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Molecular Gel as Medium or Intermediate in Functional Materials Synthesis

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1.1 Introduction

Since the 1990s, substantive development has been achieved in research related to molecular gels [1, 2]. Thousands of molecular gelators have been reported [2]. Meanwhile, with rapid development in supramolecular chemistry and nanoscience, in-depth understanding has been gained and many new research branches have emerged [3, 4]. By combining research results and theoretical calculations, theories in molecular gel study have been built. Preparation of molecular gel has also been gradually changed from the accidental discovery stage to the aimed designed stage. A typical characteristic of research on molecular gels is the interdisciplinary feature. Generally, research on molecular gels includes knowledge related to soft matter, self-assembly, rheology, thermodynamics, chemical synthesis, theoretical calculation, simulation, etc. Macroscopically, molecular gels are solid-like. Microscopically, molecular gels are made up of non-covalent interaction-based network structures consisting of a small quantity of molecular gelators and abundance of solvents [5]. The solvent molecules are trapped in the network structure via capillarity, surface tension, and other immobilization forces. Thus, molecular gels possess typical microheterogeneous structure. Different from chemical gels and polymer gels, non-covalent bonding-based network endows molecular gels prominent thermal reversibility, shear thixotropy, and stimulus response [6, 7]. These properties lay solid foundation for further application of the molecular gels. However, pronounced application of molecular gel has not been realized.

Stability is an important factor that affects the practical applications of molecular gels [8]. This is because, the formation and existence of a molecular gel is based on an equilibrium of dissolve-aggregation, which is based on a variety of non-covalent interactions [7]. The equilibrium may be broken by any tiny external disturbance, causing melting of phase transition in the molecular gel. In order to get stable molecular gels, it is necessary to strengthen the factors that are helpful to maintain the dissolve-aggregation balance. For example, high-boiling point liquids are used to

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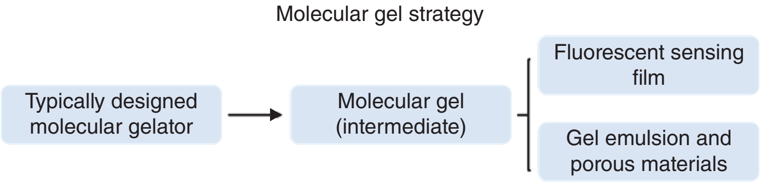
prevent gel-sol phase transitions caused by solvent volatilization [9]. Thermal insulation and vibration reduction are realized through packaging, so as to overcome the gel damage caused by vibration and heat. In fact, it is in this way that the intelligent propellant based on molecular gel is prepared.

Another way to promote the practical application of molecular gels is to use them as an intermediate to construct special materials with special structures and excellent properties, where the application of molecular gels will be highlighted [10, 11]. Based on this consideration, efforts have been devoted to the study of molecular gels as intermediates in functional materials fabrication (Scheme 1.1), such as in fluorescent sensing film, gel emulsions, and low-density porous materials. With molecular gel strategy, a series of materials with favorable performance have been obtained. In this chapter, the application of molecular gel strategy in the preparation of fluorescence sensing thin film materials and low-density porous materials is described in combination with laboratory practice. On this basis, the main challenges of related research are proposed, and the prospect and development trend of molecular gel expansion research are prospected.



Scheme 1.1 Molecular gel strategy in fabrication of fluorescent sensing film and gel emulsion as well as porous materials.

1.2 Molecular Gel as Intermediate in Synthesizing Fluorescent Sensing Films with High Performance

Compared with homogenous chemical sensing, film-based chemical sensing owns advantages in little influence on the detection system, favorable reusability, and easy to be integrated into device. [12, 13] Among chemical sensors, fluorescent sensors have received considerable attention, because of their merits in regard to high sensitivity, multiple parameters, little consumption of reagent, as well as no reference, or even remote monitoring [14, 15]. For a film-based sensor device, fluorescent film with desired sensing performance plays a pivotal role. Thus, exploring fluorescent film with desired sensing ability will lay a solid foundation in the development of high-performance sensors. Generally, sensing performance of a fluorescent film can be evaluated by sensitivity, selectivity, response time, reversibility, reusability, and stability. Sensing behavior of a fluorescent film is not only dependent on constitution of the film, but also on microstructure of the film [12, 16]. Accordingly, rationally designed fluorescent sensing unit and suitable film fabrication strategy should be two key issues in fluorescent sensing film fabrication. A desired sensing film would show characteristics in abundance of effective sensing units, which reacts to the analyte to cause a change in fluorescence signal [17].

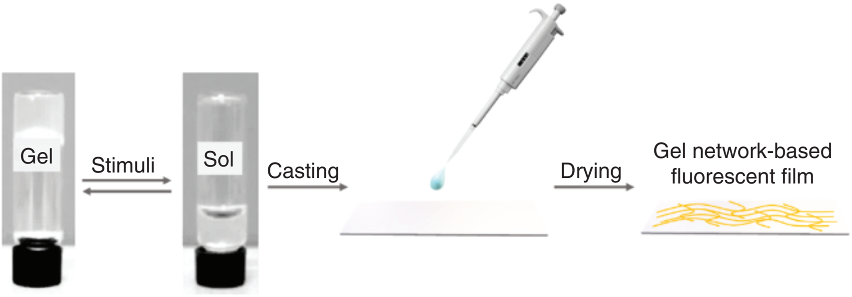


Figure 1.1 Illustration of the molecular gel for fluorescent film fabrication.

As known, solvent is the main component (more than 90%) in a molecular gel and the self-assembled supramolecular gel network accounts for only ~2%. Thus, the corresponding xerogel obtained from removing the solvent possesses features of porous network structure, which is beneficial for fluorescent sensing because of the permeability at the molecular level. Preferable permeability will lay a foundation for fast and effective interaction between the analyte and the sensing units and, therefore, result in improved sensing performance, such as fast response and high reversibility and sensitivity. In addition, shear thixotropy of some molecular gels would facilitate sensing film preparation, as they can be easily sprayed or spin coated onto the solid substrate to form porous films. Accordingly, molecular gel strategy has been developed to fabricate different types of fluorescent sensing films [17–19]. Details of the strategy are illustrated in Figure 1.1. In the strategy, fluorescent unit is introduced to the molecular design of a gelator and the achieved fluorescent molecular gels are used to construct sensing film with porous network microstructure. With the method, fluorescent films with favorable sensing performance for volatile organic compounds (VOCs), narcotics, and chemical agent have been realized and some of the sensing films have been made into devices for real-life applications.

1.2.1 Molecular Design

To make fluorescent sensing film with molecular gel strategy, structure of the molecular gelator is the basis; molecular design and synthesis play an important role. In general, there are two requirements that a molecular gelator needs to meet when it is to be used to prepare fluorescent sensing film via molecular gel strategy: (i) fluorescent unit that can respond to some typical analyte should be included and (ii) units with supramolecular binding sites should also be included to endow the molecule self-assembly ability (Scheme 1.2). Up to now, various types of fluorophores have been reported [20–22]. Based on their characteristics in molecular structures, different types of fluorophores have varied response to the analytes. For example, most of the perylene bisimide (PBI) derivatives are electron-deficient compounds and their fluorescence is easily quenched by some electron-rich compounds, such as amines and phenols. [23, 24] Fluorescence of some polycyclic aromatic hydrocarbon (PAH) derivatives shows typical difference between their monomer state and aggregated state [23]. After more than 20 years of development, abundance of gelator units have been reported, including cholesterol and its derivatives, alkanes, amino acids, and aromatic compounds. [1]. Rational combination of a fluorophore and the gelator units will enable the access of favorable fluorescent molecular gelator, which lay solid foundation for fluorescent sensing film fabrication.

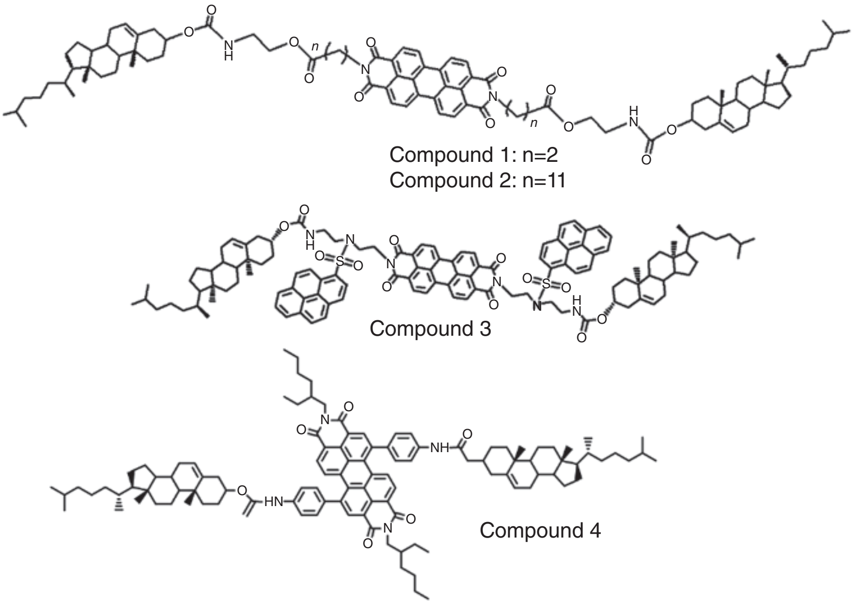
Scheme 1.2 Structure design for gelator molecules used for fluorescent film fabrication.

In Sections 1.2.2 and 1.2.3, fluorescent gelators with different molecular structures will be introduced. Based on systematic study of the self-assembly feature, gelation behavior as well as rheological properties of the gelators, fluorescent films will be obtained via techniques of drop casting or spray coating. When gelating solvent is removed, porous sensing films can be achieved. Meanwhile, porosity and microstructure of the film can be adjusted by varying the concentration of the gelator, gelating solvent, or the drying process. On that basis, the photophysical behavior and sensing performance of the films will evaluated. Furthermore, films with outstanding sensing performance will be selected to make sensor device. The molecular gel strategy will not only broaden the application of molecular gel, but also provide convenience for sensor development.

1.2.2 Molecular Gel Strategy-Based Sensing Film for VOC Vapor Detection

VOCs include a variety of chemicals, which are emitted as gases from certain solids or liquids [25, 26]. Most VOCs are toxic and some of them have short- or long-term adverse health effects, including irritation of eyes, nose, and throat, and damage to the liver, kidneys, and central nervous system. Sensors for VOCs detection would be of great help in reducing exposure risk.

Amines, especially organic amines, are recognized as important environmental pollutants and they pose a direct threat to humans [27, 28]. Meanwhile, active ingredients of some illegal chemicals are derivatives of organic amines [12]. Many PBI derivatives have shown excellent sensing performance, especially for organic amines, due to their electron-deficient nature. In addition, energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can be adjusted by varying the substituents (both the substitution type and position) [29–32]. In this way, charge transfer process between some PBI derivatives and typical amines can be tuned and sensing performance of the system can be optimized. Nevertheless, strong π–π interaction between the PBI molecules results in poor solubility of the PBI derivatives and may bring difficulties for their use through molecular gel strategy. For this reason, cholesterol groups have been involved to improve the solubility of the PBI molecules and also endow them supramolecular assembly ability.



Scheme 1.3 Molecular structures of compound 1, 2, 3, and 4.

A series of molecular systems (compounds 1~4) for organic amine sensing has been achieved by the combination of the two units (Scheme 1.3) [29–32]. The four compounds show varied assembly behavior in different solvents and it was found that sensing performance of the system was highly dependent on the assembled structure of the molecules. The molecular gel-based film was obviously superior to the film obtained by simple casting of the compounds. Sensing films obtained from molecular gel strategy show features of porous network structure: film 1 is made up of nanofibers of ~80 nm [29]; film 2 is characterized by stacking of nanoparticles of ~150 nm (Figure 1.2a) [30]; film 3 contains abundance of nanofibers of ~100 nm (Figure 1.2b) [31]; morphology of film 4 is similar to that of film 3 except for the smaller size of nanofibers [32]. The four films exhibited different sensing

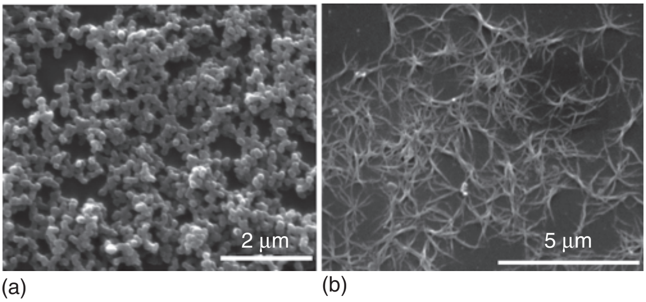


Figure 1.2 Self-assembled structures of compound 2(a) and 3(b). (a and b) SEM images of film 2 and 3 through the assembly of compound 2 and 3, respectively. Source: Adapted with permission from He et al. [31] and Shang et al. [32]. © 2016 Elsevier.

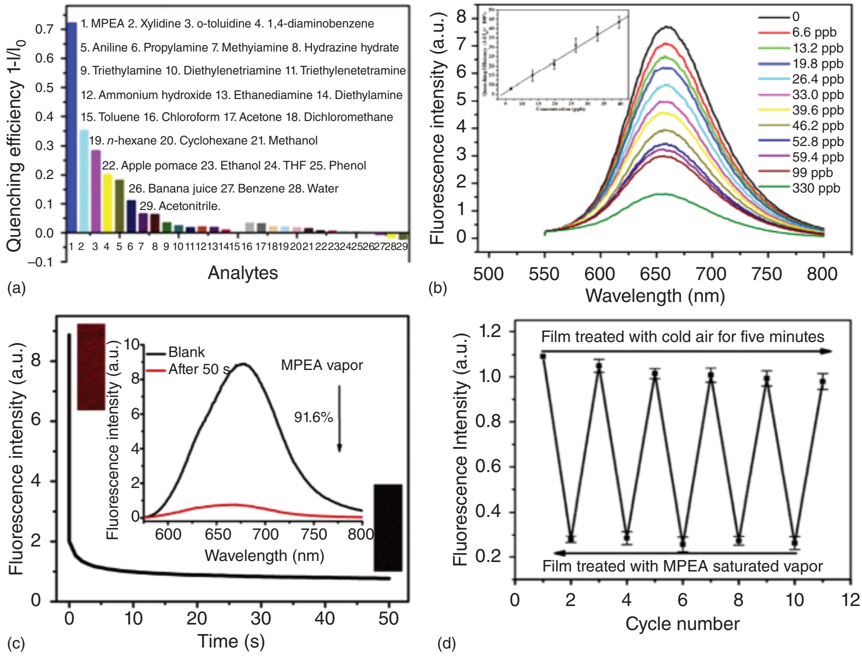
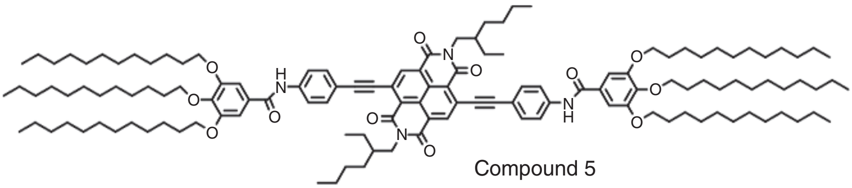


Figure 1.3 Sensing performance of some typical fluorescent films based on molecular gel strategy. (a) Fluorescence response of film 2 to a series of volatile compounds; (b) fluorescence response of film 3 to aniline; (c) fluorescence response of film 3 to *N*-methyl-phenethylamine (MEPA); (c) reversible sensing response of film 2 to MEPA vapor; inset shows the fluorescence images of the film before (up) and after (down) exposure to MEPA vapor; (d) reversible fluorescence response of film 2 to MEPA vapor. Source: He et al. [31] /Elsevier.

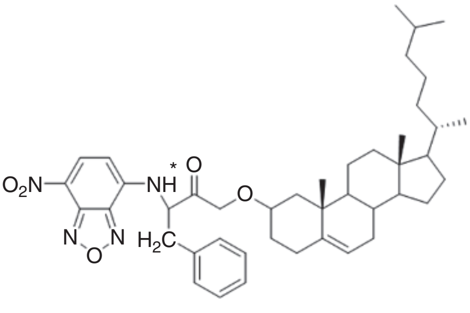
performance and showed favorable sensing performance (sensitivity, response time, and reversibility) in organic amine and its analogues, such as methylamphetamine detection (Figure 1.3). Fluorescence of film can be quenched by most commonly used amines tested with quenching efficiencies in the range of 60~80%. Sensing performance of film 2 is similar to that of film 1, but the quenching efficiencies are different (40~85%). Film 3 showed remarkable fluorescence response (~90% quenching efficiency) to methylamphetamine, an analogue of narcotics. Detection limit of film 3 to methylamphetamine is 5.5 ppb, which offers great opportunity for narcotics detection. Detection limit of film 4 to aniline vapor is 15 ppb and a film 4-based sensor device can be used to detect simulated exhaled (with aniline vapor) sample for lung cancer patients. The different sensing behaviors of the three films should be attributed to both varied molecular structure and self-assembled microstructure of the films.

Similar to PBI, naphthalimide (NID) is also an electron-deficient fluorophore. A long-chain alkane-modified NID derivative (compound 5, Scheme 1.4) has shown strong gelation ability, and several solvents (toluene, hexane, etc.) can be gelled using the NID gelator [33]. Xerogels from toluene and hexane have different morphologies and the corresponding films show different sensing performance. The film made up of uniform nanofibers was proved to be sufficient in aniline sensing with response less than 1 s and a detection limit of 12.7 mg m^{-3} ppm.



Scheme 1.4 Molecular structure of compound 5.

7-Nitrobenzofuranzan is a widely used bioimaging and bioanalysis agent, whose fluorescence is sensitive to environmental change. Using phenylalanine as the linker, a derivative of 7-nitrobenzofuranzan was connected with cholesterol and compound 6 was prepared (Scheme 1.5) [34]. Owing to the chirality of the phenylalanine (D/L) group, the isomers of compound 6 showed different gelation behaviors (Table 1.1). Systematic gelling behavior study revealed that the compound was an excellent molecular gelator and a fluorescent DMSO gel was got. The gel was sensitive to chemical stimulus: introduction of ammonia could break down the gel and further removal of the ammonia by bubbling of N_2 or air could result in the recovery of the gel. Meanwhile, the reversible sol-gel transition is accompanied by obvious fluorescence change: the DMSO gel is highly fluorescent, but the fluorescence is quenched when ammonia is introduced; the fluorescence can be recovered when the ammonia is removed. Therefore, sensing film for ammonia can be easily obtained by spray coating or high-speed coating. Microstructure as well sensing performance of the film can be optimized by changing the concentration of the compound. Under low gelator concentration, the film is characterized with loosely and randomly packed nanofibers, while the fibers become dense and uniform when concentration of the gelator is increased. With the sensing film as the key part, fluorescent sensor device for monitoring ammonia leakage was realized.



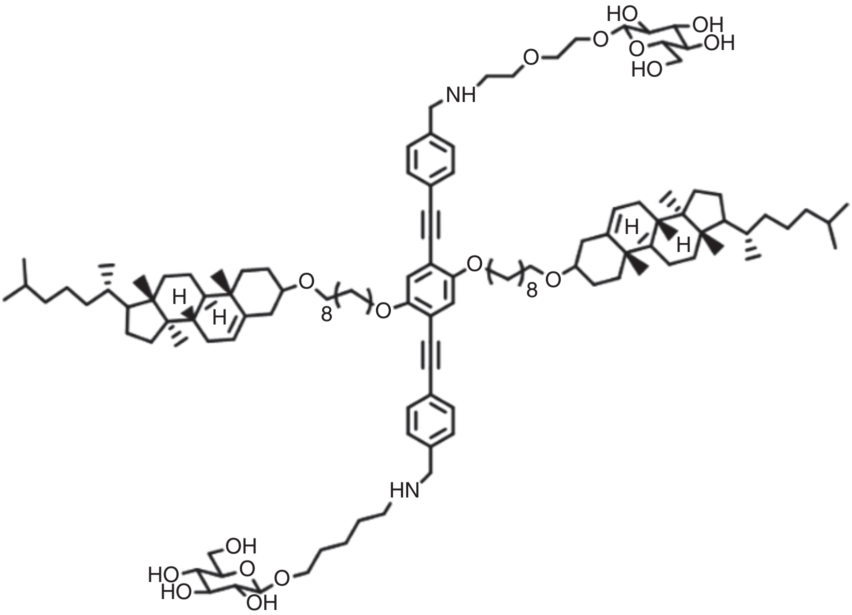
Scheme 1.5 Structure of the typically designed molecular gelator, compound 6. Source: Based on Yu et al. [34].

Table 1.1 Gelation behavior of compound 6 (2.5 wt%).

Solvent	C6-L	C6-D	Solvent	C6-L	C6-D
Methanol	I	S	*n*-Hexane	I	I
Ethanol	I	G	*n*-Heptane	I	I
n-Propanol	I	G	*n*-Octane	I	I
n-Butanol	I	G	*n*-Nonane	I	I
n-Pentanol	I	G	*n*-Decane	I	I
n-Hexanol	I	P	Cyclohexane	I	I
n-Heptanol	I	P	Acetonitrile	I	G
n-Octanol	I	P	Water	I	I
n-Nonanol	I	I	DMF	S	P
n-Decanol	I	I	DMSO	I	G
Acetone	S	P	Acetic acid	I	I
Benzene	S	S	Ethyl ether	I	I
Toluene	S	S	Ethyl acetate	S	S
THF	S	S	Dichloromethane	S	S
Pyridine	S	S	Trichloromethane	S	S

Note: I represents insoluble; S represents solution; P represents precipitate; G represents gel.

Hydrogen chloride is an extremely harmful corrosive gas, which easily causes irritation to eyes, skin, and respiratory system. Moreover, the existence of hydrogen chloride in near-earth space will lead to abnormal atmospheric processes or even affect the global environment. Thus, the detection of hydrogen chloride in gas state is of great importance. By the combination of 1,4-bis(substituted phenylacetylenyl) benzene, glucose, and cholesterol, a fluorescent molecule with typical assembly ability is constructed (compound 7, Scheme 1.6) [35]. The molecules exist in the aggregated form in chloroform, and fluorescent films consisting of numerous spherical particles can be obtained by transferring the aggregates onto a solid surface. Hydrophilicity as well morphologies of the film could be tuned by controlling the drying process. Quick drying produces hydrophobic film, but slow drying in humid air leads to hydrophilic film. The hydrophobic film is made up of particles of size 1∼3 μm; the hydrophilic film is characterized by vehicles of size ∼10 μm. Difference in film hydrophilicity and morphology causes remarkable difference in sensing performance (to hydrogen chloride vapor), which should be attributed to the interaction between the analyte and the film. Fluorescence of the hydrophilic film is sensitive to the presence of hydrogen chloride vapor with a detection limit of ∼0.4 ppb. But fluorescence of the hydrophobic film showed little change upon hydrogen chloride vapor exposure: high concentration of hydrogen chloride vapor (88 ppm or even 2860 ppm) could only cause 25% of fluorescence quenching.



Scheme 1.6 Molecular structure of compound 7. Source: Based on Sun et al. [35].

1.2.3 Molecular Gel Strategy-Based Film for Chemicals Sensing in Liquid Phase

Water pollution is one of the most challenging problems faced by humans. Methods that can be used for reliable, sensitive, and user-friendly detection of toxic chemicals in water are urgently demanded. With the advantages of molecular gel strategy in fluorescent sensing film fabrication, a series of fluorescent molecules with favorite self-assembly behavior have been synthesized [36–38], and corresponding fluorescent sensing film with typical self-assembled structure are prepared for the detection of toxic chemicals in water system. Some of the films can be used to detect toxic substances, such as nerve poison, pesticide, formaldehyde, in water. The detection is sensitive, selective, and the process can be realized either by spectroscopy, or by visualization.

1.3 Molecular Gel as Intermediate in Synthesizing Porous Materials

Because of their advantages at low density, high porosity, large surface area, and tunable pore size, porous materials are playing increasingly important roles in many fields, such as separation, catalysis, molecular recognition, bioengineering, and environmental science [39, 40]. A key point in porous materials preparation is to control the pores, including pore size, pore shape, and pore distribution. Commonly used methods for porous materials preparation includes gas foaming,

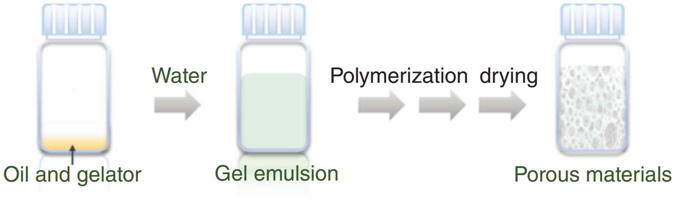


Figure 1.4 Illustration of a typical process for the preparation of molecular gelator-stabilized gel emulsions and the corresponding porous materials. Source: Based on Chen et al. [42].

porogen adding, or templating [41]. Among these methods, templating is preferred owing to its advantage in regard to facile control of pore size and distribution. Gel emulsion, also known as highly concentrated emulsion or high-internal phase ratio emulsion, is a typical template in porous materials preparation. Similar to a gel, gel emulsion is solid like, apparently. But in the microphase, a gel emulsion is totally different from a gel. There is more than one phase in a gel emulsion, usually called continuous phase and dispersed phase. Different from traditional emulsions, gel emulsions have several advantages when used as reaction intermediate. Coexistence of hydrophobic and hydrophilic domains enables good solubility of the gel emulsion system in both nonpolar and polar reactants. High viscosity of the system helps to avoid the precipitation of the product and provide basis for the formation of network structure. Water accounts for a large portion in W/O (water in oil) gel emulsion, which is benefit for the reduction of organic liquid for a consideration of both environmental protection and cost saving. The size and shape of the produced materials can be easily controlled by using a mold. Internal structure of the porous materials can be easily tuned by variation of the constitution of the gel emulsions (Figure 1.4) [42]. When used as reaction intermediate, gel emulsions can serve as both template and solvent, and they are widely used in the fabrication of low-density porous materials.

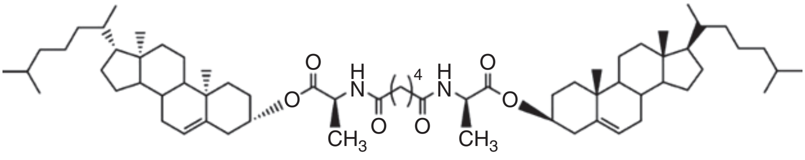
Formation of a gel emulsion is based on the stabilizer, which reduces the interfacial energy between the oil phase and the water phase [43]. Up to now, the widely used stabilizers include surfactants, micro- or nanoparticles (organic and inorganic), and molecular gelators. Usually, the stabilizer accounts for less than 3% (*w/v*) in a gel emulsion stabilized by molecular gelator, which is much lower than when surfactant is used as stabilizer. Compared with gel emulsion stabilized by micro- or nanoparticles, gel emulsions stabilized by molecular gelators possess better stability. In addition, undesired changes such as phase inversion and phase separation in particle-stabilized gel emulsions can be avoided in the molecular gelator-stabilized system. Moreover, content of the dispersed phase is not limited to a maximum of 74% in molecular gel-stabilized gel emulsion. Meanwhile, the ratio of the two phases (oil phase and water phase) in molecular gel-stabilized gel emulsion can be tuned in a wide range, which provides the basis for adjusting the internal structure of the porous materials. Low content of stabilizer is beneficial for cost saving and also for further purification of the obtained porous materials.

Based on the advantages of molecular gelator in gel emulsion stabilization, plenty of low-density porous materials have been synthesized. Details of the porous materials as well as their preliminary applications in adsorption, absorption, and environment treatment will be introduced in Sections 1.3.1 and 1.3.2.

1.3.1 Porous Materials for Removal of Oil on Water Surface

With rapid development in chemical engineering, there is increasing demand for petroleum extraction, refining, and applications. As a consequence, leakage of petroleum or the related products has become an emerging problem, which poses huge threats to ecology and human health [44, 45]. Sorption is an efficient way to reduce the risk of petroleum leakage, where sorbents with high performance are desired. It is of great significance to explore sorbents with high sorption capacity. Porous materials are widely used as sorbents. Sorption ability of porous materials is highly dependent on the constitution, internal structure, hydrophilicity, mechanical strength, as well as stability of the materials. Meanwhile, cost and the complexity of the fabrication process are important issues that need to be considered when the materials are put into application. With typically designed molecular gelator as stabilizer, a series of gel emulsions have been prepared. Polymerizable monomers, such as styrene and acrylic acid, are used as the continuous phase and water serves as the dispersed phase. Then, the gel emulsions undergo a polymerization and a subsequent drying process and thus porous materials can be achieved.

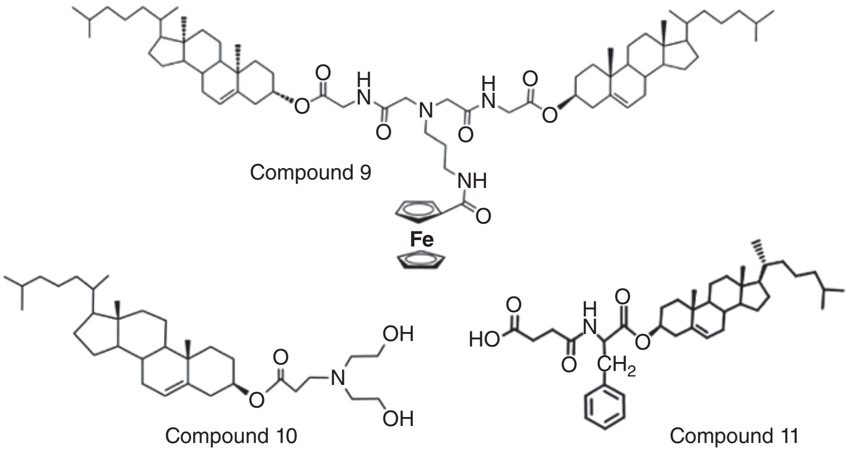
In 2009, Professor Fang's group reported the first molecular gelator-based gel emulsion stabilizer (compound 8, Scheme 1.7) [46]. The gelator contains two cholesterol groups and has a strong gelling ability. With the gelator, different types of oils can be gelated, including *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, kerosene, diesel, and gasoline. Based on the gels, a series of gel emulsions (W/O type) were made by introducing water into the gelling system. Microscopic studies and rheological measurement suggested that the gel emulsions are stable and have typical foaming structure. Gelators based on the combination of cholesterol and ferrocene have also been proven to be capable in the stabilization of gel emulsion. Some cholesterol-ferrocene gelated gels are responsive to multiple stimuli.



Compound 8

Scheme 1.7 Molecular structure of compound 8.

Molecular structures of some typical molecular gelators that can serve as stabilizers in gel emulsions formation are shown in Scheme 1.8. As an example, a series of gel emulsions of W/O type can be obtained when either of the gelators is used as a stabilizer and tert-butyl methacrylate is used as the continuous phase [47]. Polymeric porous materials with varied internal structure as well as mechanical properties can be achieved by polymerization of the different gel emulsions (Figure 1.5) [48]. The porous materials show high performance in absorption of organic liquids. Meanwhile, the absorbed solvents can be easily recovered by a squeezing process. In this way, the porous materials can be recycled and the absorption process can be repeated for more than 10 times. Except for optimization on the water content in the gel emulsion, properties as well absorption behavior of the porous material can also be enhanced by the introduction of some typical additives. For example, introducing some reactive silyl reagents is helpful to improve the mechanical strength and absorption capacity of the porous materials.


Compound 9

Compound 10

Compound 11

Scheme 1.8 Molecular structure of the gelators (compound 9–11) stabilizer used for gel emulsion and porous materials preparation.

Compound 10, which is a typical cholesterol gelator with two hydroxyl groups in the structure, can also serve as a stabilizer for W/O gel emulsions [49]. Using styrene as the continuous phase and water as the dispersed phase, a series of gel emulsions with outstanding stability can be prepared. After polymerization and drying, corresponding porous polystyrene materials were synthesized. Density of the materials can be adjusted by the variation of water content in the gel emulsions and polystyrene materials with ultralow density was presented. The preparation can be processed under mild conditions, where no complex or high energy cost drying process is needed. No high-cost post-treatment is needed as the water in the polymerized materials can be removed by squeezing and simple drying at 50 °C. The porous polystyrene materials can be used to remove some organic liquids from water. The materials can be recycled by subsequent squeeze, washing with ethanol, and drying steps (Figure 1.6) [50].

Another representative molecular gelator stabilizer contains a phenylalanine group as a linker, and a carboxyl group in a cholesterol derivative (compound 11) [51]. With the stabilizer, gel emulsion with tunable rheological properties can be

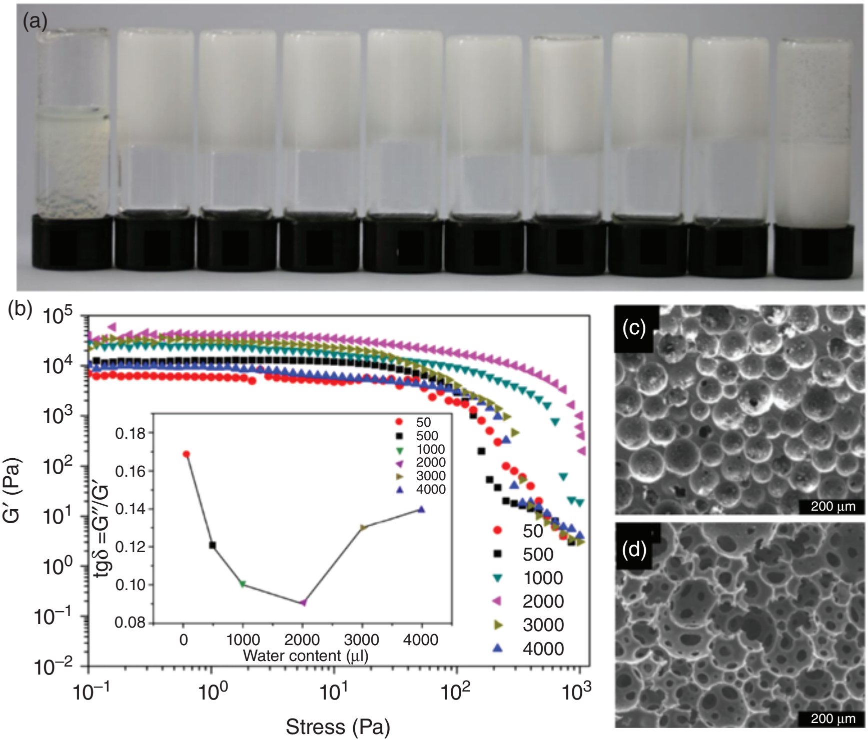


Figure 1.5 Typical gel emulsions and porous materials prepared by using molecular gelator as stabilizer. (a) Photos of the styrene gel. Photos of gel emulsion with different amounts of stabilizer. (b) Rheological behaviors of gel emulsions with different water contents. (c and d) SEM images of porous materials prepared from gel emulsions with different amounts of *n*-heptane as additives.

prepared. In addition, low-density porous materials with favorable mechanical strength and flexibility are obtained. The synthesized materials with a density of 0.18 g m^{-3} have good compressibility; the materials can be fully recovered with 70% compression and there is little change after compression (at 70% compression) for 25 times. The favorable mechanical strength lays a solid foundation for further applications of the materials.

1.3.2 Porous Materials for VOCs Adsorption

Efficient method for polluted air treatment is a great challenge, especially the removal of VOCs. Organic chemicals are not only widely used in chemical production, but also used as ingredients in household products, such as paints, detergents, disinfectors, and cosmetics. Removal of VOCs from polluted air has attracted tremendous attention around the world [52, 53]. Usually, concentrations of some VOCs are much higher indoors than outdoors, which may cause short- and long-term health effects. Among the methods for VOCs removal, adsorption is preferred because of its advantages in terms of low cost and high efficiency.

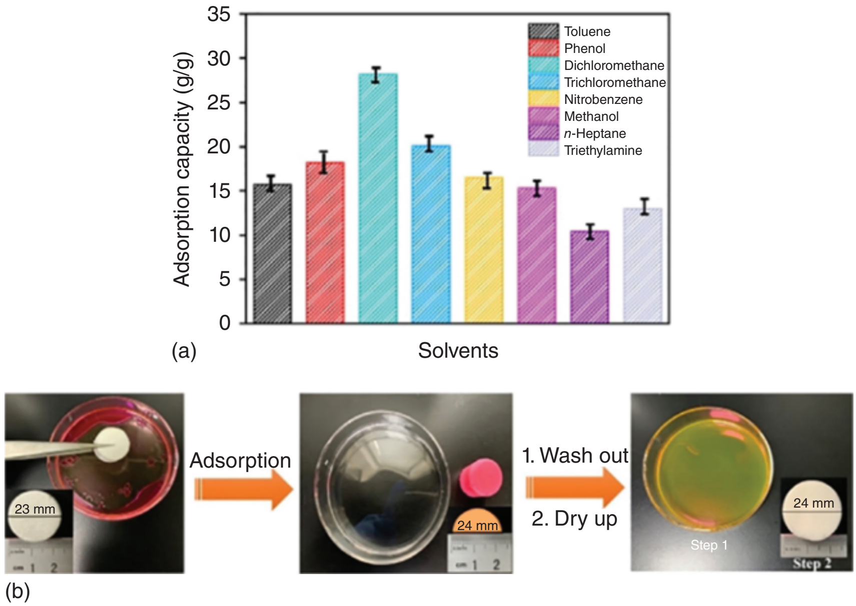
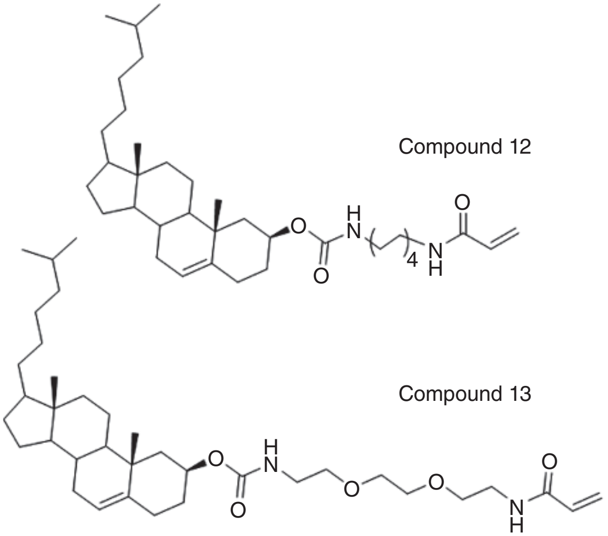


Figure 1.6 Typical application of gel emulsion-templated porous materials in organic solvent removal from water. (a) Maximum oil adsorption capacity of the porous materials. (b) shows the reusability of the materials. Source: Liu et al. [48]/Wiley.

To avoid the effect of unreacted stabilizer (molecular gelator) to the polymerized porous materials, several cholesterol derivatives with polymerizable bonds have been designed and synthesized (Scheme 1.9) [54, 55]. Using the gelators as stabilizers, a series of W/O gel emulsions (continuous phase: styrene; dispersed phase: water) have been prepared. Then, the gel emulsions were forced to undergo polymerization and drying. Accordingly, porous materials with different constitution and varied internal structures can be synthesized. Owing to the hydrophobic nature of the porous materials, they have the ability to adsorb VOCs (including benzene, toluene, ethyl benzene, and ethylene) and show higher adsorption capacity compared to the commonly used adsorbents, active carbon.

1.4 Summary and Perspectives

Physical gels, especially molecular gels made from low-molecular weight gelators and solvents are a combination of synthetic technology and supramolecular self-assembly. Different from chemical gels, gel networks of molecular gels rely on supramolecular interactions (including hydrogen bonding, π–π stacking, hydrophobic interactions, electrostatic interactions, dipole interactions) between gelator molecules, solvent molecules, and gelator-solvent molecules. The remarkable difference in structures makes the two type of gels (chemical gels and physical



Scheme 1.9 Structures of stabilizers with polymerizable bonds.

gels) show different response to external stimulus. For example, networks in both types of the gels can be broken under vigorous shearing, such as stirring, pumping, or shaking, which may result in phase separation or phase transition of the gel. It is hardly for the chemical gels to be recovered after the disruption, as the chemically bonded network is reversibly broken. But many molecular gels can be recovered when the shearing is removed. The preferable stimulus-responsive characteristics of molecular gels endow them great potential in applications of template synthesis, controlled release, tissue culturing, separation, information storage, sensing, etc. Moreover, the concentration of a gelator is usually very low in a molecular gel, which is a big advantage for further applications in molecular recognition, template synthesis, and synthetic intermediate. Introducing the molecular gel strategy to synthesize high-performance fluorescent sensing film and low-density porous materials shows some preliminary application of molecular gel in synthetic intermediate. It is expected that molecular gels will play more important roles in the research area of synthetic medium, which may include innovation in liquid–liquid extraction, cultivation of high-quality crystals, stabilization of solid–liquid suspension system extraction technology.

In addition, there are problems to be solved when molecular gel strategy is used in the synthesis of fluorescent sensing films and low-density porous materials. For example, adhesion of some fluorescent films obtained from molecular gel needs to be improved. Effect of molecular structure of the gelator stabilizer on the properties of the gel emulsions as well as the low-density porous materials needs to be given more attention. This will pave way for achieving porous materials with excellent mechanical strength and tunable internal microstructure.

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