Multicomponent Metal-Organic Frameworks

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

Doctor of Philosophy

in

Chemistry

at Massey University, Manawatū, New Zealand

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2015

For Minxuan Du

Abstract

Introducing multiple functional groups into the pores of metal-organic frameworks (MOFs) promise sophisticated properties. Precise control over the position of these functional groups would enable the 3D chemical environment of discrete void spaces to be tailored. This was an outstanding challenge prior to this work. In this thesis we present a study of the synthesis, characterization and properties of MOFs that can meet this goal. These MOFs are multicomponent in nature, being built up from three geometrically distinct organic ligands. Functional groups can be appended to these ligands and are incorporated in precise locations and with perfect order in the frameworks. The chemical environment of the pores of these MOFs is "programmed" by these functional groups. MOFs constructed in this way give rise to exceptional gas adsorption characteristics, unexpected stability towards water vapour, and tunable catalytic properties.

Contributions

All the work in this thesis was completed by Lujia Liu

except

- All elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.
- Some gas adsorption isotherms presented in Chapter 2 and 3 were measured by Dr. Matthew Hill and Dr. Kristina Konstas at CSIRO.
- Truxene, H_3hmtt, and a precursor of H_3hett were synthesized by David Lun. David Lun also conducted scale up recrystallization of some truxene-based ligands.
- ES-MS analyses for H_3hbtt and H_3hhtt were conducted by Dr. Marie Squire at University of Canterbury
- David Perl wrote a computer script to extract the data presented in Figure 4.21.
- H_2**L1**-Boc and H_2**L1** (Chapter 5), which were fully characterized in his previous work, were provided by David Lun.[1]

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 Associate Professor Shane Telfer for providing me this wonderful PhD opportunity and scholarship to carry out research in MOF chemistry. Thanks for his enthusiastic, encouraging and patient guidance to my research from the big picture all the way to technical details. Thanks for providing funding for me to attend conferences and visit Professor Randy Snurr's group in Northwestern University.

I would also like to thank my co-supervisor, Professor Geoff Jameson, for his much-valued guidance in crystallography and other scientific discussions during my research and thesis writing. I still remembered the day that he helped us to solve the structure of MUF-7a which set this thesis in motion. I also thank Dr. Pat Edwards for assisting specialized NMR experiments, Associate Professor Gareth Rowlands for discussions and advice on organic synthesis, Dr. Hui Yang for his assistance with isotherm data analyses, David Perl for writing a computer script that greatly assisted to process simulation results, Amy Toms for help with fluorescence spectroscopy, Trevor Loo and Dr. Vyacheslav Filichev for their technical assistance, and Jianyu Chen, Jordan Taylor, Niki Murray, and Dr. Matthew Savoian's assistance in optical, confocal, and scanning electron microscopy. I also thank Sebastian Blackwood, Heather Jameson, Dr. Alan Ferguson and all other current and past Telfer group members for scientific discussions and technical assistance.

A special acknowledgement goes to David Lun for his much-valued technical assistance in organic synthesis, HPLC, ES-MS, NMR training and providing some valuable ligands.

I thank Professor Randy Snurr for hosting my visit and all his group members, especially Dr. Pritha Gosh, for their training and assistance in computational MOF chemistry. I must also thank Dr. Matthew Hill, Dr. Kristina Konstas and Dr. Aaron Thornton for their assistance in measuring gas adsorption isotherms and related calculations.

I thank NeSI for providing computational resources, staff from Campbell Microanalytical Laboratory at the University of Otago for elemental analyses, Dr. Geoff Waterhouse from University of Auckland for measuring a preliminary gas adsorption isotherm, Dr. Marie Squire from University of Canterbury for some ES-MS experiments, Dr. Jack Evans for generating some hypothetical MOF structures, and Dr. Yonghwi Kim

and Professor Kimoon Kim from Pohang University of Science and Technology for generously providing a trial sample of H_3hmtt.

I would like to acknowledge the financial support from The MacDiarmid Institute for Advanced Materials and Nanotechnology for a Doctoral scholarship, Institute of Fundamental Sciences for my fourth year PhD funding, and the Chinese Scholarship Council for an Outstanding Chinese PhD student award. I also thank the IFS postgraduate travel fund and New Zealand Institute of Chemistry travel fund for supporting me to attend conferences in Dunedin, Edinburgh and Kobe, and to visit Professor Randy Snurr's group in Chicago. I greatly thank the MacDiarmid Institute for organizing and supporting annual student and postdoc symposiums and AMN-7 conference in Nelson (special thanks to Associate 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.

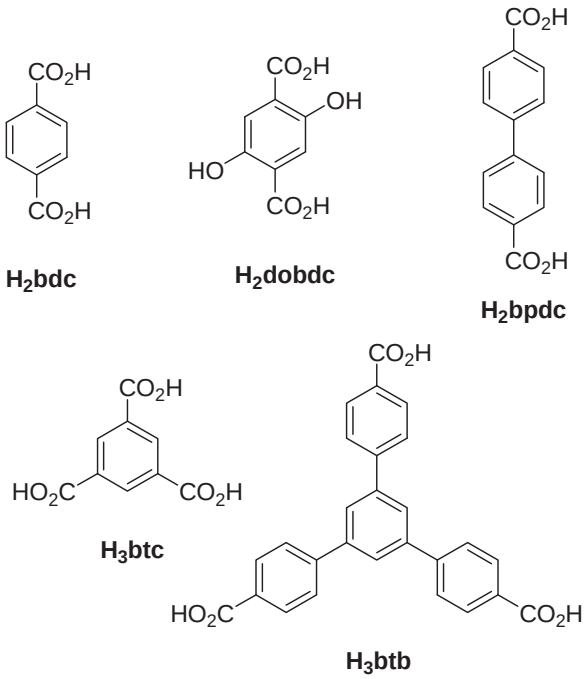
Finally, I must thank my family for their support and encouragement over the last few years. Especially I would like to thank my wife Minxuan Du for her great help, understanding and support.

Abbreviations

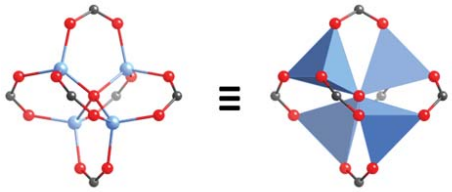
ANG	adsorbed natural gas
BET	Brunauer-Emmett-Teller
CNG	compressed natural gas
CSIRO	Commonwealth Scientific and Industrial Research Organization
DEF	*N*,*N*-diethylformamide
DFT	density functional theory
DMF	*N*,*N*-dimethylformamide
DOE	U.S. Department of Energy
GCMC	Grand Canonical Monte Carlo
HKUST	Hong Kong University of Science and Technology
IRMOF	isoreticular metal-organic framework
IUPAC	International Union of Pure and Applied Chemistry
LNG	liquefied natural gas
MAF	metal azolate framework
MC	multicomponent
MC-MOF	multicomponent metal-organic framework
MCP	microporous coordination polymer
MIL	Matérial Institut Lavoisier
MOF	metal-organic framework
MTV	multivariate
MTV-MOF	multivariate metal-organic framework
MUF	Massey University framework
NMR	nuclear magnetic resonance
PCN	porous coordination network
PCP	porous coordination polymer
PSA	pressure swing adsorption

PSD	pore size distribution
PSM	postsynthetic modification
PXRD	powder x-ray diffraction
RH	relative humidity
SBU	secondary building unit
SC-XRD	single crystal x-ray diffraction
SEM	scanning electron microscopy
STP	standard temperature and pressure
SUMOF	Stockholm University metal-organic framework
TGA	Thermogravimetric analysis
TSA	temperature swing adsorption
UiO	University of Oslo
UMCM	University of Michigan crystalline material
VSA	vacuum swing adsorption
XRD	X-ray diffraction
ZIF	zeolitic imidazolate framework

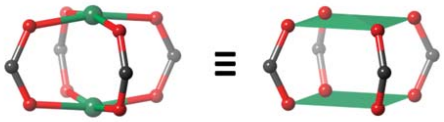
Reference chart of common ligands



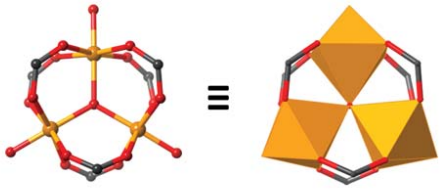
Reference chart of common metal clusters



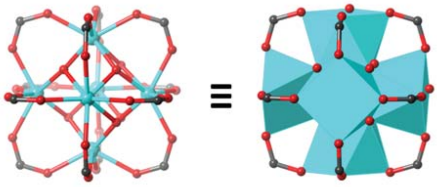
$Zn_4O(CO_2)_6$ cluster



$M_2(CO_2)_4$ paddle-wheel cluster
M = Cu(II), Zn(II)



$M_3O(CO_2)_6(H_2O)_2X$ cluster
M = Cr, Fe, V, Sc; X = F, Cl, OH



$Zr_6O_4(OH)_4(CO_2)_{12}$ cluster

Publications and thesis structure

Publications relevant to this thesis

1. **L. Liu** and S. G. Telfer, Systematic Ligand Modulation Enhances the Moisture Stability and Gas Sorption Characteristics of Quaternary Metal-Organic Frameworks, *J. Am. Chem. Soc.* **2015**, 137, 3901-3909.

   I carried out the experimental and computational work, put together the electronic supporting information, and wrote the first draft of this paper.

2. **L. Liu**, K. Konstas, M. R. Hill and S. G. Telfer, Programmed Pore Architectures in Modular Quaternary Metal-Organic Frameworks, *J. Am. Chem. Soc.* **2013**, 135, 17731-17734.

   I carried out the experimental and computational work, put together the electronic supporting information, and contributed to the writing of this paper.

Additional publications

3. J. Sirirak, D. J. Harding, P. Harding, K. S. Murray, B. Moubaraki, **L. Liu** and S. G. Telfer, Spin Crossover in *cis* Maganese(III) Quinolylaldiminates, *Eur. J. Inorg. Chem.* **2015**, 2015, 2534-2542.
4. J. Sirirak, D. J. Harding, P. Harding, **L. Liu** and S. G. Telfer, Solvatomorphism and Electronic Communication in Fe(III) N,N-Bis(salicylidene)-1,3-propanediamine Dimers, *Aust. J. Chem.* **2015**, 68, 766-773.
5. 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.
6. D. J. Harding, W. Phonsri, P. Harding, I. Gass, K. S. Murray, B. Moubaraki, J. D. Cashion, **L. Liu** and S. G. Telfer, Abrupt Spin Crossover in an Iron(III) Quinolylsalicylaldimine complex: Structural Insights and Solvent Effects, *Chem. Commun.* **2013**, 49, 6340-6342.
7. A. S. Gupta, R. K. Deshpande, **L. Liu**, G. I. N. Waterhouse and S. G. Telfer, Porosity in Metal-Organic Frameworks Following Thermolytic Postsynthetic Deprotection: Gas Sorption, Dye Uptake and Covalent Derivatisation, *CrystEngComm* **2012**, 14, 5701-5704.

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