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Towards a universal organogelator: A general mixing approach to fabricate various organic compounds into organogels

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Low-molecular-weight organogels (LMOG) have been attracting a surge interest in fabricating soft materials. Although the finding of the gelator molecules has been developed from serendipity to objective design, the achievement of the gelator molecules still needs good design and tedious organic synthesis. In this paper, we proposed a simple and general mixing approach to get the organogel for nearly all the organic compounds and even soluble nanoparticles without any modification. We have designed a universal gelator molecule, which forms organogels with more than 40 kinds of organic solvents from aploar to polar solvents. More interestingly, when other organic compounds or even nanomaterials, which are soluble in certain organic solvents, are mixed with this gelator molecule, they can form organogels no matter whether the individual compounds could form organogel or not. This method is applicable to nearly all kinds of soluble organic compounds and opens an efficient and universal way to fabricate gel materials.

organogel, hybrid system, supramolecular chemistry, self-assembly, soft matter

1 Introduction

During the last decades, there has been an increasing interest in the low-molecular-weight organogelators (LMOGs), which form supramolecular gels with various organic solvents [1, 2]. Upon gelation, the organogelators self-assemble into various nanostructures such as fiber, tape, ribbon, platelet, tubular structure and so on, which can form highly anisotropic 3-D network to immobilize the organic solvents [3–8]. The interest in the gel materials falls in lots of directions. Various nanostructures can be easily obtained through gel formation. The gels with good nanostructures can be further used as template to synthesize other hard-to-be-fabricated nanomaterials [9–12] and many functional gel materials have been developed so far. On the other hand, from any point of view in gel research, the design or selection of the gelator molecules is one of the most important issues. Although great efforts have been paid to the design of the gelator molecules and their applications, the development of novel gelator molecules still remains an important step since it serves as the basis for the gel investigation. Unfortunately, the general rule to predict the gel formation is still not clear, even if there are a huge and steady growing number of gelator molecules that have been designed and synthesized. In principle, new gelators are usually developed by modifying the structure of some parent molecules. Based on the previous studies, several scaffolds such as cholesterol-, amide-, urea-, amino acid, peptide- and sugar are suggested to be effective in promoting the gel formation [2, 6–8, 13–15]. Therefore, in order to endow the gels with some special functions, the building blocks, which are usually difficult to form gels individually, have to be incorporated into the gelator's scaffolds through covalently bonding. In such case, it usually needs a tedious synthetic way to obtain the corresponding gelators with special functional substituents.

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Besides the single component gelator, binary gels were also proposed by Smith *et al*., which utilize the supramolecular interaction between the two components to form the gelators with two different molecules connected by non-covalent bond [8]. The binary gelators expand the formation of the low-molecular-weight gels, in which the two components gelators can be self-assembly transformed into different kinds of supramolecular nanostructures to gelatinize many organic solvents and water. However, in such cases, the selection of the two components is strictly limited, since both of the components should have either similar structure or complementary substituents [16, 17].

Previously, we have designed an L-glutamic acid based organogelator, LBG, and found that it can gelatinize nearly 17 kinds of solvents [18]. Further investigation revealed that this gelator can gelatinize more than 40 kinds of organic solvents from polar to non-polar except water. More importantly and interestingly, we found that when other compounds, either gelator or non-gelator, were mixed with LBG, it could form co-gel. The selection of addable components is very wide. Here, LBG serves like an "ominisecent" host gelator, which can not only gelatinize many kinds of organic solvents, but also form co-gels no matter whether the added component is gelator. So far, several papers have reported that a co-gel could be formed when some non-gelators were mixed with certain gelator molecules [19–22]. However, either the added component or the solvent is limited. In our case, we have found that nearly all kinds of compounds, ranging from simple aliphatic acid to π-conjugated compounds and even nanomaterials, could be fabricated into organogels. In this paper, we will show the examples of how various compounds can be fabricated into gel materials. Furthermore, we will discuss the mechanism about why most of these compounds can form co-gel when mixed with our gelator molecules. Different interaction modes between the added component and our gelator molecule as well as their characteristics will be discussed.

2 Experimental

2.1 Materials

The LBG was synthesized by the amidation of Boc-L-glutamic acid with octadecylamine. Most of the mixing compounds were purchased as analytical grade and used as received. Some special dopants were synthesized according to references. Fe_3O_4 magnetic nanoparticles were synthesized by a sequential process involving the chemical co-precipitation according to the method reported by previous references. All the organic solvents were purchased from Beijing Chemical Reagents Factory. According to the grade of the solvents, some were distilled and others were used as received.

2.2 Methods

The gel formation of the gelator LBG itself was reported previously. In addition to the previously reported solvents, a series of polar and non-polar solvents was further investigated on the gel formation with the LBG by means of the inverted test-tube method.

We have fabricated the gel by mixing our gelator molecules with other organic compounds. Generally, a 5% mass ratio of dopants/LBG was used. A typical experiment was carried out as following. First, the dopants were dissolved in volatile solvents and appropriate amount was added into a screw bottle containing 5 mg LBG. After the volatile solvents were evaporated under vacuum, appropriate solvent (DMSO, toluene or 1, 2-dichlorobenzene) was added into the mixture. The screw bottle was then heated up until they were totally dissolved in the solution. After cooling down to room temperature, the transparent organogels were formed, which were confirmed by an inverse tube test. The ratio of dopants slightly influences the stability of the two-component gel. Generally, when 0 to 10% of the dopants were present, the co-gel was transparent and could be kept for two months without any collapse. When the dopants increased to 20%, only a partial organogel could be obtained in most cases. However, some dopants with long alkyl chains, such as stearic acid, octadecylamine, melamine, NK3050 and eicosanedioic acid, could form DMSO gels even when the amounts reached up to 40%–50%.

2.3 Apparatus and measurements

A quartz cell was used for the spectral measurements. CD and UV-vis spectra were obtained by using a JASCO J-810 CD and a JASCO UV-550 spectrophotometer, respectively. In the process of CD spectral measurement of the xerogel, the quartz slide was placed perpendicular to the light path and was rotated within the plane of the slide wall to avoid polarization-dependent reflections and to eliminate the possible angle dependence of the CD signals. Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer (Hitachi，Japan) using a xenon lamp as the excitation source. The FESEM images was taken using a Hitachi S-4300 system and TEM images were obtained on a JEM-100CXII electron microscope operating at accelerating voltages of 15 kV and 100 kV, respectively. In order to obtain TEM or SEM figures of the xerogel, the same procedure of co-xerogel preparation was performed on a hydrophobic silicon slide. A total of 1 μL organogel was deposited on a fresh silicon slide or copper grid surface. After that, the organogel was washed with 50 μL of the same solvent and then vacuum-dried.

3 Results

3.1 Design of the gelator molecules and the gel formation

The gelator molecule is constituted of three amide groups, a chiral center with two long alkyl chains. With such design,

the molecules have multi-sites for hydrogen bond. Two long alkyl chains facilitate the molecule to show strong hydrophobic interactions. Interestingly, this compound could gelatinize nearly all the organic solvents with relatively low critical gelation concentration (CGC). Previously, we have reported that the compound could gelatinize 17 kinds of solvents [18]. Here, we have further surveyed additional 24 kinds of solvents and found that it was really universal. Table 1 listed all of the additionally tested solvents that were arranged according to polarity index. It is clear that the compound can gelatinize the organic solvents from polar to non-polar. However, it could not gelatinize water, thus the compound can only form organogel.

Interestingly, when the gelator was mixed with different kinds of compounds, which cannot form organogels by themselves, it still could form very stable organogels. Since there are many kinds of the molecules, we have grouped them and have shown that how these materials were fabricated into organogels in the following sections.

3.2 Fatty acid

For the LMOGs, the derivatives of long chain *n*-alkanes, fatty acid and fatty amine or fluorinated alkanes could be summarized to one enormous class of simple alkyl gelator. Weiss *et al*. have reported a series of simple alkanes as LMOGs [23–25]. Very long *n*-alkanes (Cn with $n = 24–36$) can be directly used as LMOGs, which could gelatinize several organic liquids, including shorter *n*-alkanes, in low concentration [23]. However, in most cases, for the design of these kinds of simple gelators, additional functional groups are usually necessary to help the gel formation in addition to the alkyl chain. 12-Hydroxyoctadecanoic acid and its related salts are known to create hardened materials from organic liquids [2]. However, the hydroxyl group is very important to the gelation behavior of this kind of fatty acid. Obviously, not all the simple alkyl chain substituted compounds can form the organogel. Therefore, we selected several compounds with alkyl chain to mix with our powerful gelator (LBG) in different organic solvents in order to form organogels. The doping organic molecules can be fatty alcohol, fatty acid and fatty amine or fluorinated alkanes (Figure 1). In all the cases, we found that LBG form stable gels with these molecules.

Figure 1A shows the detailed molecular structures of the compounds that can form stable mixed organogels with LBG. The morphologies of these gels were investigated by scanning electron microscopy (SEM). Figure 1B displays the SEM images of the corresponding organogels from LBG and doped organic molecules. Depending on the molecular structures of secondary component, totally different morpholo-

Table 1 The gelation properties of LBG in various solvents arranged by polarity index (ε)

Solvents	Property [a]	CGC (mg mL^{-1})	ε [b]
acetic acid	WG	7.5	6.2
acetonitrile	WG	9.2	5.8
pyridine	WG	6.2	5.3
1,4-dioxane	TG	3.7	4.8
2-butanone	WG	5.7	4.7
nitrobenzene	TG	3.5	4.5
t-butanol	WG	13	4.1
n-propanol	WG	14	4.0
n-butanol	WG	12	4.0
isoamyl alcohol	WG	10	4.0
isobutanol	WG	13	3.9
n-pentanol	WG	10	3.9
isopropanol	WG	14	3.9
1,2-dichlorobenzene	TG	2.7	2.7
chlorobenzene	TG	2.5	2.7
o-xylene	TG	1.6	2.5
m-xylene	TG	1.6	2.5
p-xylene	TG	1.5	2.4
carbon tetrachloride	TG	2.2	1.6
styrene	TG	2.5	N/A
octane	WG	7.5	0
isooctane	WG	7.7	0
decalin	TG	1.5	0
aviation kerosene	WG	7.5	0

a) WG = white gel; TG = transparent gel. b) *Handbook of Physical Chemistry*.

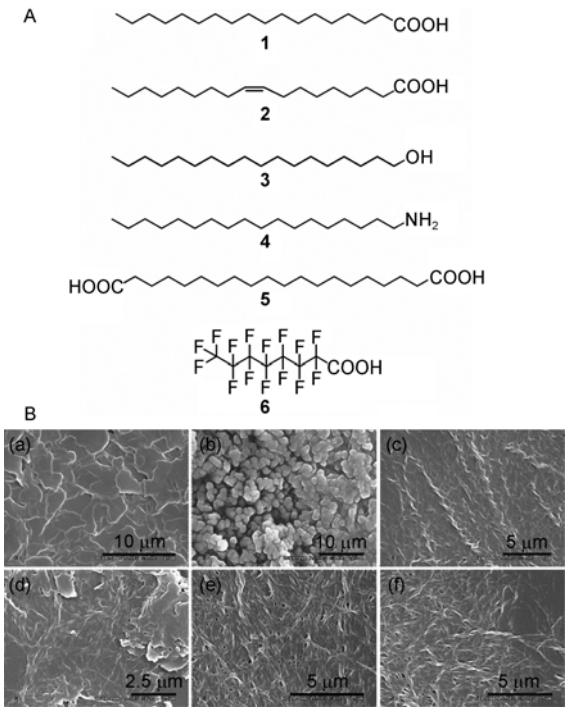


Figure 1 A, Molecular structures of alkyl compounds; B, SEM images of xerogels made from stearic acid (a), oleic acid (b), octadecanol (c), octadecylamine (d), eicosanedioic acid (e), and perfluoroheptanecarboxylic acid (f).

gies were observed in these gels. For stearic acid working as doping component, many plates were observed in the organogel systems. These plates are irregularly shaped with length and width around several micrometers (Figure 1B(a)). In contrast, when the oleic acid with one cis double bond forms mixed organogel with LBG, the corresponding assemblies change into globular nanostructures (Figure 1B(b)). The average diameters of these nanoparticles are more than 1 micrometer, and most of them are closely stacked together.

Although the morphologies from stearic acid and oleic acid mixed organogels are very different from the structures of original pure LBG gels, long nanofibers still essentially formed for all the other mixed organogels systems, including octadecanol, octadecylamine, eicosanedioic acid and perfluoroheptanecarboxylic acid. On the other hand, the detailed characteristics of all these long nanofibers are also different. The fibrous structures in octadecanol and perfluoroheptanecarboxylic acid doped gels are more or less in helical shape, while that in octadecylamine and eicosanedioic acid assembles into planar nanotapes with LBG (Figure 1B(c)–(f)). These structural features indicate that the gelator molecules and the dopants have different interactions, depending on the molecular structure of doped component.

3.3 Polar compounds

Low-molecular-weight organo- or hydrogelators based on polar compounds, such as amino acids, peptides, sugar, melamine, babituric acid, cyclodextrins and so forth, have been entirely investigated just because of the multiple sites of hydrogen bonding which are preponderant for gelator design. Generally, gelators containing polar substrates are used for gelatinizing water instead of organic solvents owing to the low solubility in organic solvents. Hamilton *et al*. [3] and van Esch *et al*. [26] have reported one enormous class of hydrogelators based on amino acids and peptides. Zinic *et al*. [27] have reported some bis(amino acid) based compounds which can be used as ambidextrous gelators: gelatinizing water as well as organic solvents. For organogelators containing polar substrates, some oil-soluble moieties such as alkyl chains and aromatic groups were introduced in the target molecules to improve the solubility in nonpolar solvents. Shinkai *et al*. [28] have reported a series of sugar- integrated gelators used for gelatinizing organic solvents. The introduction of phenyl groups improved the solubility in organic solvents as well as gelatinizing ability because of the π-π interaction. Some cylcodextrin [29] and melamine [30] derivatives can be used for organogelators due to the multiple hydrogen bonding sites. Similarly, these compounds either should be designed to have long alkyl chain to introduce hydrophobic interaction during self-assembly and gelation or have to be introduced with some other units to produce intermolecular π-π interaction to assure the gel formation.

However, these polar substrates such as glutamic acid, melamine, β-cyclodextrin and δ-gluconolactone, which cannot form organogel in organic solvents, can form stable DMSO gels by mixing them with LBG. It is interesting to find that the doping mass ratio of melamine can be expanded to 40%. From SEM images, we can estimate the interaction mode between the dopants and gelator. As shown in Figure 2B(a)–(c), the morphologies of the systems containing glutamic acid, melamine or β-cyclodextrin are similar to that of pure LBG gel. The dopants might adhere to the surface of the gelator fibres. But the morphology of the system of δ-gluconolactone and gelator complex changes a lot, suggesting a strong interaction between dopant and gelator (Figure 2B(d)).

3.4 Aromatics

The self-assembled π-systems are usually very useful to realize the organic electronic devices due to their favorable

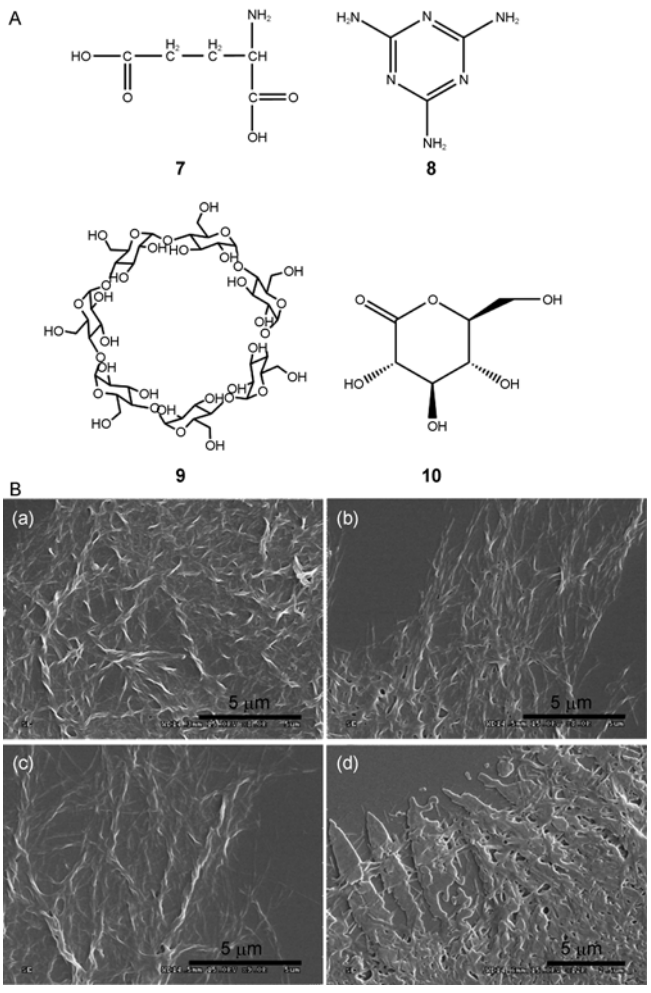


Figure 2 A, Molecular structures of polar substrate compounds; B, SEM images of xerogels obtained from glutamic acid (a), melamine (b), β-cyclodextrin (c) and δ-gluconolactone (d).

optical and electronic properties comparing with the corresponding single molecules. Therefore, LMOGs based on aromatic molecules have been extensively studied. A number of aromatic LMOGs have been designed such as anthraquinone [31], anthracene [32, 33], pyrene [34, 35] and carbazole [36] as well as large aromatics such as porphyrin [37, 38], phthalocyanine [39], triphenylene [40] and phenylenevinylene [6]. In the case of developing novel optoelectronic functional materials from organogels with π-systems, the selected aromatic molecules are generally necessary to covalently bond with some scaffolds in order to obtain good gelators and subsequently form stable organogels. Since the syntheses of some aromatic compounds with gelatinizing scaffolds are relatively complicated, this is still a hard way to obtain organogels containing aromatic molecules. However, by using our gelator, the target organogels can be easily formed by just simply mixing.

Figure 3A shows the structures of some typical aromatic molecules. All the compounds cannot form organogels individually. However, when mixing with our LBG, stable co-gels can be obtained. The morphologies of these mixed organogels were studied with SEM measurement. Interestingly, although these aromatic compounds have totally different molecular structures, they all form helical nanofibers with LBG (Figure 3B). Furthermore, since these aromatic molecules usually have strong absorption bands and also fluoresce, we studied their UV-vis and fluorescence spectra in the mixed organogels with LBG (Figure 3C). It is clear that the characteristics of these aromatics, including the feature of UV-vis and fluorescence spectra, are remained through gel formation.

3.5 Metal ion coordination compounds

In recent years, the organogels with metal complexes have attracted a great deal of interests [41, 42]. Since the metal complexes play important roles in the fields of materials chemistry, synthesis and catalysis, the development of metal-containing gels are expected to create the novel soft matters with both the properties of organogels and metal complexes.

Many of the metal complexes such as fatty acids salts [43], metal porphyrins [44] and metal phthalocyanins [45] have been known to be gelators. The metal complexes of many organic ligands like gluconamides [46], some molecules with nitrogen heterocyclic rings [47, 48] and derivatives of phosphinic acid [34] can also be used as gelators. Similarly, these coordination compounds either should be designed to have long alkyl chain to introduce hydrophobic interaction during self-assembly and gelation or have to be introduced with some other units to strengthen the intermolecular hydrogen bonding to assure the gel formation. Upon mixing with our gelator molecules, it is not necessary to modify these coordination compounds any more.

Stable organogel can be obtained from 8-hydroxyquinoline aluminum salt (AlQ_3) without long alky chains or any other hydrogen bonding substituting groups by mixing it with our gelator (Figure 4). The SEM study indicates that helical nanofibers were formed from the co-gels of AlQ_3 with LBG (Figure 4B(a)). The co-gel exhibits strong fluorescence under UV irradiation as shown in the inset of Figure 4B(a). Figure 4C shows the UV-vis and fluorescence spectrum of AlQ_3 incorporated into the co-gels. In the organogel with LBG, AlQ_3 still can be fluorescent, demonstrating that the metal complex may be in the liquid phase of the gels.

Just like the free base porphyrins, the metal porphyrin can also be integrated into the mixed gels with LBG. In the case of mixed gels containing copper porphyrin with four long alky chains, both J and H aggregation can be detected from the porphyrin aggregation in the co-gels. In addition, although the copper porphyrin does not have any chiral centre, it forms supramolecular chiral assemblies in the mixed gels with LBG (Figure 4C). The induced supramolecular chiralities are believed to be originated from the entanglement of the alkyl chains of the copper porphyrin with LBG.

3.6 Organic dyes

Dyes, with large π-conjugated systems and good absorption bands, are among the most investigated functional materials. Since the organic dyes usually have a large conjugated backbone, they will show strong π-π interaction during self-assembly, which is also very important in forming the organogels. Many gelators from the dye molecules have been reported [49, 50]. Just like the gelators based on aromatic molecules, besides the strong π-π interactions during the self-assembly, the gelators based on dyes are also usually need to be modified with some other scaffolds to introduce additional noncovalent interaction between the molecules during gelation. For example, those gelators based on porphyrins have to be appended with cholesterol or some hydrogen-bonding substituents [37, 51]. Again, the synthesis of this kind of molecules usually need long time and multistep synthesis, which usually costs money and time.

By using LBG, we have found that organogels containing dyes molecules can be obtained by simply mixing. We particularly focused on those dyes with charges, which are difficult to form gels individually (Figure 5A). Figure 5B shows the SEM pictures and the photographs of the corresponding co-gels of our gelator with many commercially available organic dyes. Uniform and transparent gels were formed in most cases. Also, depending on the molecular structures, helical fibers were obviously formed in most of these organogels.

The UV-vis spectra as well as the CD spectra of these co-gels of LBG with the dye molecules were also studied (Figure 5C). The dye molecules in the co-gels show red shifts in the absorption spectra, indicating the formation of strong J-aggregation during the assembly in the mixed gels.

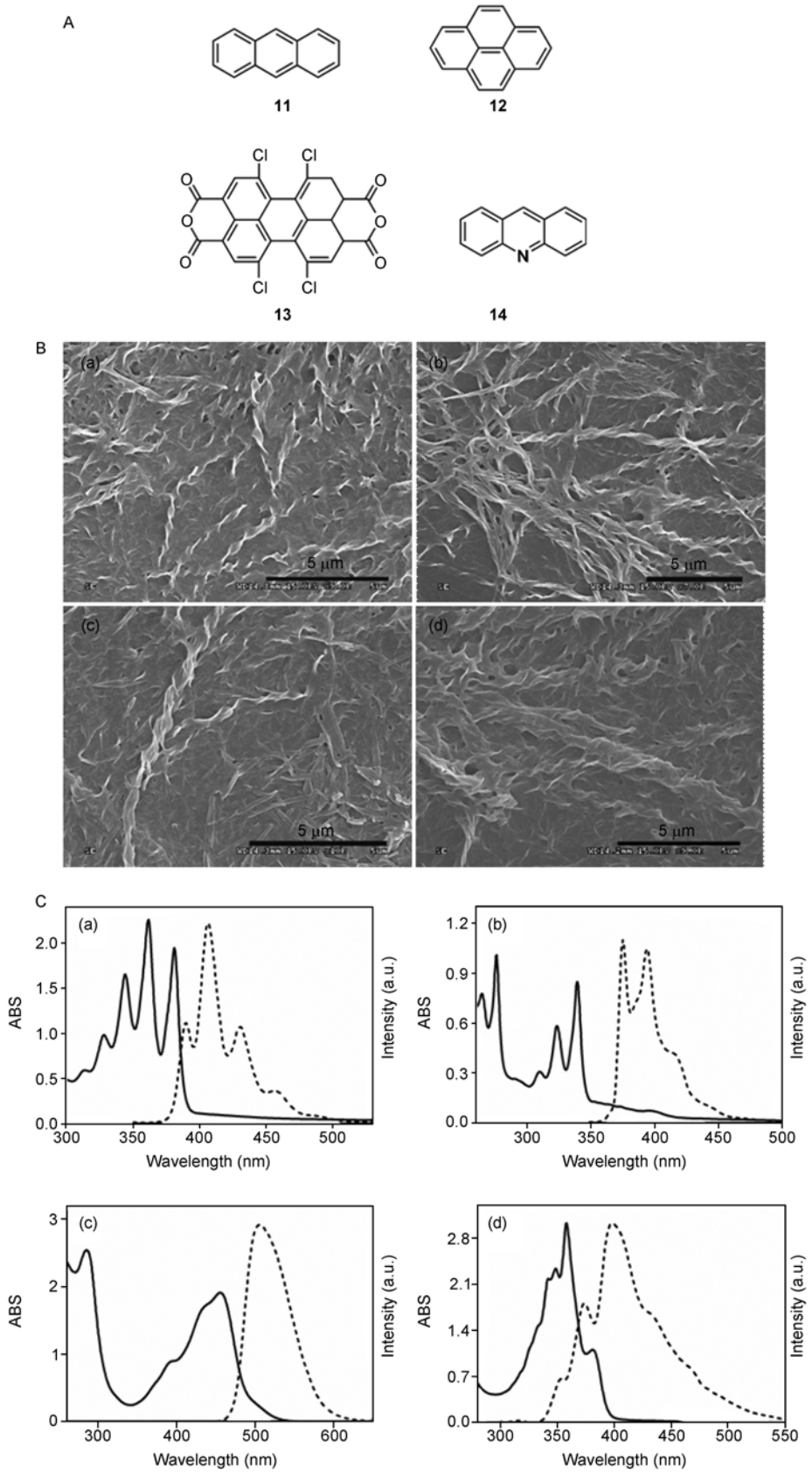


Figure 3 A, Molecular structures of aromatic compounds; B, SEM images of xerogels made from anthracene (a), pyrene (b), 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride (c), and acridine (d); C, UV-vis (solid line) and fluorescence (dash line) spectra of anthracene (a), pyrene (b), 1,6,7,12-tetrachloroperylene tetracarboxylic acid dianhydride (c), and acridine (d).

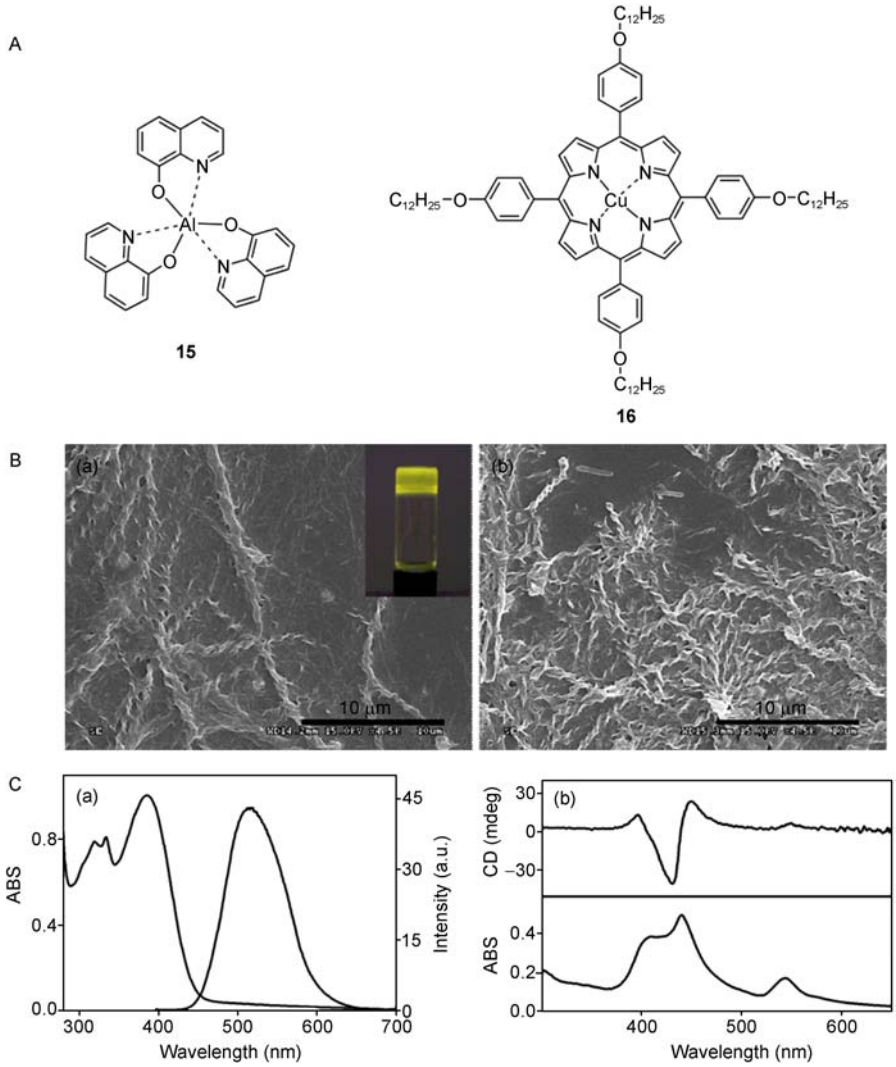


Figure 4 A, Molecular structures of metal complex compounds; B, SEM images of xerogels made from (a) 8-hydroxyquinoline aluminum salt (AlQ_3). The inset is a photograph of AlQ_3 DMSO gel exposed to UV light. (b) Cu porphyrin; C, (a) UV-vis (left) and fluorescence (right) spectrum of AlQ_3; (b) CD spectrum (upper) and the UV-vis spectrum (down) of Cu porphyrin.

Interestingly, although those dye molecules with long alky chains do not have any chiral centers, they show strong CD signals upon assembling with LBG. In principle, LBG can form helical fibers in the gel, and a strong interchain interaction between the alkyl chains in dye molecules and those from the LBG causes the transcription of the chirality of the gelator to the dye aggregation. Therefore, the induced supramolecular chirality of the dyes may originate from the entanglement of the alkyl chains of the compounds. If we use the dyes without any long alkyl chain, no supramolecular chirality can be obtained for the dyes in the mixed gels.

3.7 Polymer

Polymer refers to a large class of natural and synthetic materials, which have relative large molecular weight and different properties. The synthetic polymers are usually large molecule (macromolecule) composed of repeating structural units typically connected by covalent bonds [52]. Some of the polymers, whether with noncovalent bonded or covalent bonded, can form stable gel in both water and organic solvents [53–55]. However, many polymers still cannot form gels by themselves. If one wants to obtain gels from some special polymers, tedious synthetic ways are usually required.

On the other hand, the supramolecular properties of polymer molecules in the gel phase from LMOGs are still rarely studied. It is therefore very interesting to investigate the aggregation properties of the polymers in the organogels, or to study the intermolecular interactions between polymers and small organic gelators.

We have found that many functional polymers, which are unable to form gel by themselves, can be fabricated into organogels by using our LBG. These polymers have large molecular weight, and some of them may have long alky chains or many aromatic groups (Figure 6A). Interestingly,

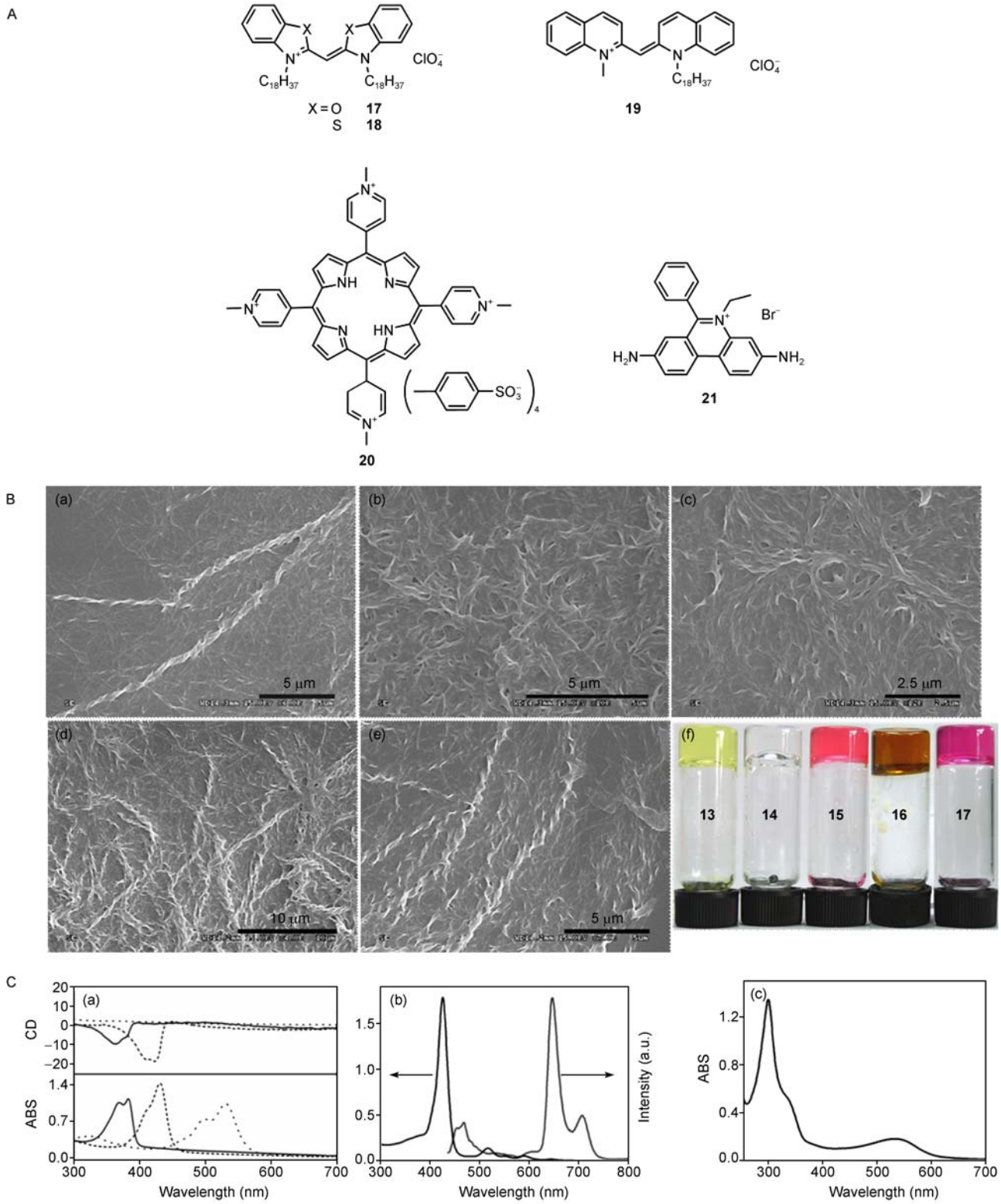


Figure 5 A, Molecular structures of dye compounds; B, SEM images of xerogels made from NK3050 (a), NK2638 (b), NK3025 (c), TMPyP (d), EB (e), the photographs of corresponding gels (f); C, (a) UV-vis (down) and CD (upper) spectra of NK3050 (blue line), NK2638 (red line), and NK3025 (black line); (b) UV-vis (black line) and fluorescence (red line) spectra of TMPyP; (c) UV-vis spectra of EB.

these polymers also assemble into different morphologies with LBG (Figure 6B). For the polymers with aromatic rings, both the UV-vis and fluorescence spectra from the co-gels are similar to those of the corresponding spectra in

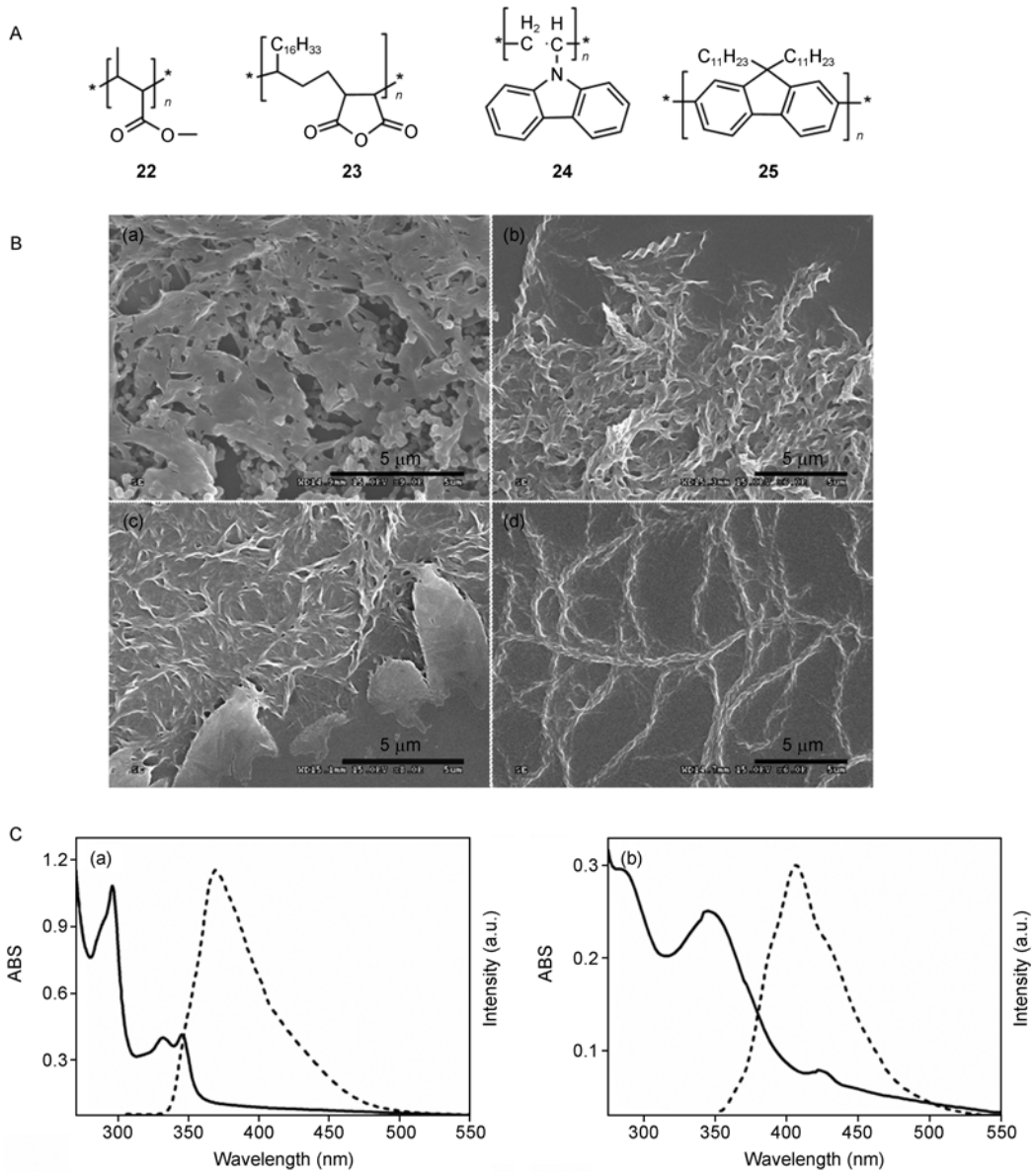


Figure 6 A, Molecular structures of polymer compounds; B, SEM images of xerogels made from PMMA (a), poly (maleic anhydride -alt-1- octadecene) (b), PVK (c), and poly (2,7-diiodo-9,9'-didodecane-9H-fluorene) (PDF) (d); C, UV-vis (solid line) and fluorescence (dash line) spectra of PVK (a) and PDF (b).

solution (Figure 6C). Through such mixing, the behavior of the polymers in the soft material can be investigated. After forming the organogels, those functional polymers such as PVK and PDF also show strong fluorescence emissions.

3.8 Nanoparticles and nanotubes

Assemblies of inorganic nanoparticles (NPs) into two- or three- dimensional architectures are of fundamental interest because of their unique optical and electronic properties [56, 57]. In order to make hybrid functional materials, inorganic nanoparticles can be either *in situ* produced or be doped inside the organic soft materials [58–60]. In this context, there has been a number of reports focusing on the doping of nanoparticles into polymers, the hybrid materials with improved performance can thus be obtained [61, 62]. The gels based on LMOGs are very important soft matters. Although the incorporation of inorganic nanoparticles into the organogels are still unusual, there has been a surge of interest in fabrication of various nanostructures by using supramolecular organogels template [9, 11, 12, 63]. On the other hand, several samples focusing on doping inorganic nanoparticles into LMOGs based organogels have been reported [64, 65]. For doping inside the organogels, gold nanoparticles can be good model. For example, Shirai *et al.* have reported an effective method, which can control the organization of Au nanoparticles into a 3-D network structure by using a site-exchange reaction. These mixtures ex-

hibited interesting optoelectronic properties, such as temperature-dependent reversible UV/vis spectral changes, as a result of the controlled and reversible aggregation of Au nanoparticles [66, 67]. Moreover, Stupp *et al*. have reported a kind of peptide based LMOGs, which can serve as scaffolds for the 1D assembly of lipophilic inorganic NPs in non-polar solvents [68].

In principle, doped inorganic nanoparticles may largely improve the functional properties of the materials and devices based on organogels. However, for the interaction of inorganic nanoparticles with molecular gels, the molecular-level understanding is still rare, even though such understanding would be useful for the design of new materials.

For developing novel soft matters doped with inorganic nanoparticles, LBG is able to be a fantastic candidate. It can form co-gels with many kinds of nanoparticles, such as CdSeS quantum dot or Fe_3O_4 magnetic nanoparticles in different solvents. Furthermore, it can form stable co-gels with C60 and carbon nanotube (Figure 7). In this case, our LBG gels are very good containers for different kinds of nanoparticles and nanotubes. Interestingly, the properties of the nano-materials could also keep constant in most cases after mixing with the gel from LBG. The quantum dots, which are doped into the co-gels, show beautiful fluorescence under UV irradiation (Figure7 A1).

Although the added molecules can be either in solid phase framework of the organogels or in liquid phase and immobilized by the framework from LBG during the gelation, all the investigated materials can form stable co-gels with LBG. In most cases, the properties of the materials keep constant after gelatinizing with LBG. Some of the molecules aggregate inside the co-gels, and form supramolecular chiral assemblies.

We have only shown some examples here. With this method, various materials can be fabricated into soft materials, which will open a large scope for the research in the field of soft materials.

4 Discussion

It is well-known that upon gel formation, the gelator molecules usually form a 3-D network structure, while the solvent was immobilized within the network. This is the general case of a single component gelator. However, when two components are present in the organogels, situation is different. In most cases, this additional component will destroy the gel formation and thus it is difficult to obtain the co-gel. In our case however, any kind of compounds mixed with our gelator seem to form the organogels. Our gelator molecules love many other compounds and get along very well with nearly all the organic compounds to form co-gels.

Although the gels are macroscopically uniform, they are generally uneven in microscopic phase. Thus there appear some types of interactions between the gelator and the dopant molecules. In the mixed gels, the interactions can be categorized into three types: binding state, semi-binding state and free-state, which can be illustrated in Scheme 1. In the binding state, the additional molecules entangled with

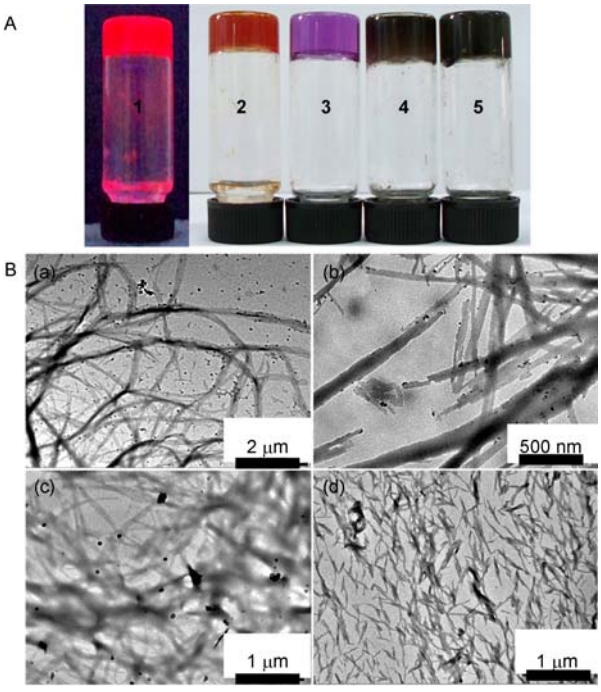
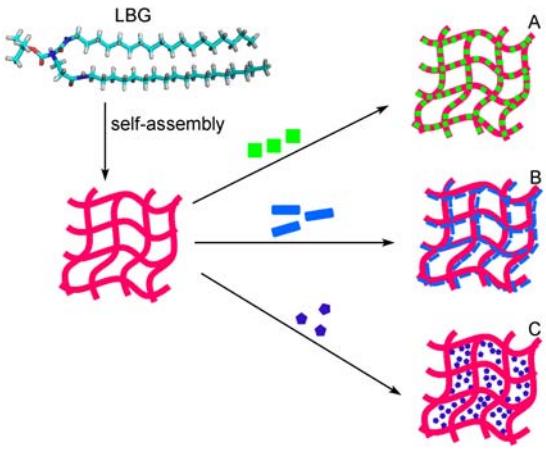


Figure 7 A, Photographs of the gel formation: (1) Toluene gel doped with CdSeS quantum dot under an UV lamp, (2) toluene gel doped with CdSeS quantum dot, (3) toluene gel doped with C60, (4) DMSO gel doped with Fe_3O_4 magnetic nanoparticles, (5) 1,3-dichlorobenzene gel doped with the single wall carbon nanotube; B, TEM images of xerogels made from the CdSeS quantum dot (a), C60 (b), Fe_3O_4 magnetic nanoparticles (c), and single wall carbon nanotube (d).



Scheme 1 Chemical structure of the gelator molecule (LBG) and its bahevaiors. LBG itself could form nanofiber structure, which immobilized the solvent to form organogels. When other components were mixed with LBG, it possibly form three kinds of organogels. In case A, the mixed component together with the LBG formed the network frame. In case B, part of the added molecules adhered to the gelator fiber structures. In case C, the added molecules existed in the solvent phase.

LBG molecules and merged into each other to form the framework or the nanofibers structures, as shown in Scheme 1A. Those compounds with long alkyl chains usually form such kind of organogels. In this case, the mixed ratio of the dopant molecules can be large. For example, stearic acid and octadecylamine could form co-gels with LBG in a mass ratio of 50%. The interactions between the gelator molecules and dopants are due to the interchains interaction and hydrogen bond between the dopants and amide groups. The second type is semi-binding state, in which the added molecules are accompanied with the gelator molecules and are arranged along the fiber structures, as shown in Scheme 1B. These cases are found in the systems such as poly (maleic-anhydride-alt-1-octadecene), Cu-porphyrin and so on. In these systems, the morphologies of the xerogels are similar to those of LBG. However, large numbers of giant helical fibers are frequently observed and the diameters are larger than that of LBG. The third type is free-state, as shown in Scheme 1C. In this case, the LBG alone form the gel framework while the doped organic molecules can be dissolved in the liquid phase and immobilized by the framework from LBG. SEM observation reveals that both components are separately observed. In this case, the doped molecules behave like in the solvents without the interference of LBG. Those molecules with larger π-conjugate system without alkyl chain substitution seem to fall into this catalogue. It is interesting the achiral dopant shows supramolecular chirality in some cases as the compounds **16**, **17**, and **18**. It is noted that in these cases, the dopant molecules interact with LBG in a binding or semi-binding state. Because LBG is a chiral molecule, the chirality could transfer from LBG to the dopants through molecular interaction.

The gelatinizing processes of all the mixed gels from our gelators and the dopants are reversible. This means that the formed organogels can be re-dissolved into the solvent upon heating, and gel again after cooling down. This sol-gel circulation can be repeated many times, and the doping organic molecules are always embedded inside the organogels after gel formation.

It should be further noted that only LBG can serve as such a universal host organogelator among many other derivatives with similar molecular structures. Actually, we have modified the compound from the head group to the long alkyl chain. It has been found that the Boc protecting group in our case is very important for good gelation properties, presumably due to its amide group for additional hydrogen bonding during gelation. In addition, two octadecyl alkyl chains are also very important, which may essentially render the compound to be a powerful gelator. In fact, if we shorten the length of alkyl chains, the universality of the gelation properties is diminished.

Our LBG can form different kinds of gels in various solutions. The given samples are mostly from DMSO gel, while in the case of polymer, nanoparticles and nanotubes working as dopants, toluene or even 1,2-dichlorobenzene were used to dissolve the corresponding materials. LBG can work very well in different solvents with various compounds. This really provides a general approach to obtain gels from nearly all the organic compounds.

5 Conclusions

In summary, we demonstrate that the L-glutamic acid based derivative (LBG), which has three amide groups, a chiral center and two long alkyl chains, can be used as a universal host organogelator. It could gelatinize more than 40 kinds of solvents. Furthermore, it can form stable co-gels upon mixing with nearly all the organic compounds and some nanoparticles in a broad range of solvents, no matter whether the mixed components can form organogel by themselves or not. The added components studied here in our mixed gels systems are just some of the examples, which including fatty acids, polar compounds, aromatics, organic dyes, metal ion coordination compounds, polymers, and nanomaterials. It is expected that many more compounds can be fabricated into the organogels upon mixing with our gelator. Thus, this report opens an efficient and universal way to fabricate soft gel materials.

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