

Studies on Interfacial Interactions in Soft Materials

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Studies on Interfacial Interactions in Soft Materials

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Chapter 1 General introduction

1-1 Interfaces and bulk

“God made the bulk; the surfaces were invented by the devil.” Professor Wolfgang Pauli, the Nobel laureate in Physics 1945, left this message to the world. In the field of solid-state physics, though the bulk properties of materials can be relatively estimated, properties from interfaces including surfaces are commonly more difficult to be simulated because molecules around interfaces have exceptional energy or are in the specific states based on the interactions among molecules or atoms.¹⁻

⁴ This kind of specificity of interfaces on materials can be observed in various research fields.

For instance, as inorganic materials, metallic materials have been developed as catalysts for various purposes such as the purification of exhaust gas^{5,6} and the enhancement of chemical reactions.⁷⁻⁹ Most of the catalytic reactions occur on the surface of the materials because that is where the active sites are located for reactions. To obtain the maximum catalytic activity from these materials, the fabrication of large active surfaces is necessary. Therefore, metal nanoparticles are commonly used because they have large surface area per unit volume, which can maximize the underlying functions of metal materials for different applications.

In terms of metal oxides, extraordinary phenomena could be observed on the surfaces. For example, Santander-Syro *et al.* have found that two-dimensional electron gases at the vacuum-cleaved surface of strontium titanate (SrTiO_3), though SrTiO_3 consists of electrically neutral TiO_2 and SrO layers.¹⁰ This conductive layer was assumed to be fabricated based on the oxygen vacancy on the cleaved surface of SrTiO_3 .

On the other hand, organic materials also have different properties between their interfaces and bulks. As a famous example, graphene has exceptional properties as compared with that of graphite as bulk materials. In 2004, Geim and Novoselov *et al.* found that one layer of graphite could be obtained by the removal of graphite surface with scotch tape.¹¹ Graphene is known to be a single layer consisting of carbon atoms organized in a two-dimensional hexagonal lattice. Moreover, graphene has high electrical conductivity and charge carrier density because of the two-dimensional electron gases, which is a promising material for transparent conductive electrodes. In addition, similarly structured materials with different atoms, such as silicene,^{12,13} germanene,^{14,15} and stanene^{16,17} have been reported in order to realize topological insulators. Scientists often tend to get interested in the bulk properties of materials, however, it has come to realize that utilizing the latent properties of interfaces would give us a new approach to invent functional materials.

1-2 Unique properties of interfaces and their applications

Molecules on the interfaces of materials have the potentials to exhibit specific properties because of the chemically active states. In this section, the applications and the exceptional behaviors of the chemical species on interfaces will be introduced.

One of the most famous examples exploiting the chemical species on the interfaces is the metal nanoparticles for catalytic reactions as described in section 1-1. For purposes such as the suppression of harmful exhaust gases from automobiles or particular chemical reactions, metal nanoparticles have been of much interest. Metal nanoparticles have large surface area per unit volume, which can realize efficient catalytic reactions. Recently, Zhang *et al.* have succeeded to prepare metal nanoparticles (platinum, palladium, rhodium, and silver) within zeolite crystals.¹⁸ Metal nanoparticles often suffer from deactivation upon metal sintering. However, metal nanoparticles in zeolite have sinter resistance. The uniform micropores of zeolite allowed reactants to have contact with the metal catalysts, leading to CO oxidation, oxidative reforming of methane, and CO₂ hydrogenation. Moreover, Choi *et al.* have produced monodisperse particles (platinum, palladium, gold, and cobalt) that can distribute onto mixed-conducting oxide electrodes as model electrochemical cells.¹⁹ They have identified the way to activate hydrogen electro-oxidation on the electrode surface of cerium oxide with metal catalysts and the approach to increase the reaction rates with different choices of metals. These results can be applied to electrodes for electrochemical reactions at high temperatures. In this way, employing and stabilizing proper metal nanoparticles give us efficient catalysts for various chemical reactions.

Molecular interactions on interfaces can also be harnessed for other applications, such as polymerization. It is well-known that some specific functional groups preferably adsorb on the surfaces of materials. For example, fatty acids tend to adsorb on metal oxides such as Al₂O₃. Meanwhile, gold surfaces are often modified through the adsorption of alkanethiols. Mizukami *et al.* found that ethanol molecules in cyclohexane formed macroclusters through hydrogen bonding on the surface of silica.²⁰ Through the utilization of these molecular macroclusters based on the interfacial interactions, Zhang *et al.* revealed that acrylic acid (AA) was adsorbed onto the surfaces of silicon oxide in AA/chloroform binary liquids and formed molecular macroclusters through hydrogen bonding, which could be utilized for polymerization.²¹ Macroclusters of AA were used to obtain flat polymer films with thickness up to 10 nm (Figure 1-2). Based on the observations, through atomic force microscopy, attenuated total reflection-FTIR spectroscopy, and ellipsometry, it was revealed that flat PAA films with linear hydrogen-bonded COOH could be obtained by only in-situ polymerization. It was demonstrated that the fabricating method was one of the effective ways to prepare molecularly uniform polymer films.

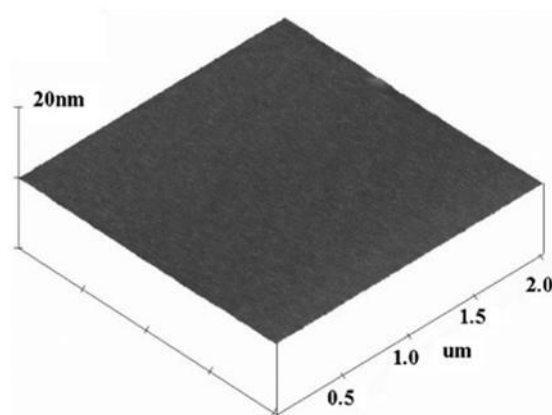


Figure 1-2. AFM images of PAA films by in-situ polymerization of AA.²¹

As aforementioned, preparing and stabilizing metal nanoparticles can give us efficient catalytic reactions because of their large active surfaces. Moreover, interactions on the interfaces are of much use for fabricating molecular layers. Fabricating appropriate interfaces would realize peculiar chemical reactions or extraordinary phenomena.

1-3 Limitation of interface chemistry

Employing interfaces would lead us to understand the unique properties or behaviors of molecules. However, there are still several problems needed to be solved and they require further understanding before introducing interface chemistry for applications.

For instance, there have been technical limitations on the evaluations of molecules on interfaces because of the extremely small amount of signals from molecules. Generally, only the molecules that are a few tens of nm from the interfaces would experience the molecule-interface interaction.²¹ Therefore, even though it is possible to evaluate the structures or dynamics of molecules on interfaces through measurements such as ellipsometry²² or scanning tunneling microscopy (STM),²³ there have been some difficulties estimating the properties of molecules on interfaces.

It also has been hard to construct materials with large interfaces that have chemically or physically active sites and prolonged functional stability. As described in section 1-2, in terms of metal nanoparticles, not only the methodology to create nanoparticles but also that to suppress the aggregation of nanoparticles is necessary in order to maintain the reactivity as catalysts. Moreover, though it is possible to control the polymerization reflecting molecular interactions on interfaces, the materials are commonly limited to two-dimensional. This aspect has suppressed the application of interfacial interactions of molecules to bulk properties of three-dimensional materials.

Interface chemistry has been in rapid progress and is introduced to many applications such as coating²⁴ or adhesion²⁵ technologies. Further understanding of the relationship between the interfacial interactions and the bulk properties of materials would give us new directions to devise novel promising materials. Especially, as compared with inorganic materials, organic materials such as gels or polymer materials have more flexibility in molecular designs and are easily produced as three-dimensional materials. This aspect can connect interfacial interaction with the bulk properties of materials, especially with three-dimensional materials having thousands of interfacial active sites within them. Based on these backgrounds, three-dimensional materials having enormous number of interfacial active sites are promising.

1-4 Chemistry based on self-assembly to fabricate large active interfaces

In order to overcome the potential problems about the utilization of molecules on interfaces for bulk properties, fabricating large active interfaces is essential. Expanding the area of interfaces makes the total interactions between molecules and interfaces stronger, and specific bulk properties could be displayed because of the large number of molecules that are affected by interfacial interactions. Additionally, the enhancement of molecular interactions on interfaces would make it possible to evaluate the properties. To realize the fabrication of large active interfaces, chemistry about self-assembly would be one of the promising solutions.

Self-assembly of molecules is upon the spontaneous association of molecules through thermodynamic or kinetic conditions. Based on the features of molecular self-assembly, not only simple structures such as micelles or self-assembled monolayers (SAMs) but also complicated structures like living cells could be built up. In 1977, Kunitake *et al.* reported for the first time that synthetic amphiphilic molecules formed self-assembled lipid bilayer membranes (Figure 1-4-1).²⁶ Optimizing the balance of hydrophobic and hydrophilic moieties of amphiphilic molecules realized the spontaneous formation of the self-assembled lipid bilayer membranes in water. The chemistry about molecular self-assembly has since then expanded to supramolecular chemistry.

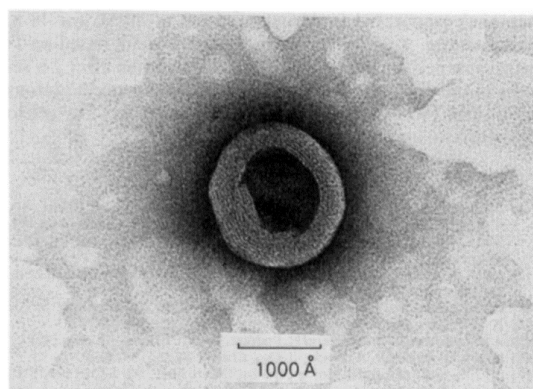


Figure 1-4-1. A TEM image of didodecyldimethylammonium bromide vesicles.²⁶

Paying attention to the interfaces established on molecular self-assembly, soft materials, such as supramolecular gels, is one of the most attractive classes of materials because there are tremendous interfaces between self-assembled structures and solvents in these materials. Though thousands of soft materials fabricated on molecular self-assembly have been created, there are limited materials with

unique interactions between the self-assembled structures and the surrounding solute or solvent molecules. For instance, Liu and Sun *et al.* have prepared anisotropic hydrogels with titanate nanosheets (TiNS) and polymers.^{27,28} Under the magnetic field, spontaneously TiNS aligned cofacially through the diamagnetic property and the repulsion force based on the negative charges on the surface of TiNS. After the polymerization of acrylamide derivatives, hydrogels with the supramolecular structure of TiNS were obtained. Utilizing the interactions on TiNS gave the hydrogel exceptional properties such as anisotropic rheological property and actuation behavior. Moreover, Wang *et al.* have prepared hydrogels with a mixture of clay nanosheets and a dendritic molecular binder.²⁹ Although the amounts of clay and binder molecules are quite small (2-3 and 0.4 wt%, respectively), this hydrogel could be utilized for shape-persistent and free-standing objects due to the strong mechanical strength. Moreover, the hydrogel showed rapid and complete self-healing properties. These peculiar properties derived from the electrostatic interactions between the binder molecules and the clay nanosheets.

Furthermore, molecular self-assembled structures in soft materials can also create large functional interfaces. For instance, Chin *et al.* have polymerized di(ethylene glycol) methyl ether methacrylate, oligo(ethylene glycol) methyl ether methacrylate and *N,N'*-methylenebisacrylamide as thermoresponsive polymers on long peptide supramolecular nanofibers which are aligned by weak shear forces (Figure 1-4-2).³⁰ The hierarchically ordered tubes exhibited reversible anisotropic actuation depending on the temperature change with contraction perpendicular to the direction of nanofiber alignment.

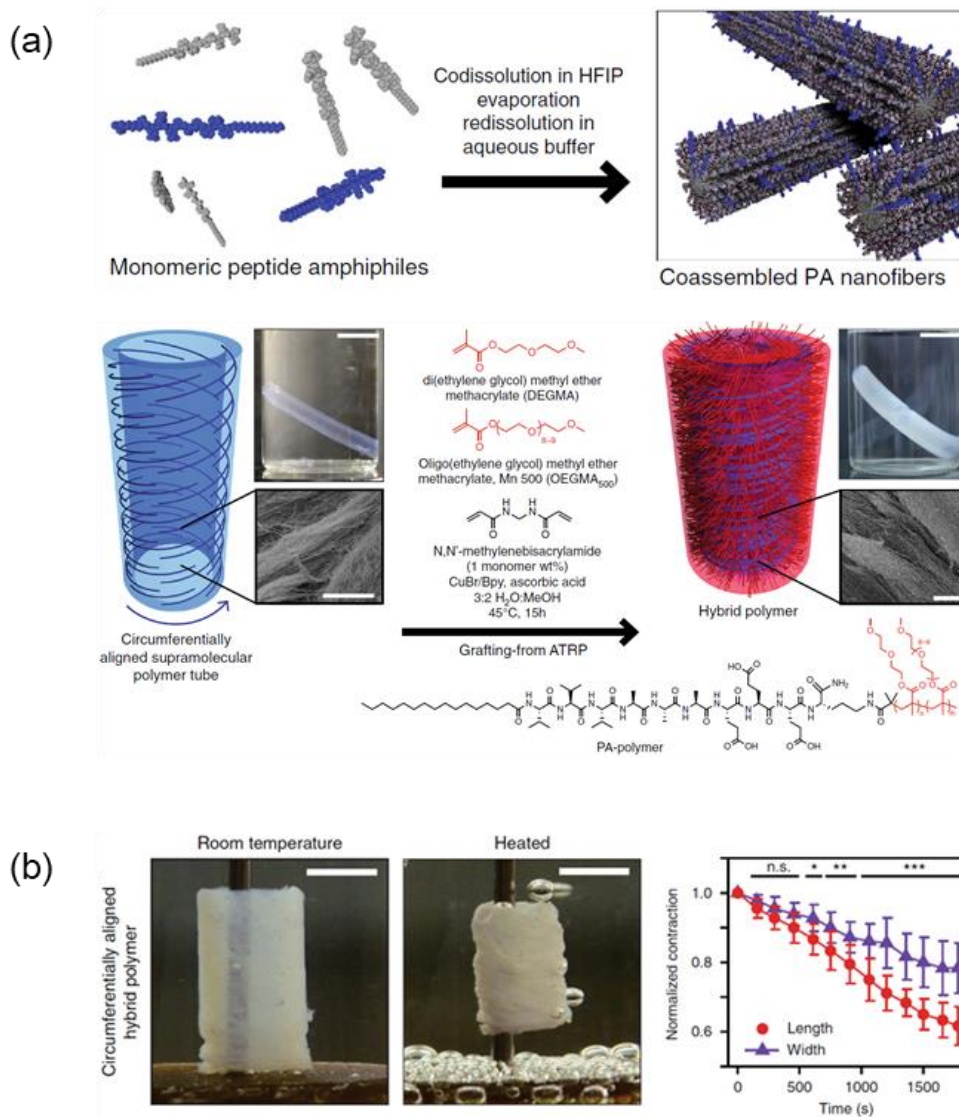


Figure 1-4-2. (a). Preparation scheme of the soft materials based on the hybrid polymer. (b) Anisotropic actuation in hybrids.³⁰

In soft materials with self-assembled structures, extremely large interfaces are created and molecules have intermolecular interactions with the interfaces. Though each interaction is quite small, totalizing the interactions would give us novel properties as bulk materials. In this point, elucidating the relationship between interfacial interactions and bulk properties could propose a strategy to invent new functional materials.

1-5 Motivation and Outline of this dissertation

In order to reveal the latent properties of soft materials, such as gels and polymer materials, we have taken notice of the interfaces fabricated in those materials as described in section 1-4.

In terms of gel materials, many types of gels have been developed for various purposes such as sensing,³¹ actuators,^{28,32} and cell cultivation.^{33,34} Gel materials can be briefly classified as hydrogels consisting of water as solvent and organogels entrapping a variety of organic solvents. For hydrogels, it is possible to combine them with various water-soluble compounds such as ionic species and drugs. Therefore, researches on hydrogels have been in rapid progress not only in materials science but also in the biological field. Especially in supramolecular hydrogels which have homogeneous molecular self-assembled nanofibrous networks, tuning the molecular interactions on the interfaces of the structures can give hydrogels unique properties such as adhesion³⁵ and mechanical toughness.³⁶ As one of the conventional methods to fabricate supramolecular hydrogels, noncovalent bonding, such as hydrogen bonding, π - π stacking, and hydrophobic interaction, is quite important for the fabrication of hydrogels.³⁷ Meanwhile, coordination bonding between metal ions and ligands can also promote the fabrication of nanofibrous networks in water. Especially, coordination bonding-based hydrogels have some particular properties such as electrostatic interactions on the interfaces of self-assembled structures³⁸ and responsivity to external stimuli^{39,40} because coordinated structures potentially have ionic properties upon the metal ions and association-dissociation properties based on the coordination bonding. Though many types of coordination bonding-based hydrogels have been reported, molecular dynamics in the hydrogels have not been focused well. This is because most of the coordination bonding-based hydrogels contain paramagnetic metal ions, which has prevented common approaches, such as NMR, to get information about the dynamics of the species forming coordinated structures. Moreover, most of the metal ions are harmful to our bodies. This feature has suppressed the possibility of coordination bonding-based hydrogels to be utilized in the biological field. A new type of coordination bonding-based hydrogels, which can be evaluated for the dynamics of the components and is relatively harmless to our bodies, has been promising for applications such as biotherapy. Taking the advantage of the molecular interactions on the interfaces of the self-assembled structures from the coordinated structures containing relatively harmless metal ions, such as zinc(II) ions, in water, it is expected to represent morphological change and specific responsivity of the bulk hydrogels which can be utilized for the biological field.

We are also interested in research related to the dielectric properties of gel materials. It is expected that applying an external electric field would align the orientation of the solvent molecules

contained in the gel materials, leading to specific phenomena such as polar switching behaviors with appropriate interactions between the solvent molecules and the frameworks. However, there are some potential limitations in the coordination bonding-based hydrogels when we apply electric bias to these materials. For instance, electrolysis of water and redox reactions of metal complexes could be disturbing when the dielectric properties of the gels are evaluated. Moreover, water as a solvent would suppress the possibility of designing suitable frameworks for gelation. To avoid these potential problems related to hydrogels, we utilized supramolecular organogels for the research on fabricating dielectric materials. Supramolecular organogels consisting of molecular self-assembled nanofibers can immobilize organic solvents within the networks. They have exhibited specific properties, such as photoresponsive morphological transformations⁴¹ or reentrant gel-sol-gel transitions,⁴² utilizing the self-assembling properties of the components. Flexibility in selecting organic solvents would realize the optimization of molecular interactions between the solvent molecules and the frameworks, leading to extraordinary dielectric behaviors of the gels. With that aim in mind, we focused on the preparations of unique dielectric systems with supramolecular organogels. Ferroelectric materials are part of the dielectric materials. However, these materials can be spontaneously polarized by altering the direction of the external electric field, leading to the hysteresis curves represented by the Polarization (P) - Electric field (E) loops (Polar switching). Therefore, ferroelectric materials have been applied for memory materials (FeRAM) and already incorporated into integrated circuit cards.⁴³ Focusing on organic ferroelectrics having some advantages, such as flexible molecular design and being environmentally-friendly, various types of organic ferroelectric materials have been reported⁴⁴⁻⁵² but there has been no example of liquid-state organic ferroelectrics. Naturally, molecular liquids having large dipole moments could show polarizing responses to the weak electric field. They have not been considered as components for ferroelectrics because such polar liquid molecules would not preserve macroscopic dipoles after removing the electric potential. However, we expect that if the mobility of the solvent molecules can be controlled by appropriate intermolecular interactions on interfaces of the structures in soft materials, the resulting behavior can denote the polar switching phenomenon as bulk property. Therefore, in this dissertation, we describe the exceptional properties of soft materials with the aim to link the molecular interactions on the interfaces in soft materials to the bulk properties.

In Chapter 2, we prepared hydrogels by mixing zinc(II) phenanthroline complexes with additional bridging ligands such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and quinuclidine in water. It was hypothesized that the additional ligand molecules would coordinate to the zinc center of the zinc(II) phenanthroline complexes and self-assemble into nanofibers consisting of cationic coordinated structures that would eventually lead to the formation of hydrogels. To exploit the electrostatic

interactions on the interface of nanofibers in the gels, solute molecules, such as salts and ionic drugs, were introduced to the gels and the physical properties, the responsivity for external stimuli and the drug release property of the hydrogels were evaluated.

In Chapter 3, in order to connect molecular interactions in gels with the electrical properties as bulk, we evaluated the dielectric properties of organogels with dipolar aromatic liquids. Liquid molecules with large dipole moments potentially can follow the direction of the electric field. However, the relaxation of the orientation occurs easily because of the mobility of liquid molecules. To overcome these problems, we employed the interface of the self-assembled structures in the gel materials to suppress the orientational relaxation of polar liquids. Therefore, we prepared organogels using organic aromatic solvents with large dipoles, such as nitrobenzene, and organogelators that could form fibrous networks in organic solvents through hydrogen bonding. After obtaining the organogels, dielectric properties of the gels were evaluated.

In Chapter 4, in order to confirm the generality of polar switching phenomena utilizing organogels of dipolar solvents in Chapter 3, solid dispersions were prepared with dipolar aromatic molecules and an organogelator. The relation between the phase transition behaviors and the dielectric properties of the solid dispersions was evaluated.

The gel and solid dispersion systems in Chapters 3 and 4 have some potential problems such as low processibility and poor controllability of dielectric properties. In order to overcome these problems, in Chapter 5, we introduced porous polymer films containing large surface upon the pores. These materials have some advantages such as flexibility and easy-to-tune pore size. It is expected that polar molecules could be confined on the surface of the inner pores, which led to the demonstration of the polar switching behavior of the composite films.

Chapter 6 summarizes this dissertation and suggests future works in the area of soft materials utilizing interfacial interactions.

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Chapter 2 Thermally stable and pH responsive hydrogels utilizing zinc(II) phenanthroline complexes

2-1 Introduction

Supramolecular hydrogels consist of molecular self-assembled nanofibrous networks and water as a solvent.¹ Comparing with covalent polymer-based hydrogels, supramolecular hydrogels have the potential to exhibit a variety of unique properties such as self-healing²⁻⁶ and responsivity to external stimuli.^{2-4,7} Therefore, supramolecular hydrogels have been of much interest not only in materials science but also in the biological field.^{1,8} Among supramolecular hydrogels, the gels containing metal ions are especially classified as supramolecular metallo-hydrogels. Supramolecular metallo-hydrogels have often exhibited unique properties utilizing the interactions between metal ions and ligands. High flexibility on the selection of metal ions for fabricating coordinated structures in water has realized the development of functional hydrogels through the utilization of metal ions for various purposes such as sensing⁹ and mechanical applications.^{4,10} Supramolecular metallo-hydrogels can be fabricated through noncovalent bonding and coordination bonding. Noncovalent bonding-based hydrogels have been fabricated by intermolecular interactions exemplified by hydrogen bonding, electrostatic interaction, π - π interaction, and hydrophobic interaction on the ligands of metal complexes (e.g., Cu^{2+} , Zn^{2+} , Ru^{2+}).¹¹⁻¹³ For instance, Shen *et al.* prepared hydrogels utilizing Cu^{2+} and phenylalanine, and the formation of hydrogels was controlled by the enantiomeric excess of phenylalanine as ligand (Figure 2-1-1a).¹¹ Coordination bonding-based hydrogels, on the other hand, can be prepared through the formation of infinite coordinated structures in water. In terms of coordination bonding-based hydrogels, there have been several conventional strategies to prepare hydrogels such as the linking of metal ions (e.g., Pd^{2+} , Co^{3+}) through cyano functional groups (Figure 2-1-1b).¹⁴⁻¹⁶ Moreover, polyethylene glycol (PEG) ligand-based hydrogels with metal ions (e.g., Zn^{2+} , La^{3+} , Co^{2+} , Eu^{3+} , Figure 2-1-1c)^{2,10,17-19} and heterocyclic amine-based hydrogels (e.g., Pd^{2+} , Cu^{2+})^{20,21} have also been reported as coordination bonding-based hydrogels.

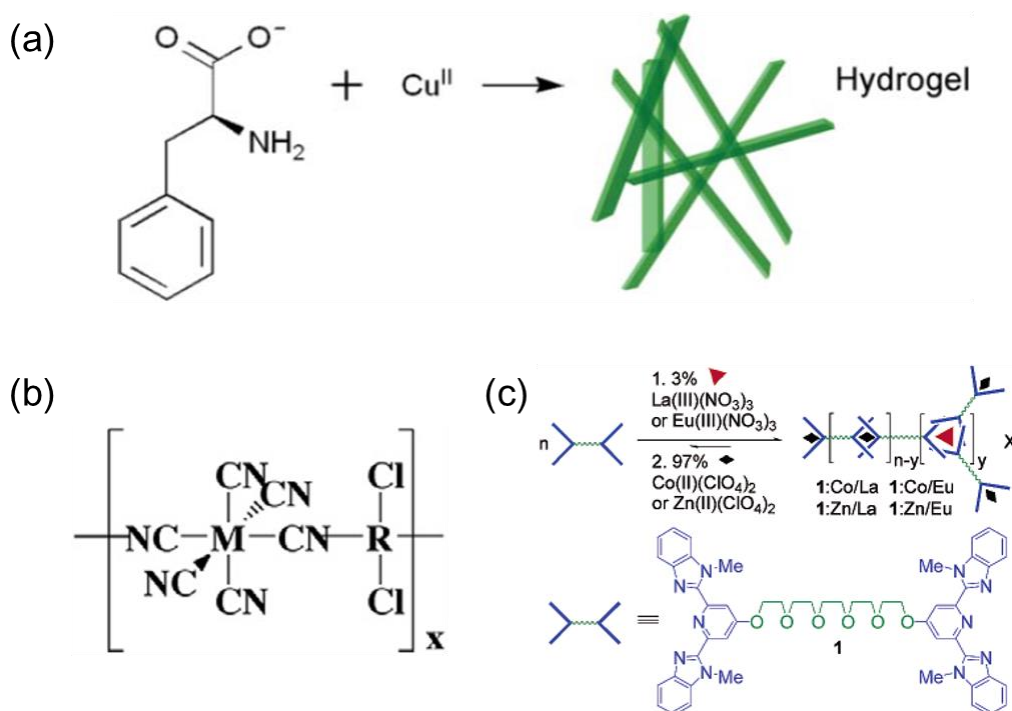


Figure 2-1-1. Hydrogels based on metal complexes. (a) Hydrogel utilizing molecular self-assembly of copper(II) complex.¹¹ (b) Hydrogel utilizing the linking of metal ions ($\text{M} = \text{Co}^{3+}$, $\text{R} = \text{Pd}^{2+}$) through cyano functional groups.¹⁶ (c) Hydrogel utilizing ligands with polyethylene glycol (PEG).¹⁸

Though many types of supramolecular metallo-hydrogels have been reported, molecular dynamics in the hydrogels have not been focused well. This is because most of the coordination bonding-based hydrogels contain paramagnetic metal ions, which has prevented common approaches, such as NMR, to get the information about the dynamics of the species forming coordinated structures. Moreover, most of the metal ions are harmful to our bodies. This feature has suppressed the possibility of utilizing supramolecular metallo-hydrogels in the biological field. A new type of supramolecular metallo-hydrogels, which can be evaluated for the dynamics of the components and is relatively harmless to our bodies, has been promising for applications, such as biotherapy.

Therefore, in this study, we focused on the fabrication of zinc(II)-containing supramolecular metallo-hydrogels because of the diamagnetic nature.^{22,23} Additionally, zinc(II) ions are abundant in our bodies and are relatively more biocompatible than other metal ions depending on the concentrations.^{24,25} In the field of supramolecular chemistry, bidentate moieties such as 2,2'-bipyridyl and 1,10-phenanthroline have been introduced as ligands for functional zinc(II) complexes^{26–28} and coordination polymers.²⁹ Heteroleptic zinc(II) complexes have also been developed through the utilization of two different bidentate ligands.³⁰ Moreover, the crystal structure of the zinc(II) complex

prepared from ZnCl_2 and DABCO has already been reported as a one-dimensional coordinated structure (Figure 2-1-2).³¹ Based on these previous researches, zinc(II) complexes with bidentate ligands are expected to have the possibility to form one-dimensional coordination polymers in water through the coordination of the complexes with subsequent bidentate linkers such as terephthalic acid or 1,4-diazabicyclo[2.2.2]octane (DABCO), which would induce the formation of hydrogels. These linkers have commonly been utilized for infinite coordinated structures, such as metal-organic frameworks (MOFs).^{32–34} Additionally, introducing amine-based linkers, such as DABCO, has the potential to render the hydrogels the pH responsivity based on the protonation of the amine moieties, which could be utilized for biotherapy as drug delivery carriers. Therefore, in this chapter, we fabricated hydrogels based on zinc(II) complexes and revealed the novel properties of the supramolecular metallo-hydrogels for biological applications.

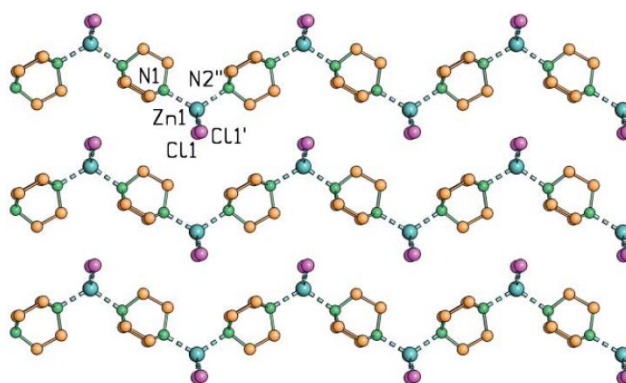


Figure 2-1-2. The crystal structure consisting of ZnCl_2 and DABCO.³¹

2-2 Results and Discussion

2-2-1 Coordination behaviors of zinc(II) complexes

Zinc(II)-1,10-phenanthroline dichloride (ZnPT2Cl) has been reported as a tetrahedral zinc(II) complex.³⁵ ZnPT2Cl and zinc(II)-5-methyl-1,10-phenanthroline dichloride (ZnMPT2Cl) were synthesized according to the literature procedure (Figure 2-2-1-1a).³⁶ The solubility of ZnMPT2Cl in water (saturated concentration: ca. 75 mM) was higher than that of ZnPT2Cl (ca. 50 mM) presumably because of the lower crystallinity from the asymmetry structure of the ligand. An aqueous solution of DABCO (400 mM) was added to the suspension of ZnPT2Cl in water (final concentration: 100 mM, respectively). After the irradiation of ultrasound to the mixture of ZnPT2Cl and DABCO in water for ca. 10 min, the aqueous solution was heated at 80 °C for 30 min, followed by cooling down to room temperature overnight. After the annealing process, the clear hydrogel was obtained and visually confirmed the absence of the liquid flow by the tube inversion test (Figure 2-2-1-1b). When preparing the mixture of ZnMPT2Cl and DABCO in water through the same preparation method as ZnPT2Cl, clear hydrogel was also obtained (Figure 2-2-1-1b). In this chapter, especially the properties of ZnMPT2Cl, in particular, were focused unless otherwise noted because of its better solubility in water as the component of hydrogel.

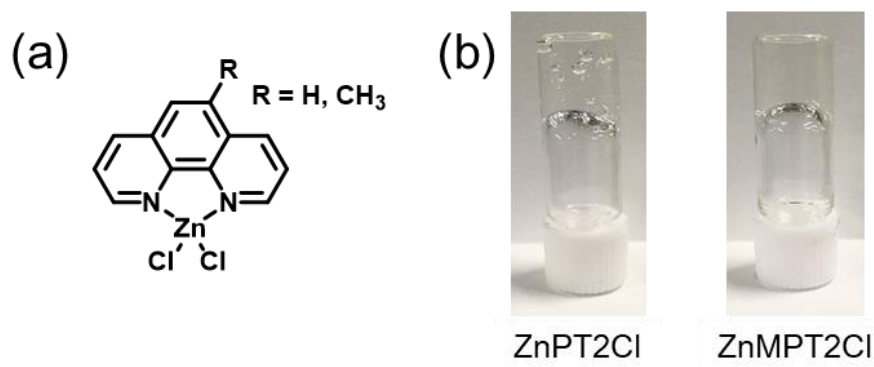


Figure 2-2-1-1. (a) The chemical structure of zinc(II) complexes and (b) the optical images of the hydrogels (zinc(II) complexes (100 mM), DABCO (100 mM)).

In terms of the linker ligand, different types of ligands, such as pyrazine and terephthalic acid, were introduced. After mixing ZnMPT2Cl and pyrazine in D₂O (30 mM, respectively), the ¹H peak representing pyrazine shifted from 8.59 ppm to 8.56 ppm (Figure 2-2-1-2). However, the gelation behavior was not observed, indicating that the coordination of pyrazine to ZnMPT2Cl was weaker than that of DABCO because of the lower electron density of the *sp*² nitrogen atoms of pyrazine.

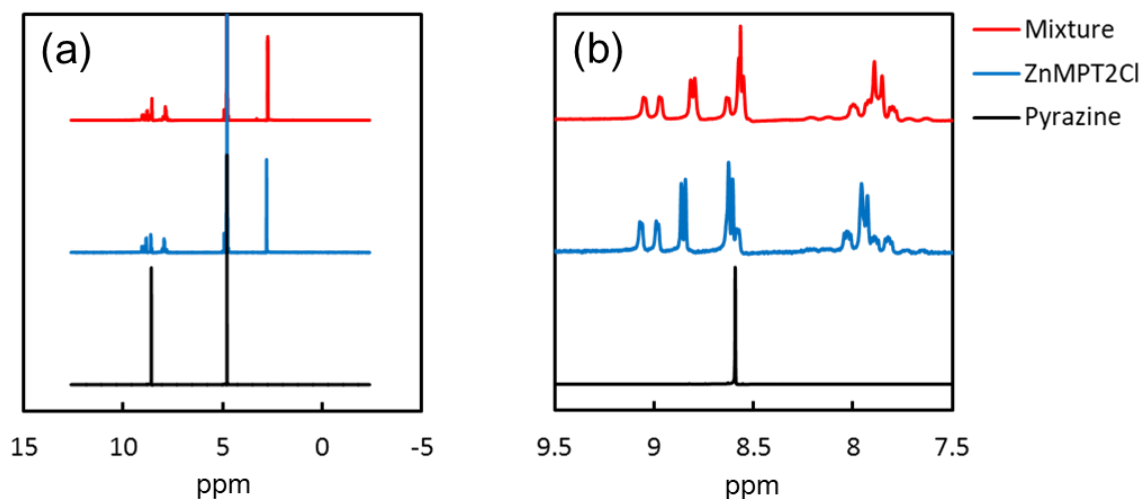


Figure 2-2-1-2. The ¹H NMR spectra of ZnMPT2Cl, pyrazine, and the mixture in D₂O (30 mM, respectively). (a) All range. (b) Magnified range.

On the other hand, crystals were obtained after dropwisely adding an aqueous solution of ZnMPT2Cl (25 mM) to a DMF solution of terephthalic acid (25 mM). Though the single crystal was not at its optimal quality, the single-crystal X-ray diffraction suggested that terephthalic acid linked ZnMPT2Cl and formed one-dimensional coordination polymers (Figure 2-2-1-3). Upon the coordination of the anionic linker (terephthalate unit), the zinc(II) complex became neutral and crystallized out from the solution. These results revealed that neutral linker ligand coordinating to the zinc center of ZnMPT2Cl strongly was essential to the formation of the hydrogel.

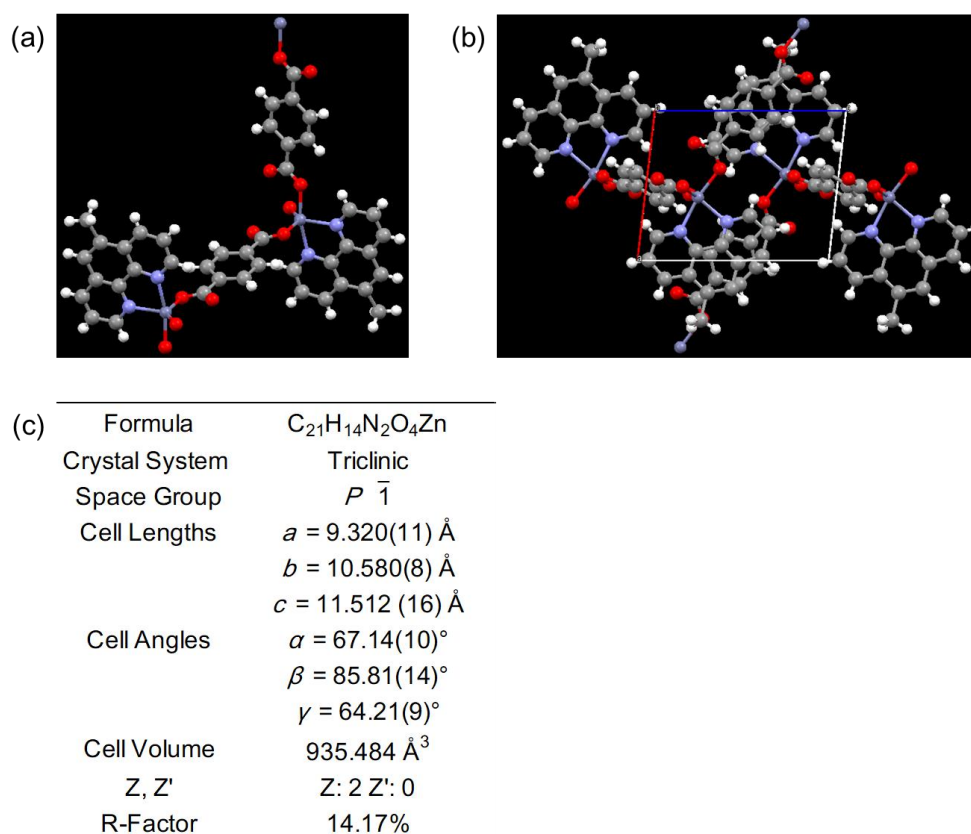


Figure 2-2-1-3. Crystal structure based on ZnMPT2Cl and terephthalic acid. (a) One chain of the coordination polymer. (b) Cell packing of the coordination polymer. (c) Crystal parameters.

To reveal the mechanism of the hydrogel formation from zinc(II) complexes and DABCO, quinuclidine (Figure 2-2-1-4a), which is a monodentate ligand, was mixed with ZnMPT2Cl in water as a comparative experiment. An aqueous solution of quinuclidine (400 mM) was added to the suspension of ZnMPT2Cl in water (final concentration: 50 mM, respectively). By the same procedure as the mixture of ZnMPT2Cl and DABCO, the clear hydrogel was obtained and confirmed the absence of the liquid flow by the tube inversion test. However, it is to note that the clear gel became turbid (Figure 2-2-1-4b), indicating that the size of the self-assembled structures formed in water grew larger over time. These results implied that there are some potential mechanisms for the formation of hydrogels, such as the formation of coordination polymer or the molecular self-assembly of zinc(II) complexes after the coordination of DABCO or quinuclidine.

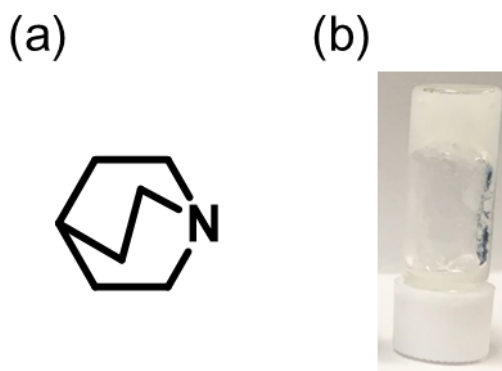


Figure 2-2-1-4. (a) The chemical structure of quinuclidine and (b) the optical images of the turbid hydrogel (ZnMPT2Cl 50 mM, quinuclidine 50 mM).

2-2-2 Rheological properties of the mixture from zinc(II) complexes and DABCO in water

The rheological properties of the mixtures of zinc(II) complexes and DABCO at different concentrations in water were evaluated by the rheometer. When the concentrations of ZnMPT2Cl and DABCO were below 60 mM, the values of storage modulus (G') and loss modulus (G'') are almost the same depending on the concentrations of ZnMPT2Cl and DABCO (Figure 2-2-2a). However, when the concentrations reached 80 mM, the value of G' (ca. 9.3 Pa) became obviously larger than that of G'' (ca. 5.9 Pa), and the values of G' and G'' became ca. 15 Pa and ca. 8.0 Pa, respectively at the concentrations of 100 mM. These results indicated that the critical gelation concentration (cgc) of ZnMPT2Cl with DABCO in water is between 60–80 mM. The cgc of ZnPT2Cl with DABCO was found to be almost the same as that of ZnMPT2Cl (between 60–80 mM), indicating that the methyl functional group of ZnMPT2Cl did not affect the gelation behavior (Figure 2-2-2b).

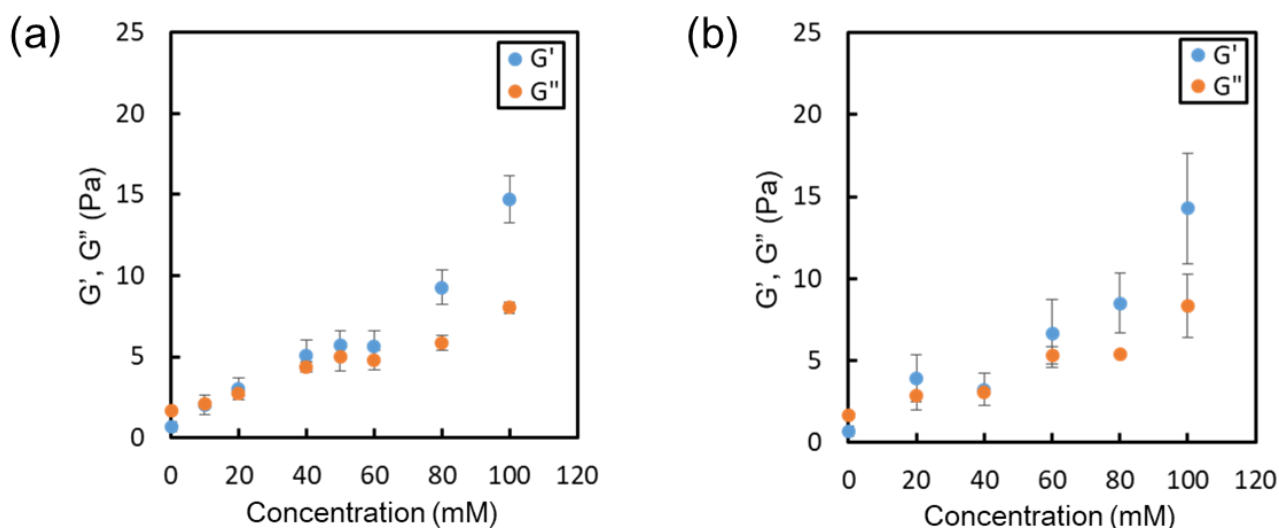


Figure 2-2-2. Rheology measurements at different concentrations (0-100 mM, strain 0.1%, angular frequency 100 rad/s, 25 °C). (a) ZnMPT2Cl and DABCO in water. (b) ZnPT2Cl and DABCO in water.

2-2-3 Morphologies of the hydrogels from zinc(II) complexes and DABCO or quinuclidine

The morphology of the aggregates in water was observed by transmission electron microscope (TEM). Hydrogels were prepared by the same procedure as described in section 2-2-1 with zinc(II) complexes and DABCO in water (100 mM, respectively). The TEM samples were prepared by placing the TEM grids on the surface of the gels and peeling off after making the contact,³⁷ followed by drying under vacuum. TEM images clearly exhibited the formation of nanofibers with a diameter of tens of nanometer (Figure 2-2-3-1). These observations elucidated that zinc(II) complexes and DABCO formed nanofiber-like structures in water, which contributed to the formation of hydrogels.

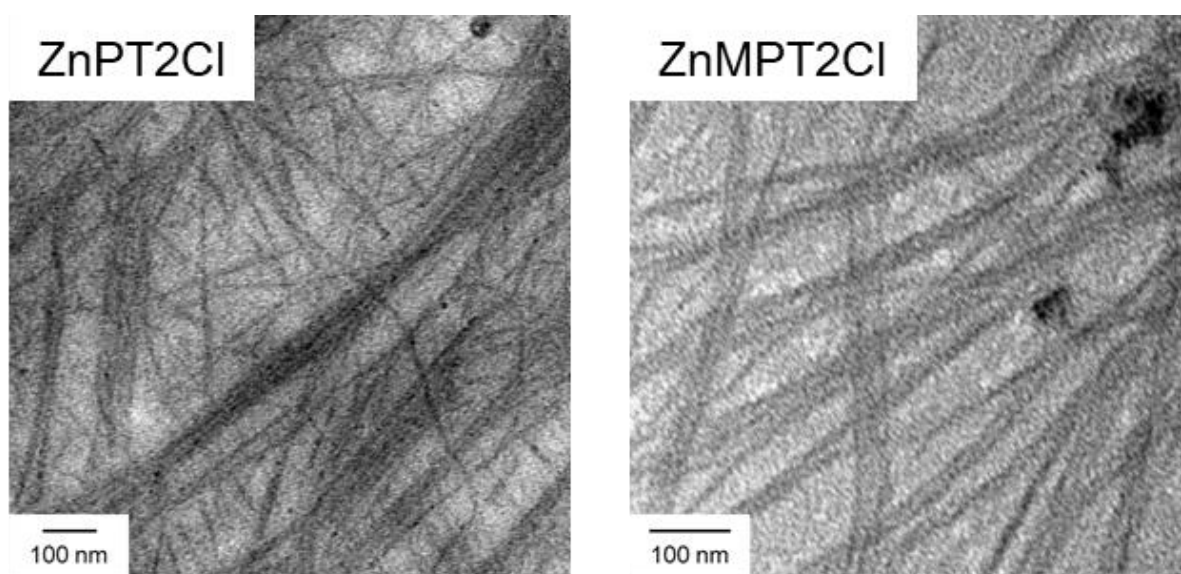


Figure 2-2-3-1. The TEM images of the xerogels (zinc(II) complexes (100 mM), DABCO (100 mM) without staining).

The morphology of the aggregates in water after mixing ZnMPT2Cl and quinuclidine was observed by scanning electron microscope (SEM). The SEM samples were prepared by placing freshly cleaved mica on the surface of the gel (ZnMPT2Cl (50 mM), quinuclidine (50 mM)) and peeling off after making the contact,³⁷ followed by drying under vacuum. SEM images exhibited the formation of fibrous structures with a diameter of ca. 1 μm (Figure 2-2-3-2). The fibers are more crystalline and thicker than those prepared by mixing ZnMPT2Cl and DABCO in water, suggesting that the formation mechanisms of the fibrous structures in water are different between DABCO and quinuclidine.

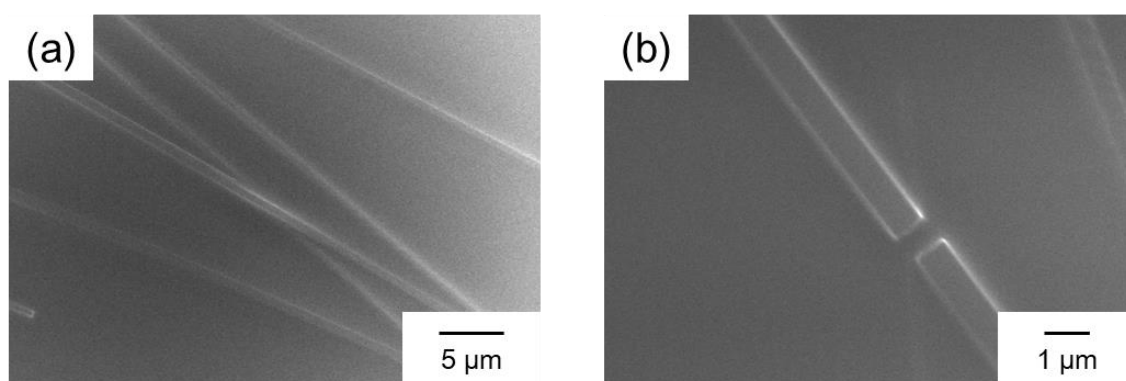


Figure 2-2-3-2. The SEM images of the xerogel (ZnMPT2Cl (50 mM), quinuclidine (50 mM)). (a) Low magnification. (b) High magnification.

2-2-4 Coordination behaviors of ZnMPT2Cl and DABCO or quinuclidine

To confirm the coordination of ZnMPT2Cl and DABCO in water, ^1H NMR measurement was undertaken with a D_2O sample of the mixture of ZnMPT2Cl and DABCO (14 mM, respectively). The peak attributed to DABCO at ca. 2.8 ppm (Figure 2-2-4-1a) was shifted to ca. 3.2 ppm (Figure 2-2-4-1c) after mixing with ZnMPT2Cl in D_2O , indicating that DABCO coordinated to the zinc center of ZnMPT2Cl and the electron density around the protons of DABCO decreased (Figure 2-2-4-1).

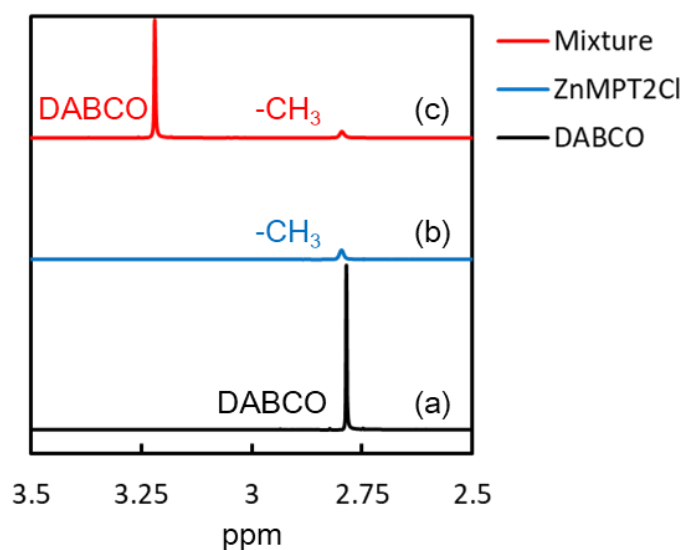


Figure 2-2-4-1. ^1H NMR spectra of (a) DABCO (14 mM in D_2O), (b) ZnMPT2Cl (14 mM in D_2O), and (c) the mixture of ZnMPT2Cl and DABCO (14 mM, respectively in D_2O).

^1H NMR measurement was also undertaken for the mixture of ZnMPT2Cl and quinuclidine in D_2O (10 mM, respectively). The peaks attributed to quinuclidine at ca. 1.7 (x, Figure 2-2-4-2a), 1.9 (y, Figure 2-2-4-2a) and 2.9 ppm (z, Figure 2-2-4-2a) were shifted to ca. 1.9, 2.1 and 3.3 ppm, respectively (Figure 2-2-4-2c) after mixing with ZnMPT2Cl in D_2O , indicating that quinuclidine also coordinated to the zinc center of ZnMPT2Cl.

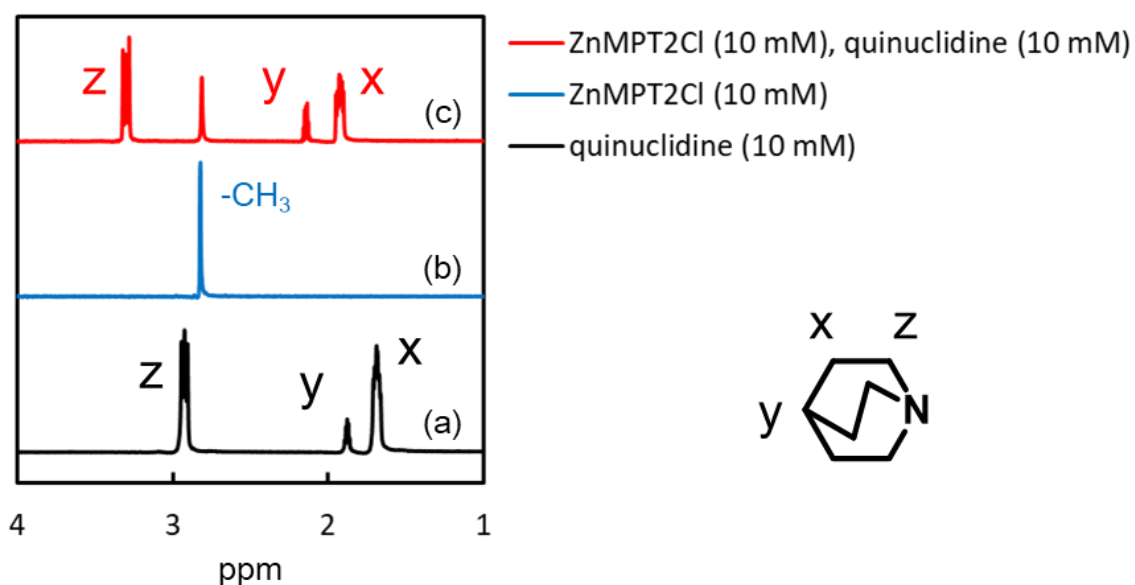


Figure 2-2-4-2. ^1H NMR spectra of (a) quinuclidine (10 mM in D_2O), (b) ZnMPT2Cl (10 mM in D_2O), and (c) the mixture of ZnMPT2Cl and quinuclidine (10 mM, respectively in D_2O).

Job plot based on the ^1H NMR spectra at different concentrations of ZnMPT2Cl and DABCO (0-10 mM, in D_2O) revealed that ZnMPT2Cl and DABCO coordinated at 1:1 ratio, suggesting that ZnMPT2Cl and DABCO formed one-dimensional coordination polymer (Figure 2-2-4-3, 4). It is to note that after mixing ZnMPT2Cl and DABCO in D_2O , only one peak derived from DABCO was observed, which indicated that DABCO molecules rapidly coordinated to and dissociated from the zinc center of ZnMPT2Cl as compared with the timescale of the ^1H NMR measurement.

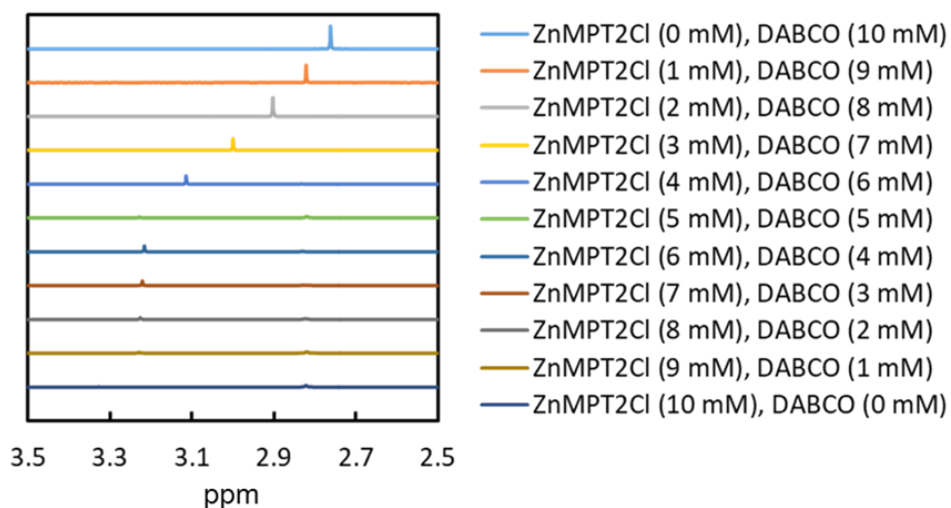


Figure 2-2-4-3. ^1H NMR spectra for the mixtures of ZnMPT2Cl and DABCO at different concentrations in D_2O (0-10 mM, respectively).

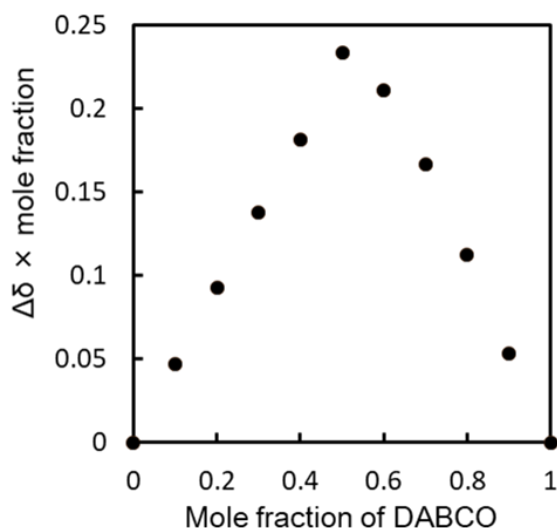


Figure 2-2-4-4. Job plot from the ^1H peak shift derived from DABCO observed on the ^1H NMR spectra for the mixtures of ZnMPT2Cl and DABCO (0-10 mM in D_2O).

To confirm the formation of the coordinated structure in water, the diffusion constants of each species were determined by DOSY-NMR spectroscopy. The values of the diffusion constants for ZnMPT2Cl and DABCO at low concentrations (10 mM, respectively in D₂O) are ca. 0.3×10^{-9} and 0.8×10^{-9} m²/s, respectively (Figure 2-2-4-5). This result indicated that ZnMPT2Cl and DABCO isolated in D₂O because of the labile property of zinc(II) ion in solution.^{38,39} However, the diffusion constant of DABCO (ca. $0.9 \pm 0.8 \times 10^{-9}$ m²/s) in D₂O became closer to that of ZnMPT2Cl (ca. 0.3×10^{-9} m²/s) at the concentrations of 50 mM (Figure 2-2-4-6). Moreover, two species of DABCO which had obviously different diffusion constants ($1.0 \pm 0.3 \times 10^{-9}$ m²/s and $0.4 \pm 0.3 \times 10^{-9}$ m²/s) were confirmed at the concentrations of 100 mM (Figure 2-2-4-7). The diffusion constant of the slower species of DABCO ($0.4 \pm 0.3 \times 10^{-9}$ m²/s) was almost the same as that of ZnMPT2Cl. These results revealed that the equilibrium on the coordination of ZnMPT2Cl and DABCO shifted to the coordinated state at higher concentrations.

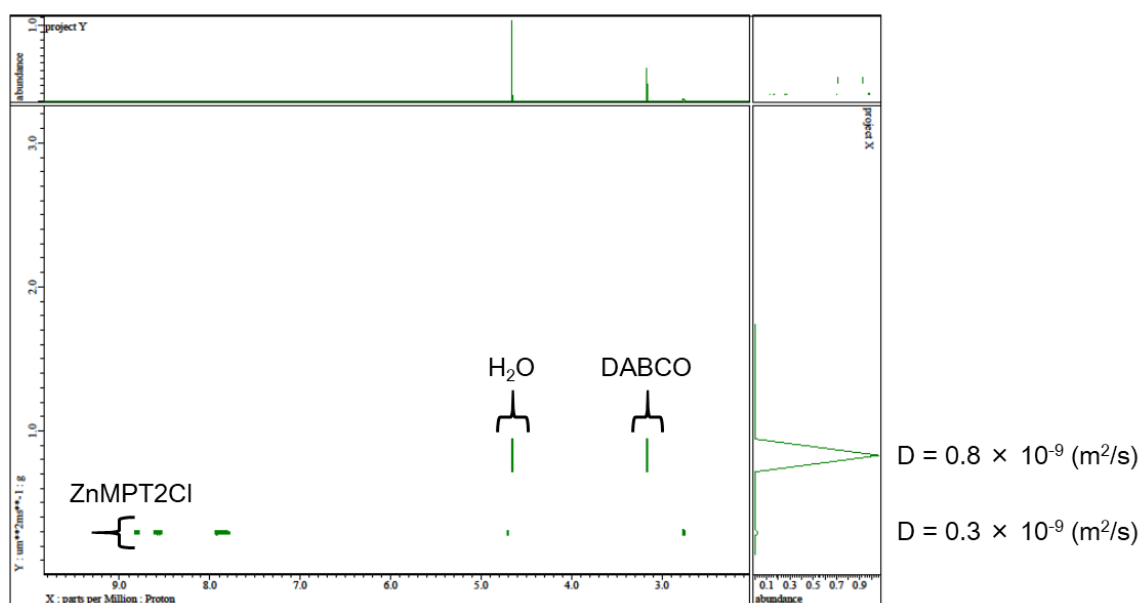


Figure 2-2-4-5. DOSY-NMR spectrum of the mixture of ZnMPT2Cl and DABCO in D₂O (10 mM, respectively).

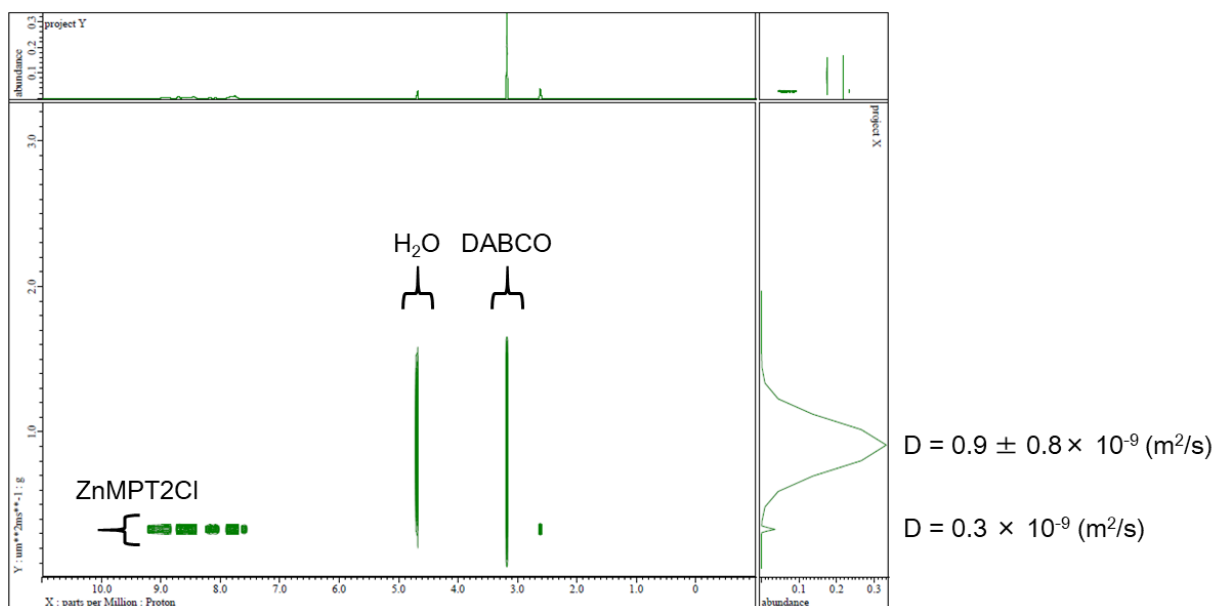


Figure 2-2-4-6. DOSY-NMR spectrum of the mixture of ZnMPT2Cl and DABCO in D_2O (50 mM, respectively).

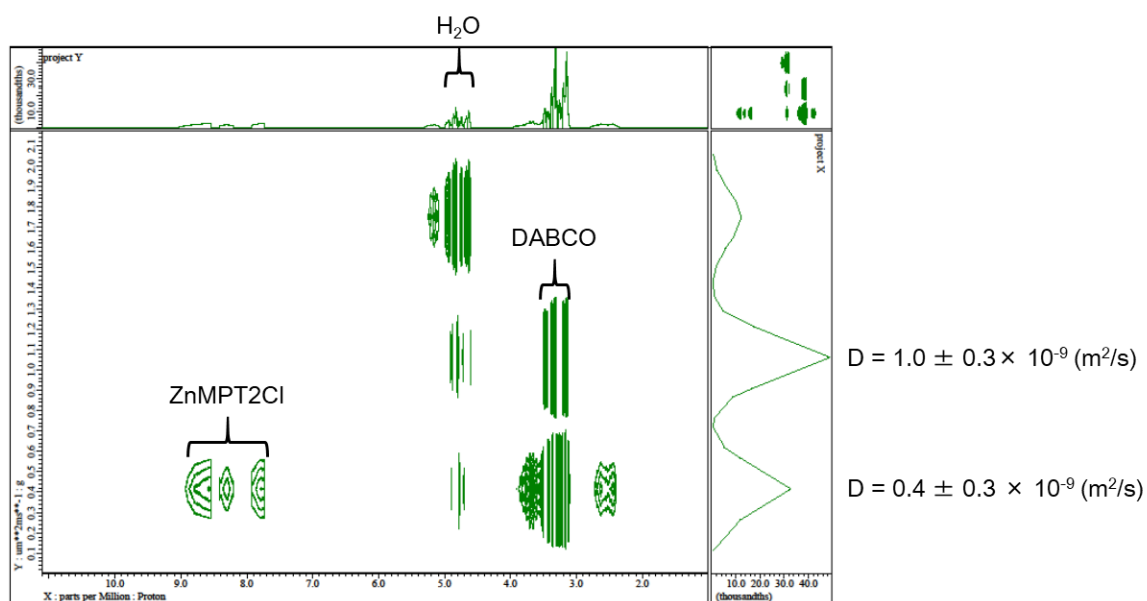


Figure 2-2-4-7. DOSY-NMR spectrum of the mixture of ZnMPT2Cl and DABCO in D_2O (100 mM, respectively).

2-2-5 Coordinated structure of ZnMPT2Cl and DABCO

In order to get more insight into the structure of the nanofibers, powder X-ray diffraction analyses were conducted on the hydrogel and xerogel of the ZnMPT2Cl-DABCO mixture. The xerogel was prepared by the evaporation of water from the hydrogel (100 mM, respectively) under ambient conditions. DABCO showed diffraction peaks at $2\theta = 16.99^\circ$, 19.66° , 27.78° , and 32.78° (corresponding $d = 5.21$ Å, 4.51 Å, 3.21 Å, and 2.73 Å, respectively, Figure 2-2-5a). ZnMPT2Cl showed obvious diffraction peaks at $2\theta = 5.58^\circ$, 5.99° , 9.72° , 10.12° , 11.28° , 12.04° , 14.11° , 14.72° , 16.23° , 20.47° , 21.43° , 23.04° , and 26.37° (corresponding $d = 15.83$ Å, 14.74 Å, 9.09 Å, 8.73 Å, 7.84 Å, 7.34 Å, 6.27 Å, 6.01 Å, 5.46 Å, 4.34 Å, 4.14 Å, 3.86 Å, and 3.38 Å, respectively, Figure 2-2-5b). Though the hydrogel (ZnMPT2Cl 100 mM, DABCO 100 mM) showed no apparent diffraction peaks (Figure 2-2-5c), the xerogel showed diffraction peaks at $2\theta = 4.73^\circ$, 6.49° , 8.00° , 10.83° , 15.42° , 16.89° , 20.57° , and 31.52° (corresponding $d = 18.67$ Å, 13.61 Å, 11.01 Å, 8.16 Å, 5.74 Å, 5.25 Å, 4.31 Å, and 2.64 Å, respectively, Figure 2-2-5d), which are different from those of pristine ZnMPT2Cl and DABCO. It was elucidated that a new coordinated structure was formed upon mixing ZnMPT2Cl and DABCO. However, the molecular packing of the coordinated structure in the hydrogel is still unclear.

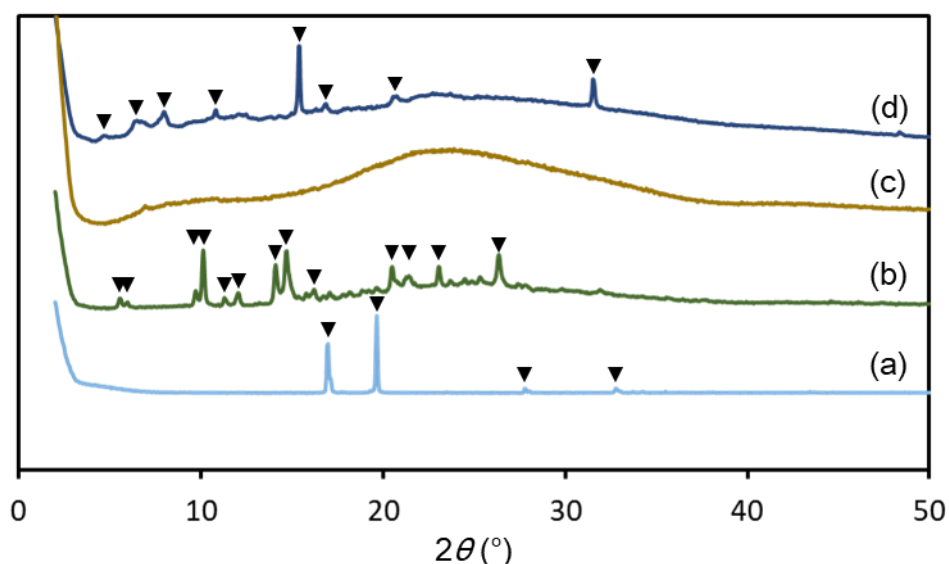


Figure 2-2-5. Powder X-ray diffraction patterns of (a) DABCO, (b) ZnMPT2Cl, (c) hydrogel (ZnMPT2Cl 100 mM, DABCO 100 mM) and (d) xerogel (ZnMPT2Cl 100 mM, DABCO 100 mM).

2-2-6 Thermal stability of the hydrogel

The phenanthroline moiety of ZnMPT2Cl is hydrophobic and interactions, such as hydrophobic interaction, among the self-assembled structures based on the coordination of ZnMPT2Cl and DABCO would provide the hydrogel thermal stability. To confirm the thermal stability of the hydrogel (ZnMPT2Cl 100 mM and DABCO 100 mM), differential scanning calorimetry (DSC) measurements were conducted (scan rate of 1 °C/min, Figure 2-2-6a). Gel-to-solid (freezing of water: -20 °C, $\Delta H = -5.3$ kJ/mol, $\Delta S = -21$ J/mol·K) and solid-to-gel (melting of ice: 2 °C, $\Delta H = +5.4$ kJ/mol, $\Delta S = +20$ J/mol·K) transition behaviors of the hydrogel were observed in the cooling and heating processes, respectively. However, the gel-to-sol transition was not detected even at higher temperatures. It was suggested that the hydrogel has good thermal stability presumably due to the hydrophobic interaction or the π - π interaction based on the phenanthroline moieties among the coordinated structures at high concentrations.

Rheological measurements of the hydrogel (ZnMPT2Cl 100 mM and DABCO 100 mM) at different temperatures revealed that G' was higher than G'' at the broad temperature range (Figure 2-2-6b). This result also supported that interactions, such as hydrophobic interaction and π - π interaction based on the phenanthroline moieties, among the coordinated structures were strong enough to maintain the self-assembled structures in the hydrogel. It should be mentioned that the values of G' and G'' (ca. 14 and 7 Pa, respectively at 25 °C) increased at higher temperatures (ca. 22 and 8 Pa, respectively at 80 °C) probably due to the evaporation of water during the measurements.

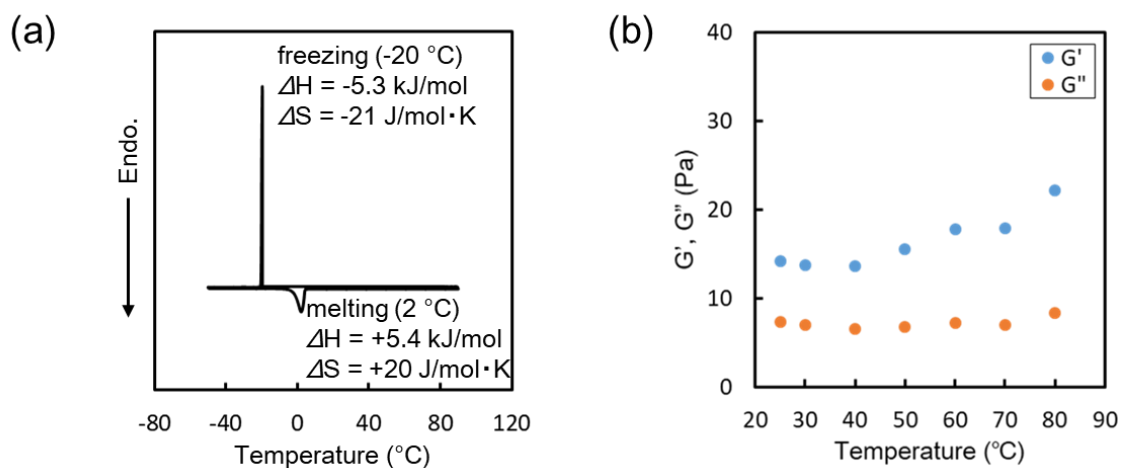


Figure 2-2-6. The assessment of the thermal stability of the hydrogel (ZnMPT2Cl 100 mM and DABCO 100 mM). (a) DSC measurement (scan rate of 1 °C/min). ΔH and ΔS were calculated based on the mole number of water. (b) Rheology measurements at different temperatures (strain 0.1%, angular frequency 100 rad/s, temperature 25-80 °C). The measurements were conducted soon after each hydrogel was put and heated on a sample plate at different temperatures.

2-2-7 Morphological and rheological changes of the hydrogel by adding multivalent anion

After mixing zinc(II) complexes with DABCO in water, it was suggested that cationic coordinated structures were presumably formed and self-assembled into nanofibers. Based on the addition of multivalent anions such as Na_2SO_4 , the binding between the coordinated structures as well as the bundled nanofibers was expected to be stronger, which would lead to a morphological change in the self-assembled structures and an enhancement on rheological stiffness of the hydrogels.

Hydrogels were prepared with the addition of Na_2SO_4 at different concentrations before the same annealing process described in section 2-2-1. When the concentration of Na_2SO_4 was below 200 mM with ZnMPT2Cl and DABCO (100 mM, respectively), clear hydrogels were obtained (Figure 2-2-7-1a-d). However, adding more than 400 mM of Na_2SO_4 gave a turbid hydrogel, suggesting that the structures in the hydrogel became larger due to hierarchical aggregation (Figure 2-2-7-1e). From the TEM images of the hydrogels (ZnMPT2Cl 100 mM, DABCO 100 mM) with different concentrations of Na_2SO_4 (100-400 mM), the morphological change of nanofibers with diameters of a few tens of nm to nanoribbons with widths of more than 100 nm induced by the presence of a larger amount of Na_2SO_4 could be seen (Figure 2-2-7-2). The multivalent anions presumably crosslinked the cationic coordinated structures or the self-assembled structures as macro domains. The rheological measurements revealed that adding a higher concentration of Na_2SO_4 enhanced the value of G' (ca. 49 Pa (Na_2SO_4 400 mM)), which suggested that the stiffness of the hydrogel increased based on the creation of the nanoribbons from the aggregation of the nanofibers (Figure 2-2-7-3).

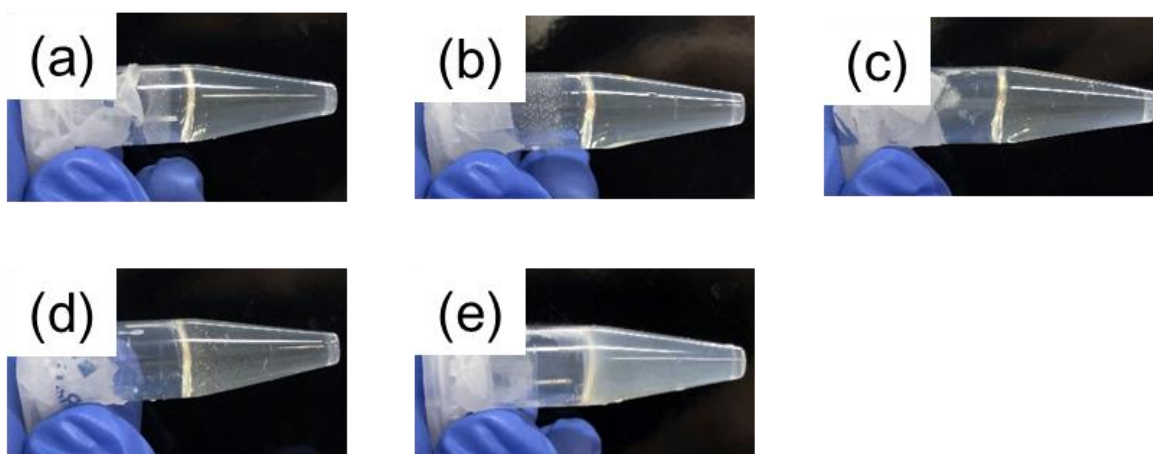


Figure 2-2-7-1. The optical images of the hydrogels (ZnMPT2Cl 100 mM, DABCO 100 mM) with different concentrations of Na_2SO_4 . (a) 1 mM. (b) 10 mM. (c) 100 mM. (d) 200 mM. (e) 400 mM.

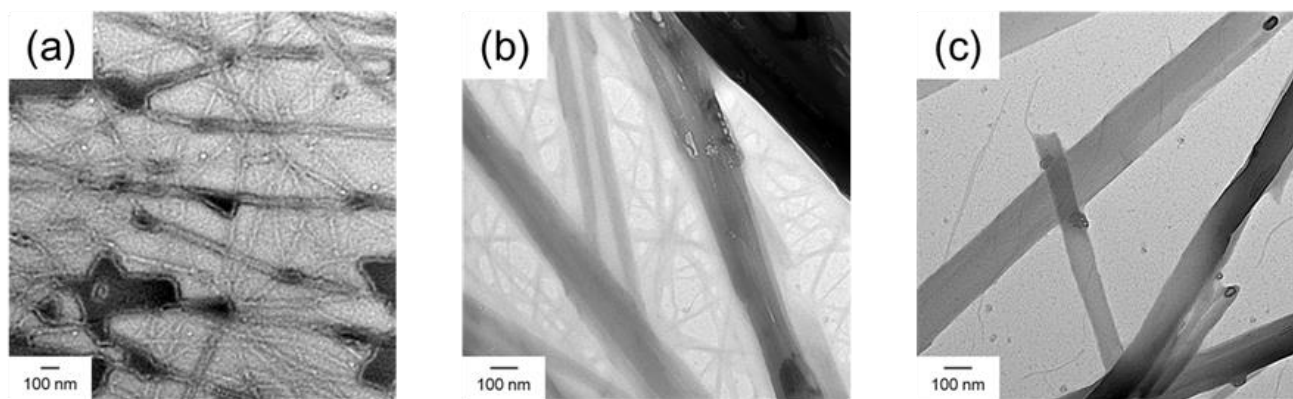


Figure 2-2-7-2. The TEM images of the hydrogels (ZnMPT2Cl 100 mM, DABCO 100 mM) with different concentrations of Na_2SO_4 transferred onto TEM grids by contacting the gel surfaces with the substrates and peeling off afterward, following by drying in vacuo. (a) 100 mM. (b) 200 mM. (c) 400 mM.

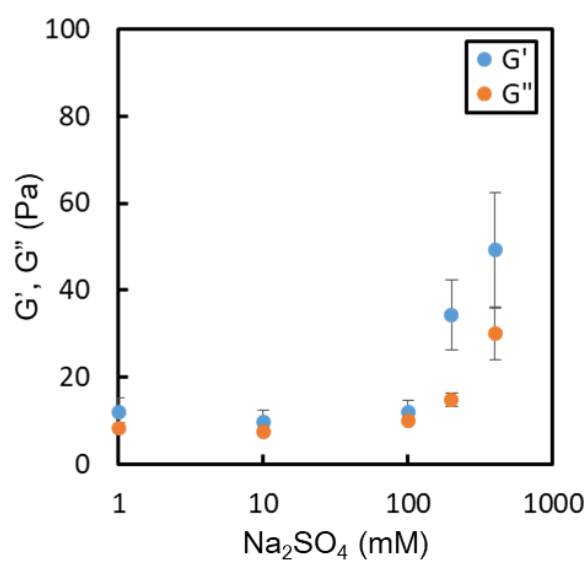


Figure 2-2-7-3. Rheology measurements for the hydrogels with different concentrations of Na_2SO_4 (ZnMPT2Cl 100 mM, DABCO 100 mM, Na_2SO_4 1-400 mM, strain 0.1%, angular frequency 100 rad/s, 25 °C).

2-2-8 Protonating behaviors of the hydrogel

The formation of the hydrogel was attributed to the coordination of DABCO to the metal center of zinc(II) complexes. DABCO coordinating to the zinc center would be protonated with the addition of acids such as hydrochloric acid (HCl), which could render the hydrogel being responsive to the pH values of external environments. Based on the ^1H NMR spectra of DABCO in D_2O with different concentrations of deuterium chloride (DCl), the ^1H peak derived from DABCO experienced a downfield shift from ca. 2.8 ppm (DCl: 0 mM) to ca. 3.8 ppm (DCl: more than ca. 100 mM), indicating the protonation of DABCO (Figure 2-2-8-1). When the concentration of DABCO was more than 100 mM, the chemical shift of the ^1H peak became almost consistent (ca. 3.8 ppm, Figure 2-2-8-2). This result suggested that DABCO was completely protonated by adding ca. 100 mM of DCl.

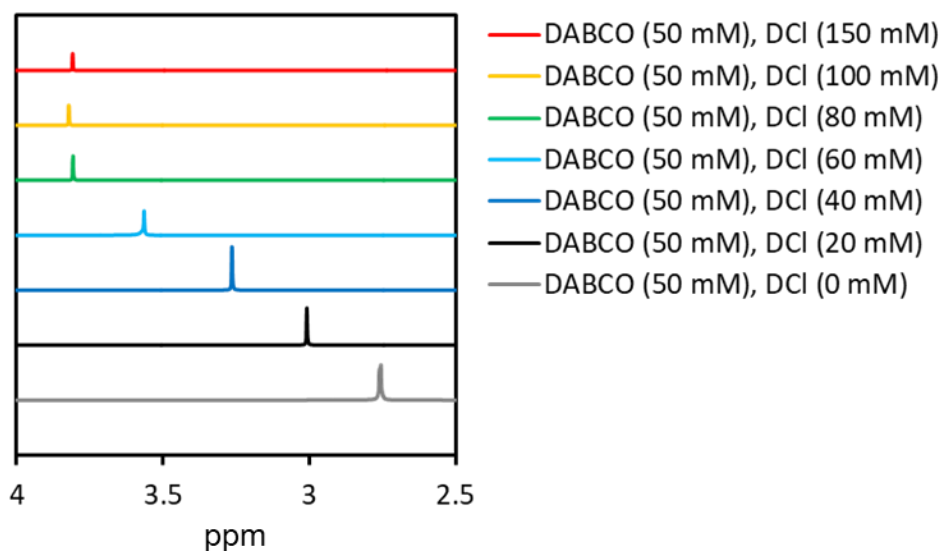


Figure 2-2-8-1. The ^1H NMR spectra of DABCO in D_2O with different concentrations of DCl (DABCO 50 mM, DCl 0-150 mM).

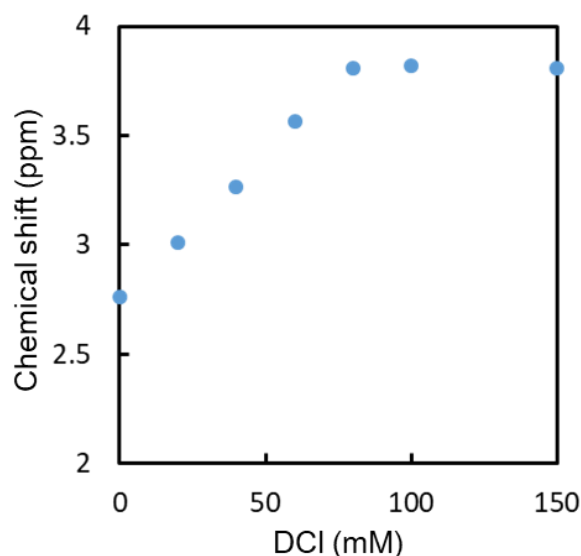


Figure 2-2-8-2. The change in the chemical shift of DABCO based on the addition of different concentrations of DCl (DABCO 50 mM, DCl 0-150 mM in D₂O).

Meanwhile, the ¹H peak representing DABCO of the hydrogel (ZnMPT2Cl 50 mM, DABCO 50 mM) was almost the same (ca. 3.2 ppm) when the concentration of DCl was below 40 mM presumably because the electron density around the protons of DABCO already decreased by the coordination to the zinc center of ZnMPT2Cl. However, when the concentration of DCl reached higher than 60 mM, the ¹H peak obviously shifted from ca. 3.2 ppm to ca. 3.8 ppm and became stable again with ca. 100 mM of DCl (ca. 3.8 ppm, Figure 2-2-8-3, 4). Then, the protonating behavior of DABCO became the same as that in the uncoordinated form.

Neutralization titrations were also conducted by adding HCl aqueous solution (50 mM, each 250 μL) to control solutions (initial concentration: ZnMPT2Cl 50 mM or DABCO 50 mM in water (5 mL)) and the hydrogel (initial concentrations: ZnMPT2Cl and DABCO 50 mM, respectively in water (5 mL)) and collecting the resulting solutions by each 250 μL to confirm the pH value by a pH meter. The results of the neutralization titrations supported that DABCO contributed to the buffering effect (Figure 2-2-8-5). Additionally, the apparent value of pK_a attributed to the first protonation of DABCO changed from 8.6 to 6.1 because of the coordination of DABCO to ZnMPT2Cl (Figure 2-2-8-5).

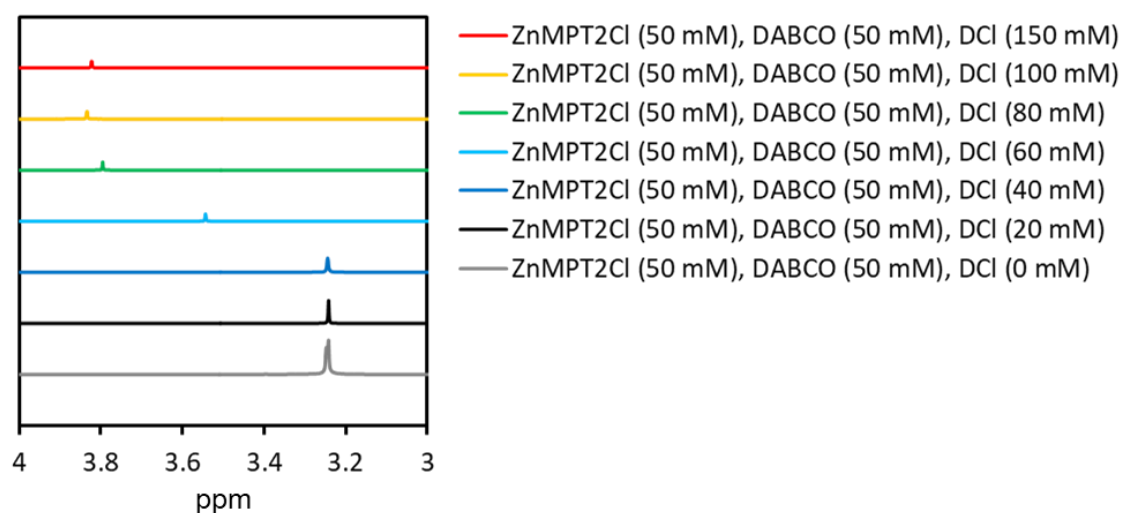


Figure 2-2-8-3. The ^1H NMR spectra of ZnMPT2Cl and DABCO in D_2O with different concentrations of DCl (ZnMPT2Cl 50 mM, DABCO 50 mM, DCl 0-150 mM).

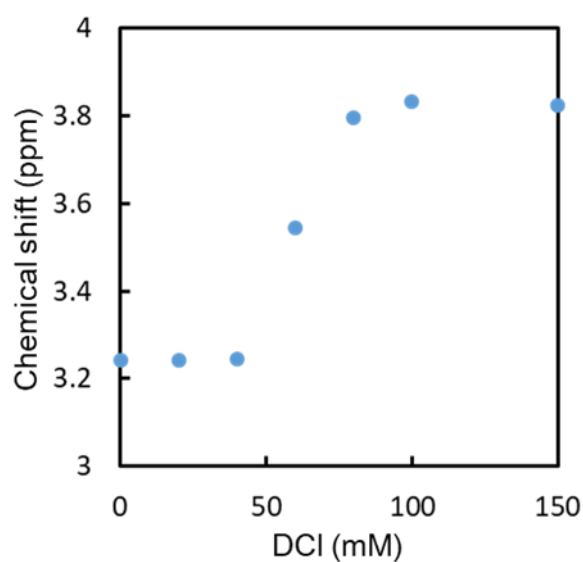


Figure 2-2-8-4. The change in the chemical shift of DABCO based on the addition of different concentrations of DCl (ZnMPT2Cl 50 mM, DABCO 50 mM, DCl 0-150 mM in D_2O).

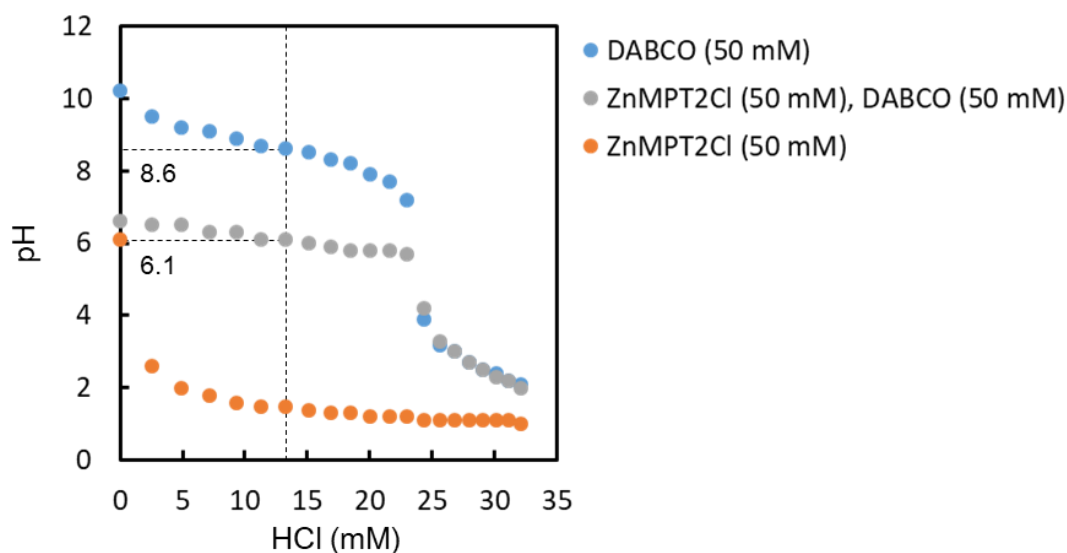


Figure 2-2-8-5. Neutralization titrations of aqueous solutions (initial concentration: ZnMPT2Cl 50 mM or DABCO 50 mM in 5 mL water) and hydrogel (initial concentrations: ZnMPT2Cl and DABCO 50 mM, respectively in 5 mL water) with HCl aqueous solution (50 mM, added by 250 μ L each).

The pH values and the rheological properties of the hydrogel (ZnMPT2Cl 50 mM, DABCO 50 mM) were evaluated with the addition of HCl (Figure 2-2-8-6). When the concentration of HCl was below 20 mM, the pH values were almost the same (pH = ca. 6.8, Figure 2-2-8-6a), which meant the buffering effect based on DABCO. The pH value dramatically changed from ca. 6.8 to ca. 6.3 by adding more than 20 mM HCl. Rheological measurements revealed that the value of G'' became larger than that of G' with more than 20 mM of HCl, indicating that the hydrogels collapsed by the addition of HCl (Figure 2-2-8-6b, c). Based on these results, it was suggested that the hydrogel had pH responsivity based on the protonation of DABCO coordinating to the zinc center of ZnMPT2Cl.

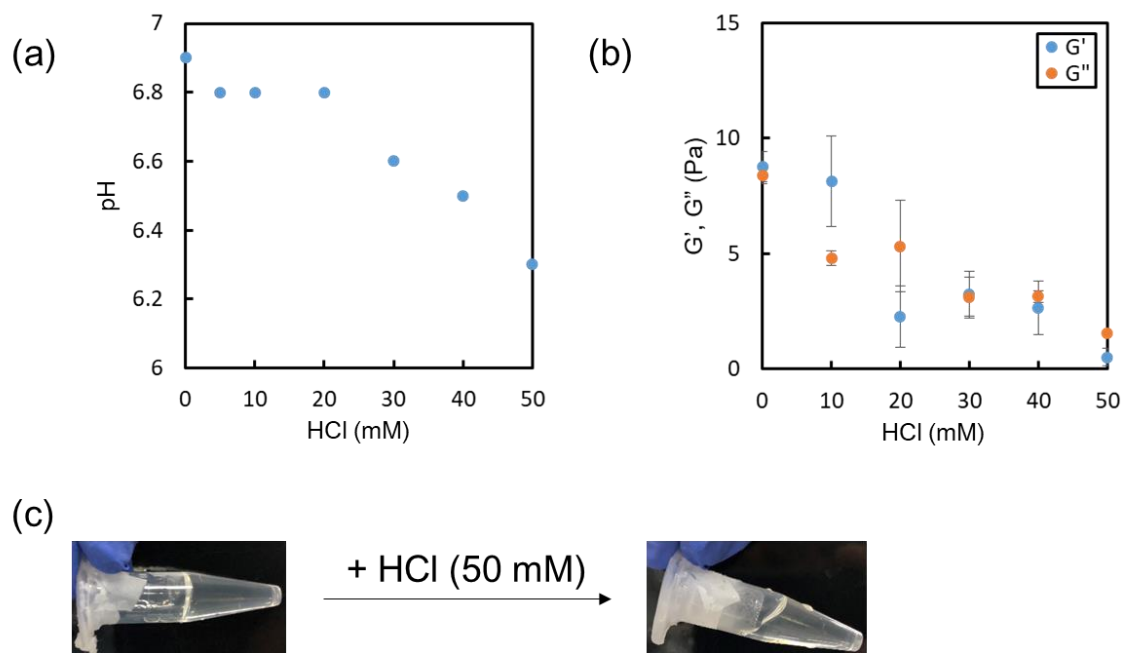


Figure 2-2-8-6. The pH responsivity of the hydrogel (ZnMPT2Cl 50 mM, DABCO 50 mM). (a) The change in the pH values of the hydrogels after adding HCl (0-50 mM). (b) Rheological measurements for the hydrogel with different concentrations of HCl (0-50 mM, strain 0.1%, angular frequency 100 rad/s). (c) Optical images of the hydrogels with and without the addition of HCl (50 mM).

2-2-9 Drug release properties of the hydrogels through the pH responsivity

Adding anionic species, such as copper(II) phthalocyanine tetrasulfonic acid tetrasodium salt, to the hydrogel of ZnMPT2Cl and DABCO induced the formation of ion complex consisting of the anions and the zinc complex because of the electrostatic interaction. Meanwhile, cationic species, such as Rhodamine B, diffused in the hydrogel through the electrostatic repulsion between the cations and the cationic self-assembled structures in the hydrogel. By combining the pH responsivity upon the coordinated structures in water and the electrostatic interaction between ionic species and the surface of self-assembled nanofibers, the hydrogel can be utilized as pH-responsive carriers for cationic species. The release property of the hydrogel was demonstrated with a model drug, doxorubicin hydrochloride (Dox, Figure 2-2-9-1). After preparing the hydrogels with the presence of Dox (ZnMPT2Cl (100 mM), DABCO (100 mM), Dox (0.5 mM), water (200 μ L)), the hydrogels were placed above Britton-Robinson buffer solutions (H_3BO_4 (40 mM), H_3PO_4 (40 mM), CH_3COOH (40 mM), NaOH, water (1800 μ L)) with different pH (pH 4-8 adjusted by NaOH aq) using dialysis film (molecular weight cut off: 6000-8000) as separator. The absorbance of Dox ($\lambda = 500$ nm) diffused to the buffer solutions were monitored by UV-vis spectroscopy (Figure 2-2-9-2). The absorbance at around $\lambda = 500$ nm derived from Dox increased over time and the increment in the absorbance was large under acidic environment (Figure 2-2-9-3). It was assumed that the hydrogel collapsed quickly based on the protonation of DABCO and released Dox to the buffer layer under acidic conditions. Generally, inside our body, extracellular pH (pHe) around cancer cells (pHe = ca. 6.9) are more acidic than that of normal cells (pHe = ca. 7.5).⁴⁰ Therefore, the hydrogels have the potential to be utilized as a pH-responsive drug carrier targeting for cancer treatments.

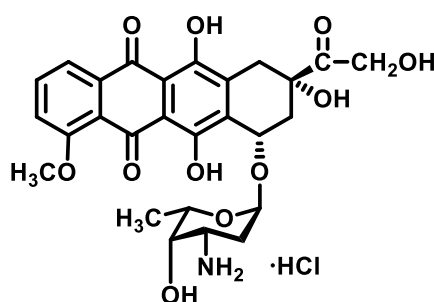


Figure 2-2-9-1. Molecular structure of doxorubicin hydrochloride (Dox).

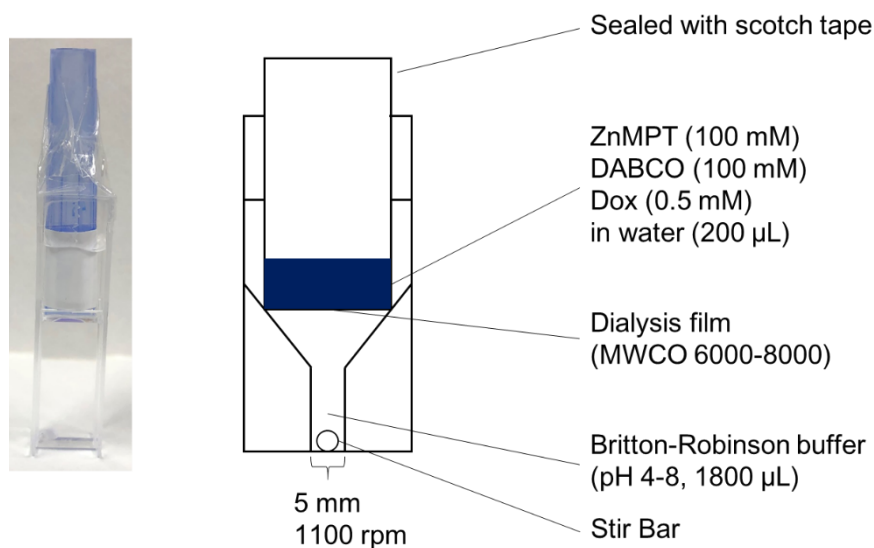


Figure 2-2-9-2. Cross-sectional illustration of the sample for evaluating of Dox release property of the hydrogel.

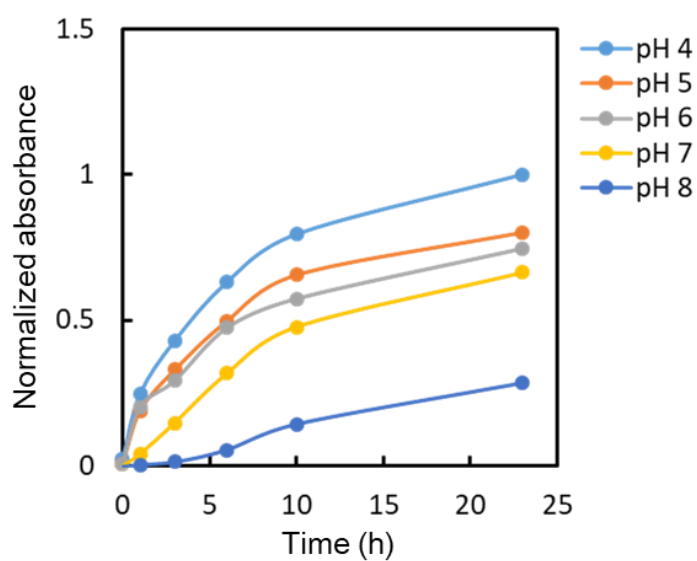


Figure 2-2-9-3. The time-dependent Dox release ability of the hydrogel evaluated by UV-vis spectroscopy (hydrogel (ZnMPT2Cl 100 mM, DABCO 100 mM, Dox 0.5 mM in water 200 μ L), and buffer (Britton-Robinson buffer 1800 μ L, pH 4–8), λ = 500 nm)).

2-2-10 Conclusion

In conclusion, mixing zinc(II) phenanthroline-based complexes and DABCO in water gave hydrogels which exhibited thermal stability and pH responsiveness. Moreover, utilizing the electrostatic interaction of interfaces on self-assembled nanofibers gave morphological and rheological changes, and controllability for the diffusion of ionic species within the hydrogels (Figure 2-2-10). DABCO coordinated to the zinc center, leading to the fabrication of nanofibrous networks in water. In this research, we successfully prepared multifunctional hydrogels upon relatively harmless zinc(II)-based coordinated structures, which have the potential to be utilized as a new drug delivery carrier.

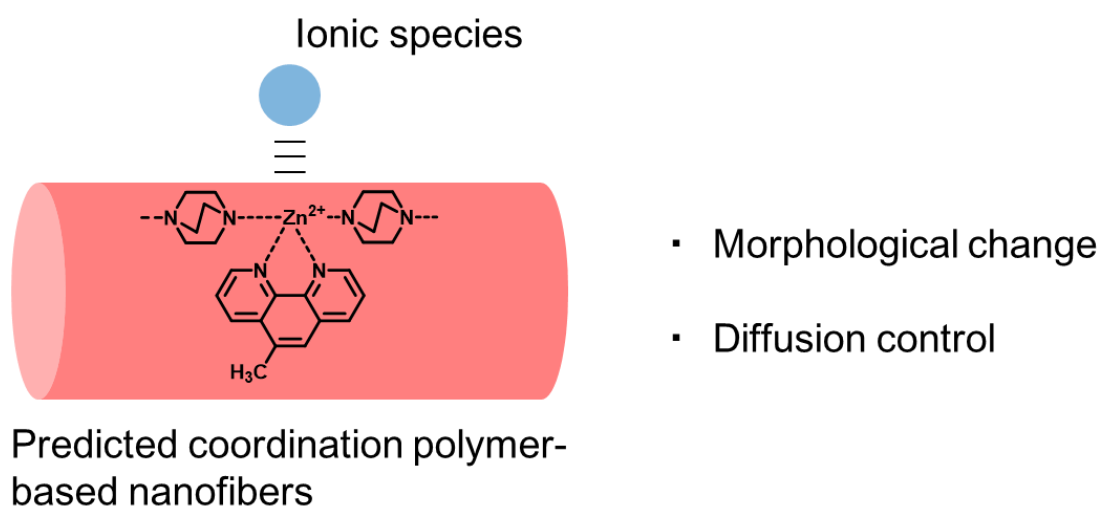
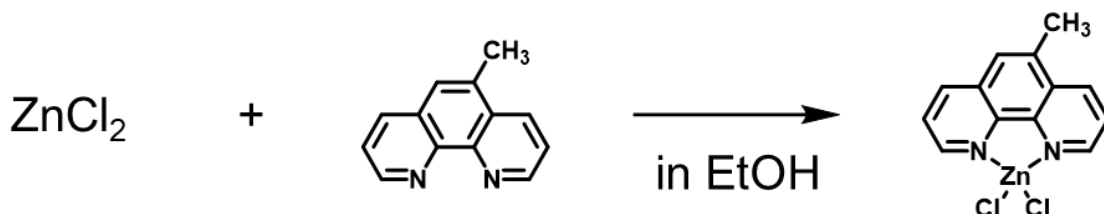


Figure 2-2-10. An illustration of this research.

2-3 Synthesis

Synthesis of zinc(II)-5-methyl-1,10-phenanthroline complex (ZnMPT2Cl)

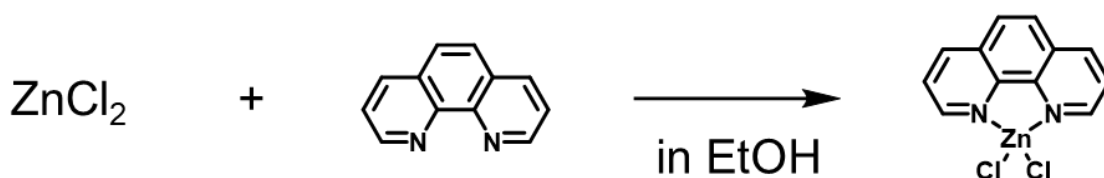


ZnMPT2Cl was synthesized according to the literature procedure.³⁶ 5-methyl-1,10-phenanthroline (895 mg, 4.61 mmol) was dissolved in ethanol (150 mL) and was added dropwisely to an ethanol solution (150 mL) of zinc chloride (945 mg, 6.93 mmol) while stirring. After refluxing the reaction solution under N_2 atmosphere for 29 h, colorless precipitate was obtained. Filtration, followed by washing with ethanol, gave pure zinc(II)-5-methyl-1,10-phenanthroline dichloride (1.20 g, 79%).

^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.83 (s, 3H), 7.97-8.08 (t, 3H), 8.73-8.91 (dd, 4H).

Elemental analysis, calculated for $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{N}_2\text{Zn}$: C, 47.27; H, 3.05; N, 8.48; found: C, 47.11; H, 2.98; N, 8.41.

Synthesis of zinc(II)-1,10-phenanthroline complex (ZnPT2Cl)



ZnPT2Cl was synthesized according to the literature procedure.³⁶ 1,10-phenanthroline (900 mg, 4.99 mmol) was dissolved in ethanol (150 mL) and was added dropwisely to an ethanol solution (150 mL) of zinc chloride (1.02 g, 7.50 mmol) while stirring. After refluxing the reaction solution under N_2 atmosphere for 19 h, colorless precipitate was obtained. Filtration, followed by washing with ethanol, gave pure zinc(II)-5-methyl-1,10-phenanthroline dichloride (1.32 g, 84%).

^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.00-8.03 (dd, 2H), 8.27 (s, 2H), 8.85-8.87 (d, 4H).

Elemental analysis, calculated for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{Zn}$: C, 45.54; H, 2.55; N, 8.85; found: C, 45.76; H, 2.54; N, 8.86.

2-4 Characterizations

^1H NMR spectra were obtained on JEOL ECZ400S spectrometer. Elemental analysis was conducted at the Elemental Analysis Center, Kyushu University. Rheology was studied with Anton Paar MCR 302. SEM images were obtained on a Hitachi SU9000 scanning electron microscope. TEM images were obtained on a JEOL JEM-2010 transmission electron microscope. Powder X-ray diffraction (PXRD) analysis was conducted on a Bruker D2 PHASER with a Cu K-alpha source ($\lambda = 1.54056 \text{ \AA}$) operated at 30 kV and 10 mA. DSC measurements were carried on a METTER TOLEDO DSC 1 STAR^e System. The pH of aqueous solutions and hydrogels were measured with a pH meter (HORIBA LAQUAtwin-pH-11B). UV-vis absorption spectra were recorded on a JASCO V-670 spectrophotometer.

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Chapter 3 Enhanced electric polarization and polar switching of dipolar aromatic liquids confined in supramolecular gel networks

3-1 Introduction

In Chapter 2, by utilizing the electrostatic interactions between ionic species and cationic coordinated structure in hydrogels, the morphological and rheological changes of hydrogels have been realized. Moreover, combining with the protonation of DABCO, the controlled release of Dox depending on the pH of the external environment was achieved. Though internal electric interactions, such as electrostatic interaction, have been focused in Chapter 2, external electric interactions such as applying an electric field to soft materials also enhance specific properties such as ion conductivity¹ or actuation² based on soft materials. However, in the case of the hydrogels consisting of coordinated structures, applying the electric field may cause electrolysis of water and redox reactions for metal ions of the metal complexes. These side reactions could suppress the utilization of the interfacial interactions between the assembled structures and solute or solvent molecules.

To overcome these problems and exploit the interfacial interactions in soft materials for the bulk properties, we have focused on organogels with electrically neutral gelator molecules. Interfacial interactions between the self-assembled structures based on the gelator molecules and organic solvent molecules were expected to lead to new functions of soft materials. Especially, utilizing the polarity of organic solvents would give the organogels unique electric property such as polar switching phenomena.

Therefore, in this chapter, we evaluated the unique dielectric properties and polar switching phenomena exerted by polar aromatic liquids confined in supramolecular organogels (Figure 3-1). We had our eyes on the gels formed from aromatic liquids with large permanent dipoles because the dipole-dipole interaction is a highly long-range effect that operates in substantial structural correlation lengths. Physical adsorption and dense alignment of such dipolar molecules on the organogel nanofiber surfaces may benefit from the cluster electrostatics³ which will promote structural ordering and cooperativity of the liquids on the surface of nanofibers in the gels. To the best of our knowledge, there are limited reports on the dielectric properties of confined organic liquids. For example, noncentrosymmetric inclusion of *p*-nitroaniline in the nanopores of molecular sieves has been demonstrated by the second-harmonic generation response⁴ and the pyroelectric property has been reported.⁵ Ethanol molecules contained in the formate-based metal-organic framework [Mn₃(HCOO)₆] (C₂H₅OH) show ferroelectricity but at the very low temperature of 160 K.⁶ Moreover, the past studies

on confined liquids have exclusively dealt with inorganic solids as host materials, and very little has been known for the dielectric properties of dipolar organic liquids confined in soft organic materials. It is expected that dipolar liquid molecules confined at the interfaces of self-assembled structures of supramolecular gels would exhibit unique dielectric properties that are distinct from those in the bulk. Herein we report the preparation of supramolecular gels by mixing the gelators with aromatic solvents having large dipole moments and the analyses of their physical and dielectric properties.

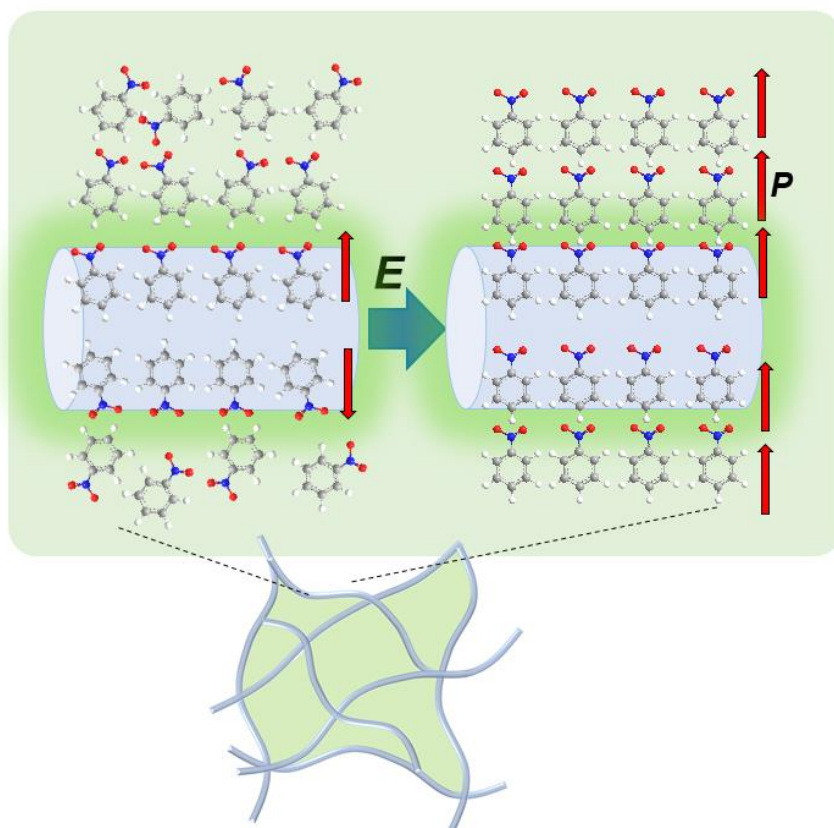


Figure 3-1. A graphic representation of the dielectric behavior of dipolar aromatic solvents such as nitrobenzene confined within the fibrous networks.

3-2 Results and Discussion

3-2-1 Gelation properties of gelator **1**

As a typical dipolar solvent, we employed nitrobenzene since it has a large permanent electric dipole moment ($\mu_D = 4.22$ debye).⁷ Nitrobenzene was purified as described in section 3-3. As for gelators, *N,N'*-bis(octadecyl)-L-boc-glutamicdiamide (**1** ($n = 14, 16, 18$), Figure 3-2-1-1) were synthesized according to the literature procedure.^{8,9} Although there are few reports on the formation of supramolecular gels in nitrobenzene,¹⁰⁻¹³ none of them reported their dielectric properties. Gelator **1** was dissolved in various solvents by heating to ca. 343 K, followed by cooling back down to room temperature naturally. The formation of gels in nitrobenzene and other reference solvents was first visually screened by the absence of flow of solvents when the vessels were inverted.

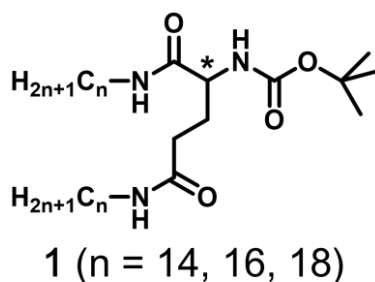


Figure 3-2-1-1. Chemical structure of the gelator **1**.

Figure 3-2-1-2a-c show the pictures of **1** ($n = 18$) dispersed in nitrobenzene at various concentrations. The gels were formed above the concentration of ca. 6 mM, as determined by the rheological measurements. In Figure 3-2-1-3a-e, time dependences of G' and G'' for the nitrobenzene gel at varying concentrations of **1** ($n = 18$) are shown. Below the concentration of 5 mM, the storage modulus G' is negligible (Figure 3-2-1-3 (a)), whereas for the concentration above 6 mM, G' gave larger value as compared with that of G'' (Figure 3-2-1-3b-e). Figure 3-2-1-3 (f) depicts the dependence of G' and G'' on the concentration of **1** ($n = 18$), showing the onset of G' value at ca. 6 mM, which corresponds to the critical gelation concentration.

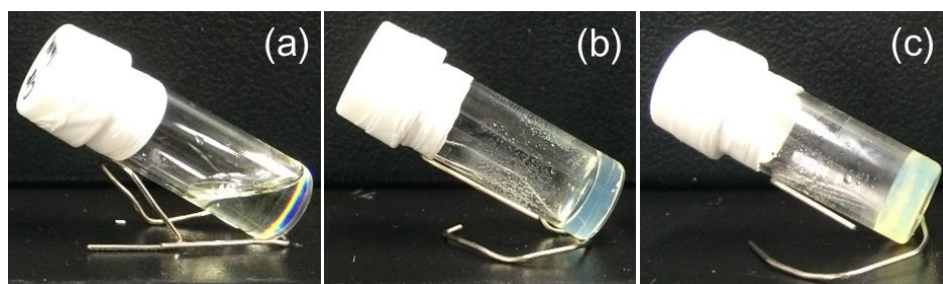


Figure 3-2-1-2. Pictures of **1** dispersed in nitrobenzene. (a) 1, (b) 10 and (c) 100 mM.

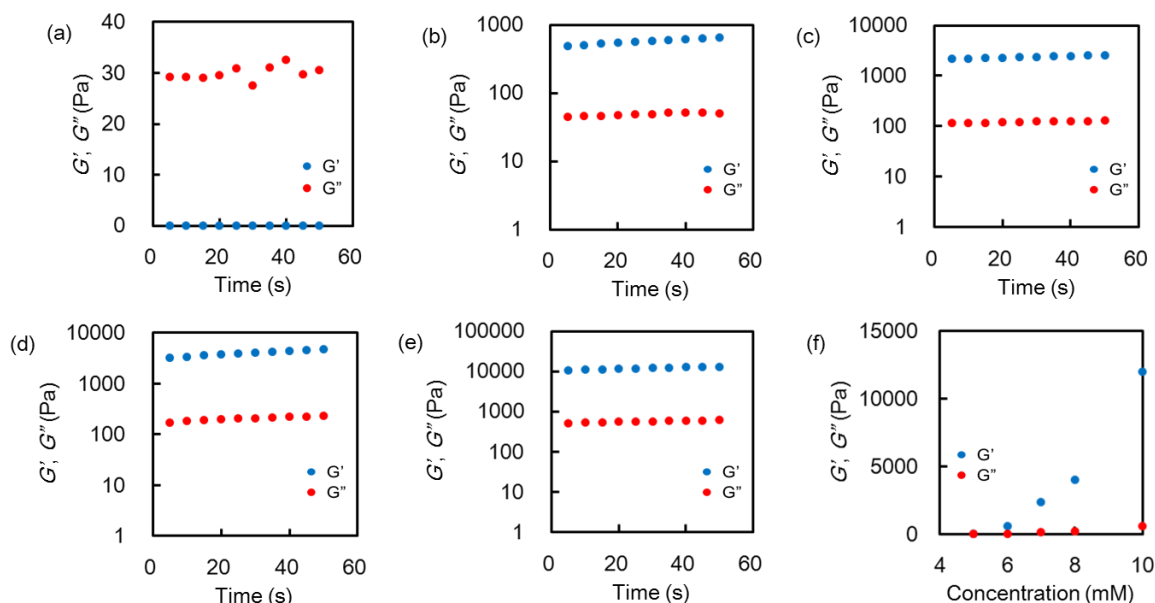


Figure 3-2-1-3. (a-e) The time-dependent and (f) concentration-dependent mechanical spectra of nitrobenzene gels prepared at gelator **1** ($n = 18$) concentrations of (a) 5, (b) 6, (c) 7, (d) 8 and (e) 10 mM (strain: 0.1%, angular frequency: 100 rad/s).

The effect of alkyl chain length of **1** ($n = 14, 16, 18$) on the rheological data of nitrobenzene gels is summarized in Figure 3-2-1-4. All the compounds showed larger G' than the corresponding G'' , which is consistent with the gel formation. We note that the shorter alkyl-chained **1** ($n = 14$) showed smaller G' value as compared with those of the longer-chained gelators **1** ($n = 16, 18$), reflecting less rigidity of the gel due to weaker intermolecular interactions among the shorter alkyl chains.

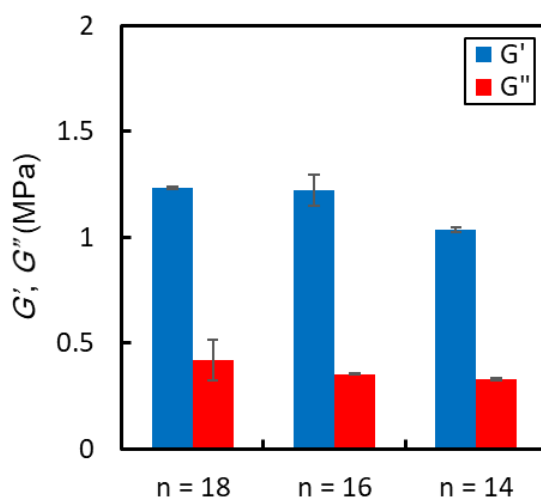


Figure 3-2-1-4. Rheological properties of nitrobenzene gels prepared with different gelators **1** ($n = 18, 16, 14$). concentration, 100 mM. temperature at 298 K, strain: 0.1%, angular frequency: 100 rad/s. Data were obtained after keeping the gels on a sample plate at 298 K for 5 min.

3-2-2 Morphologies of organogels

The morphology of **1** ($n = 18$) self-assembled in nitrobenzene was then investigated by using atomic force microscopy (AFM, Figure 3-2-2-1) and transmission and scanning electron microscopy (TEM, SEM, Figure 3-2-2-2). The AFM images in Figure 3-2-2-1a was obtained for the specimen prepared by drop-casting 1 mM nitrobenzene dispersion on a mica surface. Well-developed nanofibrous structures were abundantly observed, and the formation of nanofibers in 1 mM dispersion was also confirmed by TEM observation (Figure 3-2-2-2a). The morphologies in the gel state were observed by transferring the surface layer of nitrobenzene gels (concentrations, 10 and 100 mM) onto mica surfaces through contacting the gel surfaces with the substrates on gel surfaces and peeling off afterward.¹⁴ Entangled bundles of fibrous structures are seen in the 10 mM-gel sample (Figure 3-2-2-1b), while twisted helical superstructures were evident for the 100 mM-gel (Figure 3-2-2-1c). SEM images obtained for the dried specimens show dense accumulation of the nanofiber aggregates (Figure 3-2-2-2b,c). These results indicate that compound **1** ($n = 18$) spontaneously self-assembles in nitrobenzene to fabricate nanofibrous networks that can confine nitrobenzene molecules in the interstitial domains of the gel. TEM images of organogels **1** formed in non-polar solvents such as toluene and mesitylene also showed nanofibrous structures (Figures 3-2-2-2d,e). We confirmed that the shorter-chained **1** ($n = 14, 16$) also give bundles of helical nanofibers in nitrobenzene gel, as confirmed by AFM (Figure 3-2-2-3). Powder X-ray diffraction patterns of **1** ($n = 14, 16, 18$) are shown in Figure 3-2-2-4a, in which the compounds with longer alkyl chains give fewer diffractions, indicating lower crystallinity. In contrast, the shorter chained **1** ($n = 14$) displayed many diffractions that indicate a higher crystallinity in the powdery state. Meanwhile, broad scattering patterns are obtained for nitrobenzene gels (100 mM) which are not dependent on the chemical structure (Figure 3-2-2-4b). The self-assembling phenomena in organic media are directed by solvophobic interactions, i.e., the solute-solvent immiscibilities (enthalpic force) that arise from the differences in cohesive energy between the solute (gelator molecule **1** in this case) and the solvent.¹⁵ The cohesive energies of organic solvents are small, while the gelators **1** ($n = 14, 16, 18$) form developed nanofibrous aggregates in nitrobenzene gels because the multiple hydrogen bond networks provide large cohesive energy together with the van der Waals interactions among oriented alkyl chains. The alkyl chain moiety of the gelator also serves as a solvophilic group¹⁵ and is more or less solvated by nitrobenzene molecules.

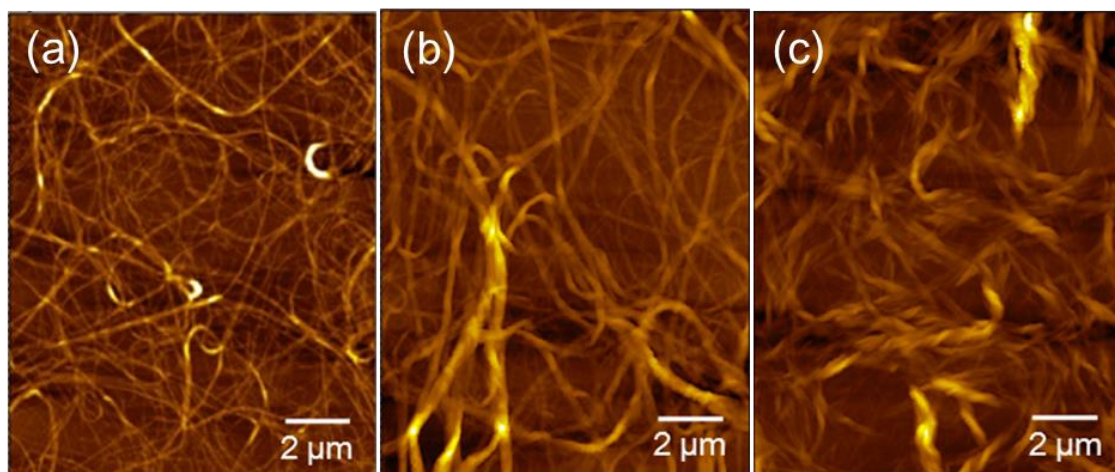


Figure 3-2-2-1. AFM images of nitrobenzene gels on mica. (a) $[1 (n = 18)] = 1 \text{ mM}$, (b) $[1 (n = 18)] = 10 \text{ mM}$. (c) $[1 (n = 18)] = 100 \text{ mM}$.

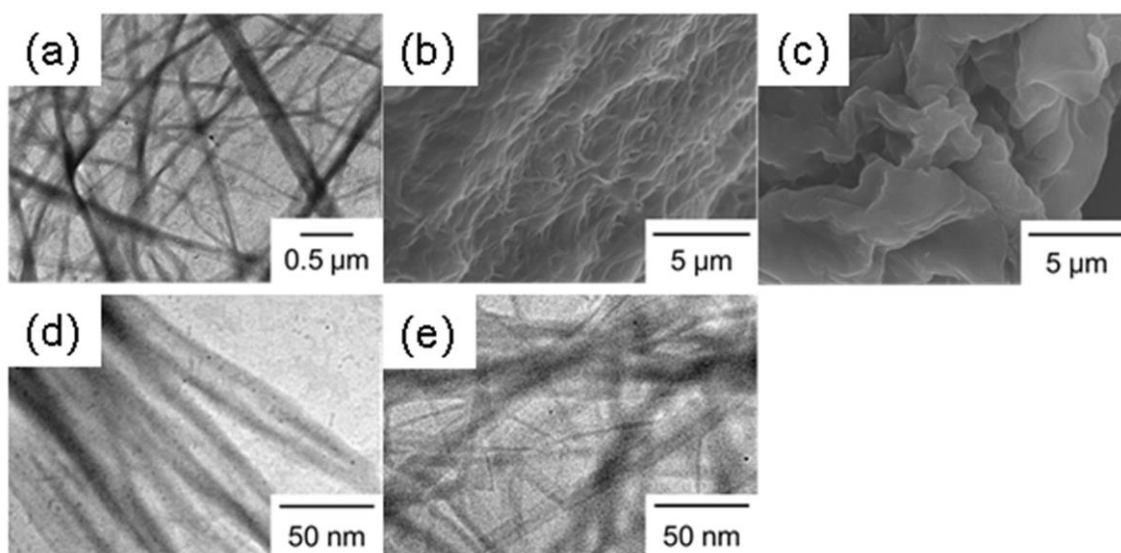


Figure 3-2-2-2. (a) A TEM image of a dried nitrobenzene solution of **1** ($n = 18$) (1 mM) prepared by drop-casting the solution onto a carbon-coated TEM grid and post-stained with uranyl acetate. (b,c) SEM images of nitrobenzene gels ($[1 (n = 18)] = 10$ and 100 mM , respectively) transferred onto mica surfaces. The samples were prepared by contacting the substrates on gel surfaces and peeling them off after a few seconds. TEM images of (d) toluene and (e) mesitylene gels ($[1 (n = 18)] = 100 \text{ mM}$), respectively. The surface of each gel is transferred onto the TEM grids by placing them and succeeding peeling off from the gel surface. The specimens were post-stained with uranyl acetate.

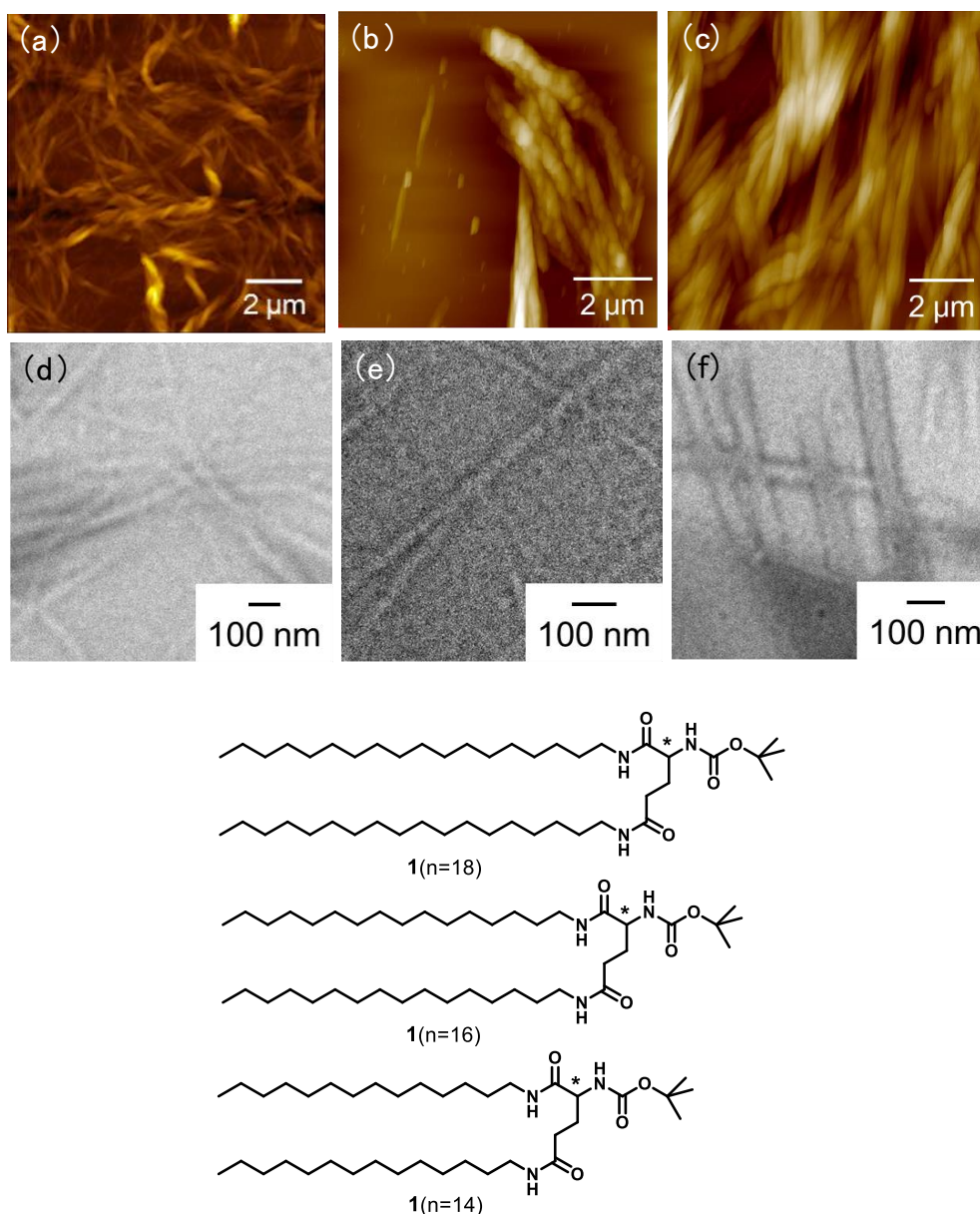


Figure 3-2-2-3. (a)-(c): Comparison of AFM images of nitrobenzene gels formed from different gelators **1** (a) $n = 18$. (b) $n = 16$. (c) $n = 14$. Concentrations, 100 mM. The AFM specimens were prepared on freshly cleaved mica surfaces as described in the text. (d)-(f): TEM images of nitrobenzene gels formed from gelators **1** (d) $n = 18$, (e) $n = 16$, and (f) $n = 14$ (concentration, 100 mM). The nanofibrous structures were transferred onto carbon-coated TEM grids by placing them on the gel surfaces and peeling off a moment later. The TEM specimens were post-stained with uranyl acetate.

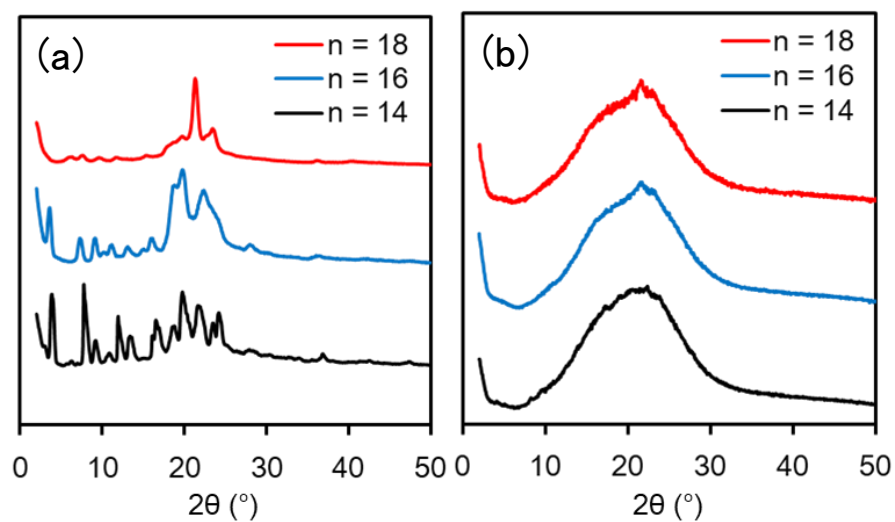


Figure 3-2-2-4. X-ray diffraction patterns of (a) **1** ($n = 18, 16$ and 14) in the powdery state, (b) nitrobenzene gels **1** ($n = 18, 16$ and 14), concentration, 100 mM.

3-2-3 Phase transition behaviors of nitrobenzene and the gels

Thermal characteristics of the 100-mM nitrobenzene gel were then investigated by using differential scanning calorimetry (DSC, Figure 3-2-3-1). The melting point of nitrobenzene in gel **1** ($n = 18$) was denoted by the endothermic peak at 279 K, which is identical to that observed for pure nitrobenzene (Figure 3-2-3-1a). Upon further heating, a broad endothermic peak at ca. 324 K (Figure 3-2-3-1b), which is attributed to the dissolution of the gel. Cooling the solution (i.e., sol), gave a sharper exothermic peak at 317 K, at which the sol gelatinized reversibly. The changes in enthalpy (ΔH) and entropy (ΔS) associated with these peaks are calculated to be ca. 22 kJ/mol and ca. 70 J/(mol·K), respectively (Figure 3-2-3-1b).

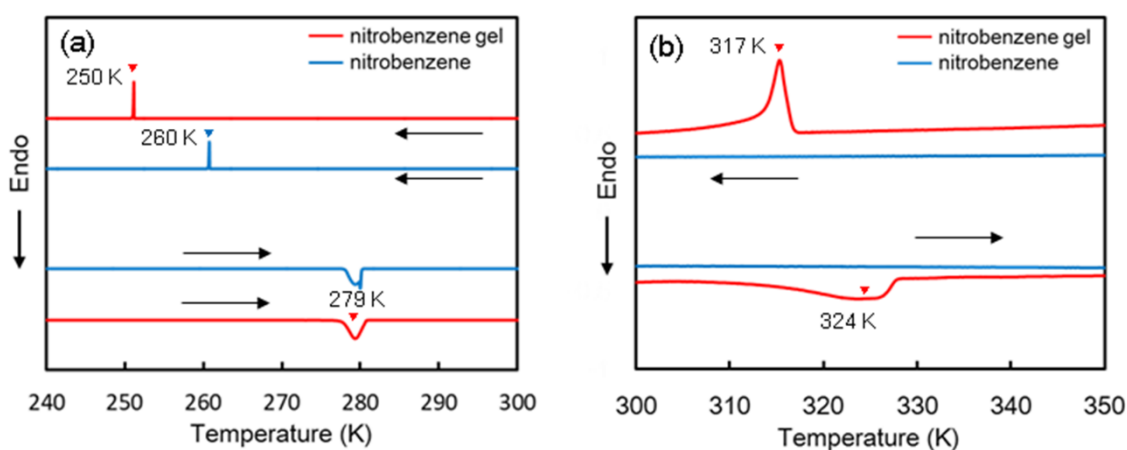


Figure 3-2-3-1. DSC thermograms of nitrobenzene gel (**1** ($n = 18$)) = 100 mM) and nitrobenzene (scan rate = 1 K/min).

The sol-to-gel transition of the nitrobenzene gel is further confirmed by measuring G' and G'' in the course of cooling the melted-gel solution (Figure 3-2-3-2). Upon cooling the sol, G' and G'' started to increase at ca. 325 K, and reached almost constant values at 317 K. Below this temperature, the value of G' exceeded that of G'' and the thermally reversible formation of nitrobenzene gel was rheologically confirmed.

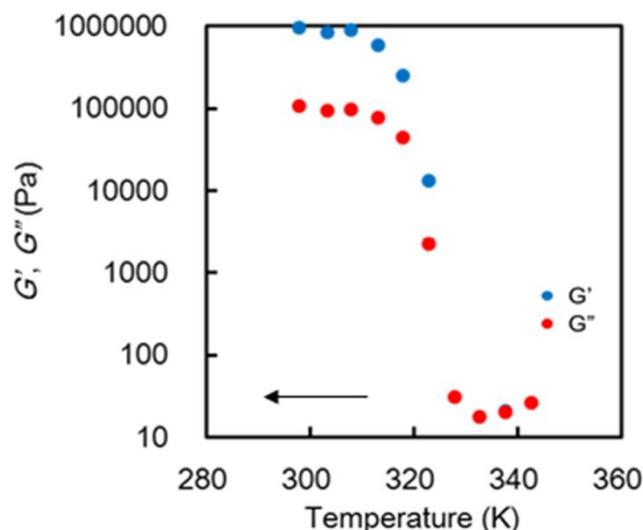


Figure 3-2-3-2. The temperature-dependent mechanical spectrum of nitrobenzene gel (**1** ($n = 18$)) = 100 mM, cooling process, strain = 0.1%, angular frequency = 100 rad/s). Data were obtained soon after putting and heating the gel to 342 K on a sample plate in order to prevent the evaporation of nitrobenzene.

In the course of DSC measurement, we noticed that pure nitrobenzene reveals a freezing temperature at 260 K which is considerably lower than the melting temperature at 279 K (Figure 3-2-3-1a). The observed lowering of freezing temperature is ascribed to the supercooled state, which has been rationalized to the presence of locally favored structures that differ from the crystalline symmetry.^{16,17} The crystals of nitrobenzene are monoclinic with four molecules in the unit cell (Figure 3-2-3-3),¹⁸ whereas the formation of antiparallel dimers was suggested for nitrobenzene in non-polar solvents at elevated concentrations.¹⁹ It is, therefore, possible that a unique frustration exists in pure nitrobenzene between the local domain structures directed by dipole-dipole interactions and less-ordered liquid structures that are prone to crystallization.²⁰ Meanwhile, nitrobenzene gel gave an exothermic peak at 250 K (Figure 3-2-3-1a) which is assigned to the freezing point of nitrobenzene in the gel. This temperature is lowered further by 10 K as compared with that of pure nitrobenzene at 260 K. The salient decrease of the freezing point in the supramolecular gel indicates the presence of interactions between the confined nitrobenzene molecules and the nanofibrous networks. A similar decrement of freezing temperature of nitrobenzene in the gel was also observed for **1** ($n = 16$) (Figure 3-2-3-4). On the other hand, the shorter-chained **1** ($n = 14$) gave a freezing point at 259 K in the gel which is very close to that of pure nitrobenzene. Thus, interactions between the fibrous gel networks

and nitrobenzene are dependent on the alkyl chain length of the gelators. **1** ($n = 14$) has smaller intermolecular interactions with nitrobenzene as compared to the longer alkyl-chained **1** ($n = 16, 18$).

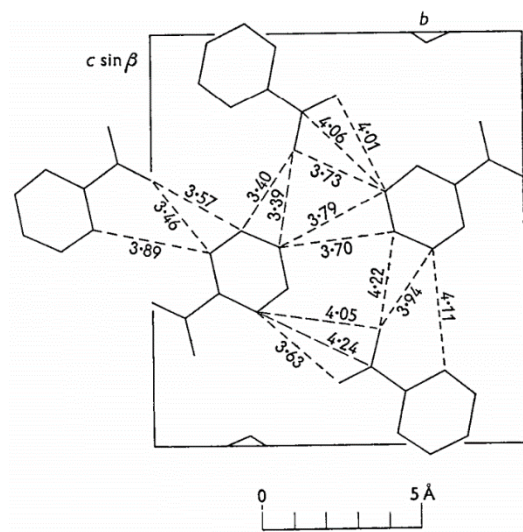


Figure 3-2-3-3. Crystal structure of nitrobenzene at 243 K.¹⁸

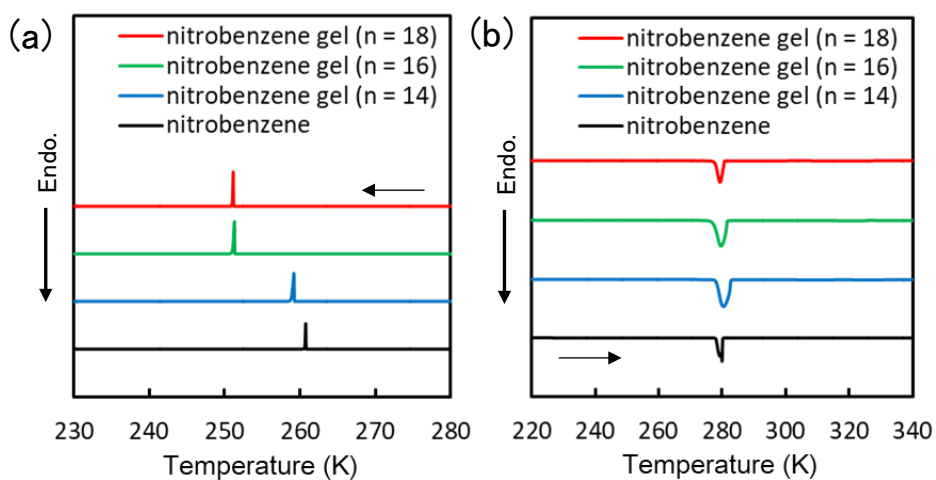


Figure 3-2-3-4. DSC thermograms of nitrobenzene and nitrobenzene gels of **1** ($n = 14, 16, 18$). (a) the cooling process from 280 K to 230 K and (b) the heating process from 220 K to 340 K. [**1** ($n = 14, 16, 18$)] = 100 mM in nitrobenzene, recorded at a scan speed of 1 K/min.

3-2-4 Dielectric properties of various solvents and their gels

The dielectric properties of the nitrobenzene gels were investigated by introducing them into glass liquid crystal (LC) cells sandwiched by two bare ITO electrodes (spacing; 20 μm , non-polyimide coated, working area; 0.25 cm^2 , Figure 3-2-4-1). To prepare the samples for dielectric studies, gels ([**1**] = 100 mM) were placed at the opening of the 20- μm -thick LC cells and was heated up to 343 K on a hot plate, at which the gels liquefied and the solution slowly transferred into the cells. After the cells were filled with the melted-gel solutions, they were slowly cooled down to room temperature to reform gels. A reference sample was also prepared by introducing pure nitrobenzene into a blank LC cell. The dielectric behaviors of nitrobenzene gel **1** and pure nitrobenzene were examined at 298 K under the application of AC voltage (0.5 V/ μm , frequency, 1 Hz). Molecules having intrinsic dipoles display dipolar (or orientational) polarization under the applied external electric field (E), which is lost when the electric field is removed ($P = 0$ at $E = 0$).

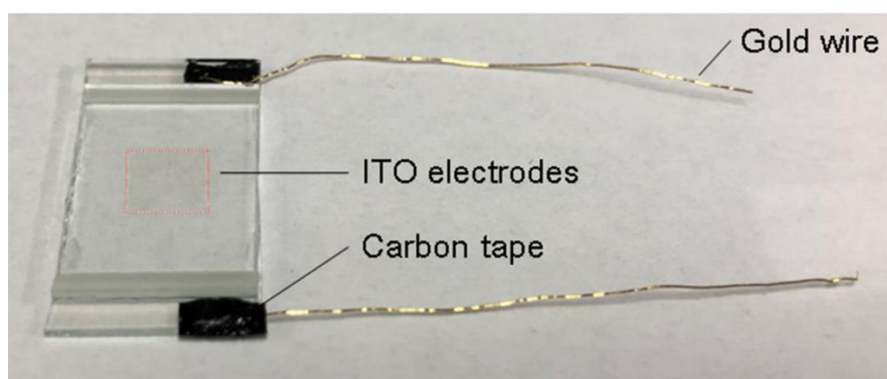


Figure 3-2-4-1. The ITO-containing liquid crystal (LC) cell setup for the dielectric measurements. LC cells with bare ITO electrodes are employed because the common LC cells have polyimide films coated on ITO electrodes, which turned out to be swollen with nitrobenzene. To eliminate the contribution of nitrobenzene-containing polyimide surface layers on the enhancement of dipolar polarization, we used the LC cells with bare ITO surfaces.

Interestingly, the polarization-electric field (P - E) curve obtained for the nitrobenzene gel of **1** ($n = 18$, 100 mM) exhibits a feature of hysteresis, with a remnant polarization (P_r) of 59 $\mu\text{C}/\text{cm}^2$ and a coercive electric field (E_c) of ± 2.5 kV/cm at 298 K as determined from x- and y-intercepts of the P - E hysteresis loops (Figure 3-2-4-2a). Here, P_r and E_c are defined as the quantity of P at $E = 0$ kV/cm, and the quantity of E at $P = 0$ $\mu\text{C}/\text{cm}^2$, respectively. Such an anomalous hysteresis was not observed for

pure nitrobenzene (P_r , $0.64 \mu\text{C}/\text{cm}^2$, Figure 3-2-4-2a and 3-2-4-3a). The strength of P_r observed for nitrobenzene gel is almost two orders of magnitude larger than that revealed by the solvent alone. Importantly, the gel sample exhibited current peaks in the current-electric field (I - E) loop, at which the positions correspond to the coercive fields at ca. $\pm 2.5 \text{ kV}/\text{cm}$ (Figure 3-2-4-2b). These are the characteristics of inversion current that reflects the polarization inversion of nitrobenzene molecules confined in the gel. Other peaks are noticeable in the I - E loop for the nitrobenzene gel at around $\pm 0.8 \text{ kV}/\text{cm}$, possibly reflecting that the confined nitrobenzene molecules are not in homogeneous environment and form different types of domains. It is reasonable to assume that nitrobenzene molecules in the present gel system are classified into three categories: (i) those strongly interacted with the surfaces of the self-assembled nanofibers, (ii) those inward the interstitial space of the gels and weakly associated with nanofibers, (iii) those adsorbed near the ITO electrodes. These domains are continuously connected in the interstitial space of gels, and the boundary of each domain is not strict. As described in the introduction, molecules with large permanent dipoles are expected to show long-ranged dipole-dipole interactions that operate in fair structural correlation lengths. This explains the observed P - E hysteresis in Figure 3-2-4-2, i.e., the inversion of nitrobenzene molecules confined in the interstitial spaces occurred cooperatively. It is to note that the spontaneous polarization of the nitrobenzene gel **1** ($n = 18$) is more than two orders of magnitude higher when compared with the typical literature values reported for ferroelectric smectic and columnar liquid crystalline phases (50 - $500 \text{ nC}/\text{cm}^2$),²¹⁻²³ and exceeds that of poly(vinylidene fluoride) (PVDF, $P_r = 8 \mu\text{C}/\text{cm}^2$), a representative ferroelectric polymer.^{24,25} Both P_r and E_c were found to be dependent on the applied voltage and the measurement frequency in the range of $1 - 1000 \text{ Hz}$ (Figure 3-2-4-4). The P_r values became smaller at higher frequencies ($> 100 \text{ Hz}$), indicating that the motional frequency of dipole inversion in the gel state is relatively slow. These results indicate that gelation not only confined nitrobenzene molecules within the nanofibrous networks but also promoted their electric field-directed macroscopic alignment and enhanced the dipolar polarization.

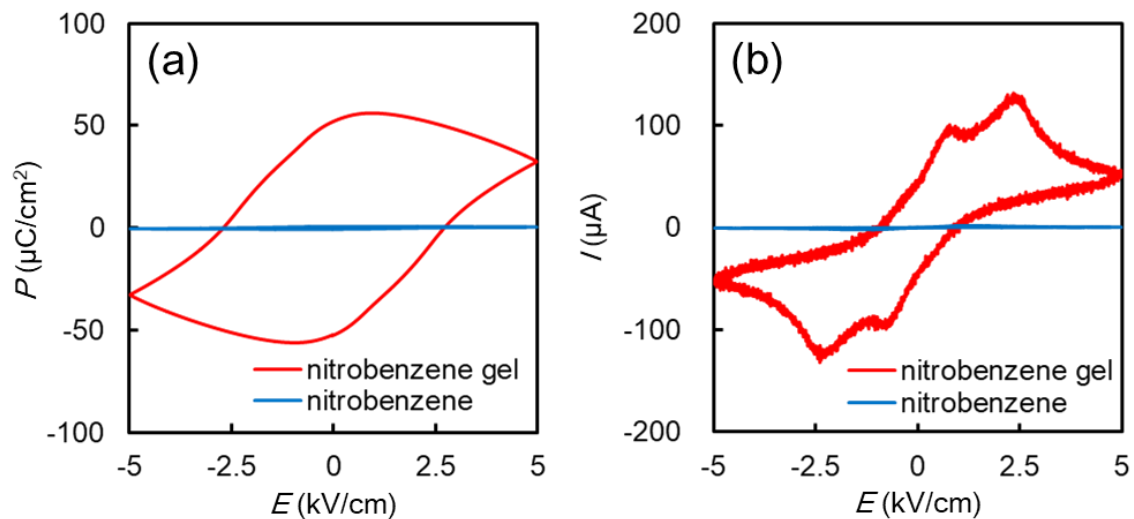


Figure 3-2-4-2. (a) Polarization – electric field (P - E) loops and (b) current – electric field (I - E) loops of nitrobenzene and its gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) recorded at 10 V, 1 Hz, 298 K. The P - E and I - E data displayed are the average of 50 cycles of measurements.

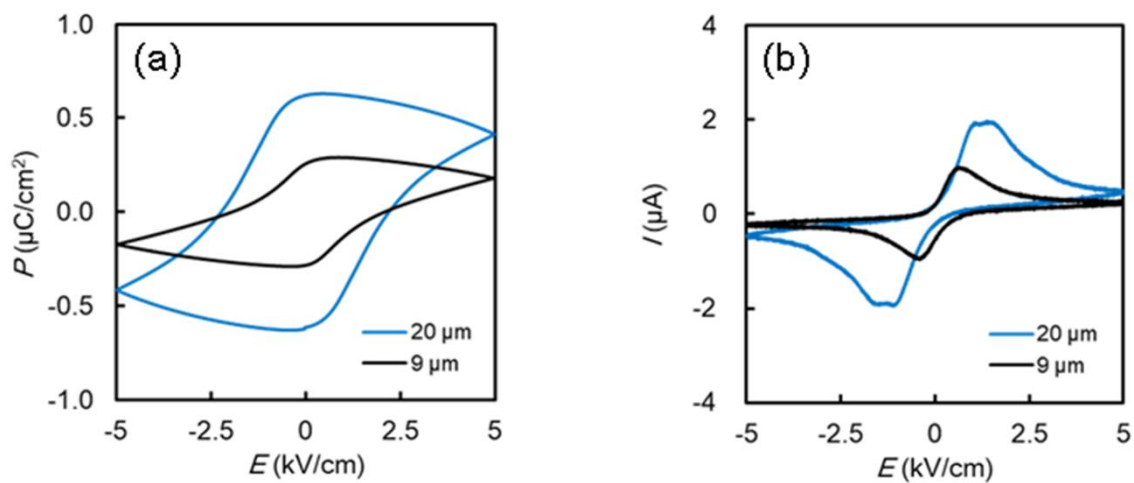


Figure 3-2-4-3. The (a) P - E and (b) I - E loops of nitrobenzene (without gelator **1**) filled in LC cells having different spacer distance between the ITO electrodes (9 and 20 μm). The data are obtained under the applied AC voltage of 5 kV/cm, 1 Hz, at 298 K and are averaged for 50-cycle measurements.

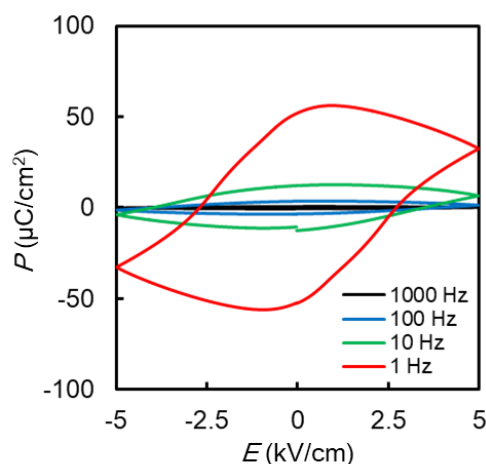


Figure 3-2-4-4. The P - E loops of nitrobenzene gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) recorded at various conditions (10 V, 1-1000 Hz, 298 K). Data are averaged for 50-cycle measurements.

We presumed that the interactions between the surface of fibrous nanofibers and nitrobenzene play essential roles in the observed P - E hysteresis, and this nanointerface-induced polarization mechanism is further supported by the dependence of P_r on the concentration of **1** ($n = 18$) (Figure 3-2-4-5). A discontinuous change was observed above the critical gelation concentration of 6 mM, and the P_r value showed an increase from ca. $20 \mu\text{C}/\text{cm}^2$ ($[1 \text{ (n = 18)}] = 20 \text{ mM}$) to ca. $59 \mu\text{C}/\text{cm}^2$ at higher concentration of **1** ($n = 18$) (100 mM). As observed in AFM images (Figures 3-2-2-1), the increase in the gelator concentration enhanced the density of nanofibrous networks. As a result, more contact areas between the confined nitrobenzene molecules and gel nanofibers were created. The presence of interactions between the nitrobenzene molecules and the nanofiber surface has been denoted by the lowering of freezing point (Figures 3-2-3-1). It is natural that the solvation of tangled nanofibers by nitrobenzene also involves the partitioning of nitrobenzene molecules in the solvophilic alkyl chain moiety of the gelators, as observed for the adaptive uptake of the aromatic triplet-triplet annihilation-based upconversion (TTA-UC) chromophores inside the gel nanofibers **1**.⁸

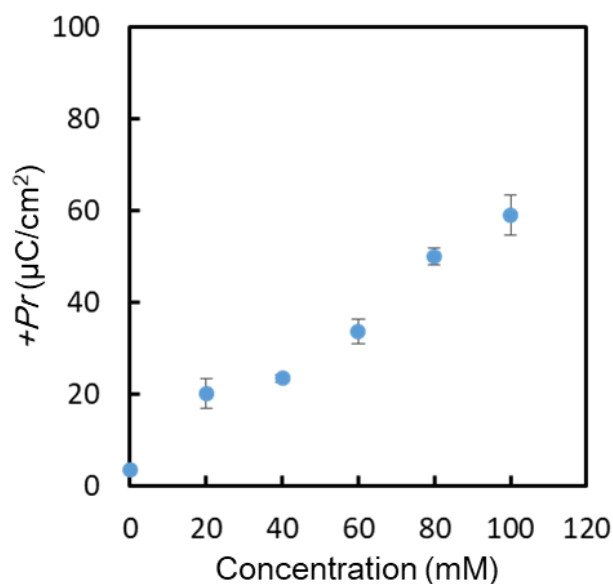


Figure 3-2-4-5. Dependence of the magnitude of positive remanent polarization ($+P_r$) on the concentrations of **1** ($n = 18$) in nitrobenzene gels.

If such partitioning of nitrobenzene molecules inside nanofibrous aggregates contributes to the polar switching phenomena of the gels with enhanced P_r , it will show dependence on the accommodation capacity of the self-assembled nanofibers which is correlated with the length of lipophilic alkyl chains. Figure 3-2-4-6a compares the P - E loops observed for nitrobenzene gels of **1** with different alkyl-chain length ($n = 18, 16, 14$). The observed P_r is the largest for the longer-alkyl chain gelator **1** ($n = 18$), and the polarization decreased in the order of shortening the alkyl-chain length n of **1**. E_c also decreased in this order, and the inversion current peaks observed for **1** ($n = 18$) in the I - E loops became weakened for the shorter-chained gelators (Figure 3-2-4-6b). These observations are consistent with the weaker intermolecular interactions observed between **1** ($n = 14$) and nitrobenzene (Figure 3-2-1-4 and Figure 3-2-3-4) and in line with our expectations that strong interactions of nitrobenzene molecules and the gel nanofibers are essential to exert the P - E hysteresis loops. The longer-chained gelator provides enhanced interactions, suggesting that its alkyl-chain moieties serve as solubilization sites for the nitrobenzene molecules. It might also be related to the enhanced rigidity of the nanofiber networks for longer-chained gelators (Figure 3-2-1-4).

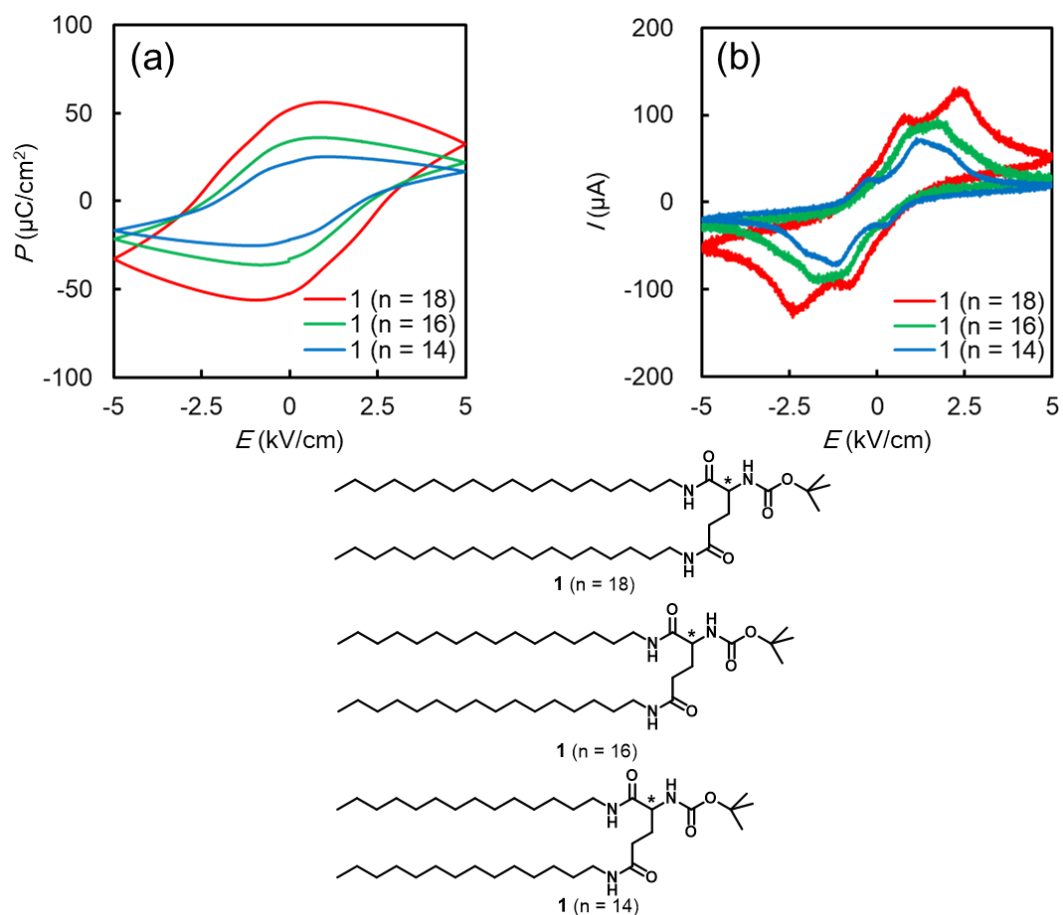


Figure 3-2-4-6. The (a) P - E and (b) I - E loops of nitrobenzene gel prepared with gelators having different lengths of alkyl chains (100 mM) recorded 10 V, 1 Hz, 298 K. Data are averaged for 50-cycle measurements.

The whole gel seems to be responsible for the unique dielectric properties, as indicated by the P - E hysteresis loop measured with a LC cell with a narrower spacer of 9 μm . It showed a remnant polarization P_r of $\pm 24 \mu\text{C}/\text{cm}^2$, which is almost proportional to the gel thickness (Figure 3-2-4-7).

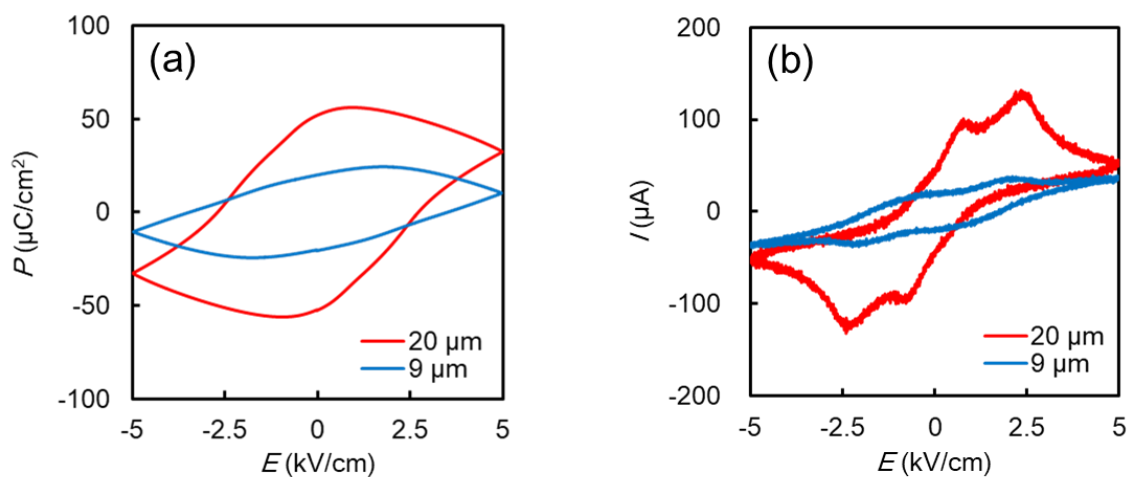


Figure 3-2-4-7. The (a) P - E and (b) I - E loops of nitrobenzene gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) recorded with LC cells having different spacers (9 and 20 μm) between the ITO electrodes. The results were recorded 5 kV/cm , 1 Hz, 298 K. Data are averaged for 50-cycle measurements.

Meanwhile, as shown in Figure 3-2-4-3, nitrobenzene alone showed a hysteresis in the P - E loop with P_r of $0.64 \mu\text{C}/\text{cm}^2$ and E_c of $2.2 \text{ kV}/\text{cm}$. The hysteresis observed even for pure nitrobenzene could be ascribed to the electric field-assisted physisorption and alignment of nitrobenzene molecules at the ITO surface. We noticed that the remnant polarization P_r value of pure nitrobenzene was also dependent on cell thickness (Figure 3-2-4-3a). The value of the inversion current also showed a decrease when the gap between the ITO electrodes is smaller (Figure 3-2-4-3b). This observed dependence on the cell thickness implies that the dielectric property of pure nitrobenzene is derived not only from the surface mono-layers of nitrobenzene molecules physisorbed on the ITO electrodes but also from the polarized layers of macroscopically oriented clusters formed near the interface. It is plausible that the physisorbed surface layers of nitrobenzene molecules promote the formation of polarized layers of macroscopically oriented clusters near the interface.²⁶ The dipole interactions operating among highly polar liquid molecules offer them a latent potential to form anisotropic molecular clusters, as indicated by the nano-sized ferroelectric domains of nitromethane formed in binary solutions.²⁷ The presence of domains in pure nitrobenzene has also been supported by the presence of a supercooled state (Figure 3-2-3-1). However, it is to note that the intensity of P_r observed for pure nitrobenzene ($\sim 0.64 \mu\text{C}/\text{cm}^2$) is marginal compared with the large P_r and the size of the hysteresis loop observed for the nitrobenzene gel (Figure 3-2-4-2a). Therefore, supramolecular confinement of nitrobenzene in the interstitial domains of gels **1** and the nanointerface-induced dipolar polarization are essential and responsible for the anomalous polar switching characteristics which overwhelm the dielectric property of bulk liquid.

To confirm that the salient polar switching phenomenon is unique to dipolar molecules confined in supramolecular gels, gels of **1** ($n = 18$) (100 mM) were prepared with varied aromatic liquids with several other aromatic liquids having different dipole moments: benzonitrile ($\mu_D = 4.18$), toluene ($\mu_D = 0.36$), mesitylene ($\mu_D = 0.05$) and benzene ($\mu_D = 0.00$).²⁸ The gel formed in benzonitrile exhibited a hysteresis loop similar to that of nitrobenzene gel (Figure 3-2-4-8). We found that benzonitrile alone showed a freezing point at ca. 215 K , which is well below its melting point (ca. 260 K , Figure 3-2-4-9). The benzonitrile gel of **1** ($n = 18$) showed identical melting temperature, while the freezing point is observed at 223 K , which is higher than that of pure benzonitrile. It reflects the presence of interactions between the confined benzonitrile and the gel networks. In contrast to the gels containing dipolar nitrobenzene and benzonitrile, those formed from non-polar liquids – toluene and mesitylene – did not show enhanced polarity nor a sign of hysteresis (Figure 3-2-4-8). These observations confirm that polar liquids confined in supramolecular gel nanofibrous networks are essential for the emergence of enhanced electric polarization and polar switching phenomena. In addition, the absence of P - E

hysteresis for toluene and mesitylene-gels indicates that the intramolecular hydrogen bonding networks formed in the nanofibrous assemblies of **1** are not contributing to the present polarity switching.

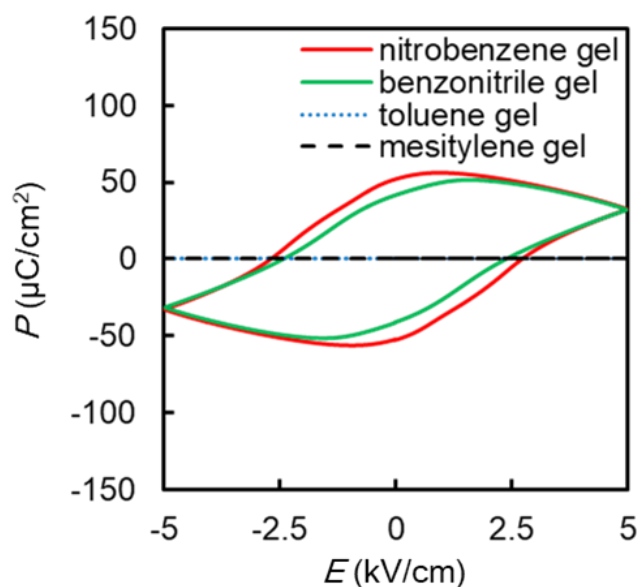


Figure 3-2-4-8. The P - E loops of gels of nitrobenzene, benzonitrile, toluene and mesitylene (100 mM) recorded at 10 V, 1 Hz, 298 K. Data are averaged for 50-cycle measurements.

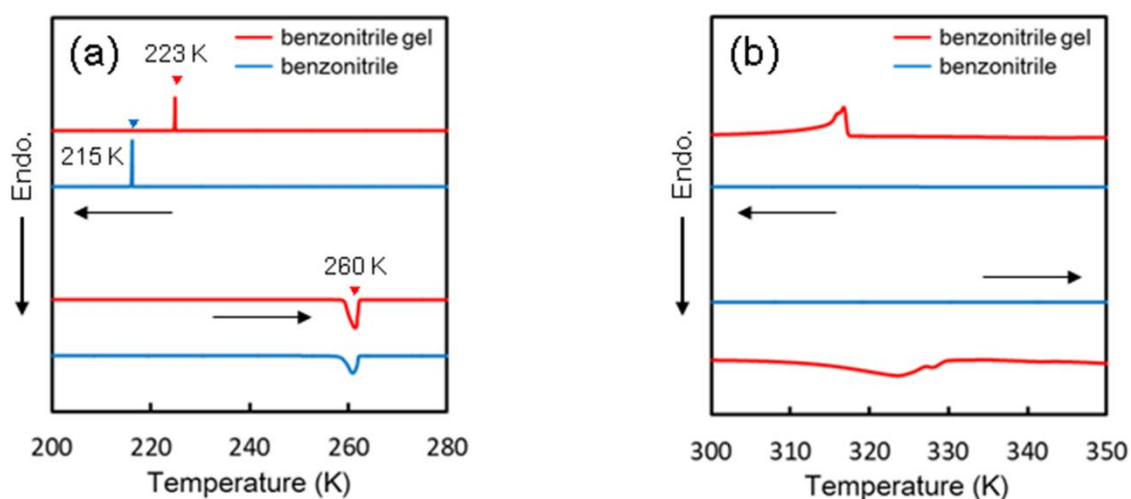


Figure 3-2-4-9. DSC thermograms of benzonitrile and its gel ($[\mathbf{1}]$ ($n = 18$) = 100 mM, scan rate = 1 K/min).

To demonstrate that the molecular orientational changes of nitrobenzene in gels are essential for the unique polar switching phenomenon, temperature-dependent P - E curves were obtained over a wide range of temperatures, including the melting point of confined nitrobenzene (Figure 3-2-4-10a). In contrast to the hysteresis loop observed at 298 K, P_r decreased upon cooling, and no hysteresis was observed below 255 K, a temperature in between the freezing point of pure nitrobenzene (260 K) and that of nitrobenzene confined in the gel (250 K). The temperature dependence of $\pm P_r$ measured while cooling the nitrobenzene gel from 298 K exhibits a rather monotonous decrease until 258 K, which is followed by a small drop at ca. 255 K (Figure 3-2-4-10b). Upon heating the frozen gel, $\pm P_r$ values started to increase near the melting temperature of nitrobenzene confined in the gel (Figure 3-2-4-11). These data clearly indicate that the hysteresis is suppressed by freezing of nitrobenzene confined in the gel, and the mobility of nitrobenzene is essential for the polar switching. Similarly, P - E loops observed for benzonitrile gel are lost below the freezing temperature of benzonitrile confined in the gel (Figure 3-2-4-12).

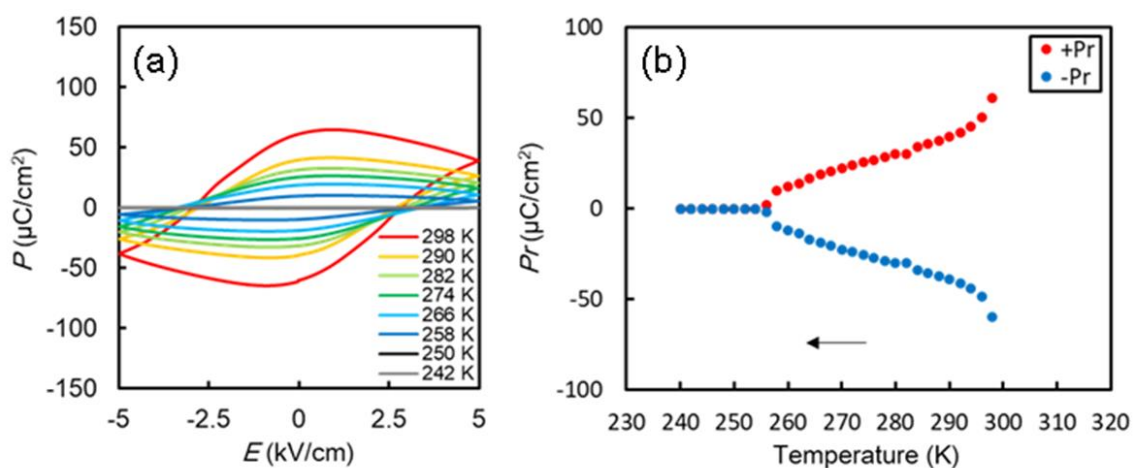


Figure 3-2-4-10. (a) P - E loops and (b) remnant polarizations of nitrobenzene gel ($[\mathbf{1}]$ ($n = 18$) = 100 mM) recorded at 10 V, 1 Hz, cooling process (298-242 K). The P - E data are averaged for 50-cycle measurements.

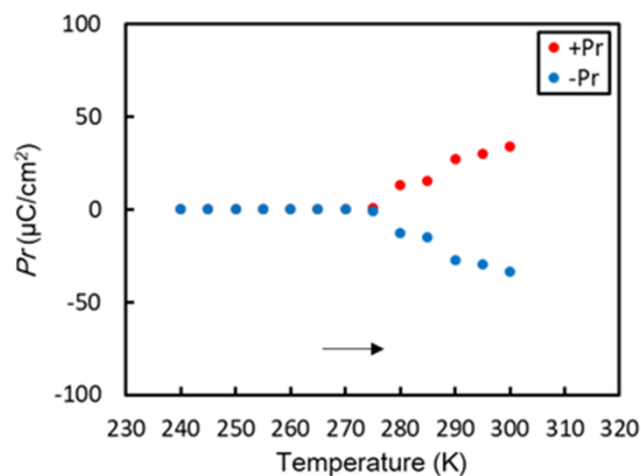


Figure 3-2-4-11. Remnant polarizations of nitrobenzene gel ($[1] (n = 18)] = 100 \text{ mM}$) recorded at 10 V, 1 Hz upon heating from 240 K to 300 K. Data are averaged for 50-cycle measurements.

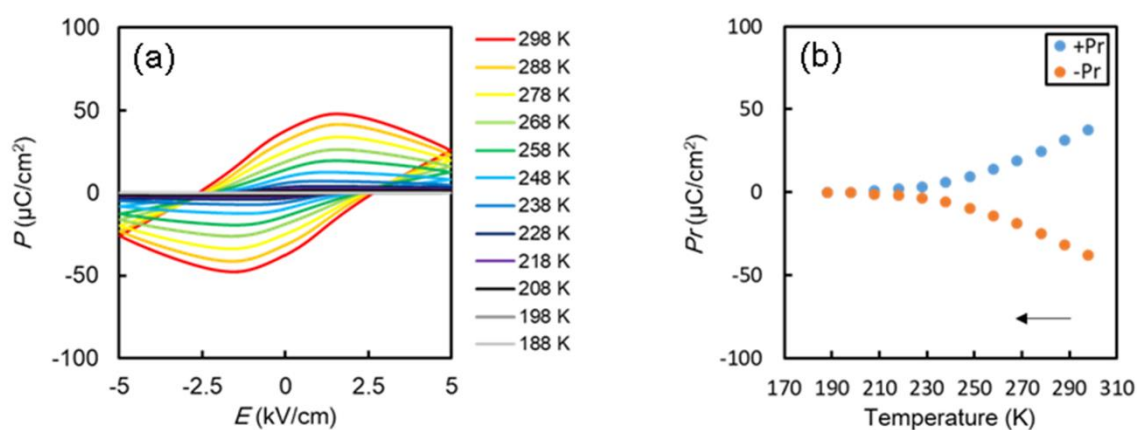


Figure 3-2-4-12. The (a) P - E loops and (b) remnant polarizations of benzonitrile gel ($[1] (n = 18)] = 100 \text{ mM}$) recorded at 10 V, 1 Hz upon cooling from 298 K to 188 K. Data are averaged for 50-cycle measurements.

To gain insight into the peculiar dielectric properties observed for supramolecular gels, positive-up-negative-down (PUND) measurements were conducted for 20- μm -thick gel samples by utilizing a pulse train with an amplitude of 5 kV/cm and a width of 100 ms.²⁹ In every PUND experiment, a negative poling pulse with the same amplitude and width was applied to the sample, followed by a sequence of two positive and two negative voltage pulses. The resulting electric displacement responses were analyzed by fitting to the ferroelectric component (FC), paraelectric component (PC), and leakage current (LC) components, respectively (Figure 3-2-4-13). Figure 3-2-4-14 shows PUND responses observed for nitrobenzene and its gel (Figure 3-2-4-14a), and their magnified pulse responses around the first positive pulse (Figure 3-2-4-14b, c), respectively. The magnitudes FC, PC, and LC obtained by the analyses of PUND pulse responses are summarized in Table 3-2-1. As can be seen from Figure 3-2-4-2a, the *P-E* loop observed for the nitrobenzene gel of **1** (*n* = 18) shows a convex region that is typical for the lossy dielectric materials exhibiting conductance,³⁰ and this would be reflected in the observed LC which is of unexplained origin. Understandably, non-polar gels formed in benzene, toluene, and mesitylene do not show appreciable dielectric responses (Table 3-2-1 and Figure 3-2-4-15).

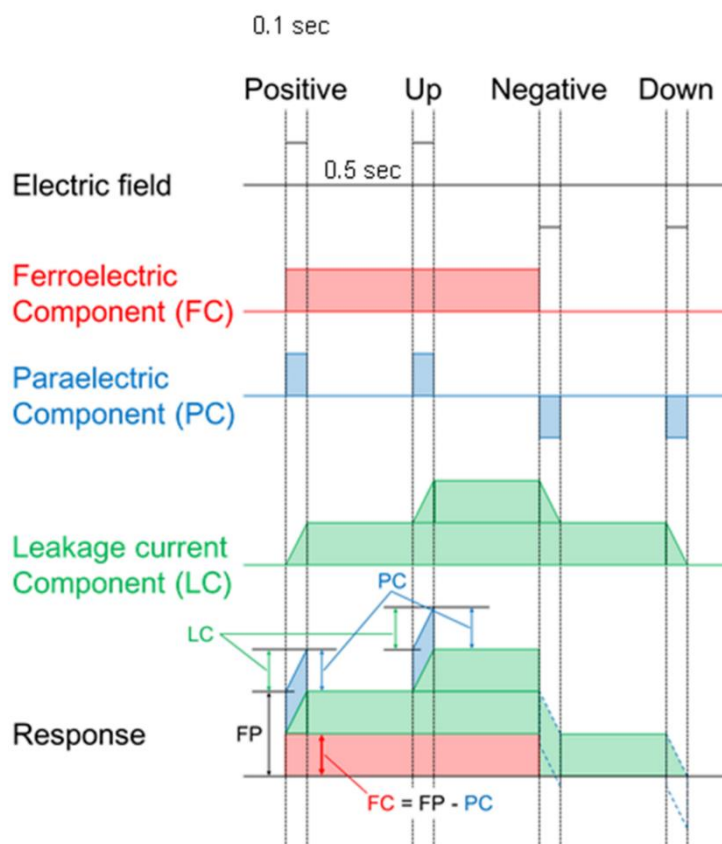


Figure 3-2-4-13. Schematic representation of the Positive-Up-Negative-Down (PUND) measurement.²⁹

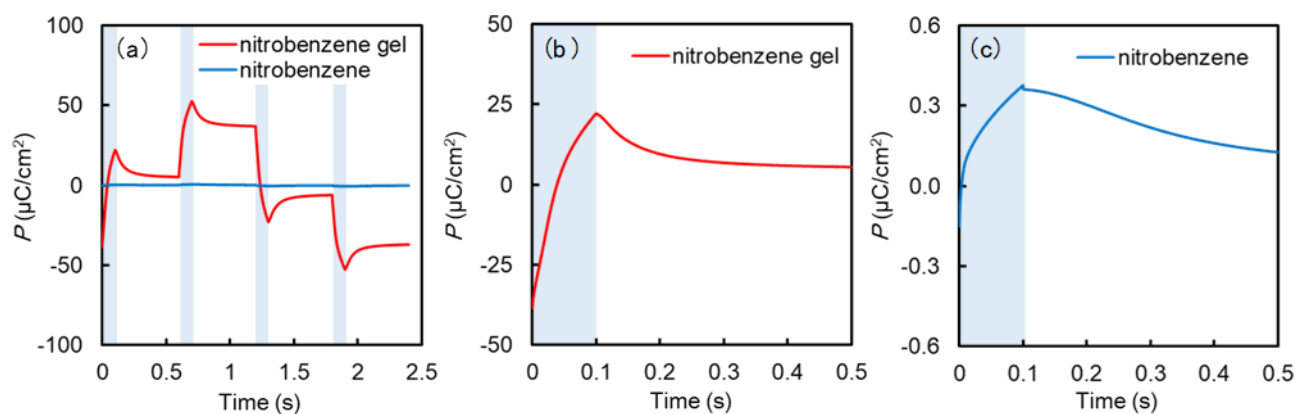


Figure 3-2-4-14. (a) PUND responses for nitrobenzene and its gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) utilizing a pulse train with an amplitude of 5 kV/cm and a width of 0.1 and 0.5 s decay time. (b) Polarization decay of nitrobenzene gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) after the first positive voltage pulse. (c) Polarization decay of nitrobenzene after the first positive voltage pulse. The blue lines indicate the application period of the pulse voltages.

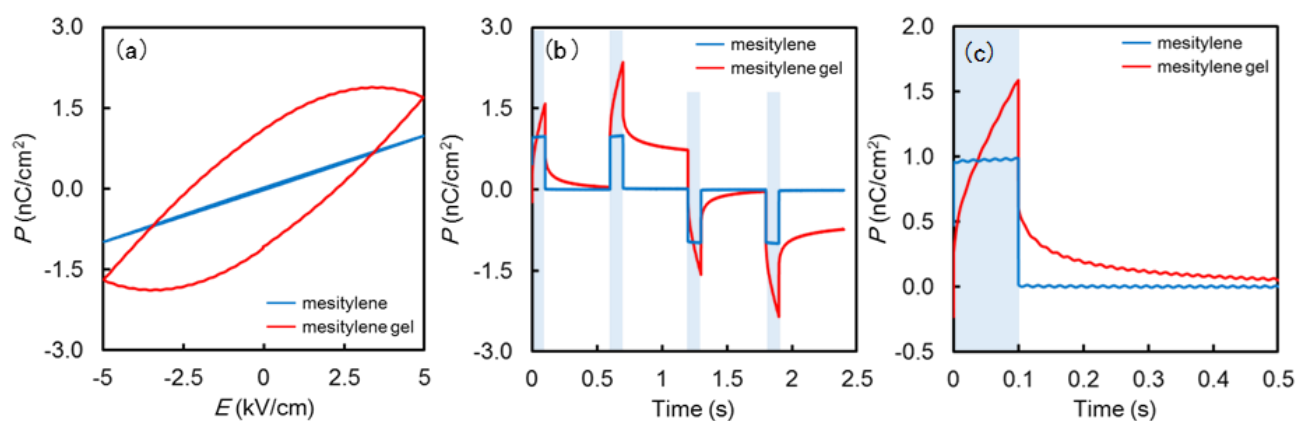


Figure 3-2-4-15. (a) The P - E loops, (b) PUND measurements and (c) polarization decay after the first positive voltage pulse of mesitylene and its gel ($[1 \text{ (n = 18)}] = 100 \text{ mM}$). The blue lines indicate the application period of the pulse voltages.

Table 3-2-1. The magnitudes of the ferroelectric component (FC), the paraelectric component (PC) and the leakage current component (LC) of different aromatic liquids and their respective gels ([**1** (n = 18)] = 100 mM) at 298 K.

	μ_D	FC ($\mu\text{C}/\text{cm}^2$)	PC ($\mu\text{C}/\text{cm}^2$)	LC ($\mu\text{A}/\text{cm}^2$)
nitrobenzene gel	-	26.5 ± 3.6	16.3 ± 1.3	218.3 ± 12
nitrobenzene	4.22	0.0	0.4 ± 0.1	2.6 ± 0.4
benzonitrile gel	-	4.4 ± 2.2	21.8 ± 1.3	184.7 ± 7.5
benzonitrile	4.18	1.1 ± 0.6	3.9 ± 1.2	38.5 ± 12
toluene gel	-	0.0	0.0	0.3
toluene	0.36	0.0	0.0	0.0
mesitylene gel	-	0.0	0.0	0.0
mesitylene	0.05	0.0	0.0	0.0
benzene gel	-	0.0	0.0	0.1
benzene	0.00	0.0	0.0	0.0

As shown in Figure 3-2-4-8, the gels of **1** (n = 18) formed in nonpolar solvents (benzene, toluene, and mesitylene) show no response in *P-E* curves. Consistently, each pure solvents showed no PUND responses. These observations indicate that the sufficient electrochemical stability of nonionic gelator molecule **1** (n = 18) under the conditions employed. Pure nitrobenzene showed a weak *P-E* hysteresis (Figure 3-2-4-3) and we ascribed this to the dipolar polarization phenomena occurring near the ITO electrodes. On the other hand, we observed a large enhancement of dipolar polarization for nitrobenzene gels of **1** (n = 14, 16, 18), which are dependent on the alkyl chain length (Figures 3-2-4-6) We note that the LC components are also larger for the gels formed in the polar solvents, as compared to those observed for each solvent. Although the LC components and their increase in polar gels are currently of unexplained origins, the observed dependence of the dielectric properties on the chemical structures (i.e, different alkyl chain length between **1** (n = 14, 16, 18)) implies that they reflect the difference in the physical properties of the gels, rather than the electrochemical reactions if any involved in the system.

To discuss the confinement effect reflected in the *P-E* loops, the FC and PC components were compared as shown in Figure 3-2-4-16. The dielectric characteristics of pure nitrobenzene (without gelator **1**) is dominated by a paraelectric component PC of $0.4 \mu\text{C}/\text{cm}^2$ as expected. Meanwhile, as illustrated in Figure 3-2-4-16, nitrobenzene gel of **1** (n = 18) shows significantly enhanced FC ($26.5 \mu\text{C}/\text{cm}^2$) that exceeds PC ($16.3 \mu\text{C}/\text{cm}^2$), which is consistent with the emergence of the *P-E* loop with hysteresis (Figure 3-2-4-2a).

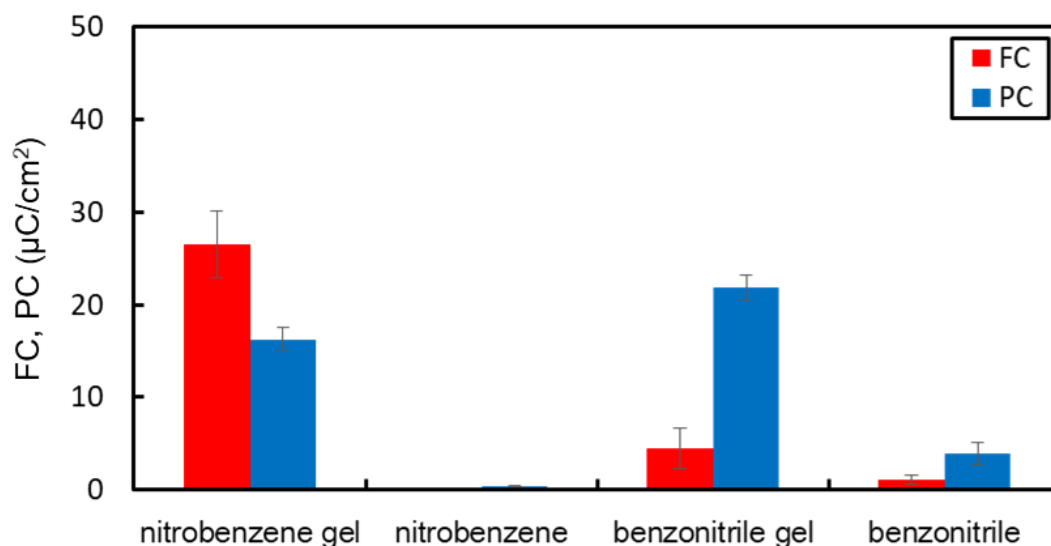


Figure 3-2-4-16. The magnitudes of the ferroelectric and paraelectric components (FC and PC respectively) of nitrobenzene, benzonitrile, and their respective gels ($[1 \text{ (n = 18)}] = 100 \text{ mM}$) at 298 K.

The correlation between the intermolecular interactions between nanofibers and nitrobenzene molecules to the relative intensity of FC and PC was investigated by performing PUND experiments at varying concentrations of **1** (n = 18) in the nitrobenzene gel (Figure 3-2-4-17). At the lower concentration of 20 mM, the value of PC is larger than that of FC. On the other hand, at the higher concentration of 100 mM, the intensity of FC becomes larger than that of PC. The density of nanofibrous networks and accordingly the total surface area of the nanofibrous assemblies in the gel increase as the concentration of **1** (n = 18) is increased. It is naturally commensurate with the fraction of nitrobenzene molecules strongly interacting with the nanofiber surfaces. These results support that FC and PC are correlated to the nitrobenzene molecules strongly interacted on the nanofiber surface and those weakly associated to the nanofibers in the interstitial space of the gels, respectively.

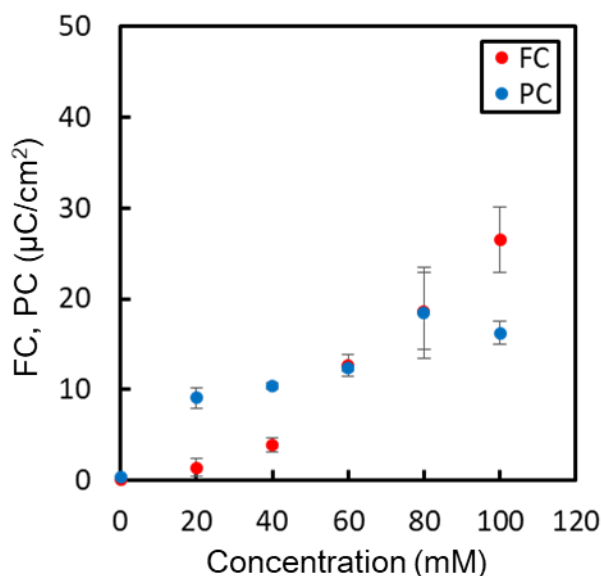


Figure 3-2-4-17. Dependence of the magnitudes of FC and PC on the concentrations of **1** ($n = 18$) in nitrobenzene gels.

On the other hand, it is to note that the dipolar polarization in the nitrobenzene gel has a finite lifetime and shows relaxation in second as depicted in Figure 3-2-4-14b. Obviously, in these nitrobenzene-nanofiber gel systems, the energy barrier between the two polar states is small to maintain the polar organization. Therefore, the nitrobenzene gel is not ferroelectric, and the observed hysteresis in the P - E loops are rather viewed as a consequence of polar switching phenomenon.³¹ Meanwhile, FC observed in the PUND measurement would reflect the presence of nitrobenzene molecules strongly interacting with the gel nanofibers. Therefore it would be appropriate to consider it as a performance index that reveals the fraction of nitrobenzene molecules strongly confined on the surface of the supramolecular gels. As can be seen from Figure 3-2-4-18, FC is most eminent for the nitrobenzene gel formed with gelator **1** ($n = 18$), and it decreases with the shortening of the alkyl-chain lengths of gelators **1** ($n = 16, 14$). The ability to accommodate and interact with nitrobenzene molecules is, therefore, higher for the longer-chained gelator **1** ($n = 18$), and this provides a simple guideline to design molecular self-assemblies that exert nanointerface-induced dipolar polarization phenomena. In the nitrobenzene gels of **1** ($n = 16, 14$), their paraelectric component (PC, $16 \mu\text{C}/\text{cm}^2$, $14 \mu\text{C}/\text{cm}^2$, respectively) also exceeds that of pure nitrobenzene ($0.4 \mu\text{C}/\text{cm}^2$) by two orders of magnitude, and thus it is clear that supramolecular gels reveal significant enhancement of the dipolar polarization for confined polar liquid molecules. In contrast to the nitrobenzene gel, the benzonitrile gel of **1** ($n = 18$)

shows PC ($21.8 \mu\text{C}/\text{cm}^2$) dominating FC ($4.4 \mu\text{C}/\text{cm}^2$). In this case, however, PC is also significantly enhanced as compared to that of benzonitrile alone (PC, $3.9 \mu\text{C}/\text{cm}^2$). The difference in the FC and PC fractions observed for nitrobenzene gel and benzonitrile gel would reflect the interactions between these dipolar solvent molecules and gel nanofiber networks that varied depending on the chemical structures.

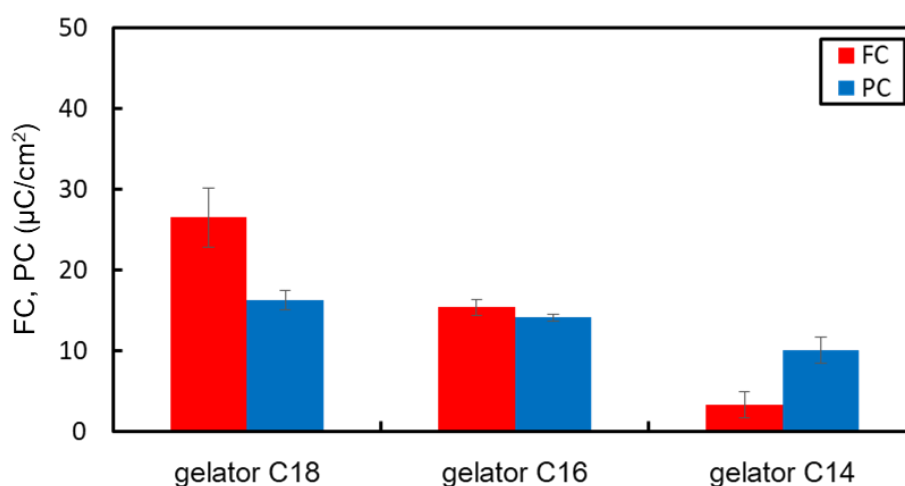


Figure 3-2-4-18. The magnitude of FC and PC of nitrobenzene gels (100 mM) prepared from gelators **1** with different alkyl chains ($n = 18, 16$ and 14) at 298 K.

To generalize the concept of nanointerface-induced dipolar polarization in supramolecular gels, we employed 12-hydroxystearic acid (12-HSA) as a typical low-molecular-weight gelator. 12-HSA (racemate) was dissolved in nitrobenzene by heating, and 12-HSA gel was obtained by cooling to room temperature (Figure 3-2-4-19). As shown in Figure 3-2-4-19, the nitrobenzene gel of 12-HSA (concentration, 100 mM) also exhibited obvious polarization in the P - E loop and humps were also confirmed in the I - E loop. However, 12-HSA gel showed a smaller P_r value as compared to that of the nitrobenzene gel of **1** ($n = 18$). The PUND experiments showed that the HSA gel showed paraelectric components (Figure 3-2-4-19e, f), and thus the chemical structure of the gelators exert significant influence on the dielectric properties of organogels.

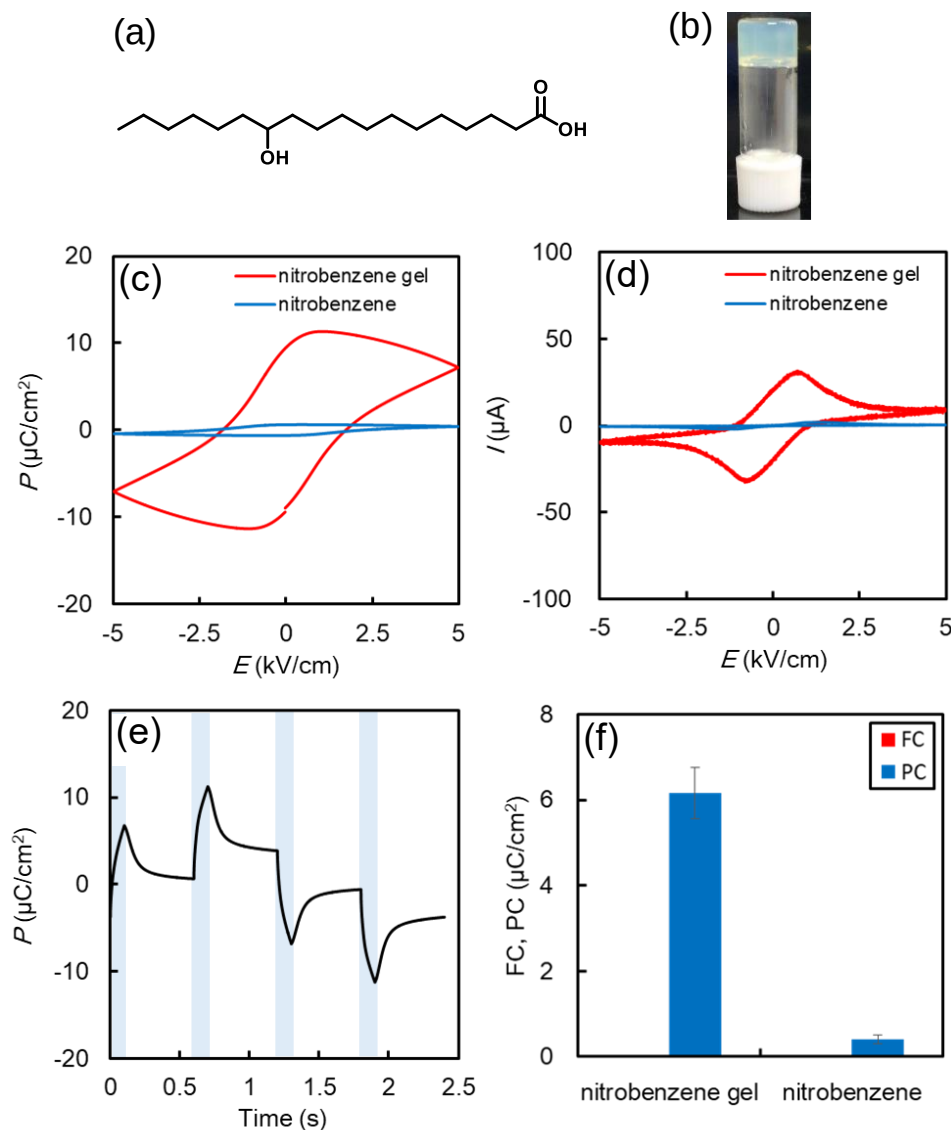


Figure 3-2-4-19. (a) Chemical structure of 12-hydroxystearic acid (racemate), (b) A picture of nitrobenzene gel by 12-hydroxystearic acid (100 mM), (c) P - E and (d) I - E loops of nitrobenzene gel formed by 12-hydroxystearic acid (100 mM). The data were recorded at 10 V, 1 Hz, temperature at 298 K. The data were averaged for 50-cycle measurements. The data for pure nitrobenzene are shown for comparison. (e) PUND response of the nitrobenzene gel with 12-hydroxystearic acid (100 mM) utilizing a pulse train with an amplitude of 5 kV/cm, a width of 0.1 and 0.5s decay time. The blue lines indicate the application of the pulse voltages. (f) The magnitudes of the paraelectric component (PC) of nitrobenzene gel formed from 12-hydroxystearic acid (100 mM) and pure nitrobenzene.

From these results, we can draw a schematic model that tentatively explains the polar liquid domains confined in supramolecular gels of **1** showing the gigantic electric polarization (Figure 3-1). Anomalous polarization switching behaviors can be observed when considerable interactions between dipolar liquids and nanofibers occur. As described at the beginning, the orientational and translational dynamics of confined liquid molecules tend to be restricted, and the nitrobenzene molecules in the interstitial domains of supramolecular gels show long-ranged interactions with the nanofibrous networks presumably mediated by the dipole-dipole interactions, as demonstrated by the strongly affected thermal phase transition characteristics. The observed anomalously enhanced electric polarization could be explained by assuming the electric-field-directed formation of macroscopically polarized layers of nitrobenzene molecules on the solvated nanofibers as schematically depicted in Figure 3-1. Physical adsorption of dipolar molecules would occur anisotropically on the surfaces of organogel nanofiber, which exert cluster electrostatics³ that promote structural ordering and cooperativity of the liquids in the bicontinuous interstitial space within the organogels. The polar switching of these bound nitrobenzene clusters occurs in response to the applied external field, which has affected the whole dielectric behavior of confined nitrobenzene molecules in the interstitial space, leading to the collective dielectric response with significantly enhanced dipolar polarization. Meanwhile, dielectric relaxation naturally occurred for the dipolar liquids confined in organogels, which involves the paraelectric relaxation from the oriented cluster domains to the less-ordered liquid structures and/or antiparallel dimers favored by the local dipole-dipole interactions in thermal equilibrium. This relaxation processes of the strongly confined nitrobenzene molecules may a temporal lag of polarization with respect to the change in direction of the external electric field. Finally, we also would like to point out the common ground between the present significant dipolar polarization effect by confined dipolar liquid domains in organogels to the disordered solid ferroelectric materials called “relaxor ferroelectrics”.^{32–34} In both cases, structural inhomogeneity, i.e., the presence of polar nano-regions inside non-polar matrices, are essential to the unusual properties. However, the present dipolar polarization by confined dipolar liquids has not been recognized and provides a new perspective in the field of soft-materials science. It may allow the development of flexible thin films that respond and amplify weak electric pulses.

3-2-5 Conclusion

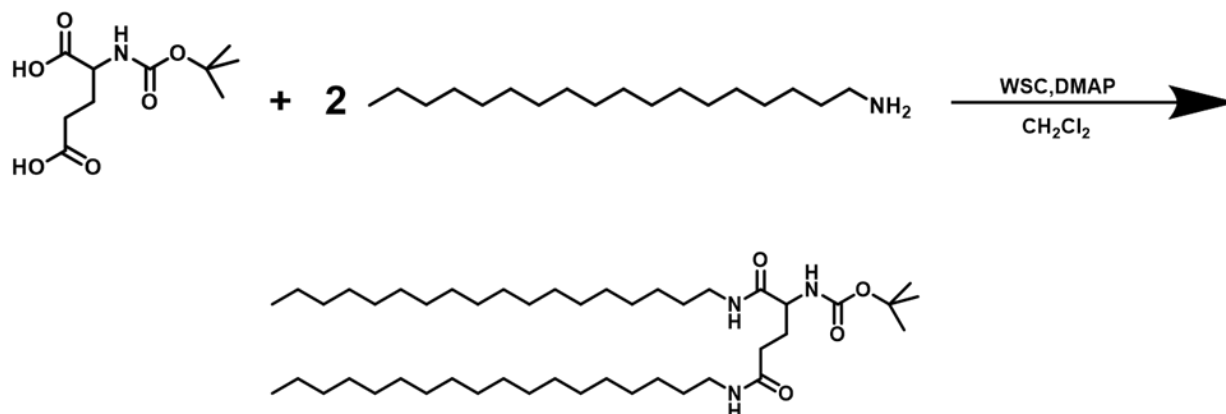
In conclusion, the confinement of polar organic solvents in the interstitial domains of organogels significantly enhanced dipolar polarization and polar switching phenomena with hysteresis in the P - E curves were observed for the chiral nitrobenzene gels. It is to note that the electric field-induced polarity switching observed for the nitrobenzene gel **1** showed remnant polarization by two orders of magnitude higher than the typical literature values reported for ferroelectric smectic and columnar liquid crystalline phases and exceeds that of poly(vinylidene fluoride). The unique polarization characteristics of polar liquids confined in supramolecular gels reflect the enhanced cooperativity in the interstitial domains, suggesting the ordering of dipoles in substantial structural correlation lengths at the interface of the confined liquids and the nanofibers. Although the nitrobenzene molecules confined in the continuous interstitial liquid phase would naturally show distributions in the orientational and translational dynamics, the dipole-dipole interactions operating in such condensed systems seem to bring out that unique collective dielectric properties. The presence of liquid domain structures under the influence of dipole-dipole interactions was indicated by the altered freezing point in the supramolecular gels. The alkyl chain moieties of the gelators would provide solubilization sites for nitrobenzene, and such stronger interactions would be accountable for the observed P - E hysteresis loops. These results illustrate that the confinement of polar liquids in supramolecular gels offer a unique means to enhance dipolar polarization properties and to achieve polar switching. By considering together the wide variety of functional organic dipolar molecules, the advantages of solution processibility, flexibility, and reconfigurability, we envisage a new family of smart soft dielectrics not available from the conventional solid inorganic materials.

3-3 Purification and Synthesis

Nitrobenzene was purchased from Tokyo Chemical Industry Co., Ltd. It was purified by distillation and successive recrystallization from anhydrous ethanol, followed by drying with molecular sieves (water content: 39 ppm). Benzonitrile was purchased from FUJIFILM Wako Pure Chemical Corporation, purified by distillation and dried with molecular sieves (water content: 46 ppm). All other solvents were purchased from FUJIFILM Wako Pure Chemical Corporation and used as received. All reagents for syntheses were used as received unless otherwise stated. All solvents for syntheses were purified before use.

Liquid crystal (LC) cells coated with ITO electrodes (area, 5 x 5 mm², cell gap of 20 μm or 9 μm, no-polyimide coating) were purchased from E.H.C. Co. Ltd.

Synthesis of *N,N'*-bis(octadecyl)-L-boc-glutamicdiamide (n = 18)

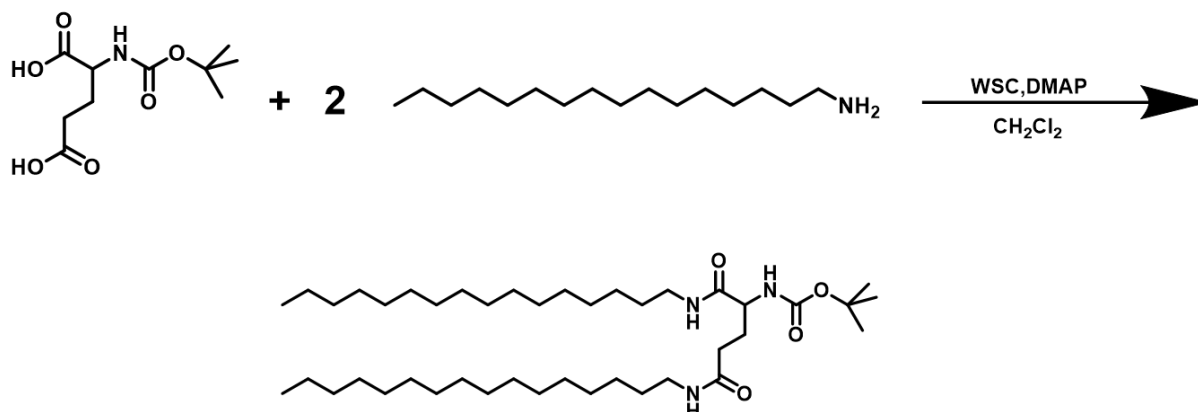


The synthesis of *N,N'*-bis(octadecyl)-L-boc-glutamicdiamide was carried out according to literature procedure.⁹ *N*-Boc-L-glutamic acid (2.01 g, 8.13 mmol) and octadecylamine (5.45 g, 20.22 mmol) were mixed in dichloromethane (65 mL) and cooled in an ice bath. WSC (3.10 g, 20.22 mmol) and DMAP (0.054 g, 0.44 mmol) were dissolved in dichloromethane (35 mL) and added into the mixture of *N*-Boc-L-glutamic acid and octadecylamine for 10 min. Additional dichloromethane (100 mL) was added to the suspension and the reaction was stirred for 160 h at room temperature. After the stirring, the suspension was washed with water (100 mL). After the centrifugation, a colorless solid was obtained. The colorless solid was dissolved in dichloromethane and the solution was added into methanol. After the centrifugation, colorless solid was obtained to give *N,N'*-bis(octadecyl)-L-boc-glutamicdiamide (3.43 g, 56%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 0.88 (t, 6H), 1.25 (s, 60H), 1.44 (m, 13H), 1.90-2.10 (m, 2H), 2.20-2.40 (m, 2H), 3.20-3.30 (m, 4H), 4.08 (q, 1 H), 5.71 (d, 1H), 6.00 (s, 1H), 6.61 (t, 1H)

Elemental analysis, calculated for C₄₆H₉₁N₃O₄: C, 73.64; H, 12.23; N, 5.60; found: C, 73.38; H, 12.16; N, 5.54

Synthesis of *N,N'*-bis(hexadecyl)-L-boc-glutamicdiamide (*n* = 16)

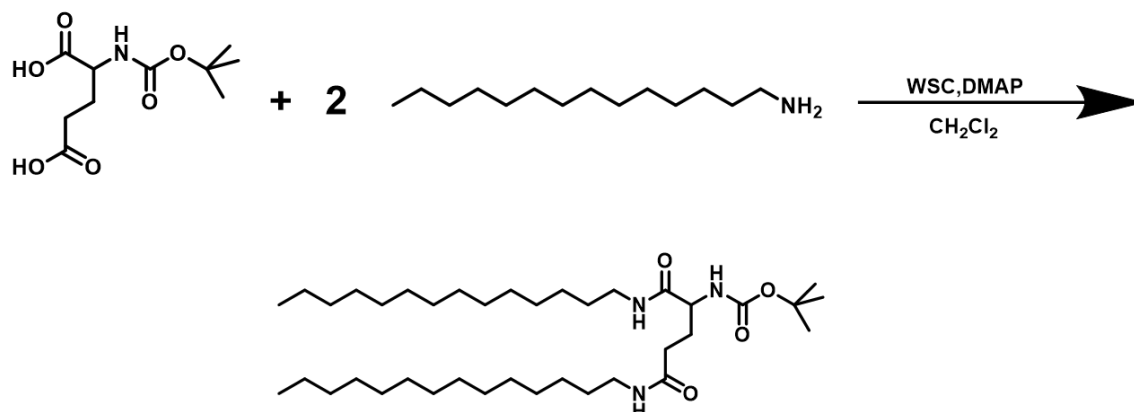


The synthesis of *N,N'*-bis(hexadecyl)-L-boc-glutamicdiamide was carried out according to literature procedure.⁹ *N*-Boc-L-glutamic acid (5.00 g, 20.2 mmol) and hexadecylamine (10.7 g, 44.5 mmol) were mixed in dichloromethane (200 mL) and was then cooled to 0 °C with an ice water bath. WSC (15.5 g, 80.9 mmol) and DMAP (0.124 g, 1.01 mmol) were dissolved in dichloromethane (100 mL) in another container to give a viscous solution. Triethylamine (6.21 mL, 44.8 mmol) was added to the reaction flask, followed by the addition of the viscous solution mixture of WSC and DMAP over a period of 10 min. An additional 100 mL of dichloromethane was added to the suspension and the reaction was stirred at ambient temperature, with a drying tube installed to the reaction flask. After stirring for 120 h, the solvent was removed by rotary evaporation to give an off-white solid. The crude product was then purified by successive recrystallization from dichloromethane/methanol mixture to yield pure *N,N'*-bis(hexadecyl)-L-boc-glutamicdiamide (colorless, 11.5 g, 82%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 0.81 (t, 6H), 1.18 (s, 52H), 1.37 (s, 9H), 1.43 (m, 4H), 1.80-2.00 (m, 2H), 2.15-2.30 (m, 2H), 3.10-3.25 (m, 4H), 4.00 (q, 1 H), 5.63 (d, 1H), 5.94 (s, 1H), 6.55 (t, 1H)

Elemental analysis, calculated for C₄₆H₉₁N₃O₄: C, 72.67; H, 12.05; N, 6.05; found: C, 72.60; H, 11.97; N, 6.05

Synthesis of *N,N'*-bis(tetradecyl)-L-boc-glutamicdiamide (*n* = 14)



The synthesis of *N,N'*-bis(tetradecyl)-L-boc-glutamicdiamide was carried out according to literature procedure.⁹ *N*-Boc-L-glutamic acid (5.00 g, 20.2 mmol) and tetradecylamine (9.49 g, 44.5 mmol) were mixed in dichloromethane (200 mL) and was then cooled to 0 °C with an ice water bath. WSC (15.5 g, 80.9 mmol) and DMAP (0.124 g, 1.01 mmol) were dissolved in dichloromethane (100 mL) in another container to give a viscous solution. Triethylamine (6.21 mL, 44.8 mmol) was added to the reaction flask, followed by the addition of the viscous solution mixture of WSC and DMAP over a period of 10 min. An additional 100 mL of dichloromethane was added to the suspension and the reaction was stirred at ambient temperature, with a drying tube installed to the reaction flask. After stirring for 120 h, the solvent was removed by rotary evaporation to give an off-white solid. The crude product was then purified by successive recrystallization from dichloromethane/methanol/acetone mixture to yield pure *N,N'*-bis(tetradecyl)-L-boc-glutamicdiamide (colorless, 9.94 g, 77%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) = 0.88 (t, 6H), 1.25 (s, 44H), 1.50 (m, 13H), 1.90-2.10 (m, 2H), 2.20-2.40 (m, 2H), 3.20-3.30 (m, 4H), 4.06 (q, 1 H), 5.67 (d, 1H), 5.94 (s, 1H), 6.55 (t, 1H)

Elemental analysis, calculated for C₄₆H₉₁N₃O₄: C, 71.53; H, 11.85; N, 6.59; found: C, 71.41; H, 11.76; N, 6.58

3-4 Characterizations

300 MHz ^1H NMR spectra were recorded on a Bruker DRX-300 spectrometer using TMS as the internal standard. Elemental analysis was obtained at the Elemental Analysis Center, Kyushu University. Rheology was performed on an Anton Paar MCR 302 rheometer. SEM images were obtained on a Hitachi S-5000 scanning electron microscope. AFM images were obtained on a Molecular Imaging Labo, Pico Plus 5500 atomic force microscope. An Olympus AC 160TS-C2 silicon cantilever was used in tapping (ac) mode. TEM image was obtained on a JEOL JEM-2010 transmission electron microscope. The DSC thermograms were obtained on a METTER TOLEDO DSC 1 STAR^e System. Powder X-ray diffraction (PXRD) analysis was conducted on a Bruker D2 PHASER with a Cu K-alpha source ($\lambda = 1.54056 \text{ \AA}$) operated at 30 kV and 10 mA. The dielectric measurements were undertaken on a Toyo Corporation ferroelectric-evaluation standard system (FCE-1) connecting to a Toyo6252 Rev. C current/charge–voltage converter, a Biomation2414B arbitrary waveform generator, a WaveBook 516E analog-to-digital converter and Linkam Hotstage 10084L (JAPAN HIGH TECH). All P - E and I - E loops were recorded with a triangular wave field. The accuracy of the polarization value was confirmed by the measurement of 20/80 lead zirconate titanate (PZT, TOSHIMA Manufacturing Co., Ltd., Area: 0.0001 cm^2 , Thickness: $0.26 \text{ }\mu\text{m}$, Voltage: 4 V, Frequency: 100 Hz, Temperature: 298 K, $+P_r$: ca. $25 \text{ }\mu\text{C}/\text{cm}^2$ (ref. $28 \text{ }\mu\text{C}/\text{cm}^2$)) as a reference sample.

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Chapter 4 Polar Switching of Dipolar Molecules Induced by Solid Dispersion-to-Organogel Phase Transition

4-1 Introduction

In Chapter 3, the confinement of polar organic solvents in the interstitial domains of organogels enhanced dipolar polarization, and polar switching phenomena with hysteresis in the P - E curves were observed for the chiral nitrobenzene gels. The unique polarization characteristics of polar liquids confined in supramolecular gels reflect the enhanced cooperativity in the interstitial domains, suggesting the ordering of dipoles in substantial structural correlation lengths at the interface of the confined liquids and the chiral nanofibers.

In order to confirm the generality of the polar switching phenomena utilizing organogels, in this chapter, we report a phase transition of gels formed from the self-assembly of low-molecular-weight gelators in molecules with a large permanent dipole. To date, the functions of low-molecular-weight organogels have largely relied on the gelatinizing molecular systems, and liquid components are rather considered merely as inert dispersion media.¹ Although gels formed by self-assembly in functional liquid materials have been investigated, such matrixes are largely restricted ionic liquids^{2,3} and liquid crystals.^{4,5} In these investigations, however, the relevance of the physicochemical properties and functions to the phase transition phenomena from solid dispersions to the gel phase have not been reported.

In this chapter, therefore, we focus on *p*-nitroanisole (*p*NA), a molecule with a large permanent dipole ($\mu_D = 4.76$ Debye).⁶ *p*NA is solid at room temperature, and the mixture of the gelator and *p*NA are expected to reveal a multiple phase transition between the solid dispersion, organogel, and the sol phase depending on temperature. An eminent enhancement of dipolar polarization and polar switching phenomena are also expected to be observed for the gel phase which is not available in the solid dispersion phase at ambient temperature (Figure 4-1).

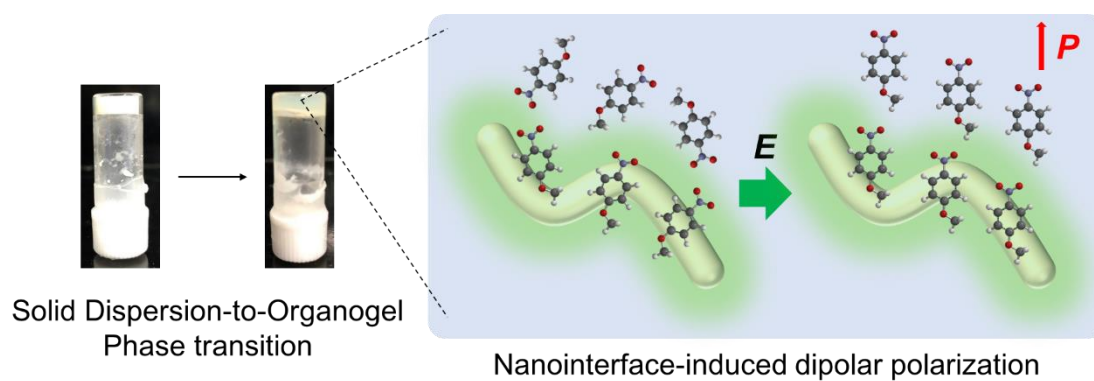


Figure 4-1. A graphic representation of the dielectric behavior of dipolar molecules, such as *p*-nitroanisole, confined within the fibrous networks in the gel state.

4-2 Results and Discussion

4-2-1 Dispersibility of gelator **1** in *p*NA

*p*NA was purified as described in 4-3. *N, N'*-bis(octadecyl)-*L*-Boc-glutamicdiamide (**1**) was synthesized according to the literature procedures.^{7,8} **1** was dissolved in *p*NA by heating to ca. 363 K (molar ratio, [**1**] : [*p*NA] = 1 : 80), and an opaque solid mixture was obtained by cooling down to ambient temperature (Figure 4-2-1-1). The employed molar ratio corresponds to the molar concentration of [**1**] = 100 mM. Powder X-ray diffraction (PXRD) pattern of the solid mixture (**1**+*p*NA) is shown in Figure 4-2-1-2, together with that of the constituents **1**, *p*NA and a simulated pattern of *p*NA from the crystal structure.⁹ The pure *p*NA shows diffractions at $2\theta = 12.90^\circ$, 16.83° , 18.85° , 19.61° , 23.70° , 25.16° , 25.92° , 27.43° , and 30.61° (Figure 4-2-1-2c), and these peaks are consistent with those simulated from the crystal structure of *p*NA⁹ (Figure 4-2-1-2d). Also, the solid mixture (**1**+*p*NA) showed essentially the same diffraction peaks as the pristine *p*NA (Figure 4-2-1-2a), and the crystalline structure of *p*NA is well maintained in the solid mixture. Meanwhile, the PXRD pattern observed for pure **1** (Figure 4-2-1-2b) is not observed in (**1**+*p*NA), indicating that **1** is dispersed in the solid mixture without phase separation.

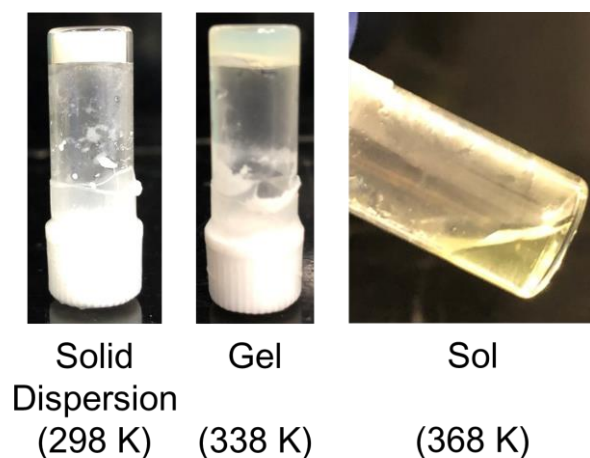


Figure 4-2-1-1. Pictures of the mixture in the heating process. Solid dispersion at 298 K, Organogel at 338 K, and sol at 368 K. ([**1**] : [*p*NA] = 1 : 80 by molar ratio)

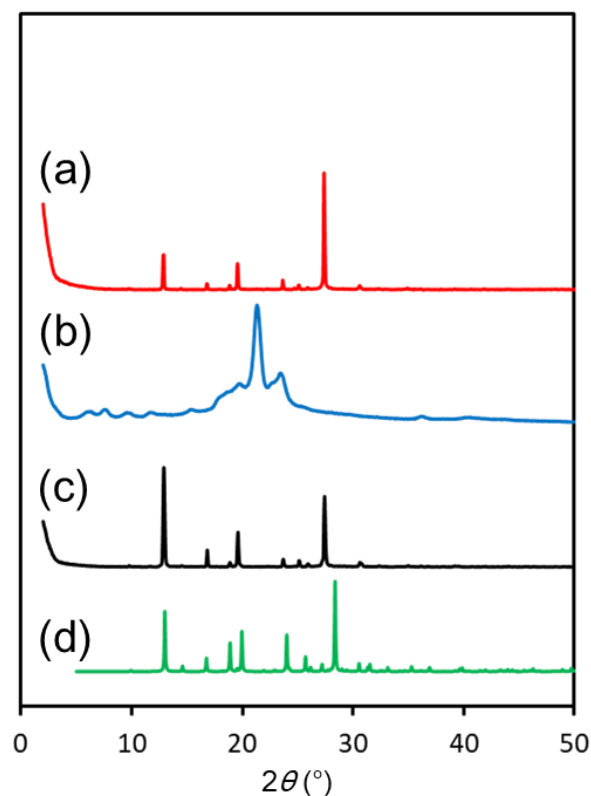


Figure 4-2-1-2. Powder X-ray diffraction patterns of the solid mixture (a, $[1] : [pNA] = 1 : 80$ by molar ratio), gelator **1** (b), pristine *pNA* (c) at 298 K and (d) simulated pattern of *pNA* from the crystal structure.⁹ The specimens (a-c) were ground well before the measurements. The solid mixture ($[1] : [pNA] = 1 : 80$ by molar ratio) showed diffraction peaks at $2\theta = 12.90^\circ, 16.83^\circ, 18.85^\circ, 19.61^\circ, 23.70^\circ, 25.11^\circ, 25.92^\circ, 27.43^\circ$, and 30.61° (corresponding $d = 6.86 \text{ \AA}, 5.26 \text{ \AA}, 4.70 \text{ \AA}, 4.52 \text{ \AA}, 3.75 \text{ \AA}, 3.54 \text{ \AA}, 3.43 \text{ \AA}, 3.25 \text{ \AA}$, and $2.92 \text{ \AA}$, respectively. Figure 4-2-1-2a) These peak positions are almost the same as those observed for pure *pNA* ($2\theta = 12.90^\circ, 16.83^\circ, 18.85^\circ, 19.61^\circ, 23.70^\circ, 25.16^\circ, 25.92^\circ, 27.43^\circ$, and 30.61° , Figure 4-2-1-2c). Figure 4-2-1-2d shows a powder XRD pattern of *pNA* simulated from the reported single-crystal data,⁹ which showed a reasonable matching with the patterns obtained from pure *pNA* (c) and also with the solid mixture (a). The diffraction patterns of the solid **1** ($2\theta = 21.22^\circ$ and 23.55° ; corresponding $d = 4.18 \text{ \AA}$ and $3.77 \text{ \AA}$, respectively) were not observed for the solid mixture, indicating no phase separation of the gelator **1** in the solid mixture.

To confirm the maintenance of the self-assembly of **1** in the solid mixtures, FT-IR spectra were measured. The FT-IR spectrum of **1** showed an N-H stretching band at 3310 cm^{-1} and a C=O stretching band at 1647 cm^{-1} , respectively (Figure 4-2-1-3). These peaks are different from 3340 cm^{-1} and 1670 cm^{-1} reported for **1** in dilute CHCl_3 solution,⁸ which are characteristics of the formation of intermolecular hydrogen bonding. On the other hand, these peaks are also observed in the solid mixture **1**+*p*NA, indicating that **1** is dispersed in the solid mixture as aggregates mediated by the hydrogen bonding. We, therefore, refer to this solid mixture as a solid dispersion.

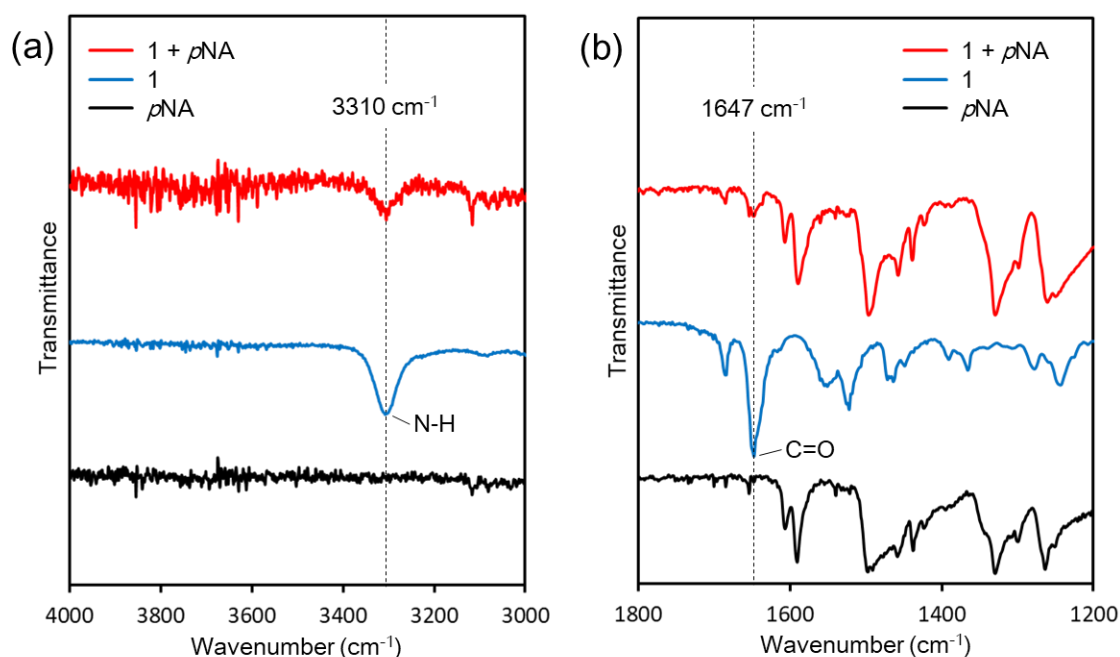


Figure 4-2-1-3. FT-IR spectroscopy of the solid dispersion ($[\mathbf{1}] : [p\text{NA}] = 1 : 80$ by molar ratio), gelator **1** and pristine *p*NA at 298 K. (a) N-H stretching band of **1**. (b) C=O stretching band of **1**.

4-2-2 Phase transition behaviors and morphology of the solid dispersion

Thermal characteristics of *p*NA and the solid dispersion ($[1] : [pNA] = 1 : 80$ by molar ratio) were then investigated by using differential scanning calorimetry (DSC, Figure 4-2-2-1, 2). As previously noted, pure *p*NA has a melting point of 326 K and it is solid at room temperature (Figure 4-2-2-1a). Meanwhile, we noticed that *p*NA showed a freezing point at 319 K, which is by 7 K lower than the melting point (Figure 4-2-2-1b). The observed lowering of the freezing temperature indicates the presence of the supercooled state, which would be rationalized to the presence of locally favored structures that differ from the crystalline symmetry. Such a supercooling phase has been also reported for nitrobenzene, in which the dipole-dipole interactions favor the formation of antiparallel dimers.¹⁰ These dimer structures are different from the monoclinic crystal structure of nitrobenzene.¹¹ It is, therefore, plausible that a similar frustration exists in liquid *p*NA between the local domain structures under the influences of dipole-dipole interactions and less-ordered liquid structures that are prone to crystallization.¹²

The solid dispersion **1**+*p*NA, meanwhile, shows a melting point at 327 K, which is close to that of pure *p*NA (at 326 K) (Figure 4-2-2-1a). Upon heating the solid dispersion above the melting point, it turned into a translucent gel (Figure 4-2-1-1). The formation of the gel phase was visually confirmed by the absence of the liquid flow in the inverted test bottles. In dark-field optical microscopy of the gel phase, however, aggregate structures of **1** were not observable. Probably, the size of these structures is below the resolution of optical microscopy. To investigate the morphology of **1** in the gel phase by atomic force microscopy (AFM), the surface of *p*NA gel ($[1] : [pNA] = 1 : 80$ by molar ratio) was transferred onto mica surfaces by contacting freshly cleaved mica substrates at 343 K and then peeling them off in a short while.¹³ To remove the matrix *p*NA by vaporization, the specimens were further heated at 343 K for 6 hrs. This compelling heat procedure was required to observe the morphology of **1** by AFM without the interference from the crystals of *p*NA otherwise coexisted at room temperature. Figure 4-2-2-2 depicts an AFM image obtained for the specimen at ambient temperature, which shows the presence of bundled fibrous nanostructures. The image looks blurred, probably due to the disfeaturing heating procedure. The formation of nanofibrous structures of **1** in organogels has been widely observed^{7,8} and it is reasonable that **1** spontaneously self-assembles also in liquid *p*NA to form nanofibrous networks. This is supported by the FT-IR data of the gel as will be discussed later. The formation of the gel phase for (**1**+*p*NA) thus indicates that liquid *p*NA molecules are confined in the interstitial domains of the self-assembled networks of **1**.

The *p*NA gel of **1** showed gel-to-sol transition by heating it to ca. 358 K (Figure 4-2-2-3). The

gel-to-sol transition occurred reversibly, and upon cooling the sol, a sol-to-gel transition was observed around 337 K (Figure 4-2-2-3). Further cooling of the gel caused the crystallization of *p*NA at 306 K (Figure 4-2-2-1b). This freezing temperature is lower than that observed for pristine *p*NA (freezing point, 319 K), and the observed decrease in the freezing point of *p*NA in the organogel is explainable by the presence of intermolecular interactions between the confined *p*NA molecules in the supercooled phase and the nanofibrous networks of **1**.

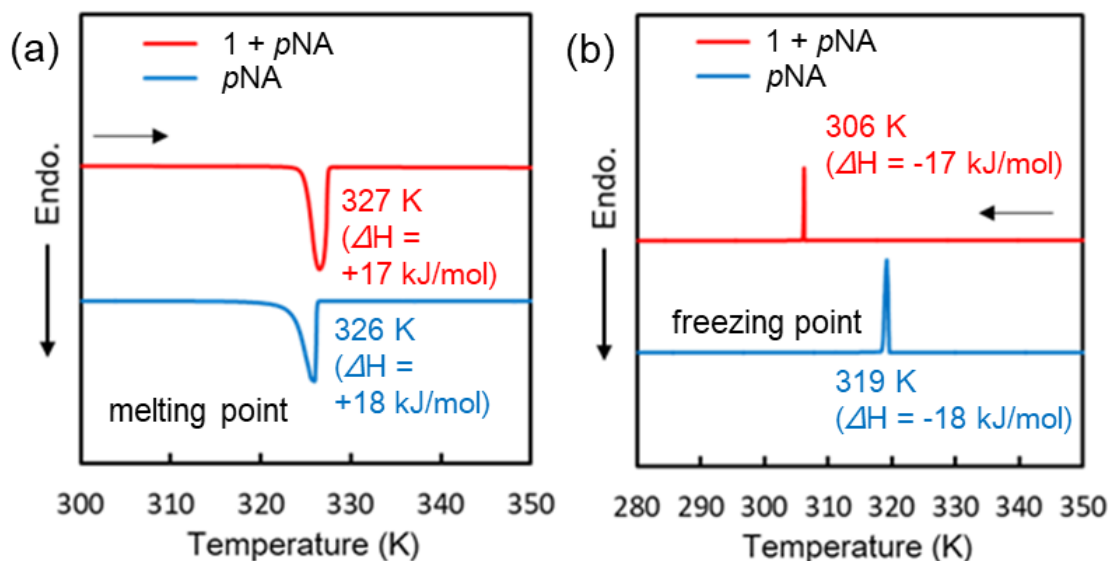


Figure 4-2-2-1. DSC thermograms of the solid dispersion of **1** and *p*NA ($[1] : [pNA] = 1 : 80$ by molar ratio) and pristine *p*NA. Scan rate = 1 K/min. (a) DSC thermograms in the heating process from 300 K to 350 K. (b) DSC thermograms in the cooling process from 350 K to 280 K. ΔH was calculated based on the mole number of *p*NA.

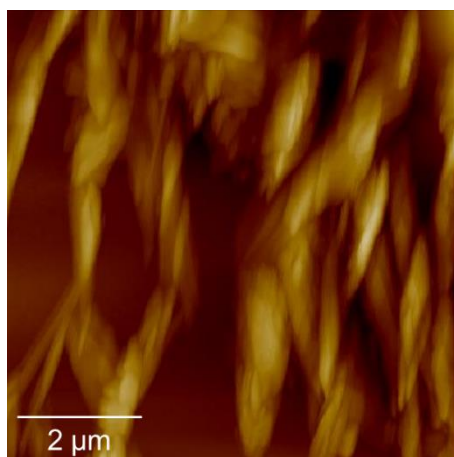


Figure 4-2-2-2. AFM image of organogel of **1** and pNA ([**1**] : [pNA] = 1 : 80 by molar ratio) at 343 K. The AFM specimen were prepared on freshly cleaved mica surfaces as described in the text. Before the AFM observations, the transferred specimen was heated at 343 K for 6 hrs to evaporate pNA.

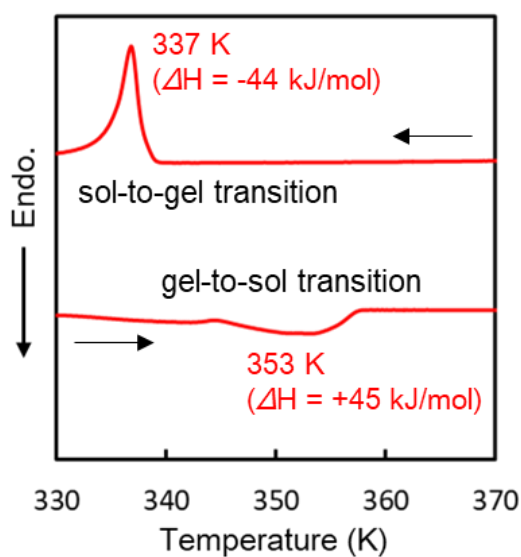


Figure 4-2-2-3. DSC thermograms of the solid dispersion in the temperature range from 330 K to 370 K. ΔH was calculated based on the mole number of **1**.

The phase transition behavior of the solid dispersion **1**+*p*NA ([**1**] : [*p*NA] = 1 : 80) was further investigated by rheological measurements (Figure 4-2-2-4). In order to prepare a homogeneous specimen, the solid dispersion was firstly heated to 358 K and the rheological measurement was conducted for the sol in the cooling process of the sol (Figure 4-2-2-4a). Upon cooling the sol from 358 K, the storage modulus (G') and the loss modulus (G'') values showed an increase and G'' reached a constant value around at 337 K, at which temperature the sol turned into the gel phase (Figure 4-2-2-2). The formation of the gel phase is also supported by the observed larger G' value as compared to the G'' value. The gel phase is maintained until cooling down to the temperature around 313 K (Figure 4-2-2-4a). Upon further cooling, G' suddenly increased at around 308 and reached a high G' of 65 MPa at 305 K which is accompanied by the disappearance of the G'' component. It reflects the crystallization of *p*NA in the gel phase to form the solid dispersion phase (Figure 4-2-2-1b). Meanwhile, the gel phase was reversibly formed upon heating the solid dispersion above the melting temperature of *p*NA, as can be seen from the sharp decrease of G' and reappearance of the loss modulus (G'') component around at 328 K (Figure 4-2-2-4b). The gel also showed gel-to-sol transition by further heating above 358 K. Thus, the rheological properties are thermally reversible which are consistent with the phase transition behaviors confirmed by DSC measurements (Figure 4-2-2-1, 2).

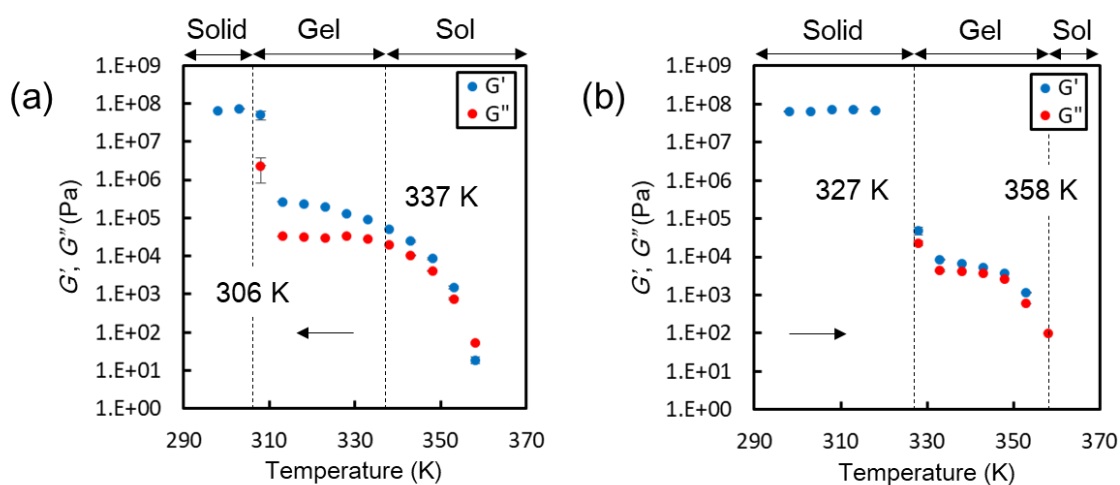


Figure 4-2-2-4. Temperature-dependent mechanical spectrum of the solid dispersion ([**1**] : [*p*NA] = 1 : 80 by molar ratio) in the (a) cooling and (b) heating processes (Temperature: 298 K–358 K, strain = 0.1%, angular frequency = 100 rad/s). To prepare a homogeneous specimen, the solid dispersion was firstly heated to 358 K on a sample plate to obtain the sol. The rheological measurement was conducted from the cooling process (a). After the cooling measurement, the sample was heated to obtain the data in the heating process (b).

The temperature dependence of FT-IR spectra was also measured (Figure 4-2-2-5). Upon heating, the hydrogen-bonded N-H stretching band of **1** shifted from 3310 cm^{-1} (298 K, solid dispersion phase) to 3316 cm^{-1} (338 K, gel phase), 3318 cm^{-1} (353 K, in the process of gel-to-sol transition) and finally disappeared at 373 K (sol phase, Figure 4-2-2-5a). On the other hand, a new high-wave number band appeared around 3420 cm^{-1} at 353 K and 373 K, suggesting that the hydrogen bonding between amide groups of **1** becomes weakened and finally broken by heating to the sol phase (Figure 4-2-2-5a). Moreover, the intensity of the C=O stretching band of **1** (1647 cm^{-1}) also showed a decrease at elevated temperatures (Figure 4-2-2-5b), supporting the molecular dissolution of **1** in the sol phase. These results confirm that the self-assembly of **1** is maintained in the solid dispersion and in the gel phase, while **1** is molecularly dissolved in the sol phase.

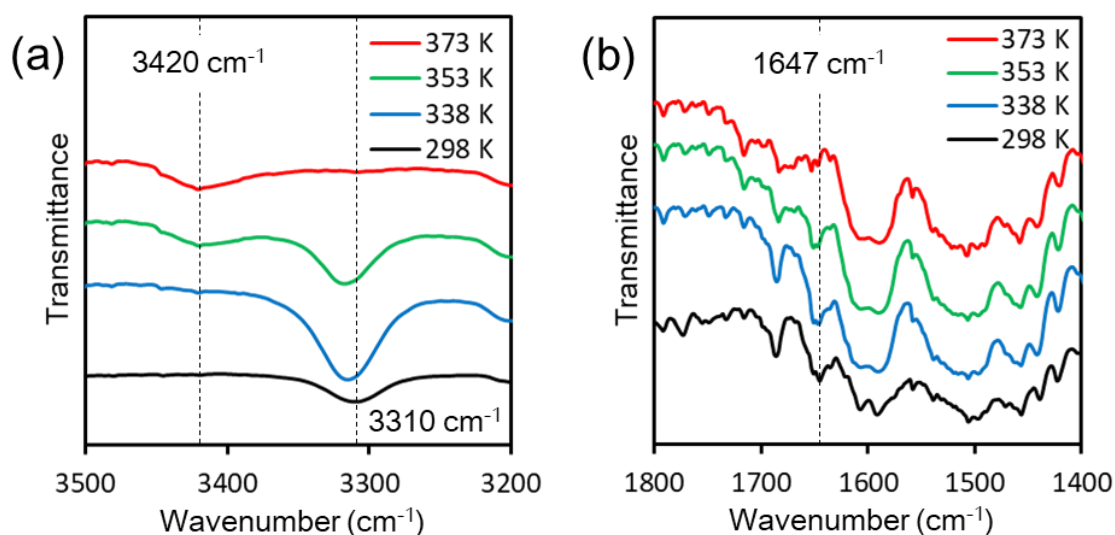


Figure 4-2-2-5. Temperature dependence of FT-IR spectroscopy of the solid dispersion ([**1**] : [pNA] = 1 : 80 by molar ratio, the heating process from 298 K to 373 K). (a) N-H stretching band of **1**. (b) C=O stretching band of **1**.

4-2-3 Dielectric properties of the solid dispersion

The dielectric properties of the solid dispersion were then investigated by introducing the liquefied sol into glass liquid crystal (LC) cells sandwiched by two bare ITO electrodes (spacing = 20 μm , non-polyimide coated, working area = 0.25 cm^2). The solid dispersion ([**1**] : [*p*NA] = 1 : 80 by molar ratio) was placed at the opening of the 20- μm -thick LC cells and was heated up to 363 K on a hot plate. The solid dispersion liquefied at this temperature, and the sol slowly transferred into the cells. After the cells were filled with the sol, they were slowly cooled down to room temperature to reform the solid dispersion in the cells. A reference sample was also prepared by introducing pristine *p*NA into a blank LC cell. The dielectric behaviors of the solid dispersion and pristine *p*NA were examined at varied temperatures under the application of AC voltage (0.5 V/ μm , frequency = 1 Hz). By applying an external electric field (*E*) to molecules having permanent dipoles, dipolar polarization is generally observed. This orientational polarization is, however, lost when the electric field is removed (i.e., no hysteresis).

The polarization-electric field (*P-E*) curve obtained for the organogel ([**1**] : [*p*NA] = 1 : 80 by molar ratio) exhibited a hysteresis with a remnant polarization (P_r) of ca. 56 $\mu\text{C}/\text{cm}^2$ and a coercive electric field (E_c) of ca. ± 4.0 kV/cm at 338 K as determined from the x- and y-intercepts of the *P-E* hysteresis loop (Figure 4-2-3-1a). Such a remarkable hysteresis was not observed for pure *p*NA (P_r , ca. 1.9 $\mu\text{C}/\text{cm}^2$, Figure 4-2-3-1a and Figure 4-2-3-2). The intensity of P_r observed for the organogel is more than an order of magnitude larger than that observed for pristine *p*NA. Importantly, the gel sample exhibited peaks in the current-electric field (*I-E*) loop, at which the positions correspond to the coercive fields at ca. ± 2.4 kV/cm (Figure 4-2-3-1b), which can be attributed to the polarization inversion of *p*NA molecules confined in the gel. We, meanwhile, noticed that the peaks of *I-E* curves observed for the organogel with **1** and *p*NA are smaller than the coercive electric field (E_c : ± 4.0 kV/cm) in the *P-E* curves (Figure 4-2-3-1a). This is probably due to the hysteresis loops show convex regions, typical for a lossy dielectric. Both the P_r and E_c values showed frequency dependence in the range of 1–1000 Hz (Figure 4-2-3-3), and the P_r values are smaller at higher frequencies (> 100 Hz). It indicates that the motional frequency of dipole inversion in the gel state is relatively slow.

It is also to note that the remnant polarization P_r value observed for the organogel is more than two orders of magnitude larger than those reported for the ferroelectric liquid crystals (50–500 nC/cm^2),^{14–16} and exceeds that of a representative ferroelectric polymer, poly(vinylidene fluoride) (PVDF, $P_r = 8$ $\mu\text{C}/\text{cm}^2$).¹⁷

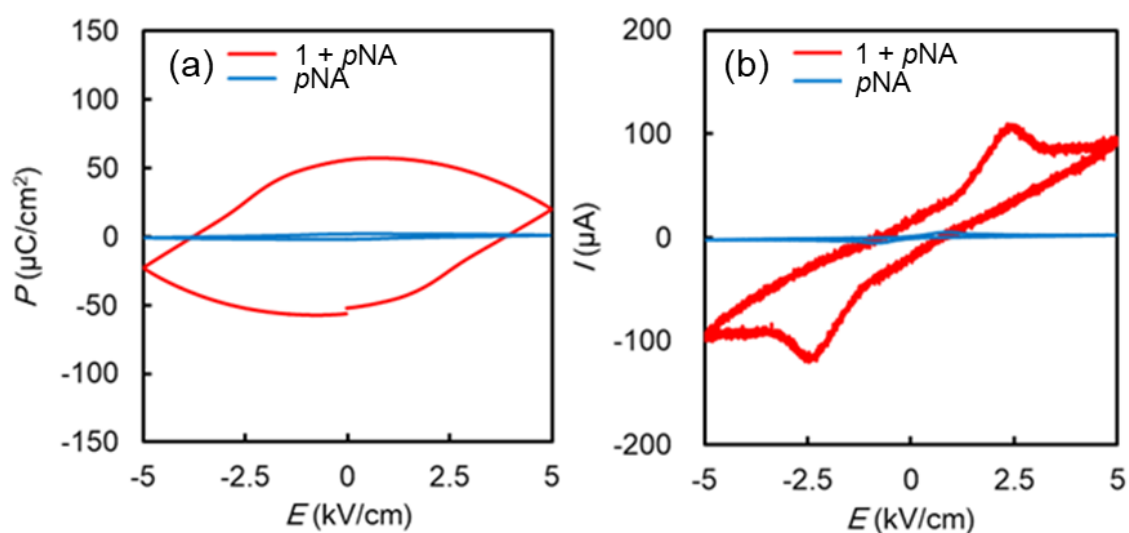


Figure 4-2-3-1. (a) P - E loops and (b) I - E loops observed for $p\text{NA}$ and the gel ($[1] : [p\text{NA}] = 1 : 80$ by molar ratio). The data were recorded by applying an AC voltage of 10 V with a frequency of 1 Hz. Temperature at 338 K. The data averaged for 50-cycle measurements.

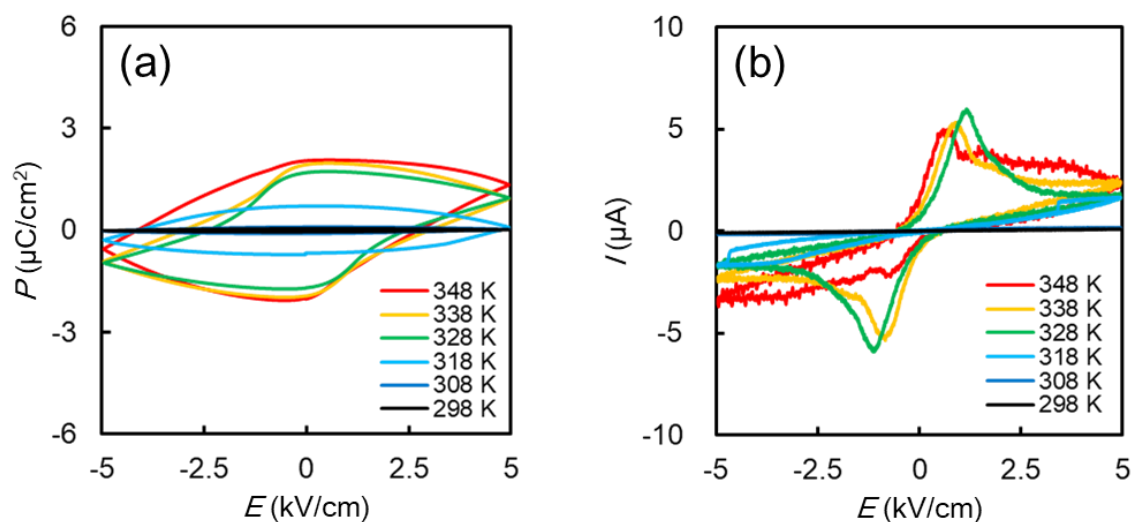


Figure 4-2-3-2. The (a) P - E and (b) I - E loops of pure $p\text{NA}$ (without gelator **1**) in the heating process from 298 K to 348 K. LC cells having 20 μm -spacer between the ITO electrodes were employed. Data recorded at 10 V, frequency of 1 Hz. Data are averaged for 50-cycle measurements.

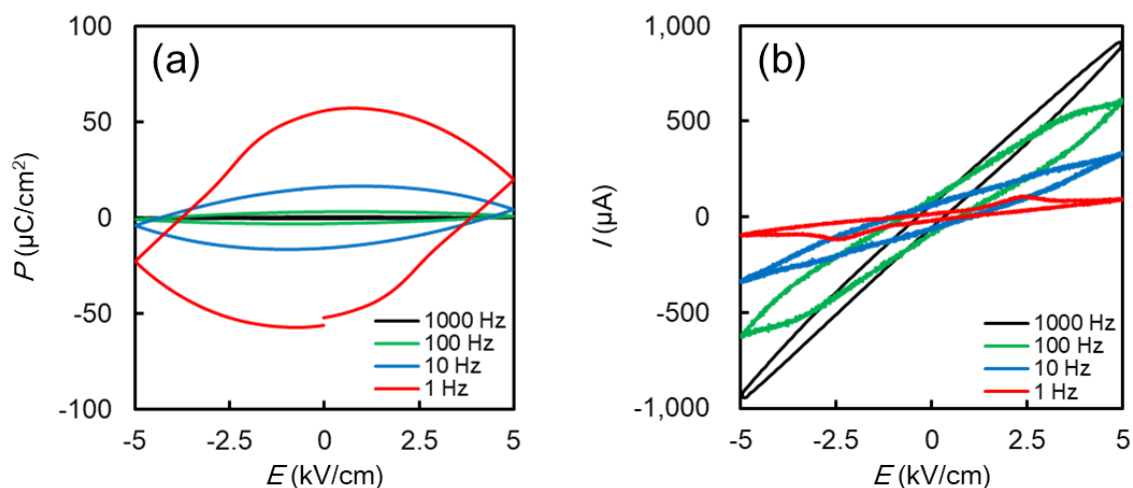


Figure 4-2-3-3. The (a) P - E and (b) I - E loops of the p NA gel ($[1] : [pNA] = 1 : 80$ by molar ratio) recorded at various conditions (10 V, 1–1000 Hz, 338 K). Data are averaged for 50-cycle measurements.

The temperature dependence of P - E and I - E curves are shown in Figure 4-2-3-4. In Figures 4-2-3-5, P_r values are plotted as a function of temperatures (the heating and cooling processes, respectively). These data show that the enhanced dipolar polarization is observed for the gel state (above the melting point of p NA, 327 K, on heating) and not in the solid dispersion phase. Apparently, the hysteresis in P - E curves is suppressed by freezing of p NA confined in the solid dispersion, and the fluidity of p NA in the gel is essential for the salient P - E hysteresis.

As discussed before, the supercooling effect observed for the gel (Figure 4-2-2-1b) indicates the presence of interactions between liquid p NA molecules with the self-assembled gel networks of **1**. It is then reasonable to consider that p NA molecules in the present gel system involve these strongly interacting with the self-assembled gel networks, and those continuously associated inward the inner interstitial space of the gel. We note that the appearance of the dipolar polarization and the P - E hysteresis occurred cooperatively with the solid-to-gel transition (Figure 4-2-3-5b). Such a cooperative transition may reflect intermolecular interactions among p NA molecules operate in substantial structural correlation lengths, presumably dipole-dipole interactions, in the interconnected interstitial space of the gel.

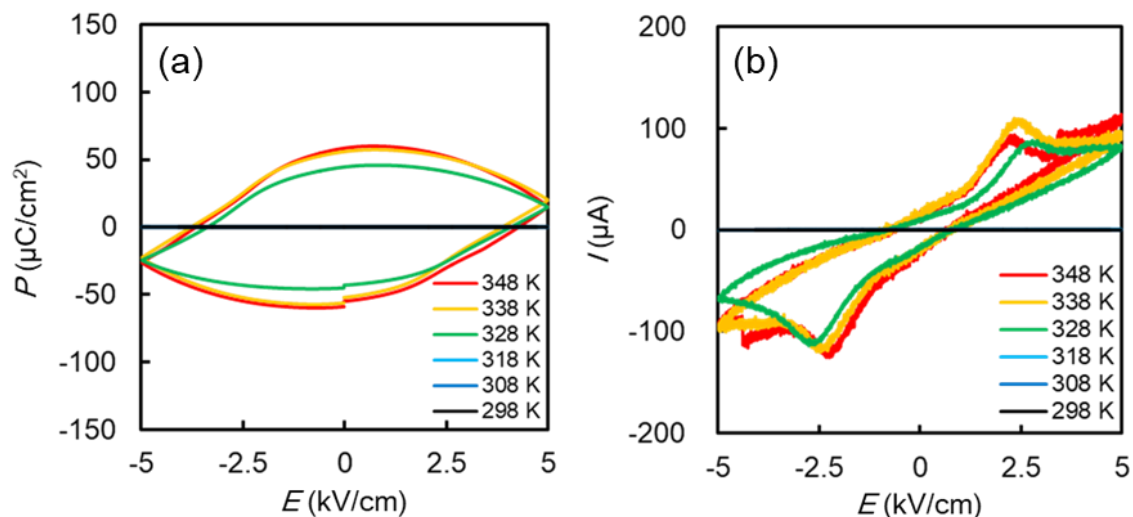


Figure 4-2-3-4. The (a) P - E and (b) I - E curves obtained for the solid dispersion (1+pNA). [1] : [pNA] = 1 : 80 by molar ratio. Temperatures at 298–348 K (heating process). The data were averaged for 50-cycle measurements.

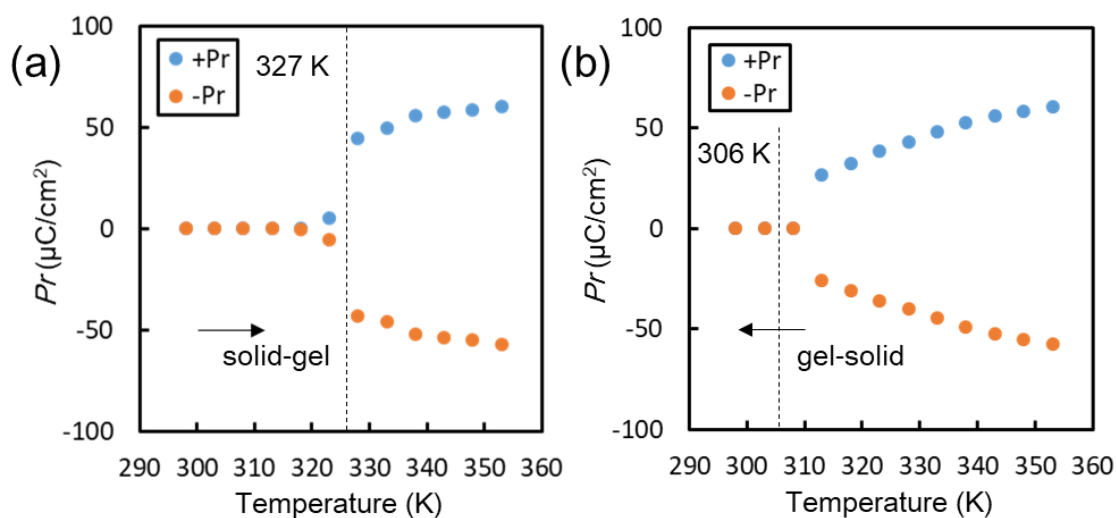
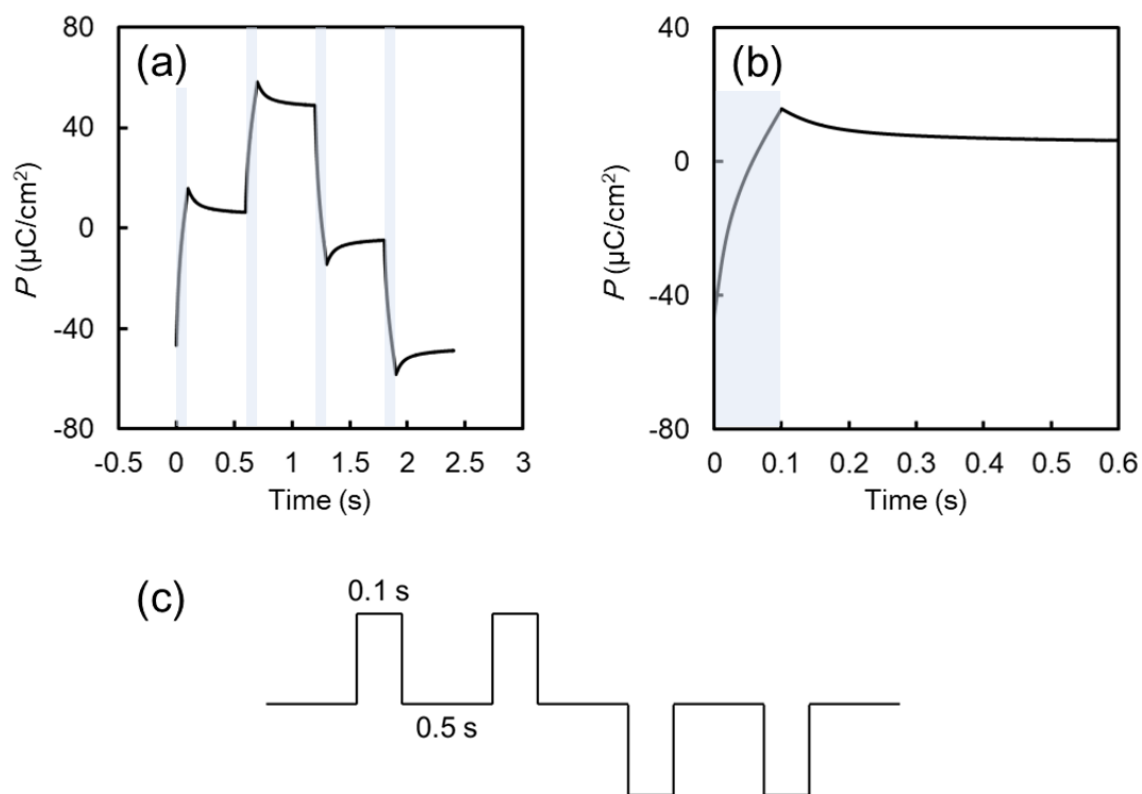


Figure 4-2-3-5. Temperature dependence of the remnant polarization ($\pm P_r$) observed for the solid dispersion ([1] : [pNA] = 1 : 80 by molar ratio). (a) Heating process from 298 K to 353 K. (b) Cooling process from 353 K to 298 K. Data recorded at applied AC voltage of 10 V with a frequency of 1 Hz. The data were averaged for 50-cycle measurements.

In the course of this study, we noticed that even *p*NA alone showed a hysteresis in the *P-E* loop with P_r of ca. $1.9 \mu\text{C}/\text{cm}^2$ and E_c of ca. $3.0 \text{ kV}/\text{cm}$ at 338 K (Figure 4-2-3-2). This could be ascribed to the electric field-assisted physisorption of *p*NA molecules near the ITO surface which promoted the formation of polarized layers of macroscopically oriented clusters near the interface, as similarly reported for the formation of ethanol macroclusters on the silica surfaces.¹⁸ This model can explain the collective polar switching following the applied external field. The presence of domains in pristine *p*NA has also been supported by the presence of a supercooled state (Figure 4-2-2-1). However, we note that the intensity of P_r observed for pristine *p*NA is nominal compared with the intensities of P_r and the hysteresis loop observed for the organogel of **1** and *p*NA (Figure 4-2-3-1).

To scrutinize the unique dielectric properties of the organogel, positive-up-negative-down (PUND)¹⁹ measurements were conducted. In PUND experiments, a negative poling pulse with the same amplitude ($5 \text{ kV}/\text{cm}$) and width (0.1 s) was applied to the sample, and it is followed by a sequence of two positive and two negative voltage pulses. The electric responses were analyzed by fitting the data to the ferroelectric component (FC), paraelectric component (PC), and leakage current component (LC), respectively. The PUND responses observed for the organogel and pristine *p*NA are shown in Figure 4-2-3-6, 7 and 8, respectively, together with the magnified pulse responses around the first positive pulse (Figure 4-2-3-6b and Figure 4-2-3-7b). The magnitudes of FC, PC, and LC obtained by the analyses of PUND pulse responses are summarized in Table 4-2-3. As noted before, the *P-E* loop observed for the organogel (Figure 4-2-3-1a) shows a convex region which is typical for the lossy dielectric materials exhibiting conductance.²⁰ This is related to the observed LC which is of inexplicable origin. To discuss the contribution of the confinement effect in the observed *P-E* loops, FC and PC were compared as shown in Figure 4-2-3-8. As expected, the dielectric characteristic of pure *p*NA is dominated by PC of ca. $0.89 \mu\text{C}/\text{cm}^2$ (Table 4-2-3, Figure 4-2-3-8). Meanwhile, the organogel shows and significantly enhanced FC (ca. $25 \mu\text{C}/\text{cm}^2$) that exceeds PC (ca. $9.4 \mu\text{C}/\text{cm}^2$), and this is consistent with the observed pronounced hysteresis in the *P-E* loop (Figure 4-2-3-1a). The presence of the FC component, therefore, would reflect the strong interactions operating between the *p*NA molecules and molecular assemblies of **1**.

On the other hand, the dipolar polarization observed for the organogel shows relaxation described in Figure 4-2-3-6. It indicates that the energy barrier between the two polar states is quite small to maintain the polar organization. Therefore, the organogel is not ferroelectric and the observed *P-E* hystereses represent the consequence of the polar switching phenomenon.²¹ The FC values observed in the PUND measurements, thus, would be better considered as a performance index that reflects the confinement effect of the *p*NA molecules in the organogel.



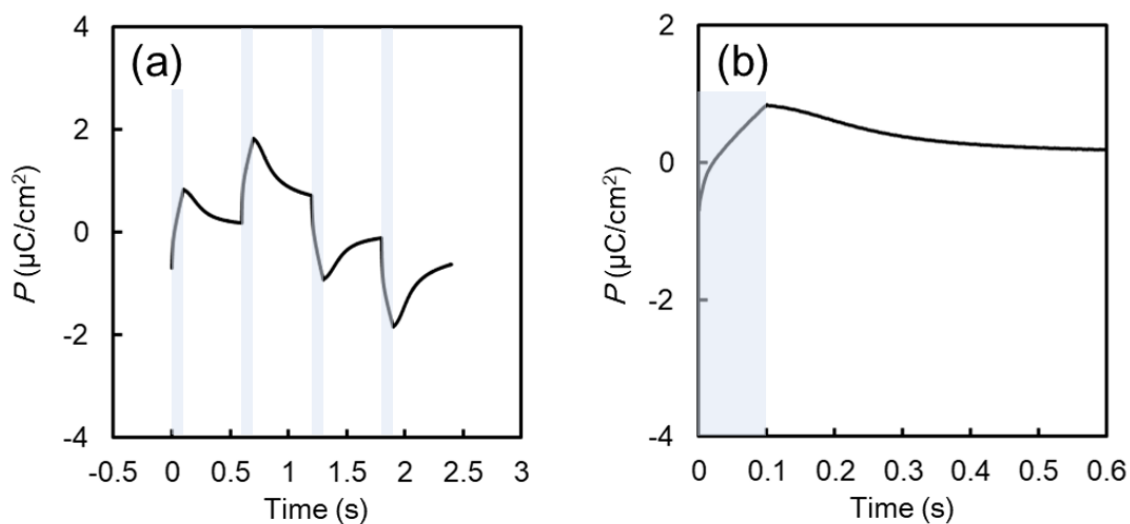


Figure 4-2-3-7. (a) PUND responses observed for pure *pNA*. Applied voltage, 5 kV/cm. Temperature at 338 K. The period of the applied voltage is shown in blue bars. (b) The polarization decay after the first positive voltage pulse in (a).

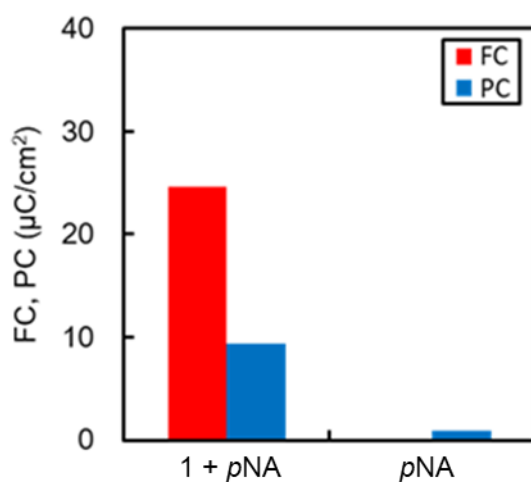


Figure 4-2-3-8. The magnitudes of FC and PC components obtained for the mixture of **1** + *pNA* ([**1**] : [*pNA*] = 1 : 80 by molar ratio) and pristine *pNA*. Temperature, 338 K.

Table 4-2-3. The magnitudes of the ferroelectric component (FC), the paraelectric component (PC) and the leakage current component (LC) of the organogel ([1] : [pNA] = 1 : 80 by molar ratio) and pristine pNA at 338 K.

	FC ($\mu\text{C}/\text{cm}^2$)	PC ($\mu\text{C}/\text{cm}^2$)	LC ($\mu\text{A}/\text{cm}^2$)
1 + pNA	25	9.4	290
pNA	0.0	0.89	8.7

4-2-4 Conclusion

It is concluded that the polarization switching behavior occurs when liquid dipolar molecules and nanofibers show considerable interactions. The presence of liquid domain structures under the influence of dipole-dipole interactions was indicated by the altered freezing point in the organogel. The confinement of polar molecules in organogels enhances the dipolar polarization and induce polar switching phenomena, i.e., the hysteresis in P - E curves. These unique features can be described as nanointerface-induced dipolar polarization. The liquid *p*NA molecules existing inward the interstitial domains seem to have long-range interactions, presumably mediated by the dipole-dipole interactions with those associating the self-assembled gel network of **1**. It leads to the cooperative changes in the dielectric properties which occurred concertedly with the solid-to-gel phase transition. By considering the wide variety of functional organic dipolar molecules and the advantages of processability as well as reconfigurability, soft dielectrics formed by self-assembly may provide new applications not available from the conventional solid inorganic materials.

4-3 Sample preparation and characterization

1. Sample preparation, Powder X-ray diffraction analysis, Fourier-transform infrared spectroscopy, DSC measurements, and rheological measurements.

*p*NA was purified by repeated recrystallization from distilled methanol. Gelator **1** was synthesized according to the literature procedures.^{7,8} Powder X-ray diffraction (PXRD) analysis was conducted on a Bruker D2 PHASER with a Cu K-alpha source ($\lambda = 1.54056 \text{ \AA}$) operated at 30 kV and 10 mA. The solid specimens for XRD measurements were well ground before the measurements to eliminate possible anisotropy of the samples. Fourier-transform infrared (FT-IR) spectroscopy was conducted with Shimadzu IRPrestige-21. DSC measurements were conducted with METTER TOLEDO, DSC 1 STARe System. The DSC isotherms were recorded at a scan speed of 1 K/min. The rheology measurements were performed on an Anton Paar MCR 302 rheometer.

2. Dielectric measurements.

Dielectric measurements were conducted for pristine *p*NA and the solid dispersion consisting of *p*NA and gelator **1**. We employed liquid crystal (LC) cells coated with ITO electrodes (area, $5 \times 5 \text{ mm}^2$, cell gap of $20 \text{ }\mu\text{m}$, no-polyimide coating, E.H.C. Co. Ltd.). The specimens were placed near the aperture of LC cells and the whole-cell samples were heated up to 363 K on a hot plate. The liquefied specimens were slowly transferred into the cells. Once the ITO working area of the cell was completely filled with the specimens, the sample was cooled down to room temperature. The specimens remained on the surface of LC cells were wiped away by using KimWipes. The dielectric measurements were undertaken on a Toyo Corporation ferroelectric-evaluation standard system (FCE-1) connecting to a Toyo6252 Rev. C current/charge–voltage converter, a Biomation2414B arbitrary waveform generator, a WaveBook 516E analog-to-digital converter and Linkam Hotstage 10084L (JAPAN HIGH TECH). All *P-E* and *I-E* loops were recorded with a triangular wave field. The accuracy of the polarization value was confirmed by the measurement of 20/80 lead zirconate titanate (PZT, TOSHIMA Manufacturing Co., Ltd., Area: 0.0001 cm^2 , Thickness: $0.26 \text{ }\mu\text{m}$, Voltage: 4 V, Frequency: 100 Hz, Temperature: 298 K, $+P_r$: ca. $25 \text{ }\mu\text{C}/\text{cm}^2$ (ref. $28 \text{ }\mu\text{C}/\text{cm}^2$)) as a reference sample.

4-4 Reference

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Chapter 5 Polar switching of dipolar molecules confined in submicron and micron-sized pores in polymer films

5-1 Introduction

In chapters 3 and 4, we reported that supramolecular gels and solid dispersions prepared from dipolar molecules, such as nitrobenzene and *p*-nitroanisole, showed a polar switching response. In these systems, it was assumed that the dipolar molecules confined on the surface of the nanofibrous network within the gel could respond to the external electric field, leading to the hysteresis in polarization-electric field loops. Therefore, it is believed that liquid molecules have the potential to exhibit polar switching by enhancing molecular interactions with surfaces.

It is essential to fabricate materials with large surface areas for controlling the orientation of polar molecules. Porous materials are promising candidates because of their large surface areas attributed to the countless pores. They have been developed for various purposes such as storage, separation, and chemical conversion of the guest molecules. Zeolite,^{1,2} silica gel^{3,4} and mesoporous silica⁵⁻⁷ are the commonly known inorganic porous materials and have been well-developed with a wide range of applications. On the other hand, organic porous materials have received a lot of attention in recent years because most of these materials are light-weighted and more environmentally friendly than their inorganic analogs. For example, activated carbons have been prepared as materials for CO₂ absorption⁸ or scaffolds for photocatalysis.⁹ Porous polymer materials have also been obtained through the microphase separation of block copolymers¹⁰ or the removal of nanoparticle template.¹¹ Recently, the development of organic-inorganic hybrids has paved the way to make promising functional porous materials. In particular, metal-organic-frameworks (MOFs) have been commonly developed for various purposes like gas adsorption,^{12,13} and drug delivery system.^{14,15}

Among all the reported types of porous materials, we set our focus on porous polymer films because of their stability and flexibility. These properties impart porous polymer films the potential for the fabrication of flexible materials that could be used in wearable devices. Functional porous polymer films have been of interest and studied by many researchers. For example, Gu *et al.* have succeeded in preparing flexible porous polystyrene films for tissue engineering.¹¹ Moreover, Watanabe *et al.* have designed and obtained porous polymer materials for the use as ionic visible indicator.¹⁶

Therefore, in this chapter, we report the confinement of molecules with a large permanent dipole in interconnected submicron and micron-sized pores formed in flexible polymer films pronouncedly enhances dipolar polarization and causes polar switching phenomena. As a dipolar molecule, we

employed *p*-nitroanisole (*p*NA) because it has a large dipole moment of 4.76 Debye.¹⁷ It was expected that the polarization of *p*NA confined in the pores in polymer films was increased compared with the bulk state and *p*NA confined in submicron-to-micron sized pores showed hysteresis in the *P-E* curves above the melting point of *p*NA (Figure 5-1).

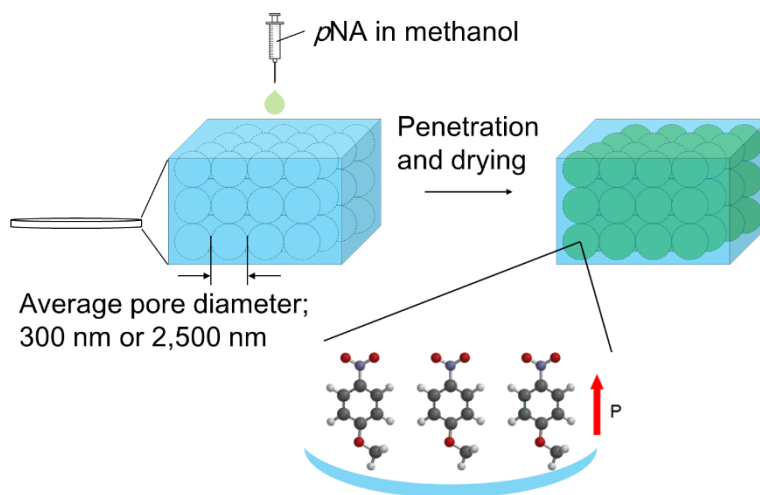


Figure 5-1. A schematic representation of the preparation of *p*NA-loaded porous polyimide films and dielectric behavior.

5-2 Results and Discussion

5-2-1 Accumulation of *p*NA into the pore of porous polyimide films

As submicron-to-micron-sized porous polymer films, we employed highly porous polyimide (PI) films (porosity ~70%, thickness, 40 μm) provided from Tokyo Ohka Kogyo Co. Ltd.. Polyimides are widely used as insulating films for the fabrication of microelectronic devices because of their high thermal and chemical stability, flexibility, insolubility in organic solvents and low electric conductivity. These features are suitable for the present purpose. The porous polymer films employed contain spherical pores of 300 nm or 2500 nm in diameter (abbreviated as PI-300 or PI-2500, respectively. film area: $1.5 \times 1.5 \text{ cm}^2$, film volume: $9 \times 10^{-3} \text{ cm}^3$, pore volume: $6.3 \times 10^{-3} \text{ cm}^3$, Figure 5-2-1-1). According to IUPAC nomenclature, materials having pore diameters of greater than 50 nm are classified as macroporous. However, we refer the present PI-300 and PI-2500 films as submicron- and micron-sized pore films because they show different host characteristics as described below. As can be seen from the scanning electron micrographs in Figure 5-2-1-1, spherical pores are interconnected in the films, giving a large surface area. To fill these pores with *p*NA, methanol solutions of *p*NA ($[p\text{NA}] = 1.27 \text{ M}$) were slowly dropped onto PI-300 or PI-2500 films horizontally supported in the air. The solutions spread on and into the film gradually and the resultant composites were dried at room temperature. The amount of *p*NA required to fill the pores in the films is roughly calculated as 51 μmol based on the density of *p*NA (1.23 g/cm^3 at RT) and the estimated pore volumes in films. The *p*NA-loaded films are referred to as *p*NA@PI-300 and *p*NA@PI-2500 films, respectively.

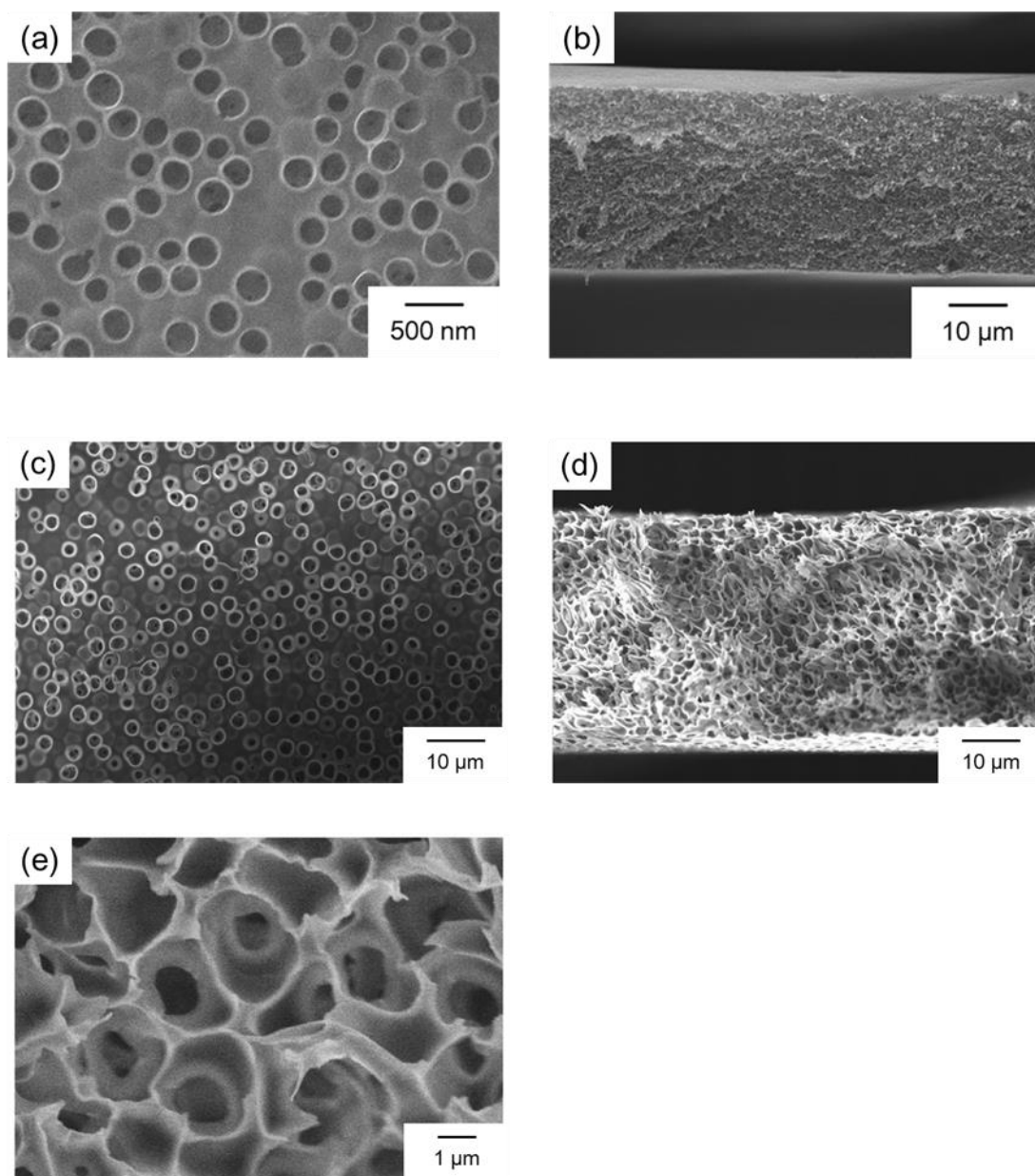


Figure 5-2-1-1. SEM images of PI-300 and PI-2500. (a) Surface image of PI-300. (b) Cross-section image of PI-300. (c) Surface image of PI-2500. (d) Cross-section image of PI-2500. (e) Magnified cross-section image of PI-2500.

The filling of *p*NA in the pores was checked for *p*NA@PI-300 films by measuring the permeability of N₂ gas with a bubble flow meter (HORIBA STEC VP-2). The permeance of N₂ gas decreased with increasing the amount of *p*NA loaded in the PI-300 film (Figure 5-2-1-2). The permeation of N₂ gas was not completely suppressed for the film containing 51 μmol of *p*NA, whereas a film doped with almost two-fold *p*NA (101 μmol) showed blocking of the gas permeance. It was employed as the experimental condition to effectively fill the pores by *p*NA molecules. As can be seen from Figure 5-2-1-1e, pores are interconnected with open channels, which may require the excess amount of *p*NA to fill all these vacancies to prevent leakage of N₂ gas.

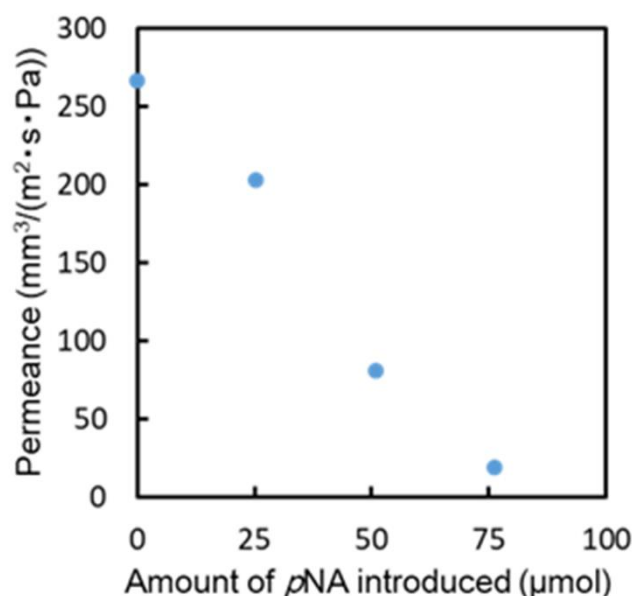


Figure 5-2-1-2. The dependence of N₂ gas permeance (0.01 MPa, 100 sccm) for PI-300 films containing varied loading amounts. N₂ gas permeance was totally blocked for PI-300 films containing more than 101 μmol of *p*NA.

5-2-2 Phase transition behaviors of *p*NA in the pores

DSC measurements were conducted for *p*NA@PI-300 films with the different loaded amount of *p*NA, and also for pure *p*NA and a pristine PI-300 film as references. Endothermic peaks were observed in the course of heating (Figure 5-2-2a) and corresponding exothermic peaks were observed in the cooling process (Figure 5-2-2b). We confirmed that the pristine PI-300 film showed no peaks in the observed temperature range (blue lines in Figure 5-2-2a,b). Pure *p*NA showed an endothermic peak at 326 K, which is ascribed to the melting temperature ($\Delta H = 17.82 \text{ kJmol}^{-1}$). In the cooling process, crystallization occurred at 319 K accompanied by an identical enthalpy change, and the solidification occurred at the lowered temperature as compared to the melting temperature at 326 K (Figure 5-2-2b). The observed lowering of the freezing temperature indicates the presence of the supercooled state, which reflects the coexistence of locally favored structures possibly mediated by dipole-dipole interactions that differ from the crystalline symmetry of *p*NA.

Meanwhile, the composite film of *p*NA (51 μmol)@PI-300 showed two melting temperatures at 318 K ($\Delta H = 2.0 \text{ kJmol}^{-1}$) and 323 K ($\Delta H = 8.77 \text{ kJmol}^{-1}$), which are lower than that observed for pure *p*NA (326 K, Figure 5-2-2a). The observation of multiple endothermic peaks in *p*NA (51 μmol)@PI-300 suggests the coexistence of *p*NA molecules that are strongly affected by the pore surface (i.e., the 318 K peak, $\Delta H = 2.0 \text{ kJmol}^{-1}$) and those less-affected inward the pores (i.e., the 323 K peak, $\Delta H = 8.77 \text{ kJmol}^{-1}$, Figure 5-2-2a). Similarly, the film *p*NA (101 μmol)@PI-300 showed peaks lower than the pristine *p*NA. The lower endothermic peaks of the film *p*NA (101 μmol)@PI-300 showed larger enthalpy changes ($\Delta H = 6.26 \text{ kJmol}^{-1}$) as compared to that of *p*NA (51 μmol)@PI-300 ($\Delta H = 2.0 \text{ kJmol}^{-1}$), indicating that the pore wall was more effectively covered by loading higher amount of *p*NA molecules. This result is consistent with the N_2 gas permeation data. In addition, we note that the total enthalpy changes associated with the melting in composite films are smaller than that of the pure *p*NA ($\Delta H = 17.82 \text{ kJmol}^{-1}$). As these composite films show no peaks at the melting temperature of bulk *p*NA, the *p*NA molecules in porous PI films appear to be well loaded in the pores without segregation on the film surface. These observations indicate that *p*NA in composite films show thermodynamic properties significantly affected by the interactions with the pore walls. The freezing temperatures are also affected in the composite films (Figure 5-2-2b), indicating that *p*NA molecules in the composite films benefit from the confinement effect.^{18–20}

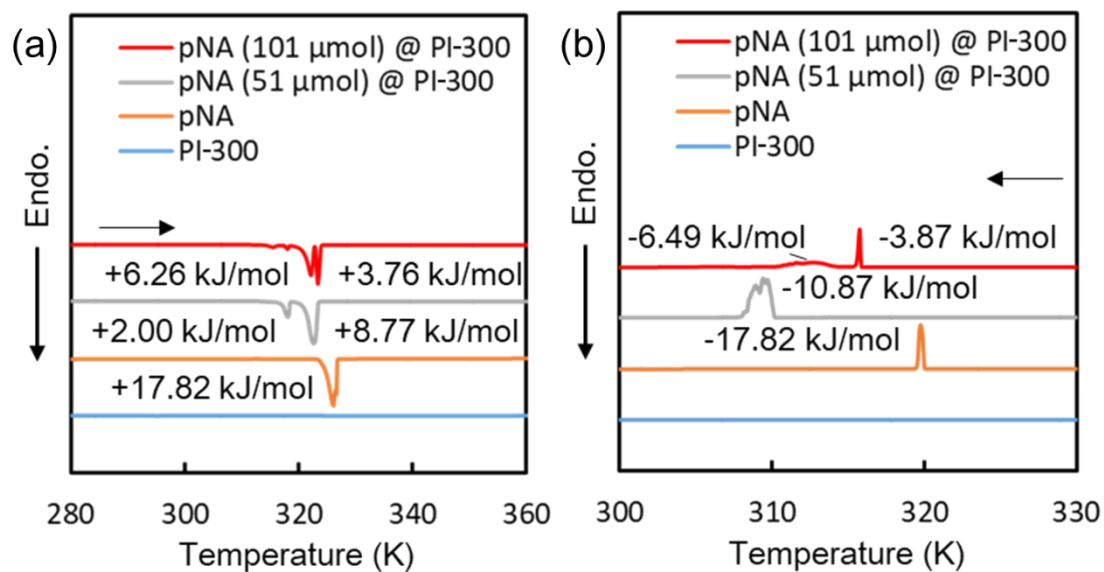


Figure 5-2-2. DSC thermograms of pNA, pNA (51 or 101 μmol)@PI-300 composite films, and PI-300 film recorded at 1 K/min. (a) Heating process. (b) Cooling process. The figures represent enthalpy changes associated with the peaks.

5-2-3 Dielectric properties of the composite films

The dielectric behaviors of pure *p*NA, pristine PI-300 film, and *p*NA (101 μmol)@PI-300 film were then examined under the application of AC voltage (2.5 kVcm^{-1} , frequency = 1 Hz, temperature at 343 K). We hereafter focus on the PI-300 film doped with 101 μmol *p*NA and abbreviate the sample just as *p*NA@PI-300 film, since the pores in these films are sufficiently filled with *p*NA molecules as indicated by the blocked gas permeability (Figure 5-2-1-2). Gold thin foil electrodes (thickness $\sim 300 \text{ nm}$) were attached to both sides of the films (Figure 5-2-3-1), and external AC voltages were applied. For dielectric measurement of pure *p*NA, it was liquefied by heating and introduced into glass liquid crystal (LC) cells containing bare ITO electrodes (spacing = 20 μm , non-polyimide coated, working area = 0.25 cm^2). In general, molecules having intrinsic dipoles display electric field-induced dipolar (or orientational) polarization (P) which is lost when the electric field (E) is removed.

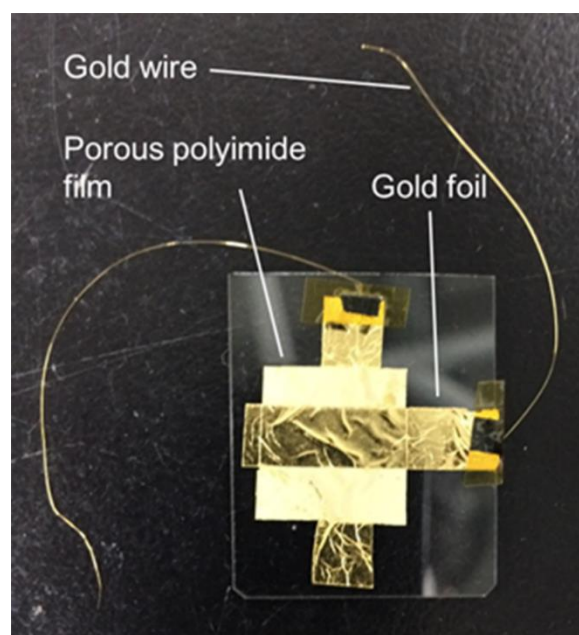


Figure 5-2-3-1. The setup of the dielectric measurement for film samples. For the dielectric measurement of pure *p*NA, glass liquid crystal (LC) cells sandwiched by two bare ITO electrodes (spacing = 20 μm , non-polyimide coated, working area = 0.25 cm^2) were employed.

The polarization-electric field (P - E) curves and the current-electric field (I - E) curves obtained for pure p NA, p NA@PI-300 film and a pristine PI-300 film are shown in Figures 5-2-3-2, 3, 4, 5, 6 and 7. p NA in the solid-state shows no dielectric response, as shown in Figure 5-2-3-3 (temperatures below 326 K). Meanwhile, at temperatures above the melting point (Figure 5-2-3-3a), the P - E loop showed a feature of hysteresis with a remnant polarization (P_r) of ca. $2 \mu\text{C}/\text{cm}^2$ and a coercive electric field (E_c) of ca. $\pm 1.3 \text{ kV}/\text{cm}$ at 343 K as determined from the x- and y-intercepts of the P - E hysteresis loops. The positive and negative peaks are observed in the I - E curves (Figure 5-2-3-3b), which are ascribable to the polarization inversion current as described later. The dipole interactions operating among highly polar liquid molecules offer them a latent potential to form anisotropic molecular clusters, as reported for the nano-sized ferroelectric domains of nitromethane formed in binary solutions.²¹ The formation of macroscopically oriented ethanol clusters on glass surfaces is also reported.²² By considering these reported self-assembling properties directed by specific intermolecular interactions in solutions and at interfaces, it is reasonable to assume that liquid p NA molecules physisorbed at the electrode surfaces promote the formation of polarized layers of macroscopically oriented clusters near the interface, mediated by the dipole-dipole interactions. They would be responsible for the polar switching phenomena with respect to the direction of the applied external field, as observed by the hysteresis in the P - E curves. The formation of such molecular clusters is supported by the observation of the supercooled state (Figure 5-2-2b).

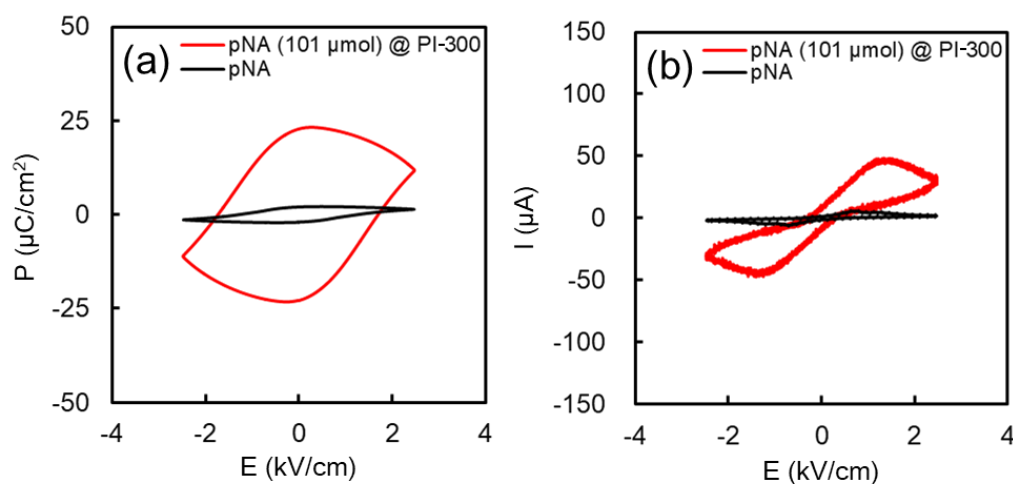


Figure 5-2-3-2. (a) The P - E and (b) I - E loops of p NA and p NA (101 μmol)@PI-300 recorded at 2.5 kV/cm, 1 Hz, 343 K. Data are the average of 50 cycles of measurements.

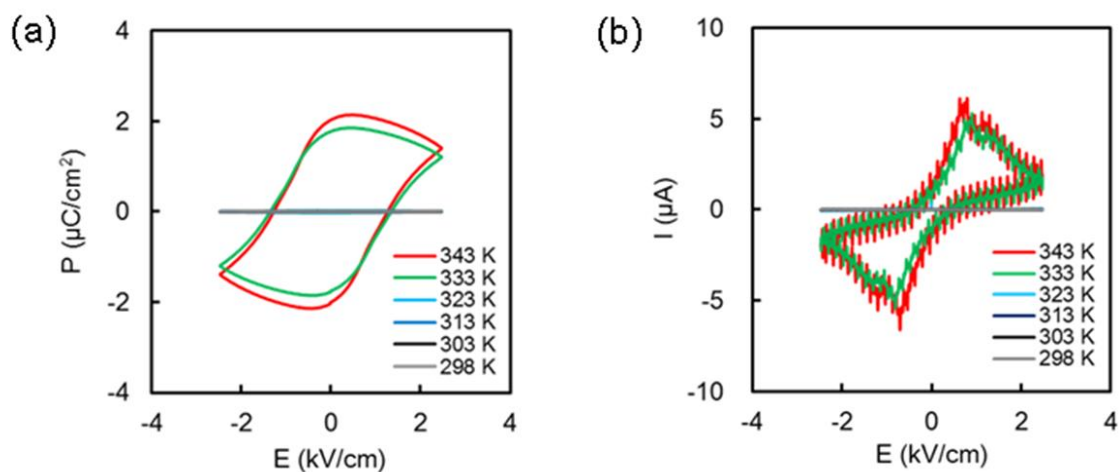


Figure 5-2-3-3. Temperature dependence of pure *p*NA recorded at 2.5 kV/cm, 1 Hz, 298–343 K. Data are the average of 50 cycles of measurements. (a) *P*-*E* loops. (b) *I*-*E* loops.

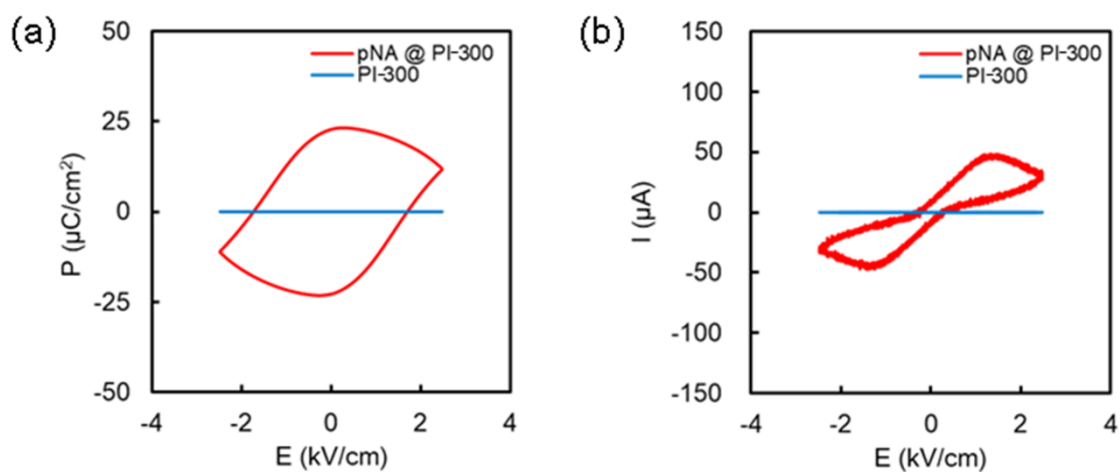


Figure 5-2-3-4. (a) The *P*-*E* and (b) *I*-*E* loops obtained for a pristine PI-300 film and a composite film *p*NA (101 μmol)@PI-300 recorded under the applied ac voltage of 2.5 kV/cm at 343 K. Frequency, 1 Hz. Data are the average of 50 cycles of measurements.

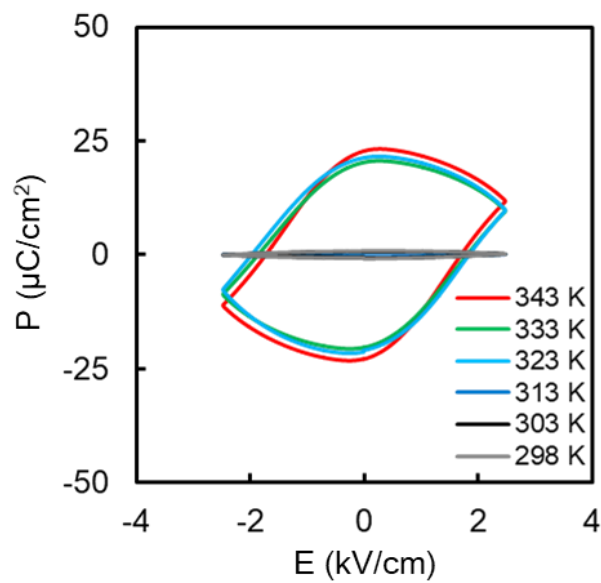


Figure 5-2-3-5. Temperature dependence of the P - E loops obtained for $p\text{NA}$ ($101 \mu\text{mol}$)@PI-300 recorded at 2.5 kV/cm , 1 Hz , heating process from 298 K to 343 K . Data are the average of 50 cycles of measurements.

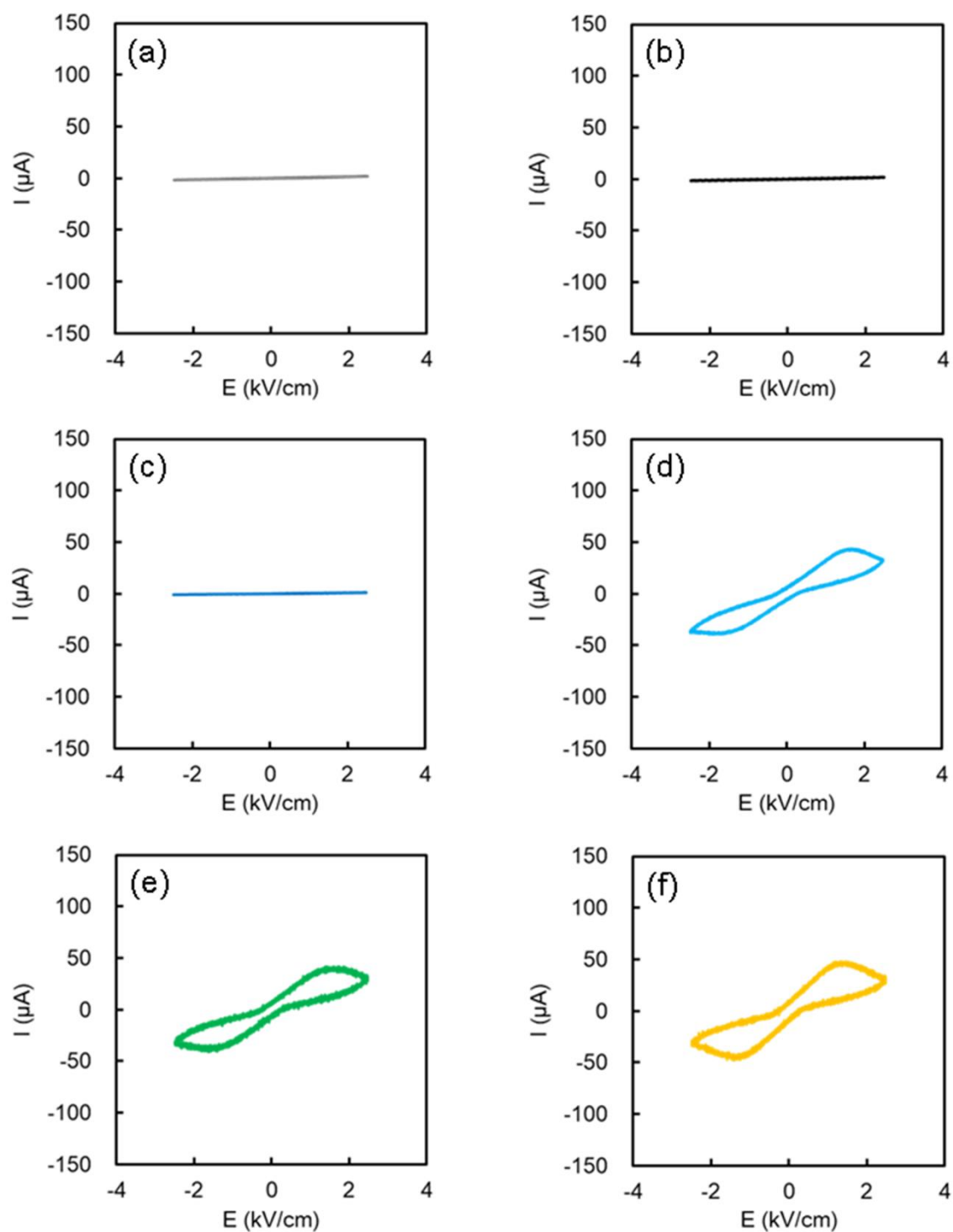


Figure 5-2-3-6. The temperature dependence of I - E loops of $p\text{NA}$ ($101\ \mu\text{mol}$)@PI-300 recorded at $2.5\ \text{kV/cm}$, $1\ \text{Hz}$. Data are the average of 50 cycles of measurements. (a) $298\ \text{K}$. (b) $303\ \text{K}$. (c) $313\ \text{K}$. (d) $323\ \text{K}$. (e) $333\ \text{K}$. (f) $343\ \text{K}$.

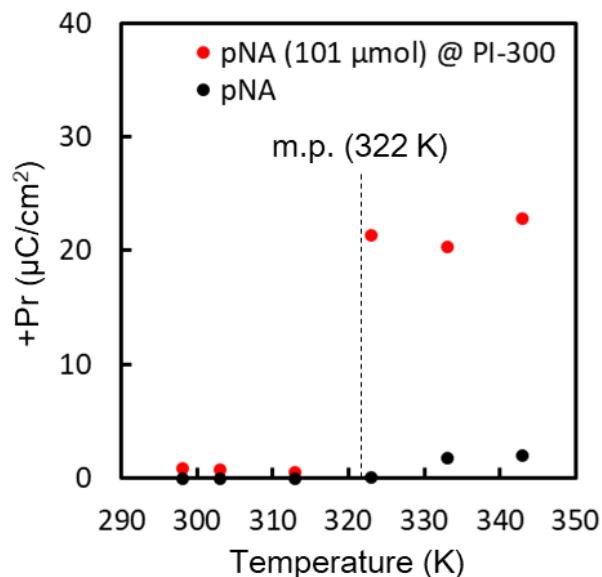


Figure 5-2-3-7. Temperature dependence of the remnant polarizations ($+P_r$) revealed by *pNA* and *pNA* (101 μmol)@PI-300 film. The P - E and I - E data displayed are the averages of 50 cycles of measurements (ca. 3 min/50 cycles).

Meanwhile, interestingly, the *pNA*@PI-300 film showed a considerably enhanced polarization and a P - E hysteresis with P_r of ca. 23 $\mu\text{C}/\text{cm}^2$ and E_c of ca. ± 1.7 kV/cm at 343 K (Figure 5-2-3-2a). This is ascribed to *pNA* molecules confined in the pores of the PI-300 film, as the host PI-300 film (without *pNA*) shows no dielectric response under the same condition (Figure 5-2-3-4a,b). It is to note that the *pNA*@PI-300 film exhibited peaks in the current-electric field (I - E) loop around at ± 1.5 kV/cm (Figure 5-2-3-2b and Figure 5-2-3-4b) with positions close to the coercive fields (Figure 5-2-3-4a). These peaks are reasonably assignable to the inversion current that reflects the polarization inversion of *pNA* molecules confined in the submicron-sized pores.²³ It indicates the dynamic molecular orientational changes of *pNA* in response to the applied AC voltages, as further supported by the temperature dependence of the P - E and I - E curves shown in Figure 5-2-3-5 and Figure 5-2-3-6, respectively. The hysteresis in P - E loop and inversion currents in I - E curves are observed for the *pNA*@PI-300 film above 323 K, a temperature around the melting point of *pNA* in the pores, while no dielectric response was observed below 313 K. As can be seen from the temperature dependence of $+P_r$ value (Figure 5-2-3-7), a sharp increase is observed by heating to 323 K while the dielectric response is totally suppressed in the crystalline *pNA* molecules confined in the pores. Thus, the mobility of *pNA* is essential for the observed polar switching.

We note that the strength of P_r observed for the *p*NA-doped film is more than an order of magnitude larger than that revealed by liquid *p*NA alone and those of the typical literature values reported for ferroelectric smectic and columnar liquid crystalline phases (50–500 nC/cm²).^{24–26} Apparently, the confinement of *p*NA molecules in pores promoted the electric-field directed macroscopic alignment which leads to the significant hysteresis in the P - E loops. We confirmed that the use of dipolar molecules is essential for the observed unique dielectric properties, as a PI-300 film loaded with non-polar naphthalene molecules showed no dielectric response even above the melting temperature (Figure 5-2-3-8).

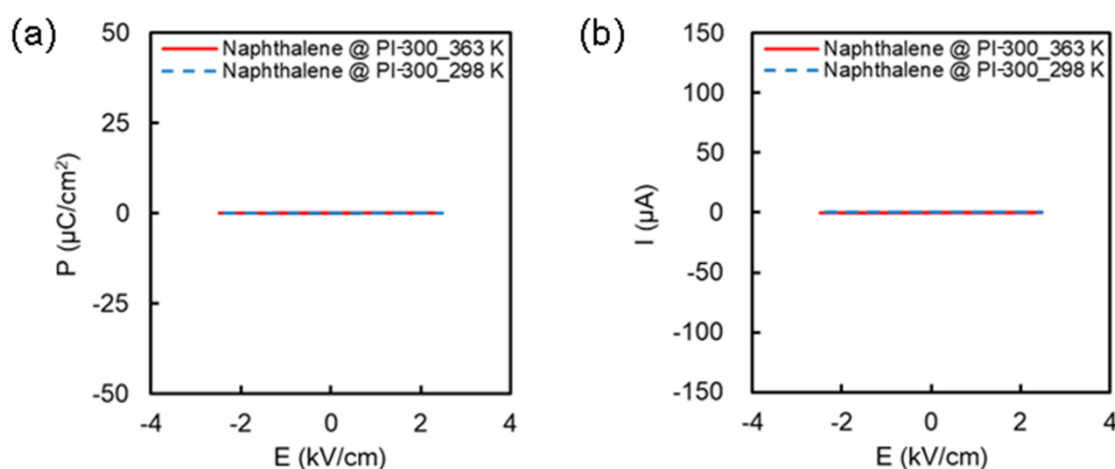


Figure 5-2-3-8. (a) The P - E and (b) I - E loops of naphthalene (101 μmol)@PI-300 recorded at 2.5 kV/cm, 1 Hz, 298 or 363 K (Melting point of naphthalene: 353 K). Data are the average of 50 cycles of measurements.

The motional frequency of the inversion of *p*NA dipole confined in the pores is relatively slow, as can be seen from the dependence of P_r value and the P - E loops on the measurement frequency in the range of 1-1000 Hz (Figure 5-2-3-9). While the P - E hysteresis loop with the inversion current is observed at the low frequency of 1 Hz, the dielectric polarization decreased at higher frequencies and disappeared at a higher frequency of 1000 Hz. The low frequency for the inversion of *p*NA dipoles would reflect the collective response of structurally ordered dipolar molecules in the viscous liquid state. The E_c value was also dependent on the applied voltage, as can be seen from Figure 5-2-3-10. Larger remnant polarization and clearer dielectric hysteresis were observed when the higher AC voltages were applied to the sample. Meanwhile, the P - E loop observed in Figure 5-2-3-2a and Figure

5-2-3-5 shows convex regions that are typical for the lossy dielectric materials exhibiting conductance,^{27,28} which are reflected in the leak current (LC) component as discussed later.

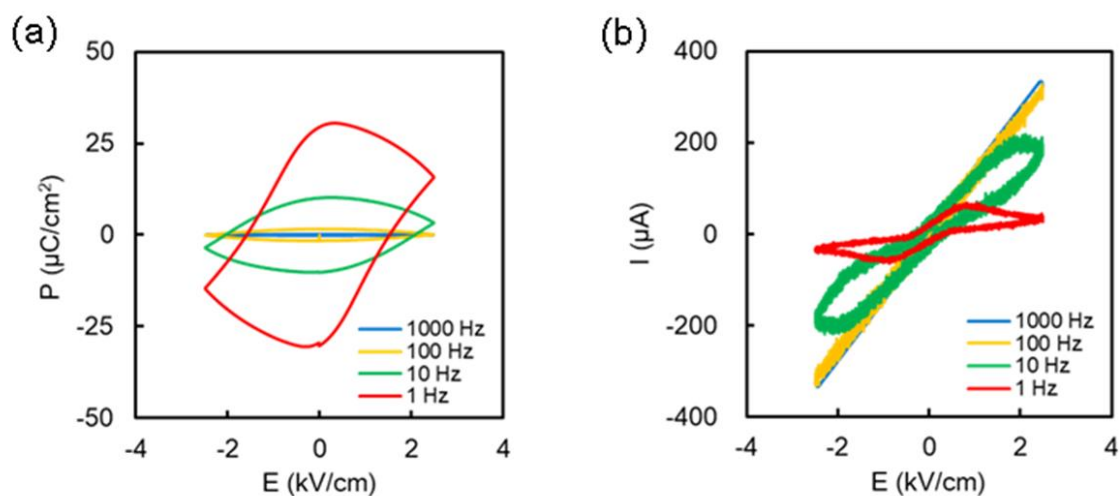


Figure 5-2-3-9. The (a) *P-E* and (b) *I-E* loops of *p*NA (101 μmol)@PI-300 recorded at 2.5 kV/cm, 1-1000 Hz, respectively, 343 K. Data are the average of 50 cycles of measurements.

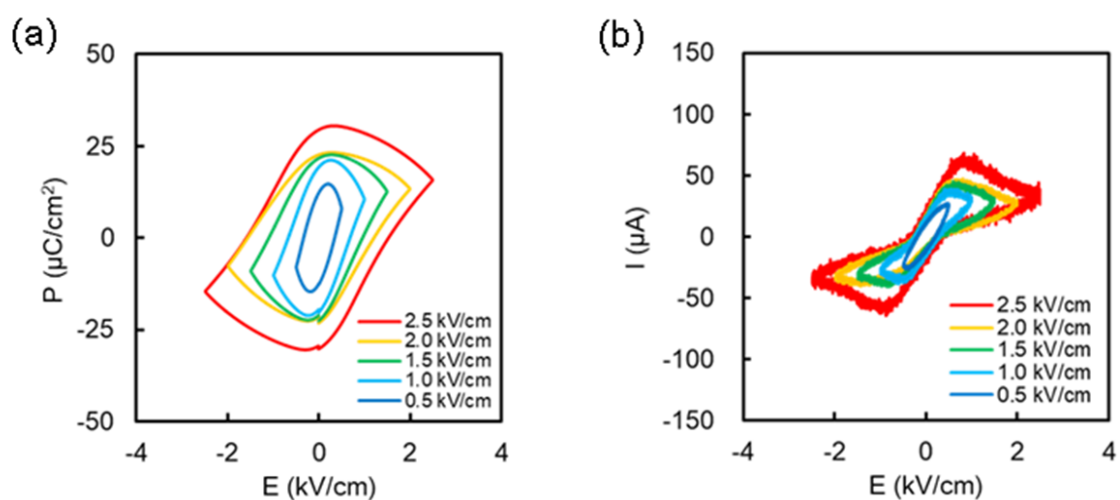


Figure 5-2-3-10. The (a) *P-E* loops and (b) *I-E* loops of *p*NA (101 μmol)@PI-300 recorded at 0.5-2.5 kV/cm, 1 Hz, 343 K. Data are the average of 50 cycles of measurements.

The interface between *p*NA and the submicron-to-micron-sized pore surfaces plays a critical role in the enhanced dipolar polarization. As shown in Figure 5-2-3-11, the remnant polarization ($+P_r$) obtained for *p*NA@PI-300 films showed an almost linear increase up to the loading amount of ca. 100 μmol , beyond that a tendency of saturation was observed at a higher loading amount of ca. 150 μmol . A similar trend was also observed for *p*NA@PI-2500 films, however, the $+P_r$ values are considerably larger for *p*NA@PI-300 films as compared to those of *p*NA@PI-2500 films. The smaller volume of each spherical pore i.e., the larger total surface area in the films increases the fraction of *p*NA molecules that are affected by the interface. Consequently, the enhanced dipolar polarization and hysteresis became more prominent for the *p*NA@PI-300 films, which is a feature consistent with the confinement effect. Thus, the PI films with pore diameters of 300 nm and 2,500 nm show distinct features which cannot be assigned to the same “macropore” category.

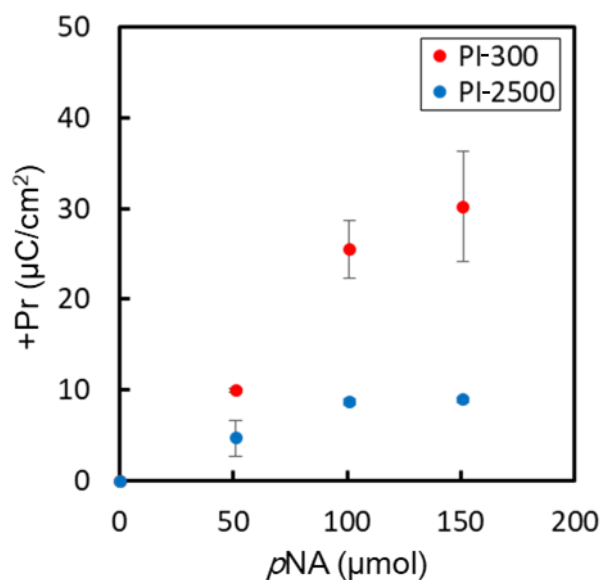


Figure 5-2-3-11. The dependence of remnant polarization ($+P_r$) observed for *p*NA@PI-300 or *p*NA@PI-2500 at the varied amount of *p*NA loaded. Ac voltage at 2.5 kV/cm, 1 Hz, 343 K.

To better understand the dipolar polarization of the present *pNA*-confined polymer systems, PUND measurements^{29,30} were conducted for pristine *pNA* (Figure 5-2-3-12), PI-300 film (without *pNA*, Figure 5-2-3-13) and for *pNA*@ PI-300 film (Figure 5-2-3-14). A pulse train with an amplitude of 2.5 kV/cm and a width of 0.1 s was applied (Figure 5-2-3-12c). In every PUND experiment, initially, a negative poling pulse was applied to the sample, and then a sequence of two positive and two negative voltage pulses followed. The resulting electric displacement responses were analyzed by fitting to the ferroelectric component (FC), paraelectric component (PC), and leakage current component (LC), respectively. The magnitudes of FC, PC, and LC obtained by the analyses of PUND pulse responses are summarized in Table 5-2-1.

The pristine PI-300 film did not show *P-E* and *I-E* response (Figure 5-2-3-4), and naturally, no PUND response was obtained. The pure *pNA* showed PC (1.24 $\mu\text{C}/\text{cm}^2$) and LC (6.38 $\mu\text{C}/\text{cm}^2$) components, as expected from the *P-E* curve observed in Figure 5-2-3-3. As can be seen from Figure 5-2-3-12a,b, the dielectric polarization generated after the pulse show decay within a second and it explains the observation of PC component. The LC component would be due to the conductance of inexplicable origin.

Interestingly, *pNA*@PI-300 film showed an FC component of 8.06 $\mu\text{C}/\text{cm}^2$ in addition to the PC (7.94 $\mu\text{C}/\text{cm}^2$) and LC components, which is consistent with the salient enhancement in the dielectric polarization and the hysteresis in *P-E* loops (Figure 5-2-3-2a). However, the dipolar polarization showed a finite lifetime also in this case and it relaxed within a second as depicted in Figure 5-2-3-14a,b. It indicates that the oriented *pNA* molecules show relaxation after releasing the external electric field. Thus, the observed hysteresis in the *P-E* loops of *pNA*@PI-300 film (Figure 5-2-3-2a and Figure 5-2-3-5) are not ascribed to ferroelectricity by definition and rather viewed as a consequence of polar switching phenomena.³¹ We consider that the FC component observed in the PUND measurement would reflect the presence of *pNA* molecules strongly interacting with the surface of nano-to-mesopores in PI-300 films. Thus the FC component is regarded as a performance index that reveals the confinement effect of *pNA* molecules in the submicron-sized porous PI films. As already discussed, the orientational and translational dynamics of confined liquid *pNA* molecules tend to be restricted, and the dipolar *pNA* molecules physisorbed at the interface would show long-ranged interactions and structuring on the pore surface presumably mediated by the dipole-dipole interactions. The presence of such interactions has been demonstrated by the significantly affected thermal phase transition characteristics (Figure 5-2-2). The enhanced dipolar polarization and the polar switching of bound *pNA* clusters thus occur in response to the applied external electric field, as a result of the collective dielectric response of *pNA* molecules confined in the submicron-sized pores.

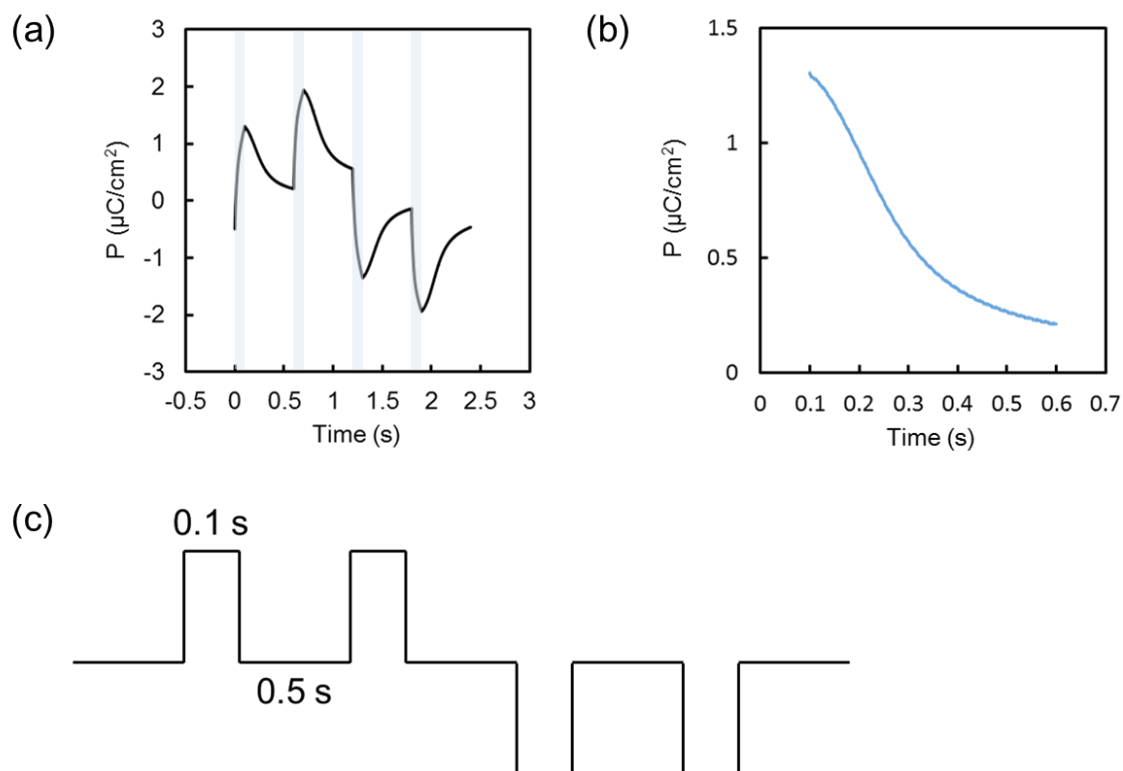


Figure 5-2-3-12. (a) PUND responses observed for pristine *p*NA. The applied sequence of voltage pulses is shown in (c). Applied voltage, 2.5 kV/cm. Temperature at 343 K. (b) The polarization decay after the first voltage pulse in (a). (c) Pulse voltage profile for the PUND measurement. The period of applied voltage and interval time are 0.1 s and 0.5 s, respectively.

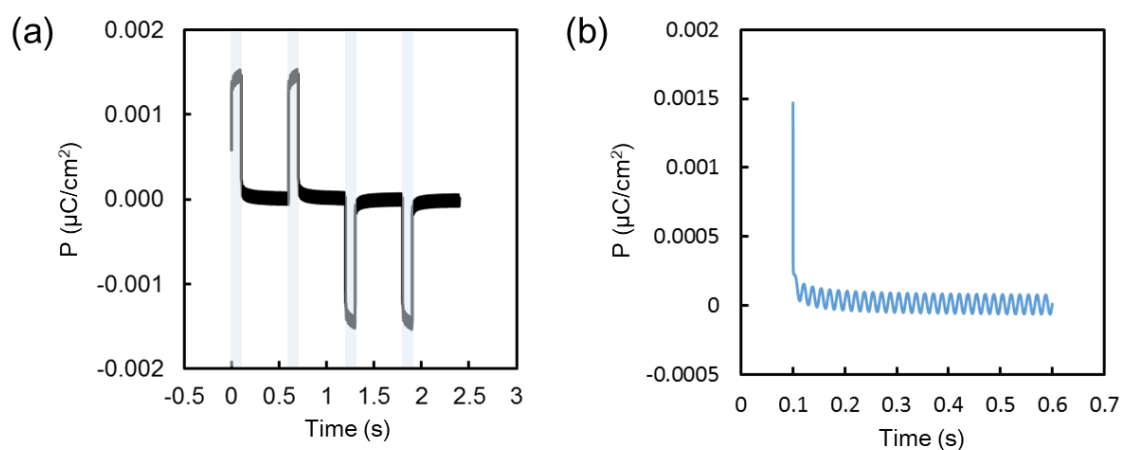


Figure 5-2-3-13. (a) PUND responses observed for pristine PI-300 film (without *pNA*). Applied voltage, 2.5 kV/cm. Temperature at 343 K. The applied sequence of voltage pulses is shown in Figure S13c. (b) The polarization decay after the first voltage pulse in (a).

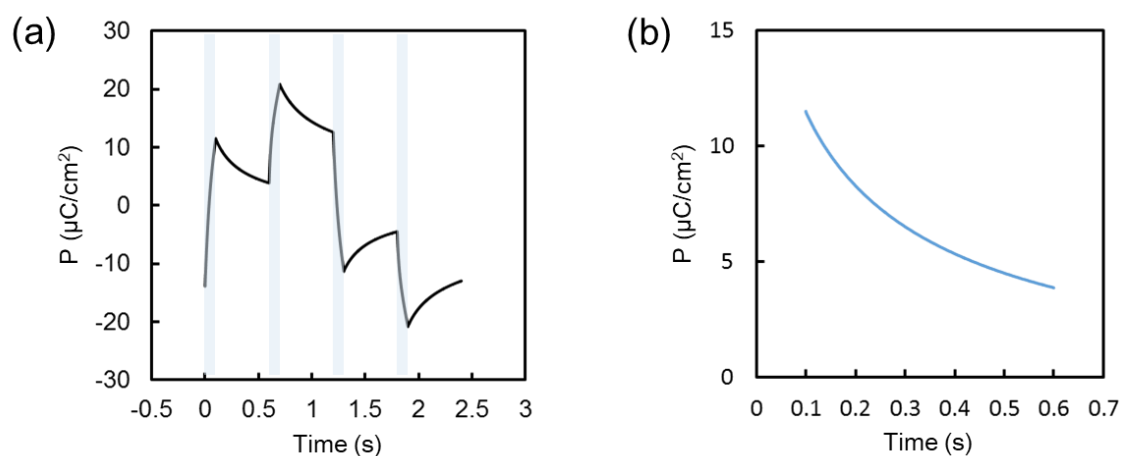


Figure 5-2-3-14. (a) PUND responses observed for *pNA* (101 μmol)@PI-300 film. Applied voltage, 2.5 kV/cm. Temperature at 343 K. The applied sequence of voltage pulses is shown in Figure S13c. (b) The polarization decay after the first voltage pulse in (a).

Table 5-2-1. The magnitude of the ferroelectric (FC), paraelectric (PC), and leakage current (LC) components obtained by analysis of PUND responses. Temperature, 343 K.

	FC ($\mu\text{C}/\text{cm}^2$)	PC ($\mu\text{C}/\text{cm}^2$)	LC ($\mu\text{A}/\text{cm}^2$)
PI-300	0.00	0.00	0.00
<i>p</i> NA	0.00	1.24	6.38
<i>p</i> NA (101 μmol)@PI-300	8.06	7.94	84.61

5-2-4 Conclusion

In conclusion, significantly enhanced dipolar polarization and polar switching was observed for liquid *p*NA confined in the submicron-to-micron sized pores in PI films. *p*NA molecules interacting with the polymer interface would form polarized layers under the applied AC voltage, which show the collective dipolar polarization and polar switching phenomena. The present findings indicate that polar liquids have the potential to exhibit unique dielectric characteristics when confined in the submicron-to-micron sized porous space. The large internal surface areas provided by these porous polymer films provide opportunities to confine functional organic liquid molecules as clusters or domains, which would allow us to deliver the full potential of confined liquids in easy-to-use film form. We envisage the introduction of photo-switchable molecular solar thermal fuels^{32,33} and photon upconversion liquids^{34–36} to these porous polymer films may lead to multi-functional materials with unique dielectric properties.

5-3 Sample preparation

1. Sample preparation and DSC measurements.

Porous polymer films are provided from Tokyo Ohka Kogyo Co. Ltd. They contain spherical pores with diameters around 300 nm (abbreviated as PI-300) or 2500 nm (abbreviated as PI-2500). The film has open pores in high density and they are interconnected to form continuous channels in the film (Figure 5-2-1-1). *p*NA was purified by repeated recrystallization from distilled methanol. Methanol solutions of *p*NA (concentration, 1.27 M) were dropped on the surface of porous films horizontally suspended in the air. The solutions spread on and into the films gradually and the resultant composites were dried at room temperature. The composite films were then heated to 363 K (above the melting point of *p*NA) for few seconds to effectively fill the pores with *p*NA and were then cooled down to room temperature. DSC measurements were conducted with METTER TOLEDO, DSC 1 STARe System. The DSC isotherms were recorded at a scan speed of 1 K/min.

2. Dielectric measurements.

To attach thin gold foils as electrodes on both sides of the film, gold foils were attached to the surface of films, followed by heating to 363 K for a few seconds and the specimens were cooled to room temperature. This heating and cooling process ensured the contact of gold foils to the composite polymer films. Gold nanowires (Nilaco Corporation, Diameter: 0.15 mm) were then attached to the gold foils by using adhesive Kapton tapes (Figure 5-2-3-1).

Dielectric measurement was also conducted for pristine *p*NA as a reference. We employed liquid crystal (LC) cells coated with ITO electrodes (area, 5 x 5 mm², cell gap of 20 μm, no-polyimide coating, E.H.C. Co. Ltd.). Crystals of *p*NA were placed near the aperture of LC cells and the whole cell samples were heated up to 363 K on a hot plate, at which temperature *p*NA liquefied and slowly transferred into the cells. Once the ITO working area of the cell was completely filled with *p*NA, the sample was cooled down to room temperature. *p*NA remained on the surface of LC cells were wiped away by using KimWipes. The dielectric measurements were undertaken on a Toyo Corporation ferroelectric-evaluation standard system (FCE-1) connecting to a Toyo6252 Rev. C current/charge–voltage converter, a Biomation2414B arbitrary waveform generator, a WaveBook 516E analog-to-digital converter and Linkam Hotstage 10084L (JAPAN HIGH TECH). All *P-E* and *I-E* loops were recorded with a triangular wave field. The accuracy of the polarization value was confirmed by the measurement of 20/80 lead zirconate titanate (PZT, TOSHIMA Manufacturing Co., Ltd., Area: 0.0001 cm², Thickness: 0.26 μm, Voltage: 4 V, Frequency: 100 Hz, Temperature: 298 K, +*P_r*: ca. 25 μC/cm² (ref. 28 μC/cm²)) as a reference sample.

5-4 Reference

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Chapter 6 Conclusions

In this dissertation, novel properties of the soft materials developed through the utilization of noncovalent, intermolecular interactions within the materials were described.

We focused on hydrogels based on coordinated structures in Chapter 2. Mixing ZnMPT2Cl with DABCO in the water medium gave hydrogel through the formation of a coordinated structure. Potentially, the self-assembled structure consisting of the metal complex is cationic. Therefore, the addition of multivalent anions, such as Na₂SO₄, crosslinked the cationic coordination structures and the bundled structures resulted in the formation of nanoribbons from nanofibers and the enhancement of the stiffness of the hydrogel. In addition, the diffusion behaviors of cationic and anionic species were quite different upon the interfacial interactions. Combining the interfacial interactions and the pH responsivity of the coordinated structure attributed to the protonation of DABCO gave us the possibility that the hydrogel could be utilized for novel pH-responsive drug carriers.

Based on the molecular design, interfacial interactions on the self-assembled structure can be tuned through the exchange of counter anion, which could control the pH responsivity of the hydrogels. Moreover, alkene functional groups can be introduced to the phenanthroline moiety, which could then be utilized for post-modification or polymerization of the zinc(II) complexes. Gong *et al.* have found that hydrogels based on double networks consisting of rigid and flexible independent networks exhibited exceptional tough mechanical properties.^{1,2,3} The enhanced toughness derived from the fracture of fragile networks, which led to the relaxation of external strains. Basically, coordination bonds are ruptured more easily than covalent bonds because of the association-dissociation property. Therefore, it is expected that utilizing alkene of the new zinc(II) complexes would realize novel double network hydrogel including covalent and coordination bonds and hydrogel would have the potential to be quite tough against external strain. Moreover, following this dissertation, interactions between the self-assembled structures could be tuned by adding multivalent anionic species.

In Chapter 3, the strategy to utilize trapped dipolar aromatic solvents in the organogels for unique dielectric properties as bulk was described. Adding gelator **1** into nitrobenzene as aromatic dipolar solvent gave organogel and the dense nanofibrous network was observed through SEM, TEM, and AFM. The organogel exhibited a polar switching phenomenon by applying AC voltage, though nitrobenzene itself showed very weak polarization. Dielectric measurements at different temperatures and those for gels prepared with several other dipolar and nonpolar solvents' gel

suggested that dipolar solvents trapped in the gel played an important role in the unique dielectric properties.

In Chapter 4, to confirm the generality of the polar switching phenomena utilizing organogels, in Chapter 3, we reported a phase transition of gels formed from the self-assembly of low-molecular-weight gelators in *p*NA, a molecule with a large permanent dipole. *p*NA is solid at room temperature, and the mixture of the gelator and *p*NA revealed a multiple phase transition between the solid dispersion, organogel, and the sol phase depending on temperature. An eminent enhancement of dipolar polarization and polar switching phenomena were observed for the gel phase which was not available in the solid dispersion phase at ambient temperature. The organogel induced by the phase transition from the solid state exhibited a polar switching phenomenon by applying an electric field, though the solid dispersion did not show the polarization. It was concluded that the polarization switching behavior occurred when dipolar molecules and nanofibers showed considerable interactions. The liquid *p*NA molecules in the gel phase had long-range interactions with the self-assembled gel network of the gelator probably mediated by the dipole-dipole interactions. The presence of liquid domain structures under the influence of dipole-dipole interactions was indicated by the altered freezing point in the organogel.

However, these systems in Chapter 3, 4 show low processability due to the softness of the gel materials. For more practical usage, the stability and flexibility of the materials are necessary. In Chapter 5, therefore, we focused on porous polyimide films as an absorbent for dipolar aromatic molecules because of their large surface area, stability, and flexibility. Above the melting point of *p*NA as dipolar guest molecules, the composite films showed a dielectric hysteresis loop. The polarization values depended on the total surface areas of porous polyimide films, which suggested that the inner surface of the pores was important for combining the domain of *p*NA. This study gave a novel concept for the fabrication of flexible memory or sensor materials in the future.

Following chapters 3, 4 and 5, it can be hypothesized that dipolar aromatic molecules could be oriented on the surface of materials when the surface is modified appropriately. Self-assembled monolayers (SAMs) are one of the promising materials, which can create homogeneous, tunable and large-scale surfaces.^{4,5} Utilizing SAMs with different functional groups would give us a sight of interfacial interactions between the dipolar aromatic molecules and the molecules on the modified surfaces.

In this dissertation, interfacial interactions in soft materials have been focused and utilized for the bulk properties. Potentially, extremely large interfaces can be created in soft materials, such as gels. As described in previous chapters, not only introducing materials, such as metal nanosheets

or clay but also self-assembly of molecules can create large and unique interfaces. In terms of self-assembled structures, molecular design can be easily modulated, which can induce changes in the morphological or chemical properties of interfaces. Taking advantage of molecular self-assembly with the flexibility of selecting solvent molecules would give us novel concepts of reconfigurable and more functional soft materials.

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