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MATERIALS  
SCIENCE

# NIMS NOW

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Innovations  
Made Possible

by **Polymers**

Materials Synthesis Technology Based on Organic Molecular Networks Project



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Made Possible

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on Organic Molecular Networks Project

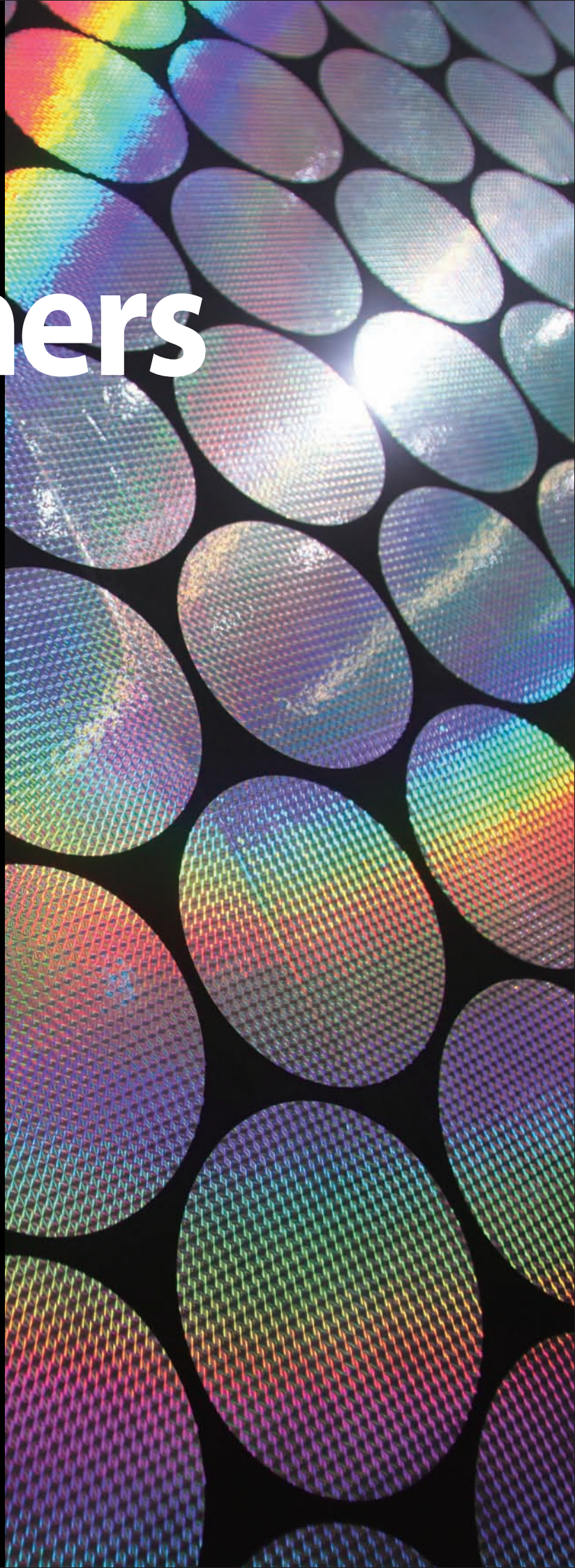
In polymer science, precision network structures that control the movement of molecules, ions, and electrons are designed and analyzed utilizing nanotechnology.

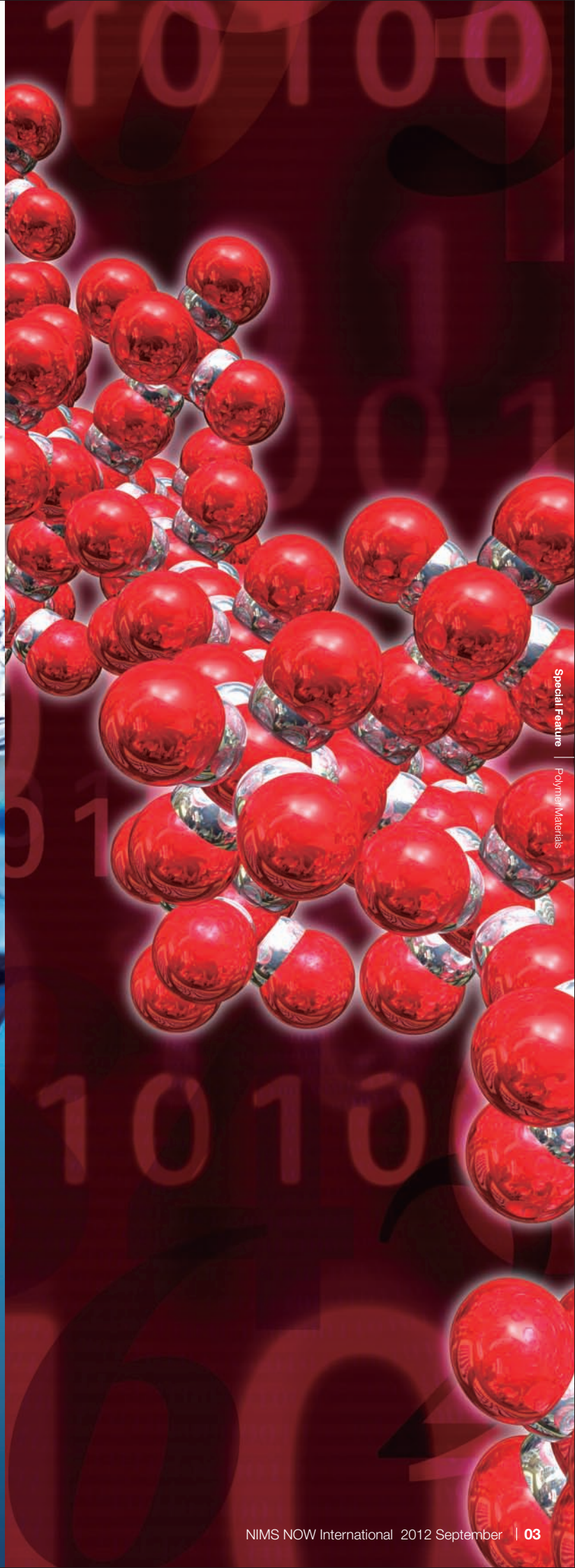
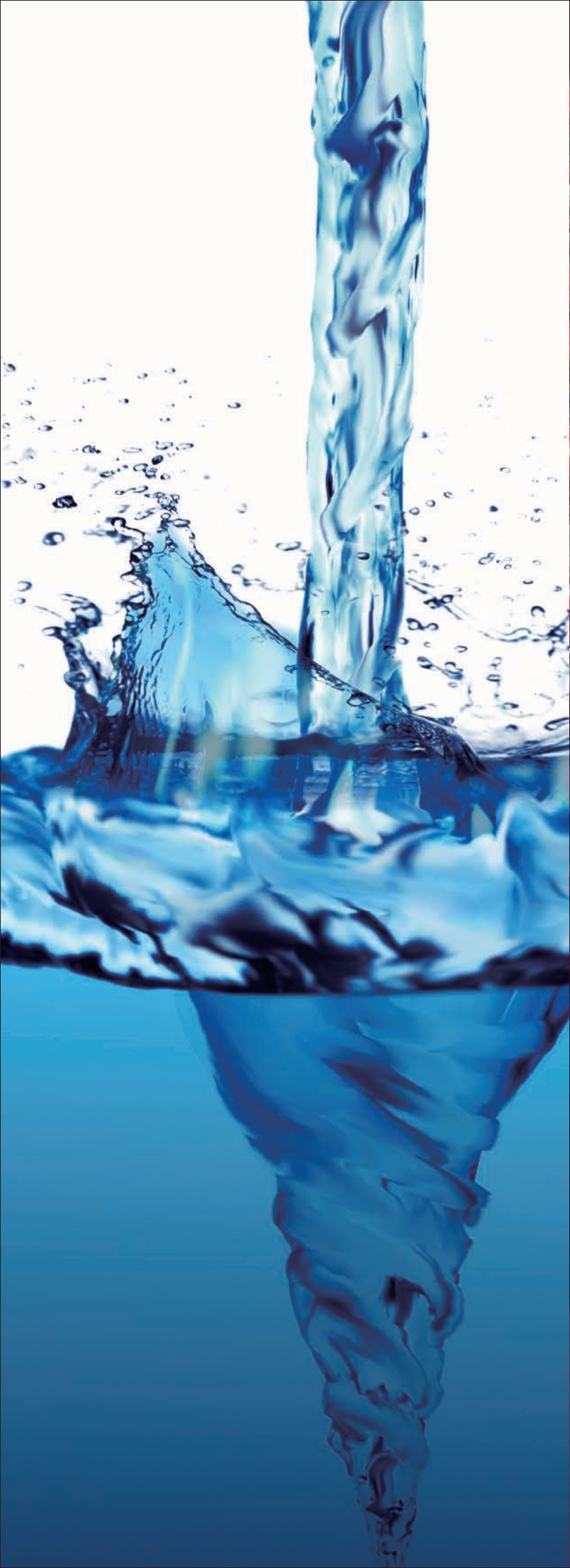
The range of applications of polymer science includes not only energy and the environment, as represented by water treatment, but also extends to information and communications and medical field. In the future, we will also explore even newer fields.

On the other hand, we are also working to meet the need for higher performance in fields where polymers have long been used, and to be meaningful, this improvement must be "dramatic."

Extending the realm of possibility, and dramatically improving existing performance: By realizing these two goals at the same time, we believe that we can truly change the world.

Because nanotech isn't magic, it's a reality that can be achieved.





Special Feature  
Polymer Materials

# Materials Synthesis Technology Based on Organic Molecular Networks Design Guidelines for Polymer Materials for Raising Performance to Its Ultimate Limit

Unit Director,  
Polymer Materials Unit, Advanced Key Technologies Division  
**Izumi Ichinose**

## Aims of NIMS in the polymer materials field

Polymer materials are actually used in a wide range of applications, from familiar materials like plastics and rubber to optical communications and electronics devices. Because polymer materials can be processed under moderate conditions, and are also lightweight and have excellent properties, their importance has steadily increased in recent years.

After NIMS was reorganized as an Independent Administrative Institution (IAI) in 2001, the polymer materials research area was gradually expanded, and polymer research was designated as a project under the NIMS Five-year Plan in 2006. Since 2011, project research has been underway with the aim of developing new polymer materials that contribute to the information technology (IT), environment and energy, and medical fields from the viewpoint of returning research results to society through innovation.

The Polymer Materials Unit is responsible for the above-mentioned project research, which is entitled "Materials Synthesis Technology Based on Organic Molecular Networks." Our aim is to substantially improve material performance by

designing precision molecular network structures which can control the movements of molecules, ions, and electrons.

Network structures are key to material design. For example, to store or separate gases and liquids, a molecular level network structure is indispensable. Likewise, to achieve high performance in displays and fuel cells, it is necessary to realize high speed transfer of electrons and ions, and to achieve this, it is important to design the optimum pathway for charge carriers. Clarifying the diffusion coefficient in organic molecular networks and the mobility of electrons and ions is also extremely important.

At NIMS, our goal is to develop non-conventional high performance polymer materials by a comprehensive approach that encompasses synthesis of polymers, formation of thin films and nanoporous materials, evaluation of molecular permeation properties, and evaluation of ion/electron conductivity. Application fields for these materials span a wide range, from materials with separation function, such as water treatment membranes, gas separation membranes, adsorbents, etc., to electron and ion conductors with the potential to become defact standards, fluorescent coating and hologram memory materials, and smart gels that can be used in displays, arti-

ficial muscle, etc. (Fig. 1).

It is also important to create materials which are tough, strong, and durable while maintaining the distinctive flexibility of polymer materials. From this viewpoint, molecular network structures are an indispensable element in controlling the mechanical properties of materials.

## The ideal form of project research

Japan's material makers have created excellent products, and many of those materials boast overwhelming strength in the market place. Polymer materials are no exception. In fact, the further upstream a material is, the global share tends to increase. However, this is no cause for complacency. To ensure high profitability in polymers, we must continue to supply basic materials which cannot be replaced with any other substitute. The key to this is ceaseless technological development. It is also essential to develop unprecedented new applications from fresh starting points. We hope to contribute to society by developing new materials that are effective in applications such as wearable electronic devices, which take advantage of the lightweight, soft texture of the material.

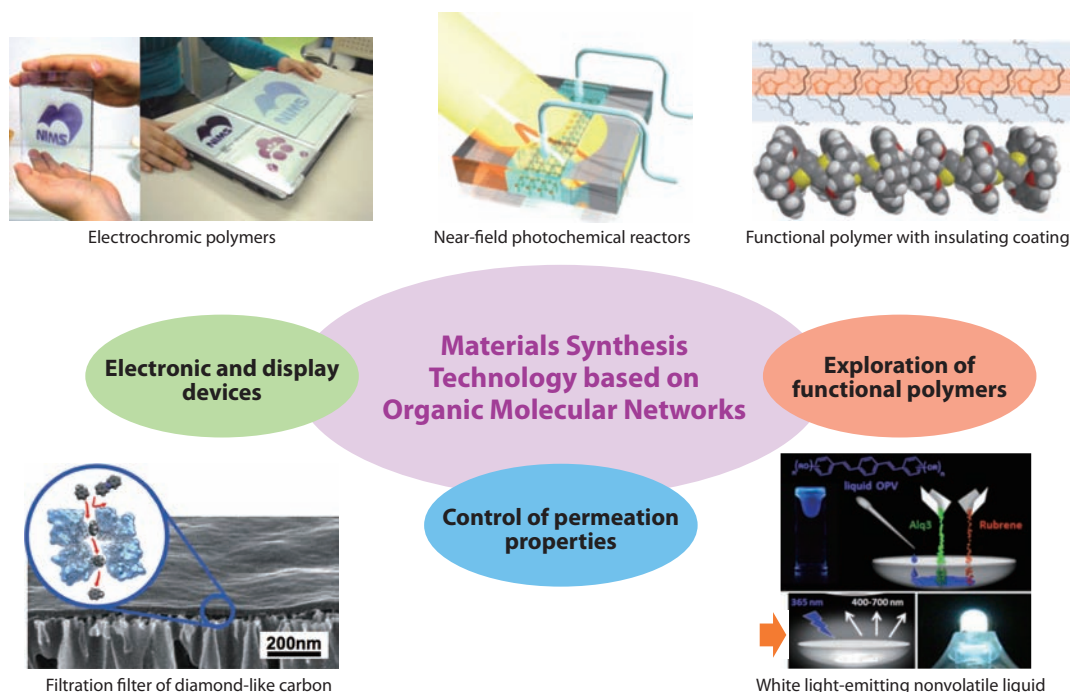


Fig. 1 Topics of polymer materials research at NIMS.

On the other hand, one role of NIMS in polymer research is to clarify design guidelines for improving the performance of materials to its ultimate limit. For this, a return to material creation is indispensable. It is important to perform molecular design of new polymer materials and actually synthesize those materials, aiming at the targeted performance. To realize the full performance of polymer materials, control of phase separation and the cross-linked structure and optimization of processing processes at the nanoscale are necessary. To improve material performance, it is important to elucidate the microstructure of the network structure and to evaluate the behavior of electrons, ions, and molecules in that structure as accurately as possible. We are working to elucidate these issues utilizing the advanced characterization technologies in the NIMS Advanced Key Technologies Division, and also proposing new characterization methods.

### From water treatment membranes to electronic paper

Research in this project is divided into the following three sub-themes (Fig. 2).

1. "Development of separation functional

materials."

In this area, we are developing water treatment membranes which are capable of efficiently separating dyes, proteins, and other substances by high density cross-linking of polymers. As a recent result, we fabricated an ultra-thin filtration membrane that is capable of purifying oil using diamond-like carbon, and succeeded in improving performance by 3 orders in comparison with commercially-available filtration membranes (see p.11). We are also developing polymer nanofibers with a network structure with the aim of application as a high volume adsorbent in place of activated carbon. Our goal is to supply new separation technologies which are effective and offer outstanding energy efficiency.

2. "Exploration of optical and electronic functions."

Here, we are developing new conductive polymers and organic light-emitting materials utilizing excellent organic synthesis technologies. Based on our research to date, we have discovered that the mobility of electrons in molecules can be dramatically improved by creating conductive polymers with rigid polymer chains. As a light-emitting material, we are developing a nonvolatile liquid which emits white light and can be coated on a variety of

materials. We also expect to pioneer new optical and electronic functions by hybridization of the materials which we are developing with fluorescent dyes, optical plastics, and similar materials.

3. "Verification of device functions."

In addition to the organic and polymer materials synthesized under the other sub-themes, we are synthesizing new cross-linked polymers, producing thin films of these materials, and evaluating their performance as electronic and display devices. In particular, we have confirmed stable, high speed oxidation-reduction behavior in organic/inorganic hybrid polymers in which transition metal ions are included in the main chain of the polymer, and applications of these materials as electronic paper and smart windows are expected. At the same time, we are also elucidating the basic physical properties of organic materials by field effect transistors.

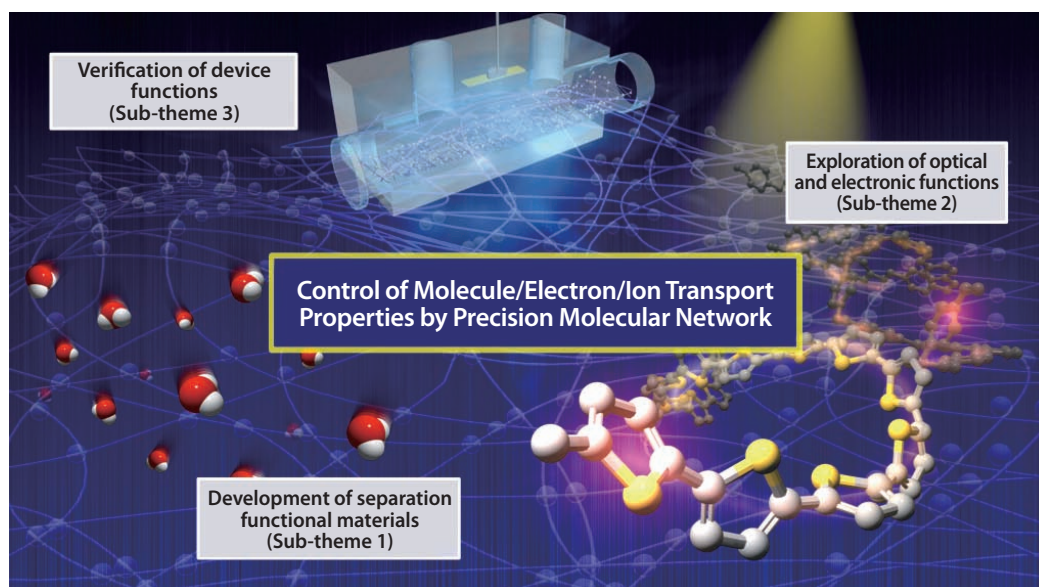


Fig. 2 Structure of research sub-themes.

## Separation Functional Materials for Solving Global Scale Problems

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### Depletion of water resources

Accompanying the rapid growth of the world's population and the economic development of the developing nations, shortages of water resources are becoming a serious global problem. Since oceans account for more than 2 times the surface area of land, a large quantity of water exists on the Earth, but because seawater contains 3-4% salt, it is impossible to drink this water directly or use it in everyday life. In many countries, pollution of rivers and groundwater is becoming more serious every year. In fact, there are only 10 or so countries where it is possible to drink tap water without some kind of treatment. Although agriculture in the regions with little water uses groundwater, the level of the groundwater is decreasing annually. The development of new ore deposits, oil fields, and gas fields is also a considerable factor in worsening water problems. Against this backdrop, excellent separation functional materials which are capable of purifying water, will be increasingly demanded in the future.

### Design of nanopores

In improving the performance of separation functional materials to their ultimate limits, rational design of the pore size is important. For example, polymer membranes that have pores with a size of 1 nm or less, which selectively permeate only water molecules, are used

in desalination of seawater. In surface water treatment, polymer membranes with a pore size of several 10 nm are necessary for removing bacteria and viruses. In the intermediate in size between these two, membranes that can separate proteins and nanoparticles are promising in the manufacture of next-generation pharmaceuticals and the high purity chemical reagents used in the semiconductor industry. Nanoscale pores can also be useful for condensing designated gases and vapors and for removing harmful substances from water. Thus, separation technology using this series of nanoporous polymers is an important part of the social infrastructure.

### Separation functional materials developed at NIMS

Because separation processes are generally highly energy intensive, improved energy efficiency can result in substantial cost reductions. Treatment speed is also a key point in the development of practical separation technology. In the NIMS Separation Functional Materials Group, our aim is to achieve overwhelmingly high speed in separation processes by developing new polymer materials (ultrathin films, membranes, and adsorbents) with pores of nanoscale size. For example, with newly-developed porous carbon films, our research has made it possible to perform high speed filtration of organic solvents such as hexane, benzene, and others which had been difficult until now, realizing improved performance more than 1000 times higher than that of commercial separation membranes. By developing thin films of cross-linked polymer nanoparticles or designing highly a dense polymer network structure, we achieved high speed separation of proteins (Fig.). Research project of high performance polymer adsorbents for removal of harmful substances dissolved in water or refining of valuable gases is also progressing.

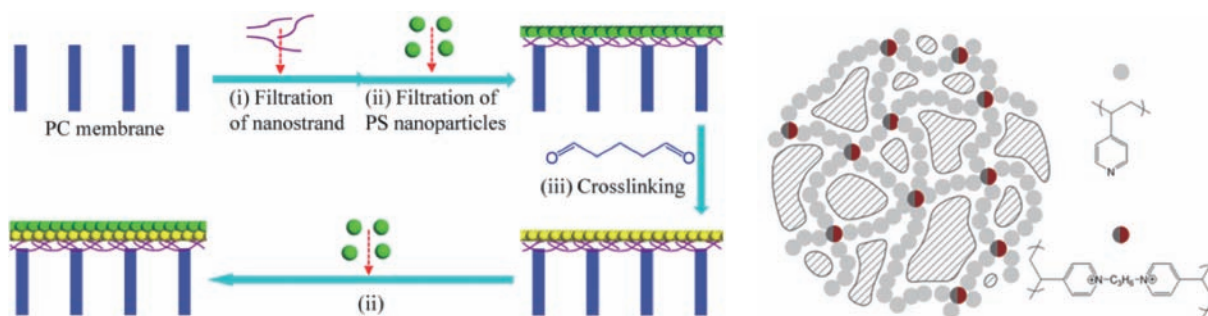


Fig. (Left) Manufacture of filtration filter by cross-linking polymer nanoparticles and (right) polymer network capable of separating proteins.

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# Aiming at Construction of Innovative Devices by Orientation and Arrangement Control of Organic Materials and Metal Nanoparticles

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## Controlling the orientation of organic molecules

We are engaged in the development of thin film forming processes that can control molecular orientation. These techniques are indispensable for realizing the "organic materials with high speed electron/ion transport" created by designing precise molecular networks, and for constructing innovative electronic devices using those organic materials.

Although it is now possible to control the stack structure of adjacent molecules by advanced molecular design, it is still difficult to control the molecular orientation at a macroscopic (actual device size) scale. To accomplish that, modification of the substrate surface on which the molecular thin film is formed, or some type of ingenuity when forming the thin films, is necessary. In this sub-theme, we are focusing on photo-aligned polyimide (PI) films as a modification of the substrate surface, and the flow coating method as a film forming solution-process that enable us to align molecules at a macroscopic scale.

The backbone structure of our PI materials can be aligned by irradiation with polarized ultraviolet light. Its two-dimensional alignment pattern can be formed easily by polarized light exposure through a photomask. To date, we have successfully induced anisotropic orientations of organic semiconducting molecules, such as pentacene and polyfluorene deriva-

tives, by using the photo-aligned PI films as a pre-deposited alignment layer. This photo-alignment technique is useful for integrating high performance organic devices, because the optimal molecular orientation can be achieved for each device on the same substrate.

The flow coating method illustrated in Fig. 1 (a) is a film forming solution-process in which preferential molecular alignment is induced by movement of the contact line (solution/substrate/air boundary line). This method enables a large area coating from a tiny amount of solution with a relatively short processing time. We succeeded in forming a highly-oriented 6,13-bis (triisopropylsilylethynyl) pentacene [TIPS-pentacene] thin film (Fig. 1 (b)), which showed a mobility of  $\sim 1 \text{ cm}^2/\text{Vs}$  in a bottom gate/bottom contact type field effect transistor (FET).<sup>1)</sup> Since there is no molecular orientation control method applicable to all kinds of molecules, we are constantly grappling with the development of new molecular orientation control methods.

## Controlling the arrangement of nanoparticles

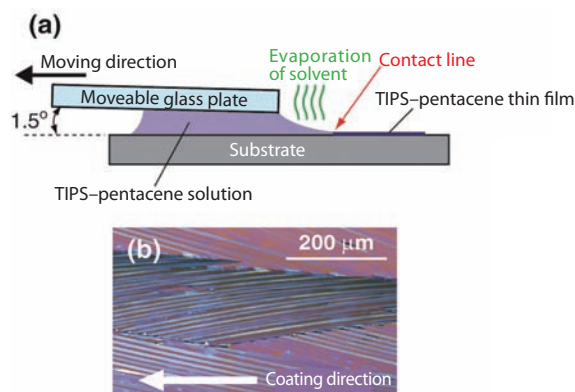
We have begun research in a new interdisciplinary field combining of chemistry and near-field light, which is generated only in the vicinity of metal nanoparticles. Near-field light is the nanotechnology that is the principle of the

scanning near field microscope (SNOM), which provides spatial resolution on the order of 50 nm. Since near-field light has physical properties of light like those of transmitted radiation, and thus is linked horizontally to a number of fields, such as telecommunications, electronic engineering, energy, and photochemistry, a wide range of applications is conceivable, including optical communications, optical sensors, photovoltaic cells, photocatalysts, etc. In these fields, it is necessary to realize large-scale communication traffic volume, sensor sensing capacity, energy power generation, and catalyst reaction material production volume. Because nanoscale point light sources are inadequate for this, practical light sources with a large area on the square centimeter to square meter order are indispensable.

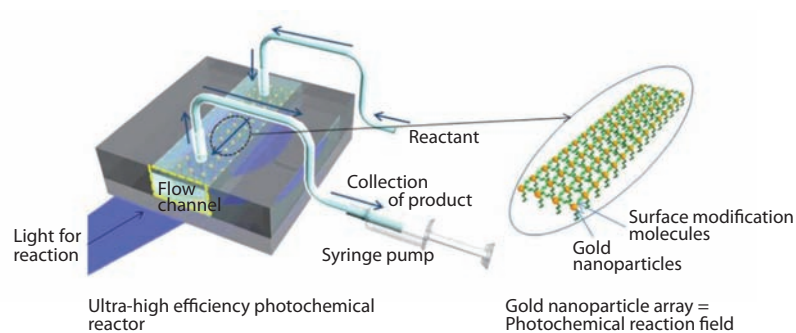
We succeeded in developing a large area near-field light source by arraying trillion of point light "near-field light" sources on a substrate with a size of  $1 \text{ cm}^2$ .<sup>2)</sup> We have also successfully conducted a test demonstration of a high efficiency photochemical reactor (Fig. 2) in which this large area near-field light source was integrated in a fluid device.

### References

1. K.Sakamoto, J.Ueno, K.Bulgarevich, K.Miki, *Appl. Phys. Lett.* **100**, 123301 (2012).
2. K.Isozaki, T.Ochiai, T.Taguchi, K.Nittoh, K.Miki, *Appl. Phys. Lett.* **97**, 221101 (2010).



**Fig. 1** (a) Flow coating method, and (b) polarizing microscope image of a highly-oriented TIPS-pentacene thin film fabricated by the flow coating method.



**Fig. 2** Ultra-high efficiency photochemical reactor using a large-area near-field light source. When the large-area near-field light source by arraying trillion of point light "near-field light" sources on a substrate with a size of  $1 \text{ cm}^2$  (right) is put in the flow channel of the fluid device, the gold nanoparticle arrays provide their vicinities strong photochemical reaction fields with the help of high intense near field lights.

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## Optically/Electronically Functionalized Organic/Polymer Materials

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### Aiming at realizing unexplored physical properties/functions of $\pi$ -conjugated organic/polymer materials

$\pi$ -conjugated organic and polymer materials can possess excellent electrical and optical properties. Strong expectations are placed on these materials as next-generation essential materials in fields related to electronics, the environment, and energy. The objectives of this sub-theme are to develop novel  $\pi$ -conjugated organic and polymer materials in which unique/uncommon properties can be recognized in the structure as such, to understand the effects of material structure on optical and electronic properties, and realize functions as targeted. The physical properties and functions of a single organic material do not necessarily determine the properties and functions of the bulk material; in many cases, it is possible to realize unexplored new optical and electronic functions by precise design and integration. For this reason, we are engaged in research with a dual focus on understanding the interactions between molecules and material synthesis based on applications/characterization of physical properties.

### Optical/electronic properties made possible by new structures

Many of the  $\pi$ -conjugated organic materials display excellent light-emitting properties. One of these is oligo phenylenevinylene (OPV), which consists of an alternating arrangement of benzene rings and double bonds. Nakanishi et al. developed an organic material, which is a liquid state at room temperature without solvent, by surrounding and isolating OPV with flexible alkyl side chains.<sup>1)</sup> Interaction between molecules is prevented by surrounding the OPV core with the branched chains, thereby maintaining the blue light-emitting property, etc. of the OPV seen in monomeric solution. A new liquid material which emits white light with high luminescence was developed by

blending a light emitting solid dopants, using this blue light-emitting liquid as a nonvolatile solvent (Fig. 1).

Sugiyasu et al. synthesized a new polymer structure like an "electric cord" by wrapping polythiophene, which is one of the semiconducting polymers, with insulating cyclic molecules (Fig. 2).<sup>2)</sup> This polymer has an extremely developed  $\pi$ -conjugated system (long conjugated wire length) originating from its rigid backbone. As a result, high charge carrier mobility along the single wire of polythiophene was realized.

Kobayashi et al. are engaged in development of electronic functions of organic salt-bridge materials under the Funding Program for Next Generation World-Leading Researchers (NEXT Program) of the Japan Society for the Promotion of Science (JSPS), and succeeded in realizing functions, beginning with conductivity, by direct

use of salt-bridge formation for manifestation of the properties of organic materials.<sup>3)</sup> Research is continuing to reveal that the electronically-active salt-bridge materials display various electronic functionalities that are greatly different from those of the conductive organic materials known to date.

1. S.S.Babu, J.Aimi, H.Ozawa, N.Shirahata, A.Saeki, S.Seki, A.Ajayaghosh, H.Mohwald, T.Nakanishi, *Angew. Chem. Int. Ed.*, 51, 3391 (2012)
2. K.Sugiyasu, Y.Honsho, R.M.Harrison, A.Sato, T.Yasuda, S.Seki, M.Takeuchi, *J. Am. Chem. Soc.*, 132, 14754 (2012)
3. Y.Kobayashi, M.Yoshioka, K.Saigo, D.Hashizume, T.Ogura, *J. Am. Chem. Soc.*, 131, 9995 (2009)

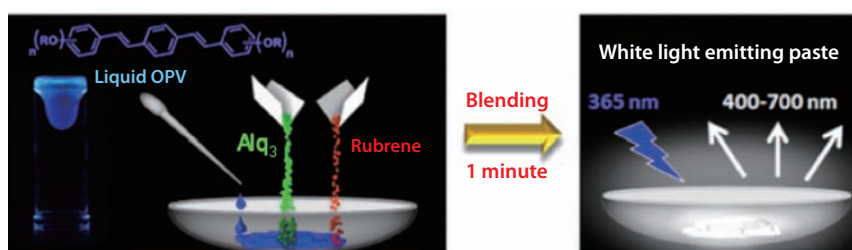


Fig. 1 White light emission using room temperature liquid material.

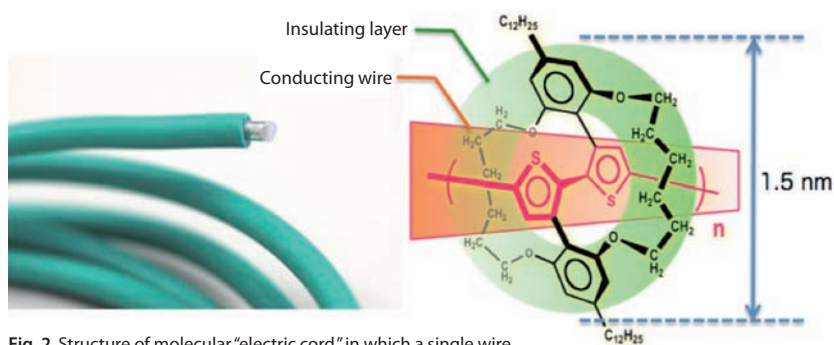


Fig. 2 Structure of molecular "electric cord," in which a single wire of a conducting polymer is covered with an insulator.

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# New Polymers Formed by Noncovalent Bonds: Discovery of Unique Electronic Functions and Application to Dream Displays

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## The world of new polymers created by noncovalent bonds

In organic macromolecules (polymers), polymer chains are formed by strong covalent bonds, producing materials which are lightweight, flexible, and strong. Plastics and other products which take advantage of these features make our lives more convenient.

In order to open the way to new functions that cannot be realized with conventional polymers, we are focusing on comparatively weak noncovalent bonds, such as hydrogen bonds, developing new polymers introducing those bonds, and applying the resulting materials to devices.<sup>1,2)</sup>

This article presents two examples of our recent research, a polymer which changes color in response to electrochemical oxidation/reduction (redox), and a polymer which emits lights when it detects vapors in the air.

## Electrochromic polymer: Power saving color electronic paper

Materials which change color in response to electrochemical redox are called electrochromic materials. Inorganic materials like tungsten oxide and organic materials like polythiophene are representative examples of these materials. We discovered that organic-metallic hybrid polymers formed by coordination bonds, which are one type of noncovalent bond, have excellent electrochromic properties.<sup>3)</sup> Because the color change in these materials is based on redox

of the metal ions, the polymer color itself depends on the charge transfer absorption from the metal ions to the organic part (Fig. 1). Unlike conventional electrochromic materials, these materials have the following features: (1) abundant color variation: it is possible to obtain a wide variety of colors, namely, red, blue, yellow, and green, by changing the metal ions and organic ligands. (2) Multicolor display: by introducing multiple metal species into the polymer, it is possible to display three or more colors by changing the voltage. (3)  $10^5$  cycles or more drive stability. Unlike organic electrochromic materials, structural changes do not occur in the organic material part, and as a result, these materials have high cyclical drive stability. On the other hand, unlike mononuclear metal complexes, these polymers are amorphous and are readily dissolved in water or methanol, enabling easy film forming by spin coating, which is an important advantage for device applications.

We have already succeeded in fabricating display devices using the polymers. As these displays have a memory property (i.e., display continues even when the power is cut off) which is not found in liquid crystal and organic EL displays, application to future newspapers and posters as power saving next-generation display devices is expected.

## Vapoluminescent polymer: Toward sensor displays that warn of danger

The phenomenon of changing light emitting

properties in the presence of vapors is called vapoluminescence. Devices made using vapoluminescent materials, if realized, will be able to detect harmful substances in the air and warn persons in the areas of the danger.

Until now, however, no material with the necessary properties had been reported. In particular, the following three properties are required: the difference during light emission and light extinction must be clear (large difference in quantum yield), the change in light emission must be rapid (within several seconds), and repeated light emission/extinction without deterioration in device performance must be possible.

We succeeded in developing a europium ions-induced polymer by newly designing the organic ligands and synthesizing the targeted polymer (Fig. 2).<sup>4)</sup> We discovered that there are large changes in the light-emitting characteristics of this polymer, depending on whether acidic or basic vapors are present in the atmosphere, and found that the newly-developed polymer satisfies all of the three above-mentioned properties required in a sensing device. Taking advantage of the amorphous property of polymers, we also succeeded in displaying characters with this polymer. Work is scheduled to advance to the applied research stage.

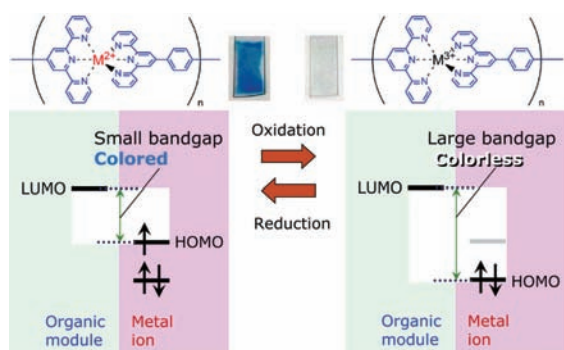


Fig. 1 Electrochromic phenomenon in an organic-metallic hybrid polymer (M=Fe), and its mechanism of color change.

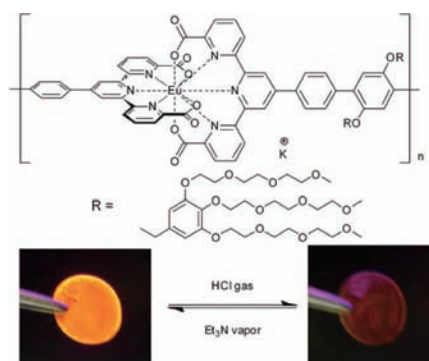


Fig. 2 Europium (Eu) ions-induced organic-metallic hybrid polymer, and its vapoluminescent change.

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## Interview

# Nanotech isn't a magic trick. Work for results rather than chasing dreams.

Izumi Ichinose, Unit Director, Polymer Materials Unit, Advanced Key Technologies Division

In 2011, NIMS launched the new project "Material Synthesis Technology Based on Organic Molecular Networks" as part of its 3rd Five-year Plan. In this interview, Dr. Izumi Ichinose, who is the Leader of this new project, discusses the current condition and future of polymer materials.

— First, could you explain what you mean by "precision molecular networks"?

**Ichinose(I):** Precision molecular networks are networks in which crosslinked polymers are expressed in a modern manner. In comparison with ordinary polymers, research on crosslinked polymers has progressed very little. The range of applications of these polymers is extremely wide, but because they are difficult to evaluate, they are still largely unexplored from the viewpoint of

basic research. In other words, although they are used industrially, scientifically speaking, their structures are complicated and they cannot be analyzed simply. For this reason, they haven't been investigated in depth. On the other hand, since crosslinking is generally associated with increased strength, it can be said that they have excellent qualities as materials. Our target is to realize high performance in crosslinked polymers by focusing on those qualities.

— How are you working to improve their properties?

**I:** To achieve a drastic improvement in the properties of polymers, it is important to elucidate the phenomena of molecular, ionic, and electronic mobility as essential physical properties. The network structure is not only important in controlling the mechanical properties of a material, it is also possible to design nanopores for water treatment membranes and gas absorbents by using this structure. Moreover, by clarifying the motion of ions and electrons, it may also become possible to design display devices based on oxidation-reduction reactions.

— What are you prioritizing in order to achieve that goal?


**I:** Rather than seeking novelty simply to attract notice, more than anything else, the effort to make steady, meaningful improvements in the intrinsic performance of polymers is important. For polymer science which treats molecules of nanoscale, nanotechnology isn't a magic trick, and it isn't a treasure chest. Rather than chasing dreams, we should make efforts that produce results. When I feel the possibility that a material that I have created might change the world, that's what gives me the greatest motivation as a researcher. You need to think and worry until then. It's also important to stop and take

a break when you can't see an exit to your work.

— So producing results is more important than anything else?

**I:** That's right. And for that reason, it isn't the end of the process when I find a new material. I pursue it to the finish. That, I feel, is the mission of a researcher. For this, it's necessary to be sensitive to movements in the world. For example, if we think about water treatments, there are drinking water, industrial water, bio applications, resources and energy, the global environment, and so on. Various materials are competing intensely in each of these applications. As a result, the required specifications are extremely high, and companies and others are engaged in continuous development. So, it's no simple matter to match what companies are doing. Therefore, we have to go out in the world in order to know reality. In this sense, maybe we should place ourselves in the same situation as companies.

— I think we can say that's an important resolution for a researcher.

**I:** I myself hope to make some kind of contribution to the environment and energy field. Because any material is a collection of many kinds of performance, it is important to work constantly to improve those properties. Bearing in mind the NIMS philosophy that "the value of materials is in their use," I want to keep an awareness of the importance of engineering. 



Izumi Ichinose See profile on page 5.

## Development of High Performance Filter of Diamond-like Carbon

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Advanced Key Technologies Division  
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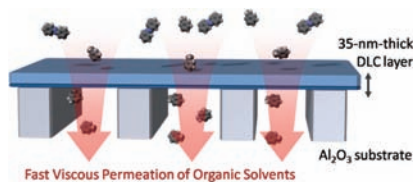
### An ultra-thin filtration membrane that can purify oil

Membrane separation technology is widely used in seawater desalination, wastewater treatment, and similar applications. Water treatment membranes with ultra-small holes around 1 nm in size are used to remove harmful substances that are dissolved in water. Japanese companies have provided leading-edge water treatment technologies in Japan and other countries, and are said to hold a share of more than 50% in the world water treatment membrane market.

However, even the best water treatment membranes have several weak points. For example, polymer membranes are gradually decomposed by acids, alkalis, hypochlorous acid, and certain other types of chemicals. Many polymer membranes become flexible when heated and swell when they absorb organic solvents. Ceramic membranes have excellent heat resistance but cannot permeate oil at high speed. Considering these problems, there are serious limitations on the range of application of today's water treatment technologies.

Filtration membranes which do not swell in the presence of organic solvents and possess high chemical resistance are indispensable for the development of new resources such as oil sand and shale gas. This is because it is necessary to treat polluted water containing oil components at low cost in these fields. Furthermore, if molecular sulfur compounds can be removed from light oil, i.e., from diesel fuel, using a high performance filtration membrane, cleaner diesel exhaust gas can be expected.

In filtration membranes, the solvent flux increases in inverse proportion to the thickness of the membrane. For this reason, a thin porous membrane with a thickness of several 10 nm must be manufactured as the separation function layer in high performance filtration membranes. We selected diamond-like carbon (DLC)<sup>1)</sup> as a materi-

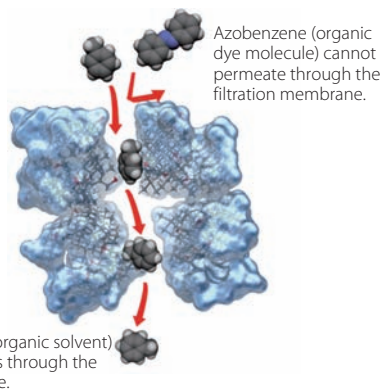


**Fig. 1** Schematic diagram of the developed ultra-high performance DLC filtration membrane. The DLC film on the porous alumina ( $\text{Al}_2\text{O}_3$ ) substrate permeates organic solvents at high speed.

al which provides adequate mechanical strength even at this ultra-thin thickness. In the process of investigating the membrane production conditions for this material, we succeeded in developing an ultra-high performance filtration membrane that can separate organic molecules at a speed 1000 faster than conventional filters.<sup>2)</sup>

### Confirmation of high speed viscous permeation of organic solvents

DLC membranes are manufactured by a membrane production method called plasma CVD.<sup>3)</sup> This production method is generally performed with the substrate heated to an elevated temperature in order to obtain a dense membrane. In contrast, we set the substrate temperature to  $-20^\circ\text{C}$  and produced a membrane with a large number of microscopic defects. The DLC membrane (Fig. 1) with a thickness of 35nm, which was formed on a substrate of porous alumina, consists of clusters of diamond-like carbon with a size of several nm. The spaces between these clusters form flow channels of approximately 1 nm in width, which water and organic solvents can pass through at high speed (Fig. 2). However, slightly larger dye molecules cannot pass through these channels. Using this membrane, it was possible to remove 94.4% of the red dye molecule, azobenzene, which has an average molecular size of 0.69 nm, and it was also possible to remove 100% of the somewhat larger dye molecule, protoporphyrin, which has a molecular width of 1.47 nm. The DLC membrane shows mechanical strength approximately 1/7 that of diamond, and it was found that this membrane can withstand filtra-



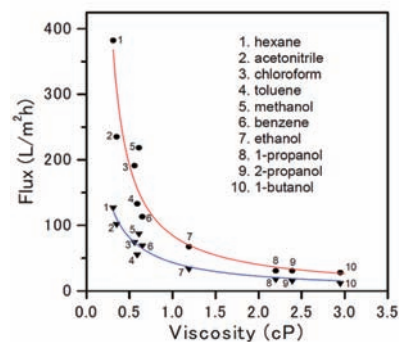
**Fig. 2** Toluene permeating through an ultra-fine flow channel. The organic solvent passes through the space of approximately 1 nm between DLC clusters several nm in size.

tion operation under a pressure of 20 atm.

In spite of the fact that the developed DLC membrane has a high rejection (filtration efficiency) for dye molecules, it can pass organic solvents at high speed. For example, in the case of hexane, which is one component of oil, the permeability is  $239 \text{ L/h}\cdot\text{m}^2\cdot\text{bar}$ . This means the membrane can pass 239 liters of hexane in 1 hour when a load with a pressure differential of 1 atmosphere is applied to a membrane area of  $1 \text{ m}^2$ . The relationship between the flux and viscosity of various solvents is plotted in Fig. 3. What is surprising here is the fact the flux is not related to the size or polarity of the solvent molecules, but increases in inverse proportion to the viscosity of the bulk. Even though the size of the pores in the DLC membrane is only 2-3 times larger than that of the solvent molecules, the flux also depends on bulk viscosity in this case. Because the DLC membrane has excellent heat and chemical resistance, use in a wide range of practical applications is expected as a high performance filter which is capable of purifying oil.

\* The evaluation of filtration performance in this research was carried out as part of the JST-CREST research project "Macroscopic Properties of Liquids in Interfacial Nanopores."

- 1) Diamond-like carbon (DLC) is an extremely hard carbon membrane; its properties vary depending mainly on the content of hydrogen.
- 2) S. Karan, S. Samitsu, X. Peng, K. Kurashima and I. Ichinose: "Ultrafast Viscous Permeation of Organic Solvents through Diamond-Like Carbon Nanosheets," *Science* 335, 444-447 (2012); <http://www.sciencemag.org/content/335/6067/444>
- 3) Plasma CVD is a technique in which a vapor deposition membrane is produced from a gas phase by plasmatizing a feedstock gas. It is the most widely used industrial coating method for DLC films.



**Fig. 3** Relationship between the permeability and viscosity of various organic solvents. The flux (flow rate in a certain area) of the organic solvents increases in inverse proportion to viscosity.



**Karan Santanu** (left) Ph.D. (Science) Received doctoral degree from Jadavpur University (India) in 2008, and has worked as a NIMS Postdoctoral Research Fellow since 2008. / **Sadaki Samitsu** (center left) See profile on page 6. / **Keiji Kurashima** (center right) Joined the National Institute for Research in Inorganic Materials (NIRIM; a predecessor of NIMS) in 1993 and has held his present position since 2011. / **Izumi Ichinose** (right) See profile on page 5.

## 1 NIMS Appoints Mr. Masaru Osanai as New Vice President

On August 1, NIMS appointed new Vice President as follows. The term of this appointment began on August 1, 2012.



Vice President Masaru Osanai:

**Masaru Osanai** : Graduated from the University of Tokyo Faculty of Law. Prior to his appointment as Vice President of NIMS, Mr. Osanai held a number of positions, including Chief of the International Exchange Policy Section, Science and Technology Policy Bureau, Ministry of Education, Culture, Sports, Science and Technology (MEXT); Professor of the National Graduate Institute for Policy Studies; Director of the London Office, Japan Society for the Promotion of Science (JSPS); Vice President and Executive Officer, Akita International University, and Director of the Research Program Department, JSPS.

## 2 Visit to NIMS

Prof. Dr. Chung-Yuan MOU, Deputy Minister of the National Science Council, Taiwan, visited NIMS on September 5, 2012.

National Science Council is a government organization belonging to Executive Yuan, the executive branch of Taiwan, and responsible for the promotion of national science & technology development, the support of academic research and the de-

velopment of science parks, analogous to the former Science and Technology Agency (presently MEXT) of Japan.

Prof. MOU is in charge of Asian region in NSC and at the same time he is affiliated with National Taiwan University as a nano-materials scientist especially for the biomedical application. He had a discussion with NIMS Vice Presidents following NIMS overview presentation. Status of the collaborations between NIMS and Taiwanese universities and research institutes, which have

been increasingly active last several years, was presented and then how to explore possible collaborations between NIMS and NSC itself was intensively discussed.



Discussion with Vice Presidents of NIMS

## Announcement : The 12th NIMS Forum

The 12th NIMS Forum will introduce two new projects which NIMS launched to carry out technological development contributing to reconstruction from the Great East Japan Earthquake of March 2011, "Structural Materials for Improved Infrastructure" and the "Elements Strategy Initiative Center for Magnetic Materials." In addition, a large

number of achievements with industrial importance will be introduced in lectures on recent research results by NIMS researchers. These include "Confinement of Radioactive Elements Using Titanium Oxide," "High Performance Filter with Resistance to Organic Solvents," "Conductive Polymer Covered with Metal Shell," and "Innovative Welding Technology Satisfying High Efficiency and High Quality," among others.

Also, the Poster Sessions will allow visitors

to exchange ideas directly with researchers. There is no admission fee for this forum. We warmly invite everyone to attend.

**Date:**  
10:00am-October 25 (Thursday), 2012

**Site:**  
Tokyo International Forum Hall B7 (Yurakucho)

**http://www.t-i-forum.co.jp/english/**  
(The NIMS Forum is held in Japanese)

## Hello from NIMS

### Dear NIMS NOW readers,

I am Carmen from Spain. Before coming to NIMS in 2010 I was living in Germany. When I arrived, the first thing that surprised me was how similar both countries (Germany and Japan) are! However, during my time here I have discovered many differences with Europe. After comparing our cultures, there are



Yukata party with friends

many things from Japanese society that I do not like or I simply do not understand but there are

many others that I REALLY enjoy: I love the different landscapes from Hokkaido to Okinawa. I like visiting shrines, temples, watching woodblock printing, learning about the history and the language. I am crazy about Japanese pottery (my boyfriend is terrified about how to bring so many plates back to Europe!). I like the kindness of the people, their respect to the elderly and their joy with children. I have lots of fun going to Izakayas, singing and dancing in Karaoke, wearing Yukata, watching Sumo or visiting parks at Sakura time. And last but not least: THE FOOD. I guess this is one of the things I will miss the most :-)

My work at NIMS has been very fruitful and I am very happy with my nice colleagues at the Nano Characterization Unit. Finally I want to write about my positive surprise

with the brave and calm reaction of the Japanese population when the earthquake and the subsequent tsunami occurred. There is still a lot of things to do and many problems to solve including Fukushima. Do not give up Japan, you have to continue being an example of survival! がんばろう日本!



Enjoying dinner with my boyfriend



With other volunteers in Miyagi



**Carmen PEREZ LEON** (Spain)  
2010-present  
Post-Doctoral Researcher  
at Nano Characterization Unit



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