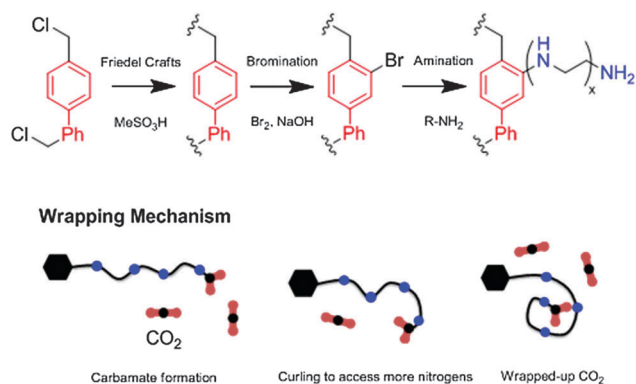

Scheme 1 Synthesis and post-synthetic modification of a nitrogen free porous support in order to monitor CO_2–amine interactions. Ethylene diamine (EDA) yields $x = 1$, diethylene triamine (DETA) $x = 2$ and triethylene tetraamine (TETA) $x = 3$. The modified COPs are labeled as COP-115-A for brominated, -B for EDA grafted, -C for DETA and -D for TETA. Wrapping mechanism is proposed based on the observed increase in CO_2 binding strength.

Table 1 Gas sorption data, heats of adsorption and CO_2/N_2 selectivities of COP-115,B,C,D

Structure	Surface area ($m^2\ g^{-1}$)	CO_2 273 K (mmol g^{-1}) 0.15/1 bar	CO_2 298 K (mmol g^{-1}) 0.15/1 bar	CO_2 323 K (mmol g^{-1}) 0.15/1 bar	Qst[a] (kJ mol^{-1})	CO_2/N_2 273 K, 1 bar[b]	CO_2/N_2 298 K, 1 bar[b]	CO_2/N_2 323 K, 1 bar[b]
COP-115	735	0.42/1.67	0.21/1.02	0.10/0.58	26.4	26	19	14
COP-115-B	638	1.06/2.45	0.82/1.81	0.35/0.94	35.9	345	253	[c]
COP-115-C	406	1.34/2.48	0.89/1.72	0.39/0.94	52.7	645	332	143
COP-115-D	299	1.45/2.48	1.04/1.80	0.36/0.73	66.1	1119	986	271

[a] Zero point coverage Qst calculated from 273 K, 298 K and 323 K. [b] Calculated using the IAST. [c] Due to very low nitrogen adsorption at 323 K, the selectivity value was not reliable.
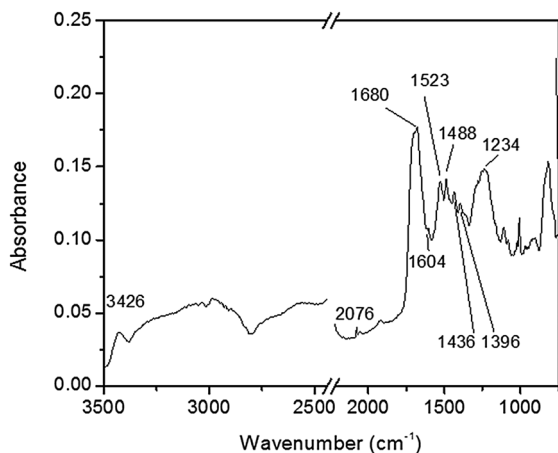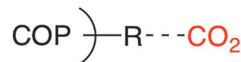

Fig. 1 *In situ* difference infrared spectrum of adsorbed CO_2 on COP-115-C. The sample was degassed prior to measurement and used as background before monitoring the CO_2 adsorption.

Fig. 2 Stepwise increase in the heat of adsorption with the increase in amine length of COP-115 series. The difference in Qst values correlate well to the number of additional H-bonds.

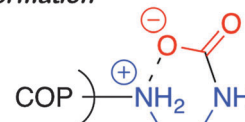other conventional methods to gauge this relationship but never succeeded.

The unmodified structure of COP-115 has Qst data in the expected range of commonly reported unfunctionalized hyper-crosslinked polymer networks, with 26 kJ mol^{-1} (Table 1).[28,41,42] These binding energies come from physisorption from near linear Langmuir adsorption profiles (Fig. S5, ESI†). Once the EDA is bound (B series) we observed the Qst to increase to above 35 kJ mol^{-1}, a little shy of the hypothetical chemisorptive threshold of 40 kJ mol^{-1} CO_2. The increase is definitely from chemisorptive amine chemistry but not significantly higher as the tethering nitrogen atom is now a predominantly aromatic one, one that is considerably less basic (Fig. 2). In the case of DETA, an additional H-bond is formed with the additional protons on the new nitrogen. The linear molecule is therefore suspected to be bent to accommodate this. The gain in the Qst is 17 kJ mol^{-1}, a value quite common for H-bonds.[43,44] TETA brings two additional nitrogens and their protons, and almost double the additional Qst value of 30 kJ mol^{-1}. It also agrees well with the fact that the additional protons are coordinating to the same oxygen, hence the Qst increase is not exactly double (34 kJ mol^{-1}) as one would expect in an ideal situation. We should note that the Qst values are calculated using the Clausius–Clapeyron equation with at least 3 temperature points, as we found that the common practice of using software generated two-point plots are not that reliable (Table S6, ESI†).

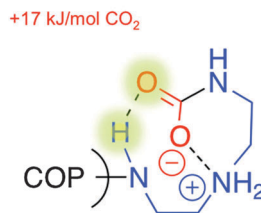In an attempt to understand the systematic increase of experimental CO_2 adsorption heat as a function of ethylene–amine chain length, we performed the density functional theory (DFT) calculations for CO_2 interacting with EDA, DETA, and TETA. The Perdew–Burke–Ernzerhof exchange–correlation functional (PBE) with the dispersion correction of Grimme (D3) was used as implemented in the Q-CHEM quantum chemistry package.[45] Due to the single bond character of the backbone of the ethylene amine oligomer, many conformational isomers are possible, among which the most stable geometries before (top) and after (bottom) the CO_2 binding are summarized in Fig. 3. The linear form is generally preferred to minimize distortive strain, while the bent form is advantageous to form intermolecular H-bonding interactions, and hence the relative importance of the two effects will determine the lowest energy structures for each amine length. For bare monomers, as seen in Fig. 3, as the chain length increases, relative stability of the bent form with the intramolecular H-bonds increases systematically due to the increasing geometric flexibility with respect to the stretched linear isomer (0, −8.9, and −15.2 kJ mol^{-1} for EDA, DETA, and TETA monomers, respectively). Calculated binding energies of CO_2 with EDA, DETA, and TETA (−25.2, −32.4, and −56.0 kJ mol^{-1}, respectively) also

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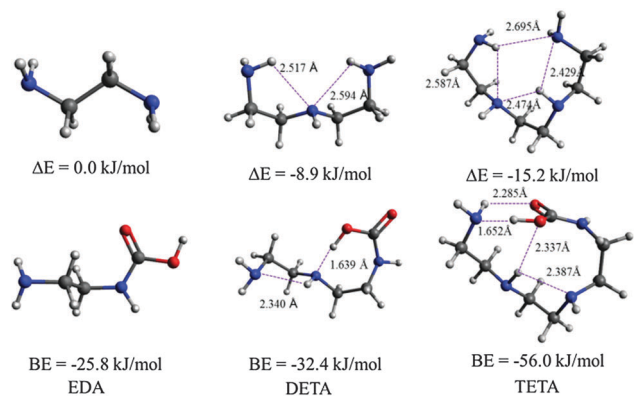
Fig. 3 Lowest energy geometries for EDA, DETA, and TETA before (top) and after (bottom) the formation of carbamic acid. ΔE is the relative energy of the lowest energy configuration for the bare monomer compared to its stretched linear isomer. BE is the binding energy obtained as E(carbamic acid) − E(CO_2) − E(oligomer) using PBE-D3/aug-cc-pVTZ//PBE-D3/aug-cc-pVDZ.

show a systematic increase as a function of chain length, agreeing qualitatively with experiments. As is visually evident in Fig. 3, this gradual increase is, again, due to the H-bonding interactions of carbamic acid with neighboring amines within the same monomer unit.

In order to verify the applicability of covalently tethered amine chains in post-combustion CO_2 capture, we measured CO_2 capacities in the presence of moisture. The simulated flue gas contained a mixture of 81.25% He, 15% CO_2 and 3.75% H_2O at 40 °C (Fig. S7, ESI†), to mimic the power plant exhausts. Helium was used instead of N_2 because of the interference of N_2 in CO_2 signals was significant in our setup. In the COP-115 series, COP-115-B and COP-115-C have similar CO_2 uptake capacities of 3.3 and 3.4 wt% respectively, which is twice as high as in dry conditions. COP-115-D shows a slightly lower uptake of 2.8 wt%, which is 1.75 times higher than the dry uptake capacity.

Conclusions

In summary, we have shown that linear chain amine molecules tend to wrap CO_2 instead of the common perception that nitrogens individually bind. In order to study this interaction, we designed a new hypercrosslinked porous polymer (COP-115) with a "greener" and industrially scalable synthesis using methanesulfonic acid as the reagent rather than $FeCl_3$. We reported a post-modification procedure that uses less harsh conditions than previous reports, effectively generating a library of amine functionalized structures. Those post-modified structures show rationally enhanced CO_2 capture capacities compared to the starting materials with having excellent CO_2/N_2 selectivities.[46–49] Heats of adsorption values show a linear relationship with the increase in amine length, an unexpected behavior that can only be explained by the additional H-bond contribution from the bent amine extensions. Our theoretical assessments verify the observations where an increasing trend is clearly observed. Simulated flue gas conditions show that aminated COPs show

enhanced and fast uptake of CO_2 from a mixture of gases. These findings will lead to corrected design considerations that take this "wrapping mechanism" into account.

Acknowledgements

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