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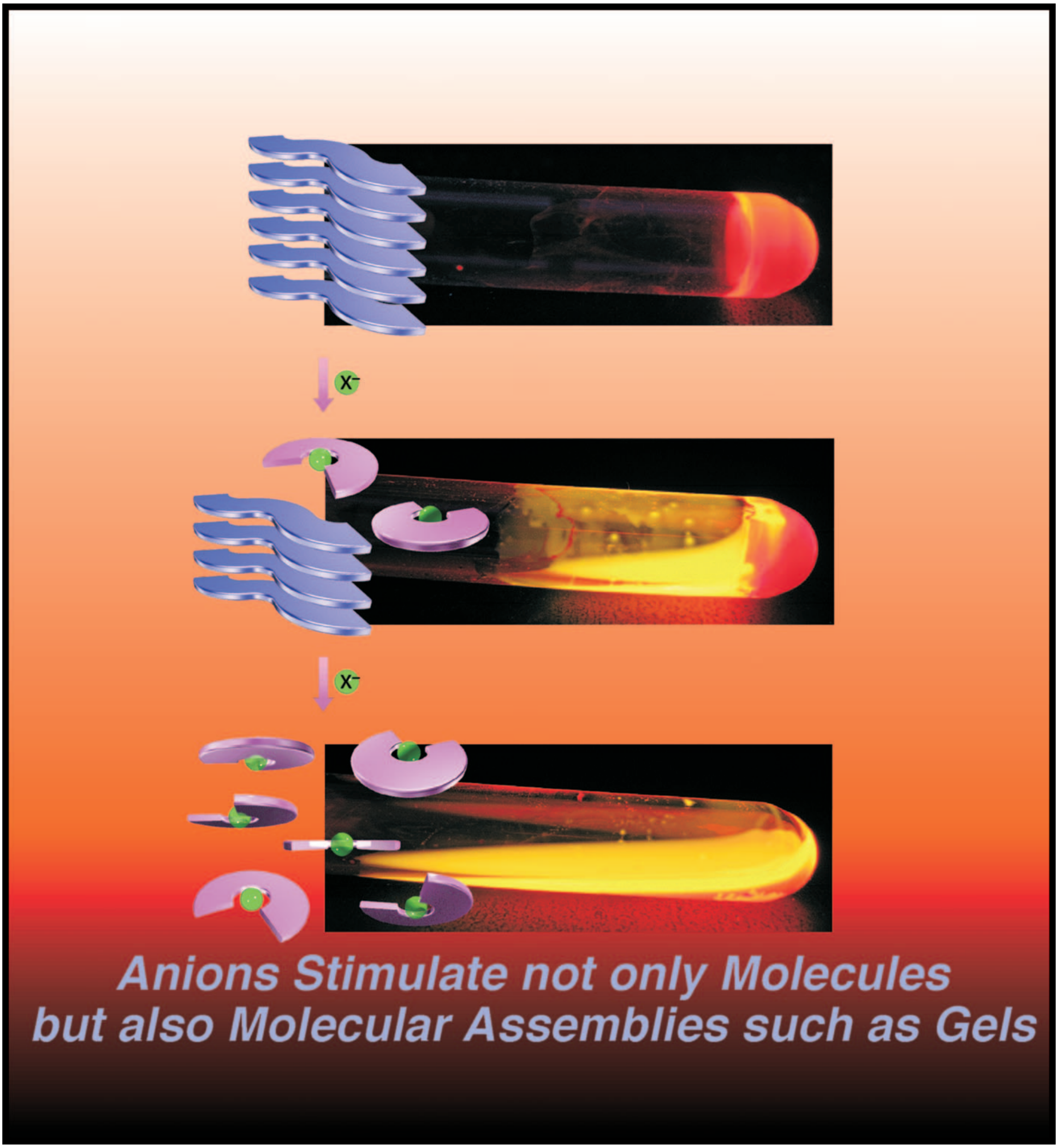
Anion-Responsive Supramolecular Gels

Hiromitsu Maeda*[a, b]



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Abstract: Supramolecular gels that change their state or structure in response to anion stimuli have been highlighted. Only a few examples exist of such supramolecular gels, the structures and properties of which can be controlled and modulated by interactions with anions. To form anion-responsive dimensionally-controlled organized structures, the constituent low-molecular-weight gelator molecules must act as anion receptors by possessing one or more of van der Waals interaction units (aliphatic chains), stacking π planes, hydrogen-bonding sites, and metal-coordination units. This Concept focuses on the gelation and transition behaviors of amide- and urea-based anion-stimulated systems, metal-coordinated systems, and novel acyclic π-conjugated oligopyrroles that act as “molecular flippers.”

Keywords: anion binding • electrostatic interaction • hydrogen bonding • pyrrole derivatives • supramolecular gels

Introduction

Soft matter has been attracting increasing attention as a “transformable” functional material, owing to its moderate mobility and flexibility, which readily enables it to change its bulk shape and properties depending on the conditions.[1] Gels are soft materials that are reasonably less mobile agglomerates with mechanical properties characteristic of a solid. Some of the gels incorporate solvent molecules into a 3D entangled network of dimensionally controlled fibril- and tape-like organized aggregates consisting of gelators; thus far, the synthesis of functional gels and the examination of their physical properties have been reported mainly on those obtained from polymer gelators.[2] In contrast, supramolecular gels are dimensionally controlled assemblies comprising low-molecular-weight molecules held together by noncovalent interactions, such as hydrogen bonding, metal coordination, van der Waals interaction, and π–π stacking; gels derived from molecular assemblies, the components of which components can be readily replaced with alternatives may provide promising material systems for drug delivery and tissue engineering.[3] Supramolecular gels that consist of molecules sensitive to a certain stimulus can be modulated and controlled by that external stimulus. For example, Shinkai et al. reported that the properties of thixotropy and the mixed valence state, which are unique to an organogel, can be controlled by mechanical and electrochemical stimuli through π-conjugated porphyrin and tetrathiafulvalene (TTF) moieties, respectively.[4] In addition, Yagai et al. produced photo-responsive organogels consisting of hydrogen-bonded aggregates of melamine-azobenzene conjugates and their complementary units.[5] In contrast to the above physical stimuli, chemical stimuli, such as the incorporation of a specific species, could afford versatile supramolecular gels that change their states depending on the interactions between the additives and gelator molecules. For example, Shinkai et al. also reported that cholesterol-substituted phenanthroline derivatives gelate various alcohols, other polar solvents, and nonpolar solvents and that propanol gel exhibits tunable electronic states and emission behaviors on the addition of trifluoroacetic acid (TFA).[6] Lehn et al. produced pH-dependent hydrogels comprising amide-bridged guanine-polyethylene glycol (PEG) hybrids in the presence of potassium ions in the form of KCl and [2.2.2]cryptand.[7] Furthermore, Xu et al. reported the synthesis of 9-fluorenylmethyloxycarbonyl (Fmoc)-substituted D-alanine dimer that forms a hydrogel through the interactions between its fluorenyl moieties, as well as through the hydrogen bonding between its amide units; the hydrogel transforms into a solution upon the addition of vancomycin.[8] In these cases, the additives (chemical stimuli) appear to behave as “inhibitors” of gel formation by interacting at the gelating sites of the building components, which are crucial for molecular assembly.

Anions play essential roles in biotic systems; for example, the chloride (Cl^-) ion is well known as the anion involved in synapse transmission in the central nervous system. Iodide (I^-) causes the depolymerization of actin filaments (F-actin) and the corresponding transition from a gel-like state to solution state, possibly by influencing the hydration shell that is thought to surround and stabilize the F-actin polymer.[9] In these cases, the anions affect biotic macromolecular systems such as protein and gel-like states. Moreover, various artificial anion receptors have been actively synthesized in this decade;[10] however, few reports currently exist on anion-controlled supramolecular gels consisting of gelator molecules with anion binding ability. To be exact, anion-responsive gel materials may include supramolecular gels consisting of anionic gelators, those comprising cationic gelators with counter anions,[11] and systems derived from ionic liquids,[11b,12] which have been and will be reviewed elsewhere.[3c] In this Concept, I will focus on supramolecular gels, the structures and properties of which are tunable by hydrogen bonding and by electrostatic interactions between anion stimuli and the gelator building components. I believe that anion-responsive supramolecular gels are not simply materials that exhibit state transitions in response to anion

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[a] Prof. Dr. H. Maeda
College of Pharmaceutical Sciences
Institute of Science and Engineering
Ritsumeikan University
Kusatsu 525–8577 (Japan)
Fax: (+81) 77-561-2659
E-mail: maedahir@ph.ritsumei.ac.jp

[b] Prof. Dr. H. Maeda
PRESTO, Japan Science and Technology Agency (JST)
Kawaguchi 332–0012 (Japan)

stimuli, but are promising "gel salts" that contain small or equivalent amounts of ionic species because of their structural design and the modifications to their building components (gelators, anions, and cations).

How to Introduce Anion-Responsive Behaviors in Supramolecular Gels

The formation of a supramolecular gel can be achieved by the incorporation of one or more types of available noncovalent interaction sites into gelator molecules, such as long alkyl chains for van der Waals interaction, suitable planes for π–π stacking, hydrogen-bonding units, and metal coordination units. In the gel state, solvent molecules exist inside entangled networks of dimensionally controlled organized structures comprising gelators (Figure 1a). Therefore, these organized structures are limited to the scale range from nanometers to micrometers. Smaller-scale materials may allow the assemblies to disperse in solutions, while larger-scale materials would afford precipitates. Crystal is one of the fairly ordered organized structures compared to dimensionally controlled ones. The initial step in the formation of a gel involves obtaining appropriate-scale (width and length) gelator molecules that can form the fibril- and tape-like structures that compose gels. Such molecular assemblies should be influenced by the external conditions, especially the solvent, temperature, concentration, etc. Among the parameters that determine gel formation, the use of anions as external chemical stimuli has only been reported in a few papers in the past five years, possibly as a result of the smaller number of candidate anion receptors that can act as gelators. Most of the anion-responsive gels reported thus far comprise anion receptors bearing amide or urea units, which also act as hydrogen bonding sites that support molecular assembly. If the hydrogen bonding donor NH sites in the amide or urea units interact with anions, the gelators may not form stable assemblies, resulting in the transformation of the gels, for example, into a solution.

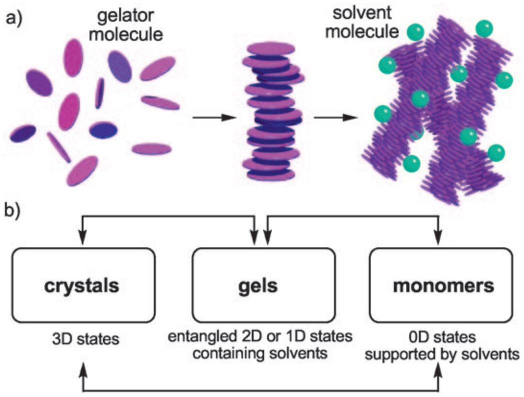

Figure 1. a) Proposed scheme of supramolecular gel formations; b) conceptual diagrams of the transitions between the three representative states: crystals, gels, and monomers.

The multimodal interactions of the gelators with anions would afford the various types of transformations (Figure 1b). Interaction of the gelator molecules with anions at the hydrogen bonding donor sites may interfere with self-assembly to afford dispersed monomers. Clearly, anion-gelator (receptor) complexes can form more ordered states, i.e., crystals, or may create the gels. Such transitions have also been observed between crystals and monomers in solution. Moreover, the solvent is the crucial factor that dominates the properties of gels; this solvent-based definition of gels conveys the diversified new features of the chemistry of supramolecular assembly and anion binding.

Amide-Based Anion-Responsive Supramolecular Gels

Amide NH units are well known anion binding sites, owing to the polarization by π conjugation with the neighboring carbonyl moiety.[10] For example, Thordarson et al. reported an alkyl-substituted pyromellite tetraamide derivative (**1**, Figure 2a) that gelates cyclohexane, hexane, diethyl ether, and toluene because of the hydrogen bonding between the gelators. The tetraamide **1** binds to anions added as tetrabutylammonium (TBA) salts through conformation changes of its amide units in dilute solutions. Therefore, the cyclohexane gel of **1** is transformed into a solution by the addition of 0.25 equiv of TBA salts (Cl^-, Br^-, I^-, AcO^-, and NO_3^-) owing to the weaker association between the gelator mole-

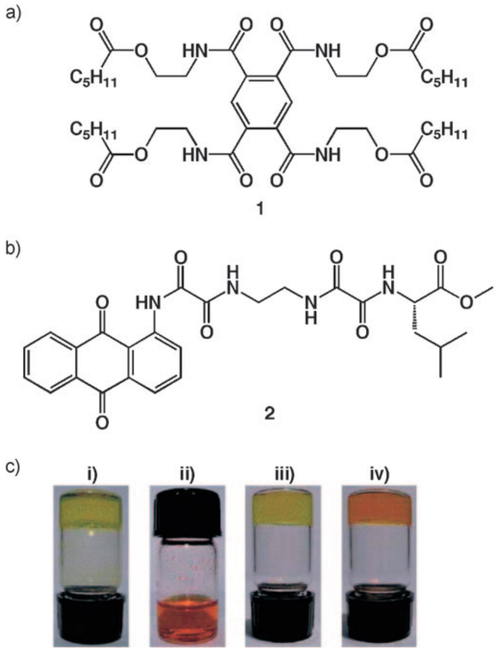

Figure 2. a) Pyromellite tetraamide derivative **1**; b) oxalamide-substituted anthraquinone derivative **2**; c) i) *p*-xylene gel of **2**, ii) *p*-xylene solution from gel of **2** with F^-, iii) ethanol gel of **2**, iv) ethanol gel of **2** with F^- (adapted from Ref. [14]).

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cules caused by the interaction with the anions at the hydrogen bonding NH sites. The transformation from gel to solution upon the addition of TBA salts as a solid on the gel surface takes time (several seconds to minutes), depending on the affinity of **1** to the anions ($Cl^- > AcO^- > Br^- > NO_3^- > I^-$). In contrast to organic salts, NaI does not induce such a transition to the solution state.[13] Žinić et al. reported an oxalamide-substituted anthraquinone (**2**, Figure 2b), which gelates alcohols (ethanol and 1-butanol) and aromatic solvents (benzene, toluene, and *p*-xylene) through π–π stacking between the gelator planes. In sharp contrast to compound **2**, the regioisomeric 2-substituted derivative only affords precipitates; this result suggests that the positions of amide-substituents significantly influence the gelation abilities. The addition of 10 equiv of TBAF transforms the *p*-xylene gel of **2** into a solution with a color change. This is owed to the interactions of F^- with amide NH groups, which interferes with the hydrogen bonding between the gelator molecules. In contrast, the ethanol gel of **2** only changes color upon the addition of F^-, which does not entirely disrupt the intermolecular interaction between the gelators, owing to the solvation of F^- by the fairly protic ethanol molecules (Figure 2c).[14]

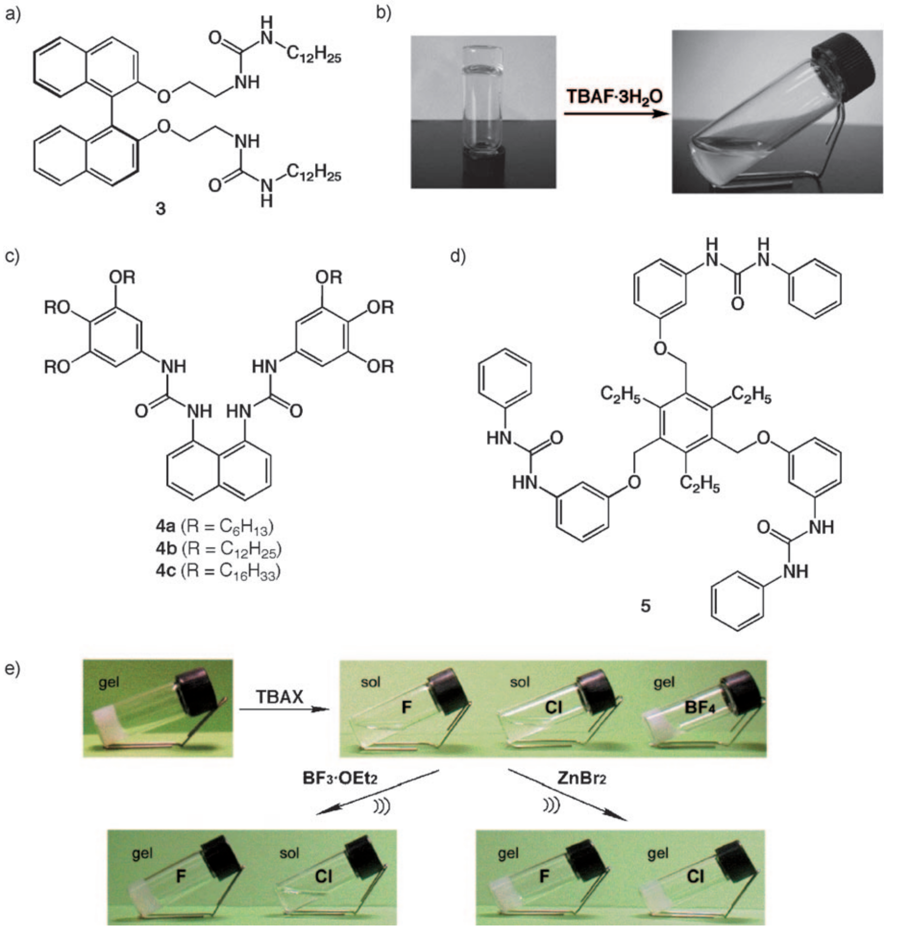

Figure 3. a) Urea-substituted binaphthyl derivative **3**; b) F^--responsive behavior of cyclohexane gel of **3** (adapted from Ref. [15]); c) urea-substituted naphthalene derivatives **4a–c**; d) benzene-coupled triurea **5**; e) anion-responsive behaviors and recovery of acetone gel of **5** (adapted from Ref. [17]).

Urea-Based Anion-Responsive Supramolecular Gels

Urea moieties are used as anion recognition sites due to their polarized NH units.[10] Zhang and Zhu et al. synthesized a urea-substituted binaphthalene derivative (**3**, Figure 3a), which gives transparent supramolecular gels ($6\,mg\,mL^{-1}$) from cyclohexane with a transition temperature of 20 °C through both hydrogen bonding and π–π stacking interaction. The addition of TBAF (1 equiv) interferes with the hydrogen bonding between the gelator molecules to afford a solution (Figure 3b). In this case, no significant absorption spectral changes caused by F^- binding have been observed as a result of the σ-bond connection between the hydrogen bonding amide units and the chromophore binaphthyl unit.[15] Alternatively, Yi and Li et al. synthesized urea-bridged hybrids of alkyl-substituted aryl units and the naphthyl moiety (**4a–c**, Figure 3c), which use hydrogen bonding and π–π stacking interactions to form emissive supramolecular gels from various solvents; the gels are decomposed to solution by F^- addition and are re-formed by H^+ addition. However, the reformed gels exhibit emission behaviors and organized structures unlike those of the original gels.[16] Recently, Yamanaka et al. synthesized a triurea-coupled benzene (**5**, Figure 3d) that affords opaque supramolecular gels from acetone by sonication. However, cooling the thermally dissolved acetone solution results in precipitation and no gel formation. Compound **5** gelates diethyl phthalate, methanol, and THF, but affords no gels from nonpolar solvents, such as hexane, toluene, and CH_2Cl_2. Hydrogen bonding at the urea units, as suggested by IR measurements of the gel, is found to be an essential factor for gel formation; this is also supported by the gelation behaviors of the derivatives lacking these interaction sites. Similar to the other examples, acetone gel is transformed to solution by the addition of TBAF and TBACl. The required amounts for the transitions increase with the ionic radii of the

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anions; this observation is correlated with the binding affinities of **5** for the corresponding anions. Furthermore, the addition of $BF_3{\cdot}OEt_2$ to the F^--mediated solution state affords the recovery of the gel state, whereas the addition of $ZnBr_2$ to the solutions mediated by anions such as halides (F^-, Cl^-, Br^-, and I^-) and AcO^- also affords supramolecular gels (Figure 3e).[17]

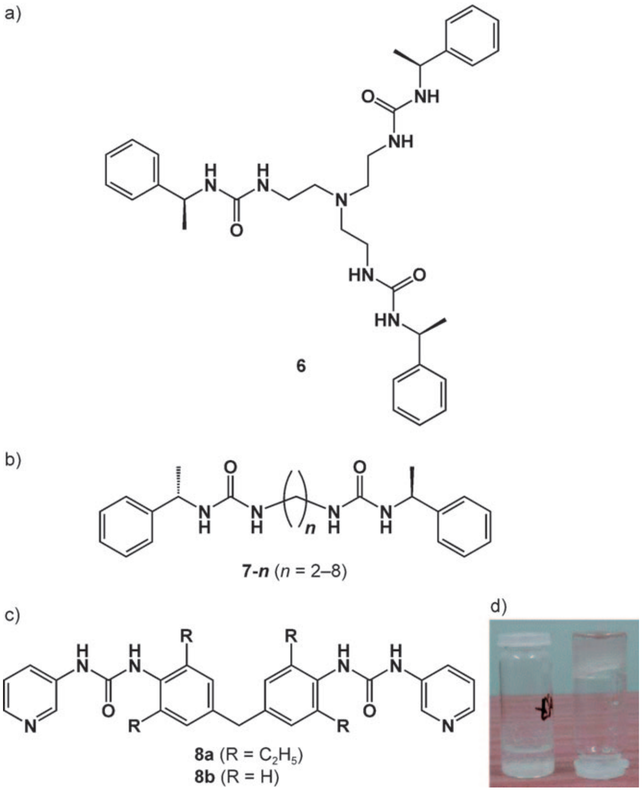

Figure 4. a) Triurea **6**; b) bisurea gelators **7-*n*** (n=2–8); c) pyridyl-substituted bisurea **8a**,**b**; d) **8b** in THF/H_2O solution from gel (left) and in THF/H_2O gel with $AgBF_4$ (right) (adapted from Ref. [20]).

Certain gel systems contain anion binding receptors, which exhibit state transitions without direct interactions with anions. Steed et al. synthesized a triurea-substituted molecule (**6**, Figure 4a) that exhibits the Cl^- affinity ($\approx 10^3\,\text{M}^{-1}$ in DMSO) and gelates DMSO–H_2O (1:1, v/v, 0.5 wt%). Addition of 1 equiv of NaCl to the gel impedes the gelation process, decreases the amount of solvents included in the gel, and thus results in the formation of both gel and crystals. Single-crystal diffraction analysis revealed that the crystals formed in the absence of Cl^- salts comprised only the gelator molecules bound through intramolecular and intermolecular hydrogen bonding between the urea units.[18] Steed et al. also reported alkyl-bridged bisurea compounds (**7-*n***, Figure 4b), which form gels when it encounters an even number of methylene units (n=2, 4, 6, 8) and no gels when it encounters an odd number of menthylene units (n= 3, 5, 7) from CH_3CN, $CHCl_3$, MeOH, toluene, and solvent mixtures such as DMSO–H_2O and MeOH–H_2O (1 wt%). This observation of the differences in the even and odd number of the spacing methylene units is correlated with the orientation of the urea units as interaction sites, which is also corroborated by X-ray diffraction analysis. The addition of anions (0.1 equiv as TBA salts) to the gels of **7-*n*** affects the storage modulus, which is augmented in the order corresponding to the addition of AcO^- (small), Cl^-, Br^-, BF_4^-, and no anions (large), as a function of the oscillation stress. The degrees to which anions inhibit gelation are, to some extent, correlated with the anion-gelator binding affinities.[19]

Aside from gel-to-solution transitions caused by the dispersion of the building units, the formation of new aggregates or crystals has also been reported. Steed et al. synthesized a pyridyl-substituted bisurea derivative (**8a**, Figure 4c) that gelates $CHCl_3$/MeOH (1:1, v/v, 10 mm) through hydrogen bonding. Bisurea **8a** keeps the gel states in metal coordination polymers on the addition of $AgPF_6$ and $AgNO_3$; the organized structures observed by scanning electron microscopy (SEM) are distinct and depend on the coexisting anionic species. In contrast, bisurea **8b**, which does not have alkyl-substituents, affords crystals by itself and gelates THF/H_2O (2:1, v/v) on the addition of $AgBF_4$ (Figure 4d). In contrast to the case of **8a**, compound **8b** forms crystals by the addition of $AgNO_3$. Single-crystal X-ray diffraction analysis has elucidated that metal coordination is essential for aggregation and that the interactions between urea units and anions affects the assembled structures; NO_3^- associates fairly well with urea sites to form crystals, whereas BF_4^- allows a more soluble state and thus supramolecular gels.[20]

Metal-Coordinated Gels Responsive to Anions

As observed in the supramolecular gels in reference [20], metal complexation of the gelator molecules is also an essential factor required to stabilize molecular assemblies in both the discrete and dispersed coordination forms. Metal-coordinated supramolecular gels can exhibit state transformation by the anion-stimulated "collapse" of the building units—the metal complexes in this case. Wu et al. obtained the amide-bridged hybrid of an alkyl-substituted aryl moiety and a pyridyl unit, which affords a Ag^+-bridged dimer complex; the triflate salt of the Ag^+ complex (**9**, Figure 5a) gelates toluene/ethanol (10:1, v/v) through hydrogen bonding and the aromatic interactions between the Ag^+ complexes. In contrast, $Co^{2+}/Cu^{2+}/Ni^{2+}$ complexes produce no gels, possibly because of their nonlinear coordination behaviors, which are not effective for the formation of organized structures. By addition of KI in ethanol, the Ag^+ complex, as a triflate salt (**9**), provides a free ligand, and as a result, a solution containing AgI precipitates is afforded (Figure 5b). The addition of excess Ag^+ salts re-forms the gel states, and, as in the case of I^-, other anions such as Br^- and Cl^- also produce transitions from gel to solution by the formation of their Ag^+ salts.[21]

The anion-driven "liberation" of metal ions has been shown to control the emission behavior. Aida et al. reported

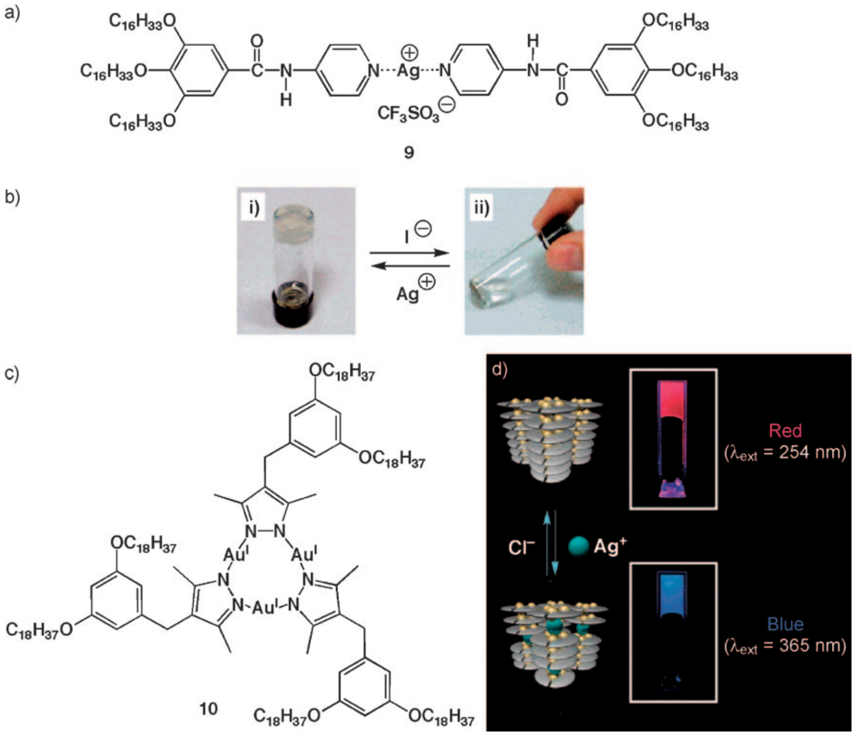

Figure 5. a) Bispyridine-Ag^+ complex **9** as a triflate salt; b) I^--driven reversible transition between i) gel and ii) solution state (adapted from Ref. [21]); c) triazole-Au^+ complex **10**; d) emission control of supramolecular gels by the addition of Ag^+/Cl^- (adapted from Ref. [22]).

an alkyl-substituted pyrazole-Au^+ trinuclear complex (**10**, Figure 5c) that forms a red-emissive supramolecular gel ($\lambda_{em}=640$ nm, $\lambda_{ex}=284$ nm) from hexane; on the addition of AgOTf, the gel is transformed into a blue-emissive gel ($\lambda_{em}=458$ nm, $\lambda_{ex}=370$ nm), which re-forms into the red-emissive gel on the addition of Cl^- as a cetyltrimethyammonium salt (Figure 5d). In this system, the Ag^+ ions, which are associated with Au^+ ions through metal-metal interaction, are partially inserted into the stacking planes of the trinuclear complexes and create a space between the planes. It is this Ag–Au interaction in the blue-emissive gel that is interfered with by the added Cl^- ions, which associate with the Ag^+ ions to re-form the red-emissive gel. Control of RGB colors by physical and chemical stimuli has been achieved by using a green-emissive solution ($\lambda_{em}=510$ nm, $\lambda_{ex}=370$ nm), which is obtained by heating a blue-emissive gel.[22]

Anions can indeed control the state of a gel without the need for specific interactions with the gelators (molecules or complexes). For example, Lee et al. prepared a dendrimer-like oxyethylene-substituted bispyridine derivative (**11**, Figure 6a) that forms coordination polymers or oligomers by Ag^+ complexation, such as dispersed helical structures and discrete cyclic conformations; the morphologies of the organized structures depend on the coexisting counter anions such as NO_3^-, BF_4^-, and $CF_3SO_3^-$. The assembled structures can be modulated by the electrostatic interactions between **11**·Ag^+ and the anions, the ionic radii of which are crucial to determining the morphologies. These dispersed and discrete coordination assemblies from **11**·Ag^+ gelate methanol; this observation suggests the formation of soft materials derived from the different topologies of coordination polymers and oligomers. The addition of F^- to the BF_4^- salt of **11**·Ag^+, which has entangled helical conformation in the gel state, results in a transformation into the solution state including free monomers **11** by formation of the AgF salt. Furthermore, $C_2F_5CO_2^-$ addition also transforms the helical structure in the gel to the fairly dispersed assemblies of linear polymers, thereby affording the solution state. In all these cases, reversible transition between the solution and gel states has been observed (Figure 6b).[23]

Pyrrole-Based Anion-Responsive Supramolecular Gels from Dipyrrolyldiketone BF_2 Complexes

Thus far, anion-responsive supramolecular gels have been illustrat-

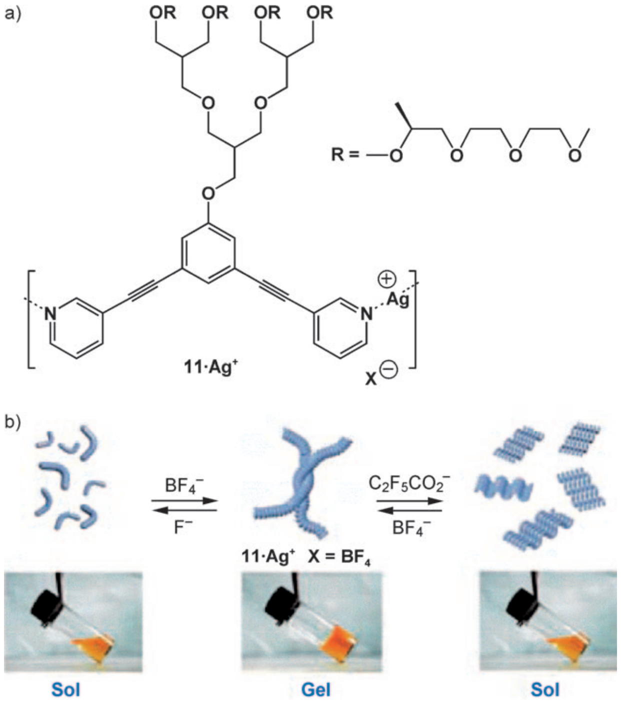

Figure 6. a) Ag^+ complex of dendrimer-like oxyethylene-substituted bispyridine derivative **11**·Ag^+; b) reversible transitions between the morphologies of the coordination polymers and the corresponding gel/solution states by anion exchanges (adapted from Ref. [23b]).

ed. To systematically examine anion-controllable gels systems, the synthesis of a series of anion-responsive gelator molecules that can be modified to form appropriate structures for desired functional materials should be considered. However, current investigations on such anion-responsive supramolecular gels appear to be quite primitive. Recently, my group at Ritsumeikan University began to focus on the synthesis of acyclic π-conjugated molecules with hydrogen bonding donor pyrrole NH site(s).[24] In these four years, we have synthesized and investigated the "molecular flippers" formed by BF_2 complexes of 1,3-dipyrrolyl-1,3-propanediones (e.g., **12a**,**b**, **13a**,**b**; Figure 7a) with planar structures, and have found that these acyclic receptors efficiently bind anions by using pyrrole NH and bridging CH sites with the inversion (flipping) of two pyrrole rings (Figure 7b).[25,26] These dipyrrolyldiketone BF_2 complexes have flexible and acyclic conformations, but form fairly planar structures in both the anion-free and anion-complex states and are, therefore, potential building subunits that can be used to form organized structures through the stacking of π-planes. X-ray structure analysis in the solid state has revealed the J-like stacking structures of the planar anion receptors (Figure 7c) and "charge-by-charge" structures that consist of receptor–anion complexes and tetraalkylammonium cations (e.g., TBA salt of **13b**·Cl^-; Figure 7d). Furthermore, modification at the periphery of the receptors makes it possible to stabilize the stacking structures in the solution state, not only in the solid state; for example, the introduction of various additional interaction moieties at the α-aryl-rings enables to the formation of molecular assemblies as soft matter that exhibit specific properties.

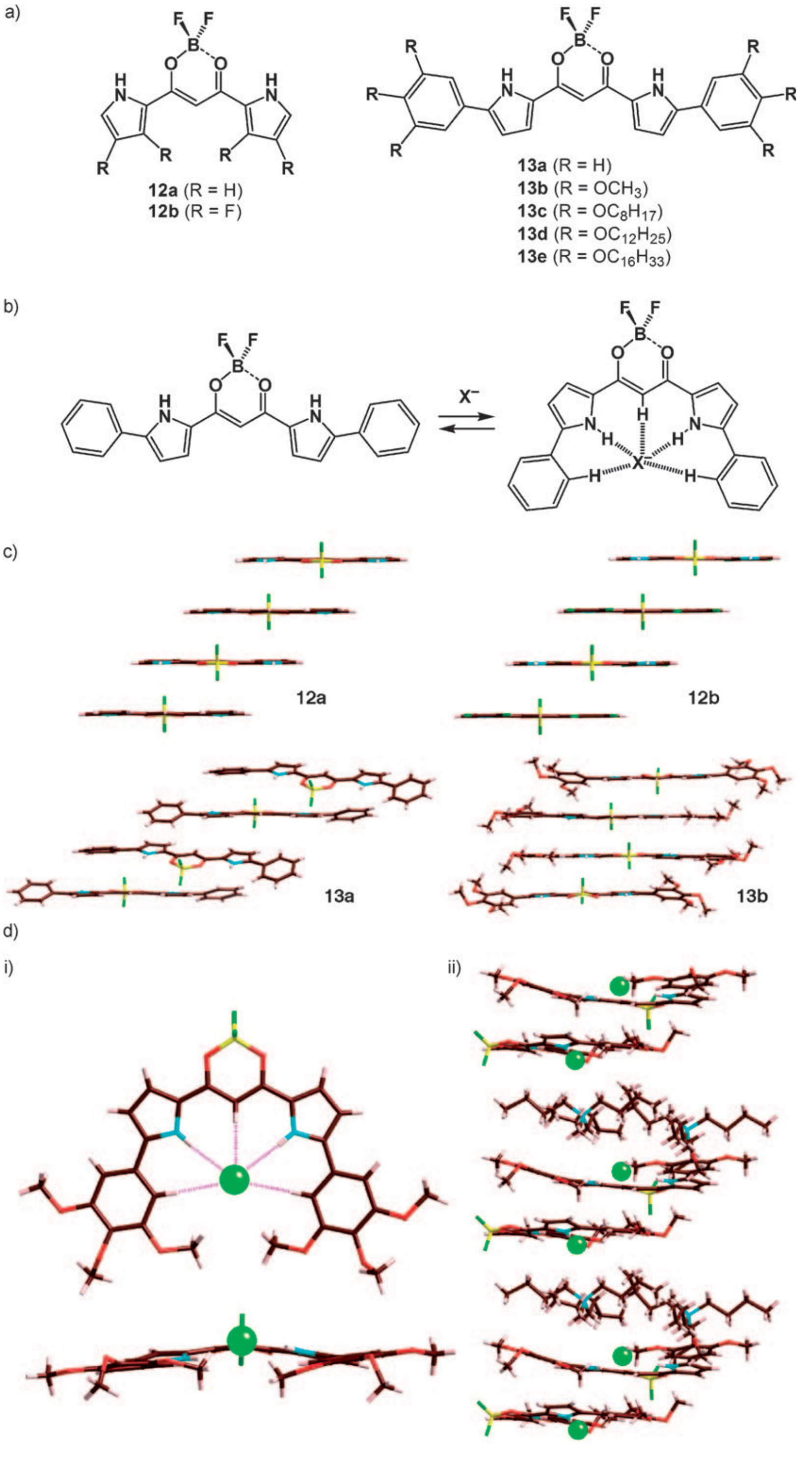

Figure 7. a) Acyclic anion receptors **12a**,**b** and **13a**–**e**; b) anion binding mode of **13a**; c) stacking structures of the anion receptors in the solid state; d) i) single molecular structure (top and side view) and ii) "charge-by-charge" structure of anion complex **13b**·Cl^- in the solid state.

Anion receptors with long alkyl chains (**13c**–**e**) have been obtained by the condensation of arylpyrroles and malonyl chloride and subsequent treatment with BF_3·OEt_2. These anion receptors gelate octane ($10\,mg\,mL^{-1}$); the transition temperatures between the gel and solution states have been found to be $T = -8.5$ (**13c**), 4.5 (**13d**), and 27.5 °C (**13e**), suggesting that the longer alkyl chains afford more stable gels. The octane gel of hexadecyloxy-substituted **13e** (10 mg mL^{-1}) exhibits split absorption bands, for example, absorption maxima at $\lambda = 525$ and 555 nm with a shoulder at $\lambda = 470$ nm; this is in contrast to the single peak at $\lambda = 493$ nm exhibited by diluted solutions containing the dispersed monomers. This observation suggests that the gels are possibly derived from assemblies consisting of both H- and J-aggregates. The octane gel has been found to exhibit emission at $\lambda = 654$ nm (excited at $\lambda = 470$ nm), which is red-shifted compared to that in the diluted condition ($\lambda_{em} = 533$ nm, $\lambda_{ex} = 493$ nm). The addition of TBA salts of anions (10 equiv) in solid form to the fluorescent octane gel results in the transition to solution state (Figure 8a); the gels are gradually transformed to solutions beginning from areas at which the solid salts have been added. The time required for complete transition depends on the type of anion employed. These transitions are significantly affected by the diffusional efficiencies of the TBA salts to the gel; in other words, once the receptor (gelator) molecules in the gel bind to the anions, the counter TBA cations, in a concerted manner, approach the anion-receptor complexes to remove the solvent molecules from the entangled fibers and afford the octane solution (Figure 8b). These transitions, in the case of the gel of **13e**, are quite distinct from the crystal states mentioned in the former part of this section (e.g., **13b**·Cl$^-$; Figure 7d), which are due to the insolubility of the TBA salt of **13b**·Cl$^-$ in apolar hydrocarbon solvents. In contrast, the absorption and emission spectra of the gel of **13e** are changed after the addition of anions suggest that the transitions are from the molecular assemblies to the dispersed monomeric states.[26a] Although intermolecular N−H···F−B hydrogen bonding may also be essential,[27] this system is a prototypical example of supramolecular gels that use π–π interactions as the main force for aggregation. Thus, anions as additives may not always act as inhibitors but also the building units of the soft materials. From this point of view, structural modifications of the anion receptors and the choice of appropriate combinations of anions, cations, receptors, and solvents are currently being investigated in order to harness the fascinating properties of supramolecular gels that are sensitive to chemical stimuli.[28]

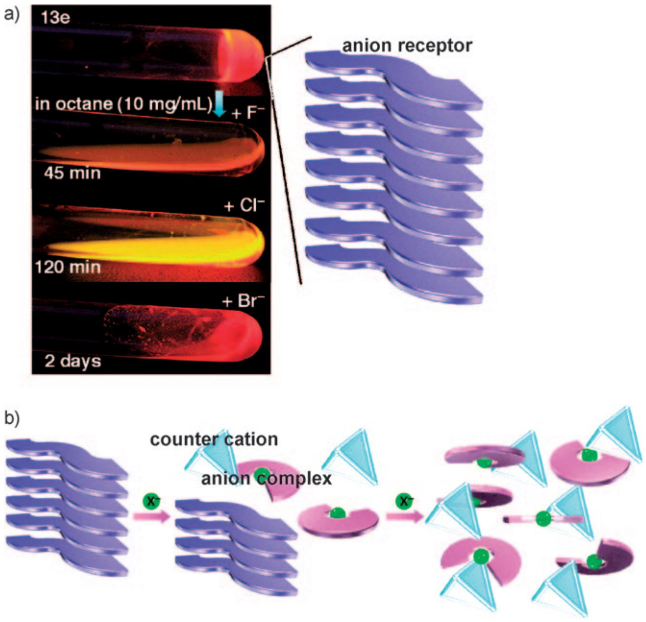

Figure 8. a) Anion-responsive behavior of octane gel of **13e** (10 mg mL^{-1}, under UV light at $\lambda = 365$ nm); b) possible anion-responsive process of gel-to-solution transition.

Conclusion

It seems unsurprising that supramolecular gels, as dimensionally controlled organized structures consisting of anion receptors, can be tuned and modulated by the interactions between the anions and binding sites or metal cations that are essential to the formation of the gels. However, these observations, which simply display the roles of anions mainly as inhibitors of gel formation, represent the "initial state" in the creation of anion-controllable functional materials. In this context, under the appropriate conditions, various anions can be incorporated into the organized structures as versatile negatively-charged building subunits with counter-cationic components. Therefore, the use of suitable anionic species as well as their counter cations will make it possible to tune and control the structures and properties of these materials, thereby making them practical. The use of appropriate molecular design and fine synthetic procedures for the subunits (gelators) will allow the formation of not only various anion-responsive supramolecular gels, but also other soft materials such as liquid crystals, colloids, micelles, etc., simply by the addition of anions.

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