Highlight Review

Electro- and Photoactive Molecular Assemblies of Liquid Crystals and Physical Gels

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Abstract

Self-organized structures of liquid crystals and self-assembled fibers have great potential as new functional materials. This article highlights self-organization of π-conjugated molecules, leading to the induction of photonic, electronic, and electrochemical properties.

◆ Introduction

Soft materials such as polymers, gels, and liquid crystals have attracted much attention because of their dynamic properties and easy processiblities.[1–12] Our strategy has been to develop new functional soft materials that show dynamic function using ordered molecular assemblies.[4–8,12] Liquid crystals are unique because molecular order and dynamic states are combined.[3–8] Liquid crystals exhibit a variety of ordered nanostructures as well as the simplest nematic structures that are widely used for informational display. Nanostructures of liquid crystals such as bicontinuous cubic, smectic, columnar, and micellar cubic phases (Figure 1) can serve as ordered functional materials. Phase transitions of these liquid-crystalline (LC) structures can also be used for the induction of dynamic properties. Unconventional molecular shapes as well as simple rod and disk shapes can function as mesogens.[3–7,13] Moreover, control of intermolecular interactions such as hydrogen bonding, ionic interactions, and charge-transfer interactions as well as π–π and van der Waals interactions is important in the design of these ordered soft materials.[5–8] Physical gels are soft composite materials consisting of solvents and self-assembled networks of gelators.[10–12] These gels form microphase-separated structures (Figure 2a). Gelators are low-molecular-weight molecules that form one-dimensional fibrous solid aggregates through hydrogen bonding or π–π interactions. The physical gels show sol–gel transitions because of noncovalent assembly. We have developed LC physical gels as a new class of soft materials (Figure 2b). For these materials, anisotropic solvents serve as functional fluids or templates for ordering of fibrous aggregates.

In this highlight review, we focus on our recent development of electro- and photofunctional liquid crystals and physical gels. Our basic materials design is the introduction of electro- and photoactive moieties such as π-conjugated systems into the molecular components of liquid crystals and physical gels. These functional groups align in the LC nanostructures, which result in the induction of anisotropy and enhanced functions. As the first topic, we describe electroactive liquid crystals based on oligothiophene, triphenylene, and viologen. We then show some examples of photoactive LC materials. In the last section, electro- and photoactive gels are described.

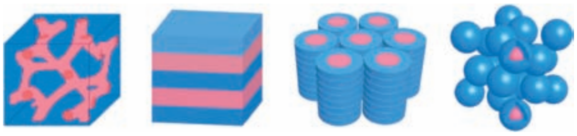

Figure 1. Schematic representations of liquid-crystalline nanostructures: bicontinuous cubic, smectic or lamellar, columnar, and micellar cubic.

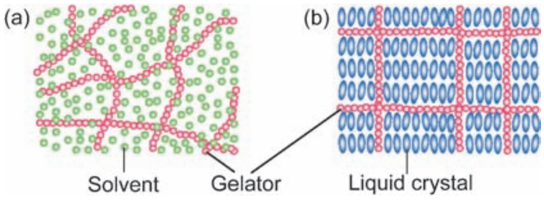

Figure 2. Schematic representations of (a) normal physical gels and (b) LC physical gels.

◆ Electroactive Liquid Crystals

Introduction of electroactive moieties into self-assembled structures is a promising approach toward the development of new electroactive materials.[14–16] If the electroactive molecules form LC structures, anisotropic electrical and electrochemical functions can be obtained. Tabushi and co-workers have reported viologen-based liquid crystals.[14a] Deschenaux and co-workers have prepared fullerene- and/or ferrocene-containing liquid crystals which exhibit redox-active properties.[14b,14c] Chang, Kitagawa, and co-workers have demonstrated cyclic voltammetric responses of a $\mathrm{Pt^{II}}$-containing metallomesogen in the LC phase.[14d] We have reported columnar liquid crystals containing redox-active units such as tetracyanoanthraquinodimethane (TCAQ),[15a] viologen,[15b] and oligothiophene.[16] All these compounds are susceptible to electrochemical oxidations or reductions. For example, oligothiophene **1** (Figure 3), which exhibits an LC columnar phase from 110 to 151 °C, is oxidized at the half-wave potential ($E_{1/2}$) of 0.35 and 0.61 V vs. $\mathrm{Fc^+/Fc}$, revealed by cyclic voltammetry.

Electrochromism is one of the significant features of redox-active materials. The spectroelectrochemical behavior of these materials was investigated by UV–vis absorption spectrosco-

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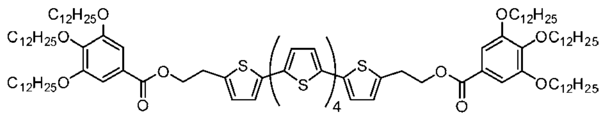

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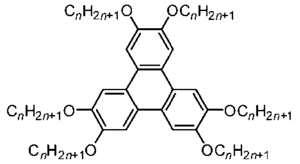
Figure 3. Molecular structures of an LC oligothiophene.



2a (*n* = 5)
2b (*n* = 6)
2c (*n* = 7)
2d (*n* = 8)
2e (*n* = 9)

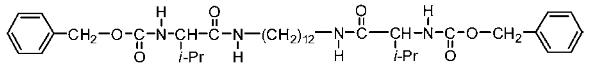


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Figure 4. Molecular structures of LC triphenylenes **2a**–**2e** and a hydrogen-bonded gelator **3**.

py.[16a] For example, the neutral form of oligothiophene **1** exhibits an absorption band centered at 440 nm. When the applied potential is increased from 0 to 0.6 V, the intensity of this absorption decreases and new absorption bands centered at 630 and 1130 nm emerge, which originate from the radical cation species of the oligothiophene core, accompanied by evident color change from yellow to blue. This electrochromic behavior of this compound is also observed in the LC state.

The LC columnar structures of oligothiophenes are capable of transporting charges. Oligothiophene **1** in the isotropic phase shows slow hole-transporting properties of the order of 10^{-6} $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, revealed by time-of-flight measurement. When the sample is cooled to the isotropic–columnar phase-transition temperature, the hole mobility of **1** discontinuously rises by two orders of magnitude. On further cooling of **1** in the columnar phase, the mobility gradually increases up to 7×10^{-3} $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at 105 °C.

Introduction of fibrous networks into hole-transporting liquid crystals is a new approach for the enhancement of hole-transporting behavior.[17] The hole mobilities of the discotic LC physical gels consisting of LC triphenylenes **2a**–**2e** and a hydrogen-bonded gelator **3** (Figure 4) are higher than those of LC triphenylenes alone. The hole mobilities of **2a**–**2e** are of the order of 10^{-4}–10^{-3} $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, whereas those of the LC gels are 1–3 × 10^{-3} $\mathrm{cm^2\,V^{-1}\,s^{-1}}$. It is noteworthy that the mobilities in the LC gels are of the order of 10^{-3} $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, while those of liquid crystals **2a**–**2e** varies over one order of magnitude depending on the length of the alkyl chains (Figure 5). This behavior suggests that finely dispersed gel fibers may properly suppress molecular fluctuation of the liquid crystals, resulting in the formation of more rigid pathways for holes in the LC gels.

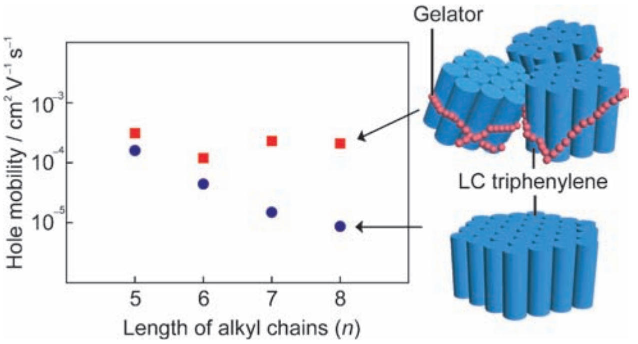
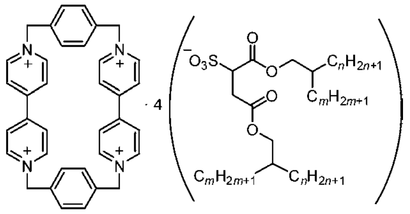
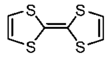


Figure 5. Dependence of the hole mobilities on the length of the alkyl chains of LC triphenylenes and schematic representations of gelation of LC triphenylenes.



4·5 (*n* = 4, *m* = 2)
4·6 (*n* = 6, *m* = 4)



TTF

Figure 6. Molecular structures of viologen-based cyclophanes and tetrathiafulvalene (TTF).

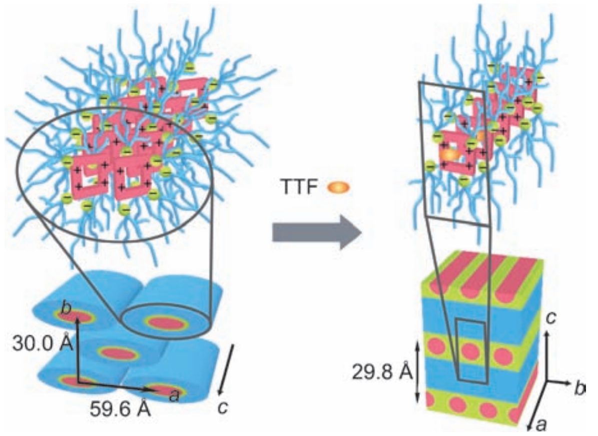


Figure 7. Schematic representation of the induction of the lamello-columnar phase for **4·6**/TTF (right) and the formation of the rectangular columnar phase of **4·6** (left).

Electroactive moieties can also be incorporated into cyclophane-based molecules. If redox-active cyclophanes form LC structures, guest recognition in aligned self-organized structures can be achieved. Recently, viologen-based LC cyclophanes have been reported (Figure 6).[18] Cyclophane **4·5** exhibits no mesomorphic properties without further addition of surfactants, whereas cyclophane **4·6** with longer alkyl chains exhibits LC properties. It is revealed that compound **4·6** forms a rectangular columnar structure and that when this compound is complexed with equimolar tetrathiafulvalene (TTF), a lamello-columnar phase is induced (Figure 7).

The existence of pseudorotaxanes where TTF molecules are located in the cavities of cyclophanes in the condensed states has been confirmed by cyclic voltammetry. Cyclic voltammogram obtained for **4·5**/TTF in a thin film state shows two successive oxidation waves (Figure 8) and a reduction wave. The two con-

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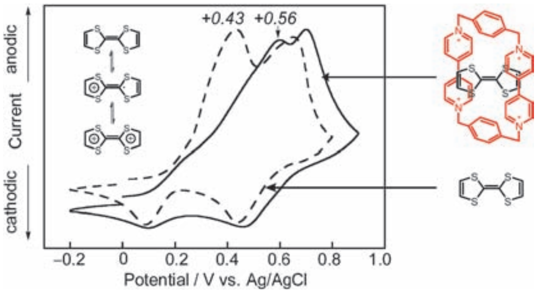

Figure 8. Cyclic voltammograms of **4·5**/TTF (1:1) (solid line) and TTF (dashed line) in thin films recorded in aqueous solutions of LiCl (0.10 M) with ITO working electrodes. The sweep rate is 30 mV s^{-1}.

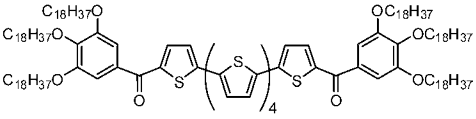

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Figure 9. Molecular structure of LC oligothiophene **7**.

secutive one-electron oxidations can be assigned to the formation of the radical cation and the dication species of TTF, respectively. The first oxidation for **4·5**/TTF occurs at the anodic peak (E_{pa}) of +0.56 V vs. Ag/AgCl, which is more positive in the position than that of TTF alone by ca. 0.13 V, suggesting that the inclusion complex between TTF and the cyclophane exists even in the condensed state.

◆ Photoactive Liquid Crystals

Use of LC materials for the development of photofunctional systems is attractive because photofunctions can be enhanced and tuned by molecular order and phase transitions.[19] Uniaxial molecular order of the LC structures induces such anisotropic photofunctions. For LC oligothiophene **7** (Figure 9),[16] which exhibits a hexagonal columnar phase from 102 to 117 °C, uniaxial orientation of the columnar structures is easily achieved by mechanical shearing of a polydomain sample of **7**. This aligned sample shows highly polarized red fluorescence with the peak at 610 nm (Figure 10). The polarization ratio of photoluminescence is ca. 11, which is nearly the same as the dichroic ratio of compound **7**.

Luminescent organic salts are a new class of materials sensing through electrostatic interactions.[20] For example, Bielawski and co-workers have reported luminescent ionic liquid crystals[21] based on benzobis(imidazolium) salts.

Recently, luminescent ionic liquid crystals based on tripodal pyridinium salts have been prepared (Figure 11).[22] These pyridinium salts **8a**–**8c** form columnar and/or micellar cubic structures over wide temperature ranges including room temperature. These pyridinium salts exhibit green photoluminescence (PL) emission both in solution and in the condensed states. As shown in Figure 12, the absorption and PL spectra of **8a** in a condensed state show peaks at 375 and 520 nm, respectively. These peak positions are almost the same as those in solution. Even when counter anions are changed, little change in the photophysical properties is observed, suggesting that the chromophores are cationic 3,4,5-trialkoxyphenyl moieties, which are electronically isolated from each other because of their mutual electrostatic repulsion even in the condensed states.

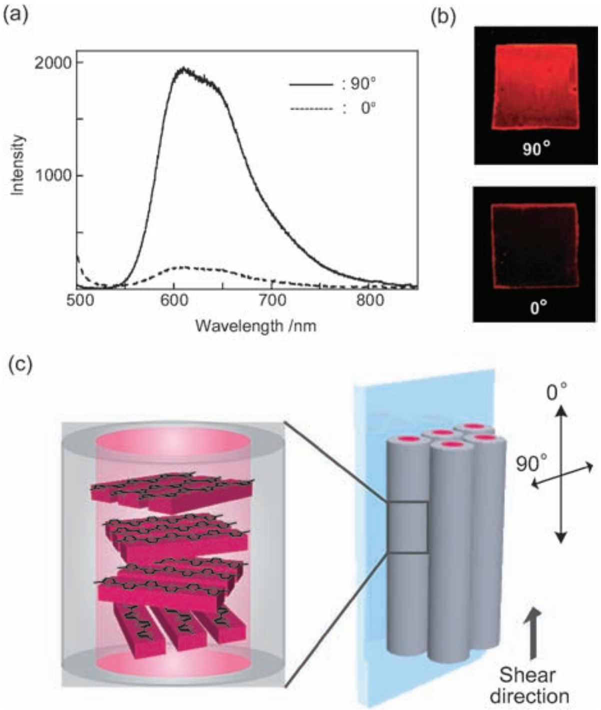
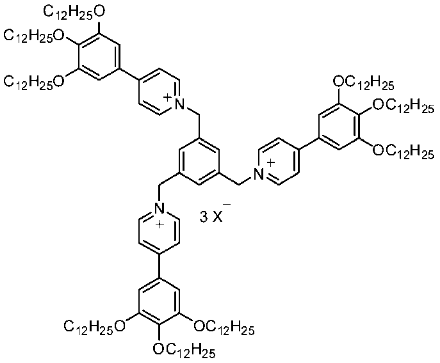


Figure 10. (a) Polarized photoluminescence spectra of a uniaxially aligned film of **7** under excitation at 488 nm, recorded through an emission polarizer set to perpendicular (solid line) and parallel (dashed line) to the shearing direction. (b) Photographs showing anisotropic emission of light from the aligned sample. (c) Schematic representations of the alignment of LC oligotiophenes.



8a (X = PF_6)
8b (X = BF_4)
8c (X = Br)

Figure 11. Molecular structures of liquid-crystalline tripodal pyridinium salts **8a**–**8c**.

◆ Electroactive Gels

Gelation of LC molecules is a promising approach toward the fabrication of a new class of ordered functional materials.[12] The formation of anisotropic phase-separated structures, which consist of liquid crystals and fibrous aggregates, can induce the enhancement of a variety of properties.

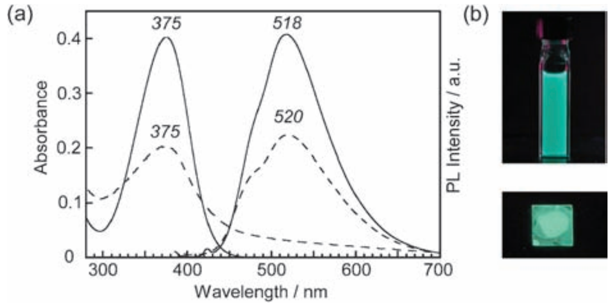


Figure 12. (a) UV–vis absorption and PL spectra of **8a** in a dichloromethane solution (solid line) and in a thin film (dashed line). (b) Photographs showing PL emission of **8a** in a solution and in a thin film.

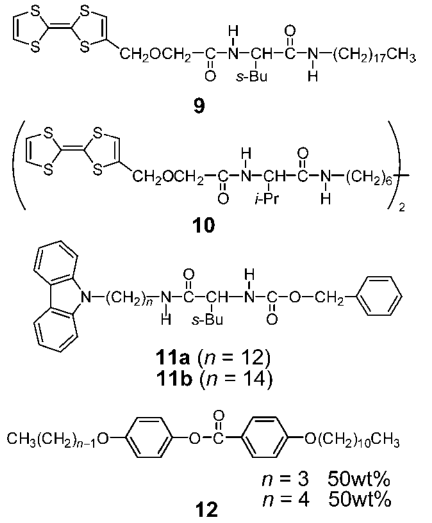


Figure 13. Molecular structures of electroactive gelators **9**–**11** and liquid crystal **12**.

TTF is known as an organic conductive material.[23] The introduction of electroactive moieties into self-assembled fibers may be a promising approach to the fabrication of a new class of functional materials.[24] In particular, if TTF moieties form one-dimensional stacks in liquid crystals, aligned electroactive fibers can be obtained. TTF derivatives **9** and **10** and carbazole derivatives **11a** and **11b** have amino acid scaffold as gel-forming units (Figure 13). They self-assemble into fibrous aggregates, resulting in gelation of aromatic liquid crystals.[25] In a nematic liquid crystal, randomly dispersed fibers are obtained, whereas aligned fibers are formed in a homogeneously oriented smectic liquid crystal **12**, which functions as a template for the alignment of the fibers. Polarized IR measurements of the oriented fibers show that **9** and **10** form intermolecular hydrogen bonding in the parallel β-sheet conformation and that the hydrogen-bonded chains formed by amino acid moieties align along the fiber direction. TTF moieties form H-aggregates in the fibers, revealed by UV–vis absorption measurements of TTF derivatives in the sol and gel states.

The electrical conductivities of randomly dispersed fibers of the TTF derivatives have been measured before and after iodine doping. The doping of the fibers leads to the formation of charge-transfer (CT) states, revealed by UV–vis–NIR measurements.

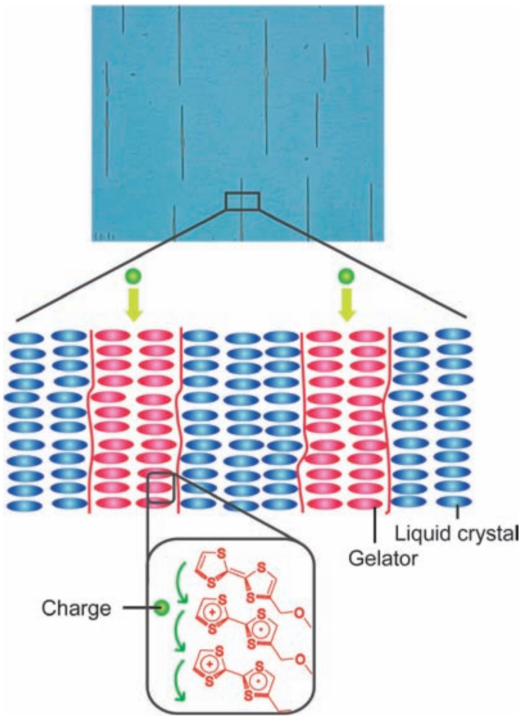


Figure 14. A photomicrograph and schematic representations of the oriented fibrous aggregate in the LC physical gel of **9**.

The conductivity of the fibers before doping is below $3 \times 10^{-10}\,\mathrm{S\,cm^{-1}}$, suggesting that the fibers behave as insulators. The conductivity increases immediately after doping up to $2 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$ with a new absorption band at 850 nm, which suggests that a full CT state is formed. The full CT state changes to a more stable mixed-valence state with a new absorption band around 2300 nm. One week after doping, the maximum conductivity of $3 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ is observed in the stable mixed-valence state (Figure 14). The XRD measurements of the fibers reveal that the molecular assembled structures are not disturbed by iodine doping.

♦ *Photoactive Gels*

The modulation of luminescent properties is also an important approach to the preparation of photofunctional materials. Self-assembly of luminescent molecules often affect luminescent color. Among self-assembled luminescent materials, fibrous aggregates are considered to be promising materials.[26] The luminescent properties can be tuned by their structures on the sol–gel transition.

To prepare self-assembled fibers with tunable fluorescent properties, luminescent pyrene units have been introduced into dendritic amino acid derivative through amide bonds (Figure 15a).[27] Pyrene derivative **13** efficiently gelates a variety of organic solvents. The infrared spectra of the gel of **13** indicates that the intermolecular hydrogen bonds between amide groups are formed, which promotes gelation. The XRD, UV–vis, and circular dichroism (CD) measurements of pyrene derivative **13** reveal that the fibrous aggregates of **13** are composed of self-assembled helical columnar structures, at the center of which pyrene moieties are located.

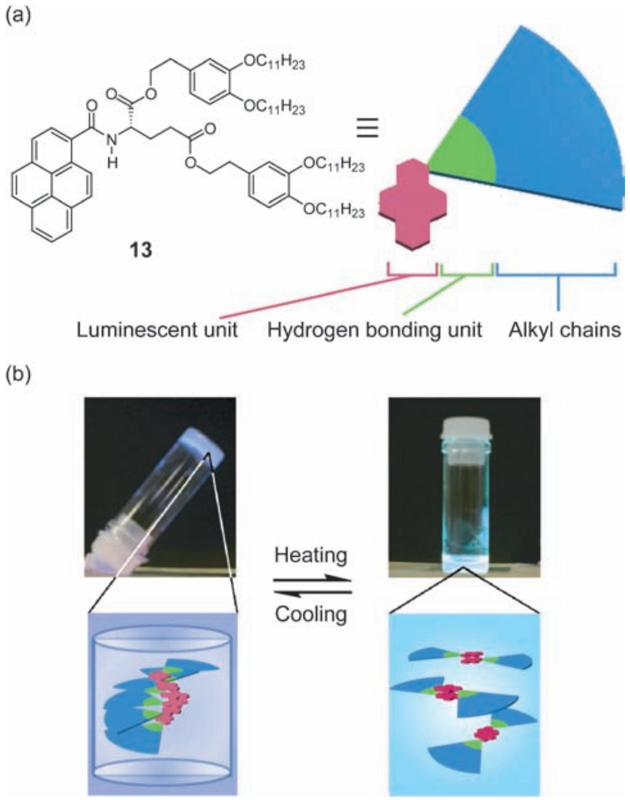


Figure 15. (a) Molecular structure of a pyrene-containing amino acid. (b) Photograph of the fluorescent gel (left) and sol (right) states of **13** and schematic illustration of the self-assembly in the gel state (left) and the excimer formation in the sol state (right).

Emission color changes are observed for compound **13** between sol and gel states under photoirradiation (Figure 15b). For the emission spectrum of **13** in the sol state, a broad structureless emission band around 480 nm is seen. On the other hand, the emission band of **13** in the gel state ($\lambda_{\max} = 396$ and 412 nm) is blue-shifted from that of **13** in the sol state. This spectral shift corresponds to the emission color change from bright-green to violet. These results are indicative of the excimer emission of pyrenes in the sol state and the monomeric emission of pyrene in the gel state of **13**. Due to the helical alignment in the gel state of **13**, pyrenes are located in the positions difficult to form excimers.

The gel–sol transitions of gels containing photochromic gelators can be induced by light irradiation as well as application of heat. Several examples of such photoresponsive gel–sol transitions have been reported.[28–30] Shinkai and co-workers have demonstrated that cholesterol derivatives containing azobenezene moieties show photoinduced sol–gel transition, triggered by cis–trans isomerization of azobenzene moieties.[28a]

Hydrogen-bonded gelator **14** containing two azobenzene units has been prepared (Figure 16).[29,30] This compound gelates organic solvents such as cyclohexanone and dodecylbenzene (Figure 17a) as well as liquid crystals by hydrogen bonding. After UV irradiation upon a gel of **14**, trans-to-cis isomerization of azobenzene moieties are induced, leading to the gel-to-sol transition (Figure 17a → 17b) with the dissociation of hydrogen bonding. When a visible light irradiates the sample in the sol state, the hydrogen-bonding is recovered, which triggers the reformation of the gel (Figure 17b → 17c). These properties are caused by the change in the polarity of the gelator, due to photoisomerization of azobenzene moieties.

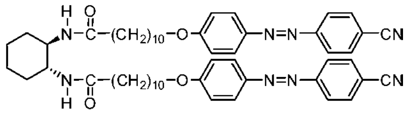


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Figure 16. Molecular structure of a gelator containing azobenzene moieties.

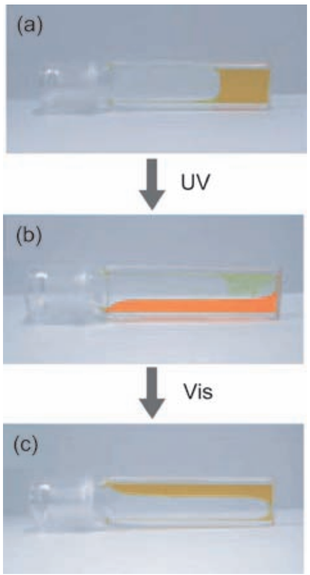

Figure 17. Photographs of **14** in cyclohexanone in the (a) gel state, (b) sol state after UV light irradiation, and (c) gel state after visible light irradiation.

◆ Summary and Outlook

We have described our recent results of functional molecular assemblies of liquid crystals and physical gels. To achieve anisotropic and enhanced properties, control of molecular order of these materials is one important factor. For nematic liquid crystals used for informational display, alignment is controlled by an alignment polymer layer. The nematic monodomain is formed and molecular order is dynamically switched by electric fields. But for nanostructured liquid crystals, such as smectic, columnar, and bicontinuous cubic phases, we cannot yet perfectly control the molecular order and properties of liquid crystals. Very recently, we have succeeded in the induction of columnar order by applying electric fields.[31] However, precise control of molecular order is still challenging.

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