

## **Macrocyclic Gelators**

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## Macrocyclic Gelators

The field of low molecular weight supramolecular gels, also known as physical gels, has grown rapidly over the last decade. In these gels small molecules (gelators) self assemble through non-covalent interactions, usually into a network of fibres, to trap solvent. Many physical gels are responsive to stimuli and often these types of gels can be reversibly converted from gel to sol. These properties make them ideal candidates for investigation into a range of potential applications, including biomedical, smart materials, sensors and catalysts. This review provides an overview of macrocyclic compounds, particularly the calixarenes, that can form supramolecular gels.

Keywords: gelator, macrocycles, calixarenes, gelating agents, supramolecular gelators

Dedicated to Professor Rocco Ungaro on the occasion of his 70th birthday and in recognition of his great contribution to the field of calixarene chemistry.

### Overview of small molecule gelators

‘The colloidal condition, the ‘gel’, is one which it is easier to recognise than to define ...’ (1) Although gel materials are difficult to define, Smith (2) defines a gel as ‘a colloidal form of matter in which a “solid-like” network is suspended within a “liquid-like” continuous phase.’ The idea that gels comprise two components (a ‘solid’ and ‘liquid’) is a central theme among many of the different definitions of a gel (3-7). Gels are colloids but not all colloids are gels (8).

Gels can be classified by their ‘solid-like’ component or their ‘liquid-like’ phase (Figure 1) (9). In chemical gels, the solid network is bound by covalent bonds cross-linking the network (e.g. polymers). This results in robust gels but the solid network cannot break down into its constituent monomers. Physical gels in contrast, typically comprise self-assembled small molecules (in the case of supramolecular gels) linked

together by non-covalent bonds (e.g. hydrogen bonds,  $\pi$ - $\pi$  stacking, hydrophobic effect (10)). As a result of non-covalent bonding, physical gels can transform back into a free-flowing liquid. Gels can also be classified by their continuous phase. Traditionally, the liquid continuous phases considered were water and organic solvents, which gave hydrogels and organogels respectively. Some gelators are capable of gelling both water and organic phases separately (11-15). Gels comprising ionic liquids ('ionogels') have been reported (16-18). Gels with a continuous phase comprising a gaseous phase are also possible if the organic solvent or supercritical fluid is removed, giving xerogels and aerogels (19) respectively. Of particular interest in this review, are low molecular weight hydrogels.

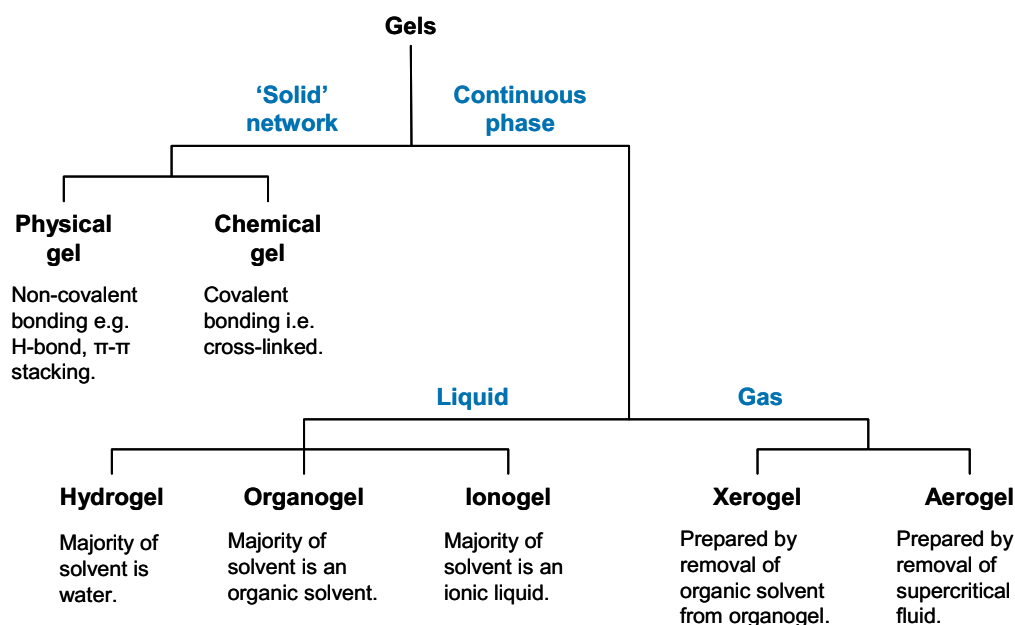


Figure 1. General classification scheme for gels.

Many gelators have been (and still are) discovered by serendipity (20-24). In light of potential applications of gels (4, 25-29), recent efforts have been directed towards the rational design of low molecular weight gelators (4, 20, 30, 31) which are primarily based on known gelator structural motifs such cholesterol (32, 33) (Figure 2) and  $C_3$ -symmetric cores with hydrogen bonding motifs (34) (Figure 3). Physical gels or

supramolecular gels (35) can be considered to be comprised of supramolecular polymers (36, 37) thus, designing self-assembly (38, 39) would aid in the synthesis of potential gelator molecules. This review will explore examples of low molecular weight gelators based on macrocyclic compounds, with an emphasis on calixarene based gelating agents.

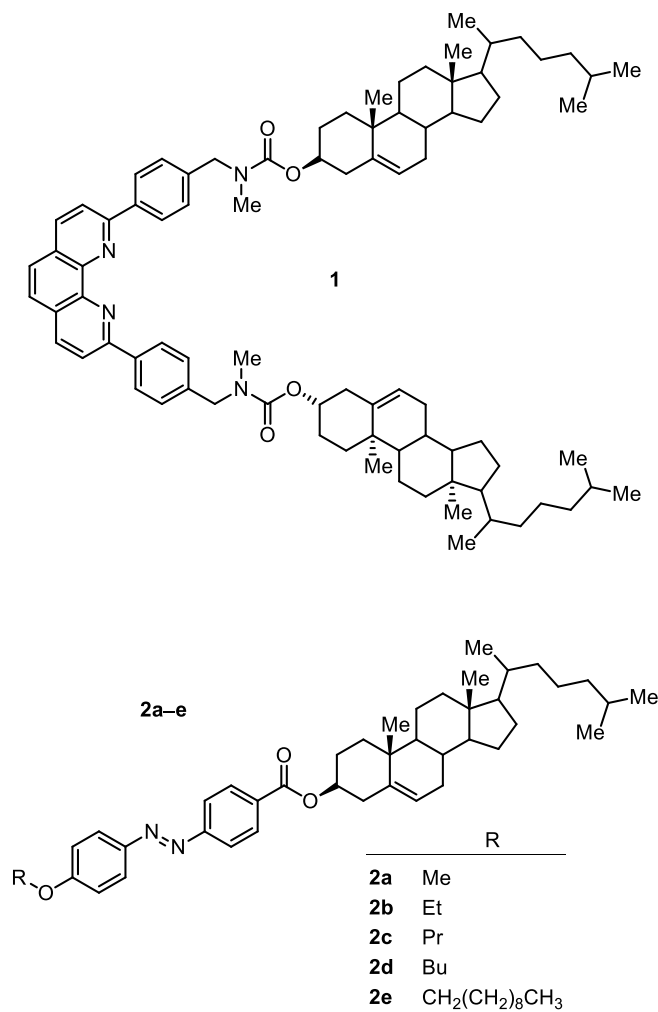


Figure 2. Examples of cholesterol-based organogelators (40, 41).

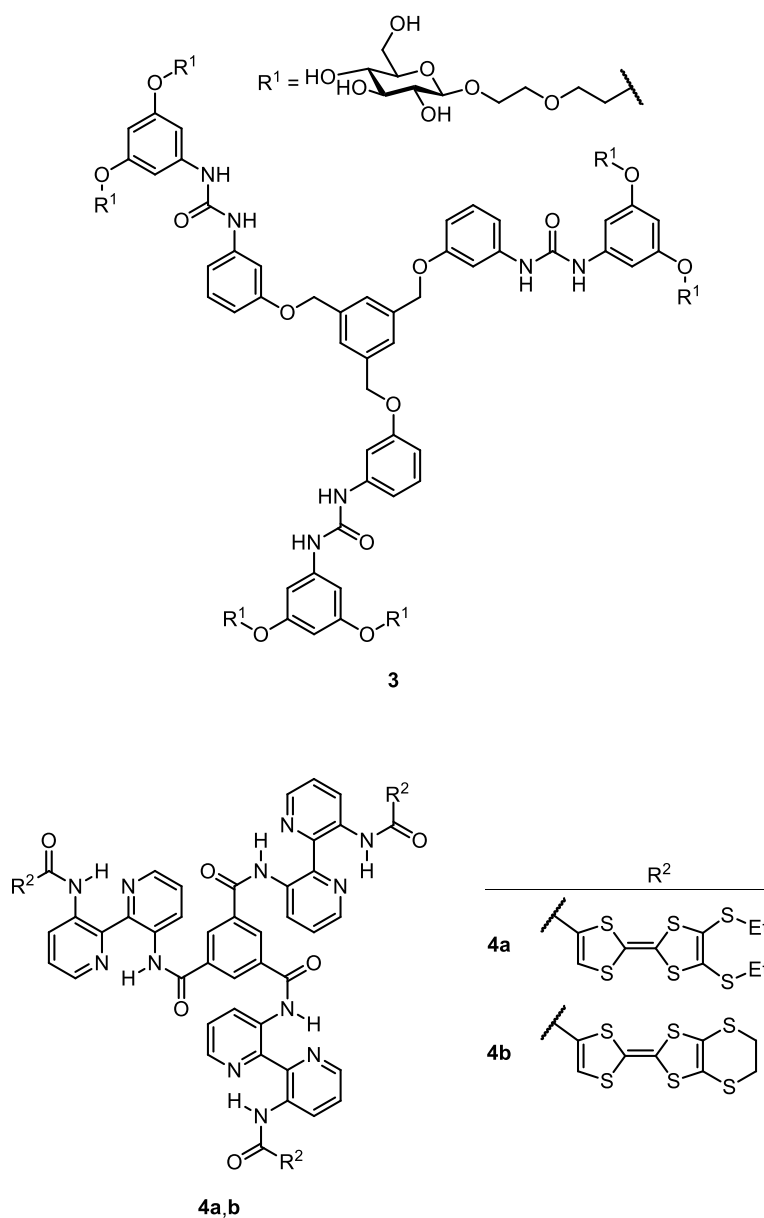


Figure 3. Examples C<sub>3</sub>-symmetric gelators (42, 43).

Gels, particularly those based on small molecule-based gelators, have generated much interest recently with a range of potential applications (4, 9, 16, 29, 30, 44, 45). Much of the recent literature shows that research efforts are being directed at biomedical applications (25, 26, 46-49) (drug delivery, tissue engineering, regenerative medicine), smart materials and sensors (which are responsive to external stimuli) (42, 50, 51), and templates for crystallisation (such as pharmaceuticals (52) and production of composite materials(53)). Other possible applications explored include using gels as reaction media (54), for catalysis (55-58), and water purification (59). Some gels, albeit

macromolecule-based, have also been applied to art conservation (60, 61). The ready accessibility and wide range of potential applications of supramolecular gels have made them a highly active research area.

### Calixarene- and resorcinarene-based gelators

A large number of gelators have been reported in the literature, however only a handful of these are macrocycles, the majority of which are calixarene- or resorcinarene-based.

#### Calixarene-based gelators

Some early examples of calixarene-based gelators were reported by Aoki et al. (62, 63). Calixarenes **5–7** (Figure 4) were acylated at the wide-rim with variable length alkyl chains. The best gelators were found to be **5c** and **7b,c** and were capable of gelling solvents such as carbon disulfide, hexane, decane, butanol, and isopropyl alcohol (by heating and cooling the gelator in the solvent). The authors proposed that  $C=O \cdots HO(\text{calixarene})$  hydrogen bonds and  $C=O \cdots C=O$  dipole-dipole interactions were the key in inducing self-assembly in organic solvents; the strength of the  $C=O \cdots HO(\text{calixarene})$  interactions were sufficient to overcome  $C=O \cdots HO(\text{alcohol})$  interactions to gel alcohols.

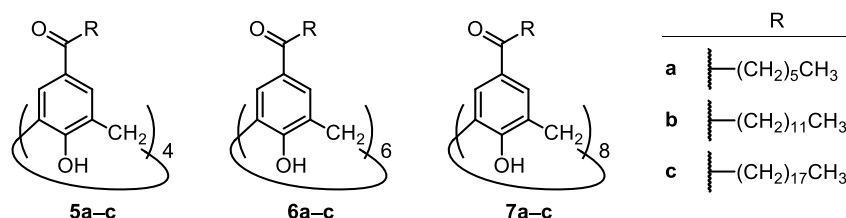


Figure 4. Calixarene-based organogelators investigated by Shinkai's group (62, 63).

In some cases, the gelator formed a gel in the presence of a second component (Figure 5). Xing et al. (64) showed that extended polymeric networks could be formed by coordination of the 3-pyridylazo moiety of calix[4]arene **8** to  $[Pd(en)(H_2O)_2](NO_3)_2$

forming a metallogel. A metallogel was observed for a range of organic solvents such as dimethylsulfoxide, tetrahydrofuran, acetic acid, chloroform, and dichloromethane. The metallogel formed in dimethylsulfoxide showed remarkable stability over a wide pH range (pH 1–13) and high temperatures (100 °C). In addition, the authors found that the metallogel could ‘uptake’ toluene from an aqueous solution with performance comparable to activated carbon.

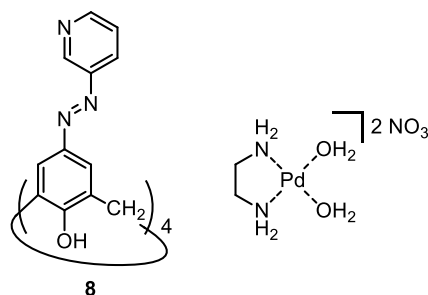


Figure 5. Calixarene **8**, functionalised with pyridyl-azobenzene moieties, formed metallogels with  $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ , where en = ethylenediamine ligand (64).

New gelators can be designed incorporating functionalities known to facilitate gel formation (4). Cholesterol-based organogelators are well known (32) and cholesterol has been appended to the narrow-rim of calix[4]arenes by Cai et al. (65) (Figure 6). Calix[4]arene **9** was found to form gels (>1.0 wt/vol%) in a mixed solvent system, acetonitrile/decane, however the acetonitrile content must be 10–60 vol/vol%. Further investigation by the authors showed that the gel was like an ‘oil-in-oil’ emulsion where acetonitrile was trapped within the **9**-decane gel; calix[4]arene **9** is soluble in decane. In addition, the **9** organogel was found to possess thixotropic properties. Thixotropic gels become liquids when shaken or stirred vigorously, (breaking non-covalent interactions between the gelator and solvent), however regain their gel state on resting (allowing supramolecular interactions to reoccur).

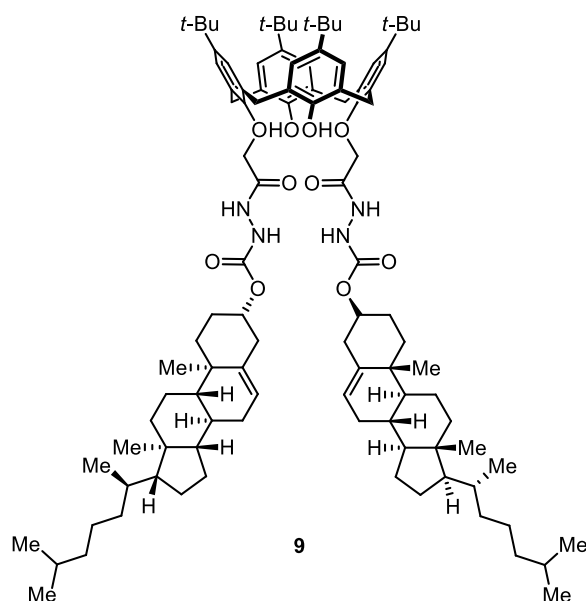


Figure 6. Cholesterol-functionalised calix[4]arene investigated by Cai et al. (65) as an organogelator.

Zheng et al. (66) investigated the formation of organogels by amine functionalised calix[4]arenes **10a–d** (Figure 7). The authors found that calix[4]arenes **10a** and **10b** could enantioselectively form a gel in the presence of 2,3-dibenzoyltartaric acid **11** (i.e. **10a–D-11** and **10b–L-11**). Gels could be formed in a variety of solvents such as dichloromethane and benzene but not in solvents that can form hydrogen bonds (e.g. diethyl ether, acetone). Characterisation of the organogels by atomic force microscopy and scanning electron microscopy (of the xerogel) showed that the gelators and tartaric acid self-assembled into fibrils. Further investigations by the group showed that achiral calix[4]arene **10c** did not form a gel whereas calix[4]arene **10d** formed a gel although it was not enantioselective.

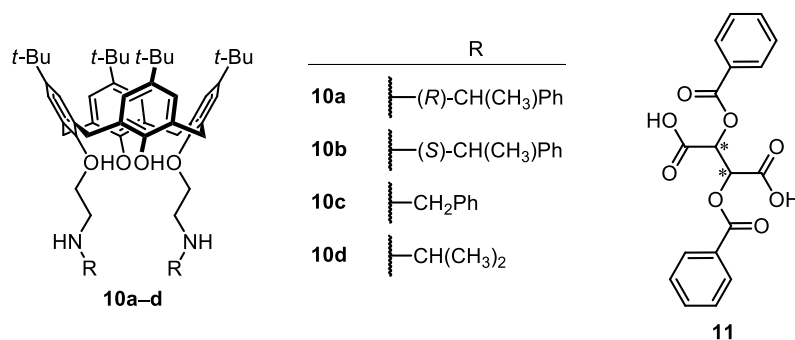




Figure 7. Chiral calix[4]arenes investigated by Zheng et al. (66) **10a–b,d** formed organogels in the presence of **11**.

Zhou et al. (67) extended their investigation into calix[4]arenes **10a–d** by substituting the *tert*-butyl substituent with long alkyl chains. Calix[4]arenes **12a–c** (Figure 8) and 2,3-dibenzoyltartaric acid **11** also formed organogels. The authors found that a solid mixture of **12a** and L-**11** (produced by dissolving both compounds in chloroform followed by removal of the solvent) dissolved in cyclohexane formed a gel after heating to 60 °C then cooling to 20 °C (like many gelators published in literature). However, heating a solid mixture of **12a** and D-**11** in cyclohexane formed a gel at 60 °C but the gel returned to a solution when cooled to 20 °C. Similar observations were made for **15b,c** with L- and D-**11**. Interestingly, **12** and L-**11** organogels formed fibres whereas **12** and D-**11** organogels formed a mixture of fibres and vesicles. The calix[4]arene **12** and D-**11** formed vesicles in cyclohexane solution (as opposed to fibrous structures). They suggested that the mixed chirality between **12** and D-**11** led to the formation of unstable fibres, therefore heat was required to destabilise the more stable vesicles.

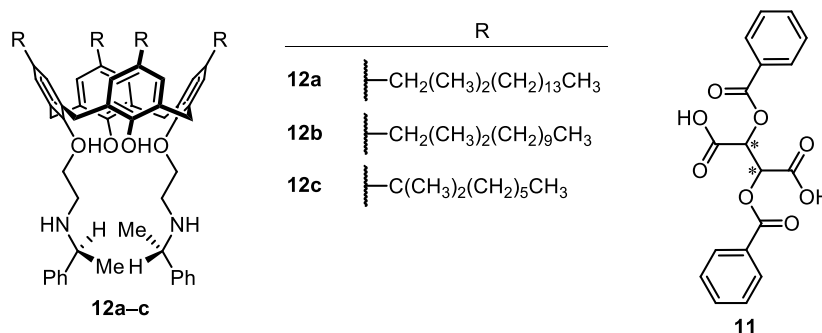


Figure 8. Chiral calix[4]arenes investigated by Zhou et al. (67) **152** formed organogels cyclohexane with L-**11** after heat and cooling. **152** and D-**151** formed organogels when heated to 60 °C but formed a solution on cooling to 20 °C.

Zheng et al. (68) further examined chiral amine interactions with 2,3-dibenzoyltartaric acid by exchanging it with the narrow-rim substituted amine. The authors attached L-2,3-dibenzoyltartaric acid via a hydrazide to the narrow-rim of a calix[4]arene to give **13** (Figure 9). Calix[4]arene **13** formed an organogel with amine (*R*)-**14** in 1,2-dichloroethane whereas (*S*)-**14** remained a solution. The calix[4]arene **13** did not form gels or exhibit chiral recognition with amines **15–17** in 1,2-dichloroethane. However, altering the solvent to a mixture of 1,2-dichloroethane and cyclohexane gave an organogel with calix[4]arene **13** and amino alcohol (*S*)-**15**. Calix[4]arene **13** with amino alcohol (1*R*,2*S*) **16**, and diamine (1*S*,2*S*) **17** gave a suspension in mixtures of 1,2-dichloroethane and cyclohexanol. Characterisation of the gels and suspensions showed solid spherical structures unlike the fibrils observed with organogels of calix[4]arenes **10a,b** and **12**.

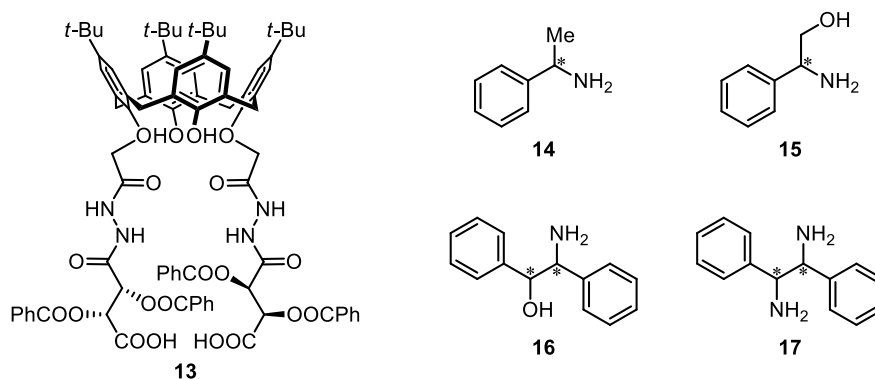


Figure 9. Calix[4]arene **13** investigated by Zheng et al. (68) for gel formation with chiral amines.

Another two-component organogel system was reported by Vreekamp et al. (69) Calix[4]arene **18** (Figure 10) substituted with 1,3,5-triazine at the wide-rim formed an organogel in the presence of an equimolar equivalent of barbituric acid **19** in chloroform. This serendipitous discovery was made during NMR experiments and the organogel was not further characterised.

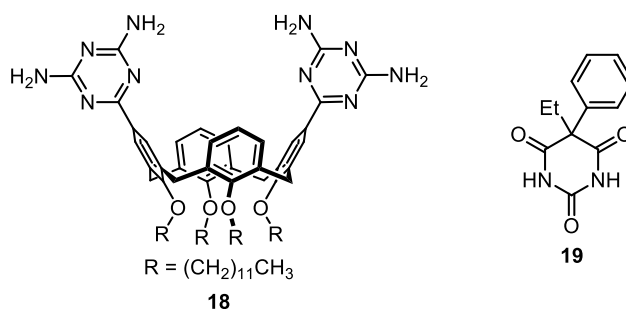


Figure 10. Calix[4]arene **18** forms a two-component organogel with **19** (69).

Dudic et al. (70) may have unintentionally prepared a hydrogelator (Figure 11) during their investigation of guanidinium-functionalised calix[4]arenes for binding to plasmid DNA. They noted that calix[4]arene **20** formed ‘a gelatinous macroscopic aggregate in water’ whereas the other calixarenes under investigation did not show signs of micellar aggregation by  $^1\text{H}$  NMR spectroscopy.

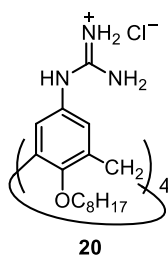


Figure 11. Potential hydrogelator prepared by Dudic et al. (70)

An amphiphilic calixarene-based hydrogel was briefly mentioned by Fujii et al. (71) (Figure 12) amongst their studies of calixarene-based micelles. The authors noted that an aqueous solution of **21** in sodium chloride formed spheres at  $\text{pH} < 6$  and cylindrical structures at  $\text{pH} > 10$  (and a mixture of structures at intermediate  $\text{pH}$ ). It was not surprising that a macroscopic gel formed at  $\text{pH} > 10$ . The gel phenomenon was not reported for the propyl and nonyl alkyl derivatives studied.

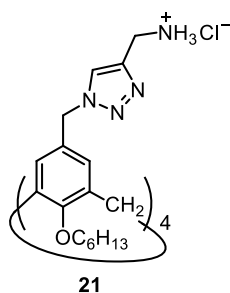


Figure 12. An amphiphilic calix[4]arene-based hydrogel investigated by Fujii et al. (71)

A water-soluble proline functionalised calix[4]arene **22a** was reported by Becker et al. (72) to form hydrogels upon the addition of electrolyte solutions. It was found that gelation was affected mainly by the anions, nitrate being the most effective. Bromide and chloride ions were also successful triggers for gelation with specific cations. These gels were stable over a wide pH range (0–7), and could be reversibly switched from gel to sol by increasing the pH above 7. Anion-tuning of low molecular weight gelators is a rapidly growing area (3, 52, 73-81).

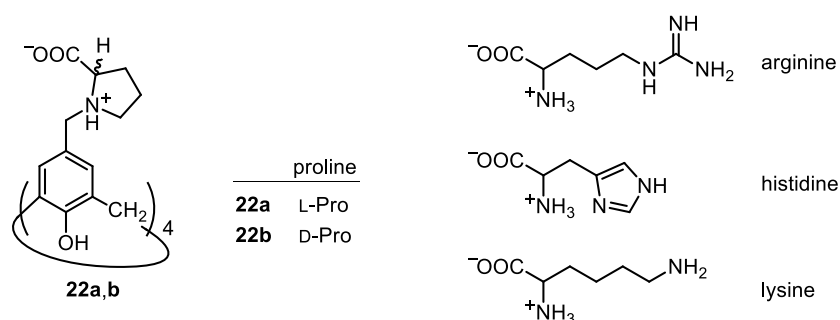


Figure 13. Proline calix[4]arene **22a,b** investigated by Becker et al. (72) and Goh et al. (82) in the presence of electrolytes. Later work by Zhang et al. (83) with basic amino acids at pH 3.

In their study of the gelation properties of racemic proline calixarene **22**, Goh et al. (82) found that the racemic gel formed by the addition of lanthanum nitrate was relatively unstable and crystallised after a few days, in contrast to the enantiopure gels that remained stable for months. An X-ray structure of the resulting crystals indicated helices in which a proline moiety of one molecule was included in the cavity of a neighbouring molecule (Figure 14). Each helix comprised only one enantiomer either

the L- or D- isomer. Furthermore, a lanthanum cation bridged two helices (one of the L- and one of the D-isomers) to form a 2-D coordination polymer. The broadening of signals in  $^1\text{H}$  NMR studies of **22a** in  $\text{D}_2\text{O}$  (without added electrolyte) with increasing concentration suggested that these molecules were self-assembling as concentrations were increased. The authors proposed a possible gelation mechanism that begins with the assembly of helices in water. The added cations may then link the strands and finally the anions play the dominant role in the aggregation of the fibres to ultimately form a gel.

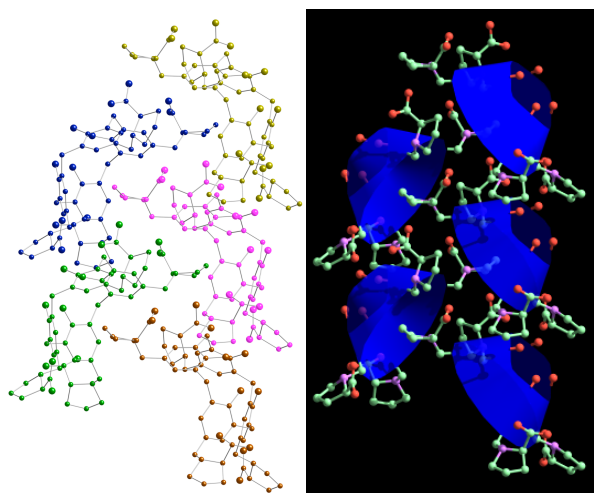


Figure 14. The helical packing of **22** found in the  $\text{La}(\text{DL-1})$  crystal structure; a ball and stick model coloured by molecule, and a schematic diagram with the calixarene backbone represented by blue ribbons (Reproduced from Ref. 82 with permission from The Royal Society of Chemistry).

Zhang et al. (83) later reported that proline calix[4]arene **22a** formed hydrogels in the presence of basic amino acids at low pH. The authors found that calix[4]arene **22a** (5 mM) formed hydrogels in the presence of arginine, histidine, or lysine (20 mM) at pH 3 (pH adjusted with hydrochloric acid). The hydrogel consisted of nanofibres, however the xerogel morphology ranged from fibres to plate-like or ribbon-like structures (dependent on the amino acid). Although the authors did not report this, it would be of interest to see if **22a** could enantioselectively form hydrogels with the basic

amino acids, and also if gels would form if the pH was adjusted with phosphoric acid rather than hydrochloric acid.

Recently, Mecca et al. (84) reported a series of amphiphilic calix[8]arene hydrogelators **23** (Figure 15). The calix[8]arenes were functionalised with either ammonium (**23a–e**) or carboxylate terminals (**23f,g**) at the wide-rim. This allows the calix[8]arenes to be pH-responsive – those calix[8]arenes with an ammonium group form hydrogels at high pH while those with carboxylates form hydrogels at low pH. The solubility of the calix[8]arenes and subsequent hydrogel stability could be tuned by varying the alkyl chain lengths.

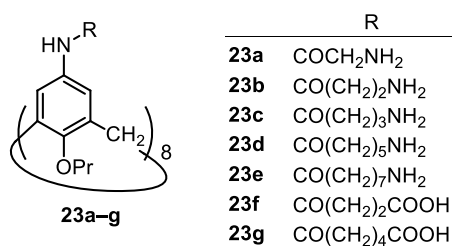


Figure 15. Water-soluble calix[8]arene hydrogelators investigated by Mecca et al. (84).

### *Resorcinarene-based gelators*

Resorcinarenes have also been shown to form gels. Haines and Harrison (85) showed that a resorcinarene functionalised with iminodiacetate **24** (Figure 16) formed hydrogels under acidic conditions. The gel was found to be pH-responsive and the gelation ability was diminished in the presence of Fe<sup>2+</sup> and Co<sup>2+</sup> and suppressed by Cu<sup>2+</sup> (presumably by the preference for coordination to copper, however this was not indicated in the paper).

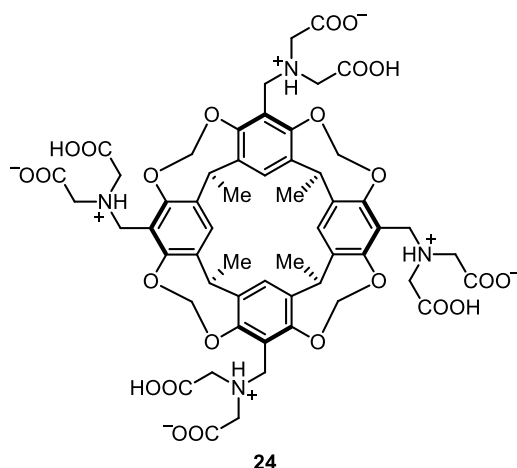


Figure 16. Resorcinarene-based hydrogelator **24** (85).

Amino-amide functionalised resorcin[4]arene **25c** (Figure 17) also formed hydrogels under acidic conditions (86). The primary amines appeared to be important for gelation as **25d** did not form a gel. Similarly, the long alkyl chains appear to be involved in gelation since **25a,b** were not reported by the authors to form gels.

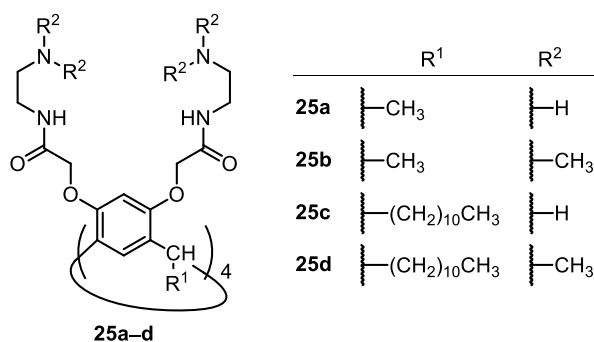


Figure 17. Resorcinarene-based hydrogelator **25a–d** (86).

### Crown ether gelators

Crown ethers have also been investigated in gel formation. Sobczuk et al. (87) proposed the application of an oligothiophene-bridged 18-crown-6 organogelator (**26**) as a memory device (Figure 18). The organogelator formed gels with a selection of ammonium species. Interestingly, chiral ammonium guests induced circular dichroism in the assembled fibrils. The memory could be stored in the chiral thermoset gel and erased by its thixotropic behaviour (mechanical stress). Previous work by Sobczuk et al. (88) on

the same gelator showed that the gel phase could be formed by heating and cooling in the absence of ammonium guests. A gel-to-sol transition could be induced with the addition of alkali cations (such as  $K^+$  and  $Cs^+$ ) which also enhanced fluorescence intensity of the solution.

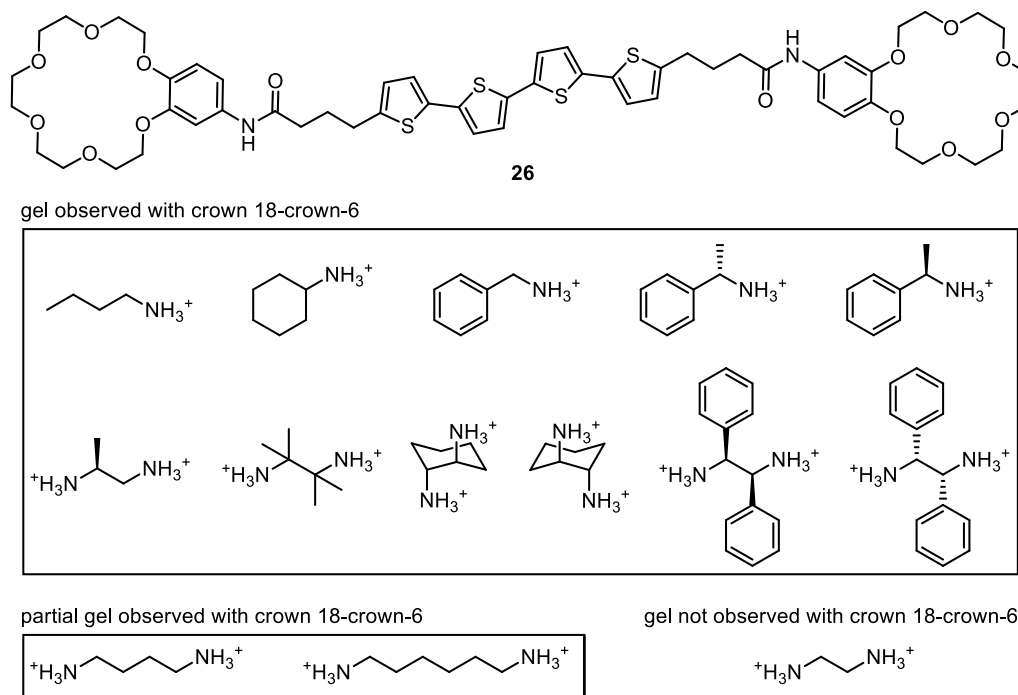


Figure 18. Oligothiophene-bridged 18-crown-6 organogelator and ammonium guests investigated by Sobczuk et al. (87). Refer to Table 1 in reference (87) for more details.

Dong et al. (89) designed an organogelator where the dibenzo[24]crown-8 (27) is linked to an ammonium moiety (Figure 19). The  $C_{12}$ -alkyl chain inserted between the crown ether and ammonium moiety favours the formation of fibrils rather than cyclic oligomers. The organogels were shown to be thermo- and pH-responsive.

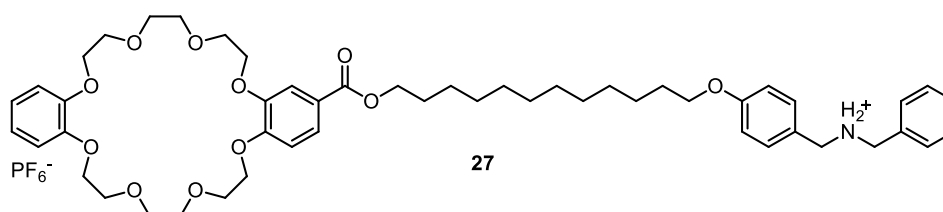


Figure 19. Crown ether-ammonium-linked organogelator investigated by Dong et al. (89)



Jung et al. (90) reports a similar crown ether–based bolaamphiphilic gelator (**28**) which exhibited improved thermostability and enhanced intensities in CD spectra of the hydrogels in the presence of dialkylammonium salts (Figure 20). Examination of the xerogel by scanning electron microscopy revealed helical fibres.

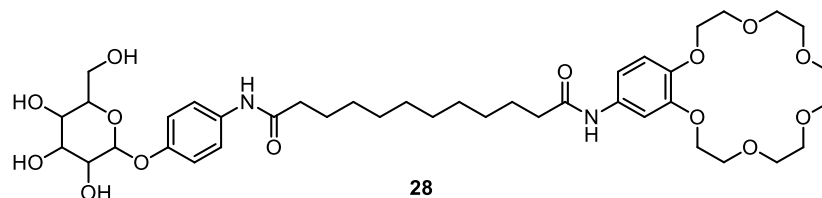


Figure 20. Crown ether-glucoside linked bolaamphiphilic gelator investigated by Jung et al. (90)

Langford et al. (91) reported tetranitrated crown ether gelators (**29**) that form gels in chlorinated solvents (Figure 21). The authors found that the dibenzo[30]crown-10 was selective for chloroform while dibenzo[24]crown-8 formed a gel in chloroform, 2-chloroethanol, and 1,2-dichloroethane. The organogels have low gel-to-sol transition temperatures (i.e. hand warming is sufficient to assist this transition).

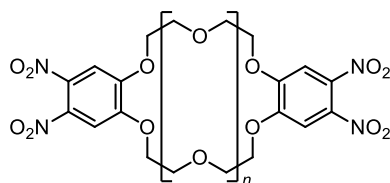


Figure 21. Tetranitrated crown ethers ( $n = 2, 3$ ) investigated by Langford et al. (91)

### Porphyrin gelators

There have also been several examples of porphyrins-based gelators. Jintoku et al. (92) noted that the limited solubility of tetraphenylporphyrin (**30a**) and its glutamide derivative (**30b**) in non-polar solutions allowed them to form a gel in those solvents (Figure 22). The coordination of the porphyrin and its derivative to  $Zn^{2+}$  increased the solubility and reduced the gel formation ability of both systems. However, the axial

coordination of the porphyrin complex influences the gelation behaviour of the Zn-porphyrin complex in addition to its chiroptical properties.

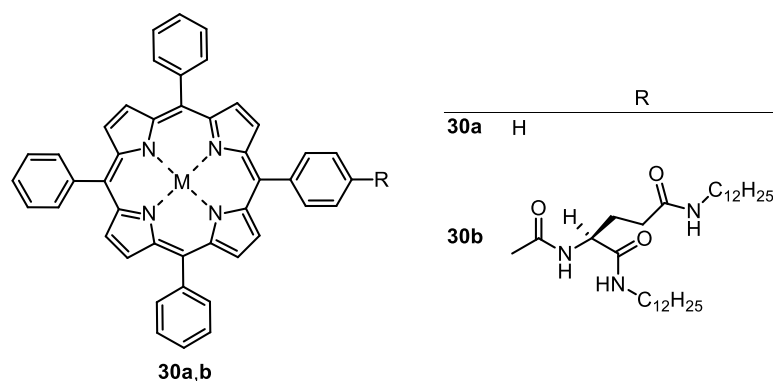


Figure 22. A porphyrin glutamide derivative was found to form a gel (92).

Li et al. (93) utilised a chiral gelator (**31**) to form a co-gel with selected porphyrins (**32**), shown in Figure 23. Unlike other co-gels reported in literature, the porphyrin and gelator are not structurally similar yet are capable of co-gelation. In addition, chiral properties were observed (through circular dichroism spectroscopy) for the porphyrin in the gel phase that were not present in the solution phase.

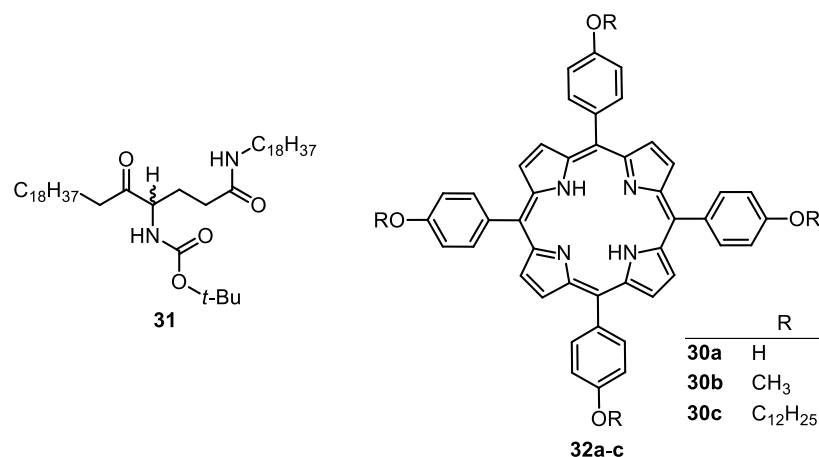


Figure 23. Li et al. (93) employed porphyrins (**32**) as a co-gel component with a known gelator (**31**).

Shinkai et al. (94-99) have investigated a number of porphyrin-based gels. Several of the porphyrins studied were found to assemble into 'sheet-like' or fibrous structures. The  $\pi$ - $\pi$  stacking of porphyrin is a key feature of the self-assembly of

porphyrin gelators. The aggregation of porphyrin gelators may be tuned by introducing functional groups at the periphery (99, 100). The peripheral groups have also been utilised in reinforcing gels (95, 96) and the formation of nanowires (97).

Setnička et al. (101) reported the first study where vibrational circular dichroism (VCD) was used to investigate sol-gel transitions. Using VCD, the authors noted that the brucine moiety was fairly rigid in the gel phase with a selection of solvents. VCD also allowed the authors to monitor changes to specific regions of the molecule (such as the C=O stretch of brucine) as the gel underwent a gel-sol transition on heating.

### Other macrocyclic gelators

A structural analogue of calixarenes, calix[4]pyrrole **33** (Figure 24), formed hydrogels in the presence of tetramethylammonium chloride and an alkali hydroxide (102). The authors found that hydrogels formed with sodium hydroxide but not with lithium or potassium hydroxides. However, reducing the pH of the solution to neutral by exposure to CO<sub>2</sub> gave hydrogels with all of the alkali hydroxides (not just sodium hydroxide).

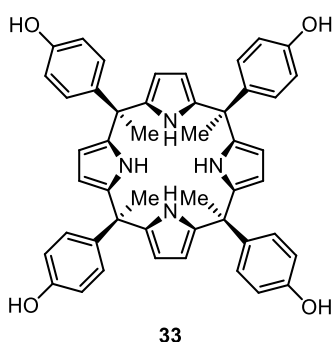
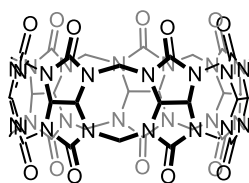


Figure 24. Calix[4]pyrrole **33** formed hydrogels in the presence of tetramethylammonium chloride and an alkali hydroxide (102).

Cucurbit[n]urils (103, 104) are another class of macrocycles. Hwang et al. (105) reported a cucurbit[7]uril-based hydrogel which was not only pH- and thermo-responsive, the hydrogel underwent a gel-sol transition in the presence of Na<sup>+</sup> and K<sup>+</sup> cations (with the cucurbit[7]uril binding to the cations). Furthermore, the inclusion of

*trans*-4,4'-diaminostilbene dihydrochloride guest within the cucurbit[7]uril host (**34**, Figure 25) allowed the authors to switch between gel and sol states by UV-irradiation; a gel was formed in the presence of *trans*-4,4'-diaminostilbene dihydrochloride while the *cis*-isomer disrupted the formation cucurbit[7]uril fibrils.



**34**

Figure 25. Cucurbit[7]uril-based hydrogelator **34** investigated by Hwang et al (105).

Ren et al. (106) reported a macrocyclic fluoropentamer (**35**), capable of gelling a range of organic solvents. The authors noted that the planar molecule was able to form organogels whereas previous literature suggested this type of motif was more likely to form vesicles. By applying rational design, the authors investigated derivatives of the fluoropentamer. The gel properties in different solvents can be tuned by the altering the R groups.

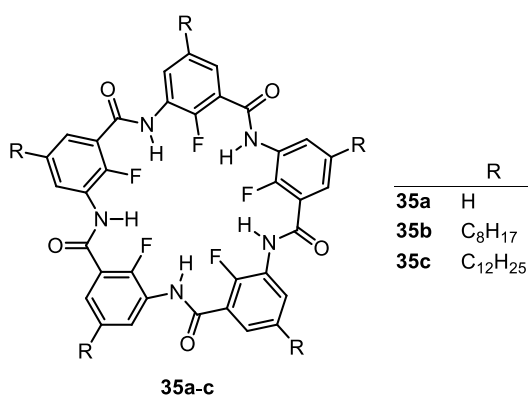


Figure 26. Macrocyclic fluoropentamer organogelator investigated by Ren et al. (106).

## Conclusions

This review provides an overview of the current work relating to macrocyclic gelating

agents. It is not meant to be comprehensive, but is intended to give a guide to the major themes in the area. The review focused on the calixarene family of macrocyclics, but also provided examples of crown ether and porphyrin based gelators. Almost all calixarene based gelators form organogels, with notable exceptions being the water-soluble proline functionalised calix[4]arene (63-65) and the calix[8]arene derivatives investigated by Mecca (66). In contrast, all the known resorcinarene-based gelators reported are hydrogelators. Although, the field of supramolecular gels has developed significantly in the last decade, there is still a need to develop gelators that are stimulus responsive for use in specific applications. Macrocyclic-based gels offer the potential to link the selectivity of the host-guest chemistry of macrocycles, to macroscopic changes in the bulk material. Examples of such interactions inducing gelation, or causing reversion to a sol are already known.(107, 108) The potential for development of increasingly selective and sensitive gelators based on known macrocyclic systems is tremendous. To achieve this efficiently, greater understanding of the structure-activity relationships for the various classes of gelators will need to be developed.

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