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Formation of hydrophobic surface using a bis-urea derived organogel
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A bis-urea derived gelator 1 was synthesised with a high yield via a simple organic reaction. The gelator could form organogel in four kinds of solvents. The organogels obtained from four kinds of solvents were systematically investigated by FESEM, UV–Vis, PL, IR, XRD and water contact angle experiments. It was interesting that the self-assembly process of gelator 1 could be tuned by solvents. The film structure and fibre were formed in different solvents. At the same time, the different morphologies all displayed hydrophobicity. Especially, the contact angle of the fibre obtained from organogel in DMF was up to 147°. This research would provide a good pattern for preparation of a special hydrophobic surface through supramolecular self-assembly.

Keywords: organogel; supramolecular; self-assembly; bis-urea; hydrophobic surfaces

1. Introduction

Supramolecular self-assembly is not only disclosing the mystery of the origin of the life, but also directs the novel smart functional materials (1). One of the main challenges is to manipulate self-assembly of designed building blocks for biomimicry natural materials with special functions such as ‘the lotus effect’. A hydrophobic surface is a surface where the water contact angle is higher than 90°. Hydrophobic surfaces have attracted growing interest due to their wide applications in the coating industry, textile industry, packaging, electronic devices, agriculture and daily life (2). Supramolecular self-assembly provides a good platform to formulate novel nanostructured materials with functional surfaces and special wettability. As a novel class of self-assembled materials, low weight molecular organogels (LOMGs), which are organised in regular nanoarchitectures through multiple weak interactions including hydrogen bonding, hydrophobic interactions, \( \pi-\pi \) interactions as well as van der Walls forces, have recently received considerable attention (3). This class of soft materials can be not only used as smart materials with environment stimuli-responsive such as pH, anions, redox agents, electric or magnetic fields, light and sound (4), but also made for surface materials with special wettability.

Recently, Yi and coworkers reported that xerogels formed from diarylamine-based two-component organogels could also express hydrophobic surfaces whose wettability switched solely by alternate irradiation of UV/visible light with change in surface morphology (5). At the same time, a variety of structures were fabricated by gelator self-assembly in the sol-gel transition such as vesicles, fibres, rings, core–shells, as well as tubes (6).

In this paper, a new bis-urea derived organogelator 1 was designed and studied (Scheme 1). By varying the solvent, film structure and fibre were obtained from the xerogel; the surface wettability of the different structure was also tuned by different solvents. All of the surface wettability obtained from organogels in different solvents exhibited high hydrophobicity with a water contact angle of > 115°. This behaviour could provide opportunities in applications for preparation of special structure and surface wettability through a supramolecular assembly.

2. Experimental section

2.1 Reagents and solvents

Organic solvents, i.e. DMF, DMSO and CH\(_2\)Cl\(_2\) were HPLC grade and obtained from Sinopharm Chemical Reagent Co. Ltd. Methyl gallate, 1-bromododecane, 1,5-diisocyanatodiphenyl ether and ethane-1,2-diamine were supplied from Aladdin reagent (Shanghai) Co., Ltd. The compound 2 was synthesised according to the reported paper (7).

2.2 Techniques and instrumentations

The \(^1\)H NMR (400 MHz) and \(^{13}\)C NMR (100 MHz) spectra were recorded on a Mercury plus-Vario instrument. Proton chemical shifts are reported in parts per million downfield from Tetramethylsilane. HRMS was recorded on LTQ-Orbitrap mass spectrometer (Thermo-Fisher, San Jose, CA). SEM images were obtained using an FE-SEM S-4800 (Hitachi) instrument. Samples were prepared by spinning the diluted gels on glass slices and...
coating with Au. Powder X-ray diffractions were generated by using a Philips PW3830 sealed-tube X-ray generator (Cu target, \( \lambda = 0.1542 \) nm) with a power of 40 kV and 50 mA. UV–vis absorption was recorded on a UV–vis 2550 spectroscope (Shimadzu). Fourier transform infrared (FTIR) spectra were collected by a Nexus 470 spectrometer (Nicolet Company) with a resolution of 2 cm\(^{-1}\), and 32 scans were accumulated to obtain an acceptable S/N ratio. The samples were prepared with KBr pellets. Original spectra were baseline-corrected by use of Omnic 5.1 software. Water contact angles were measured using the sessile drop method (Dataphysics, OCA 20). The water droplets were introduced using a micro-syringe, and images were captured to measure the angle of the liquid–solid interface; each sample was recorded at three different points.

2.3 The gelation test

The gelation test on compound 1 (25 mg mL\(^{-1}\)) was carried out with various solvents using a test tube inversion method. The tube was heated (>80°C) until the solid was dissolved, and then the sample was put into a thermostat controlled by water (>25°C). Qualitatively, gelation was considered successful if no sample flow was observed upon inversion of the container at 25°C.

2.3.1 Synthesis of molecule 1

A mixture of 1,5-diisocyanatonaphthalene (0.22 g, 1.04 mmol), 2 (1.50 g, 2.09 mmol), in anhydrous ethyl acetate (100 mL) was stirred for 24 h under nitrogen atmosphere. After the reaction was over, the precipitate was obtained from the above mixture. The precipitate was filtered and fully washed by ethyl acetate. The pale solid was the target product. Yield 70.5%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.09 (s, 4H), 7.28 (s, 2H), 7.15–7.17 (m, 4H), 6.92 (s, 4H), 6.54 (s, 2H), 3.95–4.02 (m, 12H), 3.735 (m, 4H), 3.686 (m, 4H), 1.71–1.81 (m, 12H), 1.62–1.70 (m, 12H), 1.41–1.50 (m, 12H), 1.20–1.40 (m, 84H), 0.87 (m, 18H, \( J = 6.0 \) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) : 167.7, 154.6, 147.3, 139.4, 141.2, 127.1, 125.2, 111.8, 109.0, 104.1, 69.6, 69.1, 41.2, 39.3, 31.8, 29.6, 29.5, 26.1, 22.7, 14.0 HRMS (ESI + ) calcd for C\(_{102}\)H\(_{174}\)KN\(_6\)O\(_{10}\) \([\text{M} + \text{K}^+]\) : 1682.2929; found: 1682.2948.

3. Results and discussion

The gelation properties of compound 1 were investigated using fourteen kinds of frequently-used solvents as showed in Table 1. The compound 1 could form organogels in N,N-dimethyl formamide, tetrahydrofuran, hexane and petroleum ether (by an inverse method) with a concentration of 25 mg mL\(^{-1}\). The images of organogels 1 from the above four kinds of solvents was showed in Figure S1.

Table 1. Gelation properties of compound 1 in different solvents with the minimum gelation concentrations in brackets.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Product 1</th>
<th>Solvent</th>
<th>Product 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum ether</td>
<td>OG (8.3 mg mL(^{-1}))</td>
<td>N,N-dimethyl formamide</td>
<td>TG (12.5 mg mL(^{-1}))</td>
</tr>
<tr>
<td>Toluene</td>
<td>S</td>
<td>CH(_2)Cl(_2)</td>
<td>S</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>I</td>
<td>Methanol</td>
<td>I</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>I</td>
<td>Acetone</td>
<td>I</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>I</td>
<td>Tetrahydrofuran</td>
<td>OG (25 mg mL(^{-1}))</td>
</tr>
<tr>
<td>Benzene</td>
<td>S</td>
<td>Hexane</td>
<td>TG (8.3 mg mL(^{-1}))</td>
</tr>
<tr>
<td>Ethanol</td>
<td>I</td>
<td>Dimethyl sulfoxide</td>
<td>S</td>
</tr>
</tbody>
</table>

Note: S = soluble; P = precipitate; G = gel; I = insoluble; T = transparent; O = opaque.
could be all seen from top. Under the first stratum structure, the diameter of the pore was smaller than that of the topside (Figure 1(a)). When the compound 1 was formed, i.e. the organogel in \(N,N\)-dimethyl formamide, the xerogel showed a three-dimensional network structure made by fibre with a diameter of 90 nm and a dozen microns long in Figure 1(b) and (b'). In tetrahydrofuran, an intertwined fibre structure was formed, and the whole structure was more flat than that of organogel in \(N,N\)-dimethyl formamide in Figure 1(b) and (b'). The SEM images of xerogel 1 in petroleum ether showed a multi-layered structure with some pores in Figure 1(d) and (d'). The pore was not the same as that of the organogel structure from hexane. The pore was also overlapped and not hollow. From the above results, the morphology of the self-assembly of compound 1 in organogel could be tuned by solvents.

Functional surfaces with controllable wettability have come to the forefront of research for their great potential application in daily life, industry and agriculture (8). The surface wettability of the material surfaces from different solvent were tested just as that in our previous work (5). The organogels in different solvents were dispersed on the glass cover surface and freeze-dried. The contact angle (CA) of the xerogels form hexane, \(N,N\)-dimethyl formamide, tetrahydrofuran and petroleum ether were 115°, 147°, 138° and 115°, respectively (Figure 2). The results showed the surfaces from the organogel 1 in different solvents were hydrophobic. The hydrophobicity of the fibre structure obtained from \(N,N\)-dimethyl formamide and tetrahydrofuran was larger than that of the pore structure obtained from hexane and petroleum ether.

In order to verify the nature of the intermolecular interactions constituting the self-assembly process, the absorption spectra of compound 1 in solution and gel stats from different solvents were studied, and results are shown in Figure 3. The compound 1 in hexane with the concentration of \(10^{-4}\) M had two absorption bands at 299 and 330 nm which were related to \(\pi-\pi^*\) and \(n-\pi^*\) transition bands, respectively (Figure 3(a)) (9). When the compound 1 was in gel state, the corresponding absorption bands also had a hypochromatic shift from 299 and 330 nm to 292 and 327 nm. Simultaneously, the two absorption bands of the organogel 1 changed into broad to a certain extent. This result showed that the ‘H-aggregate’ mode was employed in the gel state (10). A similar hypochromatic shift of the absorption spectra of gel 1 also existed in the other three solvents (Figure 3(b)–(d)). The UV–vis absorption spectra in non-gelation solvents such as CH\(_2\)Cl\(_2\) and DMSO are measured in Figure S2. The compound 1 in CH\(_2\)Cl\(_2\) had two absorption bands at 258 and 300 nm. When the solvent was DMSO with the same concentration,
Figure 3. (Colour online) The absorption spectra of solution and gel of 1 in different solvents: (a) hexane; (b) N,N-dimethyl formamide; (c) tetrahydrofuran; (d) petroleum ether ($C_{\text{solution}} = 10^{-4} \text{ M}$ and $C_{\text{gel}} = 25 \text{ mg mL}^{-1}$, cell length for solution, 1 cm).

Figure 4. (Colour online) The fluorescence emission spectra of solution and gel of 1 in different solvents under the excitation of 307 nm light: (a) hexane; (b) N,N-dimethyl formamide; (c) tetrahydrofuran; (d) petroleum ether ($C_{\text{solution}} = 10^{-4} \text{ M}$ and $C_{\text{gel}} = 25 \text{ mg mL}^{-1}$).
the absorption bands were at 258 and 328 nm. The second absorption band had an obvious red shift of 28 nm. These results indicated that the solvent had some effect on the self-assembly behaviour of compound 1.

The fluorescent spectra of 1 gave more information about the aggregation behaviour in gel 1 (Figure 4). The solution of compound 1 in hexane with the concentration of 10⁻⁴ M emitted 371 nm light under the excitation of 307 nm light. When gel 1 was formed in hexane, the fluorescence emission had a large red shift from 371 to 398 nm (Figure 4(a)). The fluorescence emission red shift of the gel 1 in petroleum ether also existed. The fluorescence emission of gel 1 in petroleum ether was red-shifted from 371 to 395 nm (Figure 4(d)). These results showed that the π–π stacking occurred in the sol-gel transition process when gel 1 formed in hexane and petroleum ether (11). Interestingly, the fluorescence emission of gel 1 formed from tetrahydrofuran and N,N-dimethyl formamide had no red shift compared to that of solution in the same solvent with the concentration of 10⁻⁴ M (Figure 4(b) and(c)). The solution 1 in N,N-dimethyl formamide or tetrahydrofuran all emitted 372 nm light under the excitation of 307 nm light which illustrated that gel 1 from N,N-dimethyl formamide or tetrahydrofuran was without any π–π stacking interaction. In order to further understand the π–π interaction, the concentration variable fluorescence spectra in hexane and petroleum ether were carried out and showed in Figure S3. The fluorescence spectra were all normalised. The fluorescence emission of compound 1 in hexane and petroleum ether had no shift with the solution concentration increasing. So no π–π interaction in the self-assembly process for some solvent was confirmed by these results. At the same time, the fluorescence emission spectra in non-gelation solvents such as CH₂Cl₂ and DMSO were also measured in Figure S2. The maximum emission wavelength was at 367 for CH₂Cl₂ and 377 nm for DMSO.

The nature of the hydrogen bonding of the bis-urea and imide segment was confirmed by FTIR spectrometry (Figure S4). The N–H stretching vibration bands of organogel 1 from hexane, N,N-dimethyl formamide, tetrahydrofuran and petroleum ether centred at 3322, 3305, 3305 and 3322 cm⁻¹, respectively which were typical of NH functions involved in hydrogen bonding (12). The carbonyl stretching bands of organogel 1 from hexane, N,N-dimethyl formamide, tetrahydrofuran and petroleum ether showed no difference and was all at 1636 cm⁻¹ which were assigned to hydrogen-bonded carbamate (13). This result indicated that the intermolecular hydrogen bonding was not significantly different in the gel 1 formed from different solvents. The molecular packing of the xerogel 1 from different solvents was further investigated by X-ray diffraction and showed in Figure 5. The X-ray diffraction profiles of the xerogel of 1 from tetrahydrofuran and N,N-dimethyl formamide showed a peak at 2.69° with the d-space value of 32.7 Å. However, The X-ray diffraction profiles of the xerogel of 1 from hexane and petroleum ether showed no peak at the same position. This demonstrated the self-assembly mode of organogel 1 in tetrahydrofuran and N,N-dimethyl formamide was not the same as that of hexane and petroleum ether. This result was in accordance with the SEM and fluorescence experiments results. The X-ray diffraction profiles of organogel 1 from four kinds of solvents all showed the same peak at 21.49° with the d-space value of 4.1 Å corresponding to the hydrogen bonding distance between amides (14). The weak π–π interaction only existed in the organogel from hexane and petroleum ether. The distance of a weak π–π interaction was possibly larger than a general hydrogen bonding distance. For example, Mukhopadhyay and co-worker reported valuable insights from the single crystals derived from an organogel and solution (15). The centroid-centroid distances between the two π-rings were found to be 4.316 Å. At the same time, the distance of 4.1 Å existed in organogel from four kinds of solvents. It was most reasonable that the distance of 4.1 Å interactions were assigned as intermolecular hydrogen bonds.
4. Conclusion
In summary, the organogels were prepared by a simple bisurea derivative in four commonly used solvents. The gelator was self-assembled in two different modes in four different solvents which were verified by FESEM, PL, IR and XRD experiment results. The different self-assembly modes gave rise to two different structures such as film and fibre. The different structures showed hydrophobicity with the water contact angels of 115°, 138° and 147°. The self-assembly process of low weight molecules could be tuned by solvents which provided opportunities for special functional hydrophobic surface material.

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No potential conflict of interest was reported by the authors.

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Supplemental data
Electronic Supplementary Information (ESI) available: details of FTIR experiment, images of organogel 1 in four kinds of solvents. See DOI: 10.1039/b000000x/

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