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ARTICLE

A supramolecular gel based on a glycosylated amino acid derivative with the property of gel to crystal transition

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Here we report the generation of a novel gelator from a glycosylated amino acid derivative, which contained three structural units, an aromatic residue, a carbohydrate moiety and *tert*-butyl group in a single molecule. These structural units can promote the supramolecular self-assembly of this gelator in both aprotic and protic solvents via coordinated π-π stacking, multiple hydrogen binding and van der Waals interactions. More importantly, due to their non-equilibrium natures, the organogels formed in DCM, chloroform and ethanol can undergo gel to crystal transition in storage, driven by unbalanced gelator-gelator and solvent-gelator interactions. In this process, the gelators were firstly trapped in kinetically favorable gel state, and then transferred into a more thermodynamically stable crystal state upon ageing, with the generation of microcrystals in different morphologies.

Introduction

Low-molecular-weight gelator (LMWG) was an interesting new class of small molecules that can form reversible supramolecular gels in solvents via non-covalent hydrogen bonding, van der Waals interactions and π-π stacking.[1, 2] With the development of advanced soft nanomaterials over the past few years, there has been growing interest in the design and synthesis of LMWGs from a wide spectrum of organic molecules[3-6], such as cholesterols,[7] carbamates,[8] carbazoles,[9, 10] amino acids[11-13] and carbohydrate derivatives[14, 15] for the application in chemical sensors, drug delivery, enzyme immobilization and solar cells.[16-18]

In spite of the large library of LMWGs, there is still a demand for the development of novel gelator from different origins. Among them, amino acids and carbohydrates attracted particular interests for the preparation of LMWGs with varied molecular structures and self-assembling properties, owing to their high biocompatibility, versatile molecular structure, and intrinsic chirality and capability for supramolecular interactions. For example, a number of peptide-based LMWGs have been prepared from linear or branched peptide molecules with adjustable self-assembling properties in different organic

solvents,[19-24] and a series of sugar-based gelators containing varied sugars and hydrophobic groups were made with special self-assembling behaviours in both protic and aprotic solvents.[25-29]

However, the study for the development of novel organo/hydrogelators from glycosylated amino acid is still underexplored. Recent studies have demonstrated that the integration of amino acid/peptide scaffold containing appropriate hydrophobic group and saccharide with inherent molecular chirality and multiple hydrogen binding property held great promise for the generation of new LMWG and supramolecular gel with improved structural diversity and functionality.[30] Previously, Xu and co-workers developed biocompatible hydrogelators from peptide-monosaccharide conjugates, which showed improved wound healing effects on mice,[31] Hamachi et al. displayed the preparation of ambidextrous gelators from glycosylated amino acids, which can self-assemble efficiently in both water and organic solvents,[32] and we also demonstrated that the conjugation of an amino-sugar with an amino acid/peptide derivative can generate an novel hydrogelator with multi-functionalities.[33]
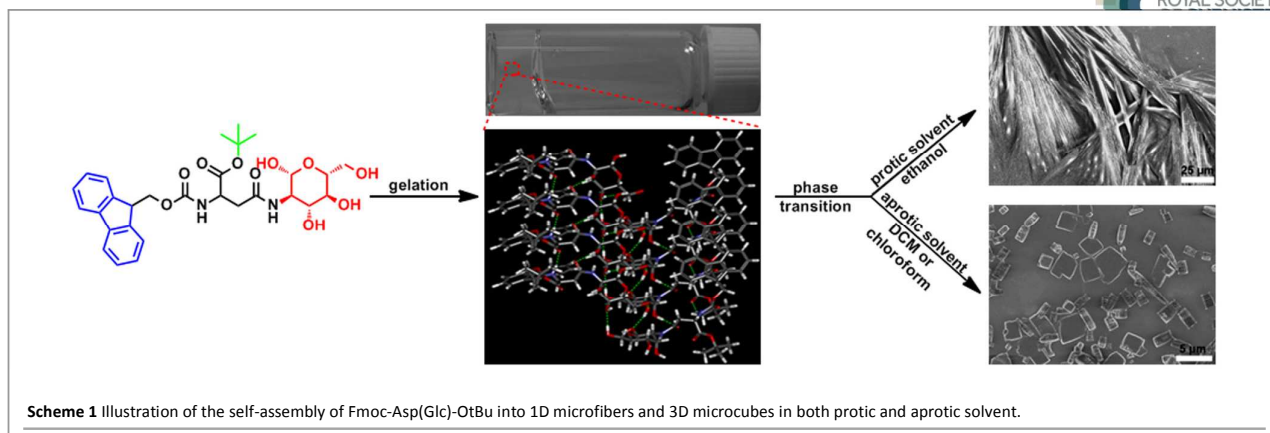
Encouraged by the successful work described above, we sought to design and synthesize a new gelator based on a glycosylated amino acid derivative, and examined its potential for supramolecular self-assembly in different solvents. As shown in Scheme 1, this molecule possessed three basic structural units, including an aromatic moiety (i.e., 9-fluorenylmethoxycarbonyl group), a carbohydrate head-residue (i.e., D-glucosamine) linked to the side chain of Fmoc-Asp-OH and a *tert*-butyl (Boc) group at the C terminal of this glycosylated amino acid derivative. These structural units can promote supramolecular self-assembly of this molecule in different solvents via π-π stacking, multiple hydrogen binding

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Scheme 1 Illustration of the self-assembly of Fmoc-Asp(Glc)-OtBu into 1D microfibers and 3D microcubes in both protic and aprotic solvent.

and van der Waals interactions.

During our research, we found that this molecule exhibited high selectivity towards the polarity of solvents for supramolecular self-assembly, and formed stable organogels in dichloromethane (DCM), chloroform, ethanol, 2-propanol and *n*-butanol, due to balanced gelator-gelator and solvent-gelator interactions.[34, 35] Moreover, the self-assembled organogels formed in DCM, chloroform and ethanol, respectively, can also undergo gel to crystal transformation in storage, because of the non-equilibrium nature of these self-assembled gels. Recent studies indicated that gelation and crystallization were orthogonal and time-resolved processes under non-equilibrium conditions,[36, 37] in which crystallization occurred over a period of hours to days, due to the presence of an energetically unfavourable nucleation step, however gelation often took place at a shorter time interval.[38, 39] Therefore during the supramolecular self-assembly process, the gelators in suitable solvents were firstly trapped in kinetically favorable gel state, and then transferred into a more thermodynamically stable crystal state upon ageing.[40-43] Since supersaturated condition was the common feature of driving force for supramolecular gelation and crystallization, a study of gelation system with phase transition property would be advantageous to gain insight into the relationship of supramolecular gelation and crystallization, and helpful for the design of new gelator with controlled self-assembling property.[44, 45]

Experimental Section

Materials and methods

Fmoc-Asp-OtBu was provided by GL Biochem (Shanghai) Ltd. D-glucosamine was purchased from Sigma-aldrich. All the other compounds were obtained from J&K Chemicals and used without further purification. ^{1}H NMR spectra were obtained on a Unity Inova 400 by using DMSO-d_6 as the solvent. CD spectroscopy study was carried out on a JASCO J-810 spectrometer. LC-MS analysis was performed on an Agilent 6120 Quadrupole LC/MS system with an ESI resource. Transmission electron micrograph (TEM) and scanning electron micrograph (SEM) images were recorded on a Tecnai G220 transmission electron microscope and a Hitachi S-4800,

respectively. Optical microscopy image was taken on an Olympus IX71 optical microscope. Fourier transform infrared spectroscopy (FTIR) characterization was performed on a Perkin-Elmer spectrophotometer. Rheological study was taken on a Thermo Scientific HAAKE RheoStress 6000 rheometer.

Sythesis of Fmoc-Asp(Glc)-OtBu.

Fmoc-Asp-OtBu (4.11 g, 10 mmol), NHS (1.51 g, 12 mmol) and DIC (1.38 g, 12 mmol) were dissolved in 80 mL DMF, and reacted at room temperature for 8 h. Then a solution of D-glucosamine (2.15 g, 12 mmol) in the mixed solvent of water and DMF was added, and the resulted solution was stirred at room temperature for another 24 h. After evaporation of solvent, the residues were re-dissolved in water and acidified with HCl to pH 2-3. The white precipitates were collected and purified by column chromatography over silica gel using chloroform/methanol as the eluents to afford the final product (yield: 78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ7.96-7.89 (m, 4H), 7.72-7.71 (d, 3H), 7.43-7.23 (m, 5H), 6.43-6.23 (d, 1H), 4.93-4.90 (t, 2H) 4.59-4.24 (m, 6H), 3.63-3.50 (m, 5H), 3.14-3.07 (d, 1H), 2.60-2.57 (s, 2H), 1.38 (s, 9H); MS: calcd M=572.50, obsd (M+H)[+]=573.2.

TEM and SEM measurements

The gel was placed on a single-crystal silica plate or a carbon-coated Cu grid and dried under vacuum. The sample for TEM study was stained with uranyl acetate (2.0 % (w/v)). The silica plate loaded with gel was further coated with a thin layer of platinum before SEM measurement. Then TEM and SEM images were recorded on a Tecnai G220 transmission electron microscope and a Hitachi S-4800, respectively.

Rheological measurements

Rheological test was operated on a Thermo Scientific HAAKE RheoStress 6000 rheometer with a 20 mm parallel plate, and 0.2 mL of organogel was used for this test. The dynamic strain sweep test was run from 0.1 to 10% with frequency at 6.282 rad/s at 25 ℃. The dynamic frequency sweep test was run from 200 rad/s to 0.1 rad/s, and a strain at 0.4% was used to ensure the linearity of dynamic viscoelasticity.

FTIR analysis

FTIR spectra of organogel and microcrystal in DCM were collected on a Perkin-Elmer spectrophotometer by loading the samples into a KBr cuvette. The sample was prepared by using deuterium DCM as solvent.

Wide angle X-ray diffraction

The X-ray diffraction patterns were obtained by a Shimadzu XRD-6000 diffractometer with a Ni filter and Cu$_{K\alpha}$ (λ=1.54056 Å, voltage=40 kV, current=40 mA). Each sample was scanned over the range from 5° to 30° with a step size of 0.026° and a count time of 5 seconds per step.

Molecular modelling

The ground-state geometry of gelator was optimized by using Hartree-Fock Austin Model 1 (AM1) method. And the geometric optimizations of four-molecule clusters of gelator and its packing model were performed using the DREIDING force field as implemented in the molecular modelling programs (Accelrys Inc., San Diego, CA, USA).
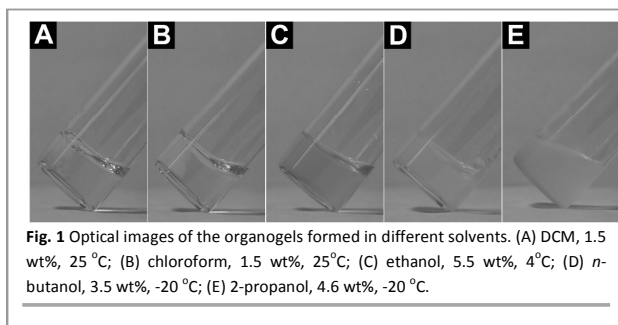
Results and discussion

Design and synthesis

The formation of Fmoc-Asp(Glc)-OtBu was achieved by treating a solution of Fmoc-Asp-OtBu in *N,N'*-

Scheme 2 Synthetic route for the preparation of Fmoc-Asp(Glc)-OtBu.
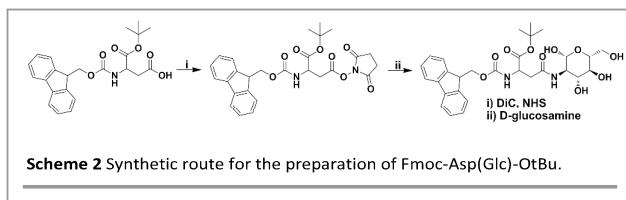
dimethylformamide (DMF) with *N*-hydroxysuccinimide (NHS) and *N,N'*-diisopropylcarbodiimide (DIC), followed by the dropwise addition of a aqueous solution of D-glucosamine (Scheme 2). In this process, the carboxylic acid group on the side chain of Fmoc-Asp-OtBu was firstly activated by NHS with the presence of DIC, and then coupled with the amine group of D-glucosamine to afford final product. After removal of reaction solvent, the product was purified by flash column, and then characterized by NMR and MS, both of which gave satisfactory analysis data corresponding to its expected molecular structure (Fig. S1 and S2). Overall, the integration of a partially protected amino acid and a amino sugar proved to be an efficient method for the preparation of a glycoamino

Fig. 1 Optical images of the organogels formed in different solvents. (A) DCM, 1.5 wt%, 25 °C; (B) chloroform, 1.5 wt%, 25°C; (C) ethanol, 5.5 wt%, 4°C; (D) *n*-butanol, 3.5 wt%, -20 °C; (E) 2-propanol, 4.6 wt%, -20 °C.

acid with regiospecific β-*N*-linkage.

Gelation test

After obtaining this compound, we tested its gelation property in various solvents such as, hexane, toluene, xylene, chlorobenzene, dichlorobenzene, ether, ethyl acetate, isobutanol, *n*-butanol, 2-propanol, ethanol, DCM, chloroform, methanol, water and DMF, ranging from protic to aprotic solvent and polar to apolar solvent. Typically, an appropriate amount of this compound was added to a sealed test tube containing one kind of organic solvent and heated gently until the sample was dissolved completely. After allowing the solution to cool to lower temperature (e.g., 25, 4, or -20 °C) for different periods of time, we examined the state of the sample by turning the tube upside down. If there was no gravitational

Table 1 The gelation ability of Fmoc-Asp(Glc)-OtBu in various organic solvents

Solvent	State[a]	CGC % wt	GT[b] at CGC (°C)
DCM	G	1.5	25
chloroform	G	1.5	25
ethanol	G	5.5	4
2-propanol	G	4.6	-20
n-butanol	G	3.5	-20
chlorobenzene	G	4.5	25
o-dichlorobenzene	G	4.5	25
m-dichlorobenzene	G	5	25
H$_2$O:ethanol (75:25)	G	2.5	25
H$_2$O:ethanol (60:40)	G	2.7	25
H$_2$O:ethanol (40:60)	G	3.7	25
H$_2$O:ethanol (25:75)	G	4.7	25
isobutanol	S	—	—
methanol	S	—	—
DMF	S	—	—
hexane	I	—	—
toluene	I	—	—
xylene	I	—	—
ether	I	—	—
ethyl acetate	I	—	—
H$_2$O	I	—	—

[a]G=gel, S=soluble, I=insoluble; [b]GT=gelation temperature

flow, the sample was termed as gel, and classified as G in Table 1. By following this procedure, we examined the gelation property of Fmoc-Asp(Glc)-OtBu in different solvents, and the results were summarized in Table 1. The compound can gel efficiently in DCM, chloroform, chlorobenzene, *m*-dichlorobenzene and *o*-dichlorobenzene at room temperature by forming translucent organogels (Fig. 1A, 1B and S3), while it afforded opaque gels in ethanol, 2-propanol and *n*-butanol, respectively, at much lower temperatures around 4°C or -20°C in 24 h (Fig. 1C, 1D and 1E). Their critical gelation concentrations were at 1.5, 1.5, 4.5, 4.5, 5.0, 5.5, 4.6 and 3.5 wt%, individually. In addition, it also exhibited the tendency to form opaque gels in the mixed solvents of water and ethanol, and the minimum gelation concentrations were highly dependent on the composition of mixed solvents (Table 1 and
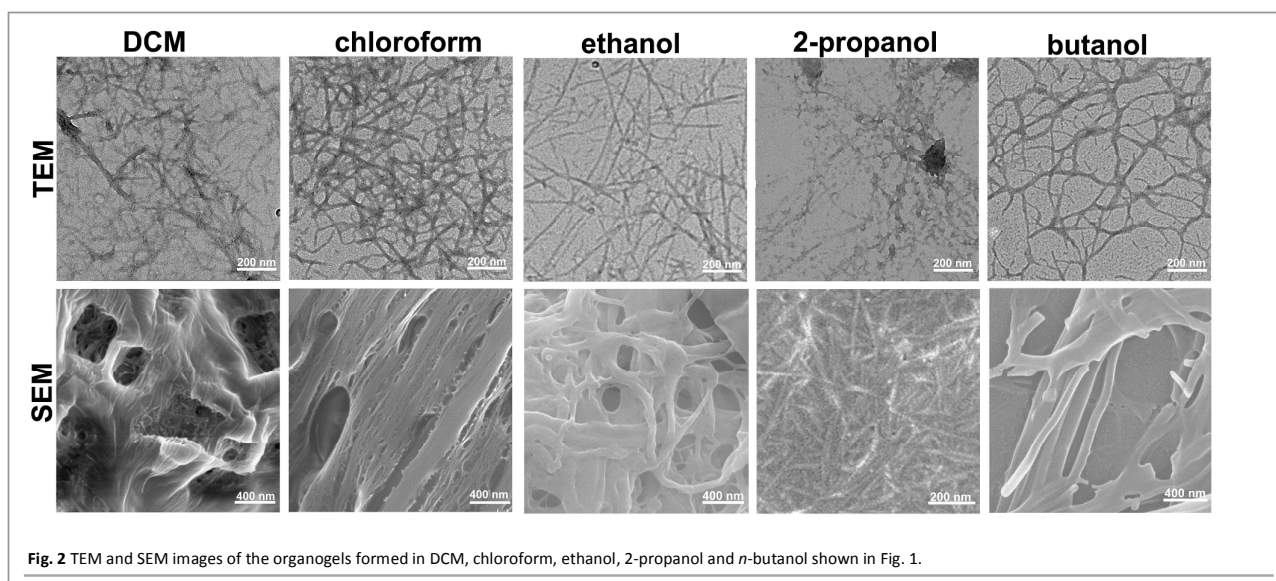
Fig. 2 TEM and SEM images of the organogels formed in DCM, chloroform, ethanol, 2-propanol and *n*-butanol shown in Fig. 1.

Fig. S3). However, this compound was insoluble in hexane, ether, toluene, xylene, ethyl acetate and water even with gentle heating (Fig. S3 and S7), due to the polarity of these solvents, but dissolved very well and formed homogenous solution in isobutanol, methanol and DMF. This study indicated that Fmoc-Asp(Glc)-OtBu can work as an effective gelator to form supramolecular gels in both protic and aprotic solvents, and its gelation property was dependent on the polarity of solvent.

Morphology

In order to obtain further insight into solvent effect on the self-assembling property of this gelator, we used transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to investigate the nano- and micro-scale structures of these gels formed in different solvents. The TEM images shown in Fig. 2 revealed that the organogels in DCM and chloroform consisted of individual nanofibers which further aggregated together to form thick fiber bundles with diameters of 20 nm and 22 nm, respectively. However, the gel in ethanol displayed the formation of well-defined nanofibrous structures tens of micrometers in length and 18 nm in width. And we also identified the formation of nanofibrous-like structures in the organogels of 2-propanol, *n*-butanol, chlorobenzene, *m*-dichlorobenzene, *o*-dichlorobenzene and mixed solvents of water and ethanol (Fig. S4-6 and S8-11). In addition, SEM analysis confirmed the morphological features of fibrous structures self-assembled from Fmoc-Asp(Glc)-OtBu, which physically cross-linked each other to form entangled bundles and immobilize organic solvents for the formation of organogels. However, structural differences among the gels in different solvents were obviously observed at micro-scale. As evidenced by SEM images shown in Fig. 2, the gel in DCM revealed the formation of entangled fibres and bundles which worked as the main microstructures to support the formation of organogel. And the gel system in chloroform and ethanol showed predominantly interwoven fibrous structures which

aggregated together to form gel network. In addition, we can confirm the formation of microstructure networks in the organogels of 2-propanol and *n*-butanol, which supported the
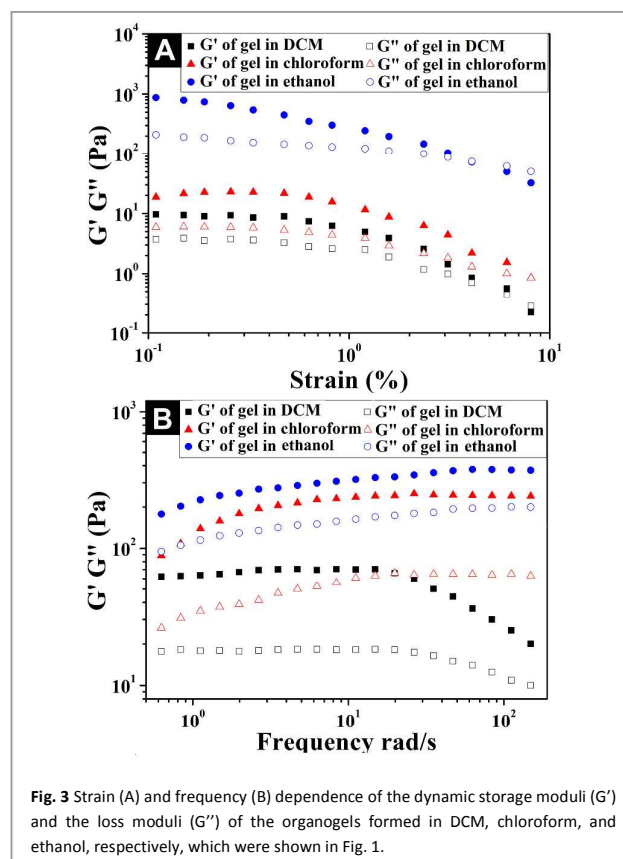

Fig. 3 Strain (A) and frequency (B) dependence of the dynamic storage moduli (G')
and the loss moduli (G'') of the organogels formed in DCM, chloroform, and
ethanol, respectively, which were shown in Fig. 1.

formation of organogels. This study demonstrated that solvent polarity played an important role in regulating the self-assembling behaviour of gelator to form nanostructures in different morphologies.
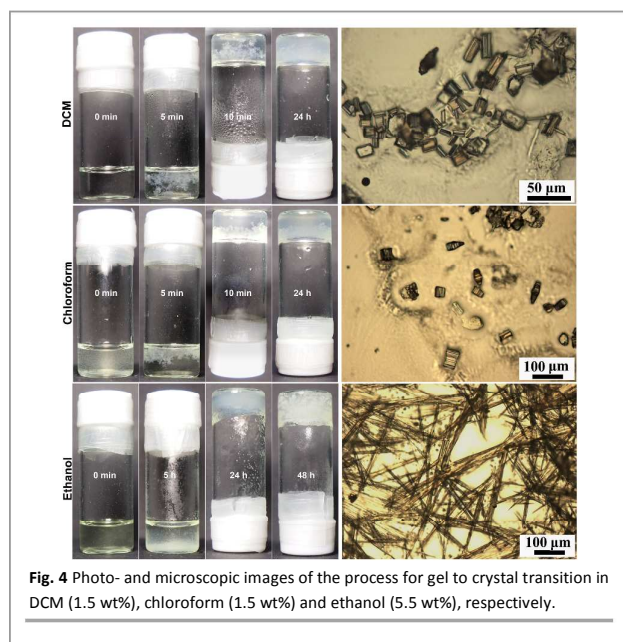
Fig. 4 Photo- and microscopic images of the process for gel to crystal transition in DCM (1.5 wt%), chloroform (1.5 wt%) and ethanol (5.5 wt%), respectively.

Rheological studies

With the application of oscillatory rheology, we investigated the viscoelastic property of organogels in different solvents. The viscoelastic behavior of a gel was determined by two key parameters, such as storage modulus (G') and loss modulus (G''), which represented the ability of a deformed gel to return to its original geometry and the tendency of a material to flow under exerted stress. For a gel material, G' is greater than G'', and G' shows low dependence on oscillatory frequency, signifying the dominant elastic behavior of the gel. From the strain and frequency sweep profiles of the organogels in different solvents shown in Fig. 3, we found that the storage moduli (G') of the organogels in chloroform and ethanol were much higher than their loss moduli (G'') within investigated oscillating strain (0.1-10%) and frequency limit (0.1-200 rad/s), confirming the formation of stable organogels and their dominantly elastic properties (Fig. S4-6 and S8-11). However, the organogel formed in DCM was mechanically weaker than that formed in chloroform and ethanol, as exemplified by the low G' value (61 Pa) and high dependence of G' value on the oscillatory frequency from 20-200 rad/s. Its abrupt decrease of storage moduli (G') within 20-200 rad/s was due to the fact that the mechanical strength of the gel matrix in DCM was not high enough to resist the exerted shear stress, with the tendency to undergo gel-sol transition under high oscillatory frequency.[46] The relatively high mechanical strength of organogels in chloroform and ethanol could be due to the formation of compact microstructure networks observed in Fig. 2.

Phase transition

In addition, we also observed that the organogels in DCM, chloroform and ethanol were metastable, because they exhibited a tendency to transfer into microscopic crystals
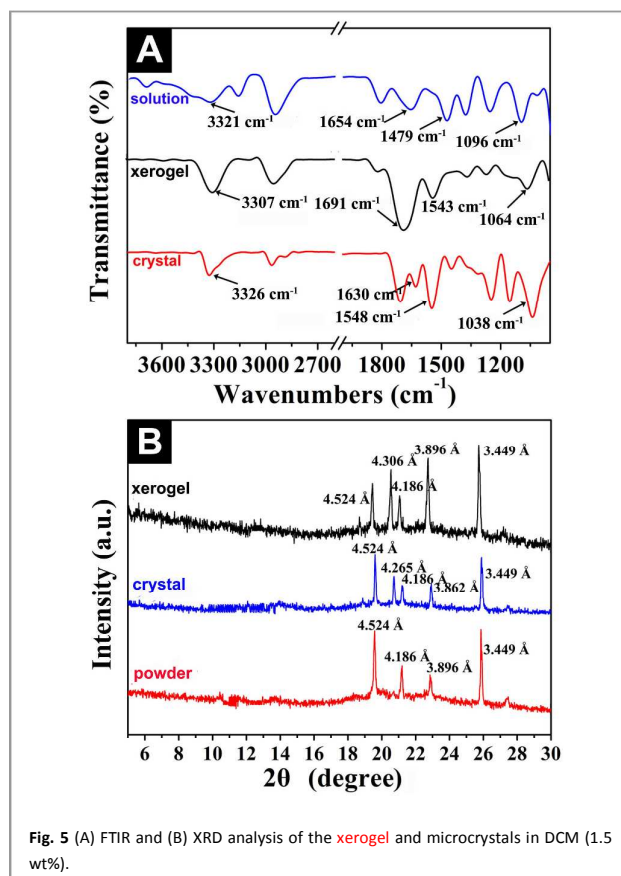
Fig. 5 (A) FTIR and (B) XRD analysis of the xerogel and microcrystals in DCM (1.5 wt%).

during storage. Typical gelation and phase transition processes of Fmoc-Asp(Glc)-OtBu in these solvents were shown in Fig. 4. In the system of DCM and chloroform, when the hot transparent solutions were cooled at room temperature, white precipitates firstly appeared at the top of the solutions in 5 min, which further aggregated together until the lower solution changed into semi-transparent gel in 10 min, and the millimetre-sized aggregates were trapped inside the gels. From the SEM images shown in Fig. S12 and S14, we confirmed that these firstly formed precipitates belonged to irregular aggregates, not crystals. Afterwards, the surrounding part of the gels changed gradually from semi-transparent to translucent in 24 h. From microscopy and SEM images in Fig. 4, S13 and S15, we confirmed the generation of significant amount of micrometre-sized crystals within gels through gel to crystal transition, which should be responsible for the cloudiness of the gels. However, for the system in ethanol, when the solution was cooled at 4°C, it gradually turned into suspension with the generation of precipitates deposited at the bottom of tube (Fig. S16). Later, the surrounding solution transformed to a translucent gel and an opaque gel gradually in 48 h, with the generation of microcrystalline fibres inside the gel (Fig. S17). These results demonstrated that there existed a phase transition from gel to crystal after the formation of gels in DCM, chloroform and ethanol, and the morphologies of microcrystals formed in this process were dependent on the polarity of the solvents.
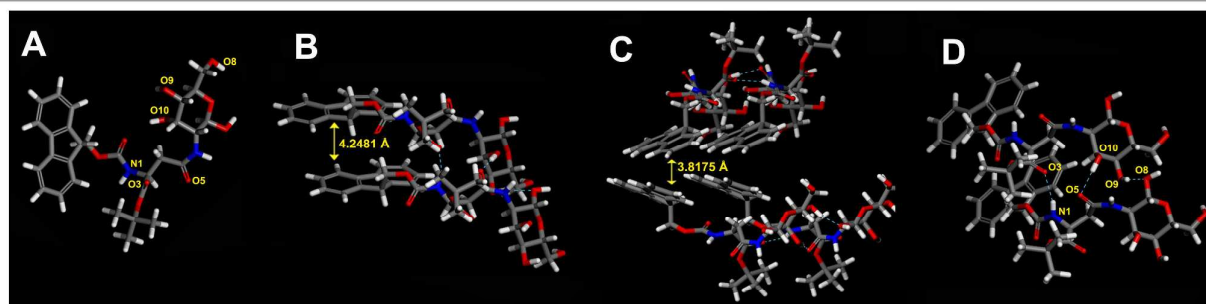
Fig. 6 (A) The molecular conformation of Fmoc-Asp(Glc)-OtBu with atom labelling for indicating the presence of hydrogen bonding interactions on these atoms. Optimized structures of molecule models of Fmoc-Asp(Glc)-OtBu showing the presence of (B) π-π stacking interaction with distance at 4.2481 Å, (C) edge-to-face interaction between two planar aromatic groups with distance at 3.8175 Å, and (D) the extended intermolecular hydrogen bond between glucose and amino acid (C: gray, H: white, N: blue, O: red). The molecular model for the supramolecular interaction of Fmoc-Asp(Glc)-OtBu was obtained from molecular mechanical (MM) calculation.

FTIR and XRD studies

With the purpose of elucidating the intermolecular interactions and molecular packing modes of the gelators in gel and microcrystal, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) experiments were carried out by using the organogel formed in DCM as an example. Fig. 5A showed the FTIR spectra of Fmoc-Asp(Glc)-OtBu at different states (e.g., solution, xerogel and crystal). It was obvious that the spectrum of the xerogel was very similar to that of the crystal in DCM, indicating that the two forms existed in the same molecular interaction patterns. As shown in Fig. 5A, the three main bands at 3328, 1651, 1536 cm^{-1} in DCM solution, corresponded to the non-hydrogen-bonded NH band and the amide I and II bands frequencies,[47] which shifted slightly to 3307, 1691, 1543 cm^{-1} for the xerogel, and 3326, 1704, 1548 cm^{-1} for the crystal, respectively, which indicated the presence of hydrogen bonding interactions between the carbonyl group and amide NH group in both gel and crystal. In addition, the stretching vibration of glycosyl ring appeared at 1095 cm^{-1} in solution and shifted to 1064 cm^{-1} and 1038 cm^{-1}, respectively, after the formation of gel and crystal, which implied that the hydroxyl groups also played important role in the supramolecular self-assembly of gelator via hydrogen-bonding interactions.[48] A transmittance band at 2967 cm^{-1} was ascribed to the CH$_3$ vibration of Fmoc-Asp(Glc)-OtBu in DCM solution, and shifted to 2953 and 2964 cm^{-1} after gelation and crystallization, due to the decreased vibration and enhanced organization of the *tert*-butyl groups via van der Waals interaction.[49] Therefore, the observed spectroscopic data suggested the involvement of both hydrogen bonding and hydrophobic interaction for the formation of ordered structure.

The molecular packing modes in different states (e.g., xerogel, crystal and powder) were further analyzed by XRD. The XRD pattern of the gel was almost identical to the result of the crystal, but different from that of the powder, confirming the similar molecular packing mode of the gelator in both gel and crystal states. As shown in Fig. 5B, the XRD traces of xerogel and crystal showed main peaks in the angle region (2θ values, 19.5°, 20.6°, 21.1°, 22.7°, and 25.7°), which corresponded to *d* values of 4,524 Å, 4.306 Å, 4.186 Å, 3.896 Å, and 3.449 Å, respectively.

Molecular modeling

With reference to the molecular structure model illustrated in Fig. 6, the peak with a *d* spacing of 4.306 Å in XRD was assigned to a vertical spacing of two stacked aromatic rings for π-π stacking interaction in gel state, and the distance was decreased to 4.265 Å after gel to crystal transition, while another peak at 22.9° with a *d* spacing value of 3.896 Å in gel corresponded to a separation distance between two planar aromatic groups for edge-to-face interaction, and the distance was shortened to 3.86 Å in crystal, indicating the occurrence of glide movement of the molecule during gel to crystal transition which was resulted from solvent and gelator interaction.[50] These data indicated that aromatic-aromatic interactions worked as a significant driving force for supramolecular gelation and subsequent phase transition. The structural model was also characterized by the presence of intermolecular hydrogen bonds between the NH group and C=O (N$_1$H¨O$_3$, 2.17 Å), and between the hydroxyl groups of glucose residues (O$_{10}$H¨O$_5$, 1.95 Å; and O$_9$H¨O$_8$, 1.98 Å). On the basis of FTIR and XRD analysis, the organogel of Fmoc-Asp(Glc)-OtBu was found to be stabilized by a combination of π-π stacking and hydrogen bonding interactions.

Conclusions

In summary, we have designed and synthesized a new gelator from a glycosylated amino acid derivative, which contained three structural units, an aromatic group, a carbohydrate moiety and alkyl residues in a single molecule. These structural units can promote the supramolecular self-assembly of this gelator in both aprotic and protic solvents via π-π stacking, multiple hydrogen binding and van der Waals interactions. More importantly, for the systems in DCM, chloroform and ethanol, the organogels can undergo phase transition from gel to crystal, induced by coordinated solvent and gelator interaction.[50] Although further studies is still required to elucidate the process of gel-crystal transition, we hope this study introduces a new gelation system with phase transition property, which would be helpful for investigating the relationship of supramolecular gelation and crystallization during the supramolecular self-assembly process of gelator.

Acknowledgements

Notes and references

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TOC
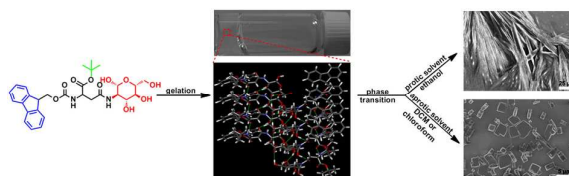
A novel gelator from a glycoamino acid derivative was discovered to perform supramolecular self-assembly and gel-crystal transition upon ageing.