

Metal- and Anion-Binding Supramolecular Gels

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1. Importance and Scope of Supramolecular Gels

Gels are a commonplace household item and are easily identified by the simple “inversion test”; turn a pot of gel upside down and it is able to support its own weight without falling out onto your shoes! Examples such as hair gel, soft contact lenses, and “Jell-o” (or “Jelly” if you are English) all pass the inversion test and are instantly recognizable. These are all examples of *hydrogels*—two-component mixtures of a small amount (typically less than 2% by weight) usually of a polymer gelator immobilizing a much larger mass of water by surface tension effects.¹ Fortunately, less recognizable is napalm, originally a gel of aluminum salts of naphthenic and palmitic acids in an organic liquid—petrol.^{2,3} Its jellylike stickiness made it a particularly deadly incendiary during the Vietnam war. Such *organogels*, gels where the bulk liquid component is organic, are more familiar in the common lithium greases in which a lithium salt of a surfactant is added to a base oil to form a lubricating gel with strongly adhering properties.⁴ As Dorothy Jordon Lloyd famously noted in 1926, gels are “... easier to recognize than to define”.^{5,6} The generally accepted definition is that advanced by Flory in 1974, that a gel has a continuous structure that is permanent on the analytical time scale and is solidlike in its rheological behavior.⁷ With very few exceptions (such as vulcanized rubber and dried gelatin, both



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of which are strictly xerogels), gels also comprise two (or more) components such that one component is a dispersion within the other. Thus, hydrogels and organogels are disper-

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sions of liquids within a solid, while *aerogels* are dispersions of a gas within a solid. In contrast, an *aerosol* is a dispersion of a liquid in a gas, while a *sol* is generally a dispersion of solid colloidal particles in a solvent. It is this multicomponent nature of gels that lies behind much of their scientific interest.

It allows the fairly systematic modification and tuning of the physical properties of the material by changing the nature or concentration of the gelling component (the *gelator*). Because the term gel was coined in the 1860s,⁸ in an era where there was little understanding of the underlying structure of materials with gel-like appearance, gels and the gelators that form them are an extraordinarily diverse class of materials, although there are, of course, many commonalities in properties and methods used to study these materials. Flory distinguishes four main types of gel:⁷

(1) well-ordered lamellar structures, including gel mesophases (e.g., soap gels and phospholipids);

(2) disordered covalent polymeric networks (e.g., vulcanized rubbers, elastin protein, condensation polymers containing polyfunctional groups, phenolic resins, paint films, and polysilicic acids);

(3) polymer networks formed through physical aggregation (e.g., gelatin); and

(4) particulate, disordered structures (e.g., precipitates consisting of highly anisotropic particles or reticular networks of fibers as in V_2O_5 gels as well as gels formed by aggregation of proteins).

Clearly traditional gel chemistry is dominated by polymers. Of more recent interest is a further type of gel (essentially a subgroup of class 4) in which the fibrous aggregates are made of small molecules that are interlinked in a noncovalent fashion. It is these "supramolecular" gels, composed of low molecular weight gelators (LMWGs), and their complexes with metal cations and small anions that are the focus of the present article. Current interest in LMWGs is growing rapidly.⁹ The molecular basis of the interactions between LMWG molecules is comparatively readily understood because of their small size and the presence of relatively few functional groups. This simplicity in turn allows their intelligent design and potential applications in areas such as those listed below.

- Tissue engineering and wound healing: gels can act as a form of nanoscaffolding encouraging the growth of slow-growing tissue such as nerves through peptide based gels.^{9–11} They can also act as selective chelators of heavy metals such as uranium in simulated uranium wounds.¹⁰

- Drug delivery: many drugs are already formulated as polymer gels for oral delivery. Small-molecule based responsive gels offer the possibility of slow release or a sudden burst of drug from a chemically triggered gel–sol transition.¹¹

- Templating or transcribing self-assembled morphology: gels have been used extensively as growth regulators for the preparation of metallic nanoparticles^{12,13} or as templates for the formation of porous or nanoimprinted polymers with catalytic activity.^{14–22} Soft gel structures have also been transcribed into hard inorganic morphologies such as CdS "nanohelices".²³ An interesting report describes the formation of the covalent polymer polymethylmethacrylate (PMMA) from an ethanol solution of the metallogel formed from $Fe(NO_3)_3$ and trimesic acid (benzene 1,3,5-tricarboxylic acid). After washing away the gel (taking advantage of its supramolecular nature), a spongy covalent polymer is left where the pores may reflect the imprint of solvent pockets or gel fibers within the gel phase (Figure 1).²⁴

- Molecular electronics: the long, fibrillar nature of gels strongly suggests that they might find applications in the construction of molecular wires. For example, compound **1** forms organized nanowire type gels in hexane that can be dried on a transmission electron microscope (TEM) substrate

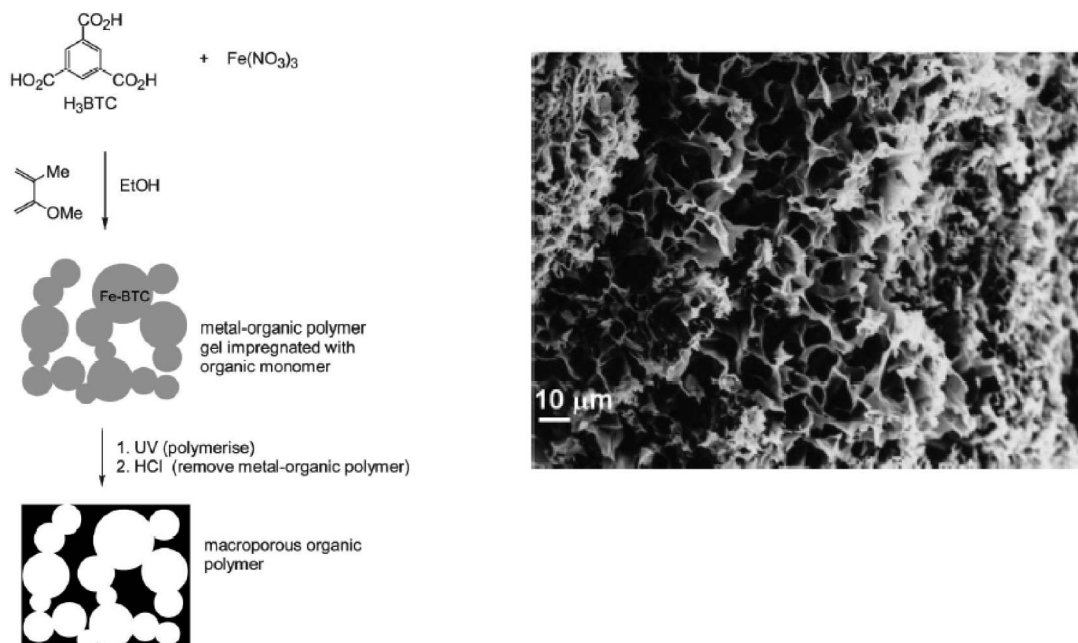
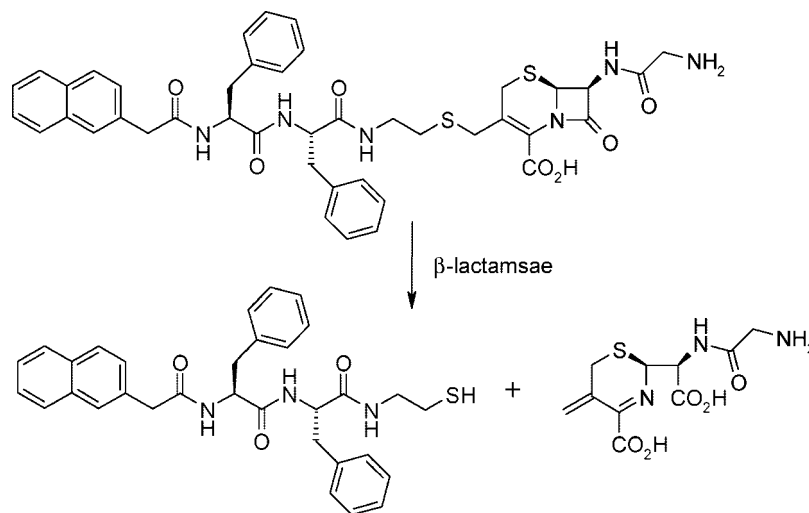
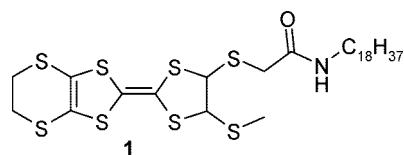


Figure 1. Templating of a covalent polymer (PMMA) by a supramolecular metallo gel of iron(III) benzene tricarboxylate (BTC). Reproduced with permission from ref 24. Copyright 2005 The Royal Society of Chemistry.

Scheme 1. β -Lactamase Catalyzed Hydrolysis of a β -Lactam Ring in Penicillin Results in Gel Formation with Potential Applications in Sensing the Presence of Penicillin-Resistant Bacteria²²



to give aerogels. Doping with iodine results in an electrically conducting thin film.¹⁹

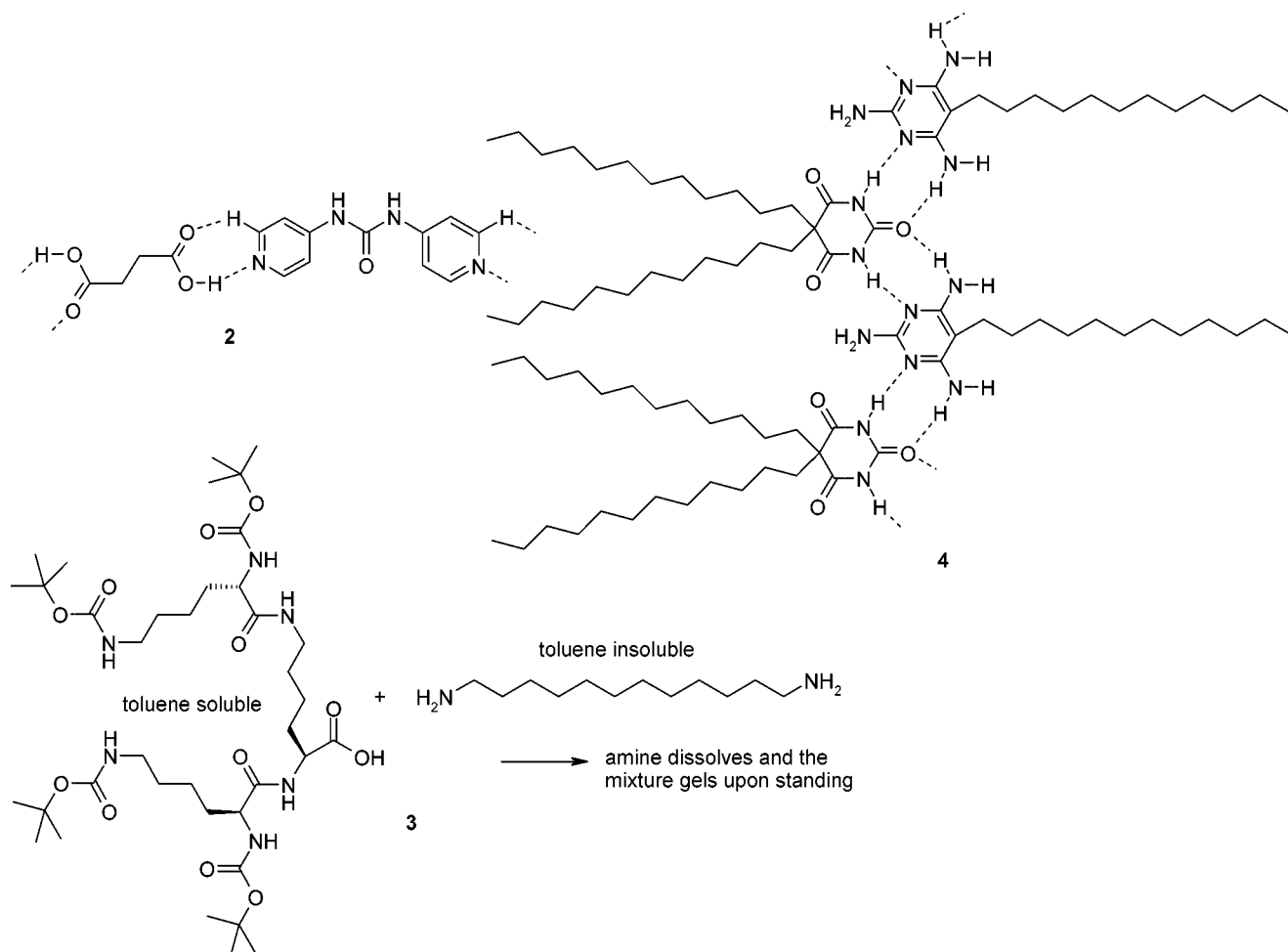


• Sensing: the compound shown in Scheme 1 is a poor gelator in itself but undergoes a reaction with β -lactamase enzyme to produce a derivative that is a good gelator. β -Lactamase catalyzed hydrolysis of a β -lactam ring in penicillin-type drugs is a significant cause of bacterial drug resistance, and hence, the formation of a gel in this reaction is a way of sensing the presence of penicillin-resistant bacteria.²²

An extraordinarily diverse range of compounds can act as LMWGs. Common examples include bis(ureas) and amides,¹⁶ nucleobase derivatives,¹⁴ fatty acids,^{15,17} steroids,^{20,21} anthryl derivatives,^{5,18,25} amino acid derivatives,^{26–30} dendrimers,^{31,32} phthalocyanines,³³ and porphyrins.^{34,35} An interesting range of two-component gelators³⁶ is also emerging, as in the work of Dastidar on dipyrindylurea carboxylic acid derivatives such as **2**³⁷ and the work of Smith on diamine-linked dendrons such as **3**.^{38,39} These examples build on earlier work on aminopyrimidine/dialkylbarbituric acid mixtures, as in **4**.^{40,41}

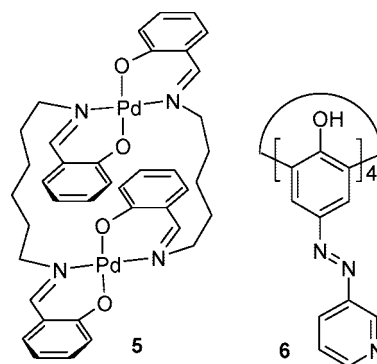
The example of the lithium greases shows that it has long been known that metals can be incorporated into gel systems. The use of metal ions as a factor in designing an effective gelator allows the vast range of diverse properties such as catalytic activity, magnetism, different coordination geometries, labile coordination interactions, and the absorption and

Scheme 2



emission of light offered by the metallic elements to enhance the tunability of the gel. As a result, *metallogels*, gels that in some way incorporate a metallic element into, usually, a LMWG, have recently become highly topical.⁴² Within the context of LMWGs, a metal can form part of the covalent structure of the gelator as in metalloporphyrin compounds,^{34,35} or the very interesting palladium(II) complex **5** that forms gels induced by sonication despite the fact that it lacks obvious hydrogen bonding or polar functional groups.⁴³ Metals can also be present as labile metal ions forming weaker coordination interactions that nevertheless enhance gel strength. For example, a coordination polymer metallogel has been formed by coordination of the pyridyl-pendant calix[4]arene **6** with the labile “Pd(en)²⁺” fragment (en = 1,2-diaminoethane) famously used by Fujita in the self-assembly of numerous discrete metallocages.⁴⁴ The resulting stable metallogel arises from the cross-linking of the calixarenes by the metal ion and exhibits uptake of small organic molecules from water—a property perhaps related to the presence of the calixarene cavity.⁴⁵ As we will see, the potential applications of metallogels are exciting and include catalytic activity,⁴⁶ Gd(III) containing gels in bioimaging,⁴⁷ and the redox-induced switching of gel–sol transitional behavior.⁴⁸ Similarly, there is rapidly growing interest in the incorporation of anions into gels and their use in tuning and switching gel behavior.^{49–59} In this review, we focus on the use of metals and anions in the control and modification of the properties and behavior of supramolecular LMWG type materials (Schemes 2 and 3).

Scheme 3



2. Gel Characterization

2.1. General Considerations

Before we embark upon a discussion of the role of metals and anions in gel structure and properties, it is worth briefly introducing the various experimental techniques used to study supramolecular gels and the supramolecular chemistry that goes with them. Because of their relatively disordered nature and structural features that extend from the molecular to multiananometer to multimicrometer scale, gels are particularly challenging to study and understand. As a result, a wide variety of experimental techniques must be brought to bear, each providing evidence that forms part of the solution to fundamental questions pertaining to the structure of the gel

and how mutual interactions of its components give rise to the observed bulk properties. Particularly key questions posed by Terech and Weiss in their classic 1997 review of LMWG systems are related to (1) the structural requirements of a LMWG to gel an organic liquid, or indeed water; (2) the relationship between the packing arrangements of gelator molecules in their bulk crystalline state and their aggregates in gels; and (3) how the packing of gelators influences the bulk physical properties of the gels.⁵ This review is a good starting point to the bases for many of these techniques as applied to gels, and we do not repeat their excellent summary here. Point 2 is of particular interest within the burgeoning topics of polymorphism and cocrystallization in crystalline organic compounds, particularly pharmaceuticals.^{60–64} Does gelation, or indeed crystal growth within gels,^{65,66} offer a new route to potentially biologically useful (or at least patentable!) polymorphs of commercial drugs, for example?

Gel characterization is primarily concerned with the gels' rheological and thermodynamic properties, particularly the gel phase diagram and gel–sol transition temperature (T_{gel} or T_{GS} , which usually differs from the transition temperature for the reverse process, T_{SG} , due to hysteresis effects). Gel rheology is perhaps the most important defining feature of a gel, and its measurement and understanding are described below. The thermodynamic properties of gels can be strongly dependent on the measurement technique with mass and/or heat transport effects and the fact that different properties are being measured, meaning that results from techniques such as differential scanning calorimetry (DSC) or temperature sweep rheometry must be interpreted with caution. In addition, of fundamental concern is the structure of the gel both on the micro- and nanoscale and at the molecular level. A wide range of microscopy techniques, particularly scanning electron microscopy (SEM), can give morphological insight, while small-angle scattering techniques such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) can provide information on correlation distances typical of colloidal systems and make use of some contrast variations, e.g., by deuteration.⁵ For example, within the context of metal-containing gels, iron(III) containing organogels based on phosphonic acid monoester, phosphonic acid, or phosphoric acid monoester have been studied by IR and NMR spectroscopies, optical microscopy, X-ray diffraction, rheology, and light scattering and SANS recently by Weiss and co-workers.⁶⁷ In this system, gelation can be induced isothermally as a result of binding the metal ion to the phosphonate groups accompanied by polymerization to give self-assembled fibrillar gel networks. The SANS measurements show that the cross-sectional radii of the cylindrical fibers are around 15 Å. The variety of techniques employed allowed significant insights into the structures of the gelator–iron(III) complexes as well as the mechanism of their formation and the gelation process. Work by Weiss' group has also resulted in a method to compare the packing in the pure gelator (obtained by single-crystal diffraction methods) with gel strand structure in gels by subtraction of the dominant amorphous liquid diffraction component from the powder diffraction pattern of the gel.⁶⁸ More recently, in collaboration with Day, we reported the use of crystal structure calculation methods usually employed for crystal structure prediction, to derive an ab initio model for a gel derived from sonication of melamine and uric acid. The rigidity of these unusual gelators allowed the calculation of some 250 000 candidate structures for the gel fibers of

formula melamine·uric acid·2H₂O, of which one of the very lowest in energy matched the observed powder X-ray diffraction (PXRD) pattern of the xerogel.⁶⁹

2.2. Rheology

Rheology⁷⁰ is the study of the deformation and flow of matter under the influence of an applied stress. Commonly a gel sample is placed between two flat plates or between two concentric cylinders and the stress is applied by moving one plate or cylinder relative to the other while the resulting strain is measured using a pressure transducer. If we apply a continuous weak stress and the material, after some deformation, eventually resists further deformation, then it is a solid. If the material eventually flows, it is a liquid. There are certain intermediate classes of behavior that fall in between these two extremes over a short time scale. If the amount of deformation of the material is proportional to applied force or stress, then the material is said to be *elastic* (like a rubber band). However, if it is the *deformation rate* that is proportional to the force or stress, then the material is said to be *viscous* (like honey). *Viscoelastic materials* exhibit some of both characteristics. While elasticity is generally the result of bond stretching along crystallographic planes in an ordered solid, viscoelasticity arises from the diffusion of molecules in an amorphous material, more like a gel. Many supramolecular gel-phase materials are viscoelastic. Liquid, solid, viscous, and elastic behaviors are recognizable under weak applied stresses. However, under high stress, a solid may begin to flow. Such materials are said to be *plastic* and have an associated *yield stress* or *plasticity threshold* beyond which the material flows.

In a rheometry experiment, the two plates or cylinders are moved back and forth relative to one another in an oscillating fashion. The elastic storage modulus (G' , the contribution of elastic, i.e., solidlike, behavior to the complex dynamic modulus) and elastic loss modulus (G'' , the contribution of viscous, i.e., liquidlike, behavior to the complex modulus), which have units of Pascals, are measured as a function of applied stress or oscillation frequency. For purely elastic materials, the stress and strain are in phase, and hence, there is an immediate stress response to the applied strain. In contrast, for purely viscous materials, the strain follows stress by a 90 degree phase lag. For viscoelastic materials, the behavior is somewhere in between and the strain lag is not zero but is less than 90°. The complex dynamic modulus (G) is used to quantify the stress–strain relationship (eq 1).

$$G = G' + iG'' \quad (1)$$

The moduli are related to the quantities σ_0 and ε_0 , the amplitudes of stress and strain, respectively, and δ , the phase shift between them. We can thus obtain G' and G'' from eqs 2 and 3.

$$G' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (2)$$

$$G'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (3)$$

There are two common rheological experiments for probing gel behavior. The linear response is determined by varying the frequency at a fixed small amplitude of stress, such that the loss and storage modulus are independent of

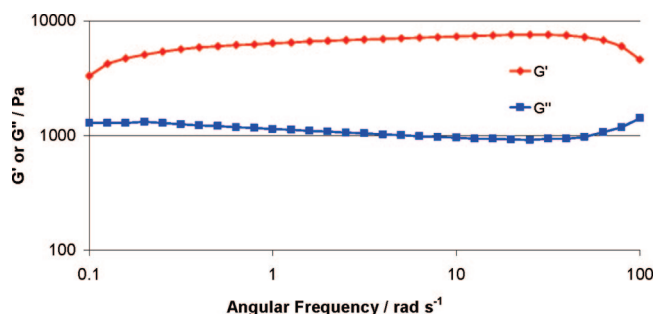


Figure 2. Frequency sweep rheometry data for a supramolecular gel. G' is invariant with frequency up to the yield point and ca. 1 order of magnitude greater than G'' .

the applied stress. Nonlinear behavior is probed using a fixed frequency and varying the amplitude of the shear stress. Below a critical value of shear stress, the yield stress, the storage modulus remains constant. Above the yield stress, G' is observed to decrease rapidly, suggesting that the network from which the gel is formed has collapsed as a consequence of the application of force. The behavior and magnitude of the storage and loss moduli and yield stress as a function of applied stress or oscillatory frequency and concentration can be modeled mathematically and lead to conclusions about the structure of the material.⁷⁰ For supramolecular gels, their structure is not simple and may be described as cellular solids, fractal/colloidal systems, or soft glassy materials.⁷¹ In order to be considered as gels (which are solidlike), the elastic modulus (G') should be invariant with frequency up to a particular yield point and should exceed G'' by at least an order of magnitude (Figure 2).

2.3. Models for Gel Rheology

It is often found that there is a simple scaling relation between concentration of the gelator and both the storage modulus and the yield stress, of the form

$$G' \propto c^\alpha; \quad \delta^* \propto c^{-\beta} \quad (4)$$

where the exponents, α and β , are typically^{53,71,72} found to be $\alpha \approx 2$ and $\beta \approx 1.5$. As noted by Sangeetha et al.,⁷¹ there are two existing quantitative theoretical frameworks that have been developed to describe colloidal gels and cellular solids. As with gels formed from small molecules, both of these materials are networklike structures, and so the models provide a promising starting point for understanding the mechanical properties of molecular gels. Colloidal gels have a structure that is random, while cellular solids have a more regular structure with well-defined cell walls. Scaling relations for the shear modulus and the yield stress with concentration for colloidal gels were derived by Shih et al.⁷³ A colloidal gel is modeled as composed of flocs with a fractal dimension, d_f , which reflects how the mass of colloidal material within a floc scales with floc size. The flocs are connected by interfloc links. The dependence of the mechanical properties on concentration is determined by the relative strength of interactions between flocs and within flocs. In the strong-link regime, the former dominate and the following is predicted,

$$G' \propto c^{(3+x)/(3-d_f)}; \quad \delta^* \propto c^{-(1+x)/(3-d_f)} \quad (5)$$

where x is the fractal dimension of the elastically effective number of interactions within a floc. In the weak-link

regime, intrafloc interactions dominate and the following is predicted,

$$G' \propto c^{1/(3-d_f)}; \quad \delta^* \propto c^{1/(3-d_f)} \quad (6)$$

From eq 5, the strong-link model permits agreement with the experimentally observed scaling of the shear modulus, but only if $x = d_f = 1$. These conditions are inconsistent with the model of an interconnected fractal colloidal gel,⁷³ which requires that (i) x be less than the fractal dimension, d_f , and (ii) in order to ensure connectivity between flocs, x must be greater than unity. Furthermore, neither model is able to correctly predict the scaling of the yield stress, regardless of the fractal dimension. Hence, this suggests that the mechanical properties of LMWGs cannot be described by analogy with colloidal gels. This is probably a consequence of the fact that the building block of a colloidal gel is a fractal object, which is then interconnected to other fractal objects. As discussed elsewhere in this review, for LMWGs the building block is typically of a well-defined fibrillar nature, with interconnections between fibers providing the percolated gel structure.

The cellular solid model⁷⁴ provides an alternative framework. For open-cell cellular materials, which consist of interconnected, via cross-links or junction points, load-bearing struts that deform by bending, this model predicts $G' \propto c^2$, in good agreement with observations. More recently, Gibson and Ashby⁷⁵ have noted that, for a wide range of materials with a wide range of cellular concentrations, $G' \approx 3E_S(c/\rho_S)^2/8$, where E_S is the Young's modulus of the struts and ρ_S is the density within the struts, which enables the mechanical properties of individual fibers to be estimated from the macroscopic properties. In addition, Gibson and Ashby^{74,75} also determined the scaling of the yield stress with concentration according to the mechanism of failure of the cellular material. If the struts buckle during deformation (elastic collapse), then $\delta_{el}^* \approx 0.05E_S(c/\rho_S)^2$, whereas if plastic collapse occurs (i.e., the struts exhibit plastic deformation), then $\delta_{pl}^* \approx 0.3\delta_S(c/\rho_S)^{1.5}$, where δ_S is the plastic yield stress of the individual struts. Again, by comparing the two scaling laws with results, it is possible to determine the yield properties of individual fibers.

However, there is a clear difference between the regularity of the structures in the cellular solid model and the more random networks observed in LMWGs. Recently, there have been a number of attempts to model the mechanical properties of random networks.^{76,77} The focus of much of this activity has been on understanding the properties of actin and cytoskeletal networks,^{78–81} which, from a physical perspective, share much in common with the networks formed from LMWGs, with the most significant difference being the extent of flexibility of the fibers that form the network, with semiflexibility playing an important role in biological network mechanical response. Within the Gibson and Ashby framework, there are two limiting regimes, bending dominated and stretching dominated. In the former, in which the modulus varies quadratically with concentration, the material can deform without the fibers having to change length by allowing deformation to occur at the junctions, so that the angle between the fibers changes. In stretching-dominated deformation, in which the modulus varies linearly with concentration, the network is geometrically constrained such that deformation can only occur by stretching of the individual fibers. Buxton and Clarke⁸² recently simulated the response of a three-dimensional random network of rods and

showed how the connectivity of the rods, as well as the concentration, influences the scaling behavior of the modulus. Connectivity is a measure of how many rods are connected, on average, at each node of the network. At a fixed concentration, the network can range from having a high density of nodes but low connectivity to a low density of nodes but high connectivity. It was shown that the transition from bending-dominated deformation at low connectivity to stretching-dominated at high connectivity is continuous between the two limiting behaviors. Hence, measurements of the scaling of the modulus with concentration enable us to infer structural features of the gel. For example, it was recently shown⁴⁹ that the addition of anions to a bis(urea) gel reduces the storage modulus by up to 2 orders of magnitude for a fixed concentration of gelator, suggesting a lower connectivity of the threads.

3. Concepts of Gel Formation

Having defined what a gel is and how to study it, we find it worthwhile to look briefly at how and why gels form before we go on to look at how metals and anions can become incorporated within a gel or influence its formation. We can consider a gel as comprising a solid matrix that immobilizes a liquid component by surface tension effects. Interestingly, it is these surface tension effects that are generally responsible for the collapse of a gel on removal of the liquid component. The bis(urea) shown in Figure 3a, for example, forms a gel in which the liquid component is supercritical CO₂. By lowering the pressure, the fluid phase can be removed in gaseous form, leaving behind an aerogel that

does not undergo microstructure collapse upon drying because the outgassing CO₂ has no surface tension.⁸³

It is the fluidlike nature of gels (allowing rapid diffusion and high mobility) coupled with their solid, "sticky" properties that is one of their most interesting features. Within a gel of a low molecular weight gelator, the solid component is formed either by cooling a solution or pregel colloidal suspension or by a precipitation process closely akin to crystallization⁸⁴ in which the solid forms rapidly in one dimension to give long fibrils, and ultimately fibers, while exhibiting little growth in the other two directions. We can think of the structure of the solid component of the gel fibrous network as having primary, secondary and tertiary components in a fashion akin to protein structure. In hydrogels, where polar groups such as the ureas shown in Figure 1 are generally highly solvated, the gelation process is generally dominated by hydrophobic effects. In organogels, directional hydrogen bonding and dipolar interactions tend to dominate. Thus, compounds like amides and ureas¹⁶ are particularly effective LWMG because of their ability to form a primary structure comprising infinite hydrogen bonded tapes in one dimension while interacting laterally by much weaker bonds such as van der Waals interactions. So, in a bis(urea) gelator (Figure 3), for example, the primary structure is made up of strands linked by the urea α -tape motif.⁸⁵ These strands give a secondary structure of fibrils and bunches of fibrils (fibers) of relatively uniform diameter. The tertiary structure arises from the mutual entanglement of linear fibers and/or the cross-linking of branching fibers to give a 3D solid network.¹ The way in which secondary structure derives from primary structure has been studied in some detail and may resemble

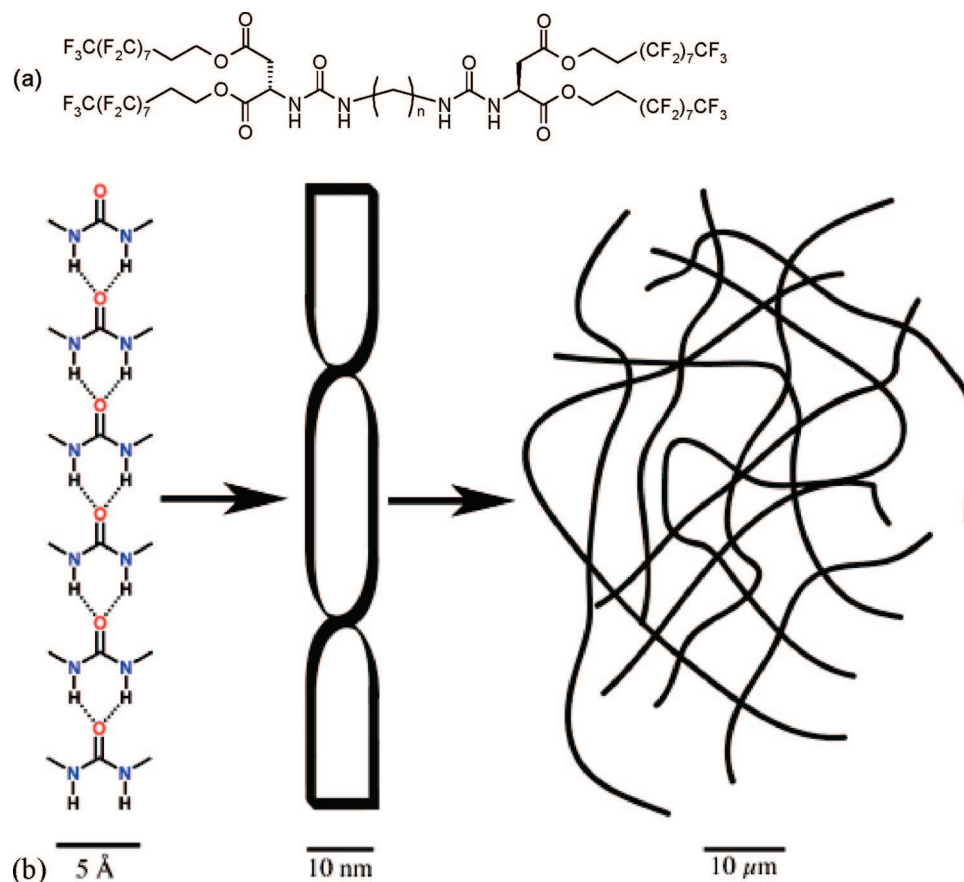


Figure 3. (a) Example of a bis(urea) gelator, and (b) the primary, secondary, and tertiary structure of a self-assembled physical gel of a urea-based LWMG. Reproduced with permission from ref 1. Copyright 2004 American Chemical Society.

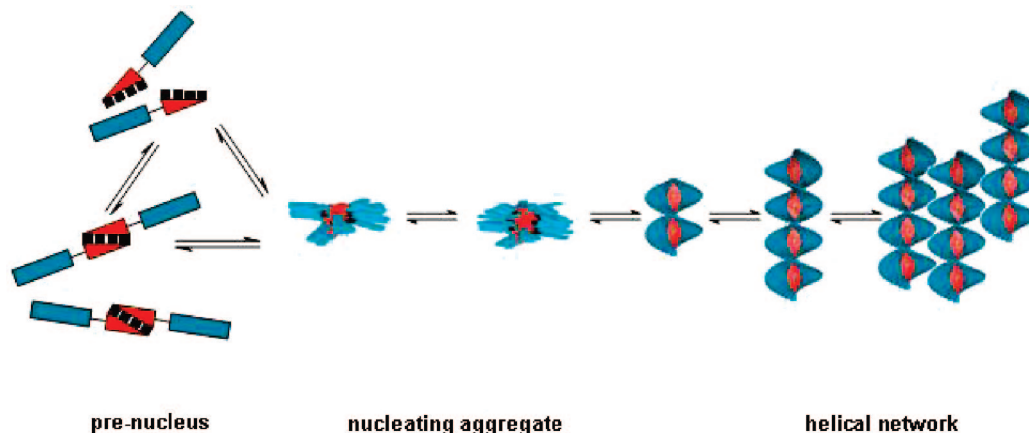


Figure 4. Hierarchical assembly of gel-phase materials as illustrated for systems developed by Meijer and co-workers. Reprinted with permission from ref 95. Copyright 2006 AAAS.

the formation of β -strand peptide fibers such as amyloids.⁸⁶ The scheme proposed by Meijer and co-workers is shown in Figure 4. While the details of various models vary, gelation is taken to be a *hierarchical* assembly process^{87,88} that generally follows a sequence involving the following steps:⁸⁹

- (1) Dimerization of two individual molecules;
- (2) Oligomer formation by interaction of dimers with further molecules;
- (3) Formation of polymer fibrils of approximately the same width as the molecular building blocks (ca. 1–2 nm) by extension of the oligomers;
- (4) Fiber formation by bundling of fibrils (ca. 20–50 nm width);
- (5) Interactions of fibers to give an effectively infinite, interconnected network spanning the entire sample (the least well understood aspect of the gelation process);
- (6) Immobilization of the solvent by the fiber network, generally by surface tension effects.

Gelation is generally in competition with other kinds of aggregation depending on the precise structure of the gelator and external conditions, and hence, the growing gel network is often in competition with other amphiphile aggregates such as micelles, vesicles, lamellae, and amorphous or microcrystalline precipitates.⁹⁰ Like crystallization, gelation is very susceptible to external factors such as the gelation temperature (T_{gel})⁹¹ and cooling rate⁹² as well as the presence of additives.^{93,94} These factors influence the rate of fibril nucleation and growth with additional branching events and, hence, a more cross-linked gel network resulting at higher temperatures.

4. Metals in Gels

Conceptually there is nothing different about a gelator containing a strongly bound metal ion within the molecule compared to a conventional organic gelator. The presence of the metal does allow additional scope for tuning gel properties, however. We can distinguish systems in which the metal acts as a linker between ligands, as in the palladium(II) complexes of **6** to give a coordination polymer, and systems in which other noncovalent interactions result in gelation and metal coordination is not directly involved in linking LMWG molecules together, as in **5**. Since gelation necessarily involves the creation of linkages between LMWG molecules, the former category is generally associated with labile metal ions. For the purpose of this review, we divide these systems into those where metals are reversibly bound

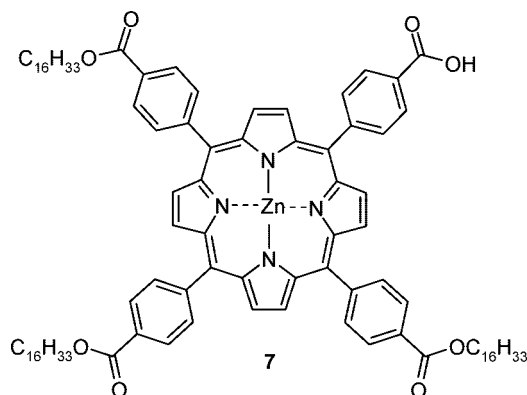
to the ligand, and in doing so assemble into 3D gelling networks, and those where labile metal bonding allows the gel to be tuned by cation or anion binding. First, however, we deal with complexes in which the metal is more integral to the structure of the gelator units that assemble into primary, secondary, and tertiary structures as described above, rather than being involved in the organization of the fibrillar network. These systems often contain substitutionally inert metal ions or those held by a multidentate or macrocyclic ligand. We will distinguish between systems where the metal is strongly bound to the ligand (as in porphyrin complexes) and those where there are discrete coordination complexes, in which an inert metal links together a number of ligands to give rise to complexes that in turn organize into gel assemblies.

4.1. Metals as Structural Components in Gels

Very prominent examples of macrocyclic ligands that bind metal ions in a nonlabile manner are the metal complexes of porphyrin derivatives. In 1996 Terech and co-workers reported gel formation from cyclohexane of the trisubstituted zinc(II) porphyrin **7**, which features three long alkyl chains attached to the porphyrin core by ester linkages and one free carboxylic acid.³⁵ Gels of **7** form at concentrations as low as 1% by weight and exhibit thixotropic behavior (Scheme 4).

In more detailed studies on these assemblies, it was noted that the free carboxylic acid as well as the contribution of the metal center was essential to gel formation because the corresponding tetraester does not show gelatinous charac-

Scheme 4



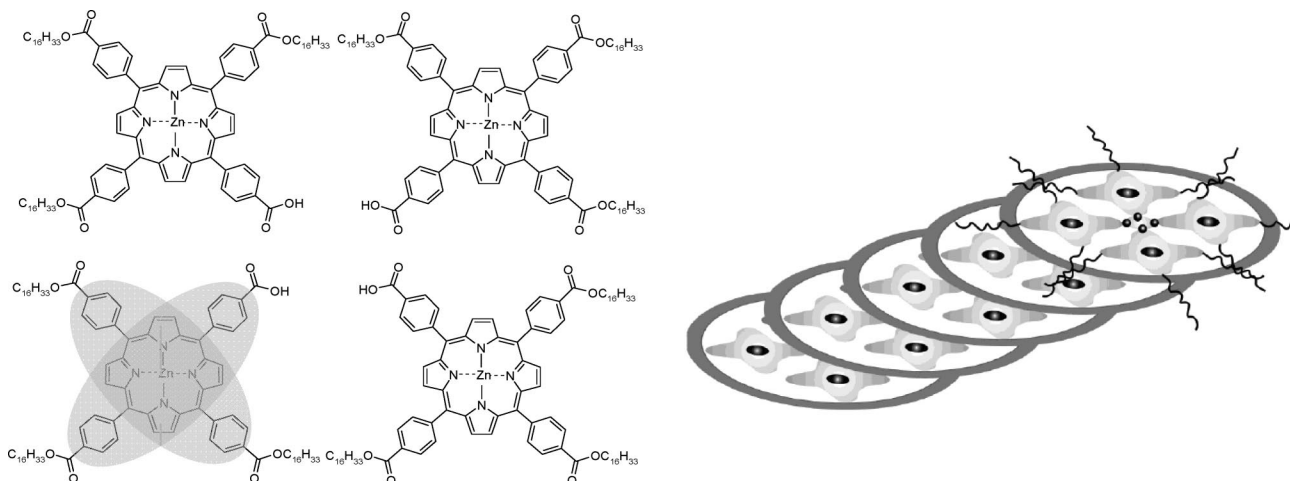
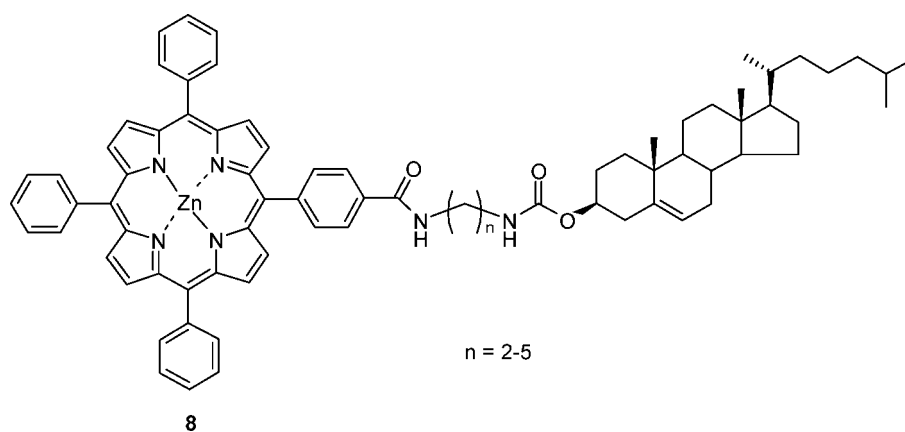


Figure 5. Proposed assembly of **7** into J-aggregates and rods with tetrameric cross sections. Adapted with permission from ref 96. Copyright 2003 American Chemical Society.

Scheme 5



teristics even at high concentrations.⁹⁶ In combination with SANS and SAXS studies, a model was proposed in which molecules of **7** participate in J-aggregates (offset-stacking) with four molecules in each section of a rodlike assembly. The rods themselves comprise a metal-containing π -rich planar region encircled by an aliphatic shell (the alkyl ester) and a polar central core (the carboxylic acid), thus demonstrating the importance of both metallic and ligand influences on the gel behavior (Figure 5).

In the framework of the proposed assembly, the thixotropic behavior of this gel can be rationalized in terms of a distribution of rigid rods of different sizes. The end-caps of these rods can form weak interactions with each other, and where more than two rods meet, a weak 3-dimensional network is established. Under shear, the rods align in the direction of the applied stress so that any 3-dimensional order is lost and the sample starts to flow freely. Upon removal of the stress, the network forms again.⁹⁷ This example illustrates how both the ligand and the metal ion act in a complementary fashion in the hierarchical self-organization process.

A great deal of work on porphyrin-based gels has been carried out by the group of Shinkai,⁹⁸ who have explored a wide variety of substituents to the porphyrin core. Their earlier work on organogelators involved the combination of porphyrins and cholesterol (the latter being a popular component of a number of LMWGs⁹⁹) to form the asymmetric zinc(II) porphyrin **8** (Scheme 5).^{34,100}

Ligand **8** was prepared with varying chain lengths of the linker between the cholesterol and porphyrin moiety, and

gelation was observed for the $n = 2$ compound in aromatic hydrocarbons such as benzene, toluene, and *p*-xylene at around 3 wt %. These gels only form at up to 5 °C, but can be stabilized at 20 °C by the addition of [60]fullerene.¹⁰⁰ A stabilization effect was also observed for a linker chain of $n = 4$, which only gels benzene and toluene in the presence of the fullerene. The odd numbered linker chain prevents gelation altogether.³⁴

On the basis of the 2:1 Zn(II) porphyrin/[60]fullerene sandwich stoichiometry determined by T_{gel} measurements and UV–visible and circular dichroism (CD) spectral observations, which showed porphyrin–fullerene interactions, Shinkai et al. proposed a sandwich structure as shown in Figure 6, where the cholesterol groups in the center form a helical stack in which the appending porphyrin moieties are preorganized to precisely sandwich the [60]fullerenes.

Further work by Shinkai et al. expanded on the idea of achieving control of the stacking mode of these porphyrin compounds as a means of self-assembly and gelation.^{101–105} The symmetrically 4-substituted compounds **9a** are versatile gelators, for example, gelling 14 (for $n = 3$) and 10 (for $n = 11$) out of 23 solvents tested. However, the *meta* analogue is a very poor gelator. Crystallographic, UV–vis, and IR spectroscopic evidence indicates that, in the organogel, the porphyrins in **9a** adopt the H aggregation (columnar stacked) mode, whereas **9b** is a sheetlike J aggregate. The H versus J aggregation mode is reflected in the bulk morphology of the materials observed by SEM with the H aggregate exhibiting a one-dimensional fibrillar structure, while **9b**

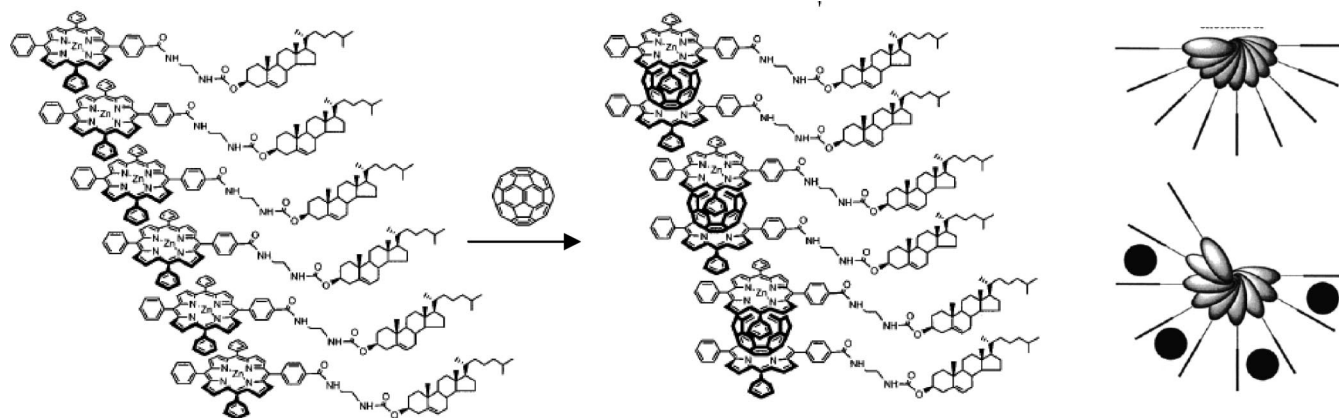
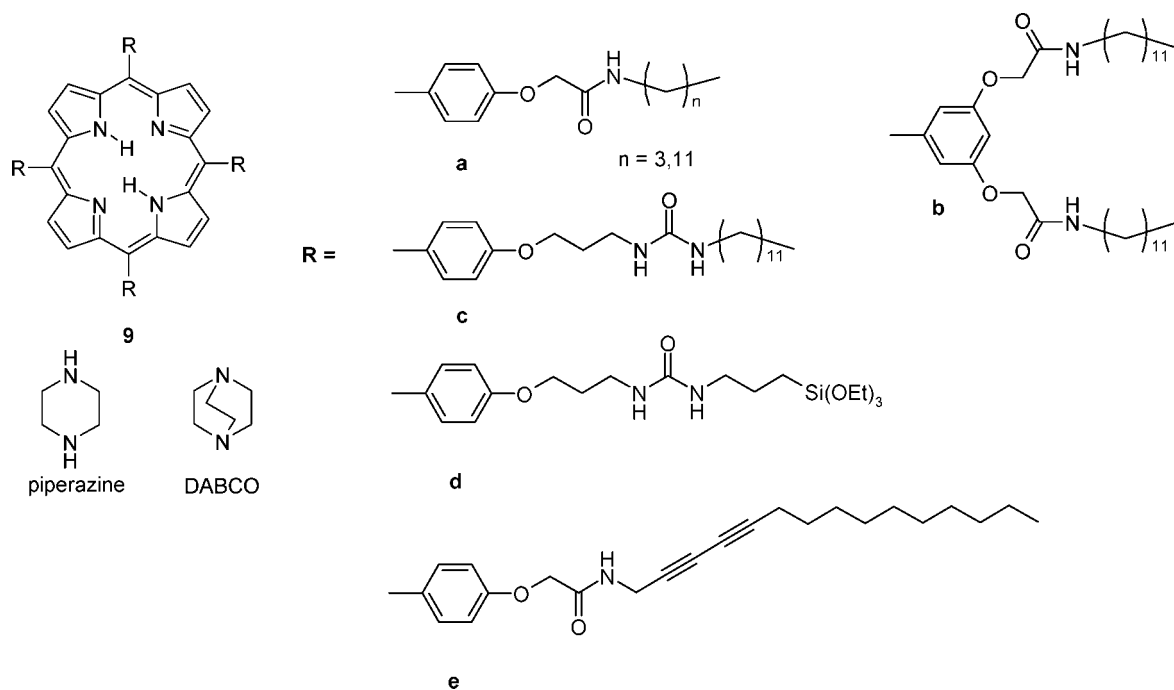


Figure 6. Sandwiching of [60]fullerene between the porphyrin moieties of **8** (left) and schematic representation of the one-dimensional organization of **8** without and with [60]fullerene. Adapted with permission from ref 34. Copyright 2001 American Chemical Society.

Scheme 6



exhibits a two-dimensional sheetlike structure.¹⁰⁵ These are all examples of how the substituents on the porphyrin can affect the assembly of the gel fibers. Interestingly, the Zn(II) complex of urea gelator **9c** (**Zn·9c**) also forms a J aggregate, which does not gel benzene, toluene, and *p*-xylene. However, addition of piperazine, which is able to link the metalloporphyrin units together via axial coordination to the Zn(II) ion, results in an H aggregate type structure and the formation of stable gels in those solvents.¹⁰¹ The stoichiometry of the **Zn·9c** piperazine complexes was found to have a great impact on the gelling behavior, with a 2:1 ratio affording gels with a one-dimensional fibrillar network at much lower concentrations and with a thixotropic character (Scheme 6).

In the 1:1 complexes, the critical gelator concentration is around one order of magnitude higher and leads to a two-dimensional sheetlike morphology of the aggregates. Addition of DABCO only allows partial gelation and results in 2D sheetlike aggregate morphologies, whereas ethylenediamine and *N,N'*-dimethylethylenediamine disrupt gel formation completely.

Again, UV-vis and IR spectroscopy together with computational modeling suggested a strong influence of the

aggregation mode on the gelling ability of these systems brought about by metalloporphyrin stacking modes and hydrogen-bonding interactions. The urea-to-urea interaction in the piperazine complex is distorted, and organization of the H aggregates is mainly in one direction. In the DABCO complex, urea-to-urea hydrogen bonding is directly parallel to the porphyrin stacking, thus enabling a 2D arrangement of the aggregates (Figure 7).

The analogous copper(II) complex **Cu·9c** is an H aggregate, even without addition of piperazine, and gels a wide variety of solvents at a concentration as low as 0.71 wt %.^{102,103} In the same study, **9d** was prepared with and without copper(II). The triethoxysilyl group increases solubility and decreases gelation ability. Compound **9d** was found to form J aggregates and only gel benzene at 10 wt %, whereas the critical gel concentration for **Cu·9d** is 2 orders of magnitude lower and *p*-xylene and anisole are also gelled. The latter organizes in H aggregates, lending more support to the view that the introduction of metals into the porphyrin facilitates this type of molecular stacking. Interestingly, the morphologies of both systems are retained upon sol-gel polycondensation of the triethoxysilyl groups, and the mechanical

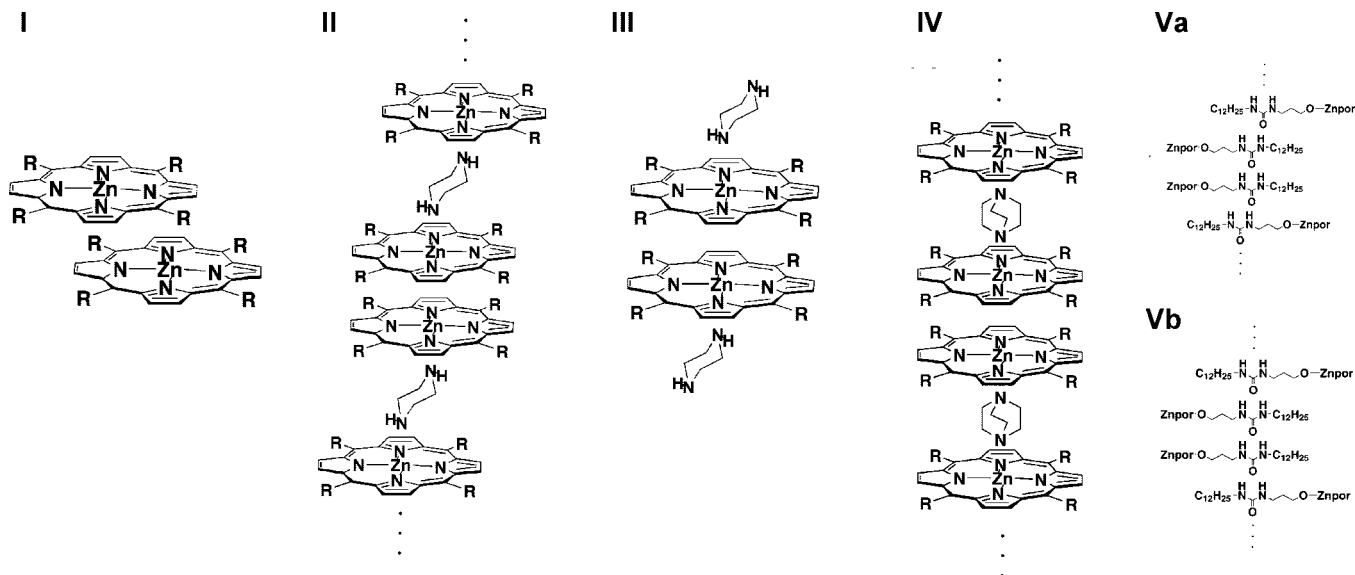
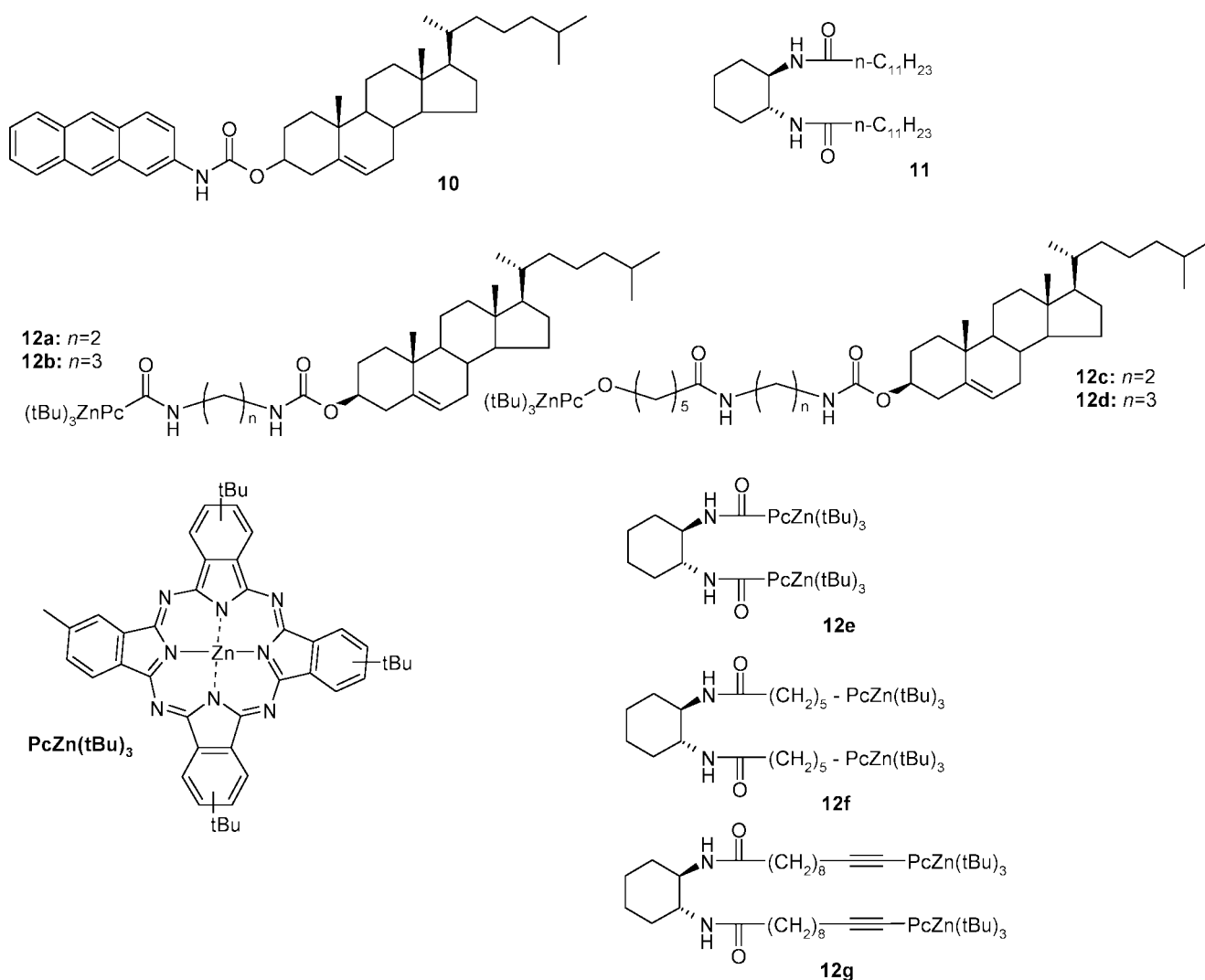


Figure 7. Illustration of different aggregation in the $\text{Zn}\cdot\mathbf{9c}$ system, for (I) $\text{Zn}\cdot\mathbf{9c}$ only, (II) $\text{Zn}\cdot\mathbf{9c}$ /piperazine 2:1, (III) $\text{Zn}\cdot\mathbf{9c}$ /piperazine 1:1, and (IV) $\text{Zn}\cdot\mathbf{9c}$ /DABCO 2:1. Also shown are the proposed urea-to-urea hydrogen-bonding motifs for (Va) $\text{Zn}\cdot\mathbf{9c}$ /piperazine 2:1 and (Vb) $\text{Zn}\cdot\mathbf{9c}$ /DABCO 2:1. Reproduced with permission from ref 101. Copyright 2006 The Royal Society of Chemistry.

Scheme 7



and thermal stability of the gels is clearly enhanced. The T_{gel} of $\mathbf{Cu}\cdot\mathbf{9d}$ after polycondensation rises to 160 °C (c.f., 50–80 °C before, depending on concentration) and the elastic

modulus G' as well as the ratio of G'/G'' increases by 1 order of magnitude indicating the transition of the system from a weak gel to a true gel.¹⁰³

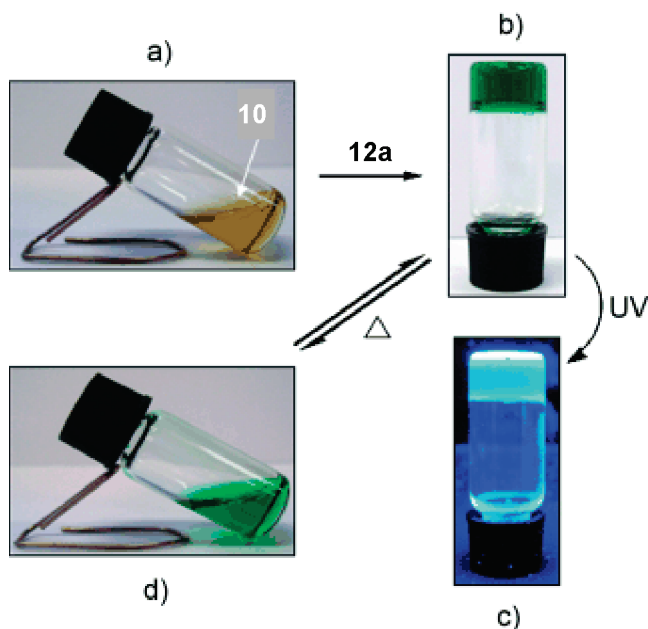


Figure 8. Photographs of (a) organogelator **10** in toluene, (b) effect of inclusion complementary compound **12a** after heating–cooling cycle, (c) the gel of **10** + **12a** under UV irradiation at 365 nm, and (d) thermally induced gel-to-sol transition. Adapted with permission from ref 107. Copyright 2008 Wiley Interscience.

Finally, **9e** and **Cu·9e** show the same trend as described above with the copper(II) porphyrin compound affording gelling properties to the system, this time in cyclohexane and decalin.¹⁰⁶ The decalin gel of **Cu·9e** shows thixotropic behavior, and the diacetylene groups could be polymerized in a first step to obtain highly elongated conducting polymers.

While metalloporphyrin gels have been studied extensively, there is now a wide variety of compounds and ligands that try to exploit metal coordination as a route to self-assembled gels. Phthalocyanines are somewhat related to porphyrins and have been demonstrated to afford if not gels then viscous solutions (Scheme 7).³³

Torres and Diaz recently carried out an extensive study on the possibility of enhancing gel strength using a “pick-and-mix” approach whereby two organogelators **10** and **11** were combined with a series of complementary structures **12a–12g** containing zinc phthalocyanines.¹⁰⁷ In general, none of the pure phthalocyanines were found to form gels on their own. Mixing of the appropriate systems in toluene (i.e., **10** with **12a–12d** and **11** with **12e–12g**) results in gelation

except where **11** was combined with **12e**, possibly due to lack of flexibility in the linking group. The gelation works best at an optimum ratio of around 20:1 of organogelator to zinc phthalocyanines, and higher concentrations of the latter usually result in breakage of the network. In the case of the cholesterol gels, both the steroidal as well as the phthalocyanine components play a role in stabilizing the assemblies. All gels were found to be thermoreversible and photoactive under UV radiation (Figure 8) but tend to break down after 17–36 days of storage. This low temporal stability combined with a low thermal stability (transition temperatures in the region between 41 and 57 °C were observed) prompted the authors to attempt strengthening of the systems by a copper(I) catalyzed azide–alkyne cycloaddition. The alkynes were again designed to be complementary to the ligand structure. For the **10** + **12a** and **11** + **12f** mixtures, this approach was found to enhance the elastic and viscous moduli as well as more than triple the temporal stability and increase the T_{gel} by nearly 20 °C.

We have already mentioned the palladium(II) complex **5** in the introductory comments.⁴³ Remarkably, this compound undergoes an abrupt transition from a stable sol in a wide variety of organic solvents to an opaque gel upon sonication. These gels are stable at room temperature and redissolve upon heating. The complex is quite particular in its gelling ability with only the *anti*-configuration of the pentylene-bridged compound being capable to rigidify the solvent. Other linker lengths, *syn*-configurations, and the mononuclear complex fail to form gels. Gelation was rationalized by assuming a bent geometry of the monomers that undergo a process of interlocking when sonicated (Figure 9).

A very recent development is the use of metallocene groups in gelators. Interesting behavior is shown by the undecyltrimethylammonium bromide appended ferrocene **13** as reported by Abe and co-workers (Scheme 8).¹⁰⁸ In aqueous solutions in the presence of sodium salicylate, the reduced ferrocenyl form **13a** forms wormlike micelles that show a high degree of entanglement and make the solution extremely viscous. Although this system is not reported as a “proper” gel, this organization of long fibers resembles the 3D arrangement of fibrils in the gel state. The giant micelles can be broken up by oxidizing **13a** at low voltages to the ferrocenium form **13b** upon which shorter elliptic assemblies and monomers result, causing the viscosity to drop by a factor of 6000.

Other examples of metallocenes in organogelators follow the design approach of **8** by linking a cholesterol group via

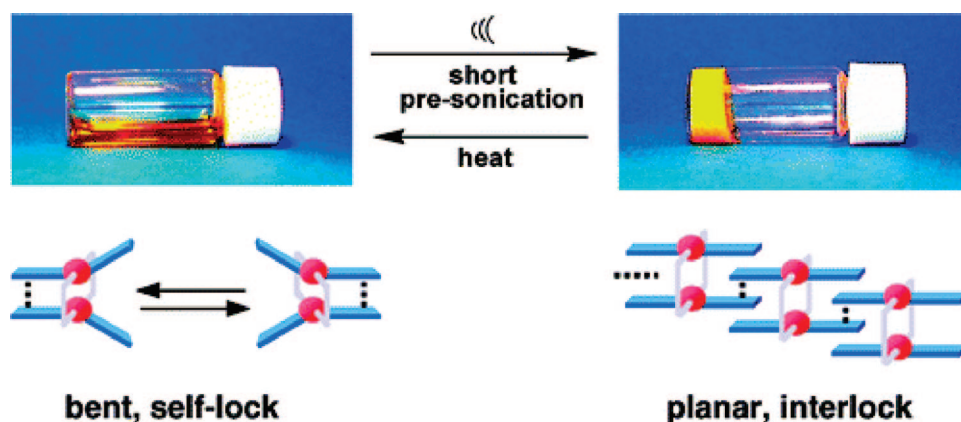
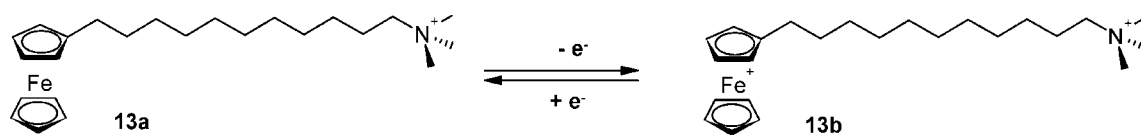
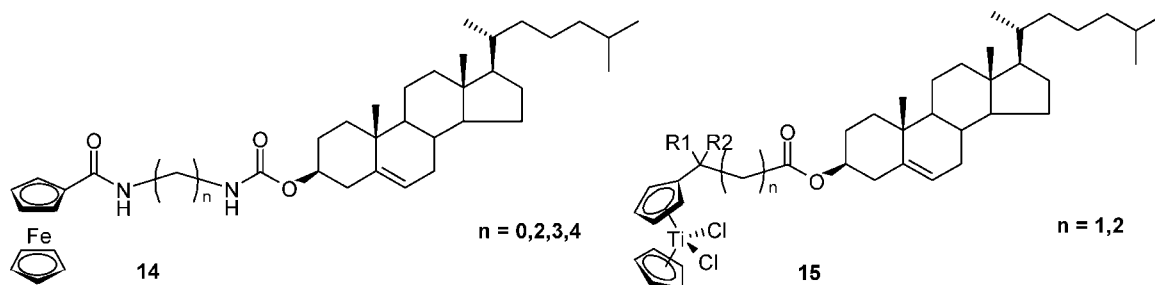


Figure 9. Illustration of gel formation of *anti*-**5** and proposed mechanism of gelation. Reproduced with permission from ref 43. Copyright 2005 American Chemical Society.

Scheme 8



Scheme 9



a linker to an aromatic moiety, also known as aromatic-linker-steroid (ALS) gelators.⁹⁹ The cholesterol-appended ferrocene **14** shows gelling behavior depending on the chain length of the linker (Scheme 9).^{109,110} The gelator with $n = 0$ rigidifies cyclohexane and CCl_4 at concentrations as low as 0.09% by weight. With $n = 2$, compound **14** also gels but at higher concentration, whereas for longer lengths of the spacer chain, gelling ability is lost altogether. Fourier transform infrared (FT-IR) and ^1H NMR spectroscopic studies suggest that not only the ferrocene and cholesterol unit but also the hydrogen bonds between the adjacent spacer groups are essential for the assembly of the gel network. The gel is rigid enough to be molded into films that support themselves in the wet state and is responsive to a wide range of stimuli, both chemical and mechanical (Figure 10). As well as being broken up and formed reversibly upon shaking, sonication, and heating, **14** also shows redox switching similar to that observed for **13**. In this case, oxidation was done using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and the gel network is destroyed. Subsequent reduction by NH_2NH_2 reestablishes the gel network, and the redox process could be confirmed by UV-vis spectroscopy.

Gansäuer and co-workers have investigated the properties of compounds where the cholesterol group is linked to a titanocene.^{111–113} Cholesteroidal titanocenes of general structure **15** were prepared, with a variation in the R1 substituents on the bridging methylene group and the terminal cyclopentadienyl ring. While the compound with $\text{R1} = \text{Me}$ and $n = 1$, **15** is a supergelator gelling a wide range of solvents, some of them at concentrations below 1 wt %. Other groups in place of R1 such as cyclohexyl increase the critical gelator

concentration, and permethylation of the terminal cyclopentadiene leads to loss of gelling ability. The morphology of the fibrillar network was investigated by transmission electron microscopy (TEM), cryo-SEM, and atomic force microscopy (AFM) and consists of entangled fibers, most of which show left-handed helicity with the occasional right-handed strands, which is frequently observed for these ALS-type compounds.¹¹³ The most recent studies on these titanocene gelators confirmed the dependence of the gelation potential and fiber morphologies on the choice of substitution both on the cyclopentadienyl rings and the linker moieties.¹¹²

Recent studies by Dastidar also employed the ferrocenyl moiety in developing low molecular weight gelators by a crystal engineering approach.¹¹⁴ In this work, a 1:2 salt of ferrocene-1,1'-dicarboxylic acid and dicyclohexylamine was found to be an effective gelator in a wide range of organic solvents. A 1:1 salt could also be isolated, but only showed gelation in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), showing the importance of the 1D hydrogen-bonded network present in the crystal structure of the 1:2 salt.

As an aside, ferrocenyls can also be found in metallopolymers, which on a few occasions have been observed to exhibit gelation behavior. In this context, cross-linked poly(ferrocenylsilane)s (PFSs) were found to form swellable gels in a variety of solvents and redox active due to the ferrocenyl moiety, which were then exploited in the formation of color-changing materials.^{115,116} PFS as a component in copolymers with poly(γ -benzyl-L-glutamate) (PBLG) was found to retain the gelling ability of the polypeptide by a nanoribbon mechanism.¹¹⁷

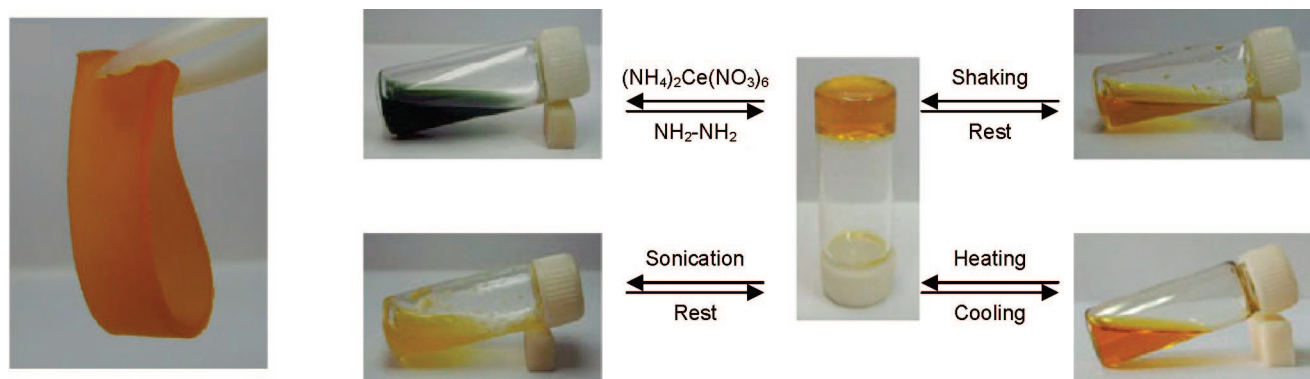
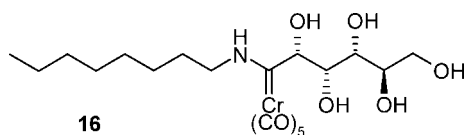
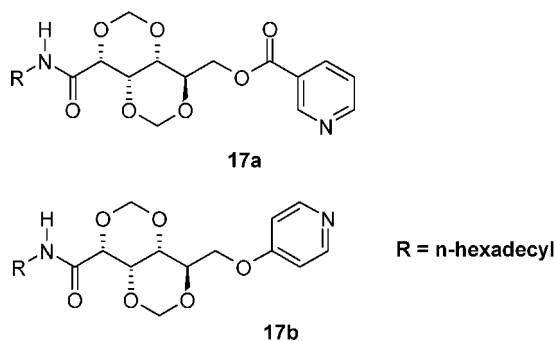


Figure 10. Gel films of **14** in cyclohexane (left) and reversible gel-sol transitions by a variety of stimuli (right).¹⁰⁹

Scheme 10



Scheme 11



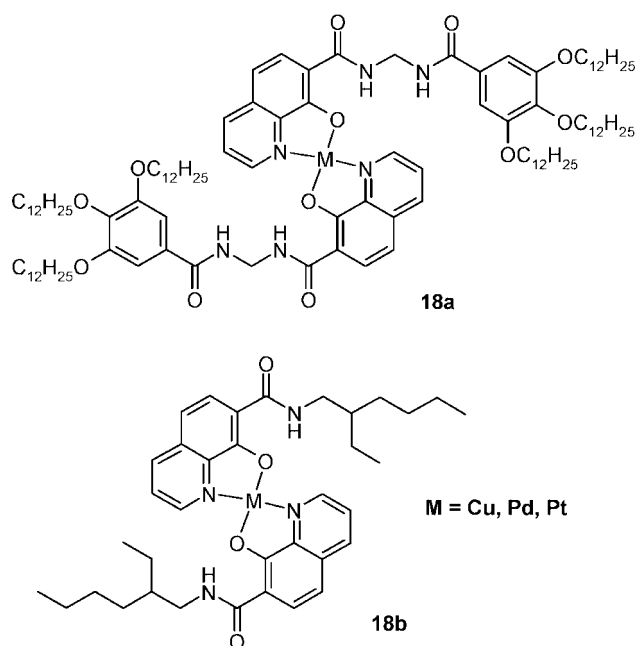
The chromium carbene complex **16** (Scheme 10) illustrates yet another strategy for designing and preparing metal-containing gelators. It was prepared as an organometallic isolobal analogue of *N*-*n*-octyl-D-gluconamide.⁴⁶ The latter forms aggregates in which the carbonyl oxygen atom is supposed to play an important role. By replacing this oxygen with the apolar pentacarbonylchromium fragment, the gluconamide is rendered almost insoluble but exhibits increased solubility in organic solvents. Compound **16** retains its gelling ability in that it forms thermoreversible gels in chloroform, dichloromethane, benzene, toluene, and mixtures thereof, that are stable over weeks. The nature of the gels depends on the rate of cooling, where slow cooling leads to clear gels and fast cooling leads to turbid gels. FT-IR analysis indicates that the local C_{4v} symmetry on the pentacarbonylchromium is reduced by hindered rotation arising from assembly of the fibers. This assembly is driven by hydrogen bonding of the hydroxyl and amino group, although it was noted that the carbonyl ligands on the chromium center may also be involved.

4.2. Discrete Metal Complex Gelators

So far we have looked at systems where the metal is irreversibly integrated into one of the ligand monomers that then assemble into primary, secondary, and tertiary gel networks. In this section, we will extend this concept and deal with discrete metal complexes formed by two or more ligands attached to the metal center. In general, as for the examples in the previous section, metal coordination is integral to the gelator shape, but interaction between the discrete complexes that leads to the formation of 3D fibrillar gel networks tends to be driven by π - π stacking, hydrogen bonding, or van der Waals forces rather than metal-ligand bonding.

Gelators involving square-planar platinum(II) as the metal center represent a prolific group in this category of discrete metal complexes. The functionalized gluconamides **17a** and **17b** (Scheme 11) are examples of a whole range of similar compounds that were tested for gelation ability, gel morphology, and imprinting of gel fibers.¹¹⁸ It was found that the complex *trans*-[Pt(**17a**)₂Cl₂] is an effective gelator in tetrahydrofuran (THF), toluene, and MeOH. The analogous *trans*-palladium(II) complex of **17a** also gels THF, and *trans*-[Pd(**17b**)₂Cl₂] does not, possibly because of a bend in the

Scheme 12

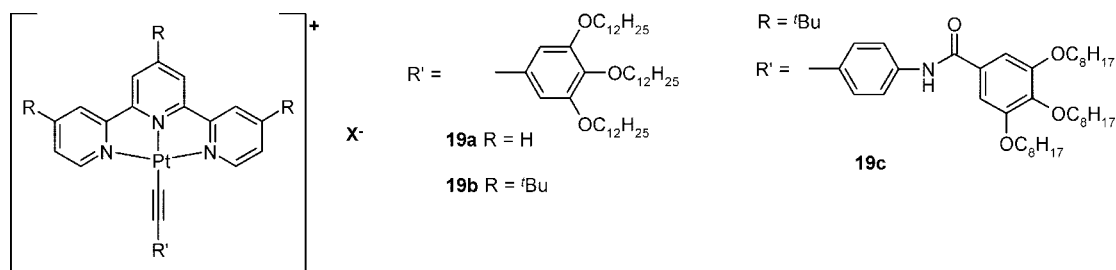


overall shape of the molecule that distorts the favorable rodlike geometry of the assemblies.

Other platinum complexes have been prepared and studied because of their interesting luminescent behavior. The group of Shinkai reported the 8-quinolinol based organogelator **Pt·18a** and its nongelating reference **Pt·18b** in a study into possible ways of protecting the excited state from O₂-quenching by “insulating” the phosphorescent group in a gel fiber with peripheral alkoxy groups (Scheme 12).^{119,120} **Pt·18a** gels 18 organic solvents out of 25 tested, some of these like *p*-xylene, cyclohexane, and other alkanes at critical gelation concentrations as low as 0.01% by weight. UV-vis spectral analysis reveals a red shift in the ligand centered π - π transition and the singlet intraligand charge transfer when going from sol to gel. This was interpreted as a *J*-aggregation mode of the 8-quinolinol platinum(II) chelate groups, which leads to thermo- and solvatochromic behavior exhibited in the absorption and emission spectra. The sol of **Pt·18a** appears yellow and emits at 460 nm when excited at 365 nm, the gel is orange and emits at 490 nm. Interestingly, the luminescence intensity in the gel phase is clearly less susceptible to O₂-quenching, thus demonstrating the insulating effect aspired to in the gel design.¹⁰⁶ Incidentally, compounds **18a** and **18b** can also be complexed by copper(II) and palladium(II) without compromising any of the gelation capacity of these systems, with gel fiber aggregation being attributed to strong π - π stacking and H-bond interaction between the amide groups. The different metallogels exhibit field emission performances, with the turn-on field depending on the type of metal in the complex. Although these fields are higher than for other organic field emission materials, the ease of preparation makes these gels interesting for photo- and electrochemical materials.¹¹⁹

Other platinum(II) containing complexes with luminescent properties were recently reported by Yam et al.¹²¹ They also made use of a 3,4,5-tris(alkoxy)phenyl group, this time in conjunction with an alkyl linker to the metal to make the cationic complexes **19a-c** (Scheme 13), which show different luminescence depending on their presence as either the trifluoromethanesulfonate (OTf) or hexafluorophosphate

Scheme 13



(PF₆) salts. UV–vis absorption studies of all OTf salts of **19a–c** showed bands indicating the presence of intraligand transitions of the alkynyl and terpyridine ligands as well as metal-to-ligand transitions. At higher concentrations, the spectra of **19a**–OTf developed a further band, which was interpreted as a Pt^{••}Pt metal–metal-to-ligand charge transfer (MMLCT). Compounds **19a**–OTf and **19b**–OTf form gels in DMSO at 0.44 and 0.75 wt %, respectively, whereas **19c**–OTf only gels benzene at 8% by weight. All gels show more or less dramatic color changes when going to a sol at elevated temperatures (Figure 11).

The origin of the color change as analyzed by both UV–vis and emission spectra over a range of temperatures was attributed to the decreasing extent of Pt^{••}Pt and π – π interactions in the **19a**–OTf, which were thus thought to be crucial in the formation of the gel. Curiously, the **19a**–PF₆ salt also gels DMSO but at a higher critical gelation concentration (0.75 wt %) and with a lower T_{gel} (42 °C compared to 55 °C). The lower-energy MMLCT bands both in absorption and emission were taken as an indication for the direct correlation of the extent of Pt^{••}Pt and π – π interactions and gel stability. The absence of these interactions in the case of **19b**–OTf and **19c**–OTf was ascribed to interference of the bulky substituent on the terpyridyl ligand.

Very recently, the authors expanded their work on these types of compounds in a full paper.¹²² The above example gives an indication of how anions can interfere with gel properties, a factor that we will return to in section 6 in more detail.

The same group extended their work on platinum(II) and reported a series of rhenium(I) complexes of general structure **20** (Scheme 14).¹²³ All of these formed gels in DMSO at a critical gelation concentration of around 1 wt %. The complexes with the *t*Bu-bpy moiety were found to be more soluble, and gels in hexane and acetone could also be achieved. In contrast to the platinum(II) compounds, no metal–metal interaction was observed. Instead, UV–vis measurements indicate that the metal–ligand charge transfer (MLCT) decreases in intensity and red-shifts when going from gel to sol, while the opposite is true for the sol-to-gel transition. Aggregation is hence likely to occur via π – π stacking interactions. All of these rhenium(I) metallo gels emit strongly between 580 and 650 nm, but most of the emission intensity is lost in the sol phase.

The platinum acetylide oligomers (PAOs) of general structure **21** make use of alkynyl and 3,4,5-tris(alkoxy)phenyl moieties and were prepared as systems to study triplet exciton transport and energy transfer (Scheme 15).¹²⁴ Compounds **21a** and **21b** thermoreversibly aggregate to gels in hydro-

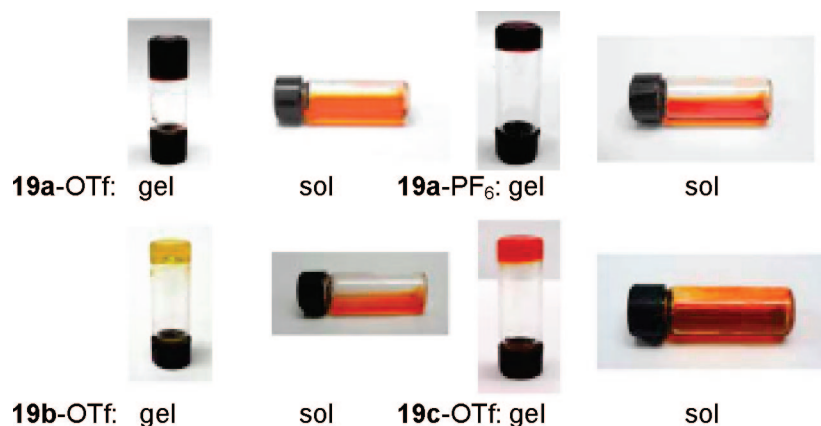
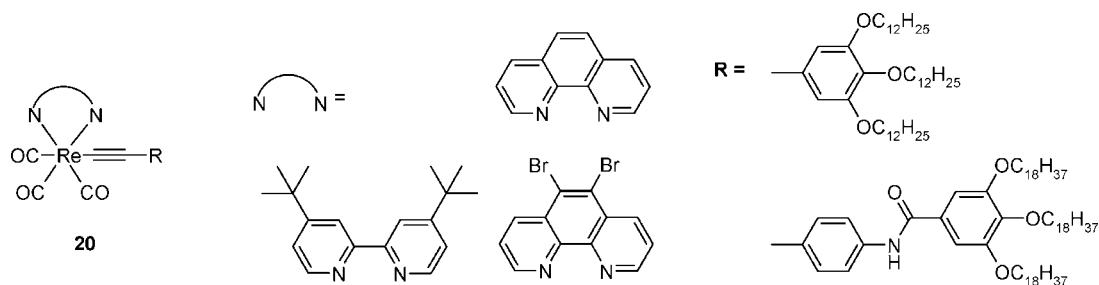
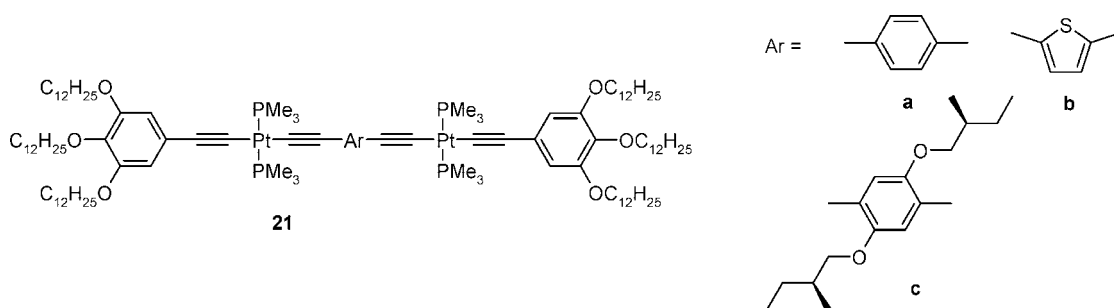


Figure 11. Photographs of gels of different platinum(II) complexes in DMSO at room temperature (gel phase) and at elevated temperature (sol phase). Reproduced by permission from ref 121. Copyright 2007 The Royal Society of Chemistry.

Scheme 14



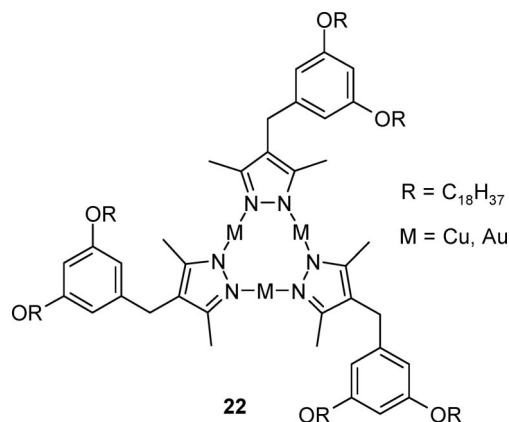
Scheme 15



carbon solvents at around 2 wt %. For **21c**, this process takes three days in *n*-dodecane and the critical gelation concentration is higher by a factor of 4. Temperature- and concentration-dependent UV–vis analyses showed a long-axis polarized π – π^* transition for the monomolecular species in the sol phase at low concentrations and high temperatures. This band broadens and diminishes while the spectra are blue-shifted, and for high concentrations and low temperatures, the absorption spectra are indicative of H-aggregates of linear π -conjugated chromophores. These spectral features were observed for all complexes, although are less pronounced for **21c**, which is likely due to steric hindrance by the branched chiral side groups. In CD measurements, these groups only give a strong signal in the H-aggregate of the settled gel state and point toward a strong exciton coupling within the chiral supramolecular environment. Charge transfer was observed in mixed gels of **21a** and **21b**, with the former acting as the energy donor and the latter acting as the acceptor. The proposed aggregation model is interesting in the context of gel organization and is shown in Figure 12. It is postulated that **21a** is present in a configuration with the central aromatic ring coplanar in relation to the plane of the PtP₂C₂ unit (*t*-conformation). The oligomers arrange into slipped stack forming sheets, which themselves pack into a lamellar configuration. On a longer-range order, these sheets may form a helically twisted ribbon structure, affording optical properties similar to those arising from the chiral packing of **21c**.

Gels where the color of phosphorescence can be tuned by chemical stimuli are formed by the planar trinuclear gold(I) pyrazolate complex **Au**•**22** (Scheme 16).¹²⁵ In this system, aggregation is driven by labile aurophilic metal–metal bonding, which organizes the complexes even at ambient temperatures into a rectangular columnar packing of a matted

Scheme 16



fibrous structure as found by XRD, and can rigidify hexane at a critical gelation concentration of 5 wt %. Organogel **Au**•**22** exhibits red luminescence under UV radiation at $\lambda = 254$ nm, whereas the sol hardly phosphoresces under the same conditions. Doping of the complex aggregates with silver(I) in the form of AgOTf leads to a blue shift in the luminescence, and after addition of 0.01 equiv of the silver(I) salt, the gel emits blue at an excitation wavelength of 365 nm. This process is reversible, and removal of the silver with cetyltrimethylammonium chloride reverts the gel to red emission. When the silver doped organogel is heated, a green luminescing sol is obtained, which upon removal of the silver returns to a virtually nonemitting sol (Figure 13).

Although no gelling behavior was reported for the related copper(I) pyrazolate complex **Cu**•**22**, it was found that similar metallophilic interactions and dichroic behavior could be exploited in the fabrication of thermally rewritable UV ink.¹²⁶

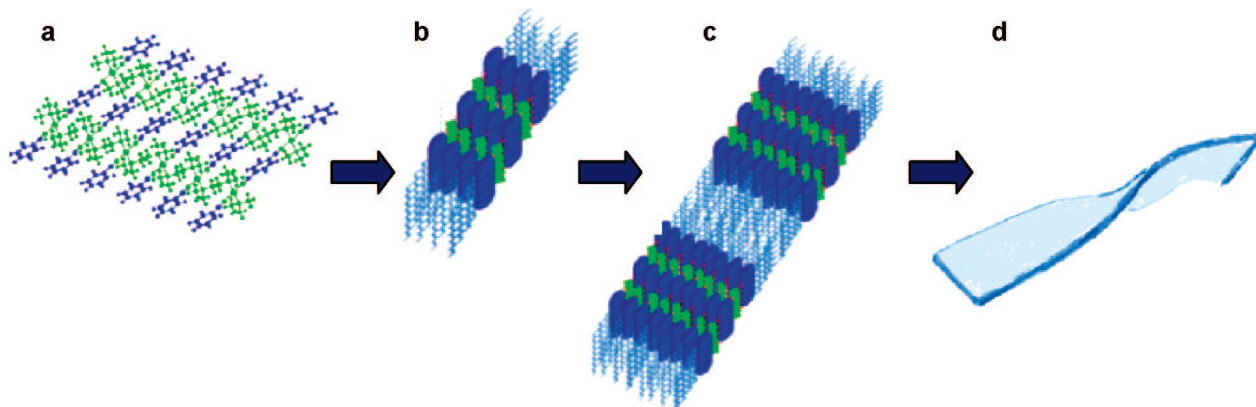


Figure 12. Proposed model for the arrangement of **21a** into supramolecular aggregates: (a) sheetlike slipped stacking of monomer in *t*-conformation, (b) stacking of the sheets, (c) lamellar packed arrangement of the stacked sheets, and (d) formation of ribbons with helical supramolecular twist. Adapted with permission from ref 124. Copyright 2008 American Chemical Society.

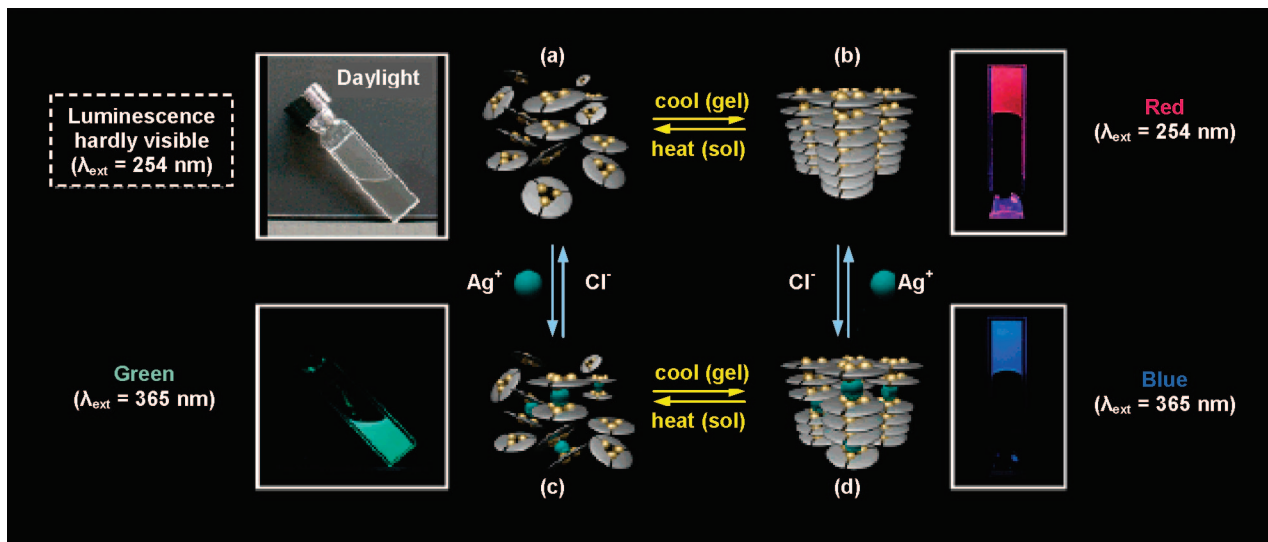
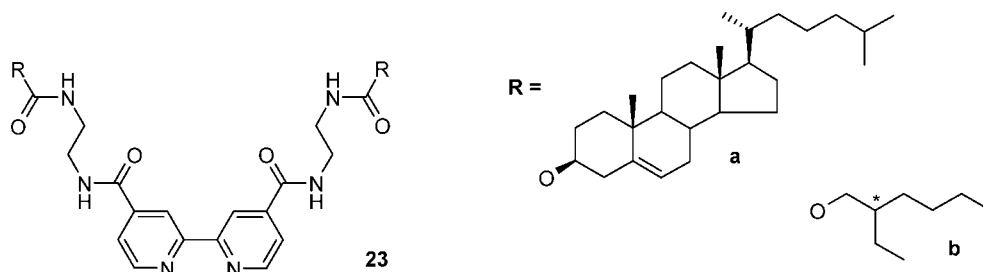


Figure 13. Luminescence profile of $\text{Au}\cdot\mathbf{22}$ in hexane and schematic representation of the self-assembly structure of (a) sol, (b) gel, (c) sol with AgOTf (0.01 equiv), and (d) gel with AgOTf (0.01 equiv). Adapted with permission from ref 125. Copyright 2005 American Chemical Society.

Scheme 17



A copper(I) containing complex that does gel was reported by Shinkai et al.⁴⁸ The 2,2'-bipyridine derivative with two cholesteryl groups **23a** forms a complex $\text{Cu(I)}\cdot(\mathbf{23a})_2$ that gels benzonitrile, 1-butyronitrile, and THF/acetonitrile (Scheme 17). The 1-butyronitrile gel was studied in greater detail, and it was found that there is a remarkable color change from reddish-brown in the sol phase to greenish-blue in the gel phase (Figure 14a).

This process is reversible many times over and, hence, does not arise from air oxidation of Cu(I) to Cu(II) but instead was attributed to a distortion in the confined environment inside the Cu(I) containing gel fibers. The color change is only observed for the cholesteryl appended ligand; $\text{Cu(I)}\cdot(\mathbf{23b})_2$ does not gelate. Furthermore, since the complexes incorporate a redox-active metal center, the systems could be reversibly switched between the sol and the gel phase by the addition of oxidizing and reducing agents (Figure 14b).

The 2,2'-bipyridyl coordinated ruthenium(II) complex in the commercially available dye Z907 (**24**) was very recently

used to induce gelation in THF and acetone by grafting it on the surface of ZnO nanospheres and nanorods (Scheme 18).¹²⁷ TEM imaging indicated localized slightly more ordered clusters of 5–10 nanorods, but no long-range order like in DNA-linked gold nanorods was observed. Rheology experiments showed a transition from a low-viscosity fluid to a very soft gel upon formation of the aggregates that is very susceptible to mechanical collapse. It is envisioned to use these kind of hybrid-aggregates in application such as solar cells.

The “tin-drum” arrangement **25** represents a rather unique complex for which gelation has been reported.¹²⁸ (Structure reproduced by permission from ref 128. Copyright 2007 The Royal Society of Chemistry.) In this system, tin assembles with carboxylate ligands to yield organotin nanoclusters. All gelators except **25e** gel benzene and are thermoreversible, which indicates that gelation is by assembly of the separate clusters by noncovalent interaction rather than chemical changes in the tin-drum, an interpretation that was supported by ¹H NMR and ¹¹⁹Sn NMR spectroscopy. Complex **25a**

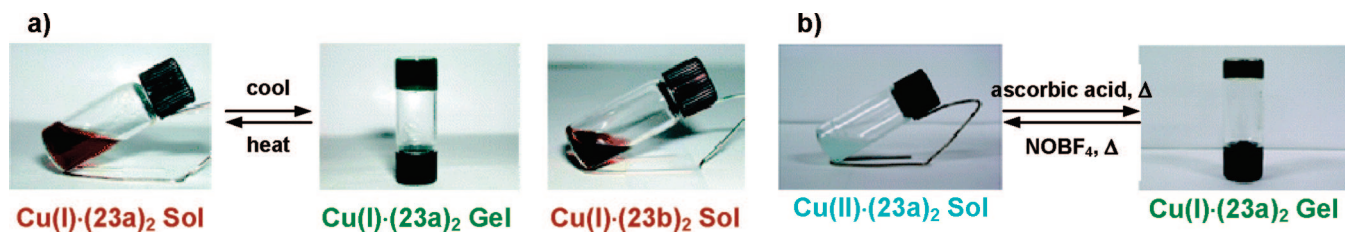
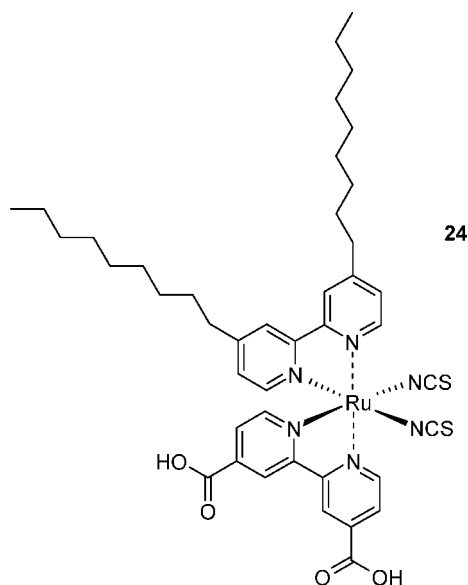


Figure 14. (a) Phase transition and thermochromic behavior of copper(I) complexes of **23a** and **23b**. (b) Phase transition and thermochromic behavior of copper complexes of **23a** upon oxidation and reduction. Adapted with permission from ref 48. Copyright 2004 American Chemical Society.

Scheme 18



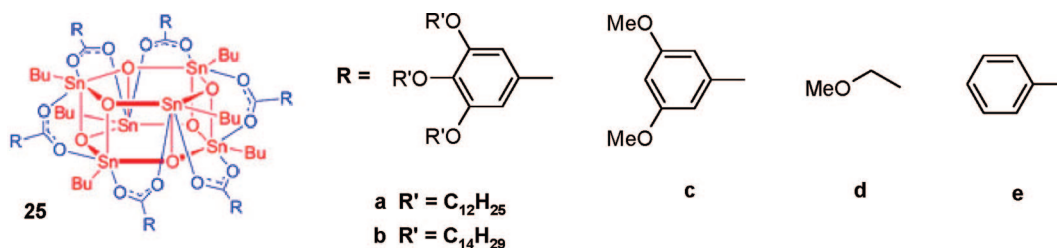
gels benzene at 2.6 wt % and **25b** is equally effective, but the absence of alkyl tail ends in **25c** and **25d** leads to less efficient gelation, suggesting that the aliphatic moieties play an important role in fiber formation (Scheme 19).

Similarly, the presence of aromatic rings was found to enhance gelling abilities, with the exception being **25e**, where the absence of the ether substituents was thought to have an even greater influence on the gelation properties by changing the solubility. XRD studies of these systems indicated a hexagonal packing of columnar fibrils. These fibrils were proposed to be formed by electrostatic interactions between $\text{Sn}(\delta^+)$ and $\text{O}(\delta^-)$ combined with π - π stacking interactions, which is supported by the packing of alkyl chains. A wide variety of carboxylic acids is hoped to enable greater control over self-assembly and tuning of gel properties.

No less unusual in the world of metalogels is the polyoxometalate-based soft material that was recently assembled from chiral aminophosphonate pentamolybdate units of the general form $[(\text{R}^*\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]^{2-}$ by Carraro et al.¹²⁹ Different aminoalkyl phosphonic acids $\text{R}^*\text{PO}_3\text{H}_2$ were employed, and Figure 15a shows the structure of $[(\text{CH}_3\text{CH}(\text{NH}_3)\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]^{2-}$ crystallized as the rubidium salt.

These assemblies have the ability to act as efficient gelators (0.2 wt %) in ethanol/water mixtures when adding the alcohol to the acidified aqueous solution (pH 3.5). Gelation was also observed with dioxane, *i*PrOH, *t*BuOH, THF, and hexafluoro-2-propanol. The gel network consists of homogeneous fibers 20–40 nm in length. In high-resolution TEM, an ordered substructure was revealed in the fibers, which is consistent in dimensions with the packing of the hydrogen-bonded polyoxometalate units. Induced cyclic dichroism showed enhanced features in the gel state attributed to the supramo-

Scheme 19



lecular organization of the compounds into twisted fibrils with a distinct handedness in the helical structure.

We will conclude this section with examples of copper(II) and palladium(II) complexes. In general, Cu(II) and Pd(II) are associated rather with labile complexes and hence lend themselves to the formation of chemically tunable gels as will be discussed later. However, the examples shown here are more characteristic of discrete metal complexes.

One of the earlier gelling complexes involving copper(II) was published by the group of Terech, who described the gelation of cyclohexane by the planar Cu(II) β -diketonate **26** substituted by eight paraffinic chains (Scheme 20).¹³⁰ This study employed electron paramagnetic resonance (EPR) techniques, otherwise seldom applied to the investigation of gels, which provided insight into the role of copper in the gelation as well as the thermodynamics and kinetics of aggregation. In this context, it was found that there were interactions between the copper atoms in the gel phase, which manifested in the reduction of the hyperfine coupling of the spectrum of the gel phase compared to the free complexes, and which indicates the aggregation of the complexes into long chains. On these grounds, copper is probably not involved in the formation of cross-links between these linear strands.

The trinuclear Cu(II) complex of inositol **27** was reported as a case where discrete complex molecules act as a hydrogelator (Scheme 21).¹³¹ The gel formation of complex **27** is not as straightforward as for many of the other examples discussed so far and involves the reaction of inositol (ins) with 3 equiv of a copper(II) 2,2'-bipyridine (bpy) complex, which in turn was obtained by reacting cupric acetate with bpy in water. After heating the solution at 60–70 °C for 30 min at pH 12.4 (NaOH), a transparent green gel forms upon cooling to room temperature. Amounts of $[\text{Cu}(\text{bpy})]^{2+}$ below 3 equiv do not lead to gelation. The xerogel can be made to form a solvated gel again by redissolving it in water and repeating the heating and cooling as described above, but no pH adjustment is necessary.

When all of the NaOH is washed out of the xerogel, structural analysis by thermogravimetry, electrospray ionization mass spectrometry (ESI-MS), and FT-IR confirms the presence of discrete complexes of **27**. These washed xerogels can be revived only in water at pH 12.4.

A series of pyridine-bridged bis(benzimidazolylidene) pincer palladium(II) complexes was prepared by Dötz and co-workers.^{132–134} The Pd(II) complex **28** was found to be a very effective gelator for a large variety of protic and aprotic organic solvents for concentrations as low as 0.2 wt % (Scheme 22). NMR and X-ray diffraction studies showed that π -stacking of the aromatic rings, van der Waals interaction between the alkyl chains, and metal–metal interactions may be important for the self-assembly. Interestingly, a gel of **28** in DMSO shows catalytic reactivity for a Michael addition of α -cyanoacetate to methyl vinyl ketone.¹³³

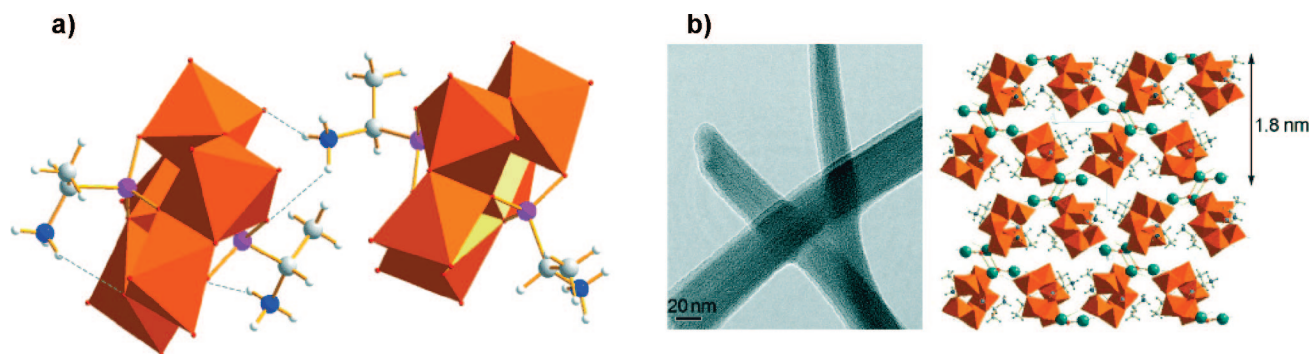
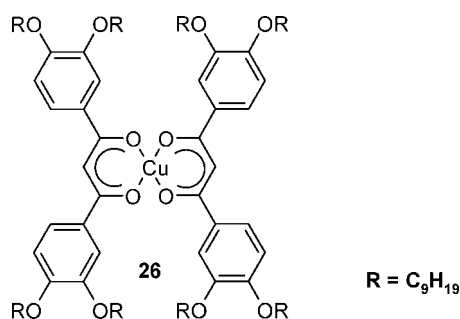
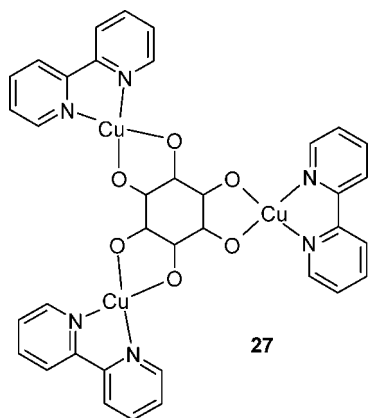


Figure 15. (a) Polyhedral/ball-and-stick representation of the two diastereomeric forms of $[(\text{CH}_3\text{CH}(\text{NH}_3)\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]^{2-}$ crystallized as the rubidium salt. MoO_6 octahedra orange, O red, P magenta, C gray, N blue, H white. (b) TEM analysis of the Na salt of $[(\text{CH}_3\text{CH}(\text{NH}_3)\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]$ and crystal packing of the Rb salt of $[(\text{CH}_3\text{CH}(\text{NH}_3)\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]$ with the same colors as above. Rb azure. Reproduced with permission from ref 129. Copyright 2008 Wiley Interscience.

Scheme 20

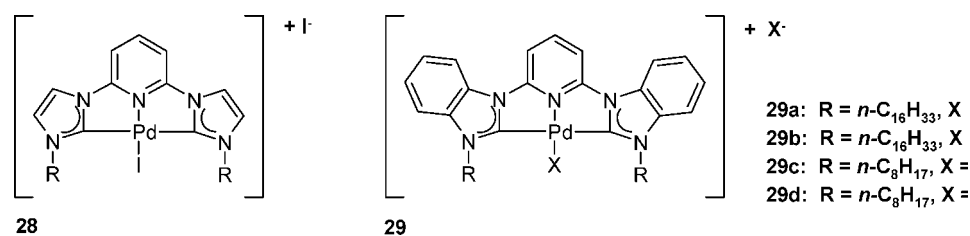


Scheme 21



The benzimidazolium salts of **29a–d** gel a wide range of solvents without the palladium center, and aggregation was also found to be driven by π -interactions as well as hydrogen bonding involving the counterion and van der Waals interactions where long alkyl chains are present.¹³² The palladium pincer complexes **29a** and **29b** show strong gelation abilities in both protic and aprotic organic solvents, with **29c** being a clearly weaker gelator and **29d** failing to show any gelation, possibly due to a lack of van der Waals interactions because

Scheme 22



of the short alkyl chains.¹³⁴ Further, **29a** and **29b** formed gels in ionic liquids, and remarkably, the conductivity of the gels was only slightly diminished compared to the pure ionic liquids, with the iodide gelator **29b** showing slightly higher conductivity than the bromide gelator **29a**, possibly related to the leaving group properties of the two anions. These gels, therefore, have interesting potential applications in electrochemical devices.

5. Metal Ion Binding by Gels and Gelators

There is increasing current interest in the use of additives such as metal cations, small inorganic anions, and ion pairs as in metal salts to tune gel properties, particularly rheological properties.^{42,135} The fast diffusion of molecules and ions into the liquidlike gel immediately suggests that gels could be either rigidified or, conversely, induced to flow by means of an ionic or molecular chemical messenger. This possibility becomes particularly intriguing in the case of the supramolecular LMWG systems in which the very interactions holding the gel fibers together are formed reversibly and are thus subject to breaking and reformation. This kind of reversibility can give rise to interesting and unusual properties such as *thixotropy*, for example, in which mechanical stress induces the breakup of the solid gel network, but that network then reforms over time.^{136–139} A very simple example of the effect ions can have on gel rheology is the addition of common salt (NaCl) to hair gel. Figure 16 shows two samples of commercial hair gel. A spatula of salt has been added to the sample on the right. After just a few seconds, the gel transforms into a solution as the salt binds to the polymer electrolytes that make up the gelator, uncoiling the polymer chains and reducing interchain interactions.

In this section, we concentrate on metallogel systems where the metal center affords a more labile binding mode compared to the examples described in the previous section. This means that ligands can reversibly bind to the metal or arrange in a different coordination geometries. This then

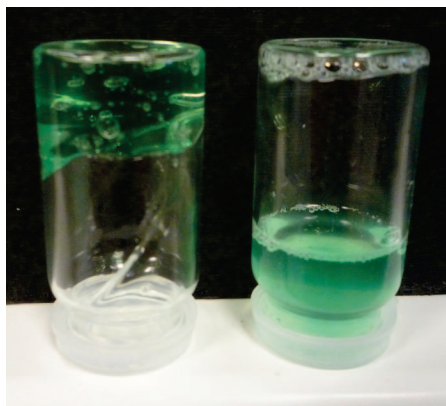
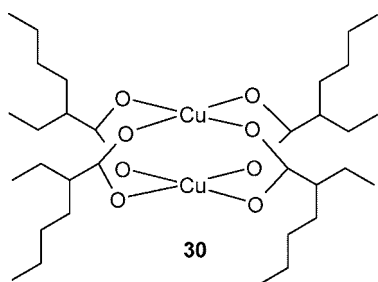


Figure 16. Two samples of commercial hair gel. A spatula of NaCl has been added to the sample on the right, resulting in the breakdown of the gel.

Scheme 23



results in metals giving gelation ability to these systems or taking it away completely. As a further consequence, these types of aggregations are susceptible to chemical stimuli such as cation and anion binding, and these will be at the center of the second part of this section as well as the next section. But first we concentrate on metals in gelling coordination polymers.

5.1. Coordination Polymers as Metallogels

As we have seen, the formation of any 3D gelating network involves the aggregation and self-assembly of some species of monomers into a larger structure. Effectively, this can be regarded as a type of polymerization. Here we specifically will refer to examples where one ligand has the ability to bridge across two metal centers and hence lead to a formal coordination polymer. One of the earliest examples of such a structure that was found to gel methylcyclohexane

was described by Terech, Guenet, and co-workers and was formed by the binuclear copper(II) tetracarboxylate **30** (Scheme 23).^{140–145}

The aggregation of this complex was first reported as an example of a “living polymer”, meaning a dynamic system where a combination of fiber breakage and recombination provides an efficient mechanism for stress relaxation and which was elucidated by dynamic rheological studies.¹⁴³ Living polymer systems have been observed mainly for aqueous surfactant micelles, and in this context, **30** provides a rare case of this kind of aggregation in an organic solvent. The local structure was probed by small-angle neutron scattering and showed characteristics of a molecular thread with only one complex of **30** in the cross section. The aggregation of the molecules in the thread was attributed to coordination bonding between the copper atom of one unit and an oxygen atom of the next unit (as indicated by the arrows in Figure 17). More detailed rheological studies in decalin as a function of temperature and concentration revealed a more complicated aggregation behavior in that there exists a concentration-dependent transition temperature T_{trans} above which the aggregates do not behave as described by the “living polymer” theory.¹⁴⁰ It was, therefore, suggested that below T_{trans} a degree of physical gelation takes place that interacts between short portions of the filaments, whose melting corresponds to the transition temperature.

As was demonstrated by complexes **28** and **29**, palladium(II) is an attractive metal for supramolecular gel assembly because of its potential use as a catalyst in these systems. Consequently, a number of coordination polymer gelators have been reported that try to make use of this possibility. The Pd(II) containing gel network **6** reported by Xu et al. has already been mentioned.^{45,146} The calix[4]arene tetrapyrrolyl ligand **6** reacts with $[\text{Pd}(\text{en})(\text{OH}_2)_2]^{2+}$ in DMSO to give orange gels of a molar ratio of Pd(II) to **6** from 1.8:1 to 2:1 and using 0.5–2% by weight. At the lower end of the concentration range, the metallogel is thermoreversible, but at the higher concentration, this is not the case, indicating a higher degree of cross-linking in the polymer. The cross-linking is thought to involve a distribution of random conformers of **6** bridged by the $\text{Pd}(\text{en})^{2+}$ ions with the solvent filling the interstitial space (Figure 18). The gels were shown to extract guest species from solvents, e.g., toluene from water or other aromatics from the gas phase.¹⁴⁷ On the other hand, they are able to retain water-soluble dyes inside the network when water was layered onto the DMSO gel and to reject cations such as Cd^{2+} dissolved in water.

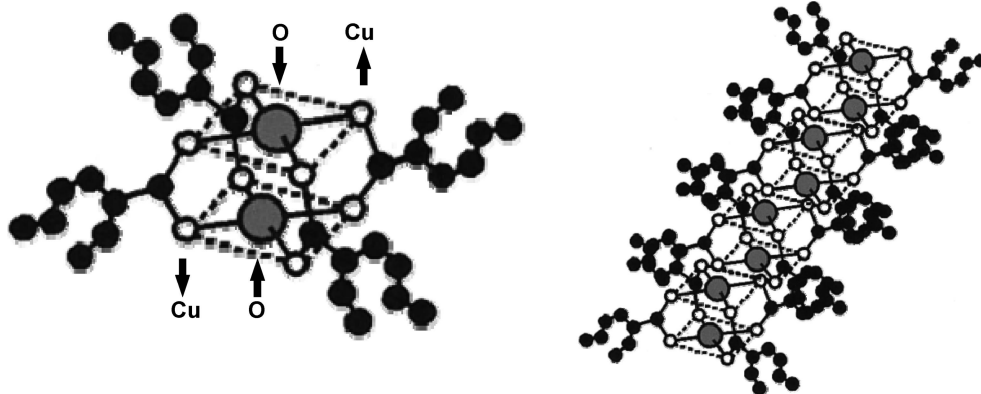


Figure 17. Schematic representation of bicopper complex **30** (left) and organization of **30** in a filament (right). Gray circles represent copper atoms, white circles represent oxygen, and black circles represent carbon. The arrows and atom labels indicate coordination to these atoms in the next unit in the fiber. Adapted with permission from ref 141. Copyright 2001 American Chemical Society.

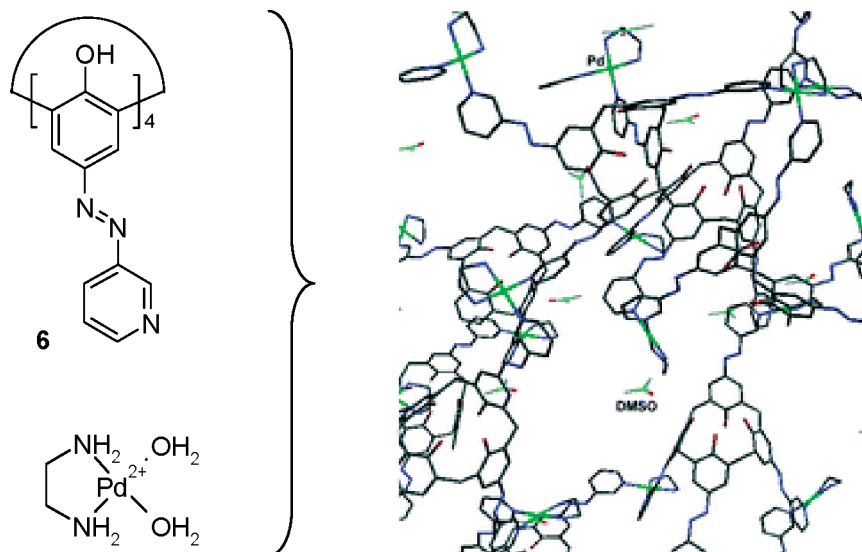
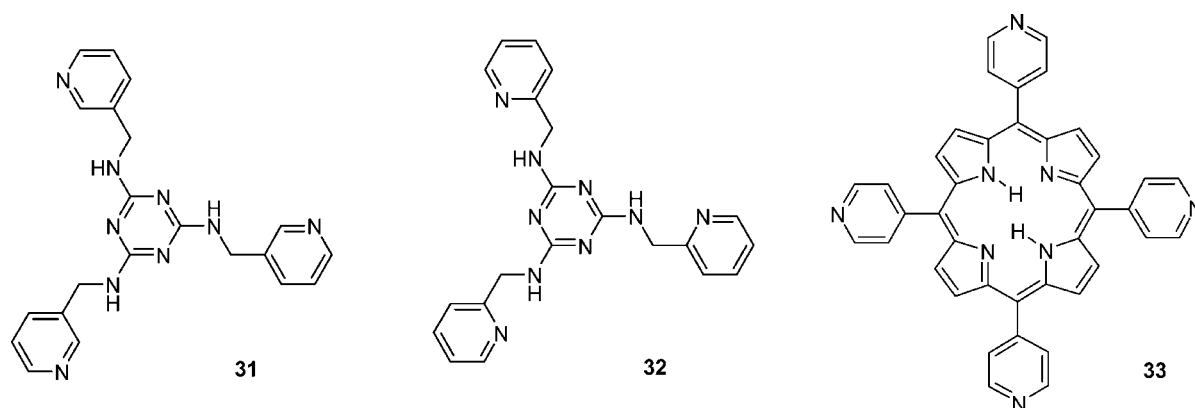
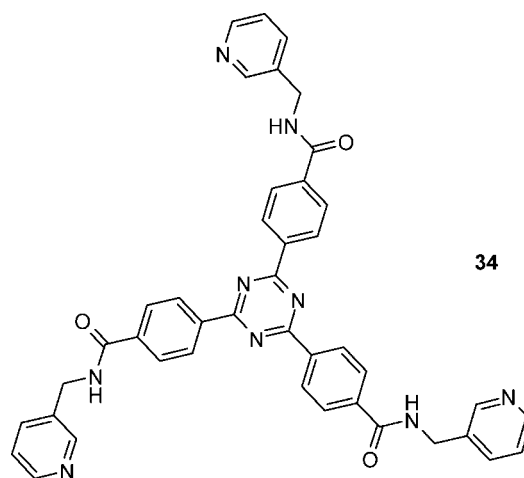


Figure 18. Formation of the possible network of the $\text{Pd}(\text{en})^{2+}$ cross-linked metallogel of **6**. Reproduced with permission from ref 45. Copyright 2002 The Royal Society of Chemistry.

Scheme 24



Scheme 25



In a subsequent paper the same group tested the Pd(II) gels of **6** as well as three new ligands **31**–**33** (Scheme 24).¹⁴⁶ **31** was found to gel only after addition of $[\text{Pd}(\text{OAc})_2]$ rather than $[\text{Pd}(\text{en})(\text{OH}_2)_2]^{2+}$, possibly because the latter caused too rapid polymerization to trap sufficient solvent inside the network.

In a very recent study, Su and co-workers presented Pd(II) metallogels from the pyridine-based tripodal ligand **34**.¹⁴⁸ These were prepared by dissolving **34** in DMSO or solvent mixtures of $\text{MeOH}-\text{CHCl}_3$ or $n\text{-BuOH}-\text{CHCl}_3$ and then adding $\text{Pd}(\text{COD})\text{Cl}_2$ and AgNO_3 in MeOH or CH_3CN to the solutions. ^1H NMR, FT-IR, and fluorescence spectroscopic analyses showed a combination of Pd–N coordination, hydrogen bonding, and π – π interactions being present in the assembly of the 3D gel network. Interestingly, the morphology of the gels depends on the ratio of Pd(II)/**34** (Scheme 25, Figure 19a,b), with an excess of palladium leading to spherical aggregates and a 1:1 ratio resulting in a more defined nanofibrous network.

In the ^1H NMR spectrum, a downfield shift is observed in the resonance assigned to the pyridyl protons, as would be expected for the coordinated fragment. For higher metal–ligand ratios, this shift is larger, suggesting a higher degree of Pd–N complexation. However, even the lowest ratios show no free ligand signals. Fluorescence spectroscopy indicates that π – π interactions are more pronounced in the

1:2 and 1:4 systems and may predominate over P–N coordination, whereas the reverse may be true for the 1:1 system.

Taking account of these observations, the authors proposed different assembly processes as shown in Figure 19c, where at low metal–ligand ratios a $\text{Pd}(\text{34})_4$ complex is organized by π – π stacking and at high ratios a more “cross-linked” 3D network is formed that relies more on Pd–N connections. The morphology was also found to have an influence on the

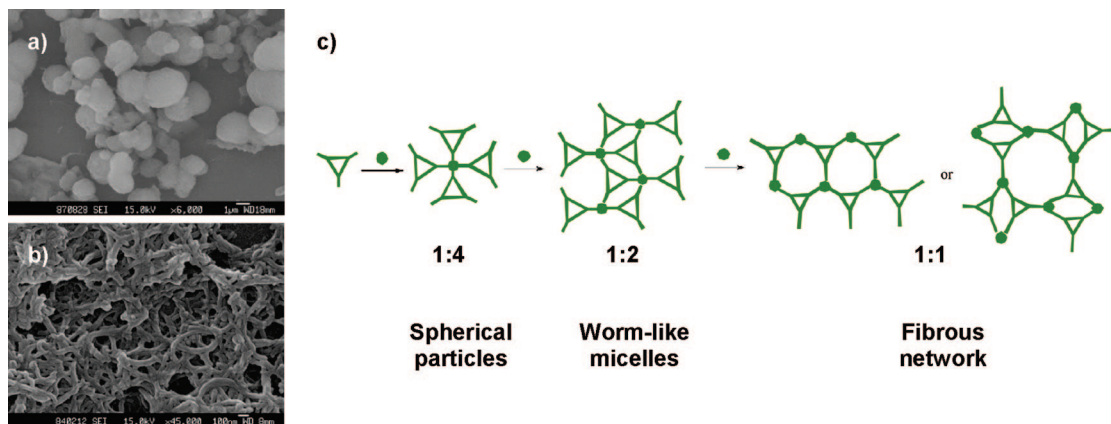
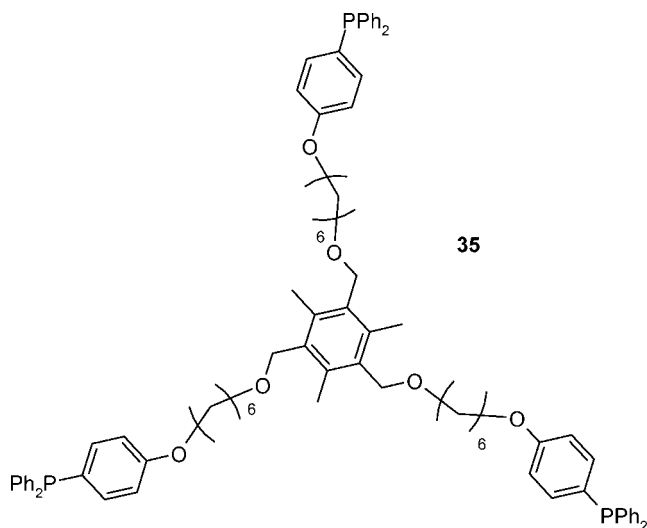
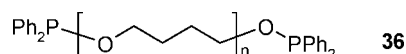


Figure 19. Morphologies of a Pd/34 gel at (a) 1:4 and (b) 1:1 ratios, and (c) proposed assembly process leading to different gel morphologies at different Pd/34 ratios. Adapted with permission from ref 148. Copyright 2009 American Chemical Society.

Scheme 26



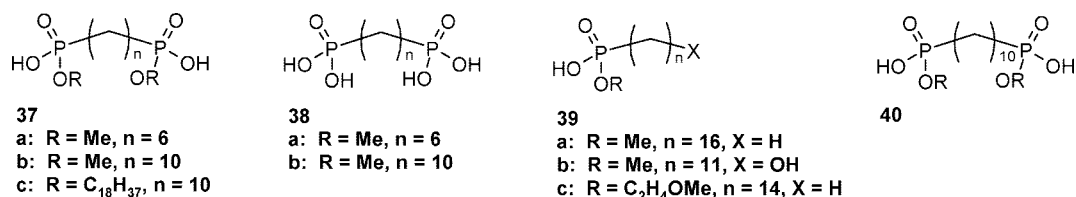
Scheme 27



catalytic activity of these systems, with a higher metal–ligand ratio affording faster catalysis of a Suzuki coupling reaction. The xerogels of these systems showed higher catalytic activity and could be recycled up to five times.

Another catalytic palladium(II) based coordination polymer is the flexibly bridged triphosphine complex of **35** (Scheme 26).¹⁴⁹ Upon the reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in toluene at 100 °C for 24 h, the complex formed a yellow gel from the reaction mixture, which had a blocklike morphology. The complexation of the triarylphosphino unit to Pd(II) forming a $\text{PdCl}_2(\text{PAR}_3)_2$ aggregate in the gel network was confirmed by ^{31}P MAS NMR studies where the singlet moved from $\delta = -7.1$ ppm to $\delta = 20$ ppm. The complex shows catalytic potential for the Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acids, with high yields being

Scheme 28



obtained even after recycling the gel four times. The wet gels are more effective than the xerogels.

Phosphorus as the coordination site in metalogels has been reported for rhodium(I) and iridium(I) containing assemblies.¹⁵⁰ The diphenylphosphinite telechelic polytetrahydrofuran derivative **36** formed reversible coordination gel networks with $[\text{RhCl}(\text{COD})_2]$ and $[\text{IrCl}(\text{COD})_2]$ in chloroform (Scheme 27).

The number of ligand molecules bound to the metal center was found to be crucial for gel formation with only the tetrakisphosphinite affording the gelling assembly. This is true for both rhodium(I) and iridium(I), although iridium forms gels more quickly and at lower concentrations. In THF, where only the trisphosphinite was detected by ^{31}P NMR spectroscopy, gelation could be induced for both metals by the addition of sodium tetraphenylborate. The gels break down after 3 min of ultrasonication but reestablish themselves after 1 min for rhodium and 1.5 h in the case of iridium. The authors explained this behavior as a result of ligand exchange without changing the stoichiometry, whereby the number of metal centers involved in the cross-linking is reduced and the gel stability is compromised.

Weiss and co-workers have studied the gelling behavior of bisphosphonate esters (**37**), phosphonic acids (**38**), mono-phosphonate esters (**39**), and a phosphoric acid ester (**40**) in the presence of different metals (Scheme 28).^{67,151,152} With Fe(III) as the complexing agents, some of these gelators have found applications in hydraulic fracturing. The gelling behavior of this wide range of ligands depends on a number of influences,⁶⁷ but in general there seems to be a trend for the monofunctional phosphonate esters **39** to show the better gelation.

A dried sample of the **Fe**•**39a** gel showed organization in a lamellar phase, whereas aggregation of the complexes in the gels is in the form of giant wormlike micelles (Figure 20a). There is a dramatic effect of the length of the spacer between the phosphorus centers, with the shorter one taking 5 weeks to form gels compared to 3 h for the $n = 10$ case.

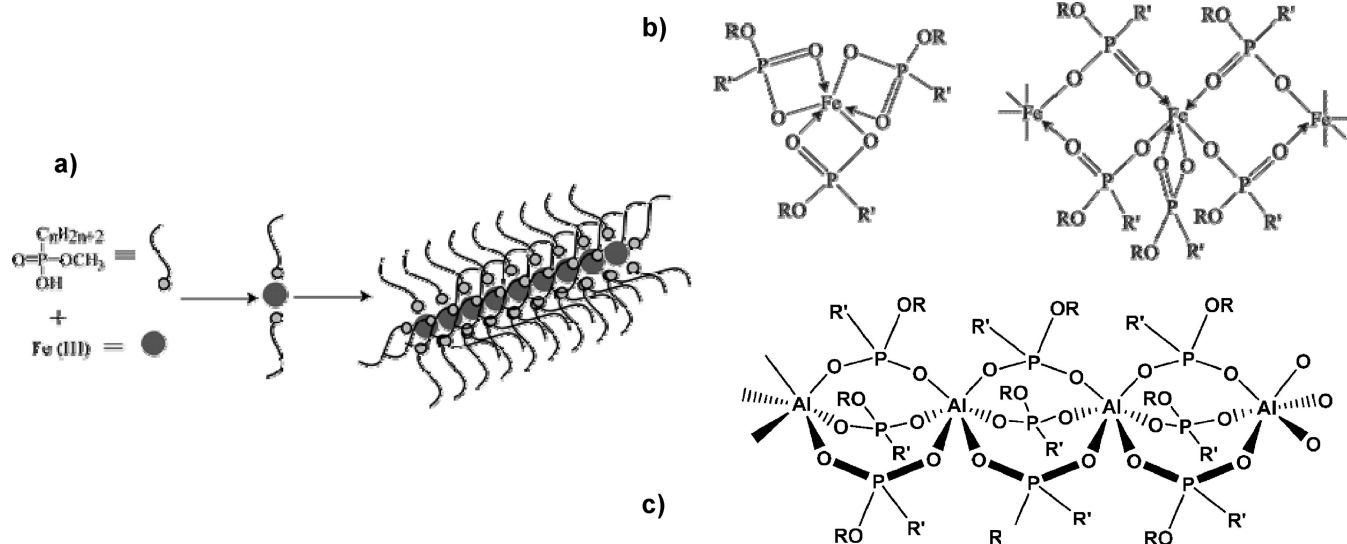


Figure 20. Representations of (a) giant wormlike micelles from an *n*-alkyl monophosphonate ester with Fe(III) (dark gray circle), of (b) two possible arrangements of Fe(III) with phosphonate esters, and of (c) a possible segment of an Al(III) complexed worm-like micelle. Reproduced with permission from refs 67 and 151. Copyright 2006 and 2008 American Chemical Society.

Clearly this class of ligand provides a wide scope for gel modulation. In a follow-up study, **39a**, its phosphonic acid derivative, and **40** were investigated as their Al(III) complexes, but only the first was found to be a good gelator in a number of solvents.¹⁵¹ Like the Fe(III) complexes, the system aggregates into inverted rodlike micelles with a possible copolymeric structure (Figure 20c). Complexation with boron(III) leads to a dramatic decrease in gelation ability, and only silicon oil could be gelled. With zirconium(IV), no gels were formed. Recently, it was demonstrated that these metal complex organogels show solution- and gel-like characteristics depending on the frequency that are consistent with living polymers.¹⁵² The rheology of these samples is dependent on the temperature and the particular metal–ligand combination.

A similar strategy as above for the formation of metallo-gels was employed by Page and Warr, who mixed aluminum isopropoxide and didodecyl phosphate surfactants in order to cause gelation in decane.^{153,154} The rheology and structures of these aggregates were reported to be very sensitive to the ratio of aluminum/surfactant (Al/P), with an increasingly viscous Newtonian liquid being present at $Al/P \leq 0.5:3$. At 1 wt % of the surfactant, a viscoelastic fluid was observed within a 0.5:3–1.0:3 of aluminum/surfactant, which became a viscoelastic solid up to a 1.5:3 ratio, and above this, phase separation occurred.¹⁵³ By rheology, this behavior was rationalized in terms of a transition of aggregate morphology from independent wormlike micelles to a physical branched gel network brought about by the increase in number of branching points with increasing amount of aluminum. This concept was recently expanded by adding the monododecyl or a branched phosphoric acid to the gel aggregates.¹⁵⁴ The former suppressed ligand binding and fibrillar network formation, but in low concentrations could help to thermally stabilize samples with low aluminum content. The latter was found to prevent fiber formation due to steric effects, which lead to shorter aggregates.

Other oxygen bridged coordination polymer metallo-gels have been reported using carboxylic acids. Moulton et al. studied the gelation behavior of a manganese containing single-molecule magnet $[Mn_{12}O_{12}(CH_3CO_2)(H_2O)_4]$ (**41**), shown in Figure 21, when bridged with 12 di- and tricar-

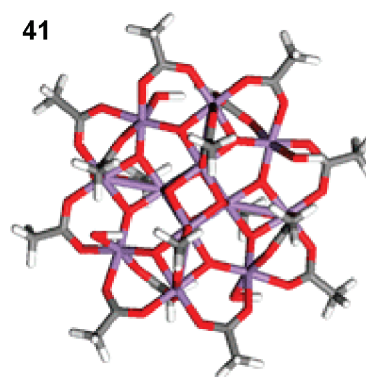


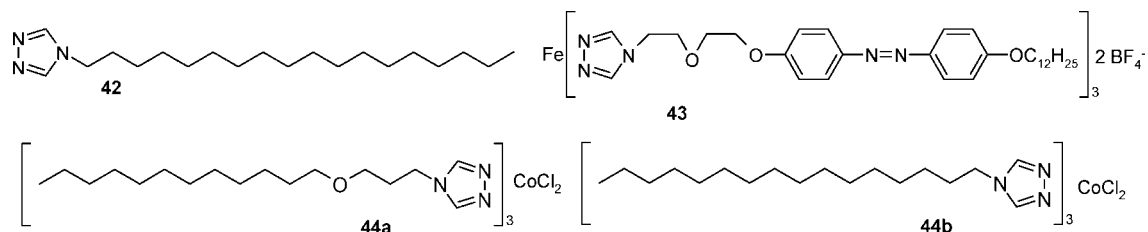
Figure 21. Structure of $[Mn_{12}O_{12}(CH_3COO)(H_2O)_4]$ (**41**) acting as a node in coordination polymers with bridging carboxylic acids. Reproduced with permission from ref 155. Copyright 2007 The Royal Society of Chemistry.

boxylic acids.¹⁵⁵ In all cases, **41** acted as a node in the polymeric network and all systems showed gel-like behavior in rheology with G' being higher than G'' in all cases. The strength of the gel depends dramatically on the nature of the linker between the carboxylates, with aromatic and conjugated spacers affording more rigid gels than aliphatic ones and shorter chains being stronger gels than long chains.

In another study, it was reported that a mixture of silver(I) hexanoate and silver(I) palmitate gave clear gels in toluene, whereas the two complexes on their own form precipitates from the same solvent.¹⁵⁶ This is thought to happen because the random distribution of the ligand chain length in the mixed silver(I) carboxylate aggregates hinders crystallization and instead a branched fibrous gel-like network is formed.

The above examples describe effective gelation by phosphorus or oxygen coordination. The vast majority of metallo-gels, however, are formed by association of metals to nitrogen, in coordination polymers based on triazoles, for example. The iron(II) containing assembly of **42** forms thermoreversible gels with spin-crossover characteristics (Scheme 29).¹⁵⁷ In the solid and in the presence of *para*-toluenesulfonate, **42** aggregates into linear polymeric structures with the substituted triazole rings in an eclipsed arrangement around the Fe(II) ions and subsequently into anisotropic rodlike species (Figure 22a). These precursors,

Scheme 29



when boiled in hydrocarbons such as decane, form a colorless viscous solution, which upon cooling transforms into a homogeneous purple gel. In the solid, this is brought about by a thermal magnetic change from the paramagnetic high-spin species at high temperatures to a diamagnetic low-spin species and is effectively reproduced in the gel phase. At around 44 °C, the gels undergo a color change accompanied by an increase in magnetic moment and are potentially useful for thermoreversible magneto-optical switches (Figure 22b).

A similar concept of creating an iron(II) polymeric metallogel was employed by Kimikazu and co-workers, who introduced an azobenzene chromophore into the triazole ligand.¹⁵⁸ The coordination of **43** around the metal centers follows a similar pattern to that of **42**. The azobenzene fragment inserted into the appendage displays photoisomerization and allows a reversible photoresponsive morphological transformation when going from a gel with *trans*-configuration in the dark to a sol upon irradiation with UV light, to give the *cis*-isomer. When stored in the dark, the sol reverts back to the gel phase, and these changes can be monitored by AFM. The same group reported a remarkable observation of another closely related triazole system in complexes with cobalt(II).¹⁵⁹ Compound **44a** forms a gel-like phase in chloroform at room temperature, whose blue color suggests a tetrahedral geometry around the metal centers. The ether functionality in the ligand is essential as **44b** does not gelate chloroform. In a complete reversal of the behavior of virtually all other reported gels, this system turned to a sol on cooling to 0 °C rather than heating. This process is accompanied by a color change to pink indicative of octahedral cobalt(II). The gel–sol transition is completely reversible and could be linked to the flexible coordination geometry of Co(II) (Figure 23). It was suggested that the thermal stability depends on a number of factors. Water was found to increase the rate of sol formation by coordination to the metal centers, which weakens the polymer but does

not break it down. The inability of the octahedral complexes to form aggregates on the grounds of enthalpy consideration may be another important factor.

Changes in coordination environment around the metal center that subsequently lead to gelation upon sonication were recently reported by You and co-workers.¹⁶⁰ Coordination polymers were formed by mixing $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$ with 4,4'-bisimidazolylbiphenyl (bibp) in methanol, resulting in a precipitate of sheetlike microparticles. Crystals acquired from diffusion of dioxane into a solution of the complex in DMSO revealed that the zinc(II) center adopts a tetrahedral geometry coordinated to four imidazole nitrogen atoms from four different bibp units whose other nitrogen atoms serve as bridging sites to adjacent identical zinc centers (Figure 24a). These units afford the formation of a 2D layer with two types of channels containing the triflate counterion (Figure 24b). While dissolving the complex only leads to precipitation in MeOH, sonication was found to dramatically change the morphology of the aggregates from sheets to long fibers and induces gelation in this solvent as well as ethanol and acetonitrile. PXRD of the xerogels indicated a difference in coordination that was proposed to result from a change from a tetrahedral geometry to a seesaw configuration (Figure 24c), making this the first example of a sonication-induced coordination geometry modification.

Fluorescent metallogels based on coumarine-derivatized glycines were reported recently by the group of Vittal.^{161,162} In basic aqueous solutions, **45a** instantly forms a hydrogel upon the addition of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$.¹⁶² These gels are pH sensitive and dissolve into colorless clear solution under acidic conditions. When zinc acetate and **45b** were mixed, a crystalline product is obtained instead of a gel. The X-ray structure of this material provides some insight into what the aggregation might look like, showing a 1D zigzag arrangement with the coumarine forming hydrophobic pockets and various hydrogen bonds. Gels of $\text{Zn} \cdot \mathbf{45a}$ show

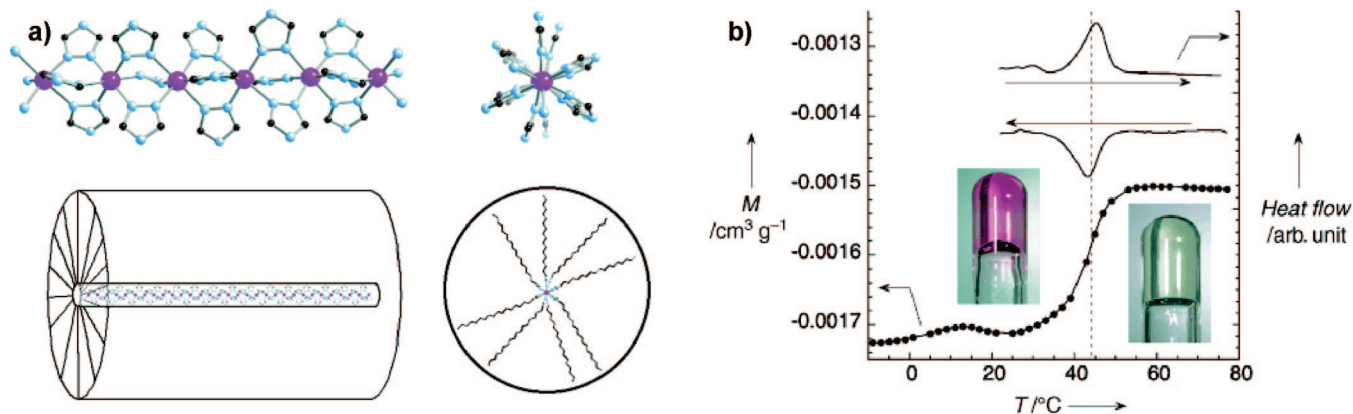


Figure 22. (a) Schematic representation of the polymeric structure of $[\text{Fe}(\mathbf{42})_n]^{2n+}$ without alkyl chain (above) and view of a cylindrical anisotropic rod formed by the polymeric chains with alkyl chains (below). (b) Demonstration of the thermoreversible magneto-optical properties of the gel at a spin-crossover temperature of 44 °C (from DSC) showing the color change and rise in massic magnetic moment at this temperature. Reproduced with permission from ref 157. Copyright 2004 Wiley Interscience.

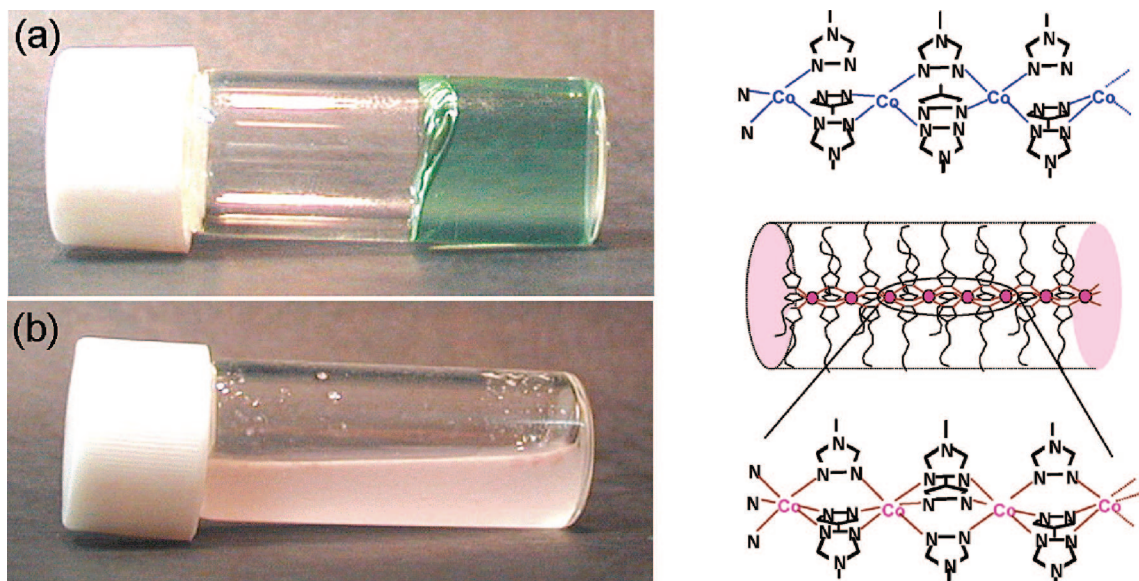


Figure 23. Pictures of **44a** in chloroform (a) as a blue gel phase at room temperature and (b) as a pale pink solution at 0 °C. On the right-hand side are shown schematic representations of the corresponding polymeric tetrahedral and octahedral complexes. Reproduced with permission from ref 159. Copyright 2004 American Chemical Society.

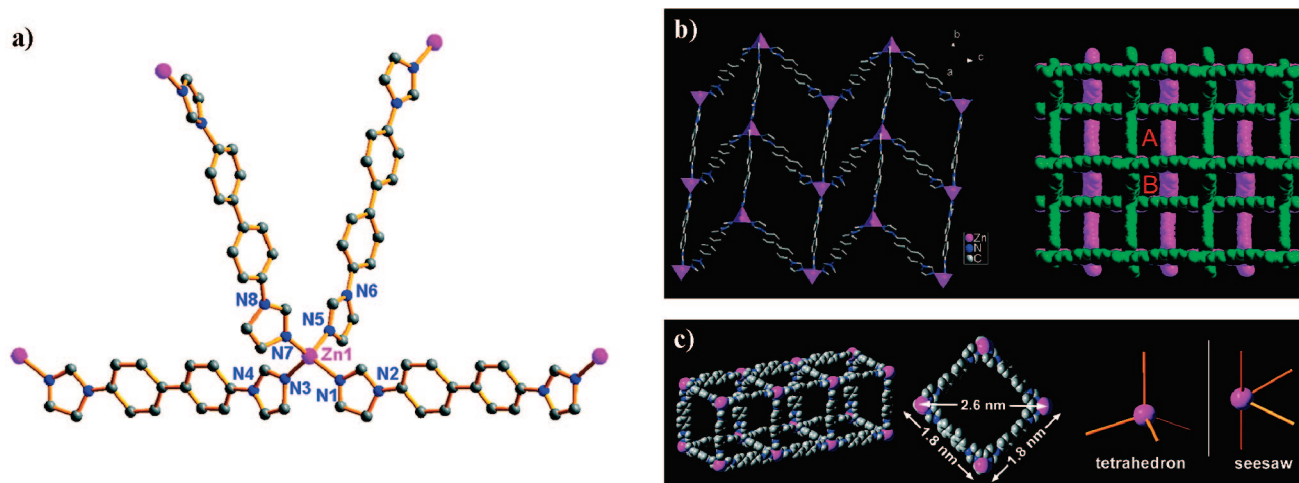
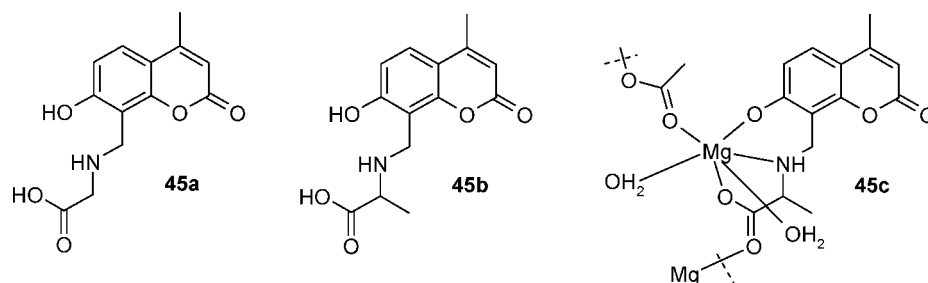


Figure 24. (a) Coordination mode of $[\text{Zn}(\text{bibp})_2(\text{OSO}_2\text{CF}_3)_2] \cdot (\text{DMSO}) \cdot (\text{dioxane}) \cdot \text{H}_2\text{O}_2$. Hydrogen atoms, solvent molecules, and nonbonding CF_3SO_3^- are omitted for clarity. (b) Infinite 2D layers of the assembled complex pink polyhedra represent the coordination geometry of zinc(II), and space-filling projection of the packing arrangement showing two types of rectangular channels A and B. (c) Proposed mode of nanofibers and coordination mode of zinc ions (pink) of tetrahedron and seesaw geometry before and after sonication, respectively. Reproduced with permission from ref 160. Copyright 2009 American Chemical Society.

Scheme 30



remarkable fluorescence enhancement over the uncomplexed ligand in the sol due to retarded nonradiative decay in the rigidified gel. Similar observations were made for magnesium coordinated metallogels.¹⁶¹ Mg(II) only forms hydrogels with **45b** by possible aggregation into polymeric strands of **45c** (Scheme 30). The magnesium gels form over a period of 20 min compared to the instant gelation brought about by the

zinc gel. It was therefore possible to perform time-dependent emission studies, which showed a great enhancement of the emission intensity as the gel fibers assemble.

Control studies with the nongelating Ca^{2+} derivative suggested that fluorescence enhancement is not due to coordination but to the process of solvent gelation. Rheological studies demonstrated the higher structural cohesive-

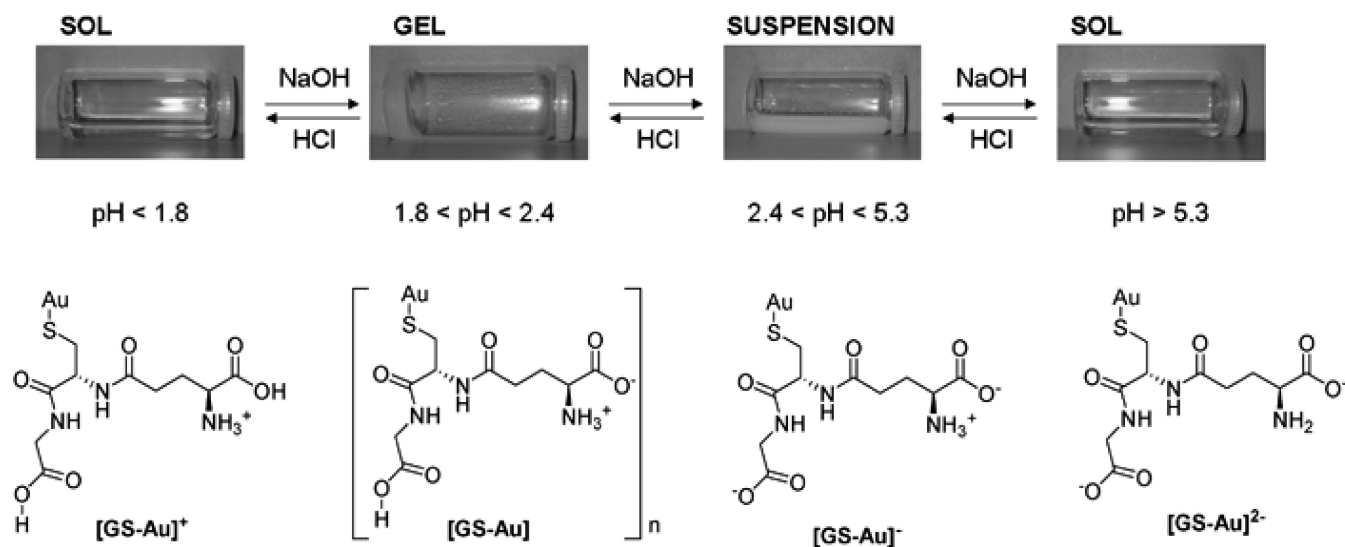
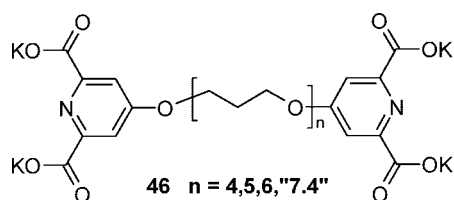


Figure 25. pH induced reversibility of GS–Au hydrogels. Reproduced with permission from ref 163. Copyright 2007 The Royal Society of Chemistry.

Scheme 31



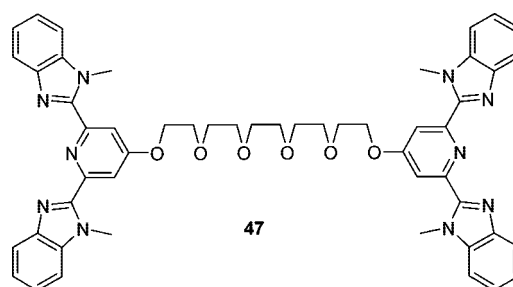
ness of **Mg·45b** over **Zn·45a** with an elastic modulus 1 order of magnitude higher and an increased T_{gel} . Applications in optoelectronic devices and biomedical uses of these gels were anticipated by the authors.

Another gel with potential biomedical applications was reported by Odriozola and co-workers and involved the polymeric coordination of gold(I) to the naturally occurring tripeptide glutathione (GSH), and silver(I) and copper(II) salts could also be used to obtain pH-responsive gels.^{163,164} Gels of GS–Au of a 1:1 glutathione–gold ratio that were thermally stable were obtained when AuCl₃ was mixed with GSH in water.

It was suggested that aurophilic interaction occurring between the gold centers in close mutual proximity contributes to the gel stability. The gels show reversible responsiveness to titrations with NaOH and HCl and are only stable in a pH range from 1.8 to 2.4. When the complex is present in its all-protonated or all-deprotonated form, the gel breaks down (Figure 25). The detailed mechanism of this behavior is currently under investigation. Very recently, anion binding to Ag(I)–GSH hydrogels was investigated further and it was found that iodide could be used to bring about a gel–sol transition, whereas a number of other anions did not have this effect.¹⁶⁵ This process was reversible upon the addition of Ag(I) into the sol. The system was found to have sensing potential when applied to the determination of I⁻ in simulated wastewater. Furthermore, the application in switchable chiral and photoluminescent devices was envisaged.

The bifunctional ligand **46** (Scheme 31) forms viscous and gel-like aggregates with neodymium(III) and lanthanum(III) in aqueous solution.^{166,167} The gelation ability with Nd³⁺ was found to depend on the chain length of the spacer moiety, and only the longer linkers $n = 6$ and “7.4” (this being a mixture of molecules with an average of 7.4 ethylene oxide

Scheme 32



units) groups afford viscoelastic properties to the system. The polymeric networks were described as equilibrium polymers formed by the alternation of rings involving a 2:2 ratio of the metal and **46**, which are connected by a single ligand to another such fragment so that one Nd center is always bonded to three ligands.

This arrangement is postulated to favor linear arrangements since branching will always lead to either an uncomplexed ligand end group, a metal with free coordination sites, or a ligand bonding to the same metal center, which are all unfavorable due to enthalpic or entropic considerations. Doping of the gel fibers with zinc leads to breakdown of the gels, as only two ligands can bind to the Zn(II) centers and the network is disrupted. The viscoelastic properties of these systems in the presence of Nd³⁺ and La³⁺ were found to be dependent on the ratio of metal to ligand and could be explained by different types of ring aggregate formation in the system.

A further step toward chemically tunable gels was taken by the group of Beck and Rowan with the multistimuli responsive metallo-supramolecular polymers using the bisterdentate bridging ligand **47** (Scheme 32).^{137,168–172} The rationale behind the ligand design is its potential to bind to transition metals in an octahedral geometry and with a 1:1 stoichiometry as well as to lanthanides with a higher coordination number with a stoichiometry of 1.5:1. Gels were formed in chloroform/acetonitrile mixtures when a small amount of Eu(III) or La(III) was added to **47** (3 mol % with respect to **47**) followed by Zn(II) or Co(II) perchlorate (97 mol % with respect to **47**) and were found to be thixotropic and thermoreversible.¹⁶⁸ Upon heating, the gels break up and

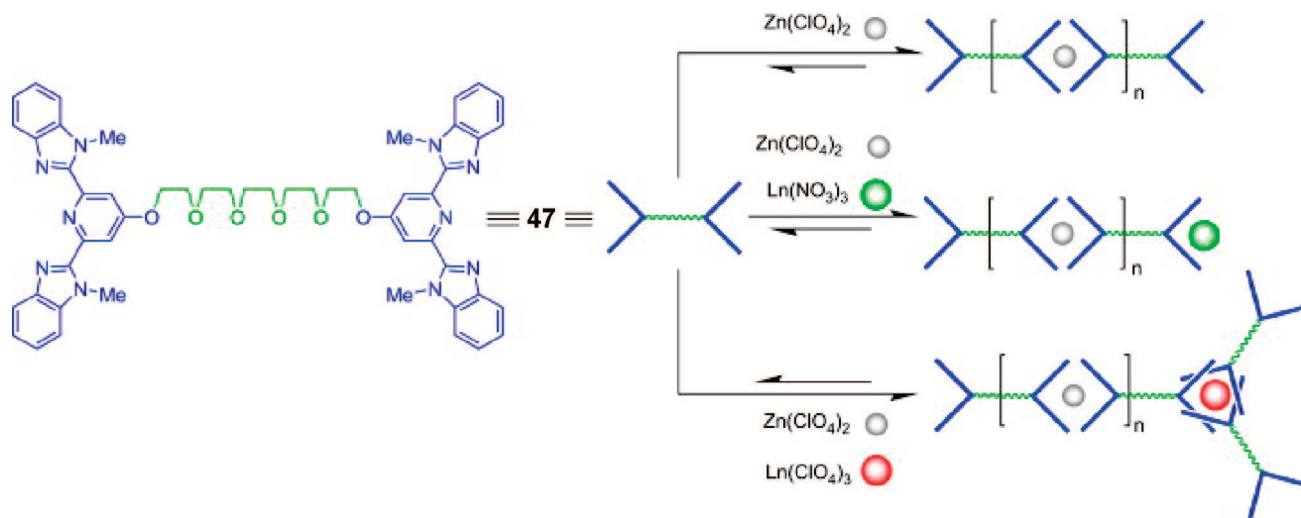


Figure 26. Representation of the possible metallosupramolecular polymeric aggregates formed from the ditopic ligand end-capped monomer **47** with transition metal ions and/or lanthanide metal ions. Reprinted with permission from ref 137. Copyright 2007 Elsevier.

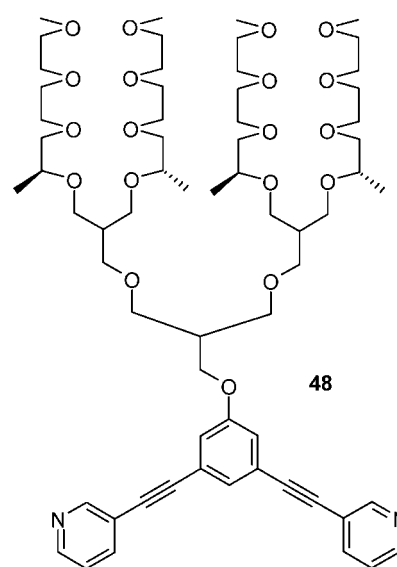
the emission bands from the lanthanides are the most affected, indicating a breaking of mainly these coordination interactions. Similarly addition of formic acid leads to breakdown of the gel network, which was attributed to ligand substitution on the lanthanide centers.

Rheological studies in connection with microscopy revealed a colloidal nature of the gel network where the systems form globular particles in contact with each other and permeated by solvent regions, rather than the fibrous network more commonly observed.^{137,170} The size of these particles depends on their mechanical history, and applied stress leads to smaller spherulites. It was argued that the increased surface area and, hence, increased interparticle cross-linking sites leads to the higher elastic moduli observed for the sonicated samples. Thixotropy arises from the ability of the spheres to regroup after shearing. The cores of the globular entities were found to have crystalline or more highly ordered character than the outer layers depending on the presence of the lanthanide cross-linkers. In this way gels assembled with only Zn(II) at the nodes are more ordered and stronger than those containing La(III), as this affords more branching in the form of a La(**47**)₃ nodes, and hence, less crystallinity and a lower yield stress are observed. Interestingly, branching is thought to be enhanced in the presence of the noncoordinating perchlorate ion compared to the nitrate ion (Figure 26), thus demonstrating the possibility of tuning gel properties. Metal-ion induced tuning of a range of self-assembled systems including gels has also been reported by Schubert and co-workers based on a polymeric ligand bis(2,2':6',2''-terpyrid-4'-yl)poly(ethylene oxide).¹⁷³ We will describe this kind of ion-based tuning in the next two sections.

5.2. Tuning Gel Properties by Ion Binding

We will now focus on gelators and gels, whose properties are directly influenced by cations or anions. In this section, we group systems where metals have been specifically reported to have a systematic influence on the gel characteristics, in particular on the rheological properties, although the distinction is somewhat arbitrary. This includes ligands that may gel on their own but whose gelation ability is either enhanced or diminished by cation binding, and although we dedicate a separate section to anion binding in gels, this also includes anion tuning, where these are thought to influence

Scheme 33



gelation abilities by binding to the metal. These systems include discrete metal complexes as well as coordination polymers; indeed, they can perhaps be viewed as particularly labile or flexible examples of such. One such case are the coordination polymers formed by the bent-shaped bipyridine with dendritic aliphatic appendages **48**, which self-assembles into supramolecular aggregates with Ag(I) (Scheme 33).^{54,59,174}

The structures of the resulting complexes in the solid state were analyzed by small-angle X-ray diffraction and found to differ as a function of the counteranion.⁵⁹ In the presence of small anions such as NO₃⁻ and BF₄⁻, helical chains are formed that organize into 2D hexagonal lattices. With the triflate ion, these chains are dimeric rather than helical and the units stack into hexagonally packed columns. All these columnar arrangements have the ability to gel aqueous solutions. The large heptafluorobutyrate counterion causes the coordination chains to organize into lamellar structures without gelation (Figure 27). Gels of silver-coordinated **48** with tetrafluoroborate also showed further tuning potential, as they dissolve upon the addition of fluoride anion, which leads to decomplexation to give the free ligand.⁵⁴ Remarkably, this process is reversible and subsequent addition of BF₄⁻ leads to reformation of the fibrous gel network.

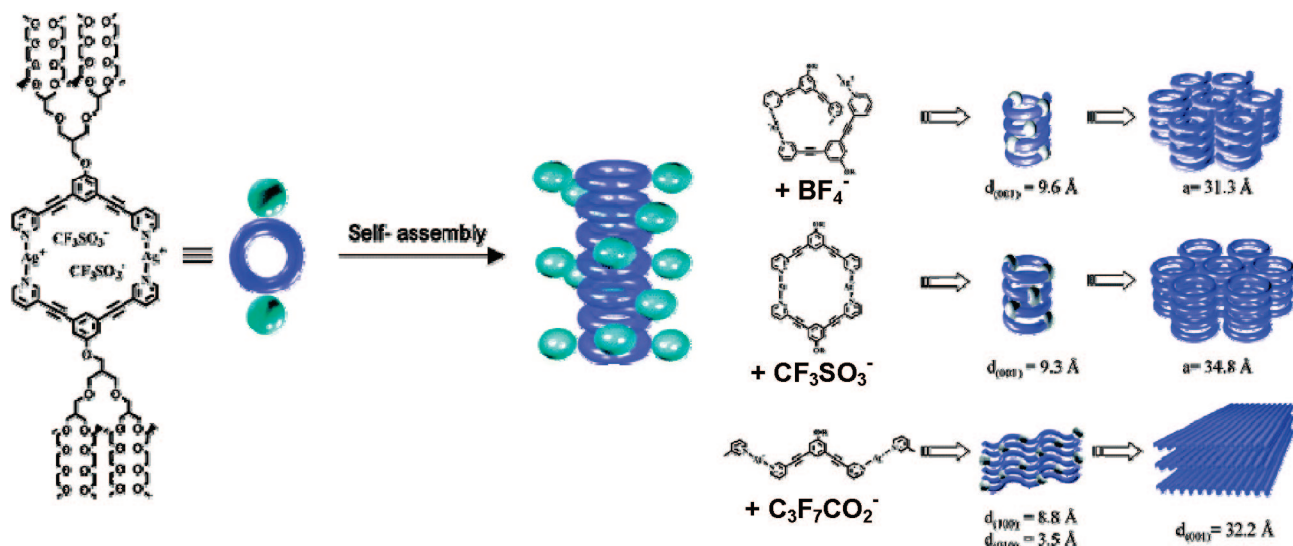
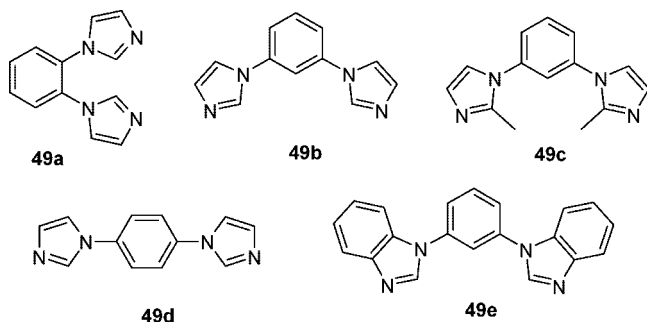


Figure 27. Schematic representation of the self-assembly of **48** with Ag(I) in the presence of different counteranions into secondary structures and subsequent self-organization. Adapted with permission from ref 59. Copyright 2004 American Chemical Society.

Scheme 34



Injection of a larger anion such as $\text{C}_2\text{F}_5\text{CO}_2^-$ also causes a transition from the gel to the sol state, which is completely reversible. In this case, gel breakage occurs because of the morphology change in the secondary structure from a helical coordination templated by the tetrafluoroborate to a lamellar arrangement brought about by a *trans*-like conformation of the ligands around the metal center.

Other compounds that aggregate with Ag(I) are the series of imidazole-appended compounds **49a–49e** (Scheme 34).¹⁷⁵ Upon addition of **49b** and **49e** dissolved in methanol to an aqueous solution of aqueous silver nitrate in a 1:1 ratio to the ligand, transparent gels were formed after a few minutes at room temperature. **49a**, **49c**, and **49f** were not able to produce gels but instead lead to precipitation out of solution. The counteranions of the silver salt had some influence on the gelation, as $\text{AgOSO}_2\text{CF}_3$ drives the formation of the gel, whereas AgBF_4 and AgSbF_6 disrupt it and afford precipitation.

Interestingly, although the ligands themselves are achiral, the aggregation of **49b** and **49e** with Ag(I) lead to chiral structures as determined by CD measurements (c.f. also Figure 28).

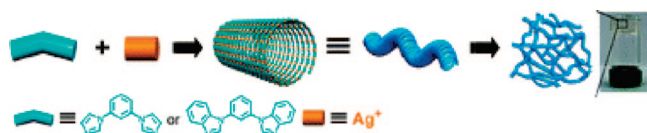
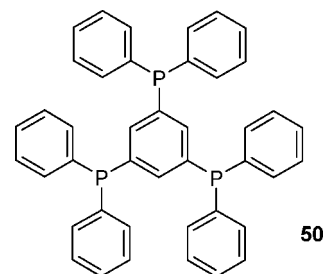


Figure 28. Schematic representation of the self-assembly process of coordination polymer gels from Ag(I) and **49b** and **49e**. Reproduced with permission from ref 175. Copyright 2008 The Royal Society of Chemistry.

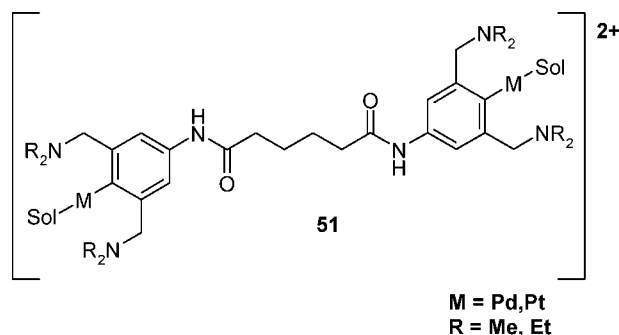
Scheme 35



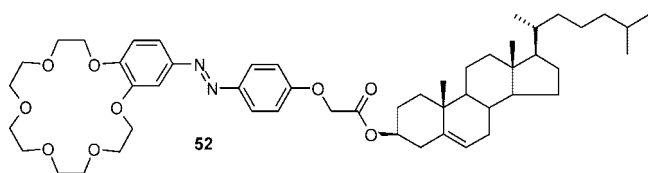
The tripodal phosphine **50** (Scheme 35) also shows affinity to form coordination polymers with silver(I) ions.^{176,177} When immersed in noncoordinating solvents such as a chloroform/nitromethane mixture and with poorly coordinating anions such as SbF_6^- , the phosphine ligand forms a highly viscous aggregate at a 1:1 ratio.¹⁷⁷ This viscous state can be envisioned as an intermediate between discrete complexes with 3:2 and 2:3 silver-to-ligand stoichiometry, which both are nonviscous in solution. While other fluoro anions (PF_6^- and BF_4^-) also produce viscous solutions, silver salts of oxoanions such as AgOTf or AgNO_3 always result in nonviscous systems and addition of these to the gel-like materials turns off the gelation ability.

A slightly more exotic example of rheology tuning is exhibited by the dimetallic pincer complex **51** (Scheme 36,^{178,179} which is unique in the context of this section in that gelation is not induced by a “conventional” metal salt but by an entire complex comprising two metal centers. The pincer unit binds the metal reversibly, but the entire organometallic cation can form labile interactions with other ligands such as pyridine and has been used as a cross-linker to gelate a mixture of poly(4-vinylpyridine) (PVP) in DMSO, linking the pyridyl groups of different polymer strands with each other. The strengths of these aggregates are different depending on the metals used in the cross-linking ligand and with Pd(II) viscous solutions are formed, whereas the Pt(II) analogues give rise to far more rigid gel networks. The mechanical dynamics of the solutions were studied in detail, and it was found that complex ligand exchange events play an important role whereby the systems undergo migration of the cross-links that also involves solvent exchange on the metal centers. In particular, the viscosity of the solutions

Scheme 36



Scheme 37



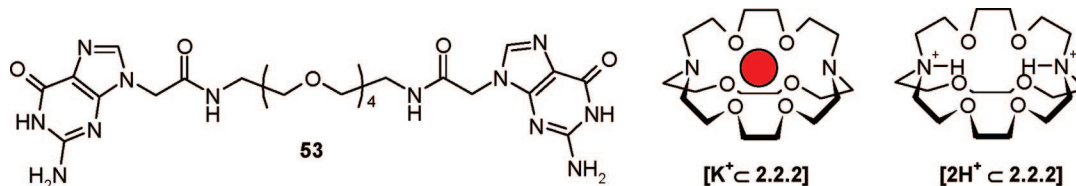
depends more on how frequently cross-links dissociate rather than for how long they became detached. It is hoped that understanding these mechanisms will lead to advances in engineering of materials.

In a recent study, Peng et al. pursued a similar strategy of linking backbone chains of a polymer, this time using iron as the metal instead of a dimetallic complex.¹⁸⁰ Introduction of iron(III) to aqueous poly(acrylic acid) (PAA) results in the formation of a heterogeneous hydrogel by rapid binding of the Fe(III) to the carboxyl groups and cross-linking of the polymer strands. When the metal is injected in the form of a citric acid chelate, the binding rate is slower and a more homogeneous gel is formed. Upon light irradiation, the gels dissolve because of the reduction of Fe(III) to Fe(II), and hence the ability to cross-link via the carboxylates is lost. The process is reversible, and oxidation of iron(II) in the presence of citric acid reestablishes the gel network.

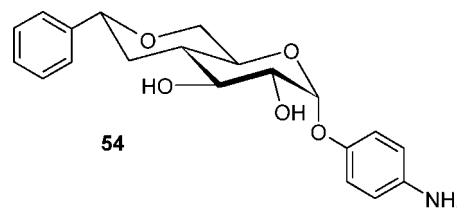
One very early gelator for which cation binding was reported to have an influence on the rheology is the cholesterol derivative **52** (Scheme 37) containing a benzocrown moiety and an azobenzene linker.¹⁸¹ Without any metal binding, this ligand gels a selection of hydrocarbons and alcohols. The gel–sol transition temperature was found to be influenced by the addition of cations, which can bind the crown ether fragment, and in the presence of Li^+ , Na^+ , K^+ , Rb^+ , and NH_4^+ , T_{gel} rises with increasing concentration by up to 20 °C and then gradually decreases. On the other hand, Cs^+ lowers the transition temperature systematically and inhibits gelation completely at higher concentrations. This was thought to be caused by a 1:2 metal-crown sandwich that may disrupt the order in the helical stacking usually observed in these cholesterol systems.

Complexation of a group I metal leading to gel tuning has been reported by Ghoussoub and Lehn, who investigated

Scheme 38



Scheme 39



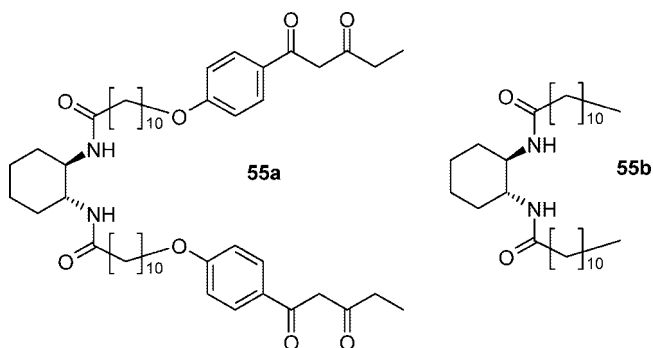
the effect of sequential binding and release of K^+ by a cryptand in the presence of the bis-guanine monomer **53** (Scheme 38).¹⁸²

Compound **53** is a gelator by itself in aqueous media, but introduction of the potassium affords an increase in T_{gel} ; however, for this system, the transition temperature plateaus at high concentrations. The gelation properties of **53** were attributed to the formation of an extended polymeric assembly driven by the formation of hydrogen bonds involving four guanine units organized in a macrocycle stabilized by the K^+ cations (a G-quartet motif). Interestingly, reversible gel–sol interconversion was achieved by the addition of [2.2.2]cryptand, which resulted in loss of the gel network, as a result of the removal of the potassium from the coordination matrix by the cryptand to form $[\text{K}^+ \subset 2.2.2]$. Subsequent addition of HCl leads to a protonation of the cryptand and K^+ release with reformation of the gel. Further acidification and neutralization allows for reversibly tunable gels.

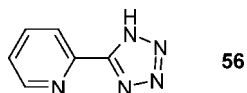
Shinkai et al. have investigated a variety of functionalized sugar-based gelators.¹⁸³ The amine containing ligand **54** (Scheme 39) gels ethanol among other solvents at 3 wt %. Interestingly, the addition of CoCl_2 and CdCl_2 to the gelator stabilizes the ethanol gel at lower concentrations (1% by weight) and increases the critical gelation temperature from -10 to 71 °C and 72 °C, respectively. AgNO_3 also increases T_{gel} but leads to precipitation of a brown solid even when stored in the dark. At lower gelator-to-Co(II) ratios, particles of CoCl_2 were adsorbed to the gel fibers, whereas at higher cobalt concentrations, a homogeneous dispersion of the metal salt into the fibers was observed by TEM. Absorption measurements suggested that the gels contain both **Co(II)·54** and **Co(II)·(54)₂**, where the bridging effect of the latter is likely to lead to gel reinforcement.

Similar effects of gel strengthening by addition of divalent metal ions such as Cu^{2+} , Ni^{2+} , and Co^{2+} were reported for a 1:4 mixture of the alkyl chain appended *trans*-(1*R*,2*R*)-diaminocyclohexane **55a** and its β -diketonato derivative **55b** in methanol (Scheme 40).¹⁸⁴ In these cases, the strengthening process is somewhat more complex and also requires the presence of triethylamine. In this manner, the strength of a nickel(II) containing gel could be increased by about 30% upon the injection of triethylamine and T_{gel} for all metal ions tested could be raised to above the boiling point of methanol. Control experiments show clearly that a mixture of metal and amine is necessary to provide mechanically robust and thermally stable gels.

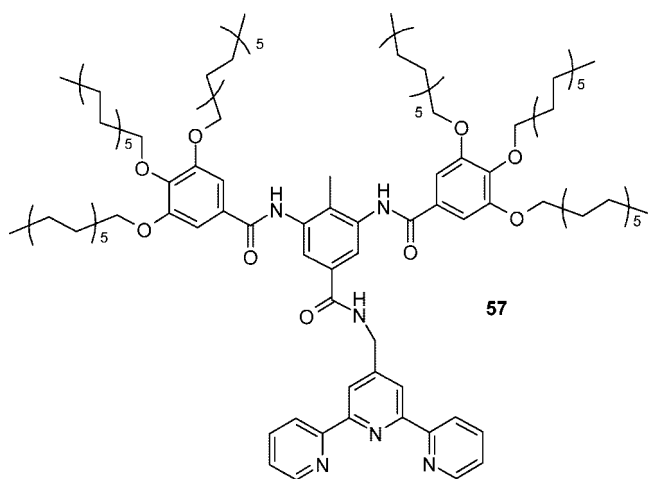
Scheme 40



Scheme 41



Scheme 42



Triethylamine was also found to be essential in the gelation of the tetrazole **56** (Scheme 41) in the presence of LaCl_3 in water.¹⁸⁵ FT-IR spectroscopy provided evidence of the formation of the gel when the complex of La(III) coordinated to the tetrazolate becomes deprotonated by the amine base. Upon the addition of water, this new form becomes entrapped in a 3D network held together by hydrogen bonding.

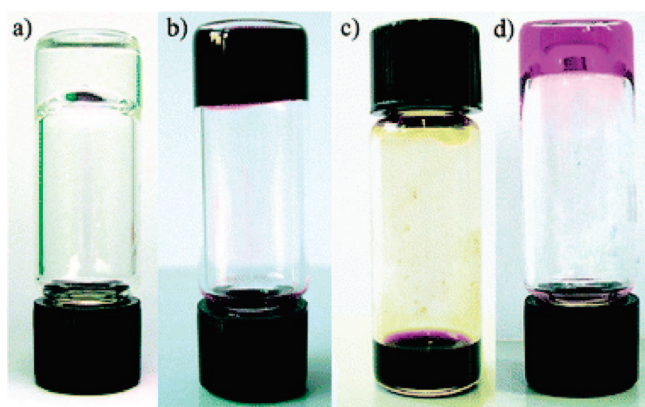
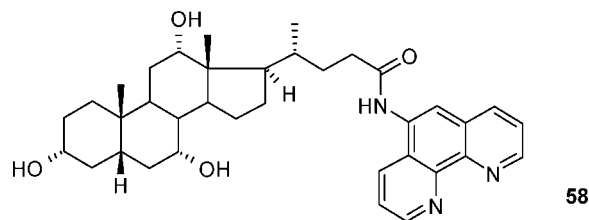


Figure 29. (a) Gelation of cyclohexane by free **57**, (b) of cyclohexane by the $[\text{Fe}(\mathbf{57})_2](\text{ClO}_4)_2$ complex, (c) precipitation of a gel of **57** doped with Fe(II). Reproduced with permission from ref 186. Copyright 2006 The Royal Society of Chemistry (RSC) for the Centre National de la Recherche Scientifique (CNRS) and the RSC.

Scheme 43



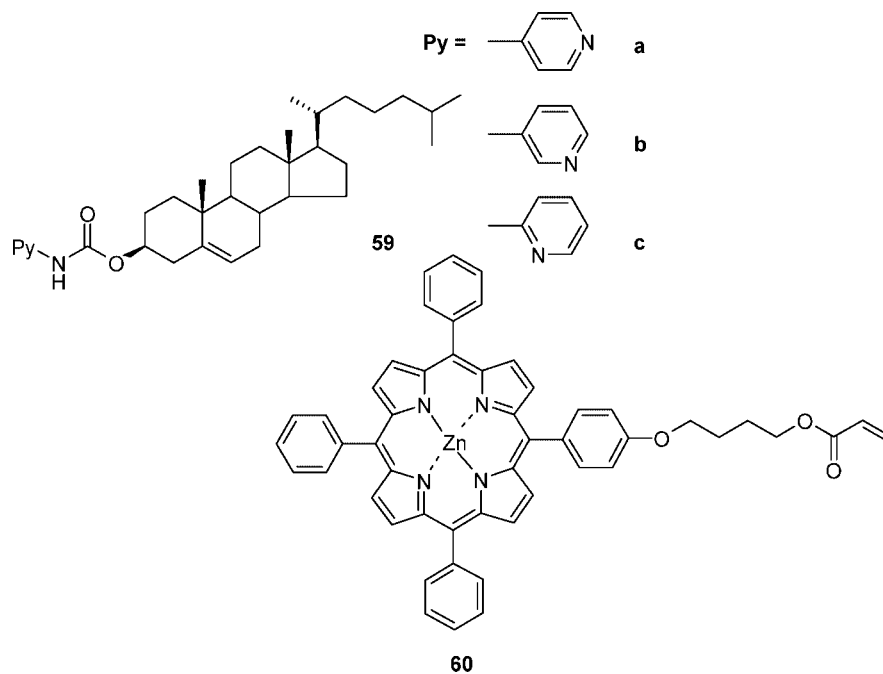
As for the other metal-containing gelators discussed herein, a great majority of tunable gels exploits the binding of metals to nitrogen atoms, mostly in the form of pyridines in some shape or form. The rather elaborate example employed the terpyridine appended 3,5-diacylamino toluene derivative **57** (Scheme 42), and its binding to iron(II) and ruthenium(II) was reported by the group of Ziessel.¹⁸⁶ The free ligand aggregates as a transparent organogel from cyclohexane at 2.6 wt %.

The Fe complex also gels the same solvent at a slightly higher critical gel concentration (3% by weight), whereas the Ru equivalent does not form gel under the same conditions (Figure 29). Both the iron gel and the ruthenium complex exhibit strong coloration stemming from metal-to-ligand charge transfer expected in the presence of terpyridine. All organogels in this system are thermoreversible and showed a tight hydrogen-bonding network involving the amide groups by FT-IR spectroscopy. The failure of the ruthenium derivative to form stable gels might be related to the chloride counterions, which could be responsible for interfering with the hydrogen bonding. A small amount of $\text{Fe}(\text{ClO}_4)_2$ in solution layered on top of a gel of free **57** led to absorption of the metal cation accompanied by the characteristic color of the complex developing inside the gel. Sprinkling an excess of the metal salt on the gel resulted in complete breakage of the assembly over a few days. Previously to this work, the same group had reported a closely related system with a phenanthroline moiety, which gelled as the free ligand but whose gelling ability was switched off by complexing to copper(I) due to disruption of the hydrogen-bonding network formed by the amide groups.¹⁸⁷

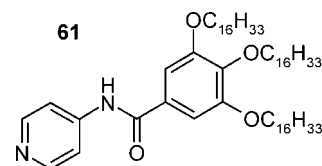
Earlier, we described the introduction of cholesterol fragments in molecules in a strategy to form aromatic-linker-steroid-type gelators. The following systems also make use of this design, employing pyridines or oligopyridines as the aromatic moiety, as in, for example, the phenanthroline containing ligand **58** (Scheme 43).¹⁸⁸ On its own, this gelator rigidifies a 1:1 MeOH–water mixture in a concentration range from 0.1 to 1.5% by weight driven mainly by the expected hydrogen bonding. Compound **58** can also undergo complexation in a 2:1 ratio with zinc(II), thus changing the gelation abilities where higher concentrations are needed to afford gel assembly. These aggregates tend to break down over time to low-viscosity liquids but can reversibly reform after short heating to 70 °C and subsequent cooling.

Gelators **59a–c** (Scheme 44) are a somewhat simpler analogue of **58** involving a pyridine containing cholesterol and result in the formation of a tunable gel with silver(I) ions.¹⁸⁹ Of the three ligands, **59a** is the most effective, gelling 16 out of 19 solvents tested, while **59b** and **59c** are markedly less successful in doing so. One possible explanation might arise from the helical stacking associated with the cholesterol group (c.f. Figure 6). The inherent dipole in the peripheral pyridines might then be most favorably aligned in the

Scheme 44



Scheme 45



4-pyridyl moiety. Ligands **59a–c** were treated with a wide range of divalent metal ions, but only the addition of AgOTf was found to have an effect on the gelling behavior, enhancing the gel–sol transition temperature for **59b** but suppressing it for the two others in diphenyl ether.

A morphology change was observed by SEM where rodlike clusters of free **59b** are present in a benzene gel, but upon the addition of AgOTf, a fibrillar aggregate was formed (Figure 30). More recent work describes gels of **59a** that were layered with a solution of the zinc porphyrin **60**, containing cross-polymerizable peripheral groups.¹⁰⁴ The porphyrin diffuses into the gel phase, thereby forming a violet complex arising from decorating the zinc center with the pyridyl groups of the gelator. After polymerization of the acryloyl end groups and removing the gelator with chloroform washing, the fibrous morphology of the gel network was retained.

Silver(I) has also been reported to assist gelation in complexes with the pyridyl containing 3,4,5-tris(alkyloxy)benzoic amide **61** (Scheme 45).⁵⁵ The free ligand cannot self-organize into gel aggregates, and it was anticipated that complexation to a linear or planar aggregate would result in a more symmetrical structure and enhanced hydrogen bonding to afford efficient aggregation. Indeed, addition of AgSO₃CF₃ in a 1:2 molar ratio yields the formation of a complex gel in a 10/1 (v/v) toluene/ethanol mixture. Other metal ions such as Co²⁺ and Cu²⁺ were also shown to coordinate to **61**, but interestingly, no gels form, meaning

that the gelation process is selective to the type of metal added. FT-IR and XRD data suggest that the linear structure found in silver complexes is essential for successful gelation, and the nonlinear complexes of cobalt and copper prevent further fibrous assemblies from forming. It was proposed that two ligands of **61** are linearly connected by a two-coordinate silver(I) ion in a symmetric fashion and further self-assemble into a primary fibril structure assisted by hydrogen bonding through the amide group. Van der Waals interactions are responsible for the secondary beltlike fibers, which in turn weave into the 3D gel network (Figure 31a). The silver gels were found to be reversibly tunable by the addition of potassium halide salts, upon which the gels break down and silver halide is formed. When this precipitate is removed, the gel reforms after addition of excess silver ions. Similar effects were observed for certain gases such as H₂S and NH₃, which break down the gel. Again, excess silver repairs the gel network (Figure 31b).

A variety of organogels based on tripodal cyclotrivenyrylene (CTV) and 1,3,5-trisubstituted benzene-type ligands has been reported recently by Hardie et al.¹⁹⁰ We focus on the gelators **62–64**, as these formed metallogels, although a series of other related compounds was also reported. Compound **62** formed gels with CuCl₂ and AgSbF₆ in DMF and DMSO, respectively. In the presence of CuBr₂, ligand **63** gels acetonitrile. Copper bromide also gels chloroform and nitromethane with **64** (Scheme 46). All these gels show dependence on the ligand-to-metal ratio, and only 3:1 stoichiometries resulted in gelation. Lower concentrations of the salts result in precipitation. While the xerogels of the copper complexes of **62** were found to contain a 3:1 metal–ligand ratio, in all other gels, elemental analysis is

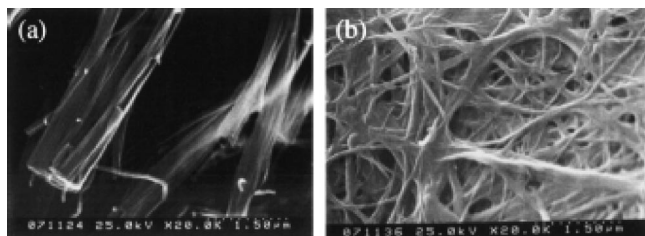


Figure 30. Silver(I) triflate induced change in xerogel morphology in **59b**. Reproduced with permission from ref 189. Copyright 2003 The Chemical Society of Japan.

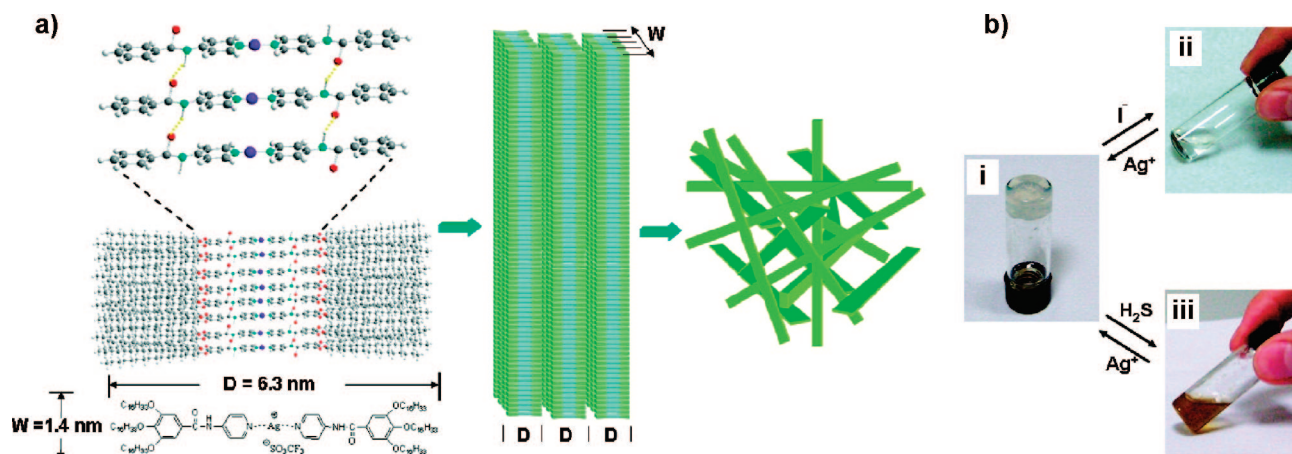
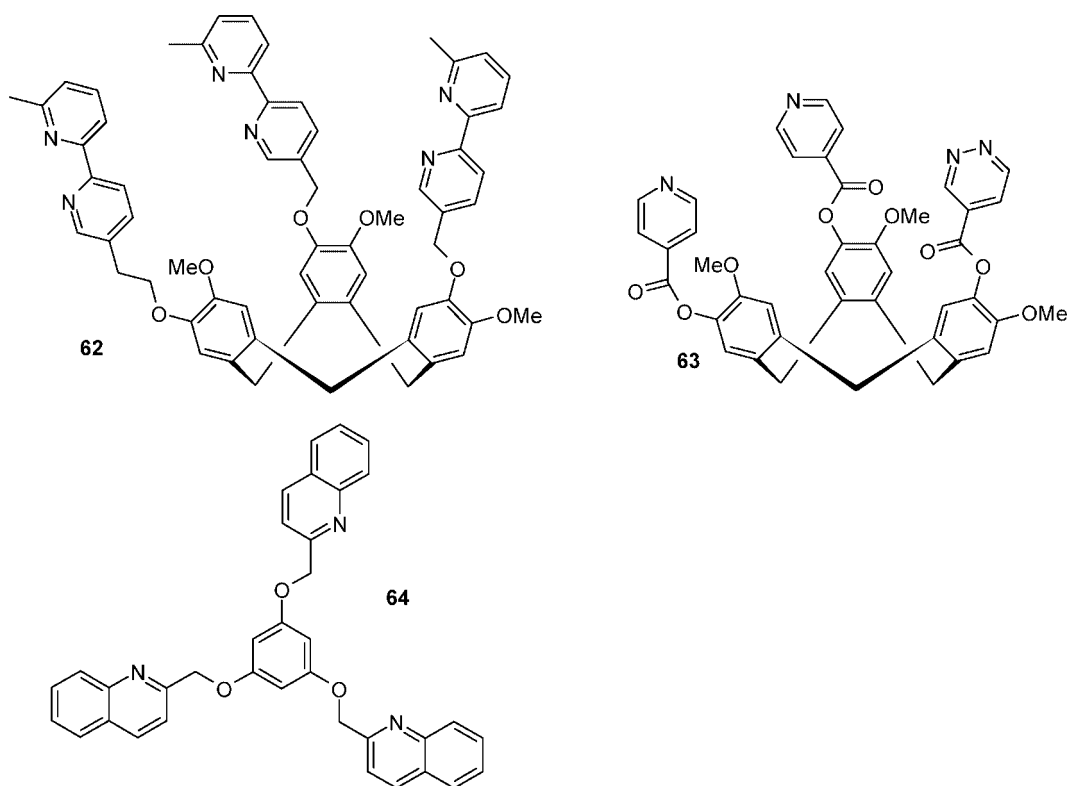


Figure 31. (a) Hierarchical structure model for $\text{Ag}(\mathbf{61})_2$ complex showing from left to right 1D molecular stacking along the direction of the hydrogen bonds as the primary gel structure, aggregation of beltlike fibers through van der Waals interactions in the secondary structure, and 3D network by interweaved fibers in the tertiary structure of the gel. (b) Reversible gel-to-sol transition of the Ag complex gel (i) to the addition of potassium iodide and hydrogen sulfate gas. Reproduced with permission from ref 55. Copyright 2007 American Chemical Society.

Scheme 46



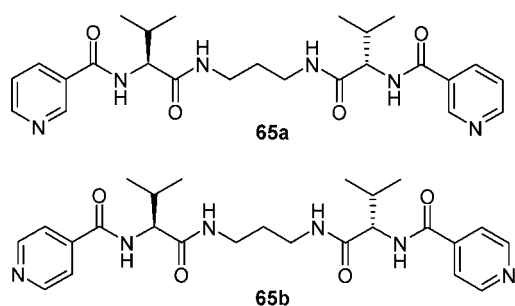
more consistent with the formation of 2:1 metal–ligand complexes. This fact may indicate that, although π – π stacking might play a role in fiber formation, coordination polymerization is probable in these systems. An X-ray crystal structure of $[\text{Ag}_2(\mathbf{64})_2](\text{NO}_3)_2$ supports the presence of π – π interactions in this type of metallogel. Gels based on the CTV ligands break up irreversibly under mechanical stress, whereas the chloroform gel of **64** is mechanoreversible at higher concentrations of the ligand and its nitromethane gel shows partial reformation.

The dipyrindine ligands **65** (Scheme 47) incorporate amide linkages and form pH-responsive gels when a solution of them in aqueous HCl is exposed to ammonia vapor.¹⁹¹ They also gel a range of organic solvents with hydrogen bonding as a driving force in the fiber creation. A layer of $\text{Pd}(\text{AcO})_2$

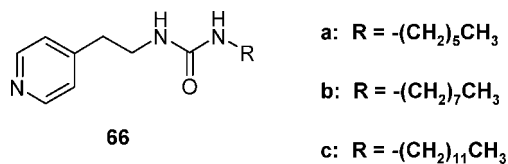
in toluene was layered on top and the gels were allowed to diffuse into them overnight. This resulted in orange coloration of the gel phase, and TEM suggested that palladium had indeed been incorporated into the fibrils. Interestingly, attempts to complex the ligands to Pd(II) outside the gel phase were unsuccessful and led to decomposition to palladium black. The metal-doped gels were found to act as an effective catalyst in the aerobic oxidation of benzyl alcohol with about 10 turnovers. This indicates some deactivation process, although the palladium inside the gel was stable toward decomposition.

Other pyridine containing gelators such as the monoureia derivatives **66** (Scheme 48) have been studied by Arai et al.¹⁹² While not able to form any gels as the free ligands, 2:1 complexes with $\text{AgC}_2\text{F}_5\text{CO}_2$ were effective gelators for

Scheme 47



Scheme 48



a number of solvents such as *p*-xylene, tetralin, and benzene. In these systems, the urea group seemed to play a crucial role in the gelation process as an amide analogue of these ligands failed to form gels with or without silver under the same conditions.

A combination of potential metal and anion-binding sites in the same gelator molecules was explored by our group based on the design of bridging two pyridyl end groups with a linker containing a bis(urea) functionality to yield compounds **67–70** (Scheme 49).¹⁹³ Of the free ligands, **69** was the only one to gel a 1:1 chloroform/MeOH mixture. Compound **68**, although not an effective gelator in its free form, was found to rigidify 2:1 THF/water solvent systems in the presence of AgBF_4 . By changing the anion to nitrate

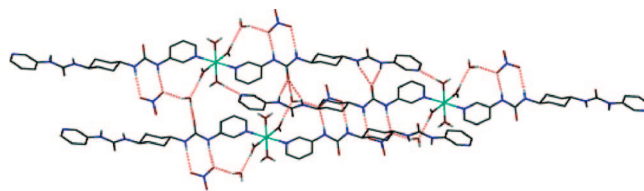


Figure 33. X-ray crystal structure of $[\text{Co}(\mathbf{67})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ showing the hydrogen-bond interactions. CH hydrogen atoms are omitted for clarity. Reproduced with permission from ref 193. Copyright 2005 The Royal Society of Chemistry.

again, gelation is inhibited, and in MeCN and chloroform, a crystalline product of the formula $[\{\text{Ag}(\mathbf{68})(\text{MeCN})\}_2](\text{NO}_3)_2 \cdot 2\text{CHCl}_3 \cdot 1.5\text{H}_2\text{O}$ was obtained. The crystal structure of this complex (Figure 32a) allowed insight into possible aggregation modes that might occur in the organization of gel fibers of related metal complexes by the formation of polar stacks in the solid state (Figure 32b).

The nitrate anions were found to be involved in hydrogen bonding to the urea groups between different complexes. It is possible that stronger urea–anion hydrogen bonding might lead to crystallization, while weaker interactions with tetrafluoroborate might result in gel formation due to better solubility.

Metal coordination also afforded gelation in **67** in the presence of copper(II) nitrate while cobalt(II) nitrate prompted the formation of yet another crystalline product of 2:1 ligand/metal stoichiometry with hydrogen-bonding interactions between ureas and anions (Figure 33).

In a recent study, we observed interesting behavior of ligand **70** with CuCl_2 .¹⁹⁴ The gelation ability in MeOH was found to depend on the concentration of the copper(II) salt, with blue translucent gels being formed at up to 0.5 equiv

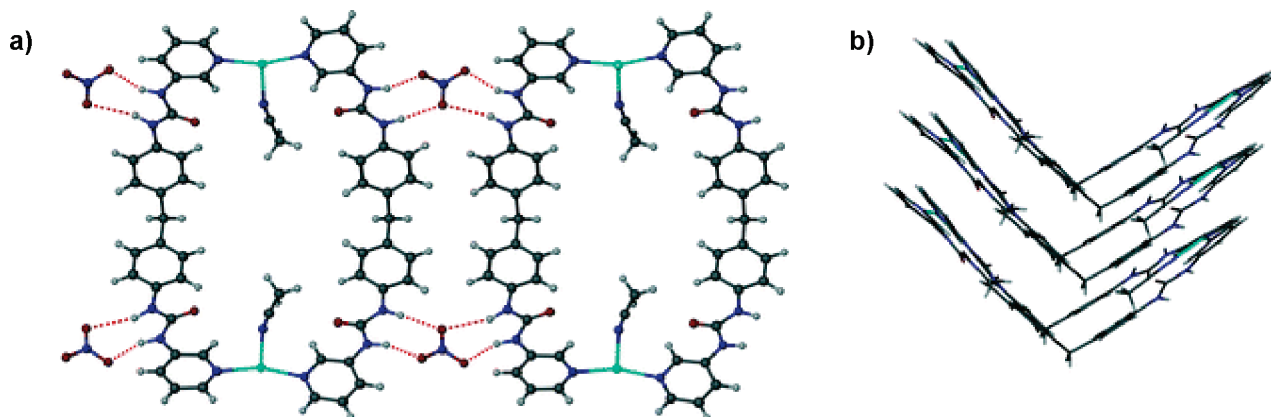
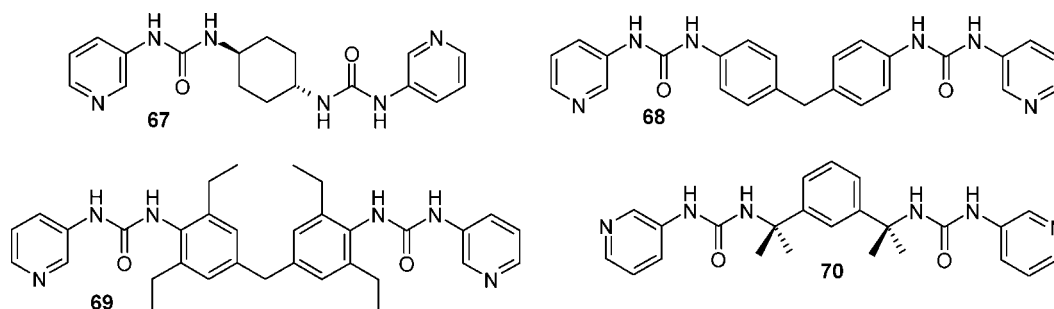


Figure 32. (a) X-ray structure of the metallomacrocycle $[\{\text{Ag}(\mathbf{68})(\text{MeCN})_2\}_2](\text{NO}_3)_2$. Each chain interacts with its neighbor via $\text{NH} \cdots \text{anion}$ hydrogen bonds. (b) Polar π -stacked chains of the macrocycles: Ag (cyan), O (red), N (blue), C (gray), and H (light gray). Reproduced with permission from ref 193. Copyright 2005 The Royal Society of Chemistry.

Scheme 49



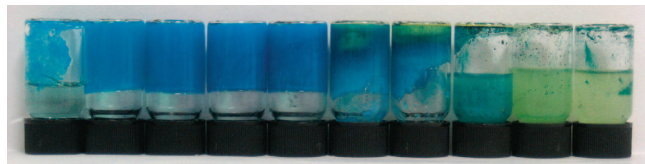


Figure 34. CuCl_2 metallogels of ligand **70** (1 wt %) in MeOH using (from left to right) 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 equiv of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Reproduced with permission from ref 194. Copyright 2009 American Chemical Society.

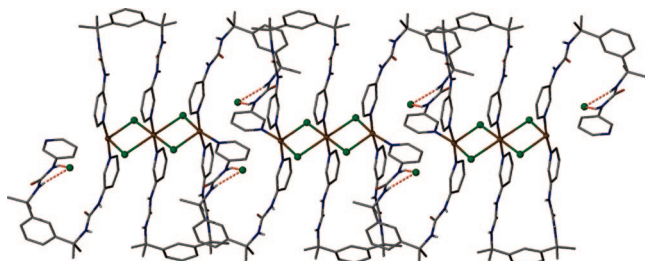
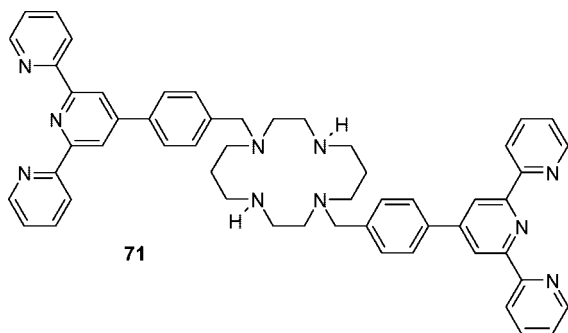


Figure 35. X-ray crystal structure of $[\text{Cu}_3(\mathbf{67})_4\text{Cl}_4]\text{Cl}_2 \cdot n\text{H}_2\text{O}$ (**2**) obtained from a 1:1 solution of **70** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in MeOH/ H_2O 7:3 extended coordination polymer structure. Reproduced with permission from ref 194. Copyright 2009 American Chemical Society.

Scheme 50



added and the formation of a green precipitate at higher concentrations (Figure 34).

At 1 equiv of the copper chloride, blue crystals were obtained and found to be formed by a coordination polymer structure of a 3:4 copper/**70** stoichiometry (Figure 35). Although no crystals could be isolated, it was possible to show by FT-IR and magic-angle spinning (MAS) NMR spectroscopy that the gel phases represent an intermediate state between the free ligand and the observed coordination polymer.

Rheology tuning with anions was also tested for these gels. The flow behavior was measured in situ during gel formation and found to be complex, with G' going through a local maximum for the pure metallogel in the early stages of gelation and then increasing dramatically after several hours. Different anions such as chloride or acetate can influence the appearance of the maximum and the strength of the final gel. These results are thought to be promising for chemical gel tuning in these versatile systems.

The polytopic bisterpyridinecyclam ligand **71** (Scheme 50), recently studied by the group of Terech, is another example of a compound that does not gel by itself but whose gelation can be induced by transition metal ions such as cobalt(II) and nickel(II).¹⁹⁵ These gels show sensitivity toward chemical, mechanical, and electrochemical stimuli. Depending on

the solvent system, different counteranions of the metal salt were found to afford spontaneous gelation, such as BF_4^- in benzonitrile, NO_3^- in acetonitrile/THF, and Cl^- in DMF (c.f. Figure 36a). Gelation could also be induced in MeOH/THF mixtures by ether diffusion or ion exchange, whereby only nitrate and chloride caused the mixture to gel. Furthermore, in DMF gels, precipitates or solutions of varying colors and viscosities could be obtained by adding CoCl_2 , NiCl_2 , and CuCl_2 in different orders to the ligand.

Viscosimetry experiments on **71** and terpyridine and cyclam reference compounds highlighted the crucial role of the incorporation of the metal ions in the cyclam unit, and for cobalt(II) and nickel(II), the data were consistent by formation of a $\text{M}^{\text{II}}(\text{terpy})_2$ species at 1 equiv added and the 2nd equiv of the metal ions attaching to the cyclam moiety. The cobalt gel in DMF was also found to undergo redox-controlled gel-to-liquid transition (Figure 36b).

Finally, heavy metals have been demonstrated to induce gelation in the polysaccharide sacran, which had been extracted from the jellylike extracellular matrix of the cyanobacterium *aphanothece sacrum*.¹⁹⁶ In a series of experiments, sacran solutions were dropped into a wide range of divalent and trivalent metal ions in solution upon which the formation of gel beads were observed (Figure 37). It was found that the polysaccharide had the strongest affinity for gel formation for trivalent metals such as indium and lanthanoids.

The mechanism of gelation was proposed to involve a nematic liquid crystalline state of the sacran chains, which electrostatically adsorb the metal ions leading to the emergence of a core-shell structure with a sol core being surrounded by a gel shell. It is envisioned that these result might be exploited in the recovery of valuable metals.

5.3. Salts as Gels and Tuning Agents

There are a remarkable number of LMWG that are salts. Of these compounds, there are the important examples that contain metals as the cationic species, e.g., Na^+ , Al^{3+} and Ca^{2+} .^{1,5,9,17,27,28,36,42,154,161,197–217} In this section, we focus on the use of these metals to tune and induce gelation. Good illustrations of the use of LMWG salts include industrially important compounds like the Li^+ salt of 12-hydroxyoctadecanoic acid²¹⁸ and the gelators (most of which are hydrogelators) based on fatty acids and their derivatives that have been used in biological situations.^{197–199} Often amino acid based gelators with carboxylic acid functionalities only gel as the appropriate salt, leading to tuning capabilities. This tuning of the gel properties has led to pH reversible gels in many cases, an important means of tuning the gelation properties of certain materials.^{27,28,202,203,205,208,213,215,217,219–229}

There have been some excellent examples of the use of specific metals and/or their salts to tune gel properties, and specific examples are given below.

Variation of the metal ion in a salt LMWG can be used to tune a gel.^{203,210} In the case of compound **72** (Scheme 51), a gel is formed when NaOH is added to a DMSO mixture. KOH and RbOH still give gels, but these gels are less stable. In the cases of LiOH, NH_4^+OH^- , and tetrabutylammonium hydroxide (TBA^+OH^-), no gels were formed, showing how important the metal is for the production of a gel.²⁰³ A similar trend was shown by compound **73** (Scheme 52), which gelled with Na^+ and Rb^+ (once again a weak gel) but not with Li^+ and K^+ .²¹⁰ The importance of the Na^+ to gelation is cleverly

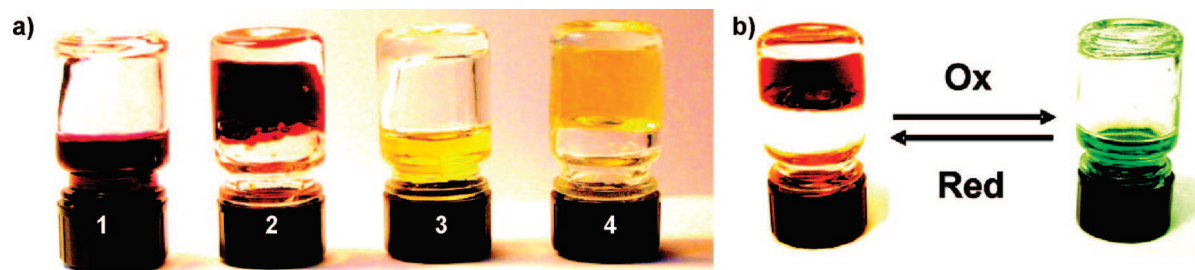


Figure 36. (a) Spontaneous gelation of **71** in acetonitrile using (1) CoCl_2 , (2) $\text{Co}(\text{NO}_3)_2$, (3) NiCl_2 , and (4) $\text{Ni}(\text{NO}_3)_2$. (b) Redox-controlled reversible gel-to-liquid transition with $\text{Co}_2(\mathbf{71})$ in DMF. Adapted with permission from ref 195. Copyright 2009 American Chemical Society.

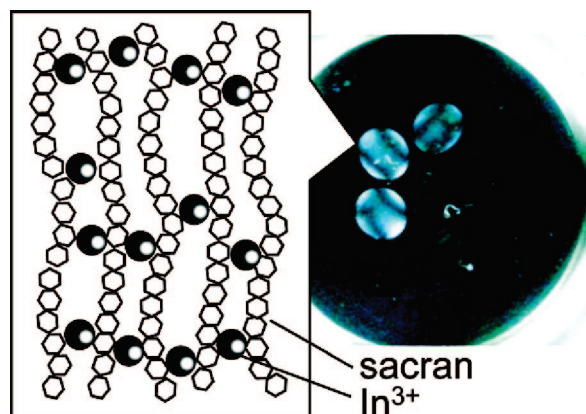
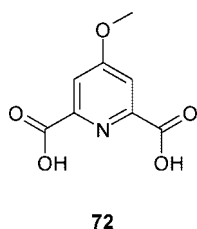


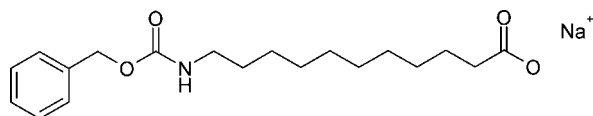
Figure 37. Image of gel bead formation by addition of a sacran solution to an indium trichloride aqueous solution and schematic representation of the network formed by adsorption of metals ions onto the sacran chains. Reproduced with permission from ref 196. Copyright 2009 American Chemical Society.

Scheme 51



72

Scheme 52



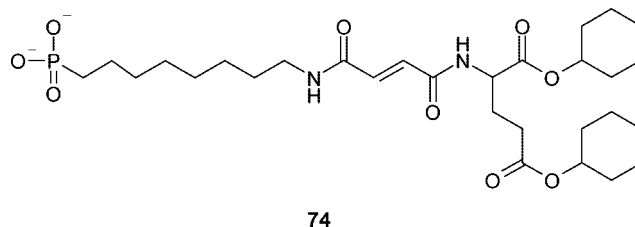
73

shown by the addition of Kryptofix [211], which selectively binds to Na^+ , preventing the gelation of a hot solution.

Ca^{2+} ions are very important physiologically and have been used, therefore, in testing gelation of some hydrogels.^{211–213} Hamachi and co-workers synthesized the excellent hydrogelator compound **74** (Scheme 53).²¹³ One of the chemical stimuli allowing for formation of the gel state was found to be Ca^{2+} (Figure 38). The reversibility of gelation can be accomplished by using EDTA (or OH^-) to bind the Ca^{2+} , and the authors cleverly use this process to release model drugs from the gel state.

Messersmith et al. cleverly use light and/or temperature-induced release of Ca^{2+} from loaded liposomes to induce gelation of a short peptide, compound **75**.²¹¹ **75** by itself is

Scheme 53



74

highly soluble in pure water, but in the presence of mM concentrations of NaCl , KCl , or CaCl_2 , a gel is formed. The authors show how they trap Ca^{2+} within liposomes that can be broken down by light or heat, and when a solution of **75** and the liposomes is stimulated, a gel results (Figure 39).

The type of metal cation within a LMWG can also have an affect on the morphology and kinetics of gelation of a gel. With compound **76** (Scheme 54), the cationic species has a drastic influence on the gel formed.²⁰² The presence of the salts NaCl , KCl , CaCl_2 , or MgCl_2 at 1 mM concentrations in water causes **76** to gel at a different rate and forms of morphology. NaCl slows the gelation period from instantaneously in pure water to approximately 7 min, and the morphology changes from spongy globules to aggregated spheres (Figure 40). KCl slows the gel formation down a little more, and a wrinkled cloth morphology results. MgCl_2 and CaCl_2 slow the gelation down to 15 min and a fused globules morphology results. The use of BaCl_2 results in precipitation and no gelation. These results clearly show how a gel can be tuned by the metal species.

6. Anion Binding by Gels and Gelators

The exploitation of metallic species in gels to tune their properties has an intuitive opposite. The principle of using anions in the tuning of gel properties is developing into a recognizable subfield.^{135,230} The principles of anion recognition are fairly well understood.^{231–235} Numerous host designs have been produced and significantly a large number use hydrogen-bonding functionalities to bind to the anions. The commonality of hydrogen bonding in anion-binding studies and in the self-association processes that result in gel formation by LMWG has influenced some research groups to begin investigations into the behavior of anions in gels. An example of this concept is the anion tuning of gelation by compound **77** (Scheme 55).²³⁶

Compound **77** contains the preorganizing triethyl benzene core^{237,238} and multiple urea-derived anion-binding moieties.²³⁶ As a LMWG, **77** forms gels in polar solvents such as acetone (critical gelation concentration, CGC 1.5 wt %), methanol (CGC 2.0 wt %), and tetrahydrofuran (CGC 5 wt %)

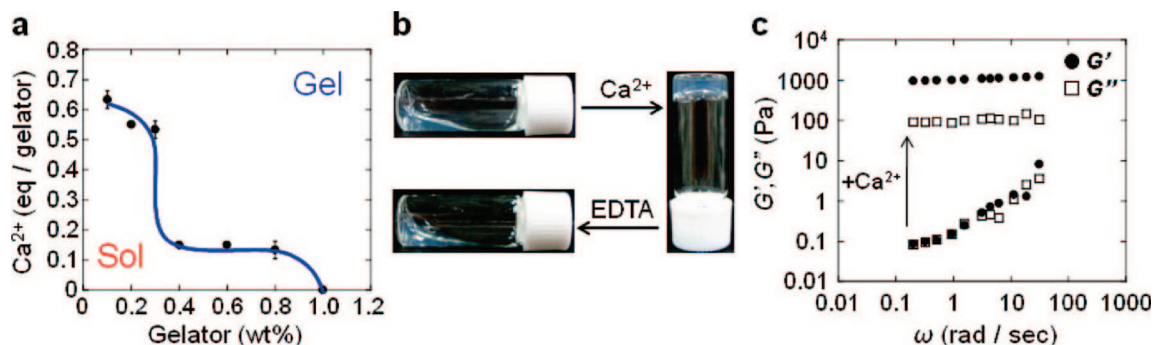


Figure 38. Ca^{2+} responsiveness of hydrogelator **74**. (a) Phase diagram of the gel–sol transition, revealing the number of equivalents of Ca^{2+} required to induce gelation at each gelator concentration. (b) Photographs of the Ca^{2+} -induced sol-to-gel transition ($[\mathbf{74}] = 0.30$ wt %; $[\text{Ca}^{2+}]/[\mathbf{74}] = 1.0$; $[\text{Na}_2\text{EDTA}]/[\text{Ca}^{2+}] = 10$). (c) Corresponding dynamic viscoelastic properties before and after the addition of Ca^{2+} . Reproduced with permission from ref 213. Copyright 2009 American Chemical Society.

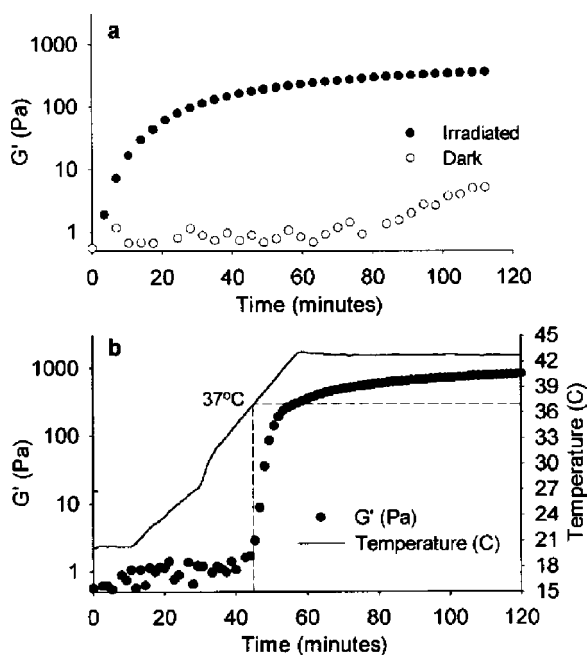
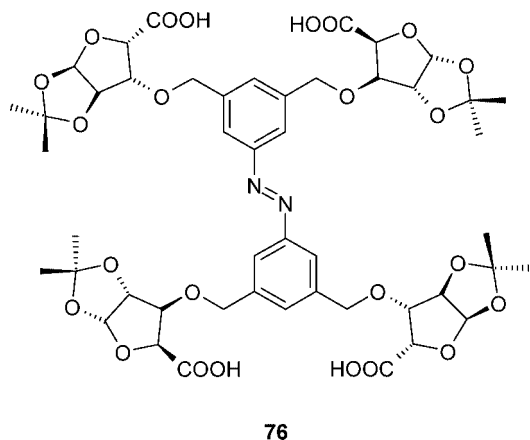


Figure 39. Rheological detection of (a) light- and (b) temperature-triggered gelation of **75**/liposome precursor fluid (12 vol % CaCl_2 -loaded liposomes in a sucrose solution of **75** (30 mg/mL)). Reproduced with permission from ref 211. Copyright 2001 American Chemical Society.

Scheme 54



%) upon brief sonication of the solution. The acetone gels of **77** respond to chemical stimuli in the form of anions, resulting in homogeneous solutions (Figure 34). The anion is added as a tetrabutylammonium salt, with the cation being

chosen for its inert properties. There is a linear correlation between the binding constants for the formation of the 3:1 complex ($\log \beta_{13}$) determined using standard solution nuclear magnetic resonance (NMR) spectroscopic titration experiments and the minimum amount of anion required for the complete gel–sol transition (indeed the very weakly bound BF_4^- does not influence the gel properties of **77** at all). The entire process is reversible and repeatable and can also be used as a means to sense or identify fluoride. Reversibility of the dissolution of the gel is demonstrated by addition of the Lewis acid $\text{BF}_3 \cdot \text{OEt}_2$ to a solution of **77** containing tetrabutylammonium fluoride (TBA^+F^-). This reverses the effect of the fluoride anion and a gel reforms upon sonication, whereas the same is not observed for the other anions. However, ZnBr_2 acts as a nonspecific chemical stimulus for regelation by binding to the added anions much more strongly than **77** (Figure 41).

Another example of the influence of anion binding on gel formation is the bis(urea) functionalized binaphthalene derived compound, **78** (Scheme 56).²³⁹ This study, primarily based around the circular dichroism (CD) of **78**, shows that the gel in cyclohexane ($\text{CGC} = 6$ mg/mL) can be destroyed by the addition of TBA^+F^- .

Maeda et al. have produced some notable results working with the anion binding and gel formation of C_3 -bridged oligopyrroles.^{51,240} A long alkyl substituted derivative of the C_3 -bridged oligopyrroles, **79**, affords a transparent emissive gel in hydrocarbon solvents such as octane ($\text{CGC} = 10$ mg/mL) (Scheme 57).

The addition of anions causes the gel to break down. This is exemplified by the break down of a **79c** gel in octane upon the addition of 10 equiv of solid TBA^+Cl^- to the upper surface of the gel, resulting in the gel becoming a solution. Additionally both the UV–vis spectra and the fluorescence are notably changed (Figure 42). The addition of different solid TBA^+ salts shows how the rate of breakdown is dependent on the anion (time required for F^- is minutes, Cl^- is 2 h, and CH_3CO_2^- is 3 h, and Ph_4B^- does not perturb the gel).

The phenomenon of gelation can be described as a form of arrested or partial crystallization.⁵ In this context, the hydrogels of **80** (Scheme 58) show an interesting transformation from gel to crystalline material when exposed to NaCl .⁵³ As Cl^- binds to **80** ($K_{11} = 1114 \text{ M}^{-1}$ by NMR spectroscopic titration), chloride complexation inhibits fiber growth along the fiber axis (and long axis of the needle-shaped crystal), allowing growth in the other two dimensions.

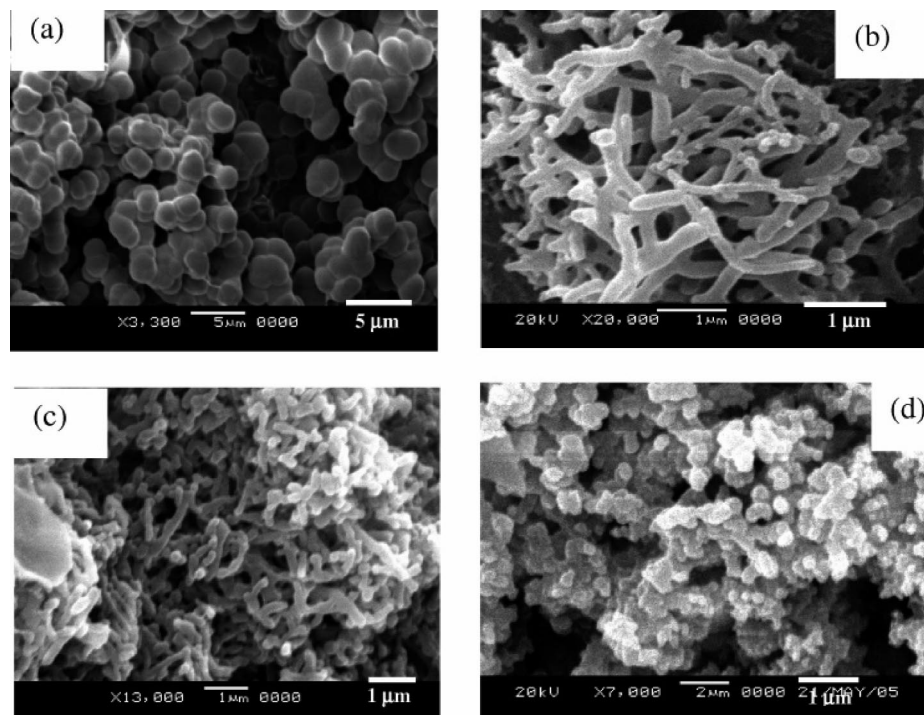
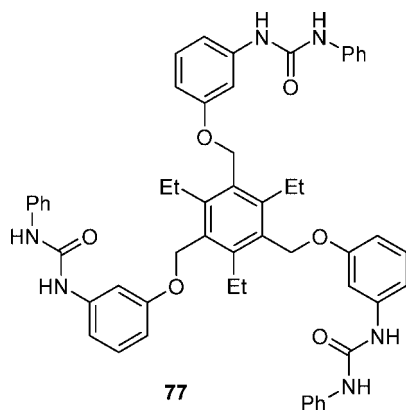


Figure 40. SEM images showing morphology of xerogels of **76** in (a) water—spongy globules (gel forms instantaneously), (b) 1 mM CaCl₂ fused globules (gel takes 15 min to form), (c) 1 mM MgCl₂ fused globules (gel takes 15 min to form), and (d) 1 mM NaCl aggregated spheres (gel takes 7 min to form). Reproduced with permission from ref 202. Copyright 2005 American Chemical Society.

Scheme 55



The strong binding of F⁻ by anion-binding hosts has its origin in the high basicity of the anion, although this can result in the deprotonation of the hydrogen-bonding moiety in some hosts. Because of the strong binding of F⁻ by hydrogen-bonding hosts, there have been a number of studies on how F⁻ affects gel formation by LMWG and the use of F⁻ as a chemical switch. A good example is the behavior of the family of compounds **81** (Scheme 59).²⁴¹

These compounds gel a variety of solvents with the R = C₁₂H₂₅ compound (**81b**) showing the greater versatility. Addition of TBA⁺F⁻ to the 1,4-dioxane **81b** gel resulted in a transition from a gel to a solution state. This process is reversed by the addition of trifluoroacetic acid (TFA). The details of these processes were probed using fluorescence spectroscopy. The photoluminescence intensity of **81b** in the gel state (λ = 433 nm) is greatly increased in comparison to that in solution (λ = 359, 376, and 396 nm) and can be attributed to the phenomenon of aggregation-induced enhanced emission. The **81b**·F⁻ aggregate in solution shows an emission band centered at 450 nm. With the addition of increasing amounts of TBA⁺F⁻ to an **81b** gel, there is a

subsequent decrease in the band at 433 nm observed for the gel and an increase in the band observed for the **81b**·F⁻ complex. Interestingly, in the solution state, **81b** that has been exposed first to TBA⁺F⁻ and then TFA has a similar emission spectrum to that of the starting **81b**; however, the reformed gel after addition of TBA⁺F⁻ and then TFA surprisingly has an emission band that is 70 nm blue-shifted. This change in the gel character (compared to the gel before addition of fluoride and TFA) is also manifest in the morphology, as shown by the scanning electron micrograph (SEM) images of the dried gels. This result highlights the continued difficulty of assigning gel structure. Are these two gels the same when it comes to content (pure **81b**), or is the new gel made of an **81b**·F⁻·H⁺ aggregate (as the authors suggest)? Indeed is the new gel some type of morphological “polymorph”?^{69,198}

An example where the gel is influenced by the interaction between the gelator in the gel state and F⁻ was reported by Žinić, Mandolini, and Cametti et al.²⁴² Working with oxalamide-derived anthraquinone compounds, they showed that compound **82** (Scheme 60) forms gels in a variety of solvents and that the properties of these gels can be tuned using anions. In *p*-xylene gels, the addition of TBA⁺F⁻ (10 equiv) causes the gel to break down and form a reddish solution. The change in color and prevention of gelation is caused by the basic F⁻ interacting with (possibly deprotonating) the NH group closest to the anthraquinone moiety in **82** (Figure 36). This effect can be prevented when the solvent used in the gel is changed. An ethanol gel does not change to a solution upon addition of TBA⁺F⁻ (10 equiv) because the fluoride is better solvated by the more polar protic solvent and, therefore, the anion cannot compete with the NH interactions that allow gelation to occur. Addition of a concentrated TBA⁺F⁻ *p*-xylene solution on top of the gel results in a gradual breakdown of the gel over 4 h (Figure 43). The fluoride ion is the only anion that behaves this way

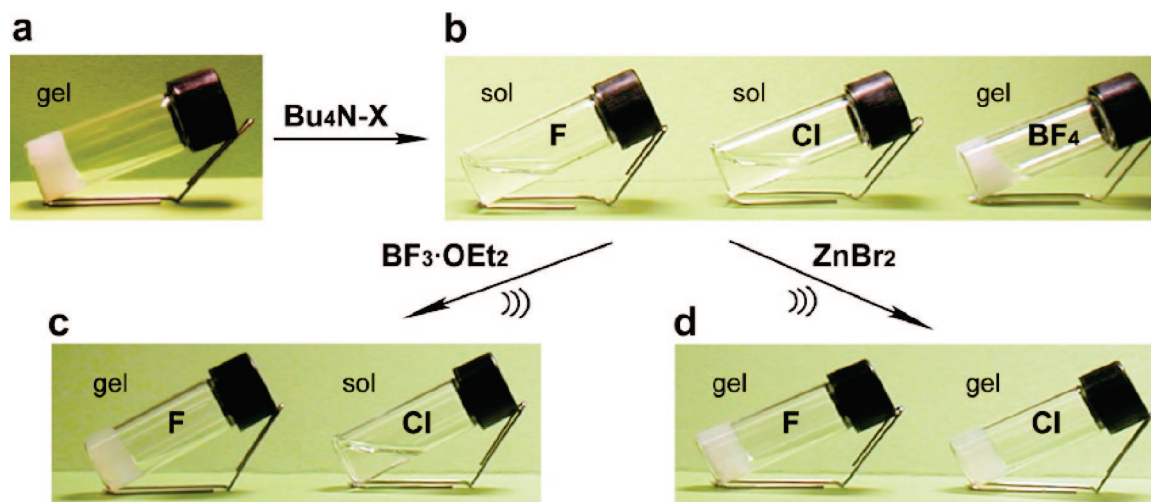
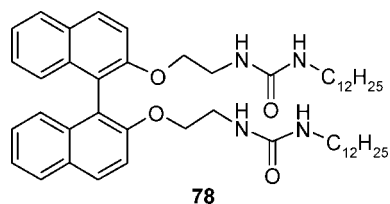
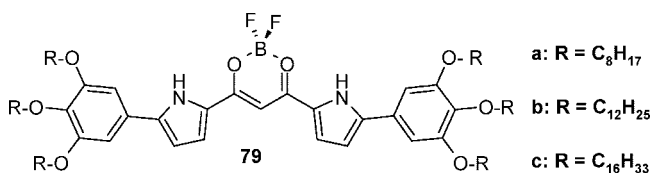


Figure 41. Photographs of acetone gel of **77** showing the transitions between gel state and liquid state upon addition of chemical stimuli ($X = F^-$, Cl^- , or BF_4^-). (a) Acetone gel of **77** (2.0 wt %); (b) acetone gel of **77** (2.0 wt %) containing (from left) 1.1 equiv of TBA^+F^- , 1.7 equiv of TBA^+Cl^- , and 10 equiv of $TBA^+BF_4^-$; (c) $BF_3 \cdot OEt_2$ (1.0 equiv for TBA^+ salt) mixture after sonication of **77** and TBA^+F^- (left) or TBA^+Cl^- (right) in acetone; (d) $ZnBr_2$ (1.0 equiv for TBA^+ salt) mixture after sonication of **77** and TBA^+F^- (left) or TBA^+Cl^- (right) in acetone. Reprinted with permission from ref 236. Copyright 2007 Elsevier.

Scheme 56



Scheme 57



with gels of **82**. This has led the authors to speculate that these fluoride responsive gels may provide the basis for a nonfluid and, therefore, more robust gel-based system for the naked-eye detection of fluoride.

Because of the selective binding of F^- by **83** (Scheme 61), a benzoxazole-based organogelator, Lee and co-workers showed that they could also visually detect F^- using a gel-based system.⁵⁷ Deprotonation by F^- causes a color change from colorless to green in **83**, so when 100 equiv of TBA salts are added to the gel, a similar effect is seen. F^- causes breakdown of the gel and generation of the color. Other anions cause breakdown of gel but do not generate the same color change except in the case of $CH_3CO_2^-$, which only gives a very pale green color.

The binding of F^- , and indeed any anion, to the hydrogen-bonding moieties of a LMWG can be used to determine the importance of those functional groups in the aggregation processes of gel formation. This is most often expressed in the form of a gel-to-sol transition. An important aspect of the study into the effects anions have on gels relates to the research done when less than a stoichiometric amount of anion is used to disrupt the formation of the gel (in comparison, most studies use an excess).^{49,50,177} Gel-to-sol transitions are not the only resultant effects caused by the addition of anions to a gel; anions can be used to change

the strength of the gel, and cases are known of both anion-induced weakening and strengthening of gels. Using rheology to study the anion-induced tuning of the gels of compounds **84** (Scheme 62), we have shown it is possible to tune the strength of a gel using anions.⁴⁹

For the compounds where $n = 2$ and 4, the addition of different anions in substoichiometric amounts results in a decrease of both G' and G'' , and a decrease in the yield stress of the gel (Figure 44). This suggests that, for a fixed concentration of gelator, the anions cause a decrease in the interconnectivity of the individual gel threads.

The degree of decrease in the storage and loss moduli approximately correlates to the anion-binding affinities of compounds **84** as determined by the solution anion-binding constants measured by 1H NMR spectroscopic titration in a sol phase above the gel-sol transition temperature. The anion binding constants for the compound $n = 2$ decrease in the sequence $CH_3CO_2^- \gg Cl^- > NO_3^- > BF_4^-$, which correlates to the decreases in the rheological values (indeed there is no change seen in G' and G'' when $TBA^+BF_4^-$ is added, even in excess). In addition to weakening gels and causing gel-to-sol transitions, anions can be used to enhance gelation.^{56,205,243,244} Addition of halide and nitrate salts to compound **85** (Scheme 63) results in the formation of hydrogels, whereas **85** by itself does not gel.⁵⁶

The anion-enhancement of gelation of **85** is suggested to be based around the Hofmeister (specific ion effect) series. A typical Hofmeister series is as follows:²⁴⁵



The more-hydrated anions (to the right) are referred to as salting-out or kosmotropic ions, and the less-hydrated anions (to the left) are known as salting-in or chaotropic ions. The salts containing the more chaotropic anions cause gelation of **85** and salts containing kosmotropic anions cause solvation. Superimposed upon this factor is the solubility-based trend in crystallization tendency. As a result, the most stable gels are formed when salts of NO_3^- and Br^- are added. It is interesting that it appears that the salts remain in the liquid phase and are not incorporated in the gel. The salts cause no noticeable perturbation of the 1H NMR spectra of **85**

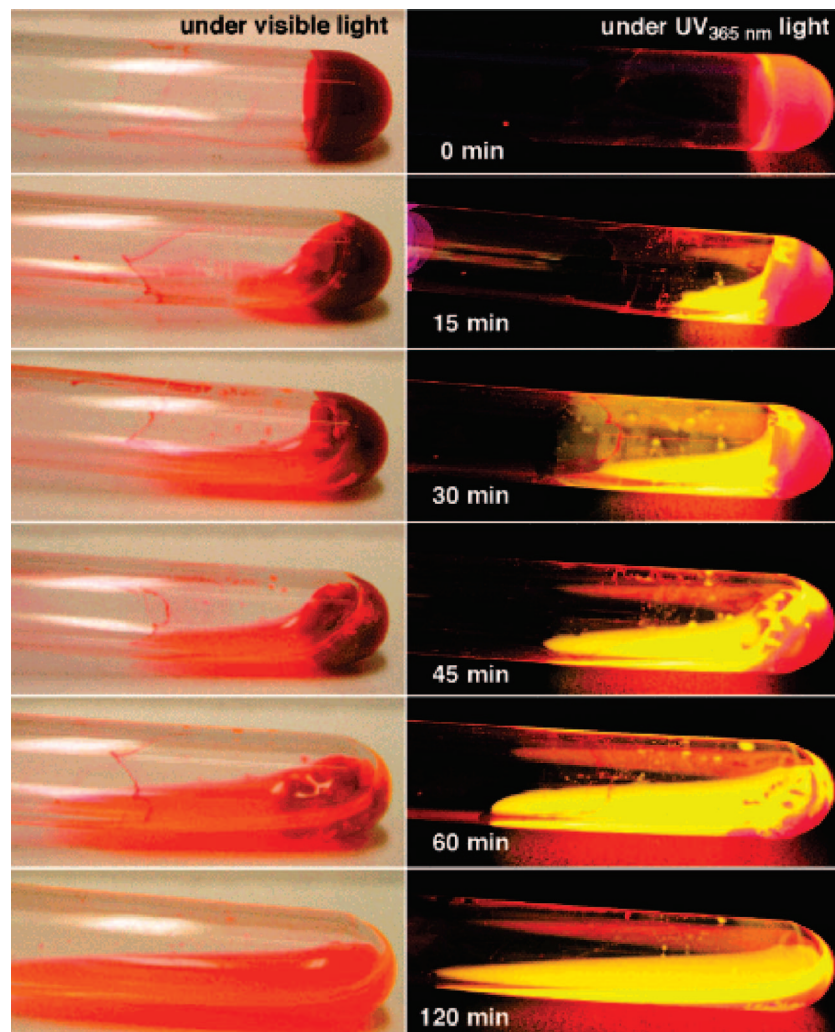
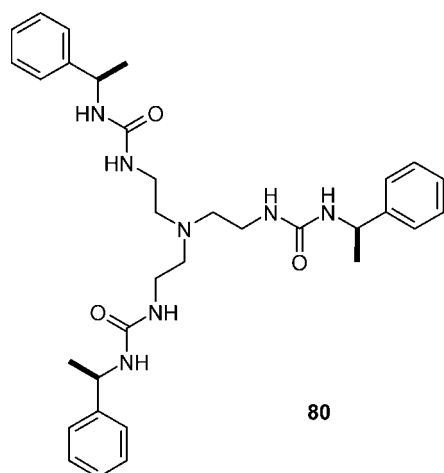


Figure 42. Transition of the supramolecular gel of **79** in octane (10 mg/mL) to a solution upon addition of 10 equiv of TBA^+Cl^- added as a solid to the top surface of the gel. The highly emissive solution generated by the decomposition of the gel has fluorescence emission at 524 and 574 nm ($\lambda_{\text{ex}} = 470$ nm), indicating that the bound Cl^- by **79** is soluble in the octane explaining the breakdown of the gel. Reproduced with permission from ref 51. Copyright 2007 American Chemical Society.

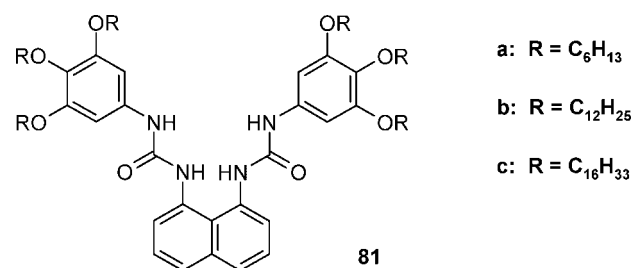
Scheme 58



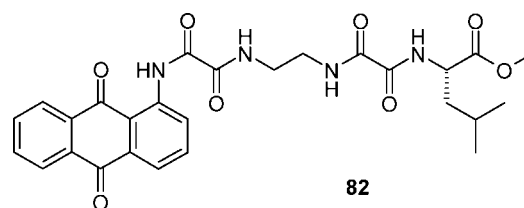
(which might indicate solution-phase binding). Even so, the anions may be helping to preorganize **85**, although poorly understood Hofmeister anion effects may be the only factor.^{53,54,59}

As we saw in the previous section, there are examples of metal-based LMWG that can be tuned using anions, e.g., compound **48** where the addition of large anions such as

Scheme 59



Scheme 60



$\text{C}_2\text{F}_5\text{CO}_2^-$ and $\text{C}_3\text{F}_7\text{CO}_2^-$ causes a breakdown of the gel as the ligand changes from a cisoid to transoid form.^{54,59} There is also the case of compound **47** that forms a colloidal gel that can be disrupted by the addition of excess ClO_4^- .¹⁷⁰ In compound **70**, complex processes result when different

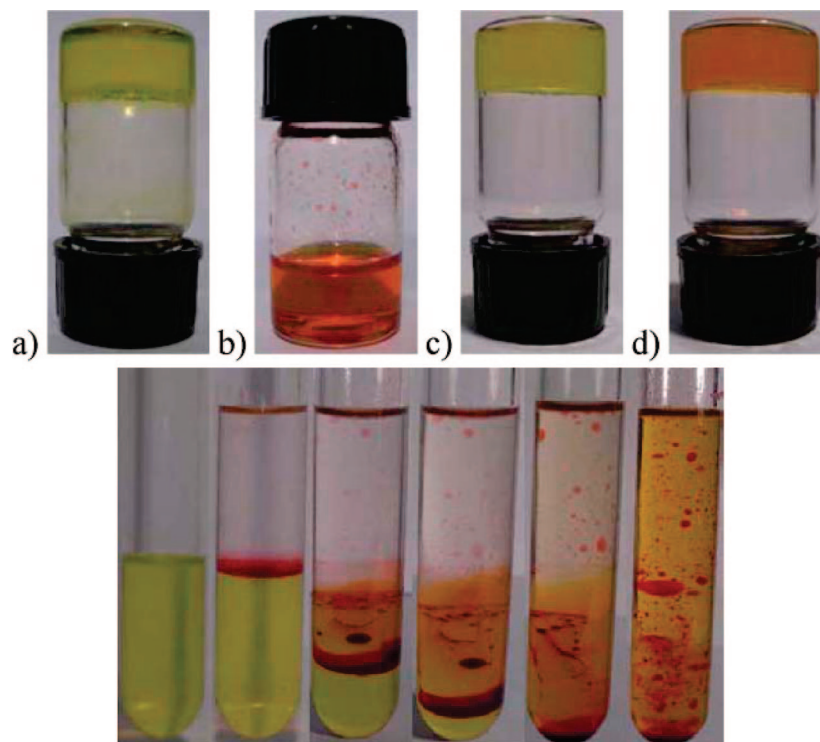
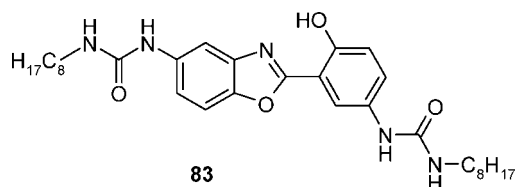
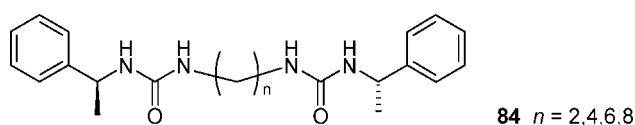


Figure 43. (a) **82** *p*-xylene gel; (b) addition of 10 equiv of TBA^+F^- to the hot *p*-xylene solution of **82** followed by cooling to RT; (c) EtOH gel; (d) reddish **82** EtOH gel after addition of 10 equiv of F^- . Diffusion of F^- from a concentrated *p*-xylene solution (50 equiv) through the **82** *p*-xylene gel. From left to right: **82** *p*-xylene gel; immediately after addition of TBA^+F^- solution; after 2, 3, and 4 h; and overnight standing. Reproduced with permission from ref 242. Copyright 2007 The Royal Society of Chemistry.

Scheme 61



Scheme 62



anions are added, which allows for the tuning of the gel strength.¹⁹⁴ Silver-based coordination LMWGs also represent an interesting group that can be tuned using anions.^{54,55,59,177} Because of the formation of insoluble silver halides and silver oxide, anions can be used to induce a gel-to-sol transition. Addition of further Ag^+ results in reformation of the gel. This has also been used to tune gel fluorescence properties in the case of compound **22**.¹²⁵

There are a large number of salts of organic anions and cations with inorganic counterions as well as purely organic salts that have been discovered to gel a wide variety of solvents.^{1,5,16,58,98,198,201,246–249} The characteristics of the anion intuitively play a crucial part in the gelation ability of these compounds. There have, however, been surprisingly few studies performed that directly look at the influence of the anion in LMWG salts, often due to the fact that a simple change in the anion results in loss of gel character all together.^{1,5,16,58,98,198,201,246–249} Studies by Dastidar and co-workers have gone against this trend and have studied examples where the anion is varied and, therefore, varies

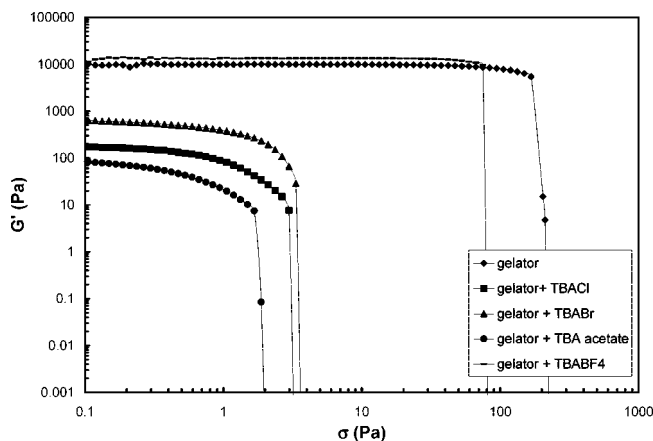
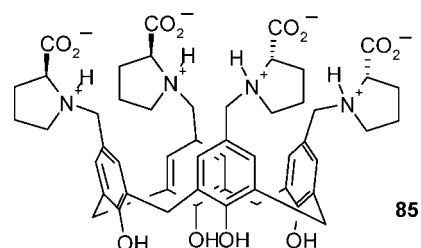


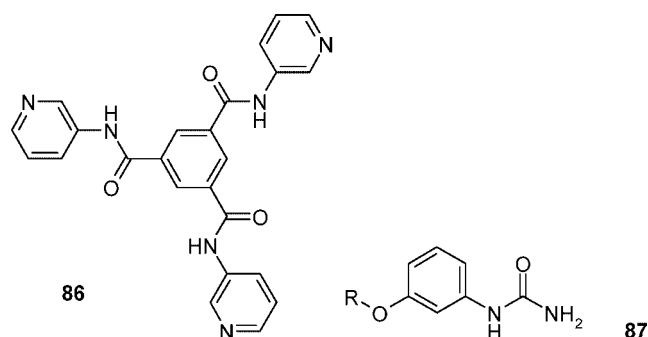
Figure 44. Influence of different anions (0.1 equiv of anion added as their TBA^+ salts) on the storage modulus (G') at a frequency of 1 Hz and a temperature of 20 °C, as a function of oscillation stress (σ) of the 1% by weight gel of **84** $n = 6$ in CHCl_3 . The lines are a guide to the eyes only. Reproduced with permission from ref 49. Copyright 2008 The Royal Society of Chemistry.

Scheme 63



the characteristics of the gel.^{248,249} This work looked at the importance of one-dimensional hydrogen-bonding networks as a means to predict and possibly design gelation using

Scheme 64



knowledge gained through the use of crystal engineering of supramolecular synthons.⁹ A study on a family of organic salts with the cation dibenzylammonium revealed that the variation in the anion in the form of both benzoate and cinnamate derivatives allowed for the tuning of the gelation process. Of the 27 anions tested, it was found that 19 of them show some form of gelation and that this tendency correlates well with the formation of one-dimensional networks in the crystal structures of the salts. This insight allows the tuning of the gel characteristics, the gel strength or stability (as measured by changes in T_{gel}), and minimum gel concentration required for full gelation of a specific solvent volume, solvent type, and gel fiber morphology.

7. Gels as Templates

One of the most exciting current areas of supramolecular gel chemistry is their potential application as templates in materials and biomaterials applications. The ion binding and slow diffusion within gels results in significant interest in their use as a basis for templating biocompatible structures or new materials such as metallic nanoparticles. In a recent example, *N,N',N''*-tris(3-pyridyl)trimesic amide (**86**; Scheme 64) has been used to form a hydrogel with applications as a matrix for the growth of biomaterials. The hydrogel pyridyl nitrogen atom and hydrogen-bonding amide group binds anions, particularly carbonate and phosphate. These bound anions act as nucleation sites for the growth of an inorganic calcium carbonate mineral phase. The resultant templated material shows obvious hydrogel fiber imprints and gives curved platelike nanostructures along the hydrogel fibrous network.²⁵⁰ The use of a LMWG in this example contrasts to much more extensive work on biomineral, particularly hydroxyapatite, deposition using polysaccharide hydrogels such as agarose.²⁵¹ While saccharide polymers are outside the scope of this review, which focuses on LMWGs, it is interesting to note that, in the case of many polysaccharide gels, the hydrogelation itself is metal-ion triggered. For example, addition of Ca^{2+} ions to alginates (block copolymers of mannuronic and guluronic acid salts obtained from seaweed) causes the cross-linking of the polymer strands in the guluronate regions, resulting in gelation in what is termed the “egg box” model.²⁵² These calcium binding sites also serve as the basis for templated biomineralization of calcium containing minerals.

A strongly growing area of gel templation is the use of LMWGs as scaffolds for the controlled growth on metallic nanoparticles. In a recent report, salt hydrogels of stearic or eicosanoic acid mixed with di- or oligomeric amines have been used as a medium for the synthesis of silver nanoparticles. The nanoparticles position themselves on the fibers

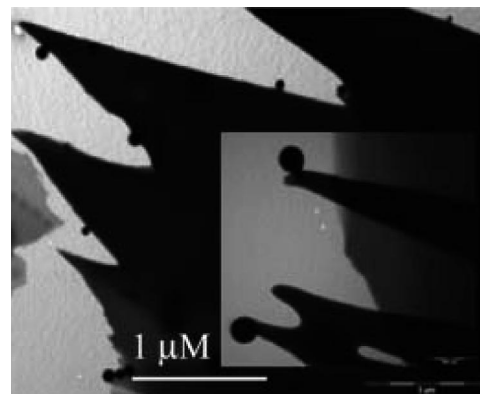


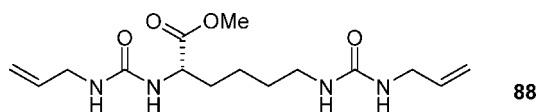
Figure 45. TEM image of a hydrogel based on gelator **87** with templated gold nanoparticles. Reproduced with permission from ref 13. Copyright 2006 The Royal Society of Chemistry.

to give ordered assembly of gel–nanoparticle composite in which the nanoparticles bind to the gel fibers.¹⁵ Related reports have described the synthesis and stabilization of gold nanoparticles using urea gelators of type **87**.¹³ Figure 45 shows the growth of spherical gold nanoparticles within the gel. Interestingly, in this system the urea acts as both a reductant for Au(III) as well as a gelator. Similarly, Smith and co-workers have reported the templation of gold nanoparticles with diameters of ca. 13 nm by UV irradiation of a dendritic supramolecular organogel containing $H AuCl_4$ and tetraoctylammonium bromide.¹² Gold nanoparticles of various shapes have also been prepared within a gel made up of peptide amphiphiles.²⁵³

As well as metallic nanoparticles, semiconductor materials have been gel templated. In one report, necklacelike arrays of TiO_2 nanoparticles have been prepared by a sol–gel polymerization using hydrogelator and tetraethylammonium 3-butyrate followed by calcination with tetrabutyl titanate ($Ti(OBu_4)$) as the titanium source. Analysis of the nanoparticles by field emission SEM (FE-SEM) gives an average diameter in the range of 200–400 nm.²⁵⁴ Sol–gel transcription has also been used to template the formation of nonspherical nanostructures. Single and double helical nano-scale structures of cadmium sulfide have been produced from growth on a self-assembled organic template. Nucleation and growth of CdS on one side of the twisted ribbonlike template leads to single helices of polycrystalline CdS, while nucleation and growth on both sides of the ribbon leads to double helices.²⁵⁵

In addition to the formation of stabilized nano-objects, gel structures themselves have been transcribed by templation into inorganic matrices. Work by the group of Shinkai has shown that the lamellar or fibrous structures of “gemini”-type cholesterol-based gelators can be transcribed into the silica structures by sol–gel polymerization of tetraethoxysilane.²⁵⁶ More recent work by Smith has resulted in gel structure transcription into polystyrene, while James has produced spongy polymethylmethacrylate structures from a metallogel as discussed in section 1.²⁴ Incidentally, the theme of the trimesic acid component in metal-containing gels has been expanded to other templated systems and catalytic applications. For example, a gel formed by trimesic acid and Fe(III) or Co(III) cations could be used to template the formation of polymer monoliths upon the addition of cross-linker and monomer to the metal–organic coordination gel.²⁵⁷ Highly micro- and macroporous aerogels were obtained from metal–organic frameworks (MOF) using iron(III) and 1,3,5-

Scheme 65



benzene tricarboxylate.²⁵⁸ Because of the nature of the pores with pore volumes of up to $5.6 \text{ cm}^3 \text{ g}^{-1}$, these gels are expected to have potential for storage or catalytic applications. Other iron–tricarboxylate based metal–organic gels could be modified to yield phosphine containing networks, which in turn could be further functionalized with palladium(II) inside the porous scaffold.²⁵⁹ These gels and their xero- and aerogels exhibited high activity in catalyzing carbon–carbon Suzuki coupling.

Finally, a remarkable recent report from Smith's group concerns the covalent capture of fibrous or spherical nanostructures (which form depending on cooling rate) derived from gelator **88** (Scheme 65) using alkene metathesis. The spherical captured structures may then be used to template the formation of hollow gold microspheres.²⁶⁰

8. Conclusions

The field of gelation by small-molecule gelators is an area of intense current activity with gelation occurring reproducibly in a wide and increasing range of organic substructure types. With the increasingly facile access to high-resolution imaging and nanoscale manipulation techniques, the structure of these materials is increasingly well-understood. The incorporation of surface functionality into such molecular gelators is synthetically relatively straightforward, allowing gels to bind and respond to a range of simple additives such as metal cations and small inorganic anions as well as molecular species. Incorporation of metals and anions within gelators allows a further degree of tuning of their materials properties, including their optical, magnetic, self-assembly, morphological, and rheological behavior. As more and more imaginative applications are devised for these new, easily handled nanomaterials, the field can only grow rapidly.

9. Acknowledgments

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