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COMMUNICATION

A novel multi-stimuli responsive gelator based on D-gluconic acetal and its potential applications

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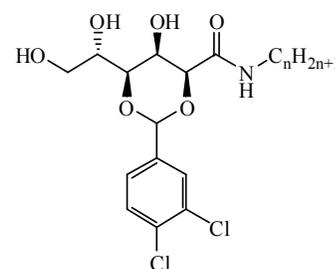
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We construct a simple-structured super gelator with multi-stimuli responsive properties, among which anion responsiveness follows Hofmeister series in a non-aqueous system. Versatile applications such as being rheological and self-healing agents, waste water treatment, spilled oil recovery and flexible optical device manufacture are integrated to the single organogelator, which was rarely reported.

Major achievements reached in supramolecular science have triggered eager search for the next-generation functional materials, especially stimuli-responsive soft matter, which could facilitate development of adaptive multifunctional materials applicable to emergent technologies.¹ As a class of stimuli-responsive soft matter, supramolecular gels are able to respond to a variety of chemical (pH change, ionic, etc.)² and physical (light, sonication, mechanical force, etc.)³ stimuli and often exhibit a reversible phase transitions due to reversible non-covalent interactions. Of particular interest is the construction of low-molecular-weight gelators (LMWGs) with multi-stimuli responsive properties, because responses to multi stimuli would give rise to more flexibility for the creation of smart materials.⁴ However, gelators with multi-stimuli responsive properties are rare because it requires a consummate integration between the gelator's structures and the environment of the noncovalent interactions.⁵ Furthermore, though different types of LMWGs with different potential applications such as self-healing,^{3a,6} waste water treatment,⁷ spilled oil recovery,⁸ flexible optical device manufacture⁹ etc. have been developed, realization of multiple applications based on one single LMWG has been rarely reported.^{7a,10} Therefore, integrating multi-stimuli responsiveness and versatile applications into a single material is a real challenge.

Carbohydrates and amides that are capable of forming hydrogen bonding have been widely used as building blocks to create a variety of molecularly assembled structures.¹¹ Meanwhile,



Gn n=2, 4, 8, 12

Figure 1 Chemical structures of gelators Gn.

incorporation of aromatic and hydrophobic segments invokes π - π stacking and van der Waals interactions, respectively, in supramolecular aggregates.¹² Inspired by the progress of research work in the area of sugar-derived LMWGs,¹¹ we decided to design structurally simple new compounds that contain the above moieties (hydrogen bonding groups, aromatic part and alkyl chain) to obtain excellent gelators. Herein a series of novel D-gluconic acetal-based gelators (Gn) with a flexible alkyl chain (Figure 1, Supporting Information Scheme S1) were synthesized. It was found that G8, as a super gelator^{5a,b} (critical gelation concentrations (CGCs) below 0.1wt%) exhibited interesting multi-stimuli responsiveness and versatile applications. For example, G8-based gels displayed chemical (base, anions) and physical (ultrasound, mechanical) stimuli and controllable phase transitions. In particular, anion responsiveness was found to follow Hofmeister series in a non-aqueous system, which was rarely recorded.¹³ Applications in versatile fields were demonstrated for G8 such as being rheological and self-healing agents, waste water treatment, spilled oil recovery and flexible optical device manufacture.

First, the gelation abilities of Gn were investigated. Nineteen different solvents including 2 mixture solvents were employed to evaluate their gelation abilities (Supporting Information, Table S1). In general, G2 and G4 can gel 5 and 11 solvents respectively, while G8 and G12 with longer alkyl chains can gel 15 of the 19 solvents. These results indicated that the length of alkyl chains had a profound effect on the gelation abilities of these compounds. It was shown that G8 can gel a wide range of organic solvents from protic/aprotic, polar/apolar solvents to mixture solvents.

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Particularly, it can gel chloroform and the mixture solvent of NMP/H₂O (1:1; v/v) at room temperature (RT). The CGC values for some aprotic solvents (hexadecane, toluene, o-dichlorobenzene and chloroform) were lower than 0.1wt%. Interestingly, the gel-sol transition temperatures (T_{gel}) in chloroform gels prepared by the two different methods (RT and heating-cooling) were both higher than the boiling point of chloroform. Furthermore, the G8-based gels formed with aprotic solvents such as higher hydrocarbon solvents and aromatic hydrocarbons are much more stable (with higher T_{gel}) than protic solvents such as alcohols and mixture solvents (NMP/H₂O). These results suggested that molecular hydrogen bond interactions between G8 molecules might be the major driving force for the self-assembly. The presence of protic solvents can compete for hydrogen bond interactions, which weakens the hydrogen bond interactions between G8 molecules, leading to the relatively less thermally stable gels.

To ascertain how the gelator molecules aggregated into the gels, FT-IR and ¹H NMR investigations were performed. In the FT-IR spectra, the absorption bands at 3450, 1650 and 1521 cm⁻¹ in CHCl₃ solution, are the characteristic vibrations of νOH (NH, amide I), νC=O (amide II) and νNH (amide II) groups. The corresponding bands of the xerogel appeared at 3389, 1639 and 1557 cm⁻¹, respectively (Supporting Information Figure S5). These data indicated that the hydroxyl and amide groups were involved in hydrogen bonding.¹⁴ Furthermore, the absorption bands of the asymmetric (ν_{as}) and symmetric (ν_{s}) CH₂ stretching appeared at 2928 and 2860 cm⁻¹ in CHCl₃ solution, whereas they shifted to 2927 and 2854 cm⁻¹, respectively, in the gel state. The shifts to the lower wavenumbers revealed a decrease in the fluidity of the alkyl chains due to the strong interaction between the alkyl chains via van der Waals forces. In order to gain more insights into the molecular arrangements within the fibers, variable concentration and temperature ¹H NMR experiments were performed in CDCl₃ (Supporting Information Figure S6). At low concentration (1.0 × 10⁻³ M), the signals of the hydroxyl protons (H_a, H_b, H_c) and amide N-H proton (H_d) appeared at 4.35 (H_a, H_b), 3.97 (H_c) and 7.54 (H_d) ppm. However, at higher concentration (4.0 × 10⁻³ M), these signals shifted to 4.37, 3.98 and 7.57 ppm, respectively. The results suggested that hydroxyl and amide N-H protons participated in the intermolecular hydrogen bonds.¹⁵ When the CDCl₃ gel of G8 was heated from 25 to 75 °C, the signals became stronger and the resolutions became better, which indicated that the signals in the CDCl₃ gel belong to the aggregate. Moreover, hydroxyl and amide N-H peaks moved upfield to 4.31, 3.96, and 7.51 ppm for H_a (H_b), H_c, H_d, respectively, when the sample was heated to 75 °C, which further confirmed the existence of intermolecular hydrogen bonds in the gel phase.^{7a} The signals did not change significantly because the compound was still in the gel state. In addition, when the temperature increased from 25 to 75 °C, the signals of the aromatic protons at 7.43 (H_e), 7.26 (H_f) and 6.41 (H_g) ppm were found to be slightly shifted upfield to 7.39 (H_e), 7.24 (H_f) and 6.32 (H_g) ppm upon increasing the temperature from 25 to 75 °C, suggesting the presence of π-π stacking interactions.¹⁶ These data suggested that a combination of hydrogen bonding, π-π-stacking and van der Waals forces was the driving forces for the self-assembly of G8 in CDCl₃. Scanning electron microscopy (SEM) studies revealed that gels of G8 aggregated into fiber structure (Supporting Information

Figure S7).

As a remarkable feature, gelator G8 was sensitive to multiple chemical and physical stimuli and the reversible phase

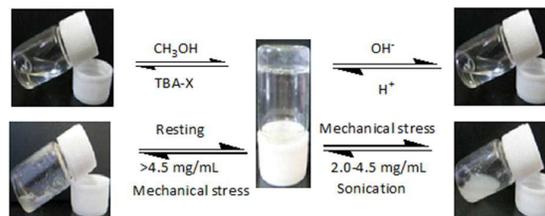


Figure 2 Phase transition of the chloroform gel of G8 triggered by chemical and physical stimuli.

transitions can be realized conveniently. As shown in Figure 2, solid TBA-F, TBA-Cl, TBA-Br, TBA-I, TBA-H₂PO₄, TBA-OAc, (molar ratio of anion:G8=2:1) were carefully placed above the chloroform gel of G8, and after the vials were left standing at RT for varying lengths of time, the gel diffused with H₂PO₄⁻ converted into solution first in 0.5 h, as assessed by the inversion test (similarly applied hereinafter). The gels with F⁻, AcO⁻, Cl⁻ and Br⁻ converted into solution after 1.5 h, 3.5 h, 18 h and 24 h, respectively. By contrast, the gel diffused with I⁻ did not convert into clear solutions, even after 48 h. These anions response influenced the gel disruption unexpectedly following the Hofmeister series in the order of H₂PO₄⁻ > F⁻ > AcO⁻ > Cl⁻ > Br⁻ > I⁻. It was noticeable that the Hofmeister series was normally observed in aqueous systems. Such anion-responsive behavior was uncommon in supramolecular gels field, in particular, in a non-aqueous system. The gel disruption may be because the addition of X⁻ resulted in the formation of X⁻⋯HNCO hydrogen bonding and destroyed the original hydrogen bonding.¹⁷ This process can be monitored by ¹H NMR spectroscopy. As shown in Figure S7, compared to the amide NH proton signal of G8 (7.54 ppm) in chloroform, the signal shifted gradually downfield due to the formation of the X⁻⋯HNCO hydrogen bonding. When 2 equivalents TBA-H₂PO₄, TBA-F, TBA-OAc, TBA-Cl or TBA-Br were added to chloroform gels, the chemical shift of NH proton appeared downfield to 7.55, 7.56, 7.57, 7.59 7.62 ppm, respectively. As expected, the chemical shift of NH proton signals also follows the order: H₂PO₄⁻ > F⁻ > AcO⁻ > Cl⁻ > Br⁻ (Supporting Information Figure S8) which indicates that these anions' influence on the gels disruption also follows the Hofmeister series. Reformation of the gels from the sol state was achieved just by adding a little excess of CH₃OH (molar ratio with respect to to anion) and opaque gels could be obtained within 5 min. The addition of CH₃OH to the collapsed 'gels' will break the X⁻⋯HNCO hydrogen bonding and recover the original intermolecular hydrogen bonding and subsequent gels state. Similarly, the gel-sol transitions could also be reversibly triggered by the addition or removal of base, such as TBA-OH. The OH⁻ also functioned as an anion which will result in the formation of OH⁻⋯HNCO hydrogen bonding, leading to the collapse of the gel (Supporting Information Figure S9).

Apart from the above-mentioned chemical stimuli, G8 also responded to physical stimuli including ultrasound and mechanical force which can also trigger the phase transitions.

In the concentration range of 2.0 to 4.5 mg/mL, stable gel was formed under ultrasonication and the gel to sol transition could be easily realized by mechanical stress. At concentrations above 4.5 mg/mL, gels could be obtained by heating-cooling and ultrasonication and gels prepared by the two methods exhibited thixotropy at RT. We then further explored the thixotropic property of G8-based gels in application-oriented solvents in industry such as toluene, o-xylene, o-dichlorobenzene, n-butyl acetate, pump oil, EG/H₂O (8:2) and NMP/H₂O (1:1) (Figure S10). Intriguingly, all gels exhibited thixotropic property, making these soft materials applicable in practical industries such as coating, ink, lubricant etc. as rheological agents.

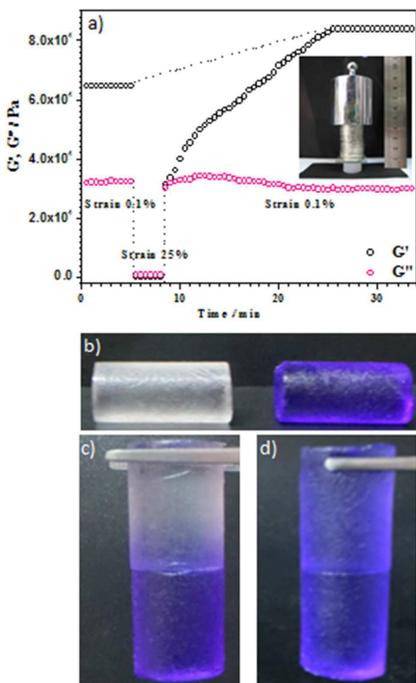


Figure 3 a) The step strain experimental data obtained from the n-butyl acetate gel of G8 (5.0% w/v). Inset: photograph of load-bearing experiment of n-butyl acetate gel of G8 (5.0% w/v). The gel withstanding the pressure of 18 chinese 1 yuan coins (108 g), glass plate (1.88 g) and 500 g weights. b-d) Illustration of self-healing behavior shown by o-dichlorobenzene gel of G8 (1.0% w/v).

In addition, these thixotropic gels displayed load-bearing and self-healing properties. As shown in Figure 3a, the n-butyl acetate gel exhibited superior mechanical strength and the G' value was higher than 64000 Pa at a concentration of 5.0% (w/v), a higher value reported in the fields of LMWGs.¹⁸ Besides, the G' value of disintegrated gel was obviously enhanced compared to the original gel. Interestingly, the gel (2.57 g) remained shape-persistent even when pressed by a heavy weight (609.88 g), which means that it can bear 237 times the weight of its own (Inset of Figure 3a). Such high load-bearing strength was a very rare property for LMWGs.¹⁹ We then investigated the self-healing properties of G8-based gels. To clearly observe the whole healing process, a designed experiment as shown in Figure 3b-d was conducted. The gel was cut into two segments and one of them was doped with methyl violet B base (Figure 3b). When the pieces joined together, they merged into a

continuous block within 10 min (Figure 3c). The whole block was violet colored after 12 h (Figure 3d), indicative of the dynamic exchange of dissolved molecules in the self-assembled fibrous network across the fusion interface during the self-healing process.²⁰

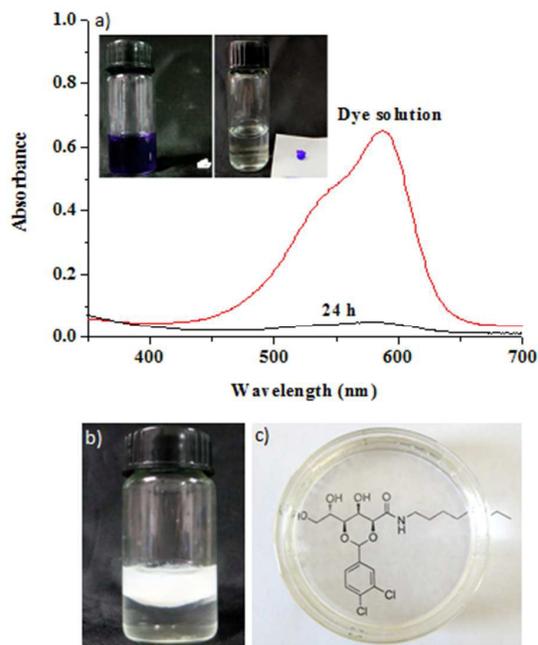


Figure 4 a) UV/Vis spectrum of aqueous solution of crystal violet indicating the adsorption of the crystal violet from water by n-butyl acetate xerogel of G8. Inset: photograph of crystal violet adsorption from water by n-butyl acetate xerogel of G8. b) Selective gelation of the pump oil layer (pump oil gel floating on water) after addition of the solution of G8. c) View of the structure of the gelator through its o-dichlorobenzene gel (0.5% w/v).

We next explored the applications of G8-based gel in the fields of waste water treatment, spilled oil recovery and flexible optical device manufacture. The xerogels could find potential applications in waste water treatment as they showed an intriguing property of adsorbing crystal violet and iodine from water (Figure 4a and Supporting Information Figure S11). Following submergence of the xerogel (20 mg) of G8 into an aqueous solution of crystal violet (7 ml, 0.2 mM), it efficiently adsorbed the crystal violet molecules from water after 24 h. Adsorption of crystal violet from aqueous solution was monitored by UV-visible spectroscopy, which revealed that the entire crystal violet molecules were transferred from water to xerogel leaving clear water. The amount of crystal violet adsorbed by G8 was 28.5 mg.g⁻¹, a better adsorption result reported in the fields of LMWGs.^{7a,10} It was reported that the phase-selective gelation requires the heating process which, however, limits the real life application, e.g. spilled oil recovery.¹¹ Thus, in our studies phase-selective gelation of pump oil in the presence of water at RT was studied (Figure 4b). A concentrated solution of gelator G8 (20 mg) in tetrahydrofuran (2 mL) was injected by a syringe into the interface between saline water (4 mL) and pump oil (2 mL). Instantaneous gelation of the pump oil layer was observed,

indicating the potential application of G8 in the real spilled oil treatment. Moreover, the o-dichlorobenzene gel at concentrations as low as 0.5% (w/v) showed moldable (Supporting Information Figure S12) and highly transparent properties (Figure 4c). These gels were so strong that they can be stable for months without losing their transparency, volume, and shape. The above features of the o-dichlorobenzene gels make them attractive for developing flexible optical devices.

In summary, we have synthesized a series of novel D-gluconic acetal-based organogelators among which G8 proved to be a super gelator exhibiting multi-stimuli responsiveness and versatile applications. For example, these gels displayed anion-, base-, ultrasonication- and mechanical-controllable phase transitions. Surprisingly, it was found that the anion responsiveness followed Hofmeister series in a non-aqueous system which was uncommon in supramolecular gels field. It was demonstrated that G8-based supramolecular gels also showed versatile applications such as being rheological and self-healing agents, waste water treatment, spilled oil recovery and flexible optical device manufacture. All these features make G8-based gels unprecedentedly intelligent soft materials. Studies on structure-gelation ability relationship and further exploring applications of these materials are still in progress.

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