

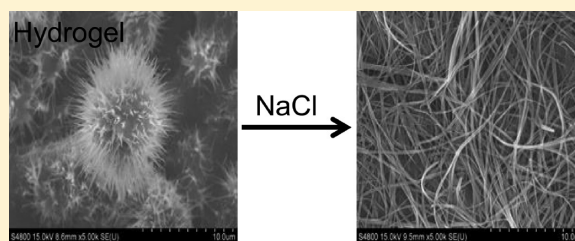
Effects of Salt on the Gelation Mechanism of a D-Sorbitol-Based Hydrogelator

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S Supporting Information

ABSTRACT: The effect of salt on the gelatinization of 2,4-(3,4-dichlorobenzylidene)-D-sorbitol (DCBS), a novel low-molecular-weight gelator, was studied. DCBS showed pronounced hydrogelation and the electron micrographs indicated that the hydrogels consists of globular aggregates. Addition of NaCl to the aqueous medium accelerated the gelation process and also caused the gel's morphology to change from globular to long fibers. In addition, the thermal properties of the hydrogels were improved with the addition of NaCl. UV-vis and fluorescence emission spectra showed that extensive aggregation of the phenyl rings was responsible for the gelation. The presence of NaCl induced a red shift in the emission peaks of DCBS and a decrease of the pyrene polarity index I_1/I_3 in the gels, which indicated that there was more π - π stacking in the hydrogels with NaCl than in the gels without NaCl. Variable-temperature ^1H NMR spectra further demonstrated that the π - π interactions were enhanced by NaCl. FTIR studies showed that hydrogen bonding was also a contributing factor in the gelation process. Wide-angle X-ray diffraction (WXR) showed that the hydrogels had a layered structure which did not change with the addition of NaCl. Density functional theory (DFT) calculations indicated the possible molecular packing of the gelator in the nanofibers.

**■ INTRODUCTION**

Low molecular weight gelators (LMWGs) have received significant attention over the past decades.¹ Stimuli responsive gels are of particular interest for applications such as drug-release formulations and sensors. Gelators responsive to light, heat, ultrasound, and chemical environments have been reported.² Within the field of LMWGs there has been a particular focus on tuning gel states by adding anions.³ Generally speaking, anions have two opposite effects on gelation.

The first is the broken effect which exploits the hydrogen bonding of the anions with the gelator molecules. Most gels reported to date are organogels which have amide or urea units as the hydrogen-bonding sites.⁴ The field of anion binding by supramolecular hosts is well established and reasonably well understood.⁵

The second anion effect is the enhancement effect, which has not been researched much. Again, organogels dominate this research and most work has been done in alcohols or DMF.⁶ Due to the competitiveness of water in ion-binding equilibria, only a few examples of anion-responsive supramolecular hydrogels have been reported. For instance, Becker et al.⁷ reported that a chiral calix[4]arene could form hydrogels when triggered by the presence of specific anions. ^1H NMR spectra indicated that the gel formation was not related to the selective binding of the anion or ion pair to the calixarene. Roy and co-workers⁸ also reported a similar observation for a series of peptide-based hydrogelators. They confirmed that the changes resulted from specific-ion effects on the gel structure, rather

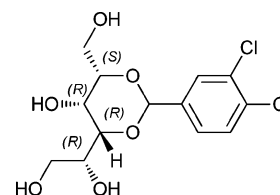
than on the sol-gel equilibrium. However, there have been surprisingly few studies that look directly at the influence of anions in hydrogels, often due to the fact that a simple change in the anion results in an improvement in the characteristics of the gel.^{6a,c,7-9}

Herein, the effects of a salt on the gelation mechanism of a hydrogelator 2,4-(3,4-dichlorobenzylidene)-D-sorbitol (DCBS) (Scheme 1) was studied. The interactions between the NaCl and the gelator were studied using FTIR, UV-vis, fluorescence, variable-temperature ^1H NMR, and wide-angle XRD.

■ EXPERIMENTAL METHODS

Chemicals and Materials. The reagents used in the study were purchased from Tianjin Chemical Reagent Factory and

Scheme 1. Chemical Structure of the Gelator, 2,4-(3,4-Dichlorobenzylidene)-D-sorbitol



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used without further purification. Pyrene was obtained from Aladdin at 99% purity and was used as received.

Synthesis of the Gelator. The gelator DCBS was easily synthesized by reacting the appropriate D-sorbitol with 3,4-dichlorobenzylidene using the method previously reported in the literature¹⁰ (Scheme S1, Supporting Information).

Preparation of the Gels. The gels were prepared by first heating solutions containing the gelators and then cooling the solutions to room temperature. The gelation properties of DCBS were evaluated by dissolving 1% (w/v) DCBS in various solvents.

Measurement of the Sol–Gel Transition Temperature (T_{gel}). A tube inversion method was used for gelation characterization. A tube containing the gel was immersed in a temperature-controlled oil bath. The temperature at which the sample started to flow was recorded as T_{gel} .

Measurement of the Critical Gelator Concentration (CGC). Critical gelator concentration (CGC) was determined by weighing up a minimum amount of gelator needed for the formation of a stable gel through the heat/cool cycle.¹¹

Solubility Measurements. HPLC was employed to determine the concentration of DCBS in the solution phase of the gels in water as well as in presence of different concentrations of NaCl at room temperature.¹² The detection wavelength was 210 nm and mobile phase was 90% methanol and 10% water.

Scanning Electron Microscope (SEM) Measurements. A sample of the xerogel was prepared by drying the gel at 25 °C for 10 days under high vacuum. SEM images of the xerogels were obtained using a Hitachi S-4800 scanning electron microscope after coating the xerogels with gold.

FTIR Measurements. The FTIR spectra of the xerogels and solutions were collected from 3000–3900 cm^{-1} with a Bruker Equinox 55 infrared spectrophotometer using KBr pellets.

UV–Vis Spectra Measurements. UV–vis absorption spectra were obtained with an Evolution 300 UV–vis spectrophotometer. The path length of the quartz cell was 1 mm.

Variable-Temperature ^1H NMR Measurements. Variable-temperature ^1H NMR spectra of 1% DCBS were recorded on a Bruker BioSpin GmbH-400 NMR spectrometer using D_2O as the solvent.

Fluorescence Emission Measurements. Pyrene was used as a fluorescence probe and its emission spectra were recorded on a Hitachi F-2500 fluorimeter. Excitation was at 334 nm with the excitation slits set for a 5 nm bandpass. Emission slit width was set to a 2.5 nm bandpass. The concentration of pyrene was $3.07 \times 10^{-7} \text{ M L}^{-1}$. The excitation wavelength was set at 259 nm for DCBS Fluorescence Emission spectra.

Wide-Angle XRD Measurements. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200-PC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) and a graphite monochromator at ambient temperature. The samples were tested from 3° to 30° at a scanning rate of $0.2^\circ/\text{step}$. The gels with or without NaCl were spread on a glass slide as a film and allowed to dry in air prior to data collection.

Calculation Methods. Geometries and energies of the stationary points were fully optimized by hybrid density functional theory (DFT) using the Gaussian 09 program suite.¹³ The most commonly used functional B3LYP poorly simulates long-range interactions. So the DFT-D method B97xD, which contains a long-range correlation, was used to calculate this system. To balance accuracy and time, the Pople basis set 6-31g(d,p) was chosen. To simulate the solvent

environment, a conductor-like polarizable continuum model (C-PCM) was used for water. The calculation of frequency, which is used to check whether the optimized geometry is the most stable one, was performed at the same level.

RESULTS AND DISCUSSION

Gelation Properties. The gelation properties of DCBS in various solvents were tested and the results are shown in Table

Table 1. Gelation Behavior of DCBS^a

solvent		solvent		solvent	
water	G	ethyl acetate	G	DMF	S
2% NaOH	G	acetonitrile	G	methanol	S
2% NaCl	G	acetone	G	ethanol	S
chlorobenzene	G	<i>n</i> -octanol	G	cyclohexane	P
<i>o</i> -xylene	G	DMSO	S	<i>n</i> -hexane	P

^aG = gel; S = solution; P = precipitate.

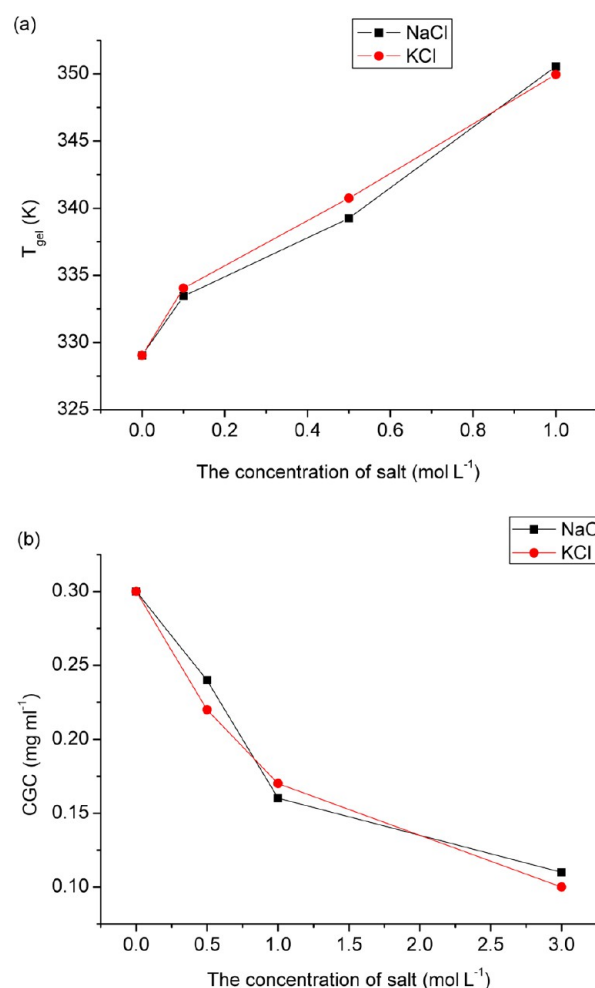


Figure 1. Effect of salt concentrations on (a) T_{gel} and (b) CGC.

1. DCBS was found to be an efficient amphiphilic gelator. It not only hardened in organic solvents such as acetone, chlorobenzene, and ethyl acetate and so on, but also hardened in water. In addition, DCBS also formed gels in water with different ions such as Na^+ , Cl^- , or OH^- .

Effect of Salt on Gelation. Thermal Properties. The thermal stabilities of the gels were investigated at different concentrations of NaCl. Using a fixed concentration of gelator

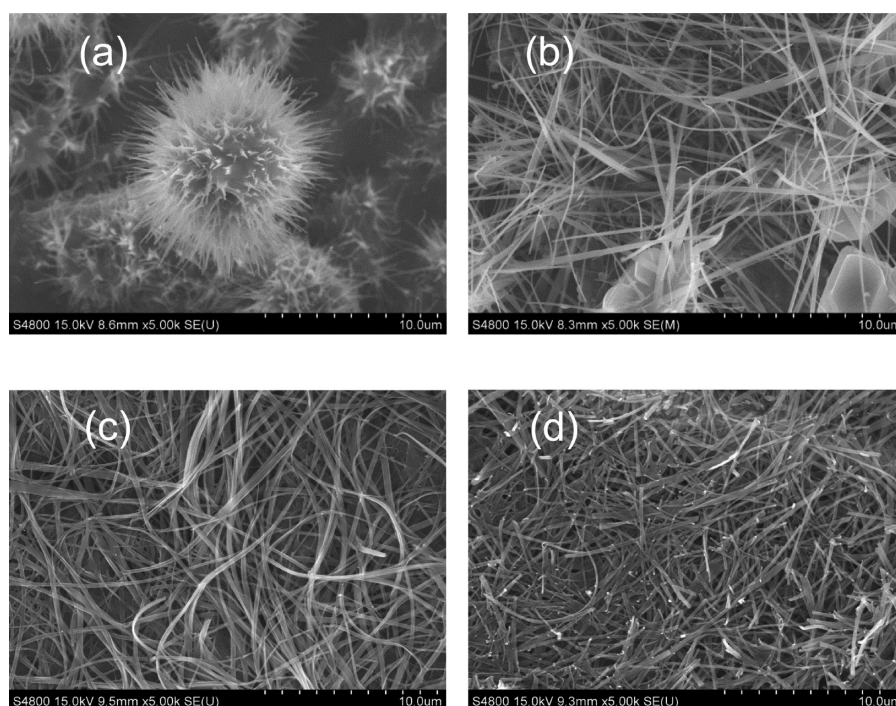


Figure 2. SEM of the DCBS xerogels made from (a) water, (b) 0.1 M NaCl solution, (c) 0.5 M NaCl solution and (d) 1 M NaCl solution.

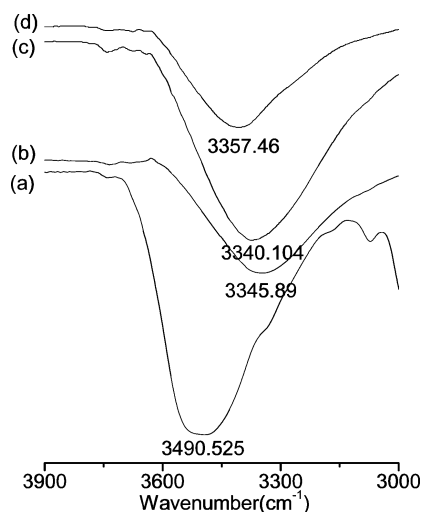


Figure 3. FTIR spectra of DCBS in (a) a solution state and in xerogel states made from (b) H₂O, (c) 0.1 M NaCl and (d) 0.5 M NaCl.

(1.0% (w/v)), the gel–sol transition temperatures (T_{gel}) were determined by the tube inversion method. The gel–sol transition temperature and critical gelator concentrations (CGCs) of the gels with different salt concentrations are shown in Figure 1.

The gel–sol transition temperature increased and the critical gelator concentration decreased with increasing NaCl concentration. This indicates that NaCl strengthens the gel networks. To determine which ion was responsible, KCl was also investigated and as shown in Figure 1, KCl had the same effect as NaCl. For the same molar concentrations of Cl[−], the hydrogels exhibited similar T_{gel} and CGCs for the two salts. From these results, it may be concluded that the cation had little effect on the gelation process, and the gel formation was mainly affected by the anion.

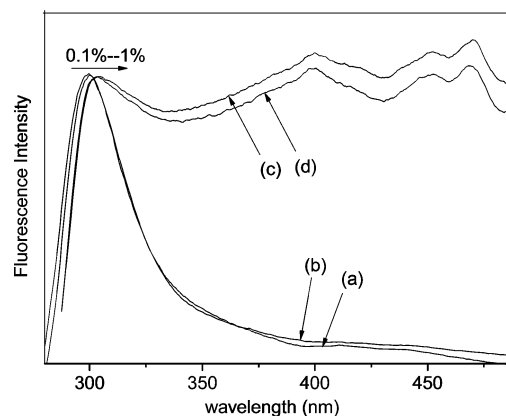


Figure 4. Fluorescence spectra of DCBS in water at different concentrations (a) 0.1%, (b) 0.3%, (c) 1%, and (d) 1% in 0.5 M NaCl solution.

To confirm this conclusion, the effects of other anions, such as Br[−], I[−], and H₂PO₄[−] were also studied and the anions concentrations were all 0.5 M. As expected, in all investigated gels the T_{gel} and CGCs were very different with different anions (Figure S1, Supporting Information).

Further, the presence of NaCl in an aqueous solvent led to a decrease in the time required for the onset of gelation. With water, the gel formation occurred after about 10 min, whereas in 1 M NaCl the DCBS gelled instantaneously.

Morphologies. The morphologies of DCBS xerogels were examined by SEM. As shown in Figure 2a, the DCBS hydrogels contain globular aggregates with fibrils. In contrast, many entangled fibers with the average width 0.21 μm was observed in the presence of NaCl (Figure 2b–d). As the concentrations of NaCl increased to 0.5 M, the fibers became longer but the average width was almost no change (Figure 2c). However, Figure 2d (1 M NaCl) showed much shorter fibers but a high fiber density than Figure 2c (0.5 M NaCl). The nice fibers in

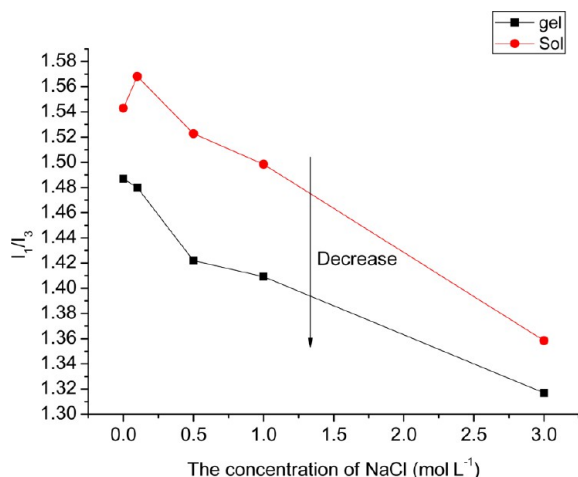


Figure 5. Pyrene polarity index in different NaCl concentrations and different temperatures. The DCBS concentration in all samples is 0.5% (w/v).

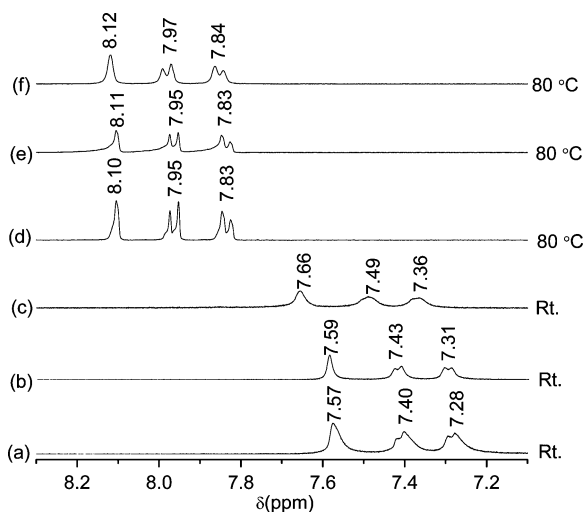


Figure 6. ¹H NMR spectra of 1% DCBS gel in (a,d) D₂O, (b,e) 0.1 M NaCl, (c,f) 1 M NaCl at different temperatures.

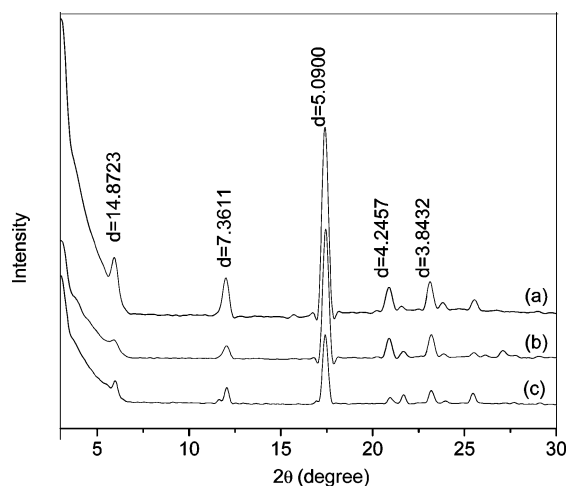


Figure 7. WXR D spectra of 1% DCBS xerogels made from (a) H₂O, (b) 0.1 M NaCl solution, and (c) 0.5 M NaCl solution.

the presence NaCl might indicate a much more ordered arrangement of DCBS molecules.

FTIR Spectra. To further insights on direct interactions between solvents and gelator, FTIR spectra of DCBS in solution state and xerogel state are measured and the results are shown in Figure 3. The FTIR spectrum of DCBS in the solution phase (a fresh solution in DMF) shows a band at 3490 cm⁻¹ which is the asymmetric stretching vibration of O–H (Figure 3a). In the xerogels (1% DCBS), the O–H bands are at 3346, 3340, and 3357 cm⁻¹ for NaCl concentrations of 0, 0.1, and 0.5 M, respectively. These values indicate that the O–H groups participate in the formation of hydrogen bonds among the gelator molecules.¹⁴ However, the blue shift for the O–H peaks of the xerogels obtained in NaCl solutions indicate that the intra- and intermolecular hydrogen bonds are slightly weakened by the introduction of NaCl. This was also seen in the report of Liu.^{6a} One possible reason may be that the self-assembly of DCBS is not only governed by intermolecular hydrogen-bonding interactions but also by other intermolecular forces such as π – π interactions and van der Waals interactions. The latter forces interfere with the hydrogen-bonding interactions because of steric mismatching.¹⁵

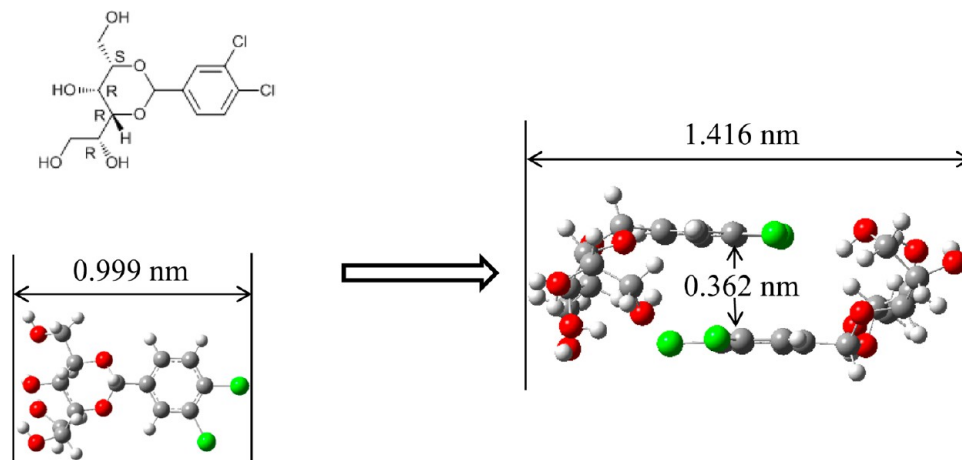
UV–Vis and Fluorescence Emission Spectra. The fluorescence emission spectra were used to monitor the interactions between the phenyl rings so as to evaluate the packing mode during formation of the gels, and the results are shown in Figure 4. The DCBS aqueous solution has a peak centered at 299 nm which red shifts to 303 nm for the 1% hydrogel. Such a red shift ($\Delta\lambda = 4$ nm) indicates that there exists π – π stacking in the hydrogel with the formation of J-type aggregates.¹⁶ An even greater red shift ($\Delta\lambda = 6$ nm) was observed in the hydrogel with 0.5 M NaCl, with peaks centered at 305 nm. It is known that the extent of the fluorescence emission shifts is consistent with the intensity of the π – π interactions between the chromophore groups.¹⁷ Therefore, the π – π stacking interactions between the DCBS chromophore groups became more extensive with the addition of NaCl, and at the micro level, this resulted in the increase of T_{gel} .

Accordingly, the UV–vis absorption spectrum was also employed to study the aggregate of DCBS hydrogel. As shown in Figure S2 (Supporting Information), from solution state to gel state, the spectra became broad together with the change of some fine structure, and a new broad absorption appeared in the longer wavelength region. These changes can be explained by the formation of a ground-state dimer, due to the resonance of a π -electron, between the benzylidene moieties at gel state.¹⁸

Since phenyl group is not a good fluorophore, DCBS gels with higher NaCl do not give nice results. It might be useful to do the study with an external fluorescence probe. Pyrene is a strongly hydrophobic probe whose emission spectrum consists of five vibronic bands. The ratio of the intensity of the first and third vibronic peaks ($I_{373\text{ nm}}/I_{384\text{ nm}}$) in the fluorescence emission spectrum shows a strong dependence on the polarity of the environment and was defined as pyrene polarity index or py-value.¹⁹ The I_1/I_3 ratio that has the highest value in water decreases with the decrease in solvent polarity. Therefore, it has been widely used as a micropolarity probe for self-assemblies.¹⁹

As shown in Figure 5, the value of I_1/I_3 in the gel state is very low compared to that in the solution state, which indicates that pyrene is preferentially solubilized in the interior hydrophobic regions of DCBS aggregates at low temperature. Most importantly, the plot showed a significantly decrease of I_1/I_3 value with the rise of salt concentration, suggesting that DCBS gel with higher NaCl have lower micropolarity due to more ordered DCBS aggregate through extensive phenyl rings π – π

Scheme 2. Optimized Self-Assembly Model of DCBS in a Gel Obtained by DFT



stacking to form a lower micropolarity hydrophobic interior. The original pyrene fluorescence emission spectra are shown in Figure S3 in the Supporting Information.

Variable-Temperature ^1H NMR Spectra. ^1H NMR spectroscopy can be used to show changes in the environment of aromatic protons which experience upfield chemical shifts when the molecules assemble via π -stacking.²⁰ Most importantly, Wang^{20c} has confirmed that, for compounds which have concentration-driven self-organization, once the molecules begin to self-organize, the aromatic protons undergo considerable upfield shifts as the concentration increases. Variable-temperature ^1H NMR experiment of DCBS in different solvents was also carried out and the results are shown in Figure 6. The ^1H NMR spectra of DCBS solution in different solvents are almost the same (Figure 6d–f) probably due to the complete dissolution of DCBS at high temperature. A large upfield chemical shift (Figure 6a–c) was observed for hydrogel with or without NaCl as temperature decreased, indicating favorable π – π stacking in the gel state at low temperature. However, it must be noted that, in a gel system, both solid fibers and the solution coexist and the ^1H NMR spectra of gels show only the molecules dissolved in the entrapped solvent.²¹ So, as shown in Figure 6a–c, the chemical shifts for the 1% DCBS hydrogel shifted downfield as the concentration of NaCl increased, from 7.57 ppm shift to 7.66 ppm, which indicates that the number of DCBS molecules dissolved in the entrapped solvent decreased after adding NaCl.

In order to confirm the conclusion, the solubility experiment of DCBS in water as well as in the presence of different concentrations of NaCl at room temperature was conducted and the results are shown in Figure S4 in the Supporting Information. It was clear that the solubility of DCBS decreased with increasing NaCl concentration. It is reasonable if we consider that the addition of ions will change the structure of water, and then change the solubility of the solute.²² Hribar et al.²³ proposed that the water structure was determined by the balance between electrostatic interactions and hydrogen bonding. Small anions such as Cl^- cause a strong electrostatic orientation of the water molecules with respect to the anion, which makes the water structure more ordered. Therefore, there are less free water molecules available to solvate the gelator. So the solubility of DCBS decreased in NaCl solutions which led to more DCBS molecules participating in self-

assembly which in turn generated more π -stacking. This may be the primary reason for the increase in T_{gel} .

Wide-Angle XRD. XRD was employed to provide an insight into the crystal structure of the DCBS xerogels and the results are shown in Figure 7. For the xerogel in water (Figure 7a) the main peaks at $2\theta = 5.94^\circ$ ($d = 1.49$ nm), $2\theta = 12.01^\circ$ ($d = 0.74$ nm), $2\theta = 17.41^\circ$ ($d = 5.09$ nm), and $2\theta = 20.91^\circ$ ($d = 0.42$ nm) have a ratio of 1:1/2:1/3:1/4, suggesting that, in this sample, the DCBS mainly assembles into a layered structure, and the interlayer distance is 1.49 nm.^{16a} This is larger than the longest length of DCBS (0.999 nm, estimated by the DFT molecular modeling, Scheme 2) but smaller than two DCBS lengths. From these results, it can be concluded that DCBS forms an interdigitated bilayer structure with a thickness of 1.49 nm in water. In addition, a peak around $2\theta = 23.12^\circ$ (0.38 nm) is characteristic of a π – π stacking distance,²⁴ which further demonstrates that there exists extensive π – π interactions between phenyl rings of DCBS. The WAXD patterns of the xerogels in the NaCl solutions (Figure 7b,c) were similar to that from water and therefore these xerogels have similar supramolecular structures.

Based on the above results, a packing mechanism for DCBS in aqueous solutions is proposed and is shown in Scheme 2. The organizational motif of DCBS in aqueous gel is dominated primarily by π – π interactions between phenyl rings, and hydrogen bonds provide the rest of the force needed for the gelation. In water, the hydroxyl groups of the DCBS are on the outside of the structure and the aromatic rings are shielded from the water. To occupy the space more effectively, the aromatic rings interdigitate.

CONCLUSIONS

DCBS, an amphiphilic gelator, was synthesized. It not only hardened in organic solvents but also in water. In addition, DCBS also formed gels in water with different ions such as Na^+ , Cl^- , or OH^- and in fact the gel–sol transition temperature increased and the critical gelator concentration decreased with increasing concentrations of NaCl. Further, the globular morphology of the hydrogel changed to entangled long fibers with the addition of NaCl. FTIR results indicated that the hydrogen-bonding interactions were slightly weakened by NaCl, and the UV–vis, fluorescence, and ^1H NMR results indicated that the π – π stacking interactions were greatly enhanced. The increased π -stacking in the hydrogels with NaCl

might be the primary reason for the increase in T_{gel} . WXR showed that all the hydrogels formed in water or NaCl solutions had layered structures. The organizational motifs in these hydrogels are dominated primarily by π - π interactions between interdigitated phenyl rings with hydrogen bonds providing the rest of the force needed for gelation.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of DCBS, effects of different anions, UV-vis spectra, pyrene fluorescence emission spectra, and solubility profile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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