



A mini review: supramolecular gels based on calix[4]arene derivatives

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Abstract

Supramolecular gels, materials with reversible phase that respond to external stimuli, form via multiple noncovalent interactions of gelator/gelator or gelator/solvent. Calix[4]arene, with an adjustable cavity and multiple modified sites, enriches the properties of supramolecular gels. The synthesis and properties of calix[4]arene supramolecular gels will be discussed and reviewed. There are three methods for constructing calix[4]arene supramolecular gels: (1) using cation- or anion-directed and assisted calix[4]arene derivatives to build a gel network; (2) using a calix[4]arene derivative and another compound together to construct a binary supramolecular gel; and (3) forming a calix[4]arene derivative self-assembled gel network. Moreover, increased interest has been shown in the application of calix[4]arene supramolecular gels.

Keywords Calix[4]arene · Supramolecular gel · Assembly

Introduction

Supramolecular gels, solid-like materials, have attracted great attention for their reversible phase and smart response to external stimuli [1] and are widely applied in controlled drug release [2], mild separation [3], smart cleaning [4], and new media for preparation [5] and purification [6, 7]. Supramolecular gels are usually formed by noncovalent interactions between gelators (Fig. 1), and their properties are enriched via introducing new interacting sites, introducing new functional groups or exploiting new noncovalent interactions and assembly [8]. Some special and functional structures, such as cholesterol [9], amino acids [10], glucose [11] and so on, are widely used as building blocks of supramolecular gels. In recent years, macrocyclic hosts such as crown ether [12], cyclodextrin [13], cucurbituril [14] and so on have been incorporated into gelators to construct excellent supramolecular gels [15].

Calix[4]arene, a cyclic oligomer condensed through phenol and formaldehyde units, has an adjustable cavity, variable conformation, an easily modified structure, convenient synthesis and unique molecular recognition of low-molecular-weight compounds, anions and cations via hydrogen bonding, electrostatic interactions, π - π stacking interactions and intermolecular forces [16]. Calix[4]arene is an excellent core structure for supramolecular assembly [17]. To date, supramolecular gels based on calix[4]arene have been reported in the following categories: (1) cation- or anion-directed and assisted calix[4]arene derivatives used to build gel networks; (2) a calix[4]arene derivative and another compound used together to construct a binary supramolecular gel; and (3) calix[4]arene derivatives self-assembled into a gel network. In this paper, the preparation and properties of all kinds of calix[4]arene supramolecular gels are reviewed.

Cation- or anion-triggered calix[4]arene derivatives supramolecular gels

Metal ligand coordination opens up a new research branch for the directed self-assembly of small molecules and is one of the main driving forces for structuring supramolecular gels [17]. Metal ions are introduced into a mixture of gelators and solvent to promote gel formation and enrich their properties. Jung and colleagues [17] described a stable metallogel of terpyridyl calix[4]arene (**1**, Fig. 2) in

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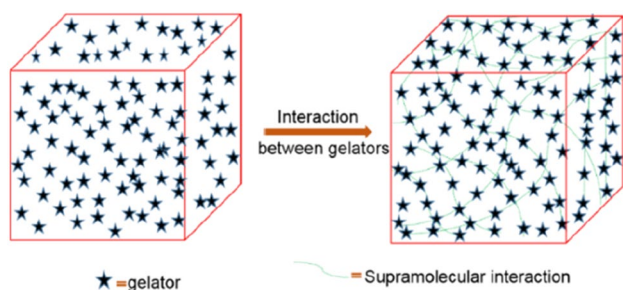
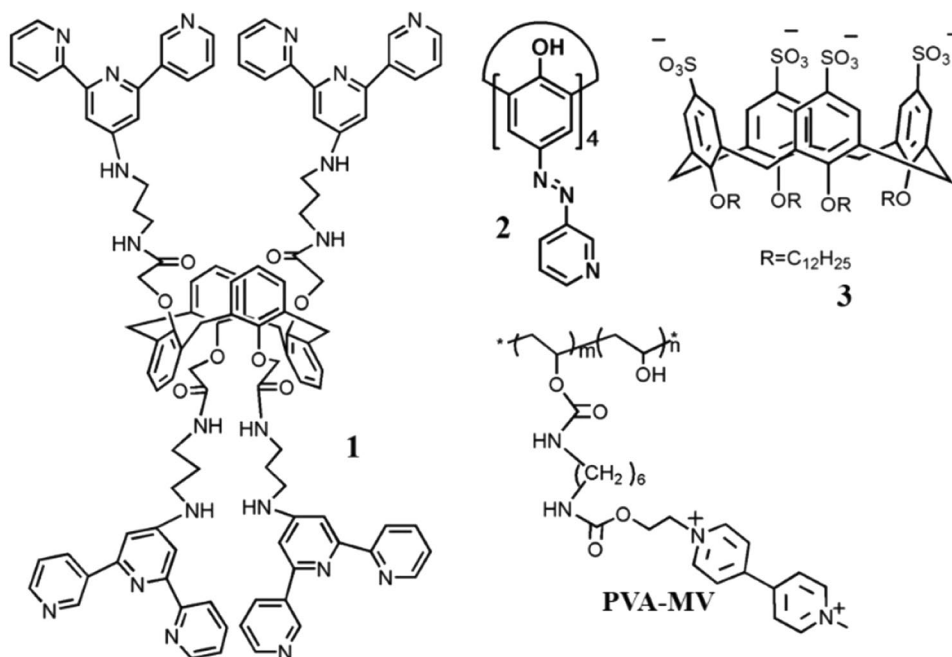


Fig. 1 Three-dimensional network formation of gelators via non-covalent interaction

the presence of Pt^{2+} (4 equiv.) at different volume ratios of $\text{DMSO}/\text{H}_2\text{O}$ (3:7–7:3, v/v) by Pt–Pt and π – π packing interactions. Further research showed that the enhancement of luminescence intensity and extension of luminescence lifetimes depended on the volume ratio of $\text{DMSO}/\text{H}_2\text{O}$.

Xu et al. [18, 19] presented a type of stable metallo-gel that spontaneously and effectively absorbed nonionic organic molecules (benzene, chlorobenzene, and malachite green) from aqueous solution up to 60 times and naphthalene from gas almost 2000 times but rejected ions, so it might be applied in chemical sensors, catalysis and separation techniques. After adding $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ to a mixture of **2** (Fig. 2)/ DMSO where the ratio of Pd(II) to **2** was 1.8:1–2:1 (mol:mol), it was found that Pd(II) cooperated with the nitrogen atom of the pyridine segment of **2** to form a metallo-gel, and more interestingly, this gel stably existed in an aqueous solution of pH 1–13 at high temperature (even up to 100 °C).

Fig. 2 Structure of **1**, **2**, **3** and PVA-MV



Liu et al. [20] prepared a supramolecular hydrogel with a porous structure and traced the gel hierarchical formation mechanism by a fluorescence probe (Nile red) in a cone-shaped SC_4AD (**3**, Fig. 2)/water solution. SC_4AD self-assembled into amphiphilic micelles, and these micelles adhered to PVA-MV chains by strongly interacting between sulfonatocalixarene cavities on the outer rim of SC_4AD micelles and viologen moieties on PVA-MV chains in water. The assembly of PVA-MV chains and SC_4AD micelles built a supramolecular gel with a sensitive response to temperature, redox conditions and ionic strength.

Lee and Park et al. [21] reported that K^+/Rb^+ ordered and assisted calix[4]arene tetraacetate (**4**, Fig. 3) to form metallo-gels in a mixture of methanol and water by coordinating with two carboxyl oxygens and two phenolic oxygens from calix[4]arene tetraacetate. They found that the Rb salt gel had a higher mechanical stability than the K salt gel and there were more metal coordination interactions and more hydrogen bonds between molecules in the Rb salt gel (Fig. 3a).

Mocerino and Ogden et al. [22] reported stable proline-functionalized calix[4]arene (**5**, Fig. 4) hydrogels at a pH range of 0–7 obtained by the addition of a specific anion and tuned the properties of the gels by altering the associated cation. They found that the influence sequence of anions on gelation was consistent with the Hofmeister series ($\text{I}^- < \text{ClO}_4^- < \text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{SO}_4^{2-}$) and the gelation ability gradually increased from right to left in their solution. Their group [23] also synthesized racemic proline-functionalized calix[4]arene (**5**, Fig. 4) and specifically studied the gel behavior of D-**5**, L-**5** and the mixture of D/L-**5** in

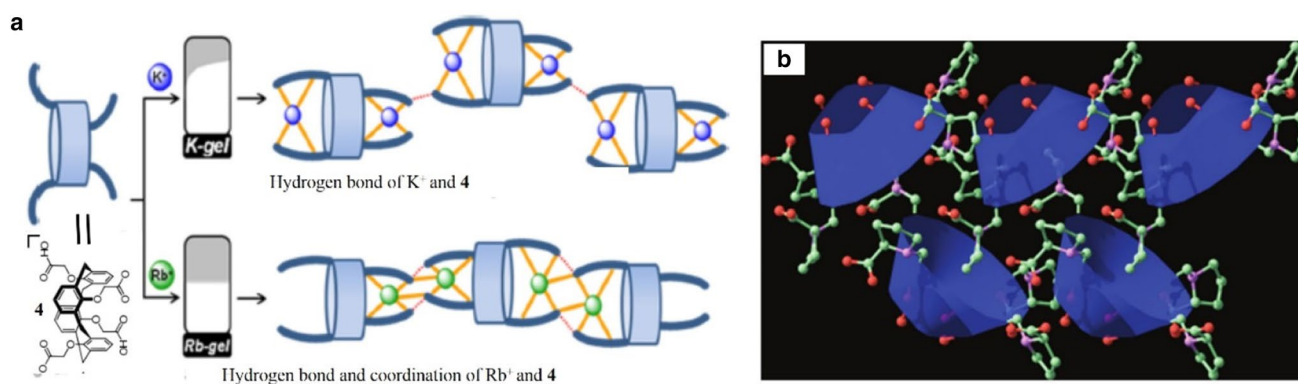


Fig. 3 3D framework formation mechanism of **4**/ K^+ , Rb^+ (a) and **5**(b)

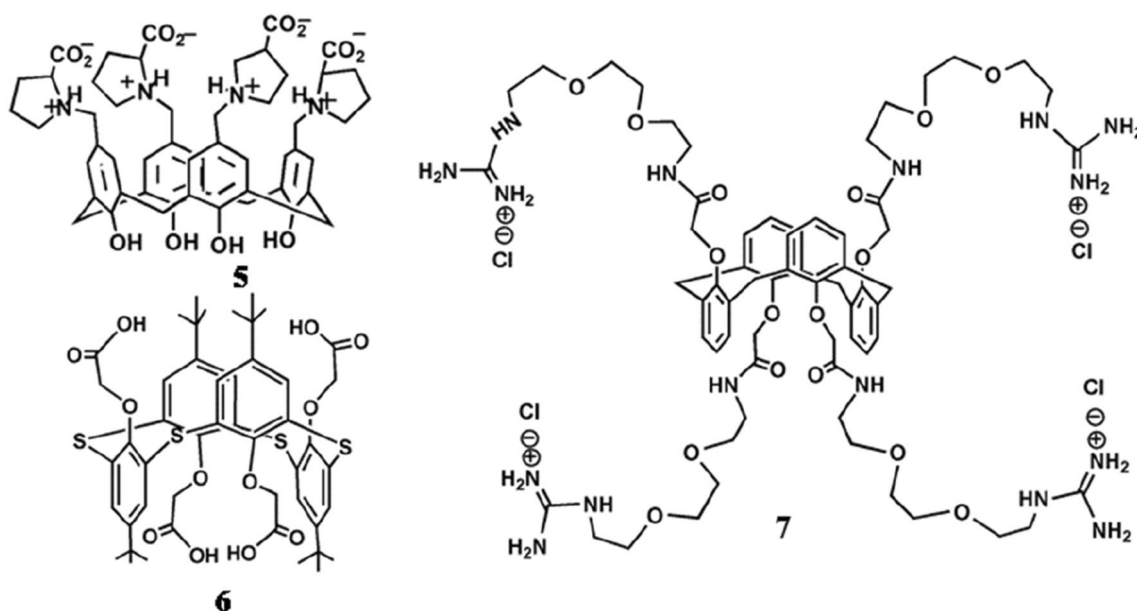


Fig. 4 Structures of **5**, **6**, **7**

aqueous lanthanum nitrate in detail. They found that racemic **5** had a minimum T_{gel} at a 1:1 M ratio of D-**5** and L-**5**. They proposed that the D(L)-proline fragment of **5** was included in the cavity of other D(L)-**5** molecules to spontaneously form a helix chain (Fig. 3b), and then those helix chains assembled into thick fibers via coordination between La ions and carboxylic oxygen from the centrosymmetrical proline moieties of two helix chains of the same isomer. Basic amino acids might appear in the form of anions or cations. Liu group [24] also created a series of hydrogels of **5** (Fig. 4) triggered by arginine, histidine, and lysine and found that the microstructure was also mediated by basic amino acids with variable side chains. They showed that the concentration of **5**, the component ratio of **5**/basic amino acid and the pH of the solution were three key factors determining the

formation of a hydrogel and that the concentration of **5**/basic amino acids affected the thermal stability of the hydrogel. They elucidated the formation mechanism of the hydrogel as follows: first, **5** aggregated into micelles, and then the micelles were linked by basic amino acids to form fibers. This gel was applied in drug delivery. After 1 year, Liu et al. [25] again reported a series of multiple-responsive hydrogels of **5** and different viologen bromides. They also found that viologen moieties with variable side chains affected the properties and morphology of the hydrogels. They investigated the stimulus responses of the hydrogels, including electrical, chemical, pH and thermal responses.

Jung et al. [26] reported a coordinated supramolecular gel of thiocalix[4]arene derivatives (**6**, Fig. 4) and Co^{2+} . They found that this gel changed color from red to blue after

treatment in volatile gases containing chlorine atoms and explained that a red octahedral Co^{2+} complex transformed into a blue tetrahedral structure with at least one cobalt(II) center in the structure of Co^{2+} coordinating with **6** in this process. The gel was applied as a chromoprobe to detect volatile gases containing chlorine. The Jung group [27] also constructed a clay nanosheet supramolecular hydrogel from clay nanosheets, acrylic sodium salt polymer (ASSP) and guanidinium-attached 1,3-alternate calix[4]arene (**7**, Fig. 4). They observed that 1,3-alternate cationic **7**, acting as a connector, bonded to clay nanosheets covered with anionic ASSP by electrostatic interaction, which built a gel framework and effectively increased the strength and elastic properties of the hydrogel.

Calix[4]arene derivatives binary supramolecular gels

A binary supramolecular gel comprises two gelators in a gel system [28]. In contrast to one-component systems, the network and properties of binary-component gel systems are also controlled by adjusting the molar ratio of the two components. In research on binary supramolecular gels conducted by the Zheng group [29–31], the chiral unit in the gelator played a crucial role and recognized other chiral components in the molecular assembly process [32, 33]. Chiral calix[4]arene derivatives (**8a–b**, **9**, **10**, Fig. 5) selectively assembled with enantiomer but did not effectively select for other chiral components in their solution. Different kinds of chiral calix[4]arene derivatives have their own assembly structure and mode. Coiled nanofibers formed with **8a/8b** and D/L-2,3-dibenzoyltartaric acid aggregated into larger ribbon-like fibers, and the optimum molar ratio of **8a** to D-2,3-dibenzoyltartaric acid was 2:1. **9a–c** formed

heat-set gels with vesicle structures with different 2,3-dibenzoyltartaric acids in cyclohexane, and the vesicle size of the gels was adjusted by changing the length of the alkyl group of the chiral calix[4]arene derivatives. More importantly, they found that the increasing unmatched interaction of **9** and D/L-2,3-dibenzoyltartaric chiral centers changed the gel behavior and microstructure at low temperature, so **9/D**-2,3-dibenzoyltartaric acid formed a gel at high temperature but a gel of **9/L**-2,3-dibenzoyltartaric acid at low temperature. L-2,3-dibenzoyltartaric acid, described in previous gels, was incorporated with calix[4]arene derivatives (**10**, Fig. 5). **10**/associated amine in gel assembled into nanofibers and nanospherical structures in suspension. Their research revealed that the association constant of **10** and some chiral amines affected the final morphology of the assembly: a larger association constant led to the formation of a gel or suspension, and with smaller constants, a solution was formed.

Jung et al. [34, 35] reported two binary hydrogels containing acid-appended calix[4]arene (**11** and **12**, Fig. 5). Though both **11** and **12** could be appended with acid, the minor difference in the linker determined the variable mechanism, structure and properties of the hydrogels. With the addition of certain amines, the solubility of **11** was improved, and a hydrogel was built by adding HCl. In this process, a spherical structure was first formed, and then a hydrogel network was assembled. **12** interacted with two D-alanines attached to 1,4-bipyridine derivatives to construct helical fibrous hydrogels by H-bonding and π - π interactions. The mechanical properties and P-type helical intensity of this hydrogel were controlled by achiral **12**.

The Steed group [36] introduced several applicable calix[4]arene-based gels for growing pharmaceutical crystal. They synthesized functionalized calix[4]arene (**13** and **14**, Fig. 6) and cultured drug crystals of

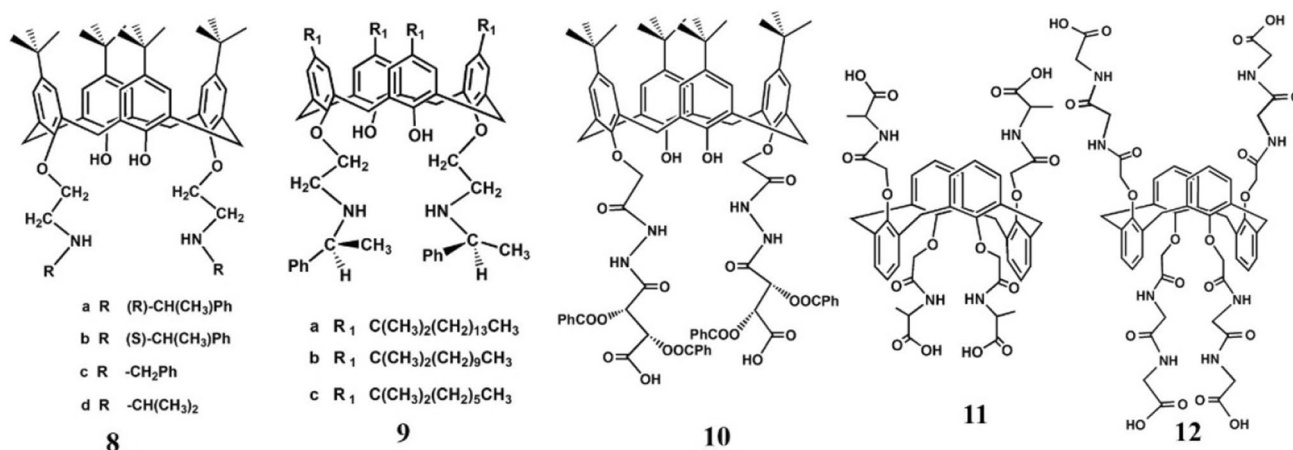


Fig. 5 Structure of **8**, **9**, **10**, **11**, **12**

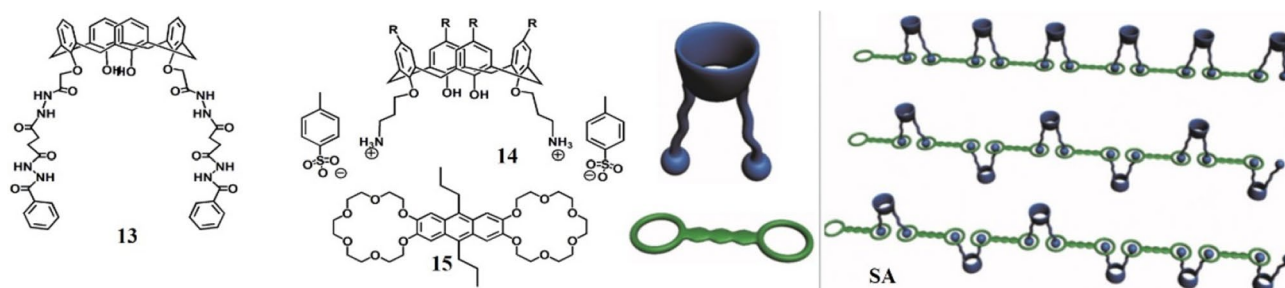


Fig. 6 Structure of compound (**13**, **14**, **15**) and self-assembly mode of **14/15(SA)**

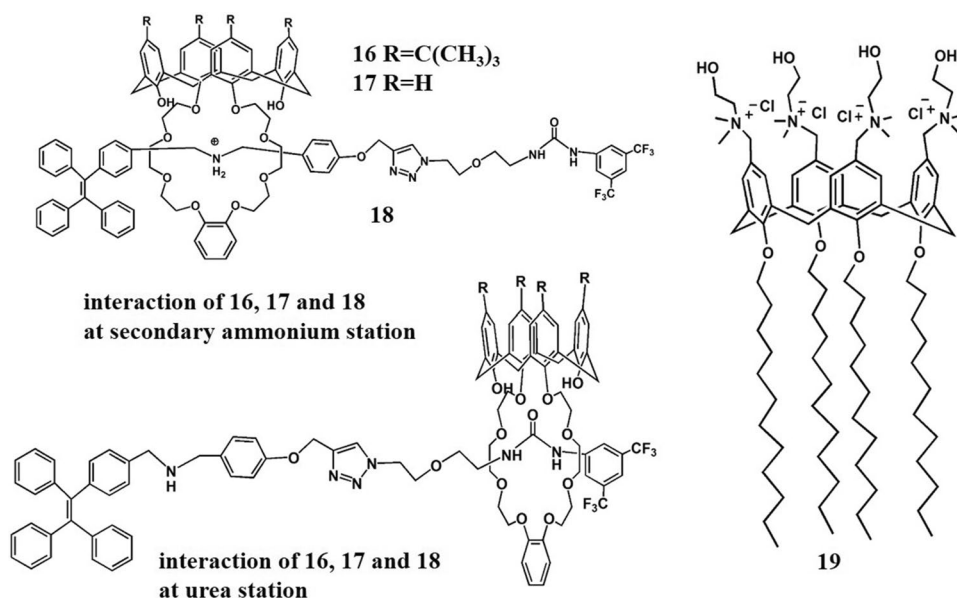
4-(4-biphenyl)-4-oxobutyric acid, 4-(benzyloxy)phenol, 3-(p-chlorophenoxy)-propane-1,2-diol, 3-(p-chlorophenoxy)propane-1,2-diol in **13**/1,2-dibromoethane gel or **14/15**/1,2,3-trichlorobenzene gel. A binary component gel of **14/15** in 1,2,3-trichlorobenzene was formed by host-guest interaction of **14-NH₃⁺** and **15-crown** (Fig. 6(SA)) and was destroyed by adding K⁺.

Arumugaperumal et al. [37] designed and synthesized calix[4]arene crown derivatives (**16**, **17**, Fig. 7) and tetraphenylethene (TPE) derivatives (**18**) incorporating secondary ammonium and urea units. They ingeniously constructed [2]rotaxanes with **16**, **17** as the wheel and **18** as the axle. Furthermore, they shuttled **16** or **17** at the ammonium and urea units of **18** by the addition of base/acid and formed four different dynamic amphiphilic [2]rotaxanes. Different [2]rotaxanes required different initial assembly conditions in the cosolvent of CH₃CN/water and

assembled into nanospheres and hollow nanospheres with wheel-stationed ammonium and urea units of **18**. Only one [2]rotaxane of **16** located at the ammonium position of **18** formed an organogel in methanol by intermolecular H-bonding, C-H... π , π - π , and hydrophobic interactions and van der Waals forces. They investigated the aggregation-inducing emission behavior of the TPE unit and morphological transformation of four different amphiphilic [2]rotaxanes in variable volume ratios of CH₃CN and water.

The Petralia and Consoli group [38] described an easily prepared, self-healing and injectable nanohydrogel of choline-calix[4]arene derivatives (**19**, Fig. 7)/PBS solution at physiologic pH in the presence of curcumin. Curcumin effectively built a bridge between micelles of **19**, which formed a nanohydrogel, and hid in or between micelles. The micellar nanohydrogel successfully prevented curcumin from rapid chemical and photochemical degradation and release at a high rate.

Fig. 7 Structure **16**, **17**, **18**, **19** and host-guest interaction of **16**, **17**, **18**



Self-assembly of calix[4]arene derivatives into supramolecular gels

Cholesterol, with a rigid skeleton and multichiral properties, has been used to construct organic supramolecular smart gel materials. Cholesterol derivative gels had good stimulus responses to light, pH, ultrasound and temperature [39]. Calix[4]arene and cholesterol were chosen as key components for the first time to construct a novel low-molecular-mass gelator (LMMG) by the Fang group [40]. They reported that a calix[4]arene derivative containing two cholesterol moieties (**20**, Fig. 8) was an efficient gelator for the cosolvent of n-decane and acetonitrile (9:1 ~ 3:2, $V_{\text{decane}}:V_{\text{acetonitril}}$). Interestingly, the gel showed an O/O porous structure and exhibited very smart thixotropic properties. On this basis, they [41] incorporated a chiral phenylalanine residue (L and D) in the linker of calix[4]arene bicholesteryl derivatives (**21**, Fig. 8) and found that L-**21** gelled n-pentanol and n-butanol, but D-**21** only formed a gel in isopropanol at room temperature. They observed that mechanical agitation or sonication not only promoted the gelation of D-**21**/isopropanol but also enhanced the strength of the gel. They investigated the morphology of D-**21** at different times with mechanical agitation in the gel process and a hexagonal molecular stacking mode in the gel. The Fang group [42] also reported that fluorescence calix[4]arene derivatives with naphthalene in the linker (**22**, Fig. 8) gelatinized many polar and nonpolar organic solvents, but the gels in benzene had smart shear

thixotropic properties and a Tgel higher than the boiling point of benzene. They also studied the morphologies of **22** in gels/solutions with benzene and the hexagonal molecular stacking mechanism of the gels (Fig. 9).

Rao et al. [43] synthesized a monocholesteryl calix[4]arene derivative (**23** Fig. 8) and found that **23** gelatinized a mixture of tetrahydrofuran and acetonitrile (1:1, v/v) even at 0.6 wt%. They investigated the stacking mode of the gel by DFT and MM. Two optimized molecules of **23** assembled a head-to-tail dimer, and then every eight dimers

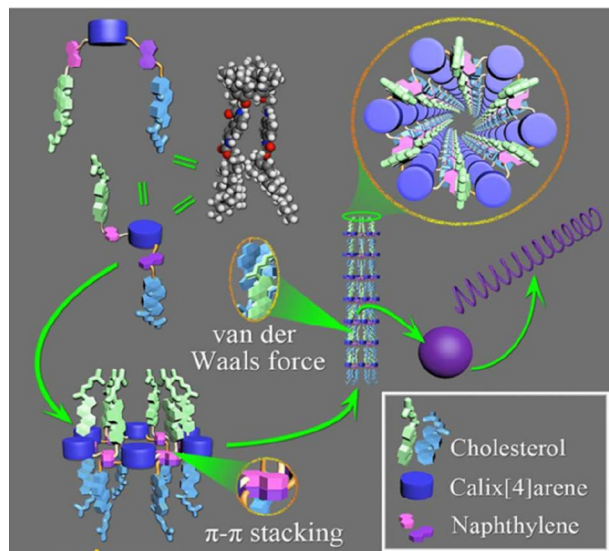
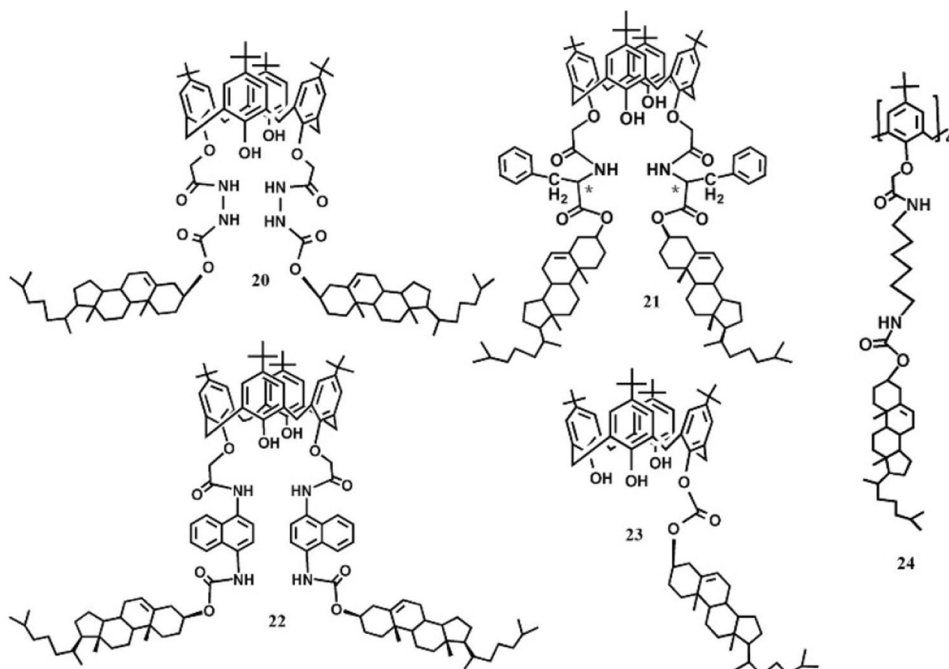


Fig. 9 Hexagonal molecular stacking mechanism

Fig. 8 Structure of **20**, **21**, **22**, **23**, **24**



arranged into a linear octamer in an end-to-end fashion. After further minimization of the linear octamer, one octamer was surrounded by six octamers to form a hexagonal heptamer. Finally, seven hexagonal heptamers assembled into a cylindrical bundle in the same mode as in the previous step. They also found that the gel could entrap a drug and easily release it into the aqueous phase, so it was applied in drug delivery.

Cai et al. [44] synthesized novel tetracholesteryl calix[4]arene derivatives (**24** Fig. 8) and discovered that **24**/kerosene formed a transparent gel at 65 °C and transformed into a fragile opaque gel at 25 °C. This phenomenon was correlated with the amount of cholesterol that participated in the stack, as shown by ¹H NMR, IR and microrheology experiments. In addition, Yang et al. [45, 46] synthesized bi/tetracholesterol calix[4]arene derivatives and studied mesomorphic behaviors and columnar molecule arrangement of these compounds, but they not investigated the gel behaviors of bi/tetracholesterol calix[4]arene derivatives.

Chung et al. [47] synthesized a series of bis(calix[4]arene) gelators (**25a–d**, Fig. 10) and found that **25a** formed organogels in different alcoholic solvents and selectively gelatinized oil in a mixture of oil/water. The driving forces of gel formation were the hydrogen bonding interaction of the down-rim phenol hydroxyl of calix[4]arene, the dipole-dipole interaction of the isoxazole fragment and the Van der Waals interaction of the tertiary butyl of calix[4]arene. They also utilized UV-vis, fluorescence and ¹H NMR spectra to prove the response of the gel solution of **25a** to Cu²⁺, Hg²⁺, and Ag⁺. Chung et al. [48] presented a bis(calix[4]arene) with anthryl group in the linker (**25**, Fig. 10) and achieved a thermoresponsive and blue-emitting organogel of **26**/CH₃CN. They studied in detail the aggregation process of the organogel from hollow spheres to a colloidal morphology. The reason for molecular assembly was attributed to van der Waals interactions between the

butyl of **26**, intermolecular hydrogen bonding interactions of each calixarene-OH, and dipole-dipole interactions between 9,10-bis(isoxazolyl)anthryl groups.

Chung et al. [49] created an organogel of azobenzene-bridged bis(calix[4]arene) (**27**, Fig. 10) and revealed that the morphological transformation of nanofibers and nanorings or closed/opened vesicles could be adjusted by modifying the UV/vis light and solvent. They attributed the driving forces of organogel formation to intermolecular H-bonding, van der Waals interactions of calix[4]arene fragments and strong dipole-dipole interactions of triazole units. In contrast, **28** modified by isoxazoles (Fig. 10) did not gel in any solvent because the triazoles in **27** have stronger dipole-dipole interactions with each other than the isoxazoles in **28**.

Zheng et al. [50] synthesized four amphiphilic calix[4]arene derivatives (**29a–d**, Fig. 11) and only obtained two temperature-responsive hydrogels of **29a–b** (Fig. 11) in a cosolvent of deionized water and ethanol. They studied the aggregates of **29a** in solution and hydrogel at different standing times after the addition of water in a mixture of **29a**/ethanol, and the results showed that **29a** first spontaneously assembled into unstable nanospheres and then dissolved to reaggregate into stable nanofibers. They used the hydrogel as a template to make hollow silicon nanofibers.

Sharma and colleagues [51] presented four thermally stable bowl-shaped bisubstituted thiacalix[4]arene derivatives (**30a–d**, Fig. 11), and only **30c–d** formed organogels in nonpolar dodecane and decane but generated precipitates in polar solvent. They observed by XRD that **30c–d** exhibited lamellar and rectangular arrangements in the xerogel. The driving forces of organogel formation were attributed to hydrogen bonding between -CH=N- and -OH groups of (**30c–d**), interactions of the sulfur bridge with nearby hydroxyl groups and π - π interactions. The

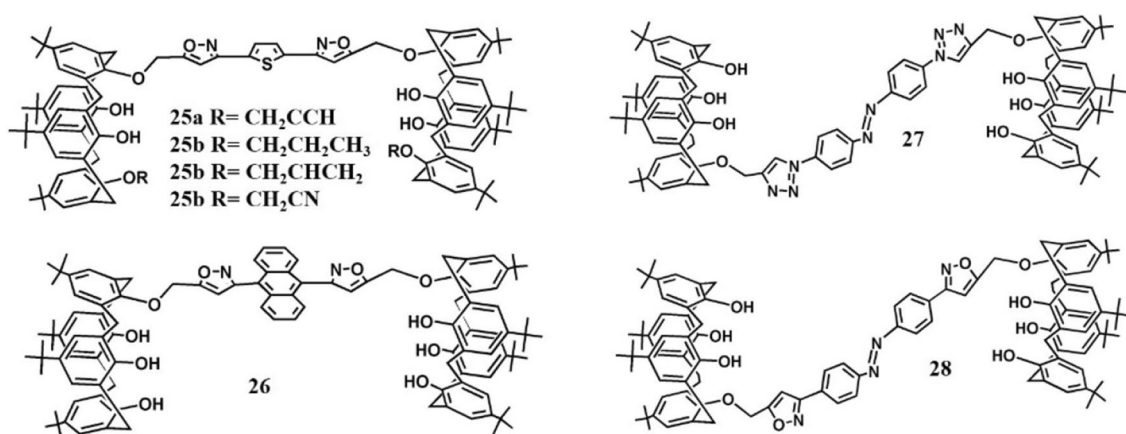


Fig. 10 Structure of **25**, **26**, **27**, **28**

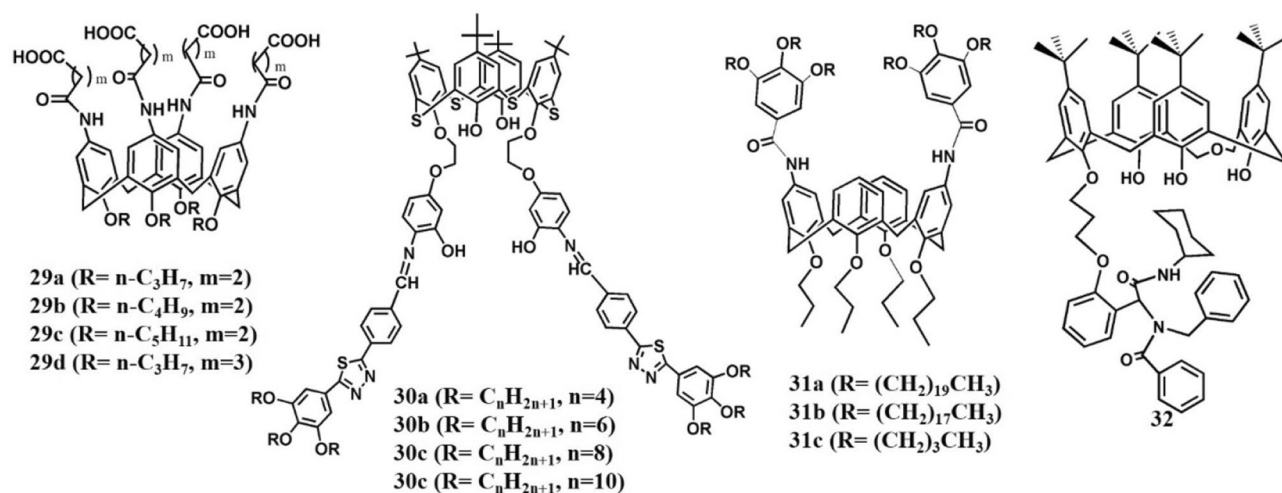


Fig. 11 Structure of **29**, **30**, **31**, **32**

electroluminescence performance of **30c** with blue light-emitting fluorescence was studied in an OLED device.

The Haino group [52] reported three 5,17-difunctionalized calix[4]arenes (**31a–c**, Fig. 11) and successfully formed two translucent organogels of **31a–b** in many organic solvents. The stacking structure of the **31a** xerogel was lamellar, according to SEM observation and X-ray detection.

Recently, Yan, Wang and colleagues [53] obtained a soft supramolecular gel based on a new functional p-tert-butyl-dihomooxalix[4]arene (**32**, Fig. 11) by the simple methods of heating, cooling and standing the mixture. This gel has good thermoreversibility, maintains its shape in water and exhibits an interconnected and homogeneous porous structure, which lays the foundation for sustained drug release.

Conclusion

Calix[4]arene units were introduced into supramolecular gels to enrich the gel properties and exploit novel applications. Supramolecular gels based on calix[4]arene derivatives have been well studied in recent decades. There are three methods that can be used to prepare this type of supramolecular gel: cation/anion-assisted supramolecular gel formation; the use of two gelators together to construct a calix[4]arene binary supramolecular gel network; and the self-assembly of calix[4]arene derivatives to form a supramolecular gel.

The properties and applications of calix[4]arene-based supramolecular gels have been increasingly studied. The design and synthesis of calix[4]arene derivatives incorporating a variety of ligands to create metallogel systems with novel versatile properties are anticipated and provide a powerful approach to make responsive soft materials. Moreover,

introducing the self-assembly of functional molecular units into calix[4]arene to form supramolecular gels is expected to lead to the construction of new nanoscale materials/devices and afford more gel media for pharmaceutical crystallization. Finally, supramolecular gels based on calix[4]arene have received increasing interest for use in absorbing metallic ions and low-molecular-weight organics and drug delivery/release.

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