Thermolabile Protecting Groups in Metal-Organic Frameworks

A thesis presented in partial fulfilment of the requirements of the degree of

Doctor of Philosophy

in

Chemistry

at Massey University, Manawatu, New Zealand

Sebastian Blackwood

2016

For Meghan Blackwood

Abstract

Prior to the work carried out for this thesis, there were no publications in which bpy was used as a ligand backbone, or in which a carboxylate was incorporated into a MOF using a TPG. Also, to the best of our knowledge there are no examples in the literature of an ethyl carbamate TPG in MOFs.

In this thesis the range of TPG protected ligands has been expanded to include 1,4-bdc (Chapter 2) and bpy (Chapters 4 and 5). The bpy-NHBoc and bpy-TBE materials are the first examples of N-donor type ligands protected by TPGs. Furthermore, the bpy-TBE ligand is the first example of a TPG protected carboxylate in a MOF.

In Chapter 2, 1,4-bdc-NH_2 was protected as both the ethyl carbamate and the *tert*-butylcarbamate, giving 1,4-bdc-NHCOOEt and 1,4-bdc-NHBoc, which there then incorporated into a MOF-5-type framework. It was envisaged that thermolysis of the carbamate esters could generate an isocyanate group, though this was not expected for 1,4-bdc-NHBoc due to the tendency of *tert*-butylcarbamates to decompose to the amine. Despite thermolysis on the TGA apparatus only generating the amine, it was found that thermolysis under vacuum enabled not only enabled ~ 60 % conversion of the ethylcarbamate to 1,4-bdc-NCO, but also a ~20 % conversion of the *tert*-butylcarbamate to 1,4-bdc-NCO. The MOF-5 analogues in this work also proved sufficiently stable to survive the thermolysis conditions with little discernible effect on the porosity of the material.

In Chapter 3, 1,3-bdc-NH_2 was protected as both the ethyl carbamate and the *tert*-butylcarbamate, giving 1,3-bdc-NHCOOEt and 1,3-bdc-NHBoc, which there then incorporated into a lon-e-type framework. It became apparent the lon-e was a poor choice in MOF for use with TPGs as the framework was prone to collapse from desolvation, and it was not possible to thermolyse the materials without complete collapse of the MOFs.

In Chapter 4, bpy-NH_2 and bpy-CO_2H were protected with TPGs to give bpy-NHBoc and bpy-TBE respectively. The ligands were combined with bpdc and zinc to obtain the BMOF-1-bpdc analogues MUF20-Aβ and MUF20-Aγ. Whilst the thermolysed materials MUF20-$A\beta^t$ and MUF20-$A\gamma^t$ demonstrated significant gas uptakes compared to their protected counterparts, comparison of MUF20-$A\beta^t$ with the directly synthesised material MUF20-Aβ' revealed significantly higher uptakes than the thermolysed materials. This discrepancy indicates that the BMOF-1-bpdc/MUF20 framework is partially degraded under thermolysis conditions. These results strongly imply that this framework is not compatible with TPGs. However, TPGs did allow for the installation of a carboxylate group into the

BMOF-1-bpdc/MUF20 framework which was not obtainable through direct synthesis methods.

In Chapter 5, bpy-TBE was combined with btb and Zn/Cu to obtain Zn-DUT-23-TBE and Cu-DUT-23-TBE. These materials were then thermolysed to produce Zn/Cu-DUT-23-CO_2H, materials that were not able to be directly synthesised using bpy-CO_2H. Unfortunately, the thermolysed materials demonstrated significant decreases in uptakes compared to their protected counterparts. However, the TPG containing materials also had markedly lower uptakes than the parent Zn-DUT-23 and Cu-DUT-23 materials, which has been attributed to pore collapse. This partial pore collapse may have sufficiently weakened the MOF framework to increase its sensitivity to the thermolysis conditions, resulting in a much larger decrease in uptake than would have been the case with a defect free material.

The results of this thesis revealed that MOF stability is a key factor in the compatibility of a material. Specifically, the MOF must be resistant to solvent removal and subsequent heating at elevated temperatures for extended periods. This is most clearly observed in Chapter 3, where the lon-e materials were very susceptible to solvent removal, and later were completely collapsed by thermolysis. These findings have led to the recommendations outlined in section 6.2 for the screening of MOFs for their compatibility with TPGs.

Contributions

All the work in this thesis was completed by Sebastian Blackwood

Except:

- Parallel syntheses of lon-e-NHBoc and lon-e-NHCOOEt for gas sorption were conducted by Yongchen Wang under supervision from Sebastian Blackwood.
- The MUF20 series was a collaborative effort between Sebastian Blackwood and Heather Jameson. As such, materials and data were freely shared. For the sake of clarity, I will be presenting the frameworks in Chapter 4, which includes experiments performed by Heather. Heather will present the rest of the MUF20 series in her thesis, which will include some of my data.

Acknowledgements

I would like to take the opportunity to thank the large number of people who have contributed to my PhD research and thesis. First, I would like to thank my supervisor Professor Shane Telfer for providing me this wonderful PhD opportunity and scholarship to carry out research in MOF chemistry. Thank you for your expert guidance on all matters throughout this PhD, from the big picture to the minutia. Thank you for providing funding for me to attend conferences and symposiums, and pushing me to be the best I can be.

I would also like to thank my co-supervisor, Associate Professor Gareth Rowlands, for his much-valued guidance during my first year when Shane was on sabbatical, as well as his expertise in organic chemistry that he generously provided throughout my PhD. I also thank Dr. Pat Edwards for assisting with specialized NMR experiments, Professor Geoff Jameson for discussions and advice on x-ray crystallography, and David Lun for his assistance and guidance in the lab. I also thank Heather Jameson, Dr. Lujia Liu, Yongchen Wang, Subo Lee, and all other current and past Telfer group members for scientific discussions and technical assistance.

I thank Dr. Marie Squire from University of Canterbury for some performing some ESI-MS experiments.

I would like to acknowledge the financial support from The MacDiarmid Institute for Advanced Materials and Nanotechnology for a Doctoral scholarship, and the Institute of Fundamental Sciences for my fourth year PhD funding. I also thank the IFS postgraduate travel fund for supporting me to attend a conference in Edinburgh. I greatly thank the MacDiarmid Institute for organizing and supporting annual student and postdoc symposiums and the AMN-7 conference in Nelson (special thanks to Professor Shane Telfer for organizing this conference).

I also thank IFS administration and technical staff for their great assistance during my PhD research and thesis writing.

I would like to take this opportunity to thanks all of my friends and family, whose encouragement and support have helped me throughout this PhD study. Finally, I would also like to thank my wife Meghan, whose love and strength have helped me every day.

Publications and thesis structure

Publications relevant to this thesis

None

Additional publications

1. A. Ferguson, L. Liu, **S. Blackwood** and S. G. Telfer, Recent Developments in Metal-Organic Framework (MOF) Chemistry, C*hemistry in New Zealand* **2014**, 78, 113-118.
2. P. Insiti, P. Jitthiang, K. Chainok, R. Chotima, J. Sirirak, **S**. **Blackwood**, A. Alkaş, S. G. Telfer, D. J. Harding, Substituent modulated packing in octahedral Ni(II) complexes, *Polyhedron* **2015**, 114, 242-248.

Table of Contents