

MERIT-WINGS Long-Term Overseas Research Report

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Host Institution: Montpellier, France

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Research Topic:

Fundamental understanding of polymer chain infiltration into MOFs through combined approach of molecular dynamics simulations and dielectric relaxation spectroscopy

Research Background

We have been applying the polymer chain infiltration into the nanopores of porous materials called Metal–Organic Frameworks (MOFs) to achieve lots of novel things including polymer structure recognition and brand new composite synthesis that are difficult to realize using conventional methods. From the viewpoint of polymer physics, it is surprising that macromolecules such as polymer chains can penetrate pores that are much smaller than their radius of gyration. Understanding the infiltration process, mechanism, and the static and dynamic states of polymer chains confined within pores is thus an intriguing and important issue—both for understanding polymer behavior in extreme confinement and for establishing fundamental insights for the application of polymer infiltration into MOF nanopore.

Our previous experimental and simulation studies have provided insights into polymer chain dynamics and thermal phase-transition-like behavior inside MOF pores.^{1,2} However, our current understanding is regrettably far from comprehensive. Many questions remain, such as global/segmental chain conformation and how chain dynamically behaves over wide time and length scales inside the pores.

In this study, I collaborated with Prof. Guillaume Maurin and Prof. Sabine Devautour-Vinot at the University of Montpellier, who specialize in equilibrium simulations and dielectric relaxation measurements of MOF/polymer composites. The goal was to gain new insights into the static and dynamic structures of polymer chains confined in MOF nanopores by combining these two approaches.

Research Results

For molecular dynamics (MD) simulations, we prepared a slab model of Zn-JAST1 as a representative MOF and a bulk model of poly(ethylene glycol) (PEG). These systems

were equilibrated under high-pressure and high-temperature conditions to obtain a simulated model structural of the experimental states.

To analyze the static structure of polymer chains confined in the pores, we extracted structural parameters such as the spatial distribution of chains within the pores, monomer density, packing state, chain segment conformation, and dihedral angle distributions, and compared these with bulk values. For example, in the segmental conformation analysis, we calculated the angles formed by three oxygen atoms on PEG chains separated by a few monomers. The distribution of these angles showed that, while the bulk PEG exhibited an almost uniform distribution across all angles, PEG confined in MOFs displayed two dominant conformations—folded “hairpin-like” segments and fully extended segments—indicating a clear structural difference induced by confinement.

To analyze dynamic structure, we ran equilibrium simulations for 50 ns and extracted parameters representing local atomic vibrations and segmental reorientation dynamics. However, due to computational cost limitations, MD simulations alone cannot provide sufficient information on long-time or long-range dynamics. Therefore, these aspects were investigated experimentally through dielectric relaxation spectroscopy of MOF/PEG composites.

The dielectric spectra revealed two distinct relaxation processes corresponding to local PEG motion and the glass–rubber transition. The local motion remained almost unchanged from bulk PEG, whereas the glass–rubber transition was observed as a slower relaxation within the MOF. Additionally, by varying the pore size of the MOF, we found that local motion was nearly independent of MOF structure, while the glass–rubber transition was strongly influenced by pore size, that is, approaching bulk behavior as the pore diameter increased.

These results provide new insights into the static and dynamic states of polymer chains confined in MOFs, complementing previous studies. The combination of MD-based short-time/short-length analyses with dielectric-based long-time/long-length analyses is a key feature of this study, offering a comprehensive understanding of chain behavior across broad time scales. My future work will focus on deepening the dynamic analysis in MD simulations and exploring correlations with experimental dielectric relaxation results.

Life in Montpellier

Montpellier is a city in southern France on the Mediterranean coast. Since my stay took place during the summer, the weather was warm and sunny, making it a pleasant environment. The long daylight hours allowed me to secure ample research time each day (approximately 8:00 a.m. to 8:30 p.m.), providing an excellent research environment. I lived in a student residence located slightly outside the city center and commuted to campus on foot.

The host laboratory was relatively small, consisting of two professors and about ten PhD students and postdocs from various countries including France, other parts of Europe, India, and Brazil. While my home laboratory in Japan emphasizes student independence, the lab of Prof. Maurin had a more structured style where professors provided clear directions and advice, which was a valuable experience in understanding different research cultures.

Thanks to an introduction by my supervisor, Prof. Uemura, I also had the opportunity to visit and give presentations at the laboratories of Prof. Vincent Ladmiraal and Prof. Sylvain Caillol, who are also part of the same research institute. These visits provided valuable discussions on my research from different perspectives and allowed me to tour the research facilities.

Although my stay lasted only six months, I was able to connect with many researchers working on MOF–polymer hybrid systems worldwide. I am grateful for this opportunity and intend to make use of these connections to further expand my research in the future.

Acknowledgments

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References

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