

**Insertion of Guest Molecules into a Mixed Ligand
Metal–Organic Framework via Single-Crystal-to-Single-
Crystal Guest Exchange**

**by Lily Giri, Rose Pesce-Rodriguez, Shashi P Karna,
and Nirupam J Trivedi**

ARL-TR-7004

July 2014

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) July 2014		2. REPORT TYPE Final		3. DATES COVERED (From - To) June 2013–December 2013	
4. TITLE AND SUBTITLE Insertion of Guest Molecules into a Mixed Ligand Metal–Organic Framework via Single-Crystal-to-Single-Crystal Guest Exchange			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Lily Giri, Rose Pesce-Rodriguez, Shashi P Karna, and Nirupam J Trivedi			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WML-B Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-7004		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Metal–organic frameworks (MOFs) are constructed from metal ions or metal ion clusters and bridging organic linkers, which provide diverse structural topologies with porous architectures. They have potential to be applied to molecular sieving, storage, ion exchange, heterogeneous catalysis, sensor technology, and optoelectronics. The robust open framework of the MOF can accommodate various guest molecules. The nanoporous lattices of MOFs have a high degree of chemical versatility and an immensely rich host–guest chemistry that include reversible guest and ion exchange and heterogeneous catalysis. In this work, we have successfully introduced two small guest molecules, viz. 3-methoxypropionitrile and nitrobenzene, in a cage of host MOF Zn ₂ NDC ₂ DPNI-DMF. The complete exchange of the reagent solvent for the new guests has been verified by gas chromatography-mass spectrometry (GC-MS), powder x-ray diffraction (PXRD), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR).					
15. SUBJECT TERMS Metal organic frame work, Porous structure, Inclusion of guest molecules					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 22	19a. NAME OF RESPONSIBLE PERSON Rose Pesce-Rodriguez
A. Report Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (410) 306-1877

Contents

List of Figures	iv
Acknowledgments	v
1. Introduction and Background	1
2. Experiment	1
2.1 Materials	1
2.2 Experimental	2
2.2.1 Solvent Exchange Method.....	2
2.2.2 Vapor Diffusion Method	2
2.3 Characterizations	3
3. Results and Discussion	3
3.1 Guest Molecule: 3-methoxypropionitrile (3MPN).....	3
3.2 Guest Molecule: Nitrobenzene (NB).....	8
4. Summary and Conclusions	11
5. References	12
List of Symbols, Abbreviations, and Acronyms	13
Distribution List	14

List of Figures

Fig. 1 (a) Crystal structure of the host MOF. The yellow polyhedra represent the Zn ions: carbon, gray; oxygen, red; and nitrogen, blue. (b) 3MPN, (c) NB, (d) NDC, and (e) DPNI d and e from Bae et al. ⁴ (used with permission)	2
Fig. 2 Total ion chromatogram for neat MOF	4
Fig. 3 Mass spectrum for 3.35-min peak in Fig. 1 (top) with library search match (bottom)	5
Fig. 4 Total ion chromatogram for guest-host complex	5
Fig. 5 Mass spectrum for 3.41-min peak in Fig. 1 (top) with library search match (bottom).	6
Fig. 6 PXRD pattern of the host MOF and the MOF + 3MPN.....	6
Fig. 7 TGA curve of neat MOF and the MOF + 3MPN complex	7
Fig. 8 FTIR spectrum of the host MOF and the MOF + 3MPN (spectra normalized to largest peak).....	8
Fig. 9 Total ion chromatogram for guest-host complex	8
Fig. 10 Mass spectrum for 5.2 min peak in Fig. 1 (top) with library search match (bottom).....	9
Fig. 11 PXRD pattern of the host MOF and the MOF + NB.....	9
Fig. 12 TGA curve of neat MOF and the MOF + NB complex.....	10
Fig. 13 FTIR spectrum of the host MOF and the MOF + NB (spectra normalized to largest peak).....	11

Acknowledgments

The authors wish to acknowledge and thank Dr Andrew P Nelson Jr of Naval Air Weapons Station, China Lake, CA, for supplying the metal–organic framework (MOF) and Shaan Sharma for his preliminary work on metal organic frameworks while at the US Army Research Laboratory (ARL) in the 2012 Summer Intern Program. This research was supported by an appointment to the Research Participation Program at ARL administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and ARL.

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1. Introduction and Background

Metal–organic framework (MOF) materials have attracted a great deal of attention during the last few years.^{1,2} These materials are formed by coordination bonds between metal ions and organic molecular ligands, leading to robust open framework structures that can accommodate various guest molecules. Organic ligands in the MOFs make the structure flexible and different from traditional microporous materials like zeolites, which are fully inorganic and thus lack synthetic flexibility. During the synthesis of MOFs, solvent molecules get trapped in the pores and can be removed via desolvation. The resulting empty framework may maintain structural integrity, yielding a porous MOF material that has a large apparent surface area. The original solvent or other guest molecules can then be adsorbed into this porous structure.

MOFs have a number of useful properties such as large internal surface areas (some as high as 10^3 – 10^5 m²/g), high thermal stability (400–500 °C), ultra low densities, and the availability of uniformly structured cavities of molecular dimensions that make them attractive candidate for a wide range of chemical and physical applications such as hydrogen and methane storage,³ chemical separations,⁴ selective chemical catalysis,⁵ photonics,⁶ and drug delivery.⁷ Here we present our work on the study of MOFs as thermally stable hosts for small molecule organic materials. We have successfully introduced two molecules, viz. 3-methoxypropionitrile (3MPN) inside the cage of a MOF and verified the inclusion by using a variety of analytical techniques, such as powder x-ray diffraction (PXRD), thermo-gravimetric analysis (TGA), Fourier transform infrared (FTIR), and gas chromatography-mass spectrometry (GC-MS).

2. Experiment

2.1 Materials

Commercial reagents were purchased from Sigma-Aldrich (ACS grade) and used as received. In this work, we used Zn₂NDC₂DPNI-DMF, as our inert MOF host, where NDC is the dianion of 1,6-naphthalene dicarboxylic acid, DPNI is N,N-di-(4-pyridyl)1,4,5,8-naphthalenetetracarboxy-diimide, and DMF is N,N dimethylformamide, which is employed as a reaction medium during the synthesis and is subsequently displaced by the guest molecule. This MOF is constructed with zinc (Zn) atoms as metal centers, and NDC and DPNI molecules as ligands, as shown in Fig. 1a. Our first guest molecule is 3MPN and the second molecule is nitrobenzene (NB). The structures of these two guest molecules are shown in Fig. 1b and Fig. 1c.

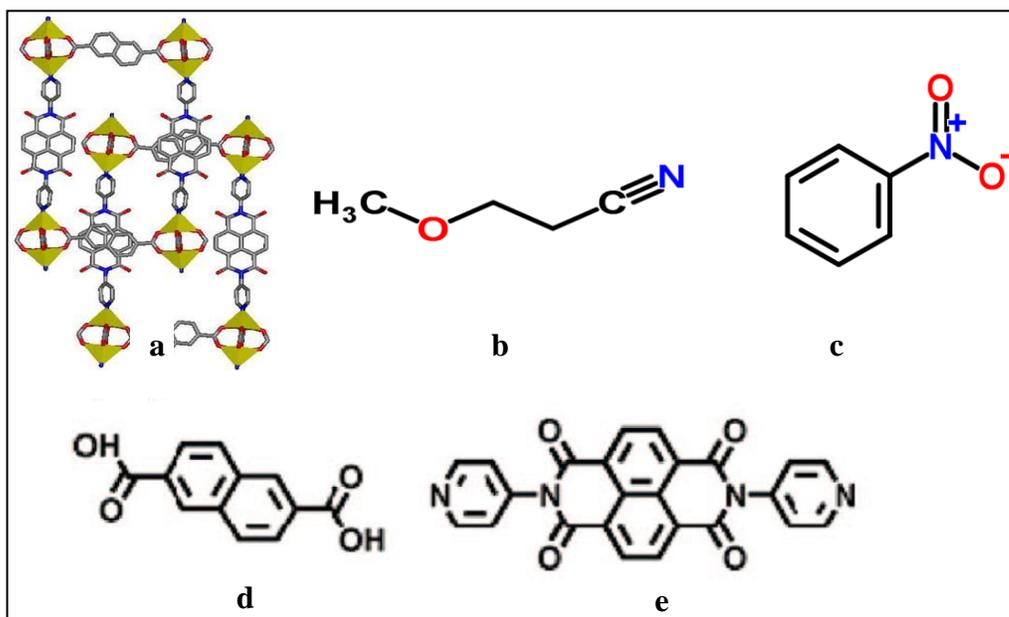


Fig. 1 (a) Crystal structure of the host MOF. The yellow polyhedra represent the Zn ions: carbon, gray; oxygen, red; and nitrogen, blue. (b) 3MPN, (c) NB, (d) NDC, and (e) DPNI d and e from Bae et al.⁴ (used with permission)

2.2 Experimental

Distilled de-ionized water was used for all solution preparations. All glassware was cleaned in the order: tap water and dish detergent, purified water, ethanol, and nitrogen gas to dry. Two different methods were used to include the guest molecules inside the cage of the host MOF. For our first guest molecule (3MPN), we used the solvent exchange method and, for the second molecule (NB), the vapor diffusion method was used.

2.2.1 Solvent Exchange Method

In a typical synthesis, 10 mg of the yellow MOF is mixed with 5 mL of 3MPN, resulting in a clear yellow liquid. The solution is stirred at room temperature for 3 weeks and then centrifuged. The powder left is quickly rinsed in acetone, allowed to dry, and then characterized by GC-MS, FTIR, TGA, and PXRD. The nitrile end of the 3MPN molecule has an affinity for metals, so in suspending these substances in a solution, we hypothesize that the 3MPN displaces the DMF inhabiting the framework.

2.2.2 Vapor Diffusion Method

In this method, the inclusion of the guest molecule NB was done by simply putting the MOF under NB atmosphere. Here, 1 mL of NB (guest) was placed in an open vial (2 mL) and 1 mg of the yellow MOF (host) was placed in an open DSC pan. Both the pan and the small vial

containing NB were placed in a larger vial (20 mL) and sealed. The whole system was placed in a heater base to maintain a temperature of ~35 °C.

2.3 Characterizations

Analysis of the MOF and the complexes with the MOF and the guest molecules was performed using an Agilent GC-MS (Model 6890N GC and Model 5973N MSD) system fitted with a Pyroprobe 2000 (CDS Analytical, Oxford, PA). The GC column used was a HP-5 capillary column (0.25 mm × 30 m, 0.25-mm film). The injector temperature was 200 °C and the Pyroprobe interface temperature was 175 °C. The GC oven temperature program was as follows: 50 °C isothermal for 1 min, 50–250 °C at 40 °C/min, and 250 °C isothermal for 1 min. The Pyroprobe was programmed to give a 20-s desorption pulse at 175 °C (heating rate 1000 °C/s). The sample was held within the coil of the Pyroprobe by first placing it in a quartz tube containing a small plug of glass wool and then inserting the entire tube into the coil.

All FTIR spectra were obtained using a ThermoScientific (formerly Nicolet) Nexus 870 FTIR spectrometer fitted with a Thermo Nicolet OmniSampler (attenuated total reflectance [ATR]) accessory. A deuterated triglycine sulfate (DTGS) and potassium bromide (KBr) beam splitter was used. For each spectrum, 64 scans were collected at a resolution of 4 cm⁻¹.

A TGA (TA Instruments Q500) operating under Universal Analysis software (TA Instruments) was used for the TGA measurements. All samples were run in open aluminum pans. The heating rate was 10 °C/min, and analyses were run under a nitrogen flow of 50 mL/min.

PXRD results of the samples were recorded with a Rigaku-miniflex II diffractometer using Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) in θ - 2θ geometry and with a position-sensitive detector. The diffractometer was operated at 30 kV with 15 mA and the data were collected in the 2θ range of 5–40° with a step size of 0.02° per 1.2 s.

3. Results and Discussion

3.1 Guest Molecule: 3-methoxypropionitrile (3MPN)

D-GC-MS analysis was performed to identify and confirm the presence of the guest molecule inside the MOF complex. The total ion chromatogram of the neat MOF is shown in Fig. 2, which shows the presence of a peak at 3.35 min. The mass spectrum of this peak, as well as the library search match, is shown in Fig. 3. Based on this finding, we conclude that the starting host MOF has DMF inside the MOF cage. After the inclusion of the guest molecule 3MPN, D-GC-MS analysis was performed to re-identify the constituents inside the host MOF (Fig. 4). While the total ion chromatogram of the complex shows a peak at nearly the same retention time observed for the neat MOF, the associated mass spectrum of the peak reveals that the peak is from 3MPN

(Fig. 5). The similar retention times for DMF and 3MPN are reasonable considering their respective boiling point (i.e., 153 and 165 °C). Based on D-GC-MS results, we conclude that the DMF inside the MOF cage has been completely displaced by the guest molecule 3MPN.

PXRD is a powerful technique to follow guest inclusion by performing a detailed analysis of the changes in the relative intensities of the low-index diffraction peaks, which are more or less sensitive to the cavity filling. In general, the overall intensity of the host XRD reflections will decrease upon inclusion of guest molecules due to the enhancement of the X-ray scattering contrast.⁸ Fig. 6 shows both the PXRD of the original host MOF and the MOF with the guest molecule 3MPN. As expected, the overall intensity of the host MOF with 3MPN as guest has decreased. Drastic changes in intensity of individual peaks in the XRD pattern can result from changes of distribution of electron density within the unit cell of the MOF. The electron density distribution is dependent upon the extent of filling of pores in the MOF with guest molecules and on the nature of the guest molecules. Esken et al.⁹ showed that in MOF-5, the intensity ratio of the reflections at especially $2\theta = 6.9^\circ$ and 9.7° will change upon loading the guest molecule. In this work, the relative intensity of the two low angle peaks at $2\theta = 6.8^\circ$ and 7.7° changed drastically, consistent with the inclusion of the guest molecule. PXRD of the MOF with 3MPN displays many additional reflections, which originate from the ordering of the guest molecules in the MOF with new reflections observed at $2\theta = 10^\circ$ – 20° , with the most prominent new reflection at $2\theta = 19^\circ$.

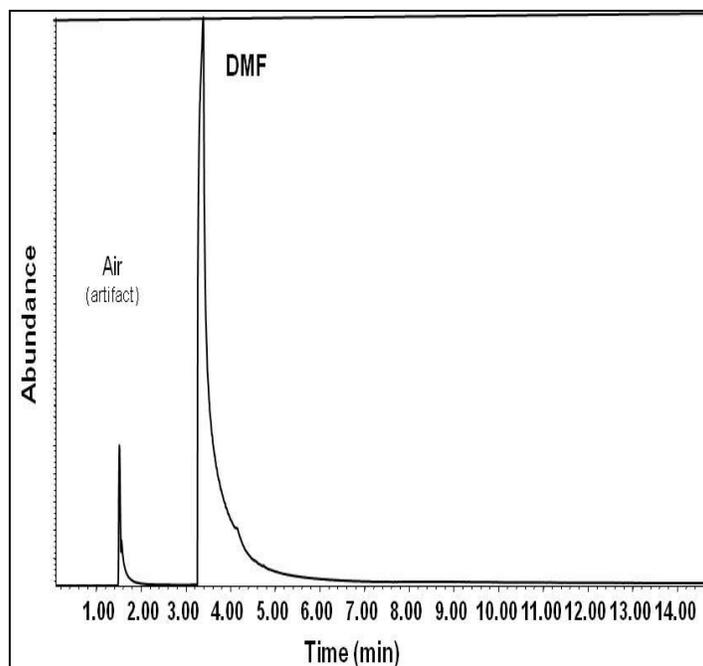


Fig. 2 Total ion chromatogram for neat MOF

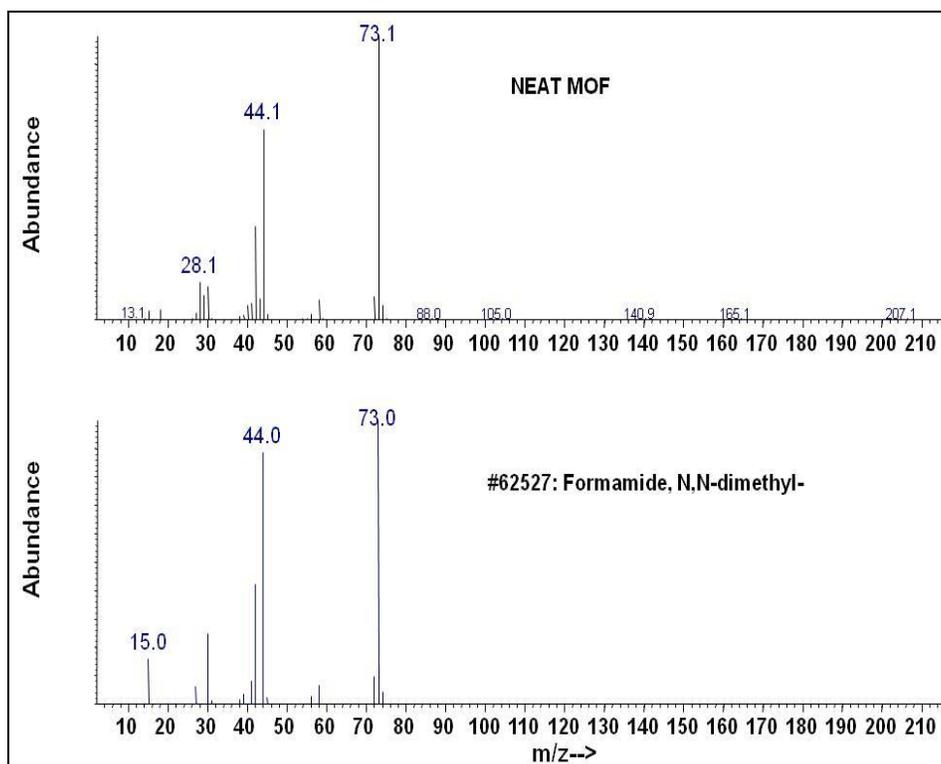


Fig. 3 Mass spectrum for 3.35-min peak in Fig. 1 (top) with library search match (bottom)

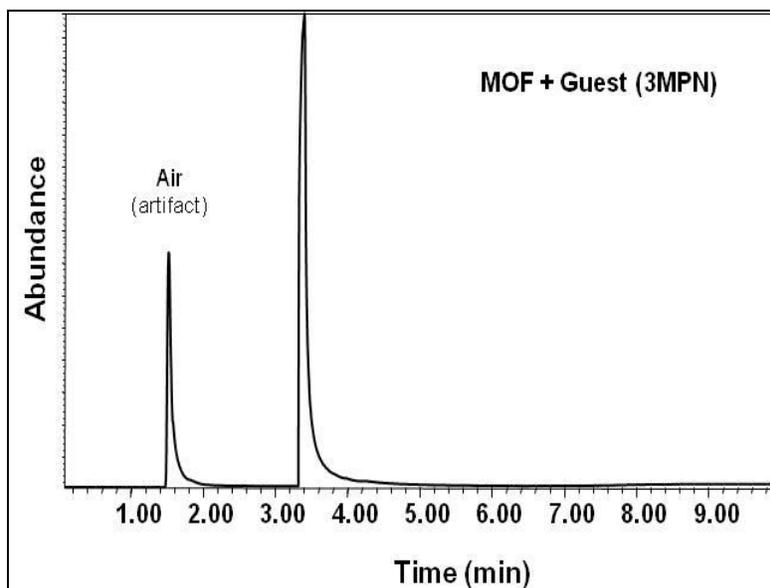


Fig. 4 Total ion chromatogram for guest-host complex

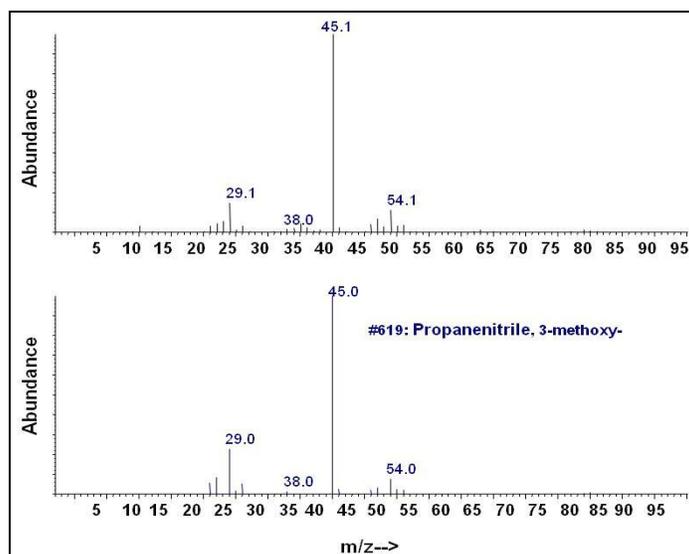


Fig. 5 Mass spectrum for 3.41-min peak in Fig. 1 (top) with library search match (bottom).

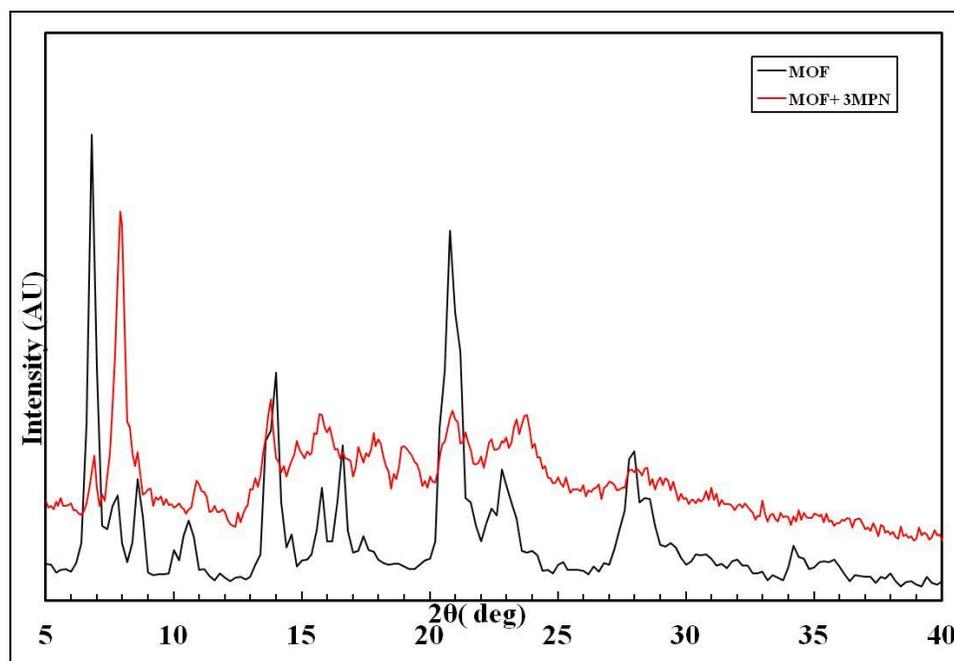


Fig. 6 PXRD pattern of the host MOF and the MOF + 3MPN

The temperature-dependent guest release and thermo-stability of the complex were explored by TGA. The TG curve shown in Fig. 7 shows a weight loss of 10% in the temperature range of 25–140 °C, which corresponds to the loss of guest molecule adsorbed on the exterior of the cage of the host MOF, and a slow weight loss of 20% between 140–400 °C, which corresponds to the

loss of the guest molecule 3MPN that was inside the MOF cage. The weight loss beyond 400 °C is attributed to the decomposition of the framework structure. It should be noticed that the release of the guest molecule by heating spans a broad temperature range up to 400 °C, which implies that the loss of 3MPN molecules from the cavities of the host MOF grid networks is a prolonged process.

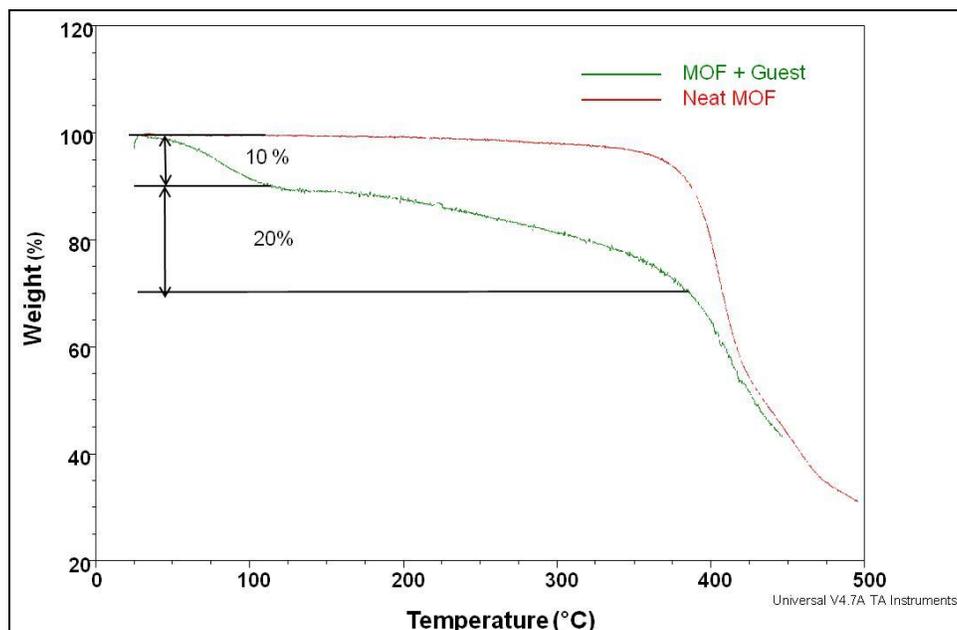


Fig. 7 TGA curve of neat MOF and the MOF + 3MPN complex

The FTIR spectrum of the host MOF and the complex (MOF + 3MPN) gave further evidence of the inclusion of the guest molecule inside the MOF cage (Fig. 8). The library spectrum of the guest molecule is taken from the Bio-Rad “Know it all” informatics system analytical addition infrared (IR) spectra database. The spectra of both 3MPN and the complex exhibits the vibration of the nitrile groups ($C\equiv N$) at 2250.8 cm^{-1} , proving the inclusion of the guest molecule inside the MOF cage. The complete removal of DMF molecules is indicated by the disappearance of the characteristic $C=O$ band of DMF at $\sim 1660\text{ cm}^{-1}$. The FTIR spectrum of the complex shows a new peak at 1638 cm^{-1} , which is not present in either the host or the guest molecule. The peaks at 1100.3 and 1115.9 cm^{-1} of the MOF spectra merges to a single peak at 1112.3 cm^{-1} in the complex spectra. An additional vibrational band at 1000.5 cm^{-1} is due to the inclusion of the guest molecule since this band is also present in the spectrum of the guest molecule but not in that of the host MOF.

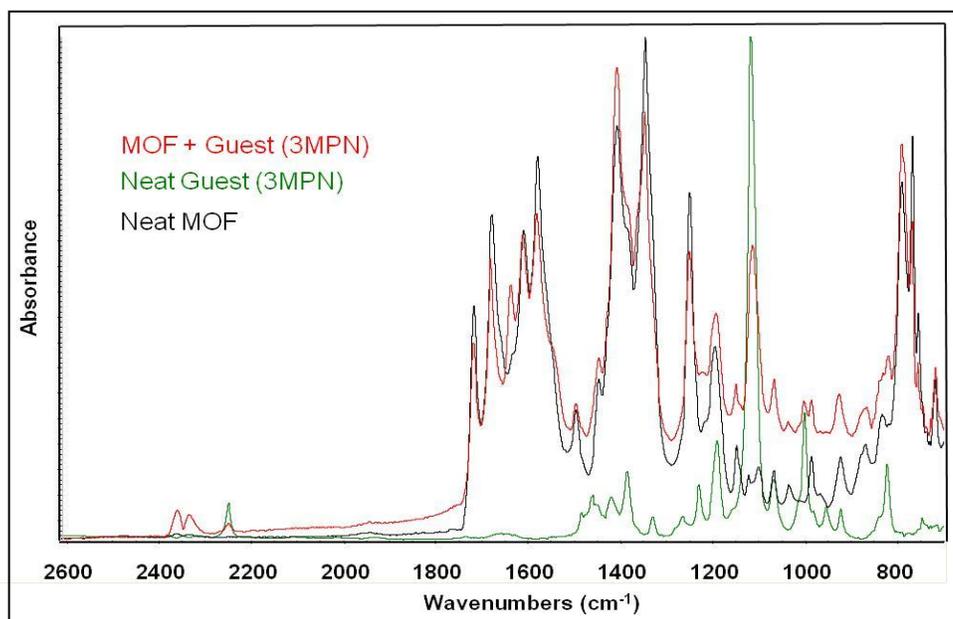


Fig. 8 FTIR spectrum of the host MOF and the MOF + 3MPN (spectra normalized to largest peak)

3.2 Guest Molecule: Nitrobenzene (NB)

The total ion chromatogram of the neat MOF shows the presence of DMF (Fig. 2 and Fig. 3) while that of the complex with the second guest molecule NB shows no trace of DMF. A new peak for NB was observed at 5.2 min, as shown in Fig. 9. The mass spectrum for this peak along with the library match for NB is shown in Fig. 10. Based on this finding, we can conclude that in the complex, the DMF molecule inside the MOF cage has been displaced by the guest molecule NB.

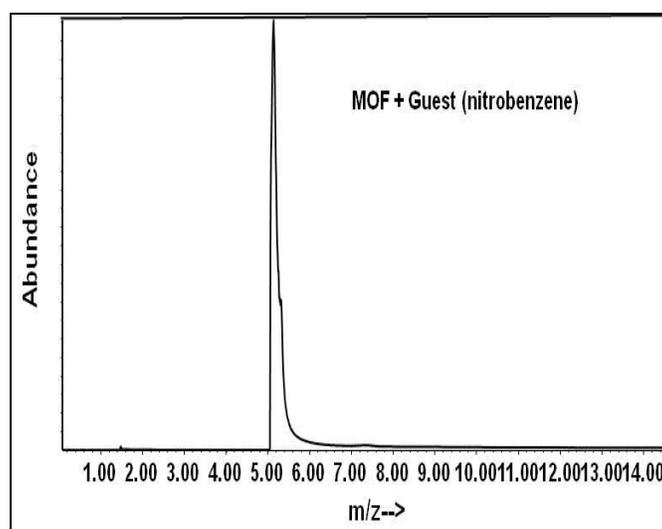


Fig. 9 Total ion chromatogram for guest-host complex

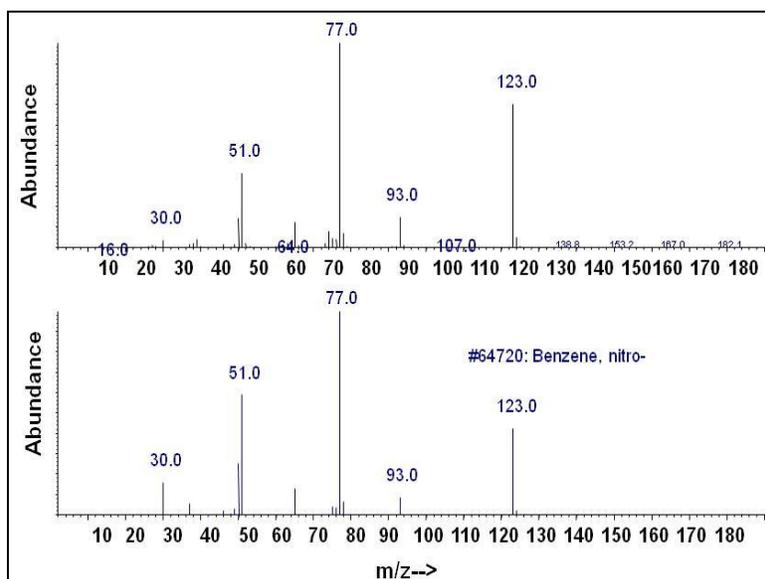


Fig. 10 Mass spectrum for 5.2 min peak in Fig. 1 (top) with library search match (bottom)

PXRD of both the original host MOF and the complex with the guest molecule NB is shown in Fig. 11. As expected, the overall intensity of the complex has decreased and relative intensity of the two low angle peaks at $2\theta = 7.9^\circ$ and 8.8° has changed proving the inclusion of the guest molecule. PXRD of the complex displays some additional reflections, which originate from the ordering of the guest molecules in the MOF with new reflections observed at $2\theta = 9\text{--}20^\circ$, with the most prominent new reflection at $2\theta = 17.9^\circ$.

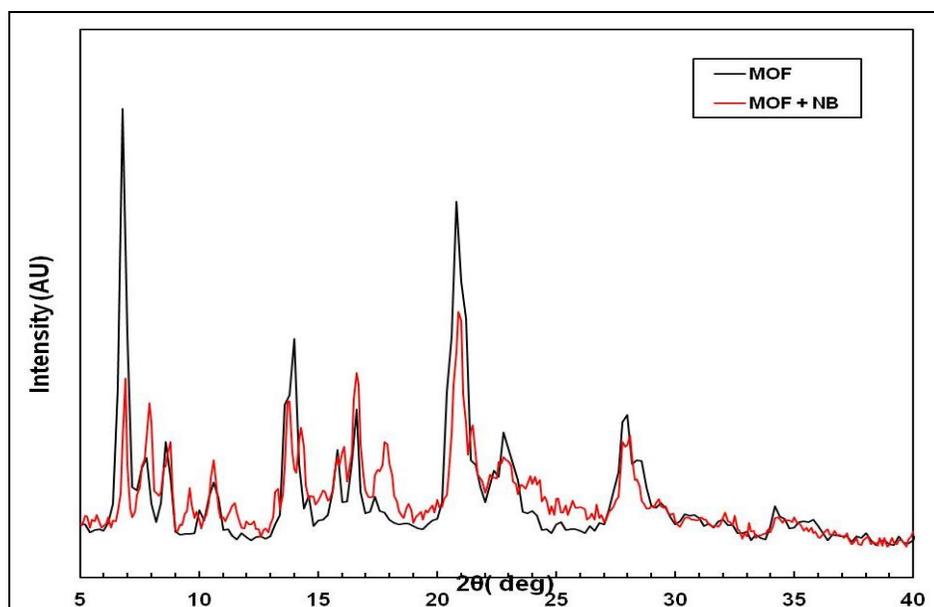


Fig. 11 PXRD pattern of the host MOF and the MOF + NB

TGA was performed to find the temperature-dependent guest release and thermo-stability of the host-guest complex. The TG curve of neat MOF and the MOF complex with the NB guest is shown in Fig. 12. The complex shows approximately 15 wt-% loss between 25–125 °C at one rate and another 15 wt-% loss between 125–400 °C. The MOF structure is observed to decompose starting at about 400 °C. We can infer that the first weight loss is from the outside guest molecule, and that the next weight loss is due the guest molecule inside the MOF cage, which took a longer time and a higher temperature to be released.

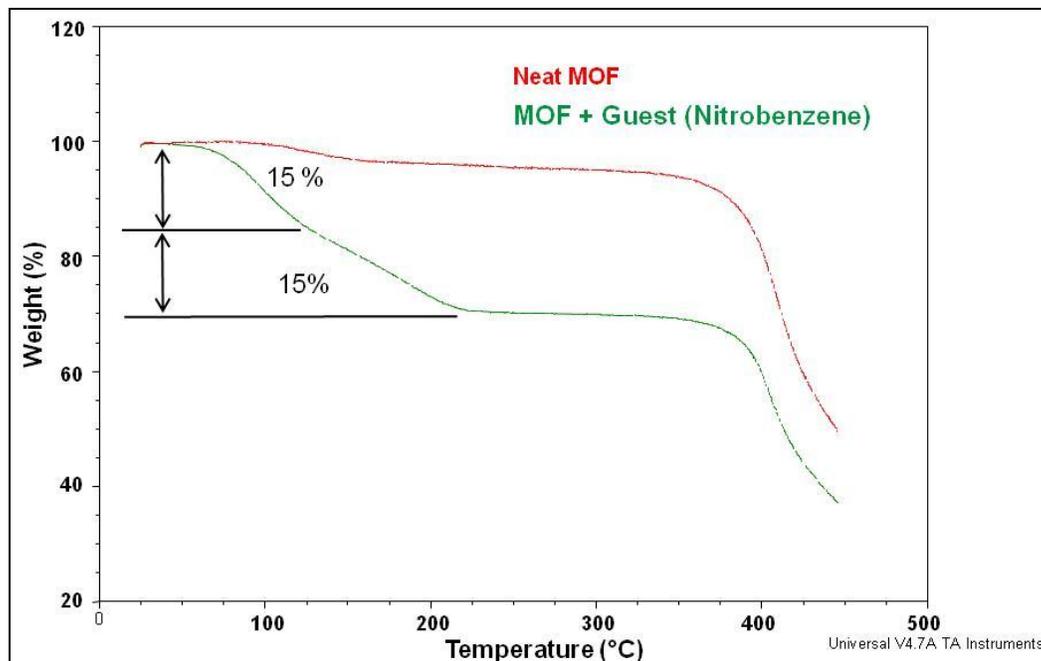


Fig. 12 TGA curve of neat MOF and the MOF + NB complex

The host MOF and the host-guest complex were also characterized by FTIR spectroscopy (Fig. 13). The complete removal of DMF molecules is indicated by the disappearance of the characteristic C=O band of DMF at $\sim 1660\text{ cm}^{-1}$. The strong band at 1523 cm^{-1} is characteristic for the asymmetric (NO_2) stretching of NB as well as two new aromatic NB bands at 1478 and 1021 cm^{-1} were also clearly visible that were not present in the MOF. The band at 851 cm^{-1} is also coming from the C-N stretch of the guest molecule NB.

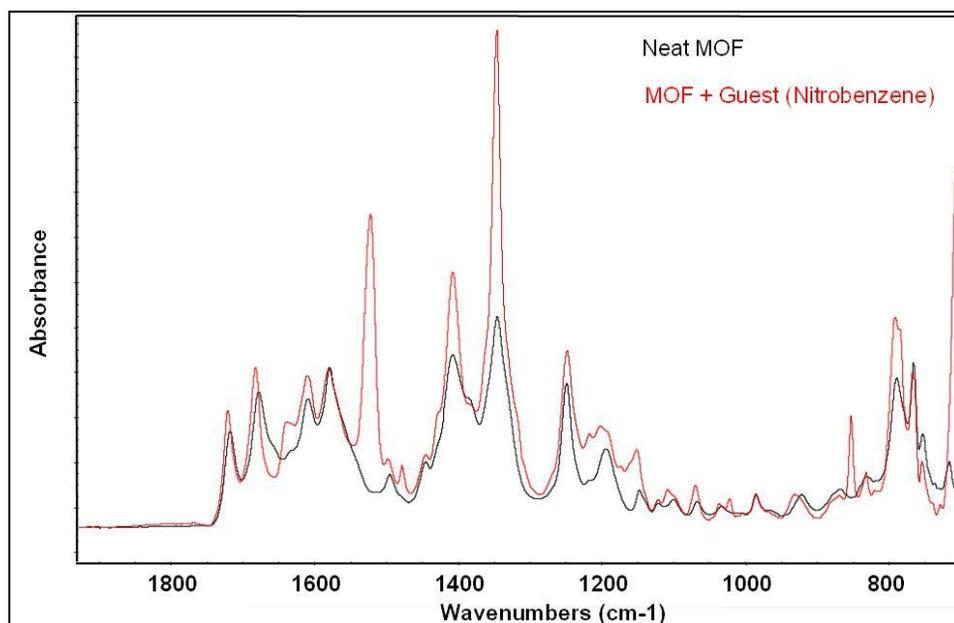


Fig. 13 FTIR spectrum of the host MOF and the MOF + NB (spectra normalized to largest peak)

4. Summary and Conclusions

We have successfully trapped two small molecules, viz. 3MPN and NB, inside the cage of a mixed ligand MOF, $Zn_2NDC_2DPNI \cdot DMF$. The complete exchange of the reagent solvent for the new guests has been verified by GC-MS, PXRD, TGA, and FTIR.

5. References

1. Collins DJ, Hong CZ. Hydrogen storage in metal–organic frameworks. *J Materials Chem.* 2007;17:3154–3160.
2. Férey G. Hybrid Porous solids: past, present, future. *Chem Soc Rev.* 2008;37(1):191–214.
3. Rowsell JLC, Yaghi OM. Strategies for hydrogen storage in metal-organic frameworks. *Angewandte Chemie Intl Ed.* 2005;44:4670–4679.
4. Bae YS, Farha OK, Spokoyny AM, Mirkin CA, Hupp JT, Snurr RQ. Carborane-based metal-organic frameworks as highly selective sorbents for CO₂ over methane. *Chem Comm.* 2008:4135–4137.
5. Cho SH, Ma BQ, Nguyen ST, Hupp JT, Albrecht-Schmitt TE. A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation. *Chem Comm.* 2006:2563–2565.
6. Evans OR, Lin W. Crystal engineering of nonlinear optical materials based on interpenetrated diamondoid coordination networks. *Chem Mat.* 2001;13:2705–2712.
7. Horcajada P, Serre C, Vallet-Regí M, Sebban M, Taulelle F, Férey G. Metal-organic frameworks as efficient materials for drug delivery. *Angewandte Chemie Intl Ed.* 2006;45:5974–5978.
8. Sauer J, Marlow F, Spliethoff B, Schüth F. Rare earth oxide coating of the walls of SBA-15. *Chem Mat.* 2002;14:217–224.
9. Esken D, Zhang X, Lebedev OI, Schröder F, Fischera RA. Pd@MOF-5: Limitations of gas-phase infiltration and solution impregnation of [Zn₄O(bdc)₃] (MOF-5) with metal–organic palladium precursors for loading with Pd nanoparticles. *J Mat Chem.* 2009;19:1314–1319.

List of Symbols, Abbreviations, and Acronyms

3MPN	3-methoxypropionitrile
ARL	US Army Research Laboratory
ATR	attenuated total reflectance
DMF	dimethylformamide
DTGS	deuterated triglycine sulfate
FTIR	Fourier transform infrared
GC-MS	gas chromatography-mass spectrometry
IR	infrared
KBr	potassium bromide
MOF	metal–organic framework
NB	nitrobenzene
PXRD	powder x-ray diffraction
TGA	thermo-gravimetric analysis
Zn	zinc

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