## Formation of a large-scale ordered honeycomb pattern by an organogelator *via* a self-assembly process<sup>†</sup>

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## We have developed a facile strategy to fabricate a large-scale, orderly-patterned honeycomb structure by using supramolecular self-assembly of a low mass organic molecule.

Large-scale pattern-arranged organic nano-structured materials have received much attention in recent years because of their orderly micro-morphology, controllable size and function, and good biocompatibility.<sup>1</sup> These materials are expected to be applied in the areas of micro-nano electronic devices, photonic crystals, catalysis, cell biology research, synthesis of new kinds of inorganic nano-materials and so on.<sup>2</sup> Usually, a large area and orderly grid nano-structure is fabricated from inorganic carbon or silica materials, colloidal films, surface modified hybrid nano-particles and LB film.<sup>3</sup> However, those approaches often require complicated multiple processing steps. Recently, spontaneously self-assembling structures or patterns formed by small organic molecules have also attracted much attention. Weiss, Shinkai and other research groups have published a number of important research works on organic nano/microstructured materials that form sphere, flake, fibre and helical ribbon structures through the supramolecular self-assembly of low mass molecular gelators.<sup>4</sup> Our previous work also focused on the formation of micro or nano-structured materials which can respond to different outside conditions with different modes and outcomes of self-assembly.<sup>5</sup> However, the preparation of large order grid-like nano-structured patterns through supramolecular self-assembly of small molecules was rarely reported in the previous literature. Very recently, Ajayaghosh for the first time reported the solvent-directed self-assembly of hierarchical macroporous structures in a linearly conjugated rigid  $\pi$  system.<sup>6</sup>

Here we designed and synthesized a novel gelator with the hydrophobic cholesteryl group and an adamantyl group on two sides of the molecule (Scheme 1). The middle part of the compound is a long chain composed of two amide bonds and a naphthalimide group with fluorescence properties. The hydrogen bonds of the amide groups and the hydrophobic interactions of the cholesteryl group enable the orientation and orderly arrangement of the molecules. The steric effect of the adamantyl group enables the molecules to maintain a certain spatial distance between them. Therefore, a spatially-ordered structure with high surface area could be formed by the effect of supramolecular selfassembly. The highlight of this work is that we adopt the approach of supramolecular self-assembly of organic gelators containing multiple intermolecular interactions to prepare a

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large-scale, orderly arranged hexagonal pattern. Moreover, a novel mechanism is proposed to clearly illustrate how the morphology dynamically changes from a sol to the substrate.

The exact description of the synthesis and characterization of 1 can be found in the ESI.† 1 can gelate a variety of organic solvents such as benzene, dichloromethane, ethyl acetate and dioxane (Table S1†). These gels are stable at room temperature for more than one week except that from ethyl acetate (ESI†) and form different microstructures in different solvents. For example, in ethyl acetate, a belt-like morphology with a width of around 200 nm was observed by scanning electron microscopy (SEM, Fig. 1a), while entangled soft fibers existed in benzene (Fig. 1b). Most notably, in dichloromethane, a large-scale, orderly patternarranged honeycomb structure was found with pore size of around 1  $\mu$ m (Fig. 1c and d). This morphology showed a dynamic change from a microporous pattern (Fig. 1e) to a nest structure (Fig. 1f and g) and finally a belt structure (Fig. 1h) when ethyl acetate was added to the CH<sub>2</sub>Cl<sub>2</sub> as a gelling solvent.

To find the optimum conditions for the formation of the ordered microstructure, SEM images of 1 in CH2Cl2 with different concentrations were examined. In this measurement,  $25 \text{ mg mL}^{-1}$ of 1 in CH<sub>2</sub>Cl<sub>2</sub> was heated, dissolved, cooled and left to gelate. This gel sample was then diluted to 10, 5.0, 2.5, 1.0, 0.5 and  $0.25 \text{ mg mL}^{-1}$ , respectively. Then the samples were respectively dropped on the surface of mica and dried for 24 h in vacuum. Surprisingly, the surfaces formed from different dilutions exhibited completely different morphology. For the sample with concentration of 10 mg mL<sup>-1</sup>, the surface morphology is a densely packed plane with very rare small vesicles or holes of a diameter of 300 nm (Fig. 2a) irregularly distributed on its surface. With decreasing concentration, notably once 5 mg mL<sup>-1</sup> was reached, the honeycomb surface morphology began to appear in a large area as shown in Fig. 2b with pore diameter of about 1 µm. With the concentration further diluted to  $2.5 \text{ mg mL}^{-1}$ , the surface pore structure became much more regular, forming a large area and orderly hexagonal porous structure as shown in Fig. 2c. However, in the case of  $1.0 \text{ mg mL}^{-1}$ , the pores became irregular again in both shape and size (Fig. 2d). Finally, the orderly porous structure gradually disappeared and broken vesicles were observed in some areas in the samples of concentration lower than  $0.5 \text{ mg mL}^{-1}$ 



Scheme 1 Molecular structure of 1.

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**Fig. 1** SEM images of the xerogel of **1** in ethyl acetate (a), benzene (b), dichloromethane (c and d), and with different ratios of  $CH_2Cl_2/CH_3COOCH_2CH_3$  (v/v), 70:30 (e), 50:50 (f), 30:70 (g), 10:90 (h). Scale bar: 2, 1, 10, 0.5, 1, 50, 10, 10  $\mu$ m, respectively.

(Fig. 2e–f). The above experiment indicated that the large-scale orderly hexagonal porous structure can form at a concentration around 2.5 mg mL<sup>-1</sup>, lower than the critical gelation concentration.

The concentration dependent SEM image indicated a dynamic process in the formation of the honeycomb structure. Ajayaghosh in his recent work proposed a mechanism for the formation of micro-porous structures, in which water droplets formed during the evaporation of solvent, thus resulting in the self-organization of the aggregates around the droplets. However, it is well known that the gelator is already aggregated before the gelling solvent has evaporated. What is the real structure of the wet gel and how is the structure of the wet gel transformed into the regular pattern on the substrate? These are questions that remain to be answered. In our present system, we found that the macro-porous structure formed by 1 is independent of the substrate species and the atmospheric humidity. Similar regular hexagonal morphologies were obtained on polished mica, glass and silica surfaces (Fig. S2<sup>+</sup>). Remarkably, micro vesicle structures were observed and confirmed by means of dynamic light scattering (DLS) and confocal laser scanning microscopy (CLSM) in a dispersion solution with concentration lower than CGC. Thus, the vesicle model was proposed as the mode of self-assembly and proven by SEM analysis and spectral study. At the start, a polydisperse spherical structure with a diameter of 1 µm formed in CH<sub>2</sub>Cl<sub>2</sub> because of the quasi amphiphilic character of the folded molecule 1 with a vesicle thickness of around 3 nm as determined by small angle X-ray scattering (Fig. 3a). Such spherical structures can be found at the edge area of the SEM image in a sample of 2.5 mg mL<sup>-1</sup> (Fig. 2g); and as the concentration decreases, the area where they can be found expands beyond just the edge. The CLSM image of a 5.0 mg mL<sup>-1</sup> dispersion shows a large area of regularly patterned vesicles (Fig. 2h). DLS data indicate that the homogenous distribution



**Fig. 2** SEM images of samples with concentration of (a) 10, (b) 5, (c) 2.5, (d) 1.0, (e) 0.5, (f)  $0.25 \text{ mg mL}^{-1}$  from CH<sub>2</sub>Cl<sub>2</sub>; (g) the edge part of the 2.5 mg mL<sup>-1</sup> sample and (h) CLSM image of the dispersion of 5 mg mL<sup>-1</sup>; the red points suggest a spherical structure higher than the focus plane. Scale bar: 1, 10, 5, 5, 5, 5, 3, 5 µm, respectively.

of the particles in both size and intensity is around 1-1.5 µm, matching the size of the spheres in the SEM images (Fig. S3<sup>†</sup>). During the process of volatilization of the solvent, the shell-like structure around the surface of the solvent was ruptured due to the pressure difference between the inside and outside of the vesicle. The balance between dissolution and nucleation was thus disturbed because gelation via fibrous or spherulitic growth depends on the degree of supersaturation. The molecules then moved to the more diluted area and reaggregated (Fig. 3b and ESI<sup>†</sup>). With further evaporation of the solution, when the liquid's surface reached the bottom of the vesicles, the molecules moved from the upper part of the vesicles and aggregated in the gap between adjacent vesicles to form the hexagonal grid-like pattern (Fig. 3c). It was noted that in the case of multilayer structure, the micro pores were inclined to form a crossbedded pattern (Fig. 3d). From our experiments, it is obvious that the concentration of the initial solution plays an important role in the formation of this regular hexagonal pattern. The pattern could be obtained only if the vesicles were closely packed and arranged in an orderly manner. Therefore in the more diluted samples or on the edge of the film, we can find scattered or broken vesicles because there weren't enough molecules to fill in the gap between the vesicles during the process of evaporation. On the other hand, the much more concentrated samples result in the rapid collapse of the crowded vesicles due to collision with one another, which is unfavourable to the formation of regular porous morphology. This obvious dynamic change and regular pattern of the morphology in the present system are quite different from those of the fibrous gels previously studied.<sup>4</sup> In our opinion, the quasi amphiphilic molecule 1 acts as a self-template and the balance between dissolution and nucleation resulting from multiple intermolecular interactions promotes the formation of the regular honeycomb pattern.

To verify the nature of the intermolecular interactions constituting the self-assembly process, the absorption and fluorescence spectra were studied (Fig. S5†). The maximum absorption of **1** located at 435 nm in CH<sub>2</sub>Cl<sub>2</sub> solution shows no wavelength change with increase in concentration. The emission of **1** was positioned at 529 nm in CH<sub>2</sub>Cl<sub>2</sub> solution (8.5 mg mL<sup>-1</sup>) and was red shifted to 537 and 557 nm for the gel (25 mg mL<sup>-1</sup>) and solid state, respectively. The comparison of the absorption and emission spectra of **1** in the solution, gel and solid state indicated the weak  $\pi$ - $\pi$  interaction of the aromatic group in the aggregated state.

Temperature-dependent FTIR spectra provide valuable information concerning the thermal stability of molecular structures from hydrogen-bonded materials.<sup>7</sup> Temperature dependent FTIR spectra of gel 1 in the temperature range of 40-30 °C were collected in order to ascertain the driving force behind the formation of the ordered structure (Fig. 4 and ESI<sup>†</sup>). Tentative band assignments are listed in Table S2.† It is important to compare the IR spectral change in the N-H and C=O stretching regions related to hydrogen bonds. In the transformation process of gel to sol, the intensity of the bands at 3220–3380 ( $\nu_{sNH}$ ) increased and the band at 1691 cm<sup>-1</sup> ( $\nu_{C=O}$ ) decreased with temperature decreasing from 40 to 30 °C. The plots of temperature vs. the intensity of  $\nu_s$  at 3315 and 1693 cm<sup>-1</sup>, respectively, show a drastic change in intensity in the temperature range between 32.5 and 36.5 °C with the steepest slope located at 34.5 °C, matching well with the  $T_g$  value. This may be the first application of two-dimensional IR to determine the gel-sol transformation point in a supramolecular gel system.



**Fig. 3** Schematic representation of the mechanism of formation of a regular pattern; (a) vesicle structure; (b) arrangement of the vesicles in solution, the red arrow indicates the direction of molecule movement with evaporation; formation of the porous pattern on (c) the first layer and (d) multilayer.

The IR analysis indicates that ordered hydrogen bonds between the amide groups in 1 form at temperatures lower than 34.5 °C at CGC. As a result, 1 can gelate solvent to form gel. Furthermore, from the analysis of the sequence order derived from 2D IR spectra (Fig. 4c,d, and ESI<sup>†</sup>), it can be seen that the sequence order for the formation of the aggregation is as follows:  $-CO-CH_2-CH_2-NH-$  (H-bonding formation)  $\rightarrow$  cholesteryl (orderly arrangement)  $\rightarrow$  CH<sub>2</sub>Cl<sub>2</sub> (fluidity prevented)  $\rightarrow$ naphthyl ( $\pi$ - $\pi$  stacking)  $\rightarrow$  adamantane (intermolecular space inserted). It is evident that the hydrogen bonding between amides and the hydrophobic interaction between cholesteryls play important roles in the formation of the regular aggregation.

The molecular packing of **1** in the xerogel state from  $CH_2Cl_2$  was further investigated by small angle X-ray scattering and powder X-ray diffraction (Fig. S6†). The scattering patterns of **1** xerogel show a series of diffraction peaks at 3.03, 1.54, 1.00 nm, indicating a lamellar structure. Molecular modeling suggested that the self-assembly of the **1** dimer with a folded conformation had a length of approximately 3.0 nm. Considering the contribution of the intermolecular H-bonding, this result supports the assumption



**Fig. 4** (a) Temperature-variable IR spectra in N–H stretching region and (b) the temperature dependent absorbance changes at 3315 and 1693 cm<sup>-1</sup> in the temperature range of 40–30 °C (0.5 °C interval). (c) and (d) are the 2D synchronous and asynchronous spectra, respectively, in the N–H stretching region in the temperature range of 36.5–32.5 °C (warm colors represent positive intensities while cold colors represent negative ones).

that this ordered structure is generated through intermolecular H-bonding with the hydrophobic parts of molecules oriented toward the surface of the layer.

In conclusion, we adopt the approach of supramolecular selfassembly of an organic gelator containing multiple intermolecular interactions to prepare a large-scale, orderly-patterned microarray. The orderly honeycomb-patterned films could be easily fabricated by casting a solution of gelator onto solid substrates followed by evaporation. The atmospheric humidity or substrate material has no crucial effect on the resulting system. A judicious thermodynamic balance among the main driving forces for selfassembly, namely hydrogen bonding, hydrophobic and  $\pi$ ... $\pi$ interaction, rationalized in terms of the solubility and cooperative self-assembly of molecules during the process of evaporation was highlighted. The vesicle model was proposed as the mode of assembly and proven by SEM, DLS analysis and spectral study. This approach may open up new possibilities for the preparation of large-scale, orderly structured materials through the supramolecular self-assembly of low mass organic molecules, which will be extremely useful in a variety of biomedical applications, such as in DNA chips, protein and cellular microarrays.

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