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Developing organic cross-linked polyamine sorbents for low temperature CO_2 capture

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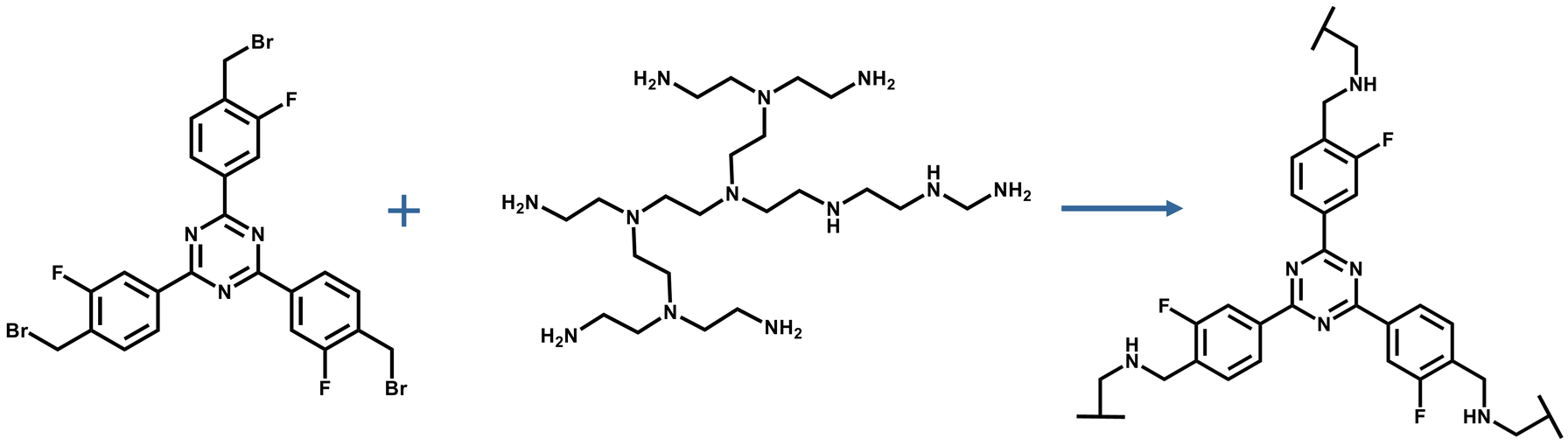
Introduction

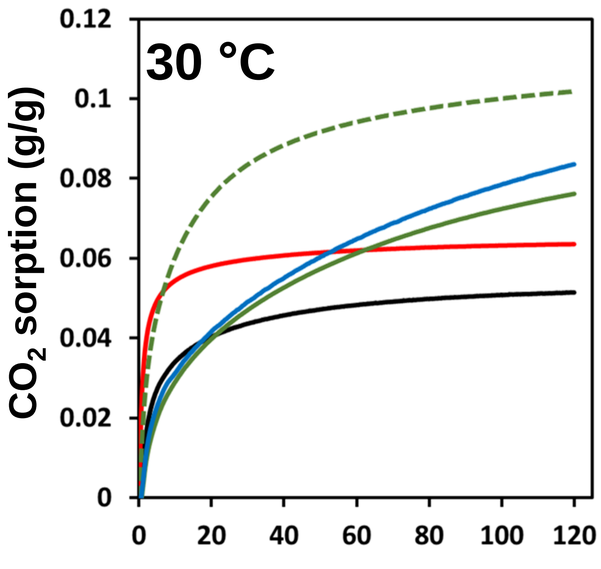
Cross-linked polyamine based CO_2 capture materials have proven highly effective sorbents. With a CO_2 capture capacity of almost 0.2 g/g, epoxy cross-linked polyethyleneimine (PEI) materials have been shown to have high CO_2 selectivity, multicycle durability and enhanced performance in the presence of moisture.[1] However, sorption at lower temperatures remains a challenge due to diffusion limitations. With growing interest in direct air capture (DAC) of CO_2, these limitations need to be overcome to allow low temperature sorption. Herein is presented a new cross-linked polyamine sorbent synthesised from a triazine based alkyl bromide cross-linker and PEI. This material shows high CO_2 uptake at 30 °C with fast kinetics, and may be suitable for development for DAC applications

Material Synthesis: PEI is cross-linked with 2,4,6-tris-(4-bromomethyl-3-fluoro-phenyl)-1,3,5-triazine (4BMFPT) in an amine:Br ratio of 1:1, 3:1, 10:1 and 25:1. The reaction proceeds at 70 °C in THF overnight, either in a vial, or in a RBF under reflux.

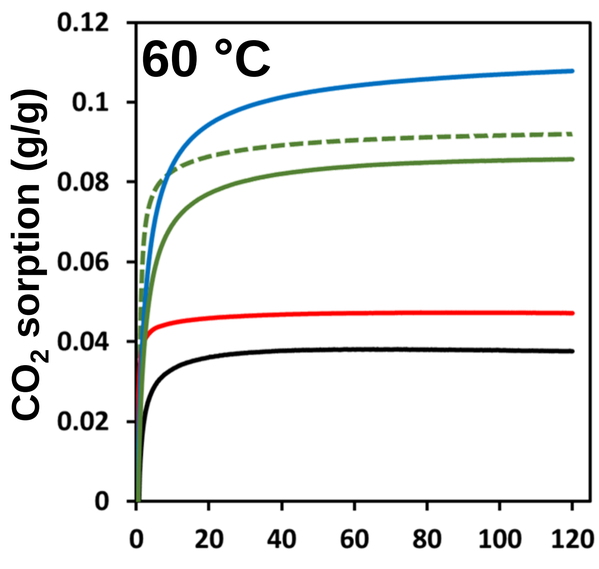


25:1 synthesised in vial (left), and 10:1 RBF synthesised in RBF (right).

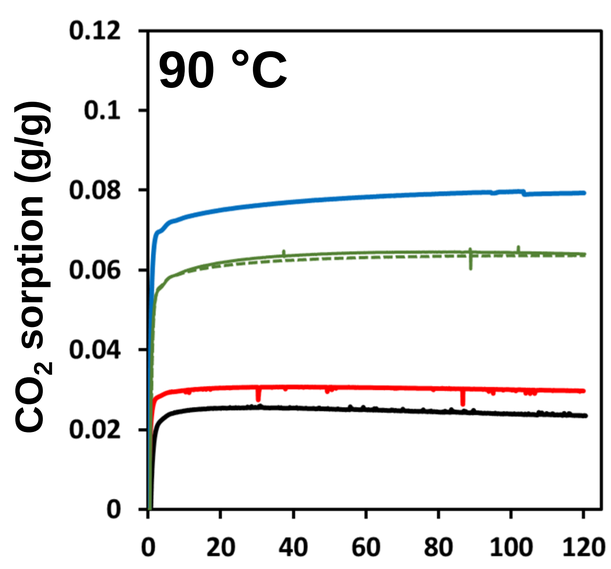
CO_2 Sorption Studies: CO_2 uptake experiments are performed at 30, 60 and 90 °C on a TGA. CO_2 flow rate of 80 ml/min, Ar 10 ml/min.



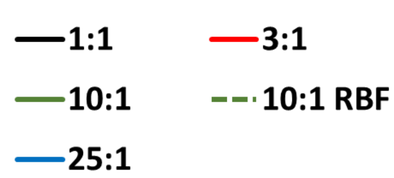
At 30 °C, 10:1 RBF shows highest sorption, reaching a final capacity of 0.102 g/g. Sorption is fastest for 1:1 and 3:1 but these have a lower uptake than 10:1 and 25:1, which show slower sorption.



All materials sorb faster at 60 than 30 °C. 1:1 and 3:1 sorb about 25% less at 60 °C than 30 °C. 25:1 shows highest sorption with a final capacity of 0.108 g/g. 10:1 RBF reduces final capacity to 0.092 g/g, but 10:1 improves.



For all materials CO_2 uptake rate further increases at 90 °C, yet final capacity is reduced. 25:1 shows highest uptake at 0.079 g/g, while both 10:1 and 10:1 RBF have similar capacities. Uptake by 1:1 and 3:1 decreases by about 37% and reduces over time.



- PEI-4BMFPT materials show higher CO_2 sorption where less cross-linker has been used.
- CO_2 uptake is faster at higher temperatures (>60 °C).
- CO_2 capacity is higher at lower temperatures (≤ 60 °C) demonstrating good CO_2 diffusion.

Conclusions and Further work

Conclusions: A range of organic cross-linked CO_2 sorbents have been produced using different starting quantities of PEI and a triazine based alkyl bromide cross-linker. The materials prepared with more cross-linker sorb CO_2 the fastest. The 10:1 material shows excellent CO_2 sorption at 30 °C, with a maximum uptake of 0.102 g/g, and an uptake of 0.075 g/g after just 20 minutes.

Further Work: Further characterisation studies including CHN and EDX are underway to understand the extend of cross-linking achieved, and the cross-linking density of each material. Further sorption studies will test the materials' CO_2 uptake in 400 ppm CO_2/N_2, and under humid conditions, to determine their applicability for DAC.

1. Hamdy, L. B.; Wakeham, R. J.; Taddei, M.; Barron, A. R.; Andreoli, E., Epoxy-cross-linked Polyamine CO_2 Sorbents Enhanced via Hydrophobic Functionalization. *Chem. Mater.* **2019**, 31, 13, 4673-4684.

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