



Modeling the Effects of Guest Molecules in Metal-Organic Frameworks

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Introduction

Metal-organic frameworks (MOFs) are a new class of porous materials which have gained major interest due to their potential applications in gas storage and carbon capture among others. Unlike other existing porous materials, MOFs are considerably more adaptable and versatile, because they allow for a large number of combinations between different inorganic and organic pieces. MOFs are constructed by connecting metal ions or clusters (sometimes referred as secondary building units, or SBUs) to organic linkers to form one-, two-, or three-dimensional structures that occasionally are stable upon solvent elimination.^[1,2]

The use of open-shell metal centers (such as Fe(II) or Co(II)) can result in MOFs that exhibit spin-crossover (SCO) behavior, meaning that the spin state of the metal centers can be controlled by means of an external perturbation (usually, the temperature). This results in drastic changes in the physical properties of the MOF, such as changes in the magnetic moment, the volume and even the color. Additionally, it has been observed that different guest molecules affect the temperature at which SCO behavior occurs.^[3]

Objectives

A computational model was used to simulate the magnetic susceptibility as a function of the temperature for the spin-crossover MOF [Fe(pz)₂Pt(CN)₄] and the effects that different guest molecules have over the magnetic properties. Among the experimentally reported guests, we investigated the effects induced by acetone, CS₂, and water. The aim of the project is to evaluate if our methodology can reproduce the experimentally observed changes in the transition temperature of the MOF, defined as the temperature with equal populations of both spin states.

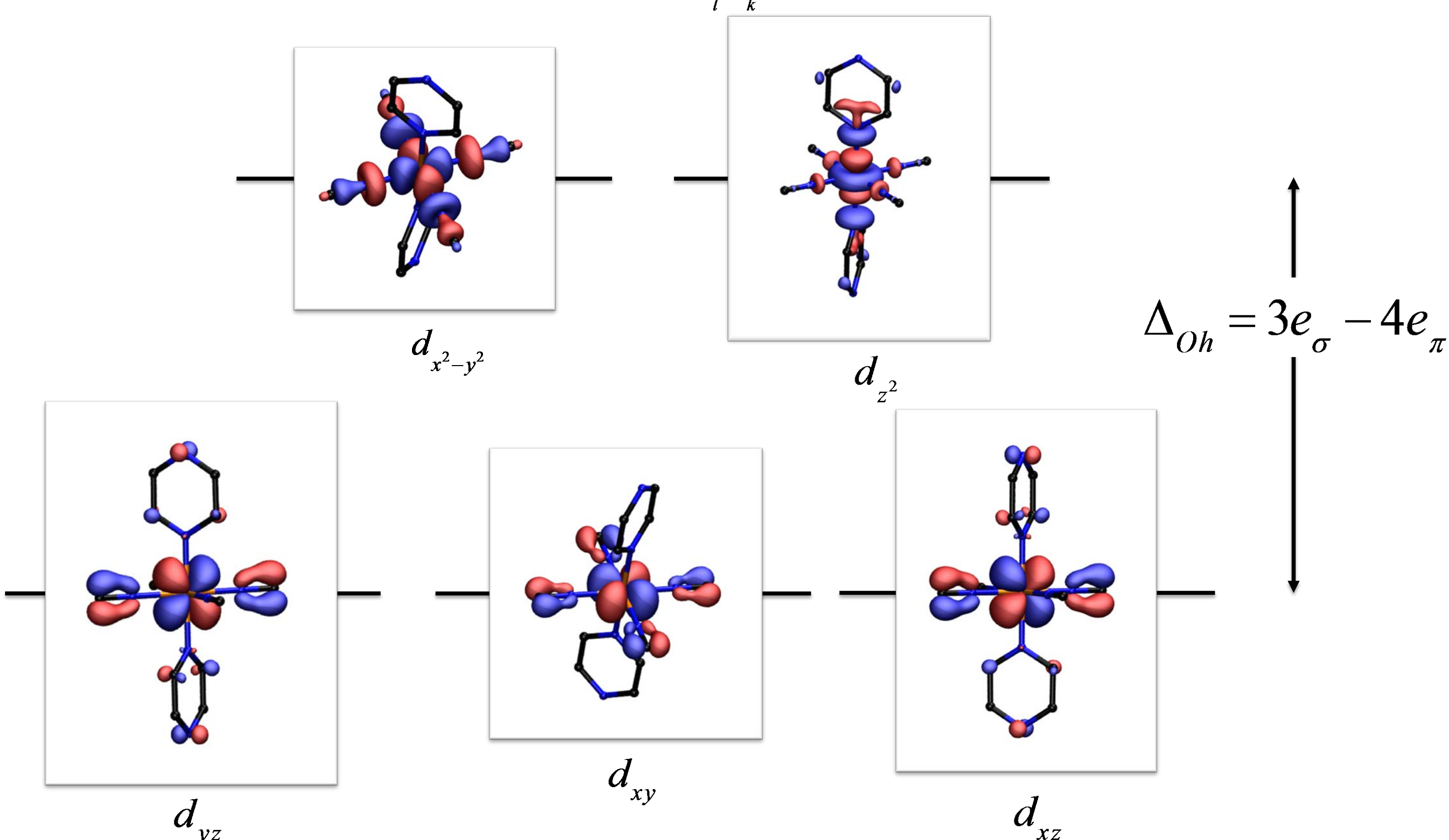
Computational Methods

- The development of *ab initio* force fields was carried out using the Gaussian09 electronic structure suite.^[4]
- The simulations were run in a "hacked" version of DL_POLY_Classic that accounts for the LFSE contribution.^[5]
- All MD simulations were performed for 250 ps in the N σ T ensemble starting from 5 randomly selected initial configurations. Sequential trajectories at increasing temperatures were carried out to model the effects induced by the thermal motion on the relative spin populations.
- Data post-processing from the output files was performed using our own codes written in Java and Fortran.

Ligand Field Molecular Mechanics

Ligand Field Molecular Mechanics (LFMM) is an *ab initio* based model that accurately includes the electronically driven effects due to the interactions of open-shell metal centers and ligands on the MOF force field. The LFMM ligand field stabilization energy (LFSE) is derived from the matrix

$$\langle d_i | V^{LF} | d_j \rangle = \sum_{l,k} \sum_{i,j} F_{ik}^l F_{kj}^l e_i^l e_k^l$$

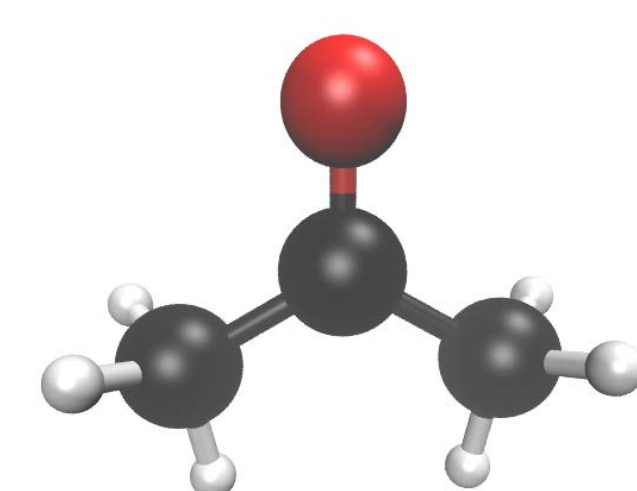
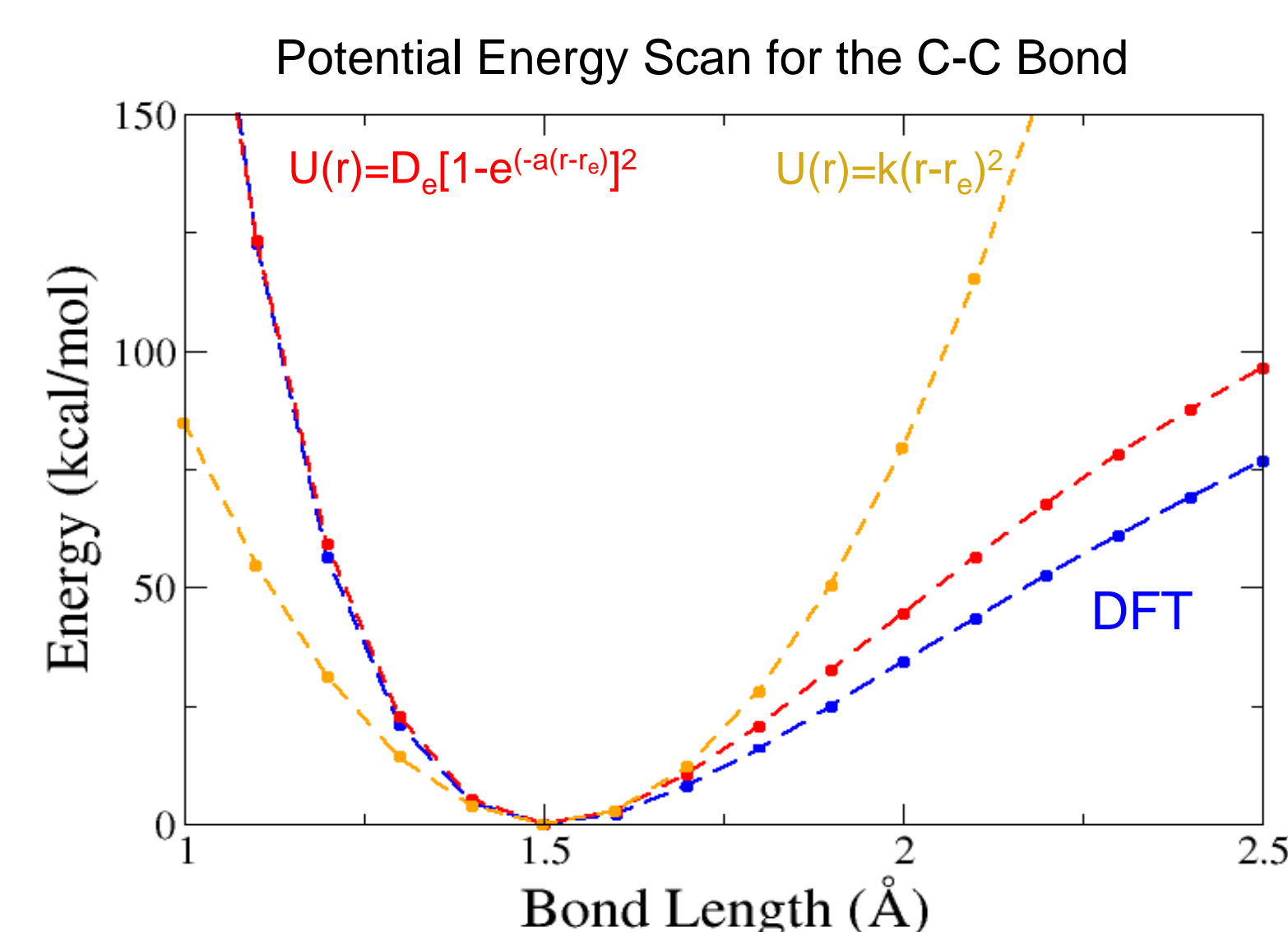


The energy gaps between the different d-based molecular orbitals can be parameterized using the bond centered $e(r)$ functions. This allows for the inclusion of the LFSE term in the MM energy functional form

Building the Guest Molecule

Guest Molecule Force Field^[6]

Intra- and inter-molecular interactions can be parameterized using different functional forms

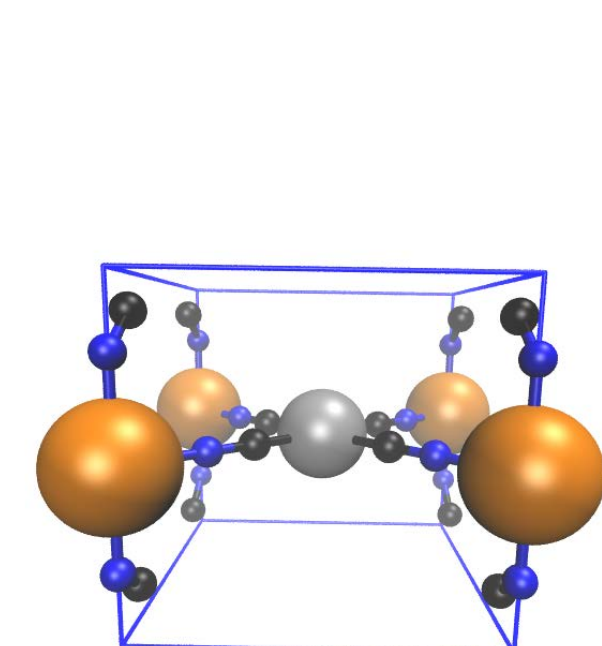


CH₃COCH₃ optimized molecule

MOF Ligand Field Force Field

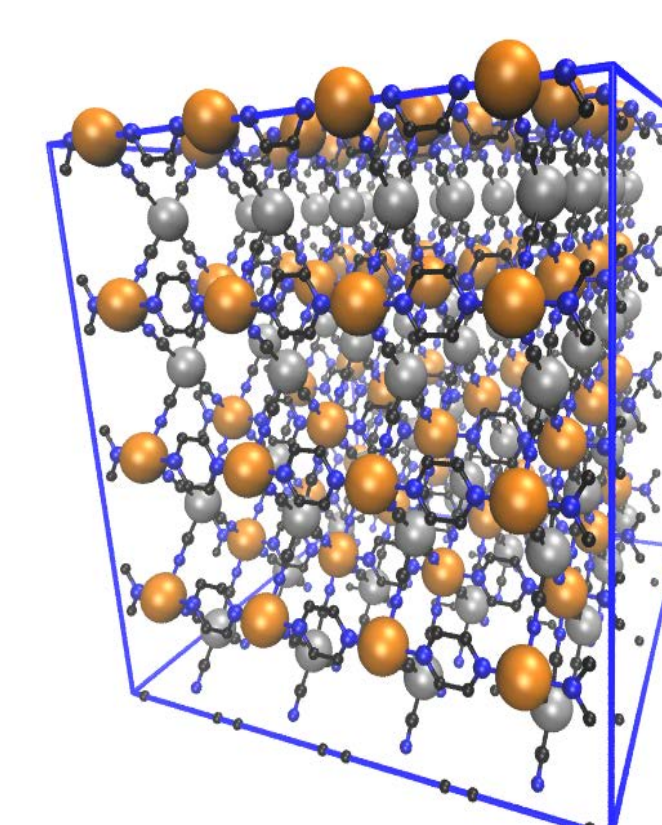
Conventional force field functional form needs to be expanded to include electronically driven effects

$$U(r) = U(r) + LFSE; LFSE = \sum_i n_i \epsilon_i$$



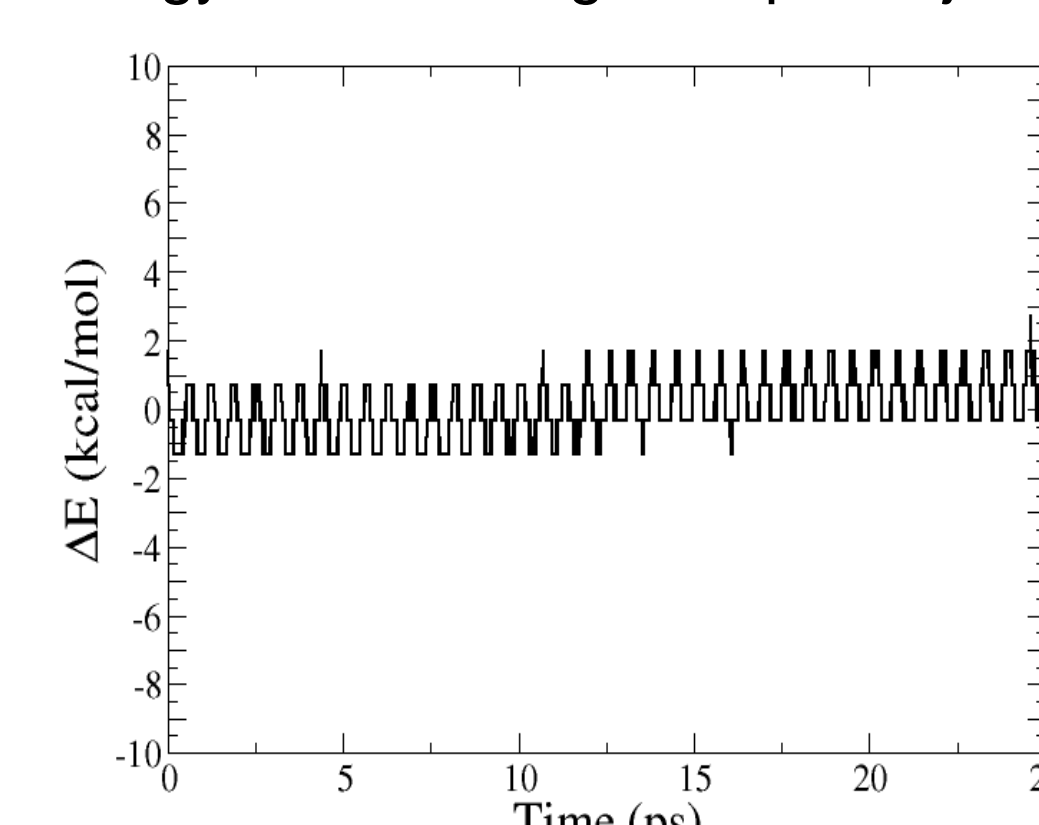
Unit cell

Unit cell replication



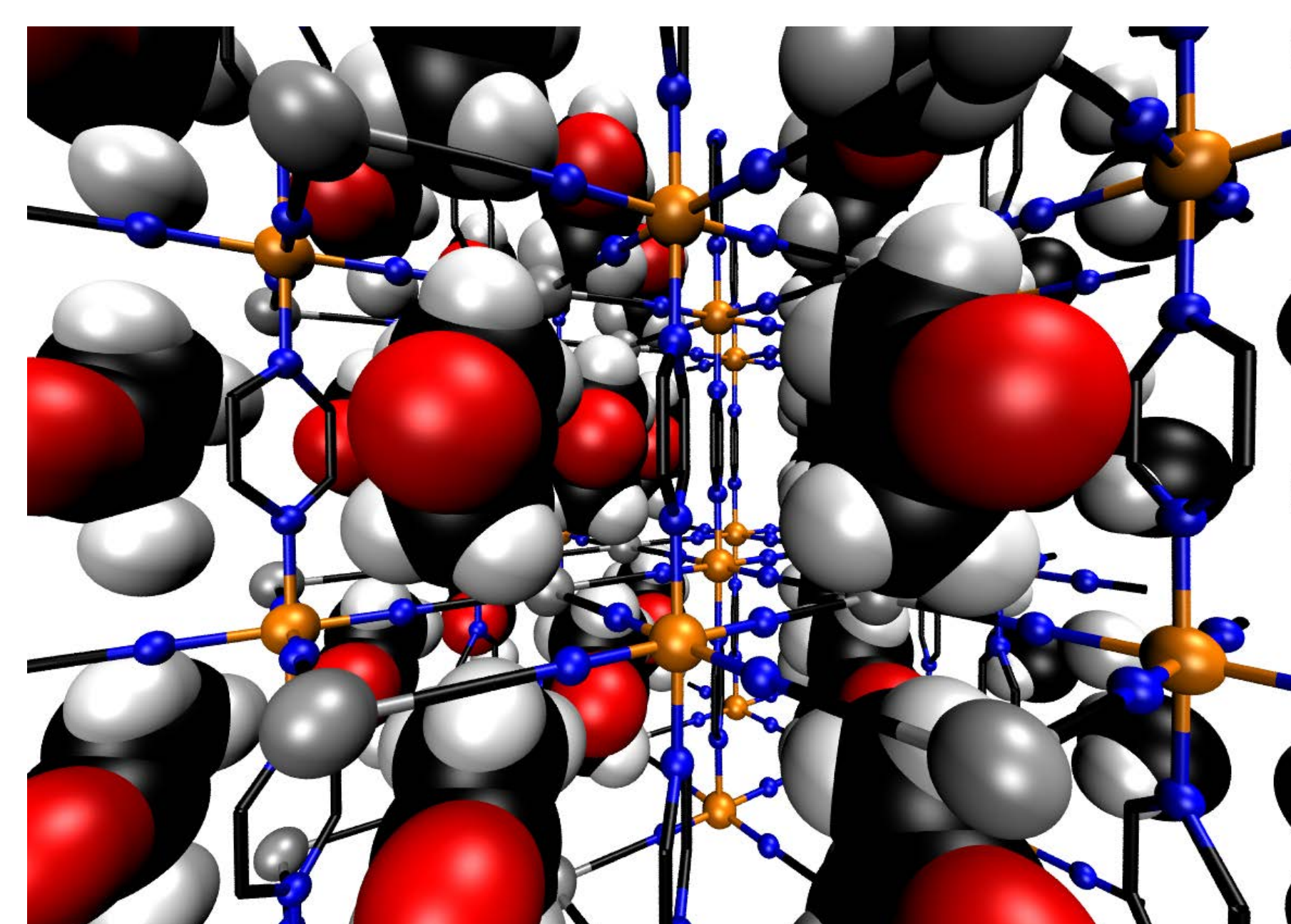
4x4x4 MOF

Energy Profile Along a 25 ps Trajectory



MOF with Guests

The guest is incorporated in the MOF structure and the overall system is equilibrated. Acetone, water and CS₂ have been used as guest molecules.



Snapshot of the [Fe(pz)₂Pt(CN)₄] MOF with acetone loaded in the pores

Acknowledgements



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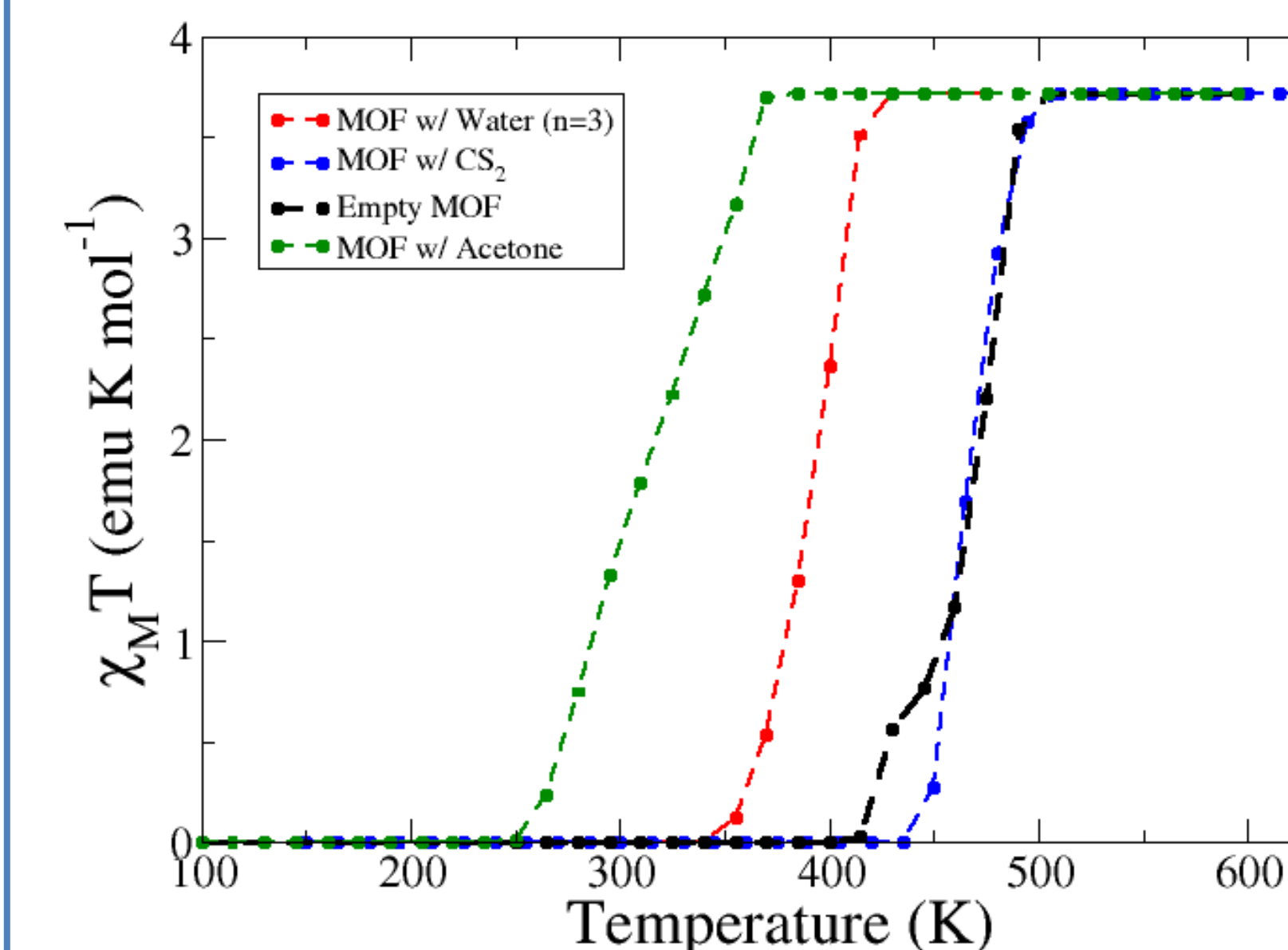
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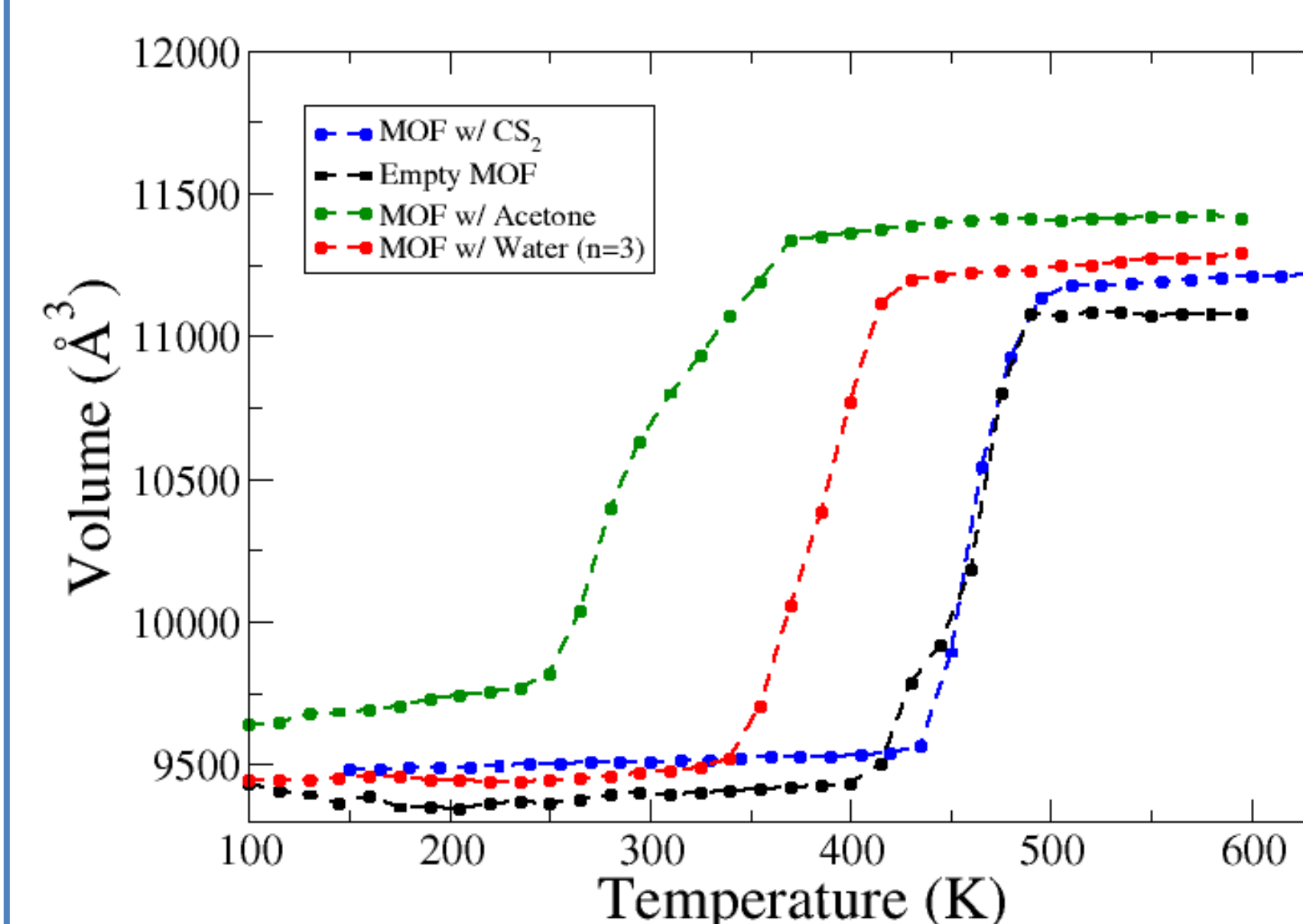
Results

Magnetic Susceptibility as a Function of the Guest



As expected, thermal vibrations induce spin crossover in the MOF, thus changing its magnetic susceptibility. Different guest molecules affect the transition temperature. Acetone and water shift $T_{1/2}$ to lower temperatures, while CS₂ induces spin crossover at a slightly higher $T_{1/2}$ than the empty MOF, in good agreement with the available experimental data.

Volume Changes as a Function of the Guest



Upon transition to the high-spin state, with associated occupation of the anti-bonding orbitals, an increase in the metal-bond lengths is expected. This is reflected in the increase of the calculated MOF volume. The volume increase correlates with the change in the magnetic moment. Bulky guests, like acetone, force the MOF to expand, thus resulting in a more pronounced effect on $T_{1/2}$.

Summary and Outlook

Our computational methodology correctly predicts the changes in the magnetic susceptibility when MOFs undergo thermal spin-crossover. Out of the three guest molecules tested, acetone and water shift the transition temperature to lower values, while a slight shift to higher values is observed for CS₂, as reported experimentally. The guest molecule size seems to play a key role in modulating the transition temperature. For large molecules, the shift in the magnetization curve can be explained by considering that the guest molecules force the framework to expand, which shifts the relative energy gap between the high- and low-spin states. The effects induced by CS₂ need further investigation.

Our methodology enable molecular-level analyses of the interactions between MOFs and different guests molecules. In addition, our calculations can be used to design and test new MOFs with specific and tunable spin-crossover properties. Understanding the physical origins of the spin crossover behavior will help in the rational design of new MOF materials with potential applications as molecular sensors and nanoscale memory devices.

References

- [1] *Metal-Organic Frameworks: Design and Application*. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2010.
- [2] *Metal-Organic Frameworks*. Wiley-VCH Verlag & CO. KGaA: Weinheim, Germany, 2011; p 392.
- [3] Ohba, M.; Yoneda, K.; Agusti, G.; Muñoz, C.; Gaspar, A.; Real, J.; Yamaki, M.; Ando, H.; Nakao, Y.; Sakai, A.; Kitagawa, S., *Angew. Chem. Int. Ed.* 2009, 48, 4767-4771.
- [4] *Gaussian 09, Revision A.01 and C.01*, Gaussian 09, Revision A.01 and C.01; Wallingford (CT), 2009.
- [5] Todorov, I. T.; Smith, W.; Trachenko, K.; Dove, M. T., *J. Mater. Chem.* 2006, 16, 1191.
- [6] *Molecular Modelling: Principles and Applications Second Edition*. Prentice Hall: