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PAPER

Hydrogelators of cyclotrimeratrylene derivatives†

Fu Cai,^a Jiang-Shan Shen,^b Jin-He Wang,^a Han Zhang,^b Jin-Song Zhao,^a Er-Man Zeng^{*a,b,c} and Yun-Bao Jiang^{*a}

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Developing cavity-based supramolecular hydrogels is in its infancy because not many such hydrogelators are available. Reported herein is our creation of rigid cavitand cyclotrimeratrylene (CTV) based hydrogelators from the molecular backbones of CTVs that were in limited cases shown to form organogels. For doing so deprotonable –COOH or protonable –NH₂ was introduced as terminal group into the rigid and hydrophobic CTV backbones. We thus successfully obtained optically anisotropic supramolecular hydrogels from these new CTVs hydrogelators with excellent thermostability and high tolerance towards strong electrolytes. The obtained CTV-1 and CTV-2 hydrogels are luminescent and exhibit reversible gel-to-sol and sol-to-gel transitions upon pH variations. The success in creating CTV-1 and CTV-2 hydrogelators on the basis of the skeleton of a CTV-organogelator suggests that balancing the hydrophilic and hydrophobic characters of the ionic and hydrophobic moieties well in the gelator molecule is important for designing a promising hydrogelator.

Introduction

Low-molecular-weight-gelators (LMWGs) can be employed to generate supramolecular hydrogels and organogels *via* the self-assembly or induced assembly under external stimuli. Most of these reported soft matters could exhibit responsive capacity towards a series of external stimuli such as temperature,¹ light,² cations or anions,³ pH,⁴ host–guest interactions,⁵ and even biologically relevant events.⁶ These supramolecular gels have thus attracted considerable attention. Therefore, it has been of particular interest to discover new molecular structures or motifs that are capable of gelling solvent molecules⁷ or to functionally modify the backbones of known gelators to improve their gelation performance.⁸ Although it remains to be not fully understood on the relationship between gelation and molecular structure, significant advances towards rationally designing gelators and/or modifying known gelator molecules have been made.^{3e,9} Deserving of notice is that macrocyclic molecules, most of which are useful host molecules such as cyclodextrins,¹⁰ crown ethers,¹¹ cucurbiturils,¹² calixarenes,¹³ and porphyrins,¹⁴ have been em-

ployed to create organogelators and hydrogelators by introducing functional groups.¹⁵ The related supramolecular gels are expected to show the host-related functionalities and interesting potentials of guest tuned gelation. Cyclotrimeratrylenes (CTVs), as a class of crown-like macrocyclic molecules with a rigid skeleton that are known to assemble into columnar stacks in the solid state, often featuring a liquid-crystalline phase,¹⁶ however, have rarely been exploited for fabricating supramolecular gels. There are actually only three available CTV-organogel examples.¹⁷ It would therefore be of significance to examine if the specific interactions that facilitate the formation of liquid-crystalline phase in the CTV solid and its rigid cavitand structure would exert any influence on the gelation of CTVs, for which a detailed investigation of the hydro-/organo-gelation would be required. From a structural point of view it is clear that the rigid CTVs without chargeable groups would be insoluble in water because of the presence of the strong π – π stacking and/or hydrophobic interactions. Although structural modifications have been attempted by grafting long alkyl chains on the periphery of the boronate-substituted CTVs and by introducing pyridine moiety into the tripodal CTVs to facilitate the organogelation,^{17a,b} the CTV-based hydrogelators have not been well accessed.^{17a}

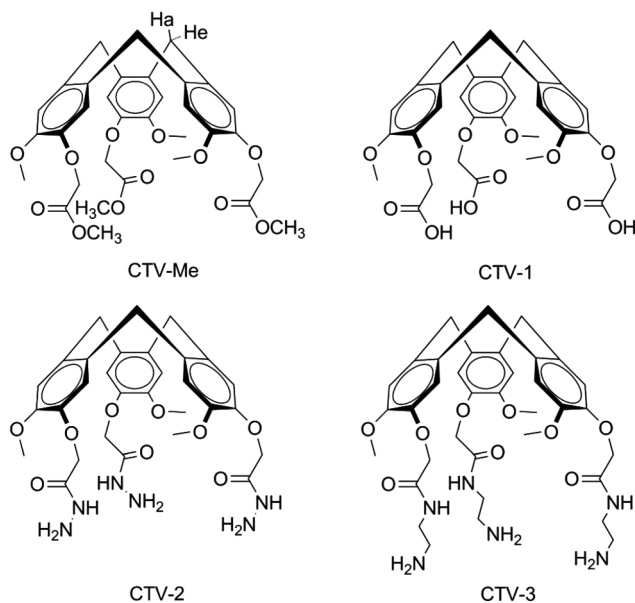
Compared to organogelators, hydrogelators should include enough hydrophilic moieties in their backbones to afford the favourable balance between the hydrophobic and hydrophilic interactions required to create effective nano-/micro- scale fibrous structures to gelate water molecules. Even by doing so the water-solubility of the resultant hydrogelator may still be limited. We thus started our efforts to create CTV-based hydrogelators from the structural skeleton of the known CTV-based organogelators, by introducing hydrophilic groups such as –COOH or –NH₂ (CTV-1 and CTV-2, Scheme 1) that can be deprotonated or protonated,

^aDepartment of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005, China. E-mail: ybjiang@xmu.edu.cn; Fax: +86 592 218 6401; Tel: +86 592 218 8372

^bInstitute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China. E-mail: emzeng@iue.ac.cn; Fax: +86 592 238 1200; Tel: +86 592 203 7248

^cAmoy Institute of Technovation, Xiamen, 361001, China

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Scheme 1 Molecular structures of the synthesized CTV derivatives.

thereby making them water-soluble by deprotonation or protonation. Optically anisotropic supramolecular hydrogels were successfully obtained from CTV-1 and CTV-2. These hydrogels were found to be highly thermostable and to exhibit excellent tolerance towards high concentrations of strong electrolytes. The fact that CTV-3, differing from CTV-2 only by three more ethylene-linkers, could not undergo hydrogelation supports the assumption that a subtle balance between the hydrophobic and hydrophilic characters of the gelator molecule is critical for a successful gelation. Thanks to the (de)protonable groups in CTV-1 and CTV-2, their hydrogels can perform reversible gel-to-sol and sol-to-gel transitions by varying the pH. The critical hydrogelation concentrations (CGCs) of the CTVs were noted to be lower than most of the reported CGCs, including those of the CTV organogels, and interesting rheologies were observed for the CTV hydrogels, likely resulting from the structural characters of the CTVs in terms of forming the liquid-crystalline phase in their solid state. The findings reported here are expected to not only provide a useful strategy for designing new hydrogelators but also shed light on the gelation behavior of the CTV-based supramolecular hydrogels that could then be subject to the investigations of host-guest interaction.

Results and discussion

CTV-1, CTV-2 and CTV-3 (Scheme 1) were prepared from CTV-Me following a reported procedure (synthetic details are supplied in the Electronic Supplementary Information, ESI†).¹⁸ Both CTV-1 and CTV-2 were found to be poorly soluble in apolar and less polar organic solvents such as dichloromethane and ethyl acetate, but well soluble in polar solvents such as *N,N*-dimethylformamide and dimethylsulphoxide (Table S1, ESI†). We noted that CTV-3 has been previously shown to be able to form organogels in 2-propanol and acetonitrile under ultrasonic processing.^{17a}

Structurally simple CTV-1 and CTV-2 were designed by introducing deprotonable $-\text{COOH}$ and protonable $-\text{NH}_2$ terminal

groups, respectively, so that CTV-1 and CTV-2 could be made water-soluble under appropriate pHs (Fig. 1a, 1c). It was observed that, when the deprotonated CTV-1 in aqueous solution was protonated by directly adding acid, entangled floccules slowly appeared. This means that CTV-1 could be a good candidate of hydrogelator. We previously showed that diffusion of CH_3COOH vapor into the alkaline solution of the gelator would allow a slow decrease in the pH of the solution that the gelator molecule is *in situ* generated slowly and therefore self-assembling of gelator molecules occurs, which is expected to be favourable for gelation.¹⁹ Employing this method, we succeeded in obtaining opaque and robust supramolecular hydrogels from CTV-1, *in situ* generated from the alkaline aqueous solution of the deprotonated CTV-1 under CH_3COOH atmosphere at room temperature within *ca.* 6 h, as judged by the inverting tube test (Fig. 1b). In the cases using protonated CTV-2 and CTV-3 as the hydrogelator precursors in aqueous solutions, NH_3 was employed as a volatile base to slowly increase the pH of the gelator solutions. Hydrogels from protonated CTV-2 were similarly formed under NH_3 within *ca.* 3–5 h, but unfortunately CTV-3 hydrogels were not obtained. CTV-3 differs structurally from CTV-2 only by three more ethylene-linkers (Scheme 1). It therefore follows that the flexible ethylene linkers in CTV-3 that may produce additional hydrophobic interactions could be a possible reason for its failure of hydrogelation. A subtle balance between the hydrophobic and hydrophilic characters of the CTV derivative is hence shown to be critical for its successful gelation. We also noted that the methyl ester of CTV-1, CTV-Me (Scheme 1) bearing no $-\text{COOH}$ group, could not be well dispersed into and gelate in aqueous solutions over a wide range of pH. This observation confirms the importance of the $-\text{COOH}$ groups in the CTV-1 molecule in facilitating its hydrogelation. Interestingly, we also found that tuning the solution pH in a similar manner was able to induce the reversible gel-to-sol and then sol-to-gel transitions in the prepared CTV-1 and CTV-2 hydrogels (Fig. 1), again likely due to the (de)protonable groups.

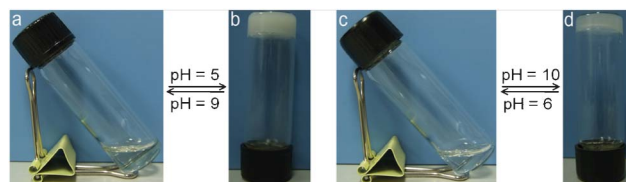


Fig. 1 pH induced gel-to-sol/sol-to-gel transitions of 10 g L^{-1} CTV-1 (a, b) and of 15 g L^{-1} CTV-2 (c, d).

The critical gelation concentration (CGC) was estimated to be 0.29% (wt) for CTV-1 and 1.1% (wt) for CTV-2 (Table 1); these are lower than most of the reported CGCs, including those of the CTV organogels.^{3d,17} It is interesting to observe that the CGC of CTV-1 is lower than that of CTV-2 by one order of magnitude, despite the small structural difference in the carboxylic acid and amide terminal functional groups (Scheme 1). This probably results from the intermolecular hydrogen bonding interactions in the gelation, since carboxylic acids could easily form a planar hydrogen bonded cyclic-dimer in the same layer whereas the amides prefer to form interlayer hydrogen bonds like that observed with 1,3,5-benzenetriamides.²⁰ This observation of the big difference in CGC caused by a small difference in the structure of the gelators also implies promising potential in tuning

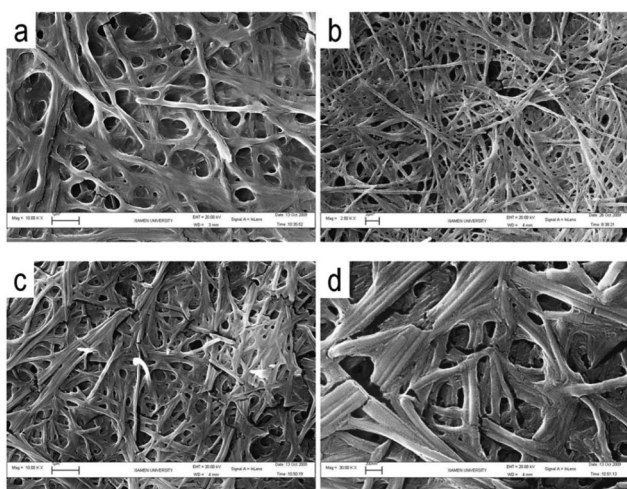
Table 1 Ionic strength effect on the hydrogelation and CGCs of CTV-1 and CTV-2 in water

KCl /mmol L ⁻¹	CGC /g L ^{-1a}	
	CTV-1	CTV-2
0	2.9	11
10	2	11
100	2	12
400	1	12
600	2	12 ^b
800	1 ^b	12 ^b

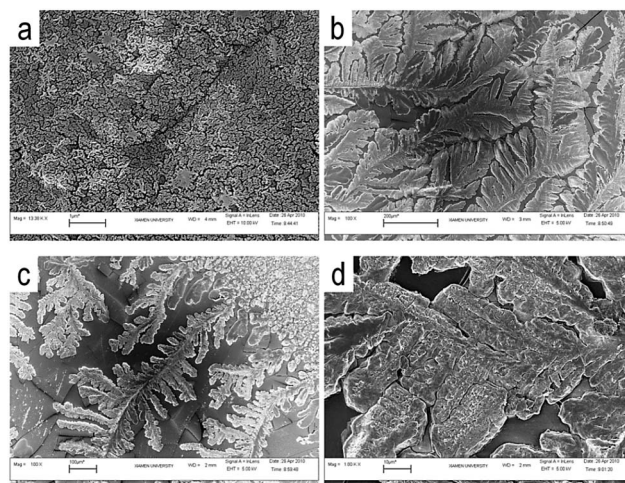
^a Opaque gel. ^b Unstable gel that starts to flow partially when shaken.

the gelation ability of the CTV hydrogelator by a slight structural modification.

The two supramolecular hydrogels were found to be stable for at least 3 months. In a sealed environment CTV-1 and CTV-2 hydrogels remained essentially unchanged when the temperature was increased from room temperature to 90 °C, which means that these CTV supramolecular hydrogels are thermostable. The morphology of CTV-1 xerogel was examined by field emission scanning electron microscopy (FESEM) (Fig. 2). It was observed that the supramolecular hydrogels were composed of very long nano-/micro-sized fibres that aggregated into cross-linked three dimensional networks. Fine striations inside flat fibres were also noted in the xerogels (Fig. 2d), which likely result from a highly compact state of the gelator molecules,^{17a,b} relating to the rigid cavitated structure of the CTVs. These fibres were too rigid to randomly cross stack, being thereby favourable for hydrogelation. It was therefore assumed that the CTV-1 molecules in aqueous solution underwent well-ordered assembling into one-dimensional structures that led to gelation once the three-dimensional structures were formed from the entangled fibres. CTV-2 xerogels, on the other hand, were found to consist mainly of aggregated clusters along shorter rod-like fabrics and to exhibit amorphous aggregates (Fig. 3), again differing substantially from the CTV-1 xerogels.

**Fig. 2** FESEM images of xerogels obtained from original supramolecular hydrogels of (a) 4 g L⁻¹, (b) 10 g L⁻¹, (c) and (d) 30 g L⁻¹ CTV-1. Scale bars are 1 μm (a, c), 2 μm (b) and 200 nm (d), respectively.

Ionic strength in solution was varied by KCl to probe the tolerance capacity of the gelation towards strong electrolytes

**Fig. 3** FESEM images of xerogels obtained from original supramolecular hydrogels of (a) 11 g L⁻¹, (b) 15 g L⁻¹, (c) and (d) 20 g L⁻¹ CTV-2. Scale bars are 1 μm (a), 200 μm (b), 100 μm (c) and 10 μm (d), respectively.

(Table 1). Opaque and stable gels were obtained in the presence of strong electrolytes over a wide range of concentrations from 10 mM to 800 mM, indicating that the hydrogelation could occur in the presence of a large amount of salt. This is important for the practical biological applications of these hydrogels. SEMs of xerogels of CTV-1 and CTV-2 made from their corresponding solutions containing KCl of varying concentrations showed more or less the same morphologies as those obtained in the absence of KCl (Figs. S1 and S2, ESI[†]). This means that KCl does not co-gelate with CTV-1 or CTV-2. It was also found that, in the presence of KCl, the CGCs were hardly changed either (Table 1), suggesting that the hydrophobic and hydrophilic interactions may operate in a synergistic manner in facilitating the gelation so that the strong electrolyte does not exert an observable influence. It is interesting to note that, in the case of CTV-1, the presence of KCl led to a shorter duration of *ca.* 2–3 h required for the gelation, and the resulting gels were more translucent than those obtained in the absence of KCl.

Both CTV-1 and CTV-2 contain the same luminophore. CTV-1 itself is however weakly luminescent in aqueous solution. In contrast, the CTV-1 hydrogel is highly luminescent under the same concentration of CTV-1, by a 5-fold enhancement in the emission intensity and a 10-nm blue-shift in the peak position, at 317 nm for the gel form with respect to 327 nm for the solution (Fig. 4a). Interestingly, the luminescence of CTV-2 in the gel state is turned on at the same position as that of the CTV-1 hydrogel, whereas its corresponding sol state is nonluminescent (Fig. 4b). These observations might be understood in terms of aggregation-induced emission.²¹ We also found that the emission wavelength of the hydrogels of CTV-1 and CTV-2 exhibited practically no dependence on the concentration of KCl in the solutions of CTV-1 and CTV-2 from which the hydrogels were made (Figs. S3 and S4, ESI[†]), again suggesting that KCl is not co-gelated with the CTVs, as indicated by the SEMs of their hydrogels (Figs. S1 and S2, ESI[†]).

Supramolecular hydrogels of both CTV-1 and CTV-2 show significant polarized optical property (Fig. 5, Figs. S5 and S6 in ESI[†]), indicative of their lyotropic anisotropic character. The two

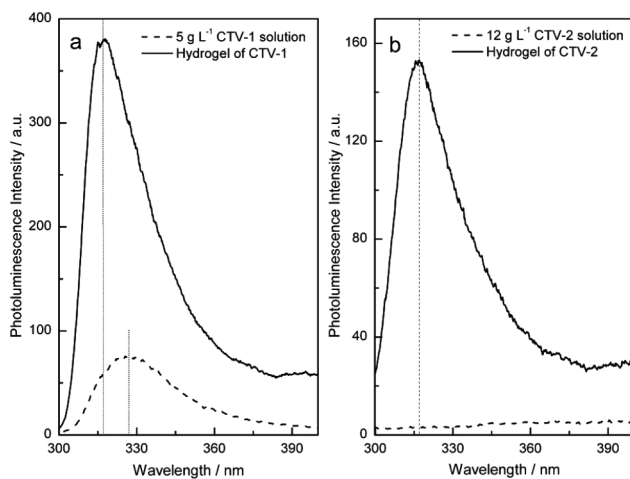


Fig. 4 Emission spectra of (a) CTV-1 in solution (pH 9) and hydrogel (pH 5) and (b) CTV-2 in solution (pH 6) and hydrogel (pH 10). [KCl] = 100 mmol L⁻¹, λ_{ex} = 290 nm.

optically anisotropic structures of the supramolecular hydrogels were also found to be stable at temperatures ranging from 30 °C to 80 °C (Fig. 5, Fig. S6 in ESI[†]). To the best of our knowledge, this is the first report of CTV-based optically anisotropic supramolecular hydrogels. This property of the CTV hydrogels can be safely assigned to the structural character of the rigid cavitanol CTVs.

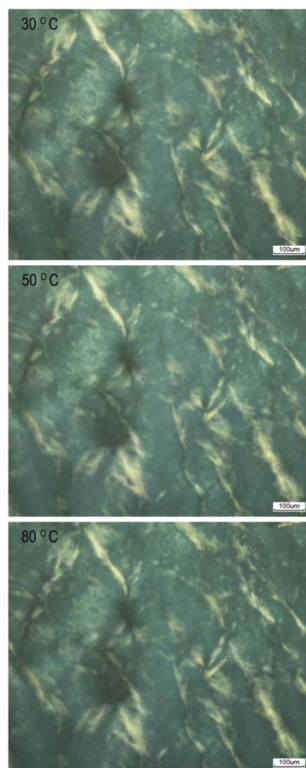


Fig. 5 Polarized optical photomicrographs of CTV-1 supramolecular hydrogel (30 g L⁻¹) at varying temperature.

Considering that weak interactions such as π - π stacking may be involved in the ordered aggregates and that the discotic molecules are capable of forming columnar, nematic, or lamellar phases,²² X-ray diffraction (XRD) was applied to probe the self-organizing

patterns of the crown-like CTV molecules in the gels. The XRD of CTV-1 xerogel shows three significant diffraction peaks (I, II, and III) at $2\theta = 7.4^\circ$, 14.9° , and 22.4° with lattice spacings of 12.0, 6.0, and 4.0 Å, respectively. The ratios of the lattice spacings are 1 : 1/2 : 1/3, which are characteristic of the lamellar packing (Fig. 6).^{3a,23} The layer spacing (D) of the aggregates obtained from the XRD pattern was *ca.* 12.0 Å, in agreement with the molecular diameter of *ca.* 15 Å calculated by the ChemOffice Chem3D software. Peak IV in the wide-angle diffraction region corresponds to a d -spacing of 3.46 Å, likely relating to the π - π stacking within the columnar structures formed from the self-assemblies of the CTV molecules. Therefore, stronger intermolecular interactions were shown to exist in the CTV-1 hydrogels compared to those of the previously reported CTV organogels that showed d -spacing of 4.5 Å^{17a} and 5.3 Å,^{17b} respectively. This can be understood in terms of the shorter lateral groups in CTV-1 that impose less steric constraint than that in the reported organogels formed from the counterparts of CTV-1 and that the CTV derivatives take offset arrangement along the axis to maximize the aromatic interactions between the crown-like molecules in a hydrophilic environment.²⁴ Both would lead to a decrease in the layer spatial separation along the column (Fig. 7). As for CTV-2 xerogel, a strong peak corresponding a d -spacing of 3.88 Å in the wide-angle XRD pattern also indicates an intermolecular stacking within its column (Fig. S7, ESI[†]). The absence of low-angle peaks in the XRD patterns, however, does not allow further analysis of the structural information of the CTV-2 xerogel.

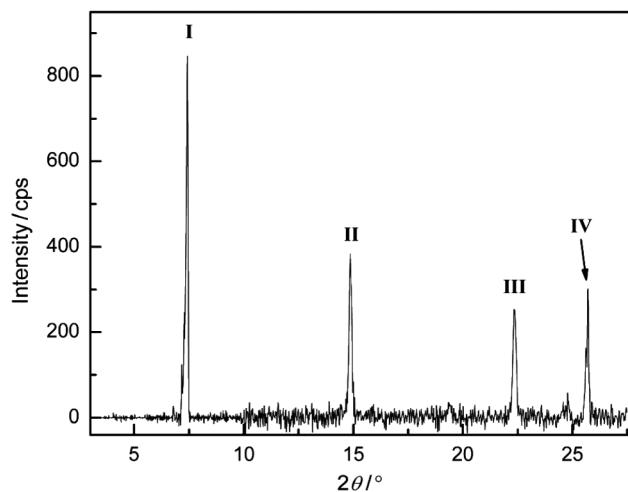


Fig. 6 X-ray diffraction pattern of CTV-1 xerogel (30 g L⁻¹).

We also recorded the XRDs of the native gels of CTV-1 and CTV-2, following a reported method.²⁵ In the XRD of the native CTV-1 gel, diffraction peaks I and II in the low-angle region occurred at 4.19° and 8.25° , corresponding to the lattice spacings of 21.1 Å and 10.7 Å, respectively (Fig. S8, ESI[†]). The ratio of lattice spacings is 1 : 1/2, consistent with that observed in the XRD of the CTV-1 xerogel (Fig. 6). The significantly larger lattice spacings in the native CTV-1 gel than those in the xerogel might be ascribed to the swelling of the lamellae. These observations further support the lamellar packing mode and the lyotropic anisotropic character of the hydrogel. Similar to that of the XRD of the CTV-2 xerogel, the low-angle region of the XRD of the native CTV-2

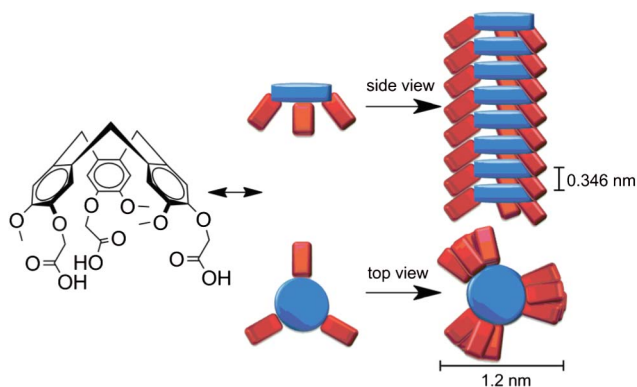


Fig. 7 Proposed self-assembling pattern of CTV-1.

hydrogel did not provide any structural information for the CTV-2 native gel (Fig. S9c, ESI†).

Such a significant difference in the morphologies of the hydrogels of CTV-1 and CTV-2 of similar structure (Scheme 1) promoted us to examine the rheologies of the CTV-1 and CTV-2 hydrogels. Rheologies under a low strain ($\gamma < 10\%$) within the linear viscoelastic (LVE) regime (Fig. 8) show that, for CTV-1 and CTV-2 hydrogels, the dynamic storage modulus G' is in general larger than the loss modulus G'' while both G' and G'' are almost independent of the strain, indicative of their gel state nature.^{3e,26} This observation also shows that the obtained hydrogels are solid-like rather than liquid-like. It should be noted that both the G' and G'' of the hydrogel of CTV-1 (10 g L^{-1}) are larger than those of the CTV-2 hydrogel (30 g L^{-1}) in the LVE regime, suggesting that the CTV-1 hydrogel fibres are intertwined more tightly to increase the elasticity of the hydrogel compared to those of the CTV-2 hydrogel.^{3e,26d} This agrees well with the observations made from their SEMs (Fig. 2 and 3). Note that both G' and G'' of the CTV-1 hydrogel, respectively, at 10^4 and 10^3 Pa are orders of magnitude are higher than some of the reported gels.^{3e}

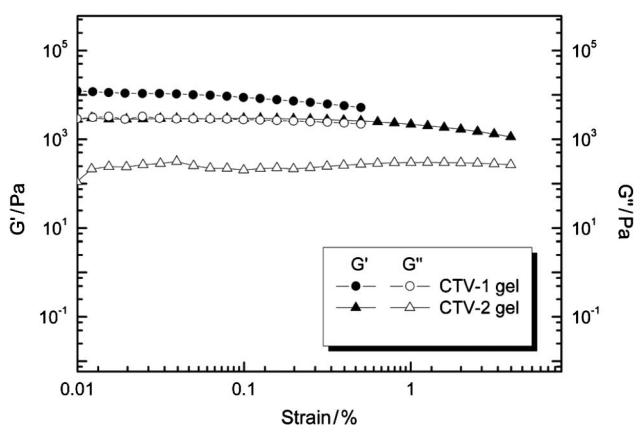


Fig. 8 Plots of storage modulus and loss modulus versus strain for hydrogels of CTV-1 (10 g L^{-1}) and CTV-2 (30 g L^{-1}) at $31 \text{ }^\circ\text{C}$.

Conclusions

Introducing ionizable $-\text{COOH}$ and $-\text{NH}_2$ terminal groups into the skeletons of CTVs, we successfully created hydrogelators

CTV-1 and CTV-2 from the rigid cavitand CTV host molecular skeleton. The present work provides a new entry to create CTV-based hydrogelators that have ionic groups in conjunction with the hydrophobic moieties of a compound capable of forming organogels that allow a balance between the hydrophilic and hydrophobic characters in the newly designed molecule would lead to a hydrogelator. Comparison of the hydrogelations of CTV-2 and CTV-3 that structurally differ only by three ethylene-linkers, supports this assumption. The highly structure sensitive hydrogelation observed between CTV-1 and CTV-2 hydrogelators confirms the critical impact of this balance. The ionizable groups in the gelator molecules also allow a slow *in situ* generation of the promising gelator in aqueous solution from its water-soluble precursor *via* solution pH variation.

The formation of the hydrogels was found to be induced by the self-assembly of the CTV molecules into extended three-dimensional networks. Both π - π stacking and hydrogen bonding are shown to be responsible for the hydrogelation. The CGCs of these CTV hydrogelators are lower than most of the reported CGCs including those of the CTV organogels and the optically anisotropic hydrogels of the CTVs exhibit a high thermostability and excellent tolerance towards strong electrolytes. Together with the luminescent and optically anisotropic characters, the CTV-based hydrogels reported here are expected to find optical and sensory/imaging applications. The possibility of interaction with external guest species and the observed highly structure-sensitive hydrogelation behavior of CTV-1 and CTV-2 provide hints to their applications.

Acknowledgements

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