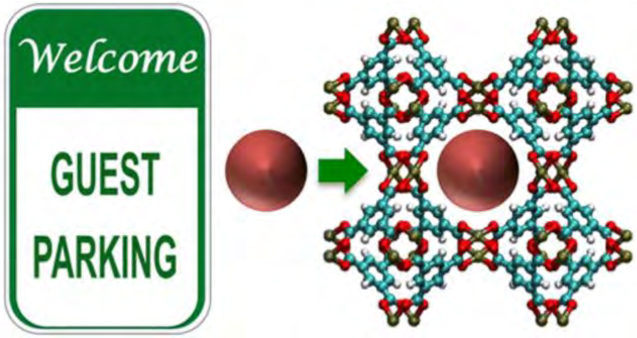


10.1021/jz5026883

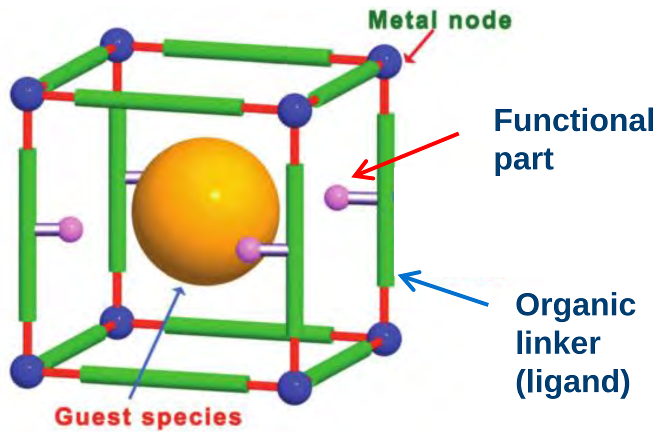
Controlled Guest Materials Formation in the Confined Environments of Metal-organic Frameworks: A Brief Introduction

Tiesheng Wang, Stoyan Smoukov*

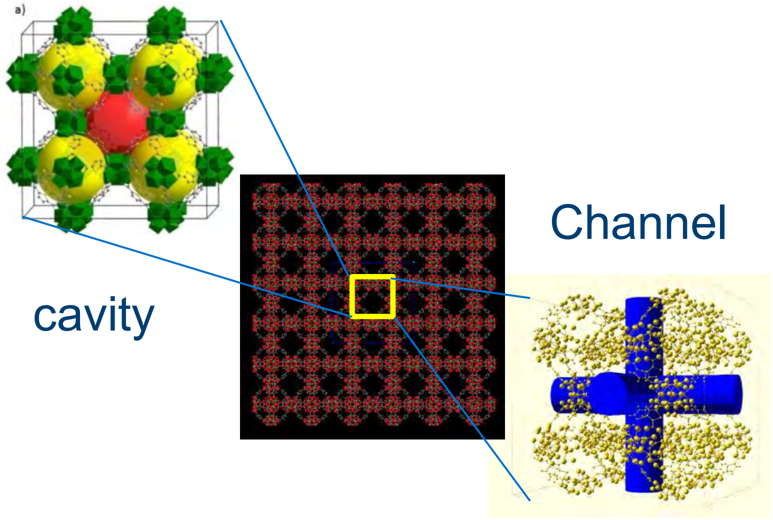
Department of Materials Science and Metallurgy, University of Cambridge

Nomenclatures:

Metal-organic Frameworks (MOFs) and the Guests

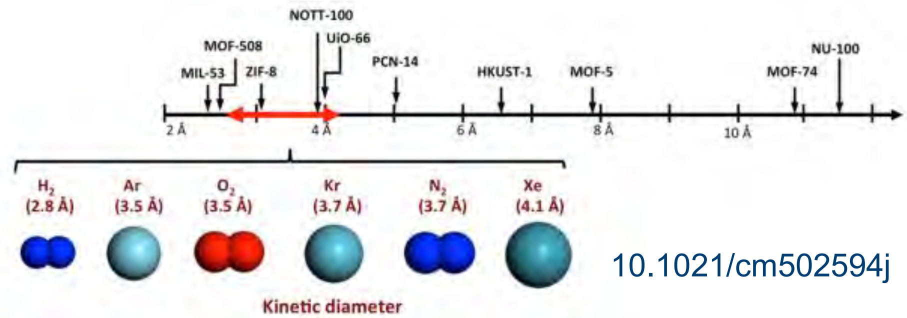


10.1039/c6cs00250a



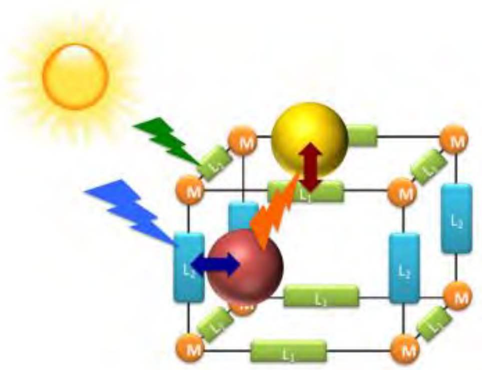
Common Features:

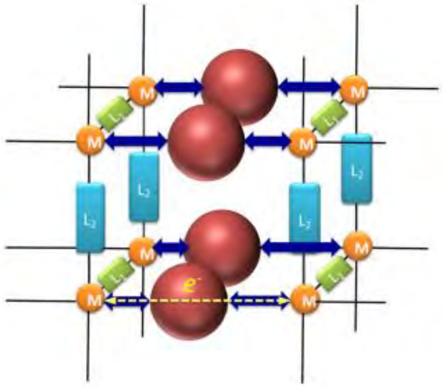
- Crystal-like
- Porous (typical pore dimension: 0.5-2.5 nm)



10.1021/cm502594j

Guests in the MOFs: An Emerging Field





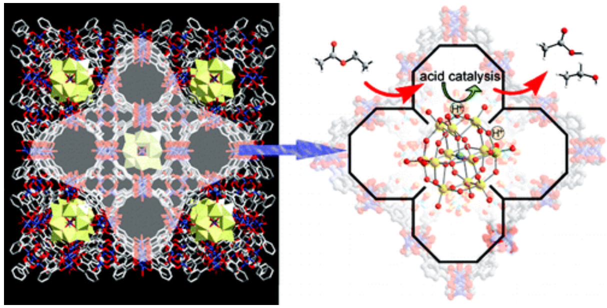
Facilitates light harvesting (e.g. photoluminescence)

Facilitates light harvesting (e.g. photoluminescence)

10.1021/jz5026883

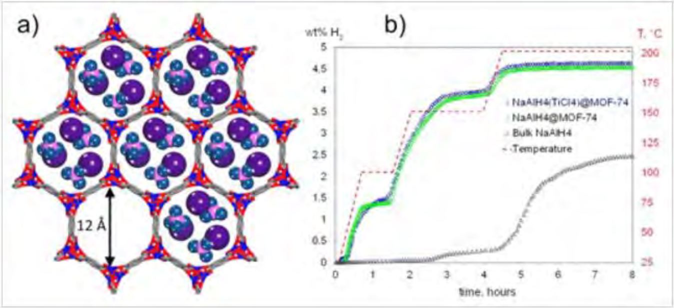
1. Guest-Induced Emergent Properties

2. Potentially used for catalysis, hydrogen storage etc.



10.1021/ja807357r

MOF prohibits conglomeration and deactivation of polyoxometalates catalysts



10.1021/nn304514c

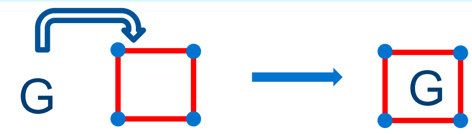
MOF-confined $NaAlH_4$ hydrogen storage

- Guest-host (MOF) interaction can lead to positive **confinement/synergistic effect**.

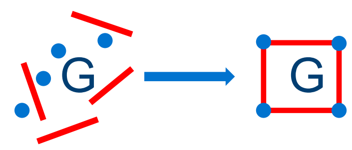
How to Put Guest Species inside MOFs?

Achieving guest species in MOF

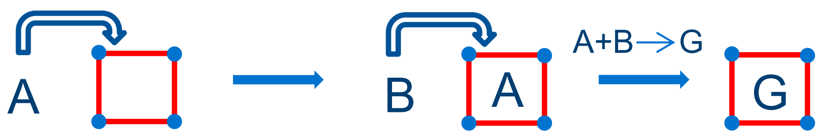
Direct impregnation (e.g. enzyme@MOF)



MOF synthesised in presence of guest species or their precursors(e.g. polyoxometalate (POM) @MOF)



Guest species formed locally (*in situ*?)



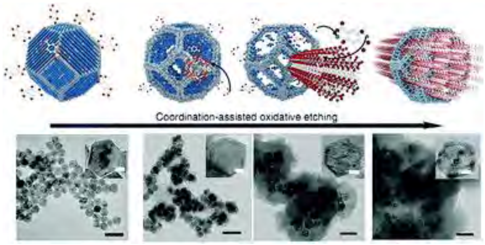
Challenges related to controlled guest materials formation locally:

- Precursor/intermediate **impregnation**
- MOF **degradation**
- Place that guest materials can formed (i.e. only inside? Or both **inside and outside**?)
- Guest materials **morphology**
- Porosity after the guests incorporation
- And the list carries on…

Inorganic Materials inside MOF: an Overview

Metal/Alloy/intermetallic composite

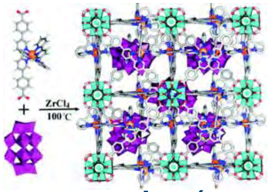
A quite mature field



10.1038/ncomms9248

Metal oxide/ polyoxometalate

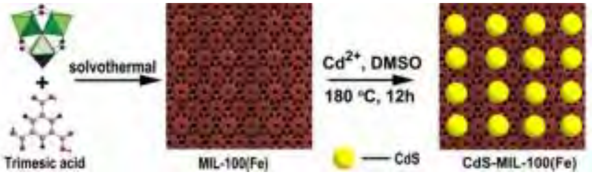
A medium mature field



10.1021/jacs.5b00075

Other metallic compounds (e.g. sulphides, phosphides)

Rarely studied

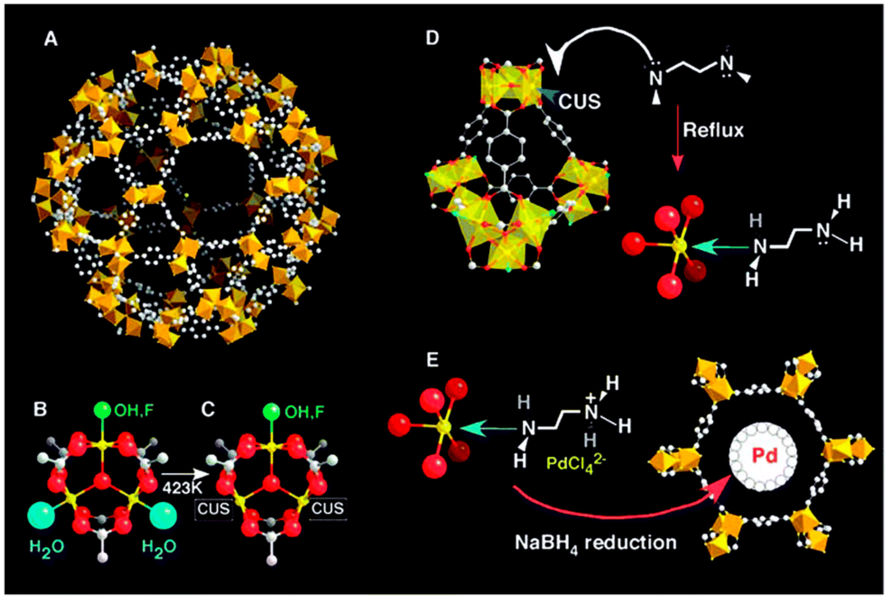


10.1007/s12274-014-0690-x

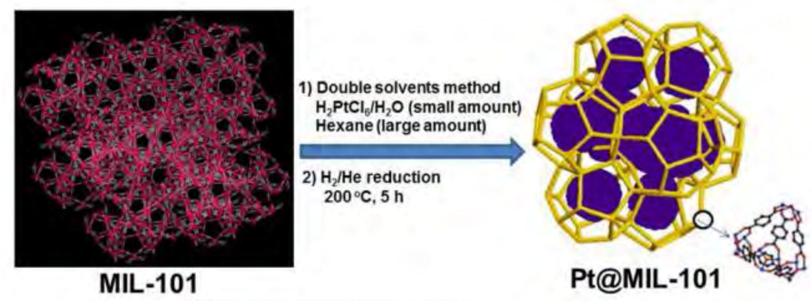
General routes to achieve inorganic materials inside (and outside) MOF:

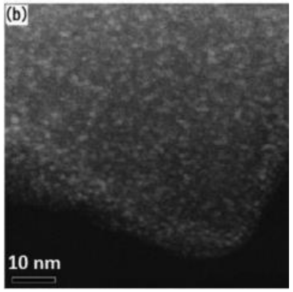
- Wet-chemistry: redox reaction
- Wet-chemistry: decomposition (maybe followed by a redox reaction)
- Vapour-phase deposition followed by decomposition or redox reaction

Controlled Precursor Impregnation



10.1002/anie.200705998



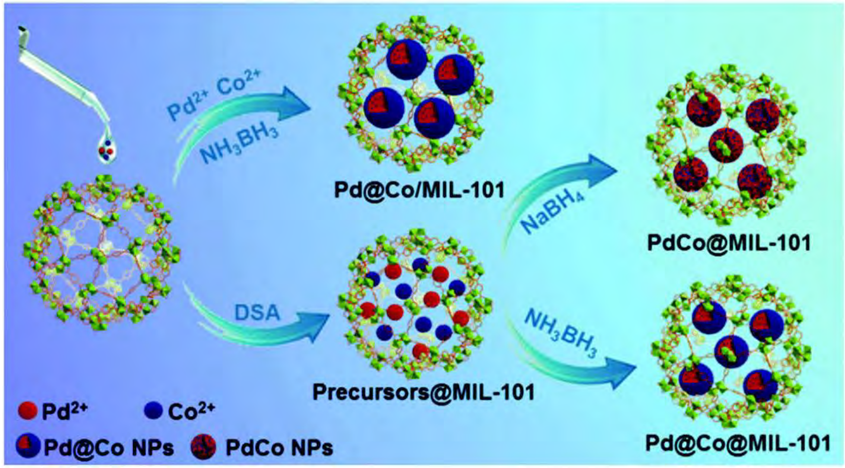


10.1021/ja3043905

Functional part of MOF is used to attract and immobilised the metal precursor.

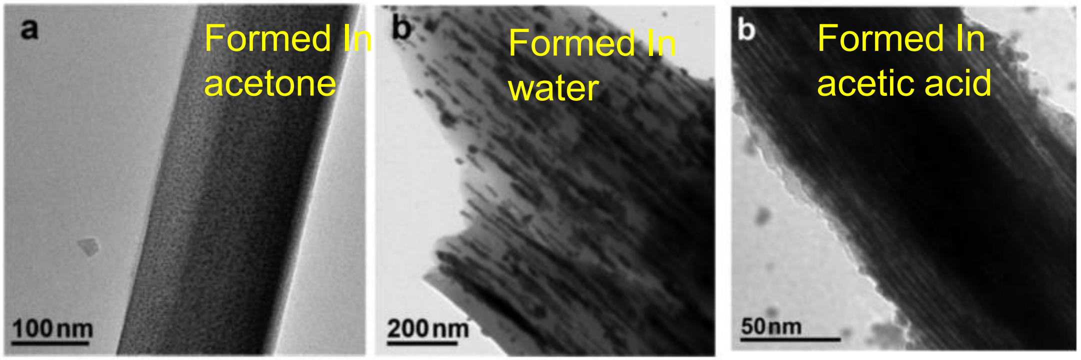
Double solvent method: guiding metal salt to the **hydrophilic** MOF in a more **hydrophobic** medium.

Controlled Material Formation Process II



10.1002/smll.201401875

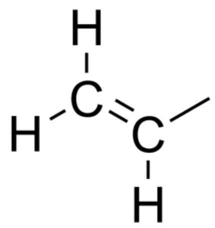
Different reducing agent may lead to different guest materials.



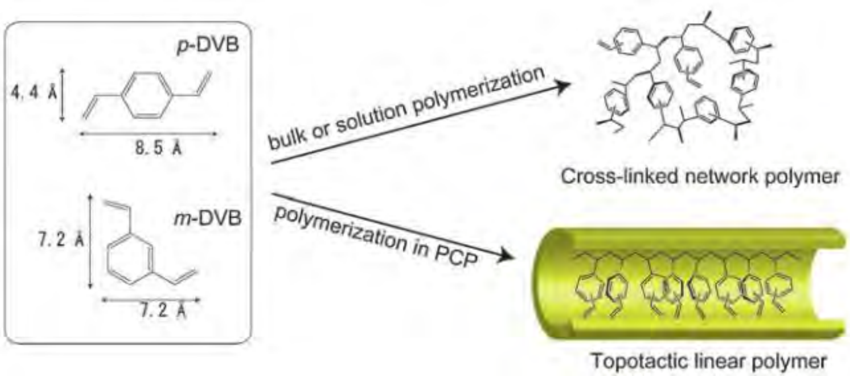
10.1021/nn5072446

Solvent may influence the morphology of the guest material.

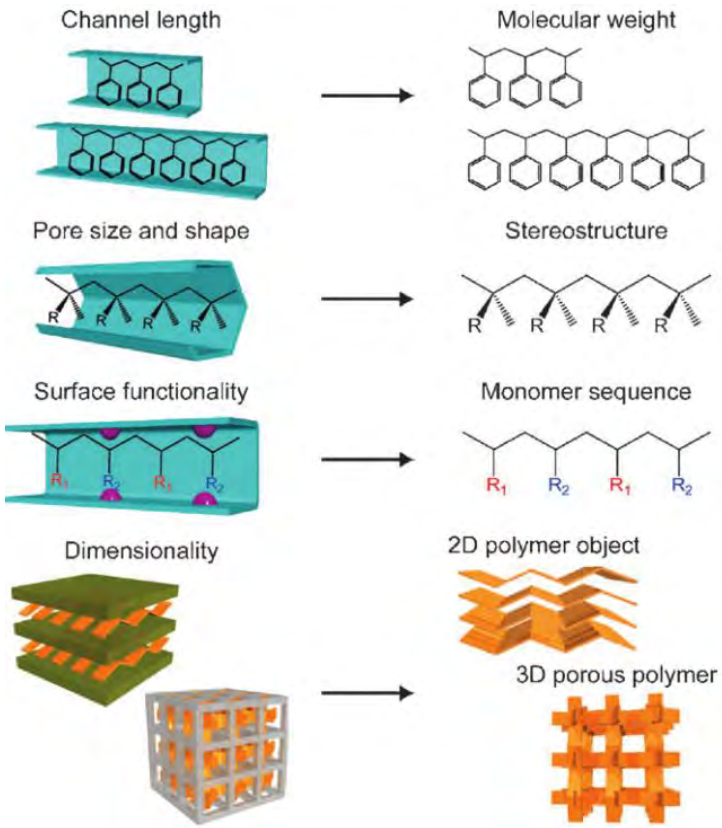
Vinyl-based Oligomers/Polymers inside MOF



Vinyl group



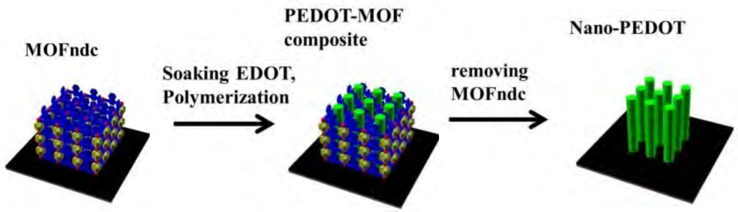
10.1002/anie.200700242

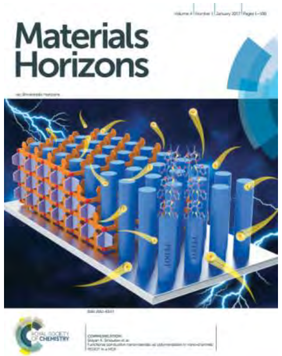


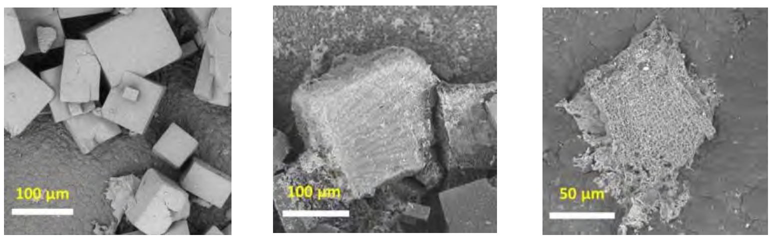
10.1039/b802583p

Conducting Oligomers/Polymers inside MOF

Liquid phase, oxidising agent used

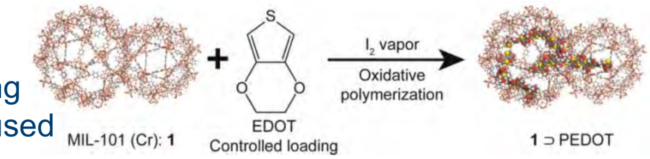


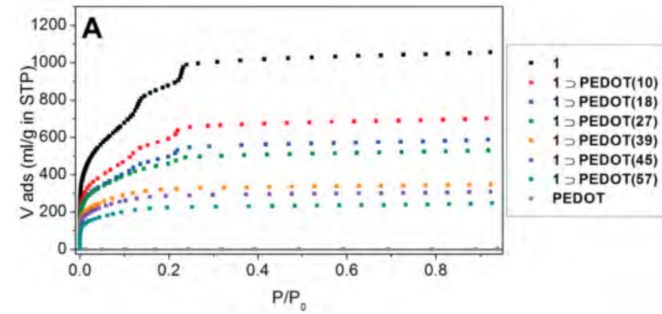


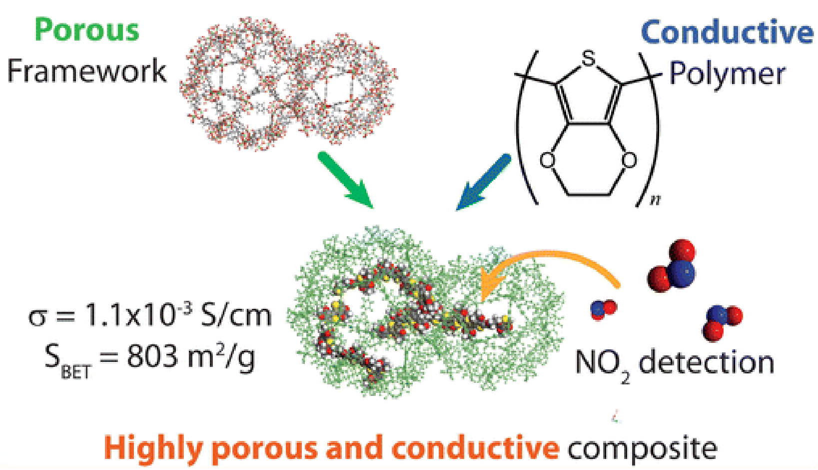


10.1039/C6MH00230G

Vapour phase, oxidising agent used

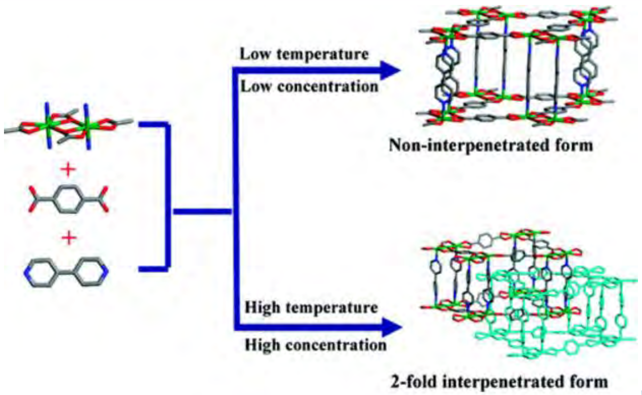






10.1021/jacs.6b05552

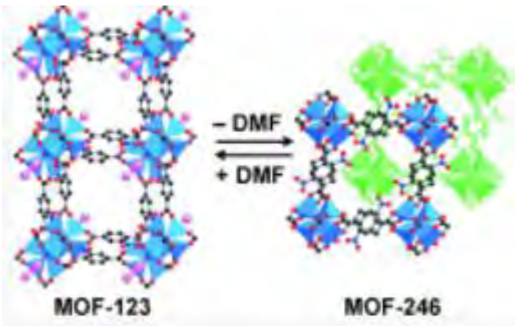
Controlled MOF-MOF interpenetration



10.1021/ja906911q

Temperature/
concentration

solvent

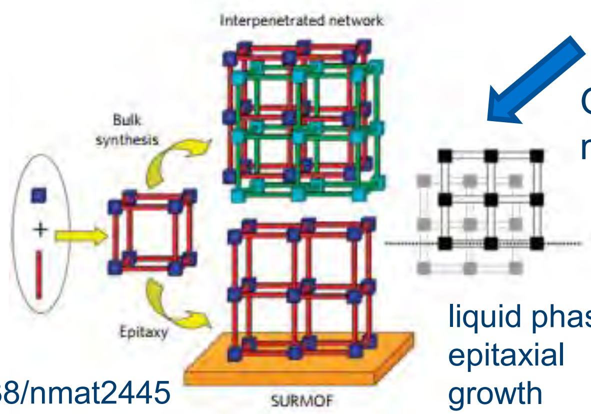


10.1002/anie.201202925

Controlled
Interpenetration

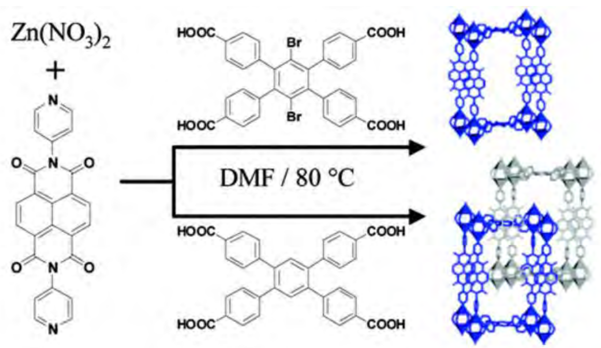
Growth
method

Ligand used



liquid phase
epitaxial
growth

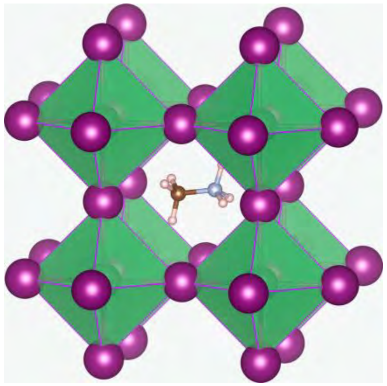
10.1038/nmat2445

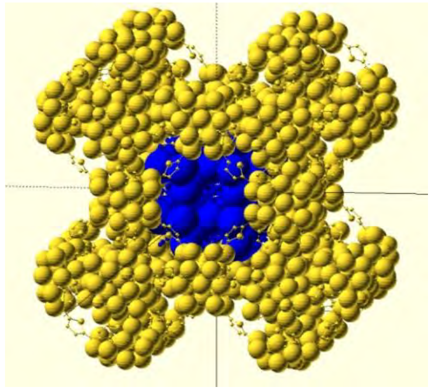


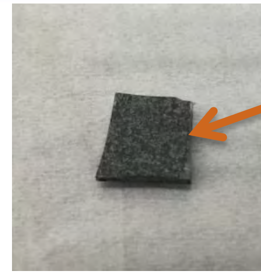
10.1021/ja909519e

Controlling the MOF-MOF interpenetration is a challenge for MOF synthesis.

Potential Hybrid ($CH_3NH_3PbI_3$, MAPI) Perovskite Incorporated inside A MOF

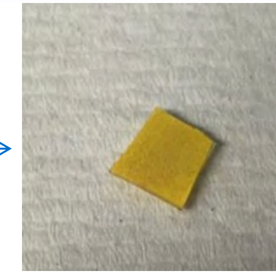






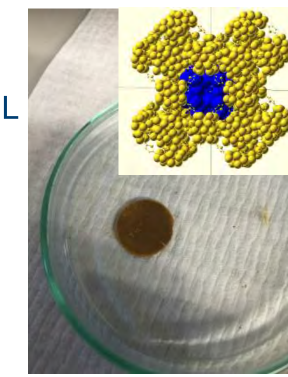
MAPI on glass

180 °C, 0.001 torr, 10 hours



+PbI_2
MAI/DMSO/GBL

180 °C, 0.001 torr, 10 hours



- Hybrid ervoskite can be synthesised by removing the solvent.
- It will **decompose to PbI_2** to if the temperature is too high – methylamine (MA) can be removed – the major issue for the **stability of hybrid perovskite solar cell**.

Unpublished work

PbI_2@MOF

Temperature applied is used to control the potential formation of MAPI only inside the MOF.

Conclusion

- ✓ **empty space** to accommodate guests.
- ✓ **Small pore dimension** - guests can be immobilised and dispersed in MOF, also confinement effect
- ✓ MOF with tuneable chemistry; Positive guest-host (MOF) interaction can lead to **synergistic effect**.

- ✓ Some typical approaches to control various materials incorporating into (sometimes also onto) MOFs.
- ✓ Factors like dimensions in space, physical/chemical interactions and other physical/chemical properties (e.g. thermal stability) need to be taken into account.

Thank you!

Dr Stoyan Smoukov, Prof. Anthony K. Cheetham FRS, Dr Yue Wu, Dr Tongtong Zhu, Dr Weiwei Li & Ms Shijing Sun
Department of Materials Science & Metallurgy

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Centre for Advanced Photonics and Electronics, Department of Engineering

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Prof. John Madden & Dr Meisam Farajollahi
Advanced Materials and Process Engineering Laboratory

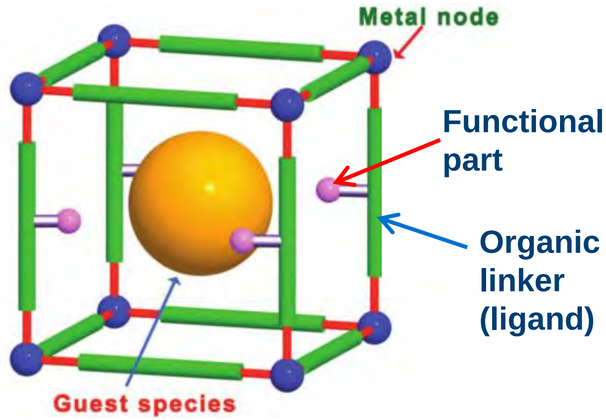
Prof. Xinhe Bao, Prof. Qiang Fu, Ms Lijun Gao
State Key Laboratory of Catalysis

Dr Sebastian Henke
Faculty of Chemistry

Dr Sneha R Bajpe
Inorganic Chemistry Laboratory

Dr Martyn McLachlan & Mr Jiaqi Zhang
Department of Materials

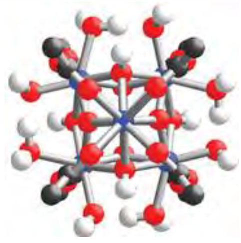
Some Concepts about MOF



Metal Node:

SUMOF-1

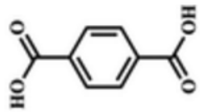
10.1039/C4CS00067F



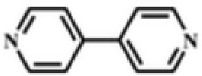
NU-1000

10.1038/nmat4238

Organic linker (ligand):



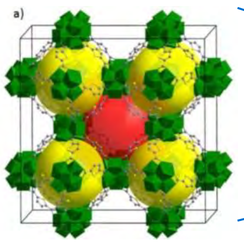
Benzene-1,4-dicarboxylic acid

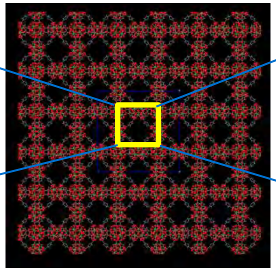


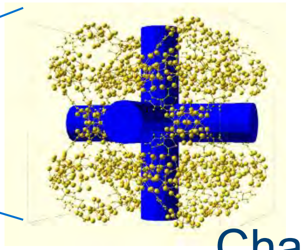
10.1039/C3CS60404G

4 4'-bipyridine

cavity



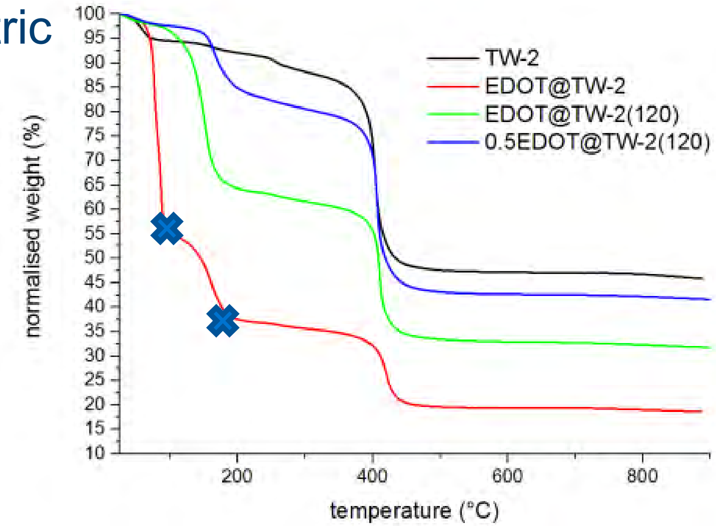


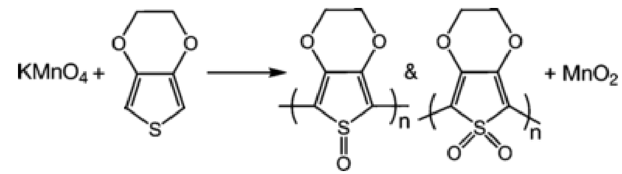


Channel

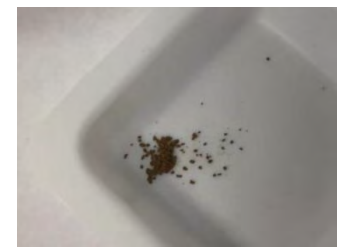
Controlled Reducing Agent Impregnation: A Novel Way to Incorporate Active Metallic Compound inside the MOF

Thermal Gravimetric Analysis





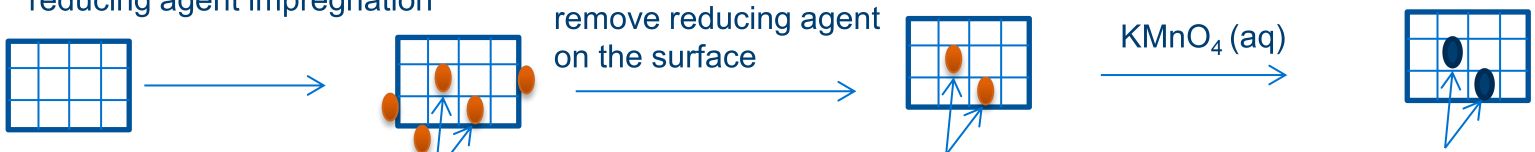
10.1021/nn1010182



reducing agent impregnation

Elevated T applied to remove reducing agent on the surface

$KMnO_4$ (aq)



TW-2 (the MOF used)

Reducing agent (EDOT)

Excess_EDOT@ TW-2

Reducing agent (EDOT)

EDOT@ TW-2

Mn_xO_y cluster embedded in the organic matrix of produced by reducing agent

MnO_2_base_guest@ TW-2

Unpublished work

Additionally, the reducing agent is trapped inside the MOF as it is immiscible with water.

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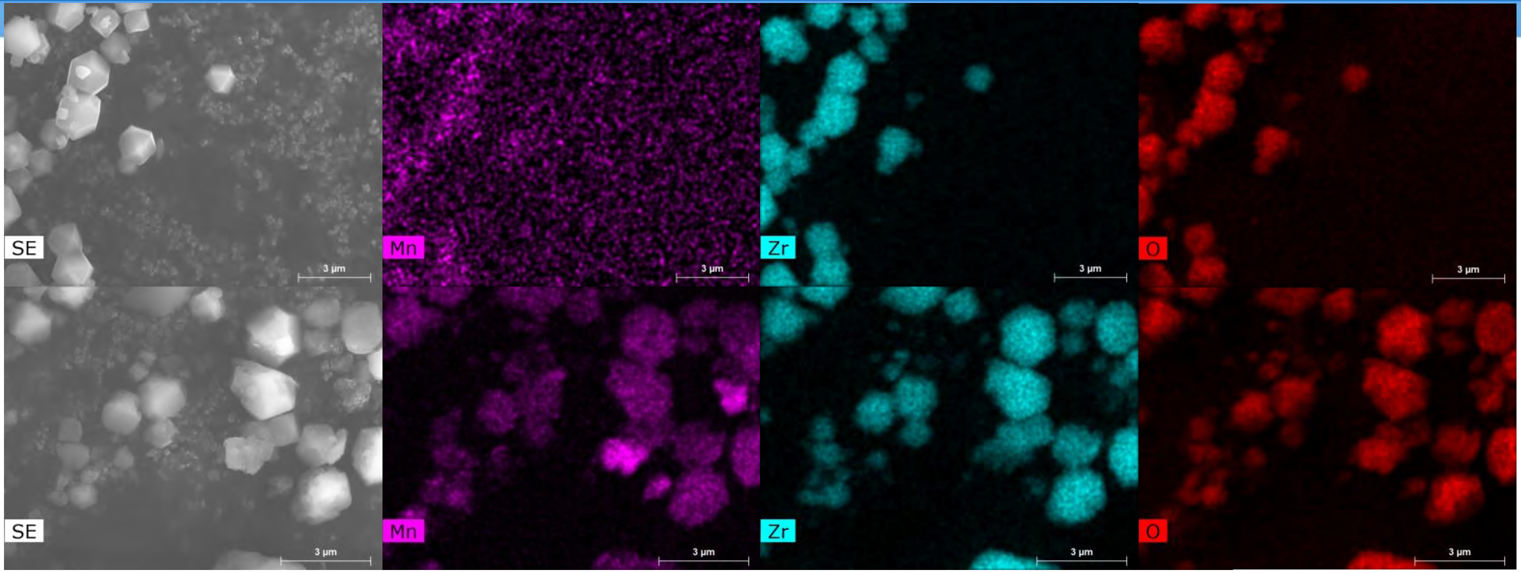
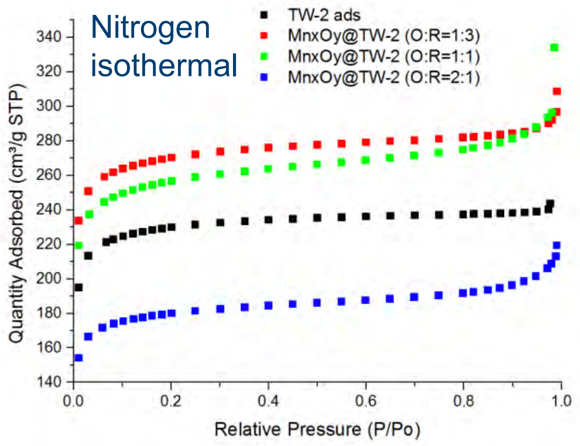
- **An alternative way to control reagent impregnation and reaction in the MOF system.**
- **Allow some metal oxides to be synthesised in MOF, which can be difficult to achieve otherwise.**

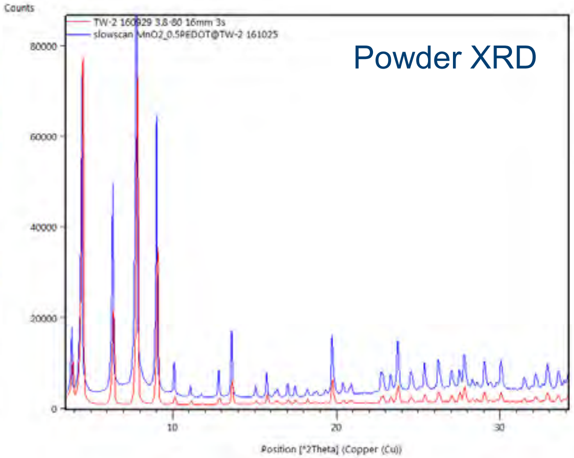
Controlled Reducing Agent Impregnation: A Novel Way to Incorporate Active Metallic Compound inside the MOF II

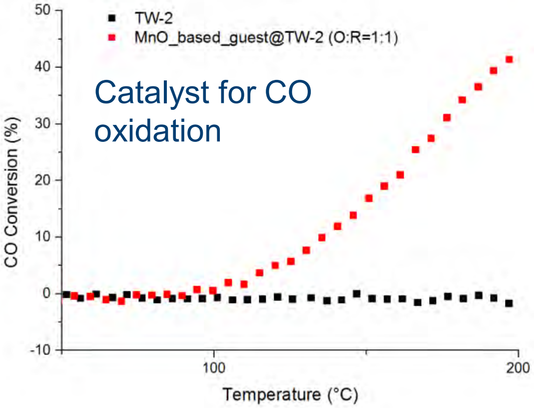


EDS elemental analysis on the pure MOF

EDS elemental analysis on MnO_2_base_guest@TW-2

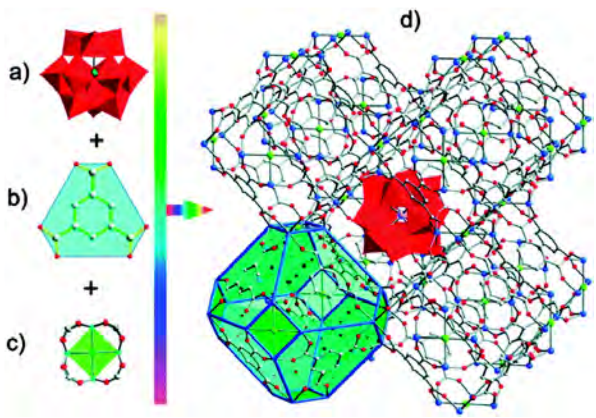






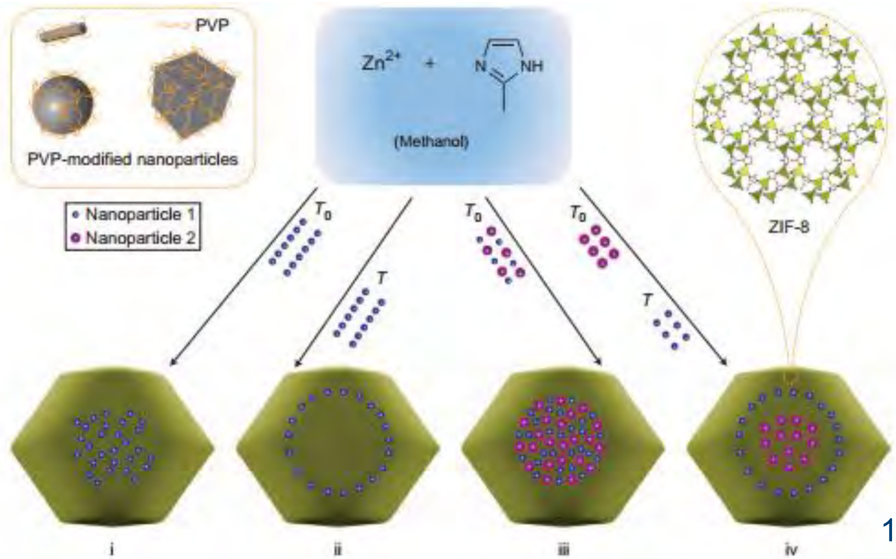
Unpublished work

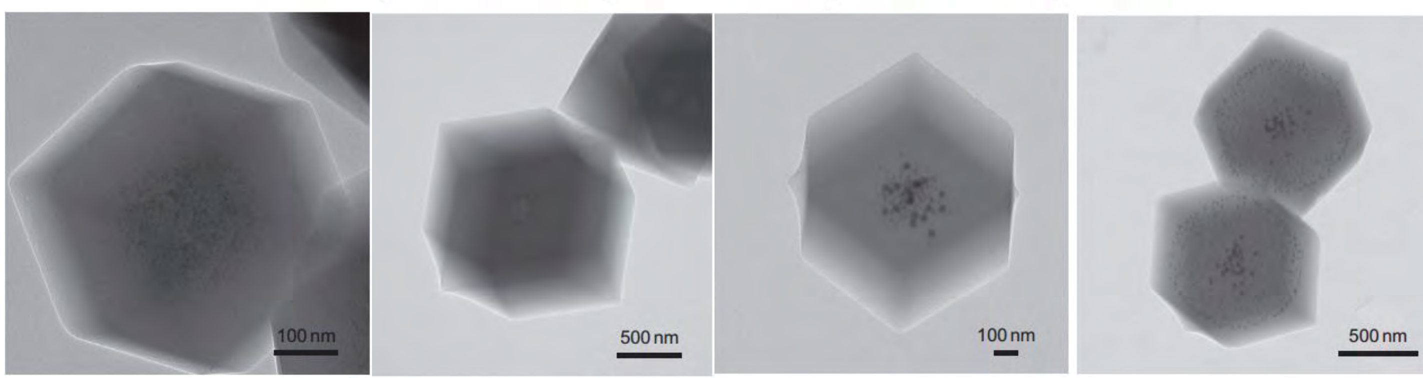
Appendix Control in Bottle-around-the-ship Approach



10.1021/ja109659k

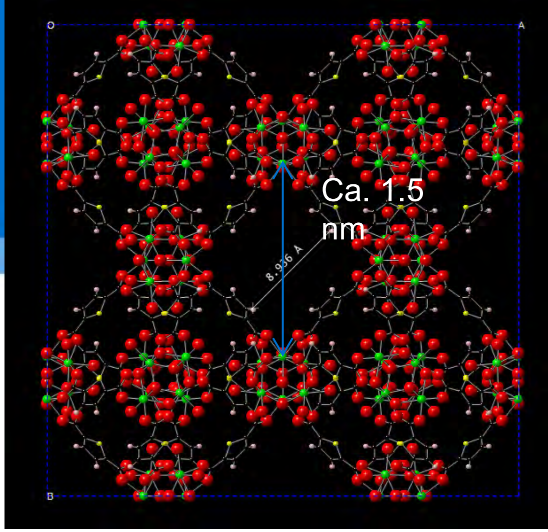
A typical polyoxometalate (POM)@MOF.

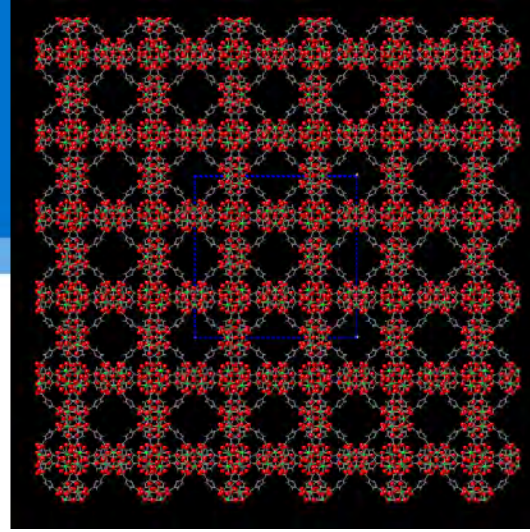




Particles can be encapsulated in MOF via surface modification.
The particle distribution inside the MOF can also be controlled.

10.1038/nchem.1272





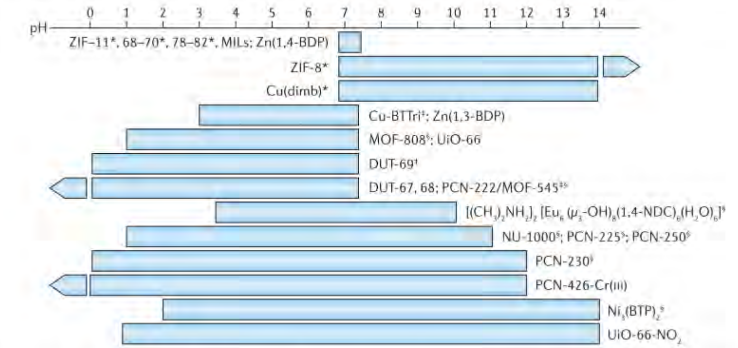
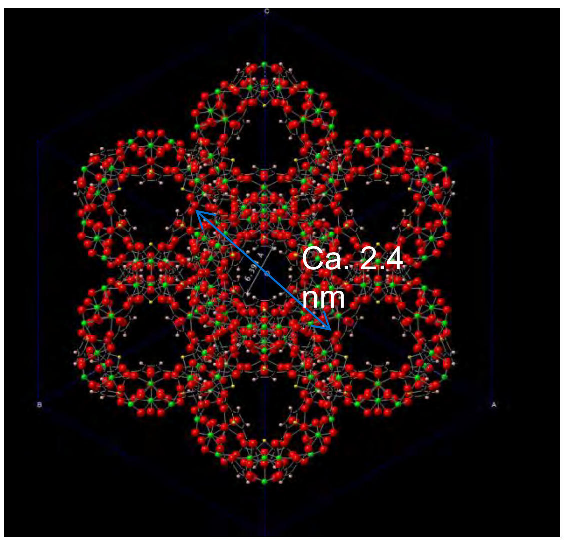
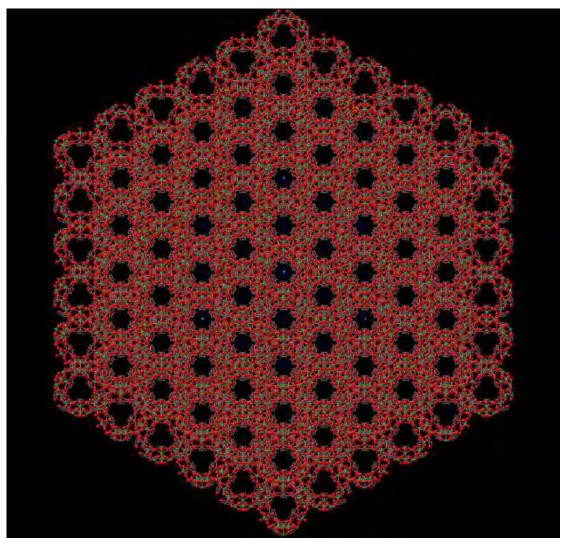
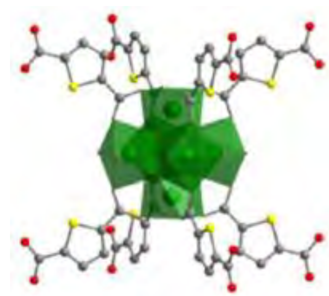


Figure 1 | **The chemical (acid–base) stability of some representative metal–organic frameworks based on literature data.** The bar length indicates the pH range that the metal–organic frameworks (MOFs) can tolerate. An arrow indicates that the MOF can withstand pH < 0 or pH > 14. Stabilities are established by powder X-ray diffraction (PXRD) apart from those marked with '§' (stability confirmed by both PXRD and gas sorption experiments). Studies of stability in aqueous base (‡) or aqueous acid (*) have yet to be reported. 1,3-BDP, 1,3-benzenedipyrozolate; 1,4-BDP, 1,4-benzenedipyrozolate; 1,4-NDC, 1,4-naphthalenedicarboxylate; BTP, 1,3,5-tris(1*H*-pyrazol-4-yl)benzene; BTTri, 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene; dimb, 1,4-bis(1*H*-imidazol-4-yl)benzene; DUT, Dresden University of Technology; MIL, Materials Institute Lavoisier; NU, Northwestern University; PCN, porous coordination network; ZIF, zeolitic imidazolate framework.

10.1038/natrevmats.2015.18



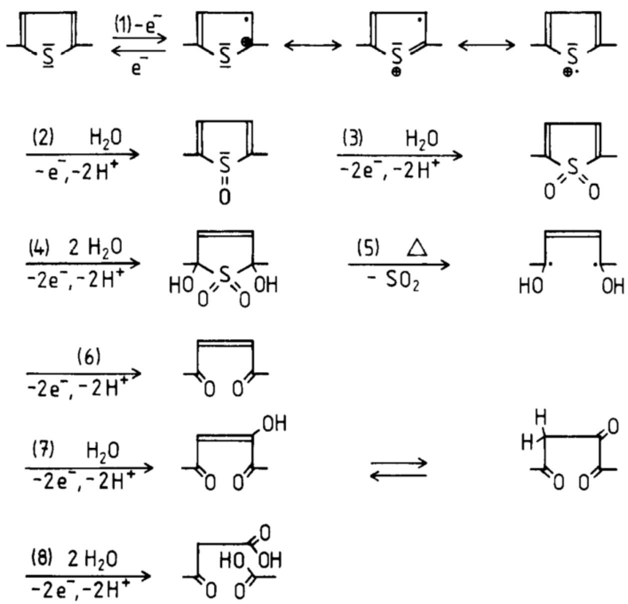


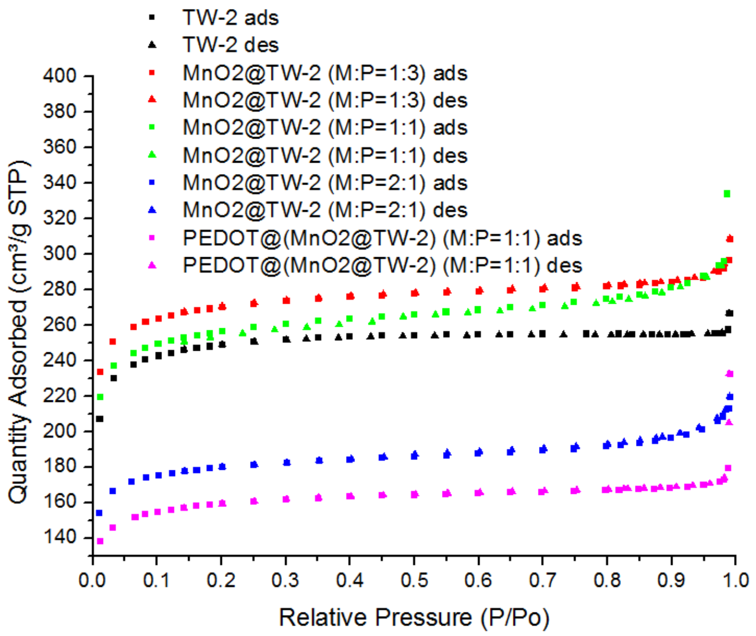


10.1021/cg301691d

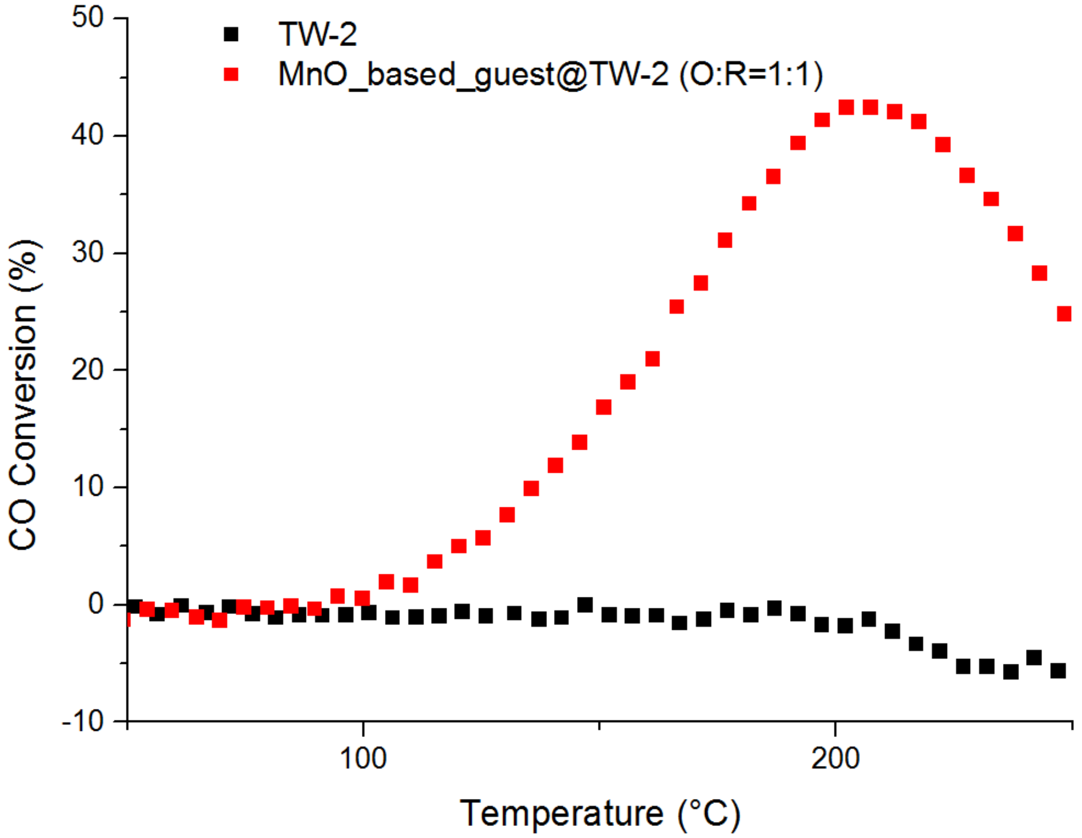
cubic

appendix



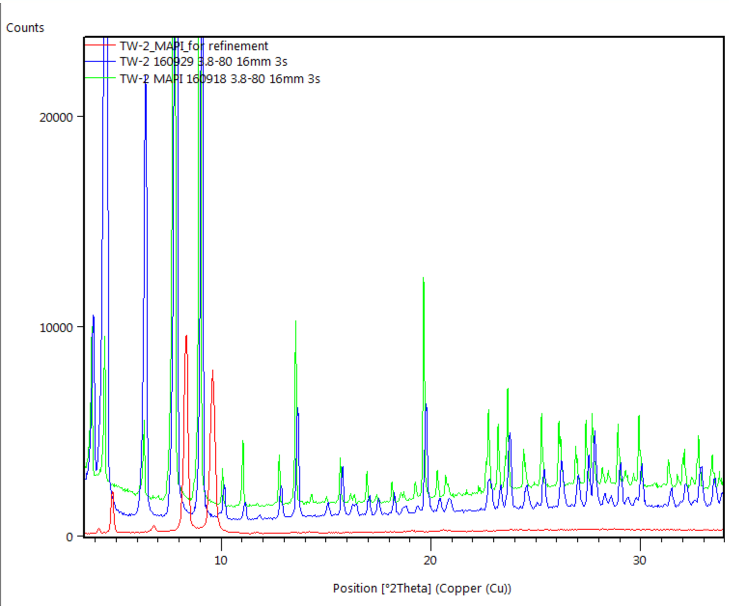

TW-2 ads
TW-2 des
MnO2@TW-2 (M:P=1:3) ads
MnO2@TW-2 (M:P=1:3) des
MnO2@TW-2 (M:P=1:1) ads
MnO2@TW-2 (M:P=1:1) des
MnO2@TW-2 (M:P=2:1) ads
MnO2@TW-2 (M:P=2:1) des
PEDOT@(MnO2@TW-2) (M:P=1:1) ads
PEDOT@(MnO2@TW-2) (M:P=1:1) des
Quantity Adsorbed (cm³/g STP)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Relative Pressure (P/Po)

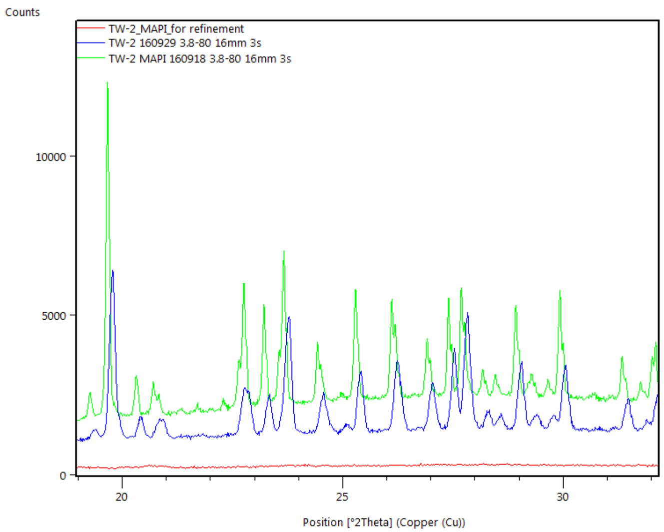
appendix

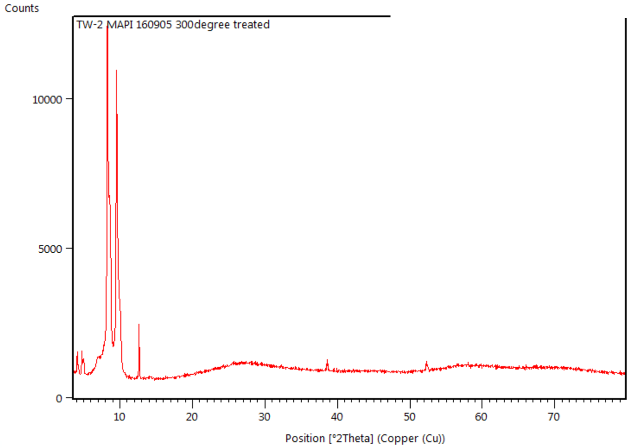


TW-2
MnO_based_guest@TW-2 (O:R=1:1)
CO Conversion (%)
50
40
30
20
10
0
-10
100
200
Temperature (°C)

appendix

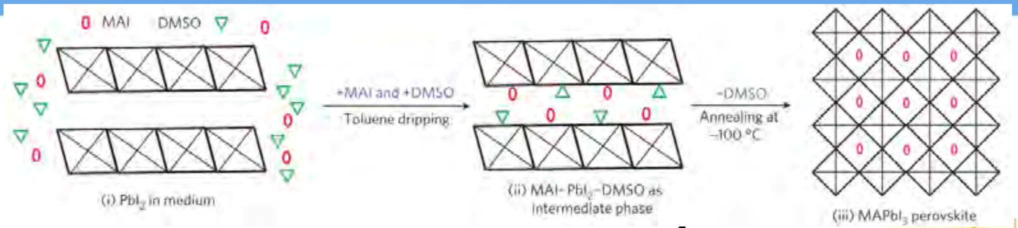






University of Cambridge

appendix



10.1038/nmat4014