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Takashi Uemura received his Ph.D. degree at Department of Polymer Chemistry, Kyoto University in 2002. He then began his academic career as Assistant Professor (2002) and then Associate Professor (2010) at Kyoto University and was promoted to Professor at the University of Tokyo in 2018. He has received a number of awards, including JSPS Prize, the Chemical Society of Japan (CSJ) Award for Young Chemists, The CSJ Award for Creative Works, the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science, and Technology. He has been appointed as Associate Editor of several international journals, such Dalton Trans. (RSC), Chem. Lett. (CSJ), and Bull. Chem. Soc. Jpn. (CSJ). His research interest is preparation of synergistic nano-hybrids between coordination compounds and polymeric materials, in particular, polymer chemistry in coordination nanopores.



Nanoporous Chem *MOFs as Polymer*

Our technology-driven society continues to advance, and with it the demand for various high-function plastics also advances, calling for precision-engineered polymers with few defects in their structures even at the molecular level. People's lives have come to strongly rely upon these plastics, but in recent decades have we also come to recognize their negative aspects in the form of the environmental and resource crises. It is against this backdrop that a new method of efficient and precise control over polymer structure has been developed - the use of porous materials called 'MOFs' as nano-sized 'factories'. With this new technology, desired polymers can be supplied and utilized effectively, and we envision a future where they may also be reclaimed post-use then re-circulated.



Chemical Plants: *Manufacturers*

By Keat Beamsley and Takashi Uemura
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POLYMERS, ALONGSIDE METALS

and ceramics, make up one of the three fundamental types of materials that enable our modern way of life. Owing to their characteristic light weight and customizable physical properties, the range of applications for polymers is continually expanding, calling for the development of polymeric materials which exhibit excellent functionality of any and all kinds. However, when we synthesize polymers, we typically do so in a flask or reactor – a macro-scale vessel. In this case, we may obtain polymeric materials at low cost and in great quantity, but their

polymer chains are unavoidably entangled, and control over their molecular structures is often difficult. If instead we were to use a reaction vessel of a scale that matches the individual size of target polymer chains, we should be able to precisely control the orientation, position, distance, and electronic state of the ingredient monomers. Thus, the vessel itself is expected to exert great influence on the polymerization reaction, and may be able to precisely control the resulting polymer structure and aggregation state from the moment it is formed.

In recent years, structurally regular porous materials formed from the self-assembly of metal ions and organic ligands – metal-organic frameworks or “MOFs” - have gathered much attention¹⁻³. The number of combinations of metal ions and ligands in these organic-inorganic hybrids are limitless, so by choosing the structural ingredients appropriately one can not only control the pore space and its dimensionality, but also its shape and the presence or absence of functional groups (Figure 1). Further, by tuning the electronic structure of these building blocks, it is possible

to impart not only a spatial structure but also electronic properties and chemical reactivity. They therefore have value as vessels for the construction of custom polymers with tailor-made structures and functionality.

MOFs, first developed in the 1990s, have mostly seen applications using gases and solvents, aiming for the adsorption and separation of these *micromolecules*. In contrast, this article describes MOF nanopores' ability to produce functional *macromolecular* (polymeric) materials. 500 publications per year now involve some combination of MOFs and polymers together, and it's not hard to see why as it becomes increasingly clear that the skillful use of MOFs allows nano-level chemical manipulation of not only organic polymers, but biological and inorganic polymers as well. As the possibilities for combinations of MOFs and polymers are endless, this area will continue to expand into a wide-reaching field with strong

impact on various academic disciplines and industries⁴⁻⁸.

Controlling polymer primary structures

DNA and proteins show us that biological systems can exert such strict control over their polymerizations' regiochemistry, stereoregularity, molecular weight, and sequence that they can't help but seem like the ultimate system when measured by the standards we currently apply to synthetic polymerization. Life's key to producing this kind of elaborate polymer structure is the highly accurate transcription of the molecular information held by nucleic acids, and it is within the organized nanopores of enzymes that it does this.

Similarly, when the micropores of MOFs are used as a vessel for polymerization, precise control over the structures of the polymers that come out becomes possible

(Figure 2)⁴⁻⁶. The history of this effort starts in 2005, with our development of the first polymerization method using a MOF nanopore⁹. Using the 1D channels of $[M_2(L)_2(\text{ted})]_n$ ($M = \text{Cu}^{2+}$ or Zn^{2+} , $L =$ terephthalate or its derivatives, $\text{ted} =$ triethylenediamine), it became clear that radical polymerization of vinyl monomers in their pores proceeds in a manner resembling living radical polymerization^{9,10}. Recently, Schmidt and Antonietti have also reported that they can exert greater control over the molecular weight by carrying out reversible addition-fragmentation chain transfer (RAFT) polymerization inside MOF spaces¹¹. Atom transfer radical polymerization (ATRP) utilizing the metals inside MOFs has also become possible, with developments progressing into precision polymerization systems using recoverable catalysts¹².

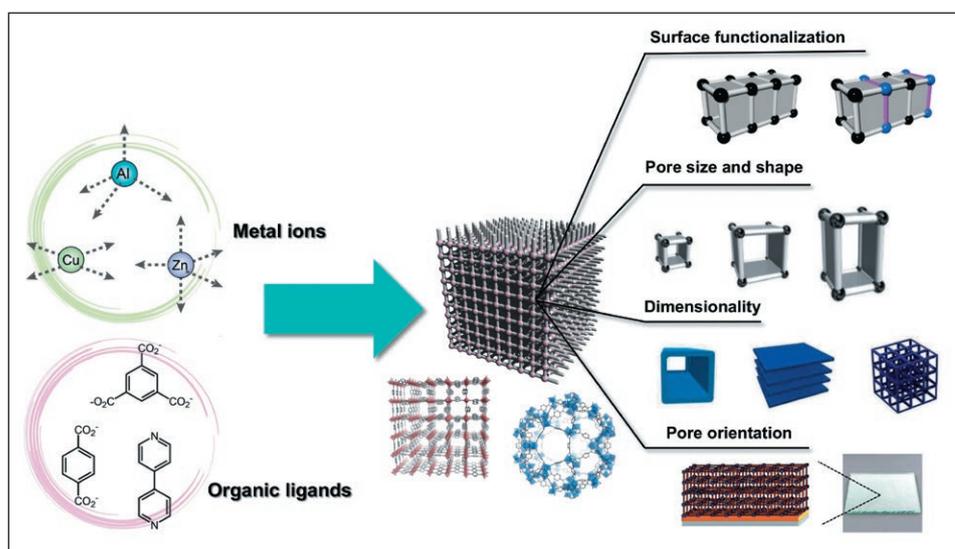


Figure 1: Schematic representation of MOFs.

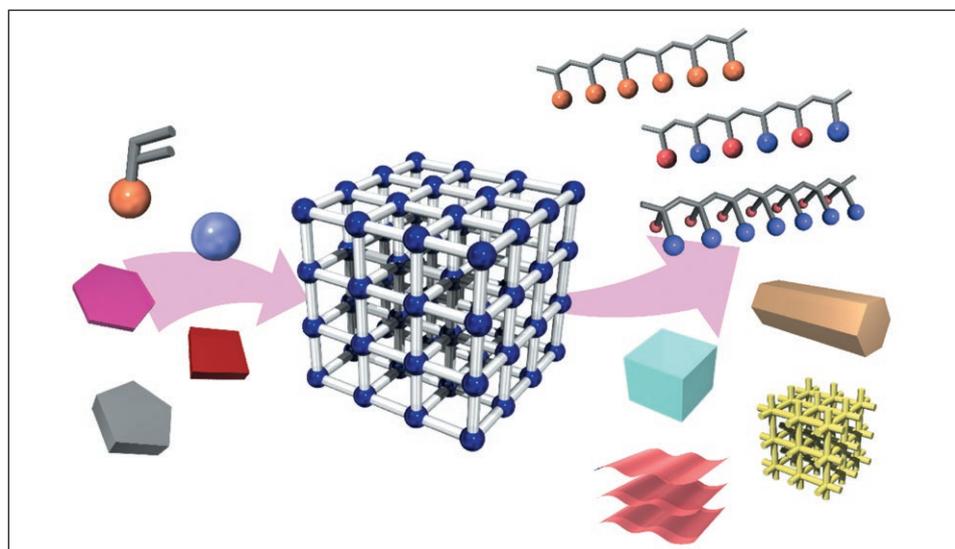


Figure 2: Polymerizations in MOFs allow multi-level controls over the structures of polymers, depending on the nanoporous structures of MOF templates.

When copolymerization is carried out in a MOF, monomer reactivities differ greatly to their behavior in solution. Recently, it was observed that immobilizing monomers on a MOF framework through coordinate or covalent bonding caused wide-ranging changes to the makeup of the resulting copolymer

Polymerization of vinyl monomers in MOF pores brings about polymers with stereoregularity that sensitively responds to the size and shape of the MOF space, as well as the presence or absence of unsaturated coordination sites^{10,13,14}. This makes the formation of highly isotactic polymers, which are otherwise difficult to achieve by radical polymerization, possible. By also using unsaturated coordination sites as polymerization catalysts, Dinca and co-workers achieved highly stereospecific polymerization of butadiene monomers using a MOF possessing cobalt-substituted metal sites¹⁵. Combining the aforementioned RAFT

and ATRP methods, simultaneous control over molecular weight, stereoregularity, and terminal structure has also become possible¹⁶.

When several kinds of monomers are simply mixed together and polymerized, the monomers usually connect randomly to one another, resulting in copolymers with no particular predetermined sequence. In contrast, when copolymerization is carried out in a MOF, monomer reactivities differ greatly to their behavior in solution. Recently, it was observed that immobilizing monomers on a MOF framework through coordinate or covalent bonding caused wide-ranging changes to the makeup of the resulting copolymer^{17,18}. For example, mixing 5-vinylisophthalate (S) and copper ions gives a MOF with a perfectly repeating space of 0.68 nm between the S units which are to act as monomers (Figure 3a)¹⁸. After introducing acrylonitrile (A) into the 1D channels of this MOF, carrying out copolymerization between the host and guest, and finally digesting the MOF, a polymer is obtained which has a structure consisting of perfectly repeating AAAS units (Figure 3b)¹⁸. This implies that precisely three A monomers fit and polymerize between each S embedded regularly along the 1D pores, and is a fascinating system for imprinting the periodicity of a MOF into a polymer.

Recently, Sada and co-workers found that the step-growth polymerization of immobilized monomers in a MOF is also capable of controlling the molecular weight of polymers, in contrast to solution processes¹⁹. Between all these studies, it has become clear that polymerization within MOF pores can play a strong part in the precision-controlled synthesis of polymers, regardless of the polymerization mechanism.

Aligning polymer chains

Polymers synthesized within MOF pores form in a state where their orientation is perfectly restricted by the crystalline space. If, perhaps, the template MOF could be removed without disturbing that state, it follows that it would be possible to control the aggregation structure of the polymers inside according to the dimensionality of the MOF used. Following this principle, it was discovered that polythiophene synthesized in a MOF's 1D pores give rod-shaped particles when said MOF is removed²⁰. Polymer chains in these particles are highly aligned along their long axis, and possess electrical conductivity on the order of 1000 times higher than that of polythiophene synthesized in solution. Further, when polythiophene chains are inserted into a chiral MOF, it has been shown that even upon removal of the MOF mold (that is, in the complete absence of a source of chirality), the isolated polythiophene continues to exhibit chirality²¹.

While this method of control over orientation and conformation is effective with respect to rigid, conjugated polymers, it remains unsuitable for the control of soft, vinyl polymers.

To that end, a polystyrene network wherein polymer chains are perfectly aligned along one axis was synthesized by partially introducing divinylated ligands – species capable of bridging the styrene chains – into the walls of a 1D channel MOF, then polymerizing styrene within²². In this system, polymer networks were crosslinked while completely aligned in a MOF space, so the alignment of the polymer chains was conserved after MOF destruction, and even withstood heat and solvent treatment. Recently, the synthesis of ultrathin-film 2D polymers of monomolecular thickness has been demonstrated by crosslinking within the

2D space of a 'pillared-layer MOF' (Figure 4)²³. These polymers display unique viscoelastic properties due to their unique topological structure, which completely excludes any interweaving of polymer chains.

While the control over polymer network structures such as functional gels and adsorbent materials holds great importance to advanced materials science and technology, the standard polymerization reactions carried out in solution inevitably form randomly arranged crosslinks, making such control difficult. By using a MOF possessing 3D connected pores as a template, however,

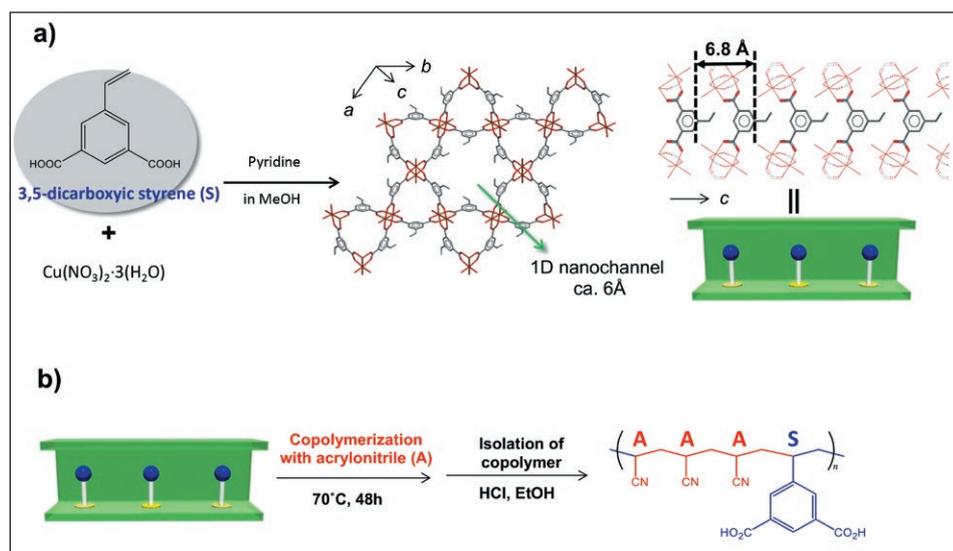


Figure 3: a) Formation of a MOF with styryl groups (S) periodically aligned along the 1D channels. b) Copolymerization of acrylonitrile with the MOF provides sequence-regulated copolymers reflecting on the periodicity of the MOF channels.

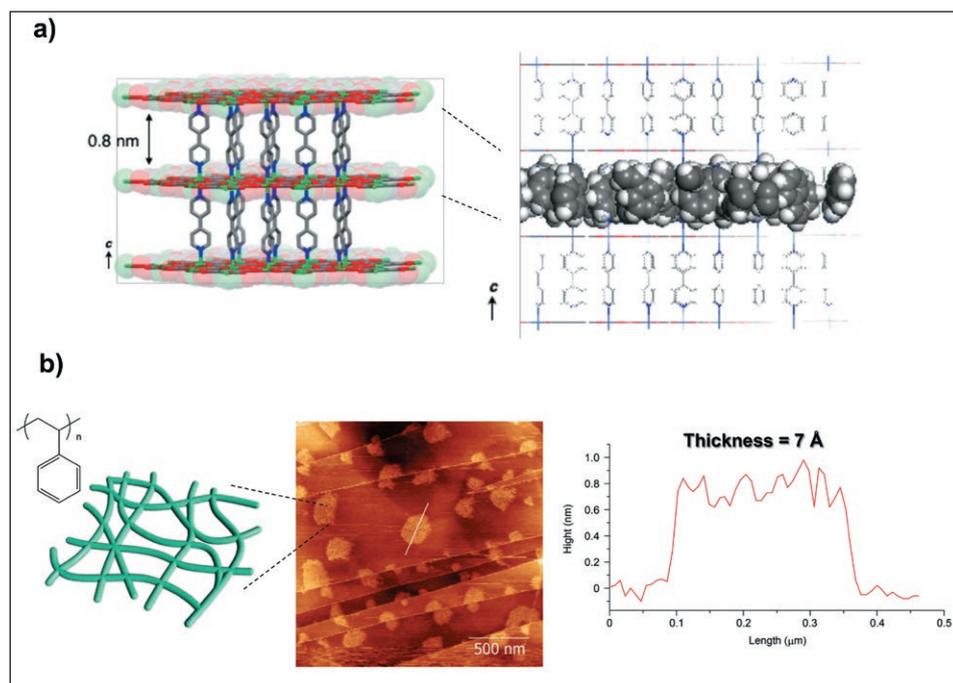


Figure 4: a) Crystal structure of a pillared-layer MOF and an MD simulation snapshot of the MOF containing styrene monomers. b) AFM image and height profile of ultrathin polystyrene film obtained from the MOF.

control of various polymer network structures becomes possible. For example, if the synthesis of a polysaccharide is carried out within the 3D channels of $[\text{Cu}_3(\text{btc})_2]$ (btc = benzene-1,3,5-tricarboxylate), polymeric particles possessing mesopores are obtained²⁴. As this type of material efficiently takes up guests such as drugs and peptide molecules, it is hoped to see use in biological applications such as drug delivery systems. Research is also being carried out into the precise control over bridged structures by carrying out host–guest cross-polymerization between monomer guests and reaction sites embedded into MOF ligands. For example, a ‘click’ coupling reaction proceeds efficiently between a tetraalkynyl guest and a MOF host possessing two azide groups on each of its ligands²⁵. Upon removal of the MOF’s metal atoms, a polymer particle with a shape reflecting that of the original MOF particle is obtained, and exposing this particle to solvent then expands it isotropically into a gel. More recently, success has also been found in designing anisotropically-expanding gels by using pillared-layer 2D MOFs as templates²⁶.

If all different types of polymeric material were mutually miscible, we could freely tune the functional properties of these polymers by simply mixing them, bringing about possibilities that would be unobtainable with mere homopolymers. However, the vast majority are instead mutually *immiscible*, resulting in the spontaneous phase separation of polymer mixtures. In our work, we have shown that mutually immiscible polymer species (such as polystyrene and methyl methacrylate) can be mixed on the molecular level by using the non-equilibrium approach of encapsulating different species of polymer inside a MOF’s pores, then removing the MOF²⁷.

Integrating MOF-polymer functions

By introducing polymer chains into MOF nanospaces, one can precisely control the

By enclosing conductive polymers like polythiophene in MOF pores, changes in hole mobility could be induced depending on the number of polymer chains aggregated together

number of interacting polymer chains, their alignment, and their surrounding environment. Accordingly, it becomes possible to characterize the physical properties of either one or several polymer chains in isolation, which are distinct from those in the bulk state. Accordingly, we have revealed that the nanoconfinement in MOF channels has marked effects on the dynamics as well as the thermal behaviors of the encapsulated polymer chains^{28,29}.

By enclosing conductive polymers like polythiophene in MOF pores, changes in hole mobility could be induced depending on the number of polymer chains aggregated together³⁰. Preparing such a host–guest complex gives a material possessing a combination of both porosity and conductivity, and this was further developed into sensor materials capable of detecting guest NO_2 gas at the ppb level by measuring their impact on host conductivity³¹. It has also been shown that donor-acceptor structures can be rationally assembled at the molecular level by forcing them to reflect anisotropic MOF framework structures. By first preparing a MOF with

titanium oxide nanowires (acceptors) present in its pores, then synthesizing polythiophene chains (donors) in the 1D channels, a perfectly alternating array structure was achieved (Figure 5)³². Investigations showed that this array creates long-lived charge separation states, with the half-life of the charged species exceeding 1 millisecond – about 1,000 times longer than that of any other reported titanium oxide system. Results like this provide a useful guide to building new materials to raise the efficiency of photoelectric devices, and draw attention to their possible applications in solar cells.

The above methods all focus on the post-synthetic introduction of polymers to form host–guest complexes. In contrast, if we instead use polymers which incorporate ligands that can make up a MOF, we may create hybrids where these materials are connected directly by covalent bonds. Cohen and co-workers are researching what they call a ‘polyMOF’ – a complex where polymers with repeating units containing terephthalate (a common MOF ligand) are incorporated directly into the MOF structure by mixing them in during the MOF synthesis process³³. Building complexes like this enhances properties such as the stability and hydrophobicity of the MOF, and there are even cases where the MOF crystals form structures resembling thin films. Recently, the Johnson group has been carrying out the synthesis of polyMOF nanoparticles using block copolymers³⁴. In this system, MOF crystals are formed around blocks of ligand moieties in the polymer while the remaining blocks encircle the outside, resulting in nanoparticles with decorated surfaces. In short, the use of block copolymers as precursors enables simultaneous control over both the MOF nanoparticles and their surfaces.

Practicality issues arise in many cases when MOFs in particle form are considered for use in real-world implementations. As such, there are times when MOFs are simply mixed with

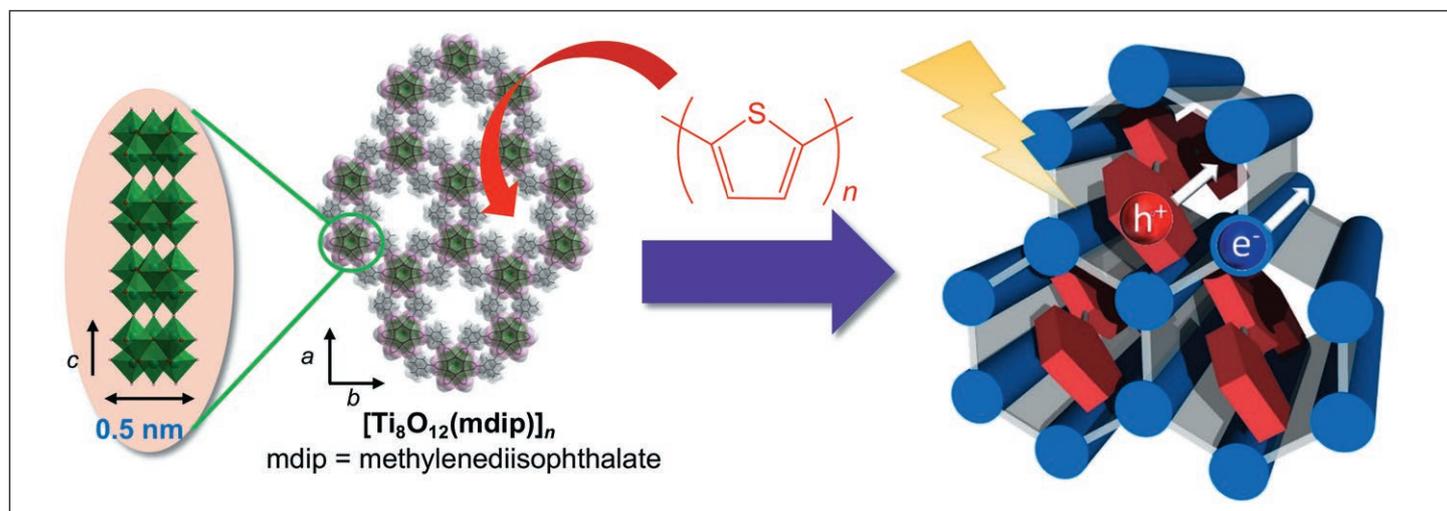


Figure 5: Fabrication of a perfectly alternating donor–acceptor architecture at the molecular level.

various polymers to form mixed-matrix membranes. Compared to the conventional inorganic fillers, MOFs' hybrid organic-inorganic structures display high compatibility with polymers. Complex membranes constructed using this method have already shown excellent functionality as gas separation membranes, nanofiltration membranes, and solid electrolytes³⁵.

Separating desired polymer chains

Polymers are made up of chains containing countless monomer units, and can thus have any number of diverse and distinct structures. While sequence disorder is of course present in the case where a mixture of several monomers is used, a statistical distribution of molecular weights is observed even if only one monomer type is used. Stereo- and regiochemical control are often difficult to achieve, and thus the polymeric materials we use in our daily lives consist of mixtures of various types of polymer chain. It goes without saying that the polymers' structures determine their physical properties, and so the isolation of specific desired polymers from mixtures is extremely important both academically and industrially. This is no simple task, however, due to the complete ineffectiveness of standard chemical separations (distillation, recrystallization, solvent extraction, etc.) with respect to polymer-polymer mixtures. Essentially, even if there were a different moiety present at some point in a polymer chain, we could not usually single that moiety out and isolate only the polymer chains that possess it in a designated location on the chain. On top of that, polymers undergo self-entanglement unique to the chain-like nature of their structures, so even in solution they exist in states which constantly bend and knot themselves together, leaving us no option but to process them as 'clumps'. For this reason, one could discriminate between polymers based on 'clump' size (which is proportional to chain length) using size-exclusion chromatography, but recognition and separation according to some minute change of structure within a long chain (large 'clump') was impossible.

Recently, our group has sought a resolution to this problem by methods utilizing the adsorption of polymers into the nanopores of MOFs^{29,36,37}. While such a description makes it sound simple, at the time it was considered common sense that the very idea of polymers adsorbing into channels on the sub-nanometer scale would be impossible, due to the great loss of entropy it would entail. In fact, there were no reported examples of their adsorption into conventional microporous materials – zeolites – either. Nevertheless, by shunning 'common sense' we were able to find that many polymers *do*, in fact, spontaneously penetrate into MOF

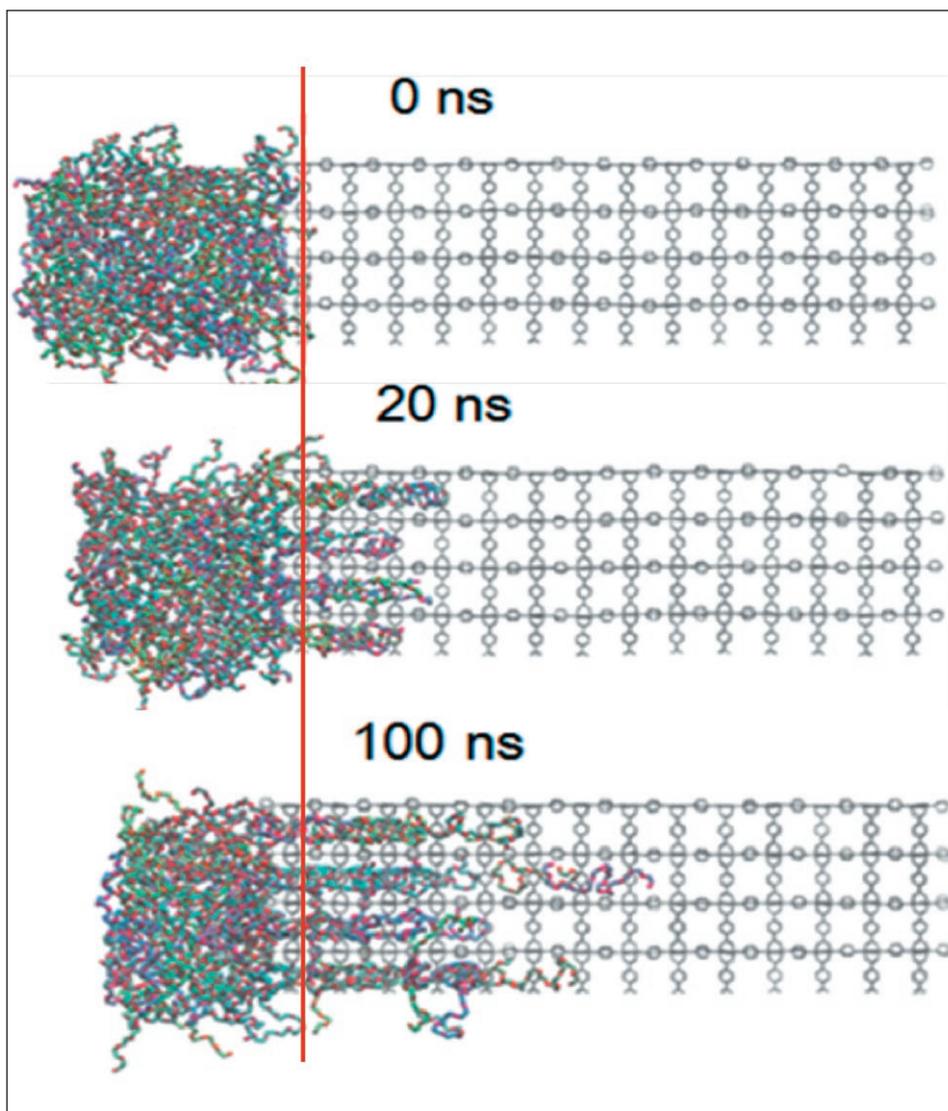


Figure 6: Time-evolved snapshots from MD simulations of PEG (Mw = 600 g/mol) intercalated in [Zn₂(terephthalate)₂(triethylenediamine)]_n.

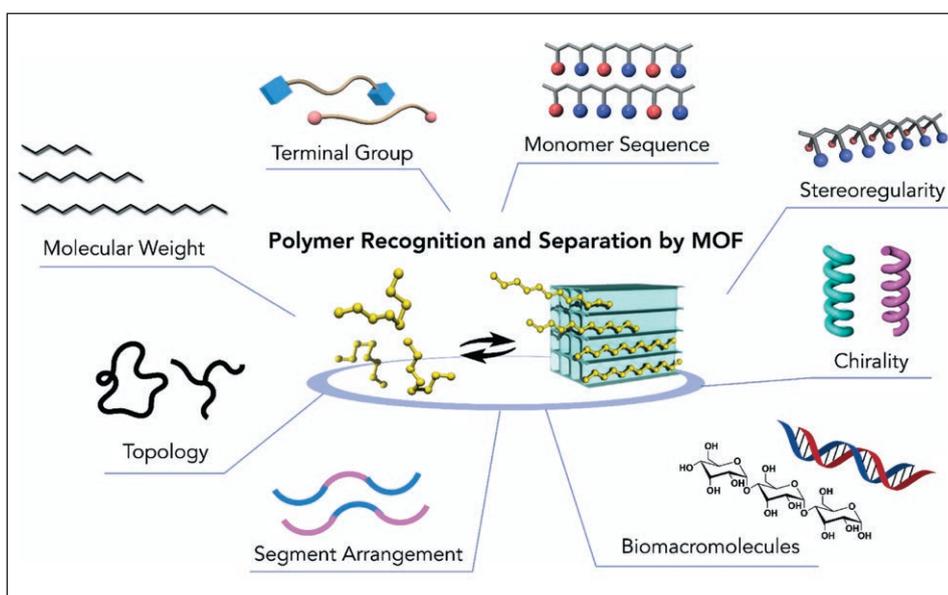


Figure 7: Well-defined nanopores of MOFs serve as a universal workspace for high-precision polymer recognition and separation, which is not possible with conventional methods.

nanospaces, even into those whose radii number in the angstroms (Figure 6).

This phenomenon opens doors to the previously non-existent concept of ‘precision polymer separation’^{7,8}. For example, polymers which differ only by terminal structure experience less and less influence from the terminals as their chains become longer (i.e. as the terminal becomes a smaller component relative to the whole chain) and so existing methods have proven incapable of recognizing and separating them based on this difference. Using MOFs, our group has succeeded in discriminating between polymer chains which possess molecular weights in the tens of thousands of Daltons, and differ only by their terminal structure³⁸. Further, we have carried out liquid chromatographic separation using prototype columns loaded with MOF particles^{37,39}. The result was a shocking level of recognition, with retention times differing enough to discriminate in response to changes as small as one atom on a long polymer chain. As this method disentangles polymer chains into linear arrays along the MOF pores, it enables structural recognition without neglecting any features within the chain, some of which might otherwise be shrouded by the outer layers of an aggregate structure. Various types of polymer separation have been realized based not only on molecular weight³⁷, but topological differences such

as cyclic-versus-linear⁴⁰, or even monomer composition within a copolymer, making this a macromolecular recognition-separation system of unparalleled precision (Figure 7).

Developing “urban oil wells”

Our new approach of polymer separation can provide structurally controlled polymers without the use of tedious synthetic techniques. These could then be used as enhanced plastics in applications such as electrical devices and medicine, bringing prosperity to our everyday lives. However, looking at the results of a survey by the Japan Plastics Industry Federation (JPIF)⁴¹, we find that for 20 years consumers’ impressions of plastics’ “usefulness” has remained consistently high, and that most are already satisfied with the ‘work’ plastic does for us (Figure 8).

A point that’s cause for concern, however, is the “Environmental friendliness” and “Resource efficiency” categories, where public opinion has abruptly fallen in recent years (Figure 8)⁴¹. One major reason for this is a raised awareness of the pollution problems plastic litter causes, and people continue to celebrate switches toward bioplastics and biodegradable materials in response to this. Such materials do not actually solve the problem in marine environments, however, and the United Nations Environment Programme (UNEP) has stated



as much – biodegradation occurs in conditions that rarely ever occur in our oceans, and concern has been raised that hiding such a fundamental problem behind an ‘eco-friendly’ image may actually worsen the situation⁴².

Returning to the survey (Figure 8), and the fact that nearly 100% of respondents were satisfied with plastics’ performance⁴¹ – one way to read this would be that what we have already is completely sufficient as-is. From that standpoint, it would be best to let a perfectly satisfactory plastic do its job again and again, so our society must consider having plastics which fulfilled their role once do so multiple times by way of recycling. The current reality, however, is that in Japan roughly 60% of waste plastic resources end up undergoing combustion (in solid fuel, electricity generation, and other applications) by a process called ‘thermal recycling’, with the range of products reused as actual plastics (‘material recycling’) restricted mainly to those made of PET⁴³. The reason renewal of other plastics remains stagnant is that they form various mixtures, complexes, and composites from which pure polymers cannot be effectively separated⁴³. So here too, we see that current technology’s inability to separate desired polymers out of a mixture is connected directly to a societal problem.

We are confident our MOF method can perform this separation, having witnessed its capabilities in lab-scale separations of simple polymer mixtures. However, real-world application will bring new technological challenges in both the processing of unpredictable mixtures and the upscaling of this process, and even if it proves to be possible in principle, there would be no meaning in doing so if the process takes an excessive amount of energy or creates an extreme environmental burden of its own. Complex socioeconomic factors will also have to be accounted for. But at the end of the line, could we not consider the plastics welling up in the streets a high-quality “urban oil well”? We dream of a future for society where plastic no longer piles up, but is used in cycles just as water and air are. ◆

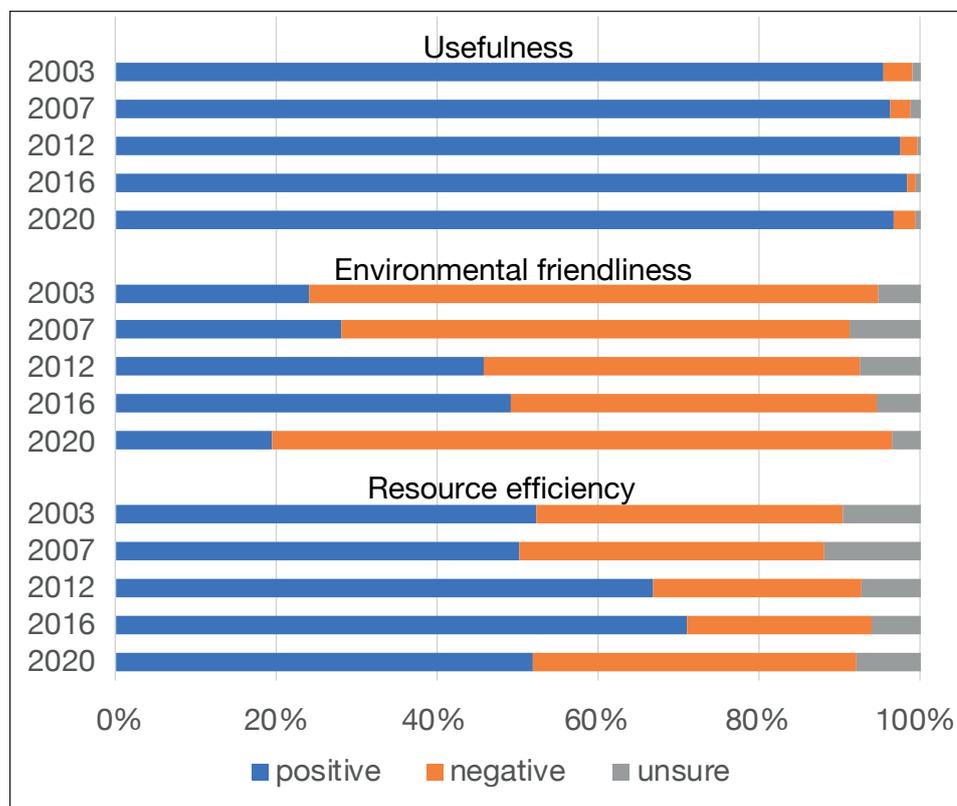


Figure 8: Impression of plastics surveyed by the Japan Plastics Industry Federation (JPIF).⁴¹

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