

## REVIEW

# Functional liquid-crystalline polymers and supramolecular liquid crystals

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The design and functions of liquid-crystalline (LC) polymers with classifying them into conventional-, supramolecular-, dendritic- and network-type LC polymers are described. LC polymers show new functions as new devices in the field of energy and environment by incorporating mesogenic moieties exhibiting photonic, electronic and ionic functions. Supramolecular LC polymers show dynamic and unique properties because the mesogenic moieties are built with non-covalent interactions. Dendritic-type LC polymers exhibit liquid crystallinity by nanosegregation of aromatic and aliphatic moieties. Dendritic fork-like mesogens have also been prepared. A variety of nonmesogenic functional building blocks including fullerene,  $\pi$ -conjugated moieties, catenane, rotaxane and others can be incorporated into LC phases by attaching these dendritic moieties. LC networks are constructed *in situ* polymerization of polymerizable nematic or nanostructured liquid crystals. The specific characteristics of the LC networks have generated new research trends to develop well-defined polymers that exhibit optical, transport and separation properties. In these materials, through suitable design of LC monomers, the preservation of smectic, columnar and bicontinuous cubic phases has been successfully used for the development of membranes with one-dimensional, two-dimensional and three-dimensional nanostructures.

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## INTRODUCTION

Liquid-crystalline (LC) polymers have attracted attention for these five decades since the discovery of LC states of synthetic rigid-rod polymers.<sup>1–3</sup> The well-designed LC polymer structures are expected to be useful in a variety of fields of new devices, energy, environment, resources and biotechnologies (Figure 1). In the history of synthetic LC polymers, aromatic polyamides **1** having rigid-rod structures were discovered to show lyotropic LC phases in 1960.<sup>4</sup> The processing of these polymers in aligned LC states leads to the formation of high-modulus high-strength fibers. In 1976, aromatic polyester **2** and polyazomethines were reported to exhibit thermotropic LC properties.<sup>5,6</sup> Since then, a variety of LC main-chain polymers have been extensively studied.<sup>5–7</sup> Representative molecular structures of the main-chain and side-chain LC polymers are shown in Figure 2. Side-chain polymers **3** and **4** have also been obtained in early 1980.<sup>8–10</sup> They were expected to show electro-optical effects and film-forming abilities.<sup>9</sup>

LC polymers having a variety of functional groups have been extensively studied (Figure 3). For example, functional main-chain LC polymers **5** have been prepared to exhibit electron conductivities and luminescence properties.<sup>11,12</sup> Photofunctional,<sup>13,14</sup> electro-active,<sup>15–18</sup> and ion-active<sup>19–24</sup> groups have been incorporated into the side chains of LC polymers. For example, LC polymers **6** and **7** bearing electro-active moieties are obtained by using  $\pi$ -conjugated molecules as

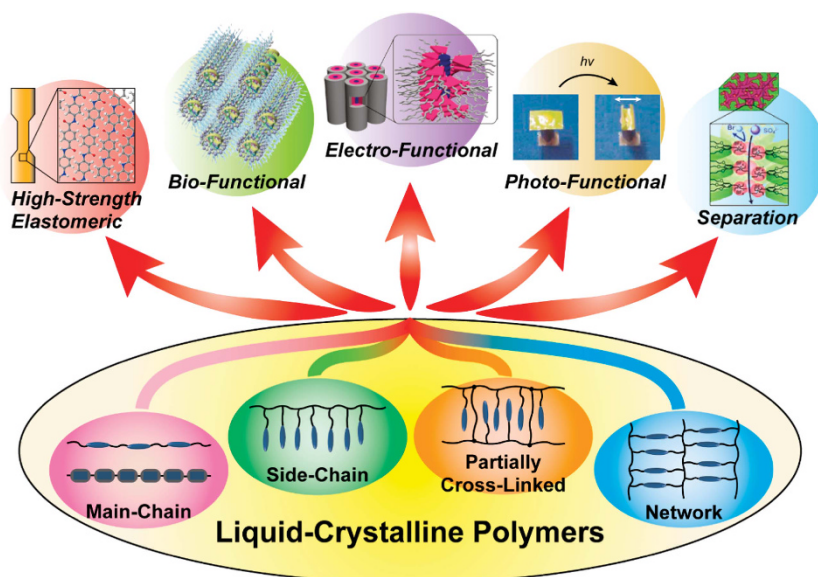
mesogenic units.<sup>15–18</sup> The introduction of azobenzene moieties into the side chain of LC polymers leads to the development of photo-responsive optical systems **8** and photo-actuators.<sup>25,26</sup> Anisotropic two-dimensional (2D) ion-conductive materials **9** and **10** are achieved by incorporation of ionic moieties or oligo(oxyethylene) units complexed with inorganic salts in the spacer or the terminal group of the side-chain LC polymers.<sup>19–22</sup> Side-chain-block LC polymers were prepared for membrane applications.<sup>27,28</sup>

In addition to these conventional structures of covalently bonded main-chain and side-chain LC polymers, newly designed functional LC polymers have been developed since late 1980's.<sup>1,2,29,30</sup> Supramolecular hydrogen-bonded LC polymers emerged by introducing supramolecular chemistry into the design of LC polymers.<sup>31–39</sup> These polymers were firstly prepared through the formation of complementary hydrogen bonds by Kato and Frechet<sup>37</sup> and Lehn,<sup>38</sup> respectively. They exhibit LC phases in their bulk states. It should be noted that non-covalent interactions can be used for the functional LC design.<sup>29,40</sup> Supramolecular approach is now well recognized and used as a new design strategy of a variety of molecular-based functional materials as new molecular architecture.

As new structures for polymer backbones, dendritic structures have been introduced to the design of LC polymers.<sup>41–44</sup> There are two types: the first type is dendrimers having many mesogenic rigid-rod groups;<sup>41,42</sup> the second type is dendrimers that show LC phases due to

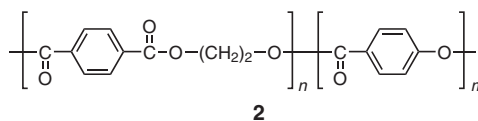
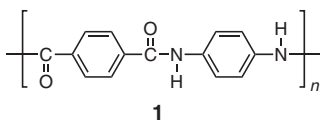
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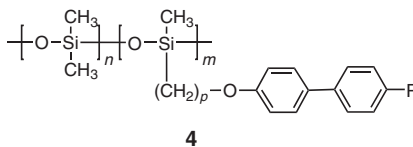
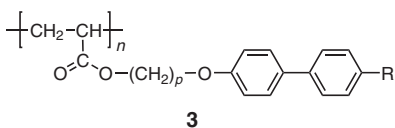


**Figure 1** Design and applications of liquid-crystalline polymers. Reproduced with permission from Wiley-VCH, American Chemical Society and Springer Nature.

#### Main-chain LC polymers



#### Side-chain LC polymers



**Figure 2** Representative molecular structures of historical LC polymers. LC, liquid crystalline.

nanosegregation.<sup>43,44</sup> This second type shows liquid crystallinity without rigid-rod mesogenic groups.

Network structures and partial cross-linked structures of the LC polymers are also useful to tune and preserve specific properties of the polymers.<sup>45</sup> Highly cross-linked side-chain-type polymers<sup>45–47</sup> and network polymerizable functional molecules<sup>48,49</sup> have been prepared to develop free-standing and mechanically tough functional polymers.

In this review, we describe development of new functional LC polymeric materials.

### SUPRAMOLECULAR DESIGN OF LC POLYMERS

The preparation and functionalization of polymeric LC assemblies based on supramolecular design are described in this section. The supramolecular approach has been utilized for the preparation of main-chain, side-chain and network LC polymers. These supramolecular LC polymers offer a unique platform for the development of dynamic functional materials.

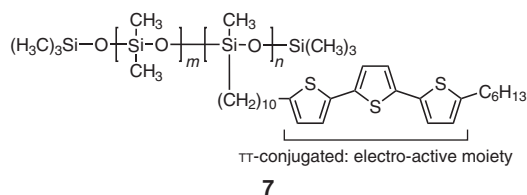
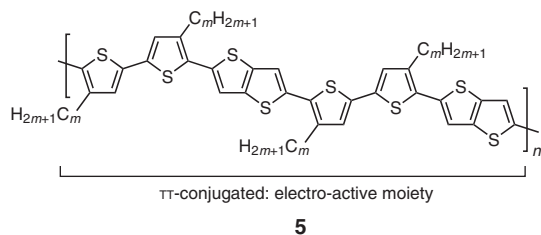
The first supramolecular hydrogen-bonded LC polymers were side-chain LC polymers **11** formed by complexation of the benzoic acid moieties in the side chain with stilbazoles (Figure 4a).<sup>37</sup> A variety of polysiloxane-based<sup>50–52</sup> and polyacrylate-based<sup>53,54</sup> side-chain LC polymers have been obtained by the formation of supramolecular mesogens through a variety of hydrogen bonds. Nonmesogenic poly

(vinylpyridine) (PVP)<sup>55–59</sup> and poly(acrylic acid) (PAA)<sup>60</sup> were also used to prepare LC polymers by the complexation with complementary hydrogen-bond donors or acceptors. A main-chain polyamide incorporating 2,6-bis(amino)pyridine units can form supramolecular complexes with a biphenylcarboxylic acid.<sup>61–63</sup> The direct attachment of supramolecular mesogens to the polymer backbone results in stabilization of the induced smectic A phase over 350 °C.

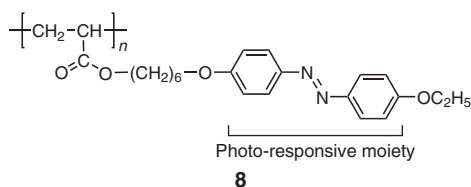
Main-chain supramolecular LC polymers were built through the formation of hydrogen bonds between two complementary bifunctional components (Figure 4b).<sup>38,39,64–66</sup> LC polymeric complex **12** was prepared through the formation of triple hydrogen bonds.<sup>38,65</sup> The influence of chirality on the mesomorphic behavior of the supramolecular polymers was studied. In a similar manner to the hydrogen-bonded side-chain LC polymers,<sup>37,50–63</sup> main-chain LC polymer **13** was synthesized by using hydrogen bonds between pyridines and benzoic acids. The complex exhibited nematic and smectic phases.<sup>39</sup> LC polymeric merocyanine dye assemblies exhibiting columnar phases were also obtained by combining triple hydrogen bonds and  $\pi$ - $\pi$  aggregation.<sup>66</sup>

Use of multifunctional components for the formation of non-covalent interactions can produce supramolecular LC network structures.<sup>67–69</sup> One of representative examples is self-assembled LC polymer network **14** formed by complexation of 4,4'-bipyridine and

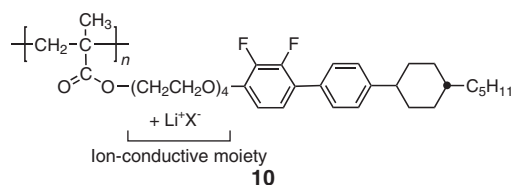
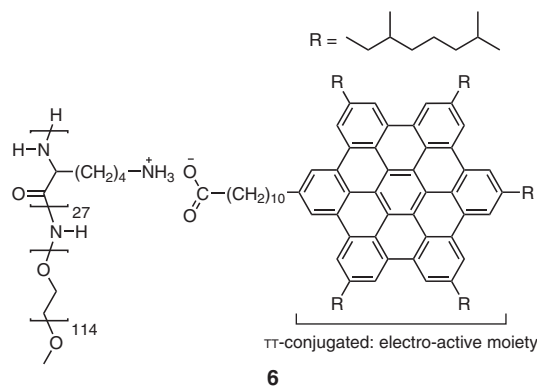
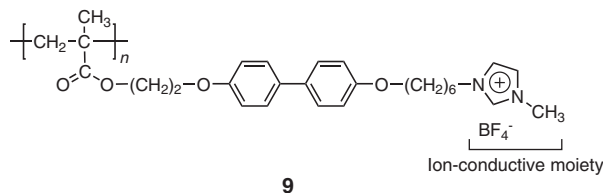
## Electro-active



## Photo-active



## Ion-active



**Figure 3** Representative molecular structures of functional LC polymers. LC, liquid crystalline.

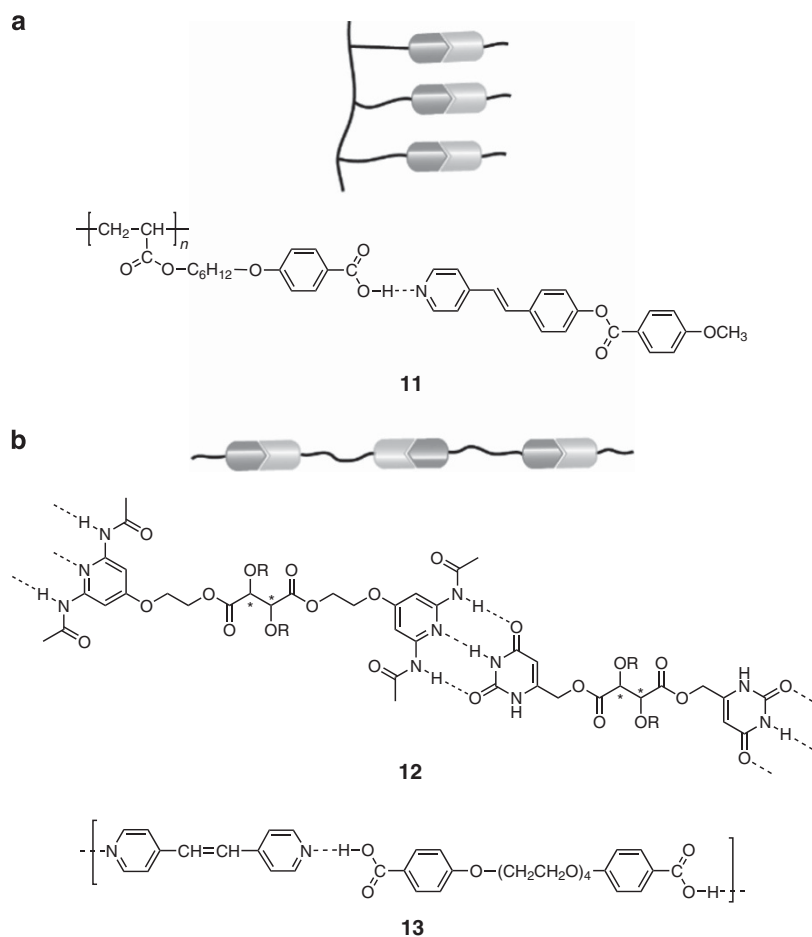
hydrogen-bond donor polymer (Figure 5).<sup>67</sup> In the network structures of **14**, 4,4'-bipyridine recognizes carboxylic acid moieties and functions as a cross-linker. Remarkably, these LC networks show reversible phase transition between isotropic and LC phases due to dynamic properties of hydrogen bonds, which is in contrast to covalently cross-linked networks. Another example is self-assembly of small molecular components to construct hydrogen-bonded network structures.<sup>68</sup> Trifunctional hydrogen-bond donors and bifunctional hydrogen-bond acceptors self-organize into nematic and smectic LC networks through the formation of hydrogen-bonded supramolecular mesogens. Chiral LC networks exhibiting cholesteric phases were also developed by using a chiral bispyridyl molecule as a cross-linker.<sup>69</sup> The helical structures of the cholesteric phase are preserved in the glassy state at room temperature.

Host-guest LC polymers built through the formation of inclusion complexes were reported.<sup>55,70–72</sup> Hydrogen bonds have a key role in the formation of host-guest complexes. Complexation of hydroxyl-functionalized polymers with clip molecules affords inclusion polymeric complexes exhibiting LC properties.<sup>70</sup> Phase transition behavior of the LC polymers is tuned by the ratio of host and guest molecules.

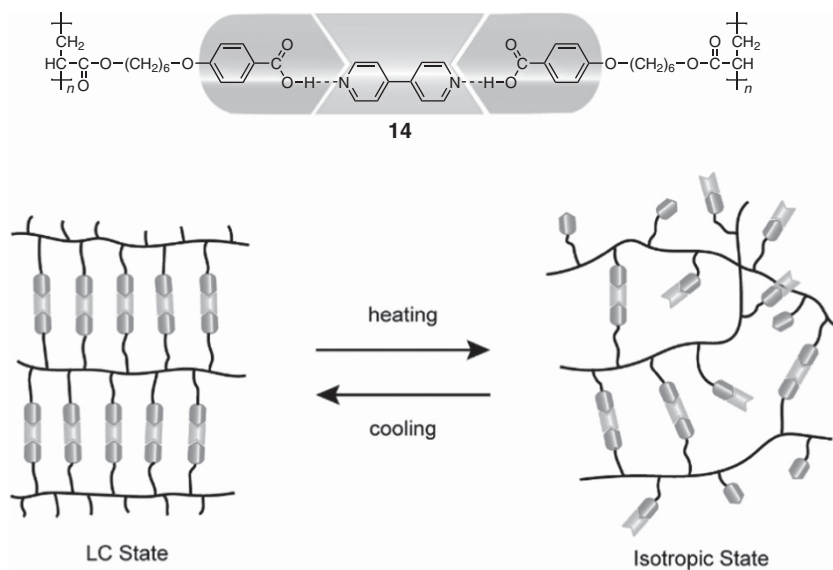
Main-chain host-guest LC polymers were developed by the formation of host-guest complexes.<sup>71,72</sup> In this case, two calixarene molecules are covalently connected through phenyl spacer, and therefore, polymeric complexes are formed by self-organization of calixarene moieties into capsules to show lyotropic LC behavior in chloroform.

The concept of hydrogen-bonded liquid crystals<sup>29–40</sup> has been extended to halogen-bonded LC complexes<sup>73–75</sup> because of the similarities of these non-covalent interactions. Halogen-bonded main-chain LC polymers were obtained by self-assembly of bifunctional halogen-bonding molecules.<sup>75</sup> In these polymeric complexes, interactions between fluoro-substituted iodobenzene and stilbazole moieties are used to form halogen-bonded adducts exhibiting LC properties.

Polyrotaxanes are mechanically interlocked polymers consisting of ring molecules threaded onto a linear polymer chain.<sup>76–80</sup> Ito and colleagues<sup>81</sup> attached mesogenic rigid-rod moieties to  $\alpha$ -cyclodextrin on the polymer backbone to synthesize LC polyrotaxanes. Detailed dielectric relaxation measurements revealed that the mesogenic moieties in LC polyrotaxanes can move and rotate around the main chain more easily than those in conventional side-chain LC



**Figure 4** Schematic illustration and representative molecular structures of (a) supramolecular side-chain LC polymer and (b) supramolecular main-chain LC polymers. LC, liquid crystalline. A full color version of this figure is available at *Polymer Journal* online.



**Figure 5** Schematic illustration and representative molecular structure of hydrogen-bonded LC network. LC, liquid crystalline. A full color version of this figure is available at *Polymer Journal* online.

polymers,<sup>82,83</sup> which provides potential applications for new stimuli-responsive materials. Main-chain LC polyrotaxanes were synthesized by polymerization of pseudorotaxane monomers prepared by intramolecular self-inclusion.<sup>84,85</sup> Formation of a cholesteric phase in a concentrated chloroform solution is confirmed by fingerprint texture observed under polarizing microscopy.

Ionic interactions based on ammonium moieties as cationic components have been employed for the formation of ionic LC polymers.<sup>86–94</sup> Ujiie and Imura<sup>88</sup> synthesized ionic LC polymers by appending azobenzene-based mesogens having ammonium groups to the poly(vinylsulfonate) through ionic interactions between ammonium and sulfonate moieties. They also studied the effects of ionic backbone on the LC behavior.<sup>89</sup> Ionic LC polymers with poly(ammonium salt) backbone exhibit smectic phases, while their non-ionic analogs show nematic phases. Acidic polymers such as PAA were used for complexation with amine-containing molecules to form ionic side-chain LC polymers.<sup>90–92</sup> LC properties were also induced for  $\omega$ - and  $\alpha,\omega$ -carboxylato and sulfonato polystyrenes by attaching ammonium-containing mesogens.<sup>93</sup> The design of ionic supramolecular LC polymers has been extended to the introduction of secondary structures into the polymers.<sup>15,94</sup> Müllen and co-workers synthesized side-chain LC polymer **6** through the formation of acid-base complexes composed of poly(ethylene oxide)-*block*-poly(L-lysine) (PEO-PLL) and carboxylic acid-functionalized hexa-*peri*-hexabenzocoronene (HBC).<sup>15</sup> The polymeric complex shows thermotropic LC phases, where the poly(L-lysine) backbones form helical structures surrounded by six discotic columns of hexa-*peri*-hexabenzocoronene. Furthermore, supramolecular helical polyacetylenes were prepared through ionic interactions between chiral acids and ammonium groups in the polymers.<sup>94</sup> The macromolecular helicity is amplified in the lyotropic cholesteric LC phases in water.

In addition to hydrogen bonds,<sup>29–40</sup> halogen bonds,<sup>74,75</sup> and ionic interactions,<sup>15,86–94</sup> charge-transfer interactions were applied for the preparation of supramolecular LC polymers.<sup>95,96</sup> Ringsdorf *et al.*<sup>95</sup> used charge-transfer interactions between electron-rich triphenylene and 2,4,7-trinitrofluorenone units to produce LC discotic polymers. Introduction of chirality into these charge-transfer polymeric complexes yields LC discotic polymers with helical order of the columns.<sup>96</sup>

On the basis of the supramolecular design described above, functional supramolecular LC polymers have been developed (Figure 6).<sup>51,97–105</sup> Ferroelectricity can be induced for hydrogen-bonded LC polymer **15** exhibiting chiral smectic C phases.<sup>51</sup> Chiral hydrogen-bond acceptors are used to form supramolecular LC polymers that show spontaneous polarization. Photonic materials made from hydrogen-bond donor polymer **16** and imidazole-containing mesogen **17** show interesting optical properties.<sup>97</sup> Reversible change of optical transmission in the visible region can be observed as a function of temperature because refractive indices of the LC materials change with the order parameter. Fluorescent supramolecular LC polymers with rigid bis(phenylethynyl)benzene moieties were constructed by the formation of hydrogen bonds between two complementary nucleobase-terminated monomers **18** and **19**.<sup>98</sup> Polarized emission and photoluminescent color tuning of fluorene derivatives were also reported by using photoreactive hydrogen-bonded LC polymers.<sup>99</sup> Photo-responsive materials were developed based on azobenzene-containing LC supramolecular polymer networks.<sup>100</sup>

Supramolecular LC polymers have been applied for ion- and electron-conductive materials.<sup>101–105</sup> Ikkala and co-workers described the development of nanostructured proton-conductive polymers combining hydrogen bonds and ionic interactions.<sup>101–103</sup> Supramolecular polymer **20** is composed of diblock copolymer poly(styrene-

*block*-(4-vinylpyridine)] (PS-*b*-PVP), *p*-toluenesulfonic acid and pentadecylphenol.<sup>103</sup> They have hierarchical nanostructures with multiple length scales, which results in anisotropic proton conduction. Using this approach, polyaniline-based supramolecular LC materials that show electrical conductivity were also reported.<sup>104</sup> Percec *et al.*<sup>105</sup> employed charge-transfer interactions to prepare electron donor-acceptor LC polymeric complexes with electronic functions. One-dimensional LC ordered structures of the electron donor-acceptor complexes are stabilized by self-assembly of acceptor polymer **21** and fluorine-substituted donor dendron **22**. The mobilities of electron donor-acceptor polymeric complexes are much higher than those of related donor and acceptor molecules in the amorphous state.

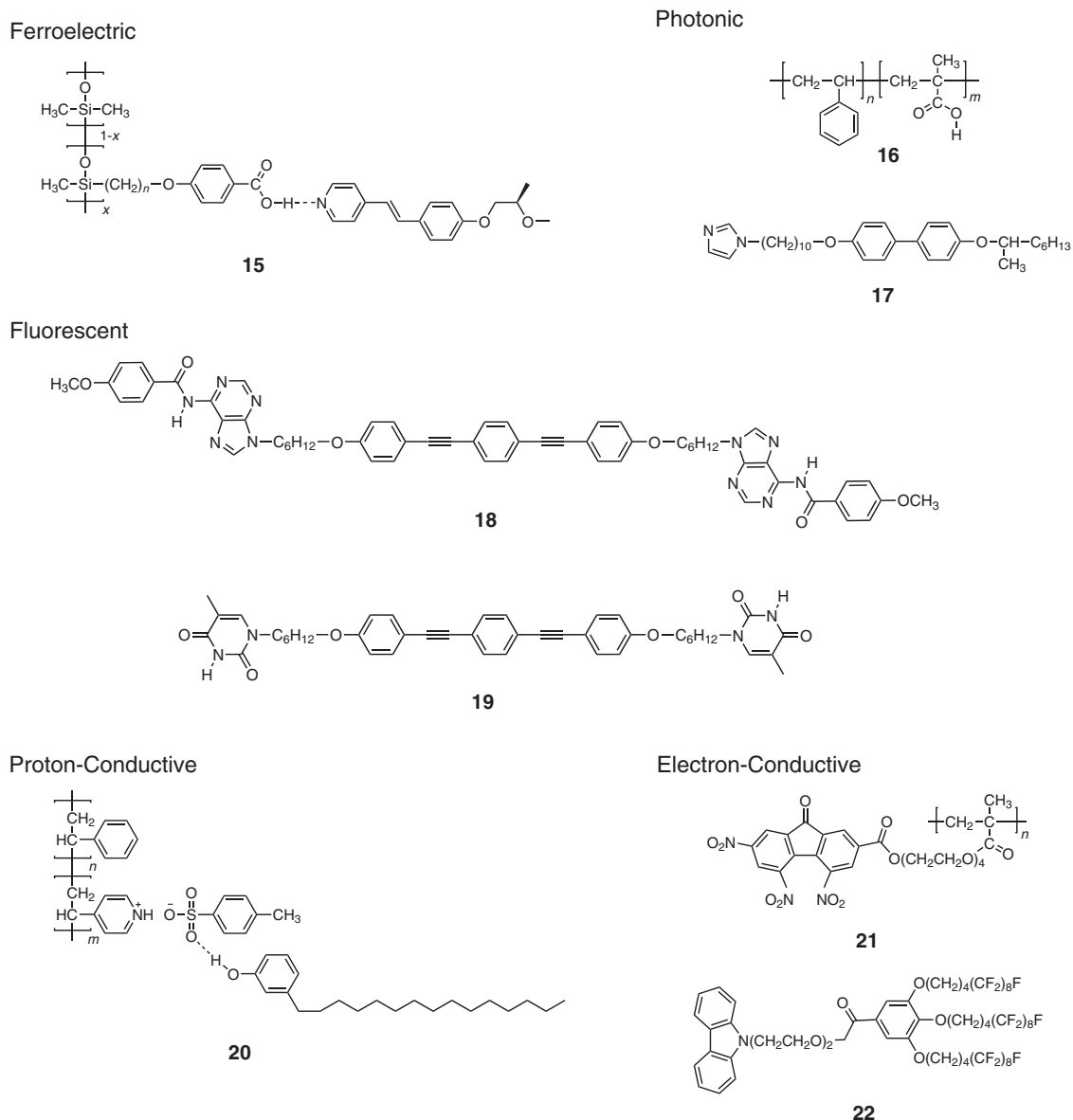
## DENDRITIC DESIGN FOR LC POLYMERS

The design of LC polymers has been applied for the development of LC dendritic molecules.<sup>43,44,106–108</sup> Dendrimers and dendrons are a class of macromolecules with repetitive branching units, which have attracted growing interest in polymer and materials science.<sup>109,110</sup> LC molecules with dendritic structures exhibit unique self-assembled behavior and functions.<sup>43,44</sup> Some representative dendritic LC molecules are shown in Figure 7. In the early stage of LC dendrimer, Percec *et al.*<sup>111</sup> synthesized and characterized thermotropic nematic LC dendritic polymer **23**. They have extended the design of LC dendrimers to cone-shaped and semicircular dendrons, which exhibit micellar cubic and columnar phases, respectively.<sup>112</sup> The LC phases can be systematically modulated by changing the volume of dendritic moieties.<sup>113,114</sup>

Attachment of rigid-rod mesogenic moieties on the terminal position of the dendrimers can produce LC dendritic molecules.<sup>41,42,115–117</sup> Shibaev and Frey elaborated LC carbosilane dendrimers decorated with terminal mesogenic groups.<sup>41,115</sup> In these molecules, the mesogenic groups are arranged only in the periphery of the dendritic macromolecules,<sup>41,115</sup> which is in contrast to the early example reported by Percec.<sup>111</sup> The type of LC phases depends on chemical nature of the terminal mesogenic groups.<sup>116</sup> Poly(amidoamine)<sup>118</sup> and poly(propyleneimine)<sup>119</sup> dendrimers have also been functionalized with mesogenic molecules at the periphery to exhibit mesomorphic behavior.<sup>42,117</sup>

The dendritic design is effective to induce liquid crystallinity for complex molecules.<sup>120–124</sup> Silsesquioxanes have been used as scaffolds of supermolecular liquid crystals because organic substituents can be easily tethered to the vertices of the polyhedra.<sup>120,121</sup> Mehl and Goodby<sup>122</sup> reported octasilsesquioxane dendrimers exhibiting LC phases by introducing cyanobiphenyl mesogens on the periphery. The mesomorphic properties can be tuned by number, density and orientation of the attachment of rigid-rod moieties bound to the central cores.<sup>123</sup> In general, laterally attached mesogens induce nematic phases, whereas terminally attached mesogens afford smectic phases.<sup>120,121</sup> By combining these two different types of mesogens, 'Janus' liquid crystal **24** has been developed.<sup>124</sup> The type of LC phases of the Janus molecules is dependent on the overall topology of the molecules.

Combination of the dendritic design and functional molecules provides dynamic self-assembled materials.<sup>125–130</sup> Fullerenes are representative electro-functional molecules that have been incorporated into LC dendrimers.<sup>125–127</sup> Chuard and Deschenaux<sup>128</sup> synthesized LC fullerenes by appending the cholesterol mesogens to the core structures. The generations, mesogenic groups and linkers of the LC dendrimers have a key role in determining the self-assembled behavior of the dendritic liquid crystals.<sup>125</sup> A variety of LC fullerenes with electro-active moieties have been reported.<sup>129,130</sup>

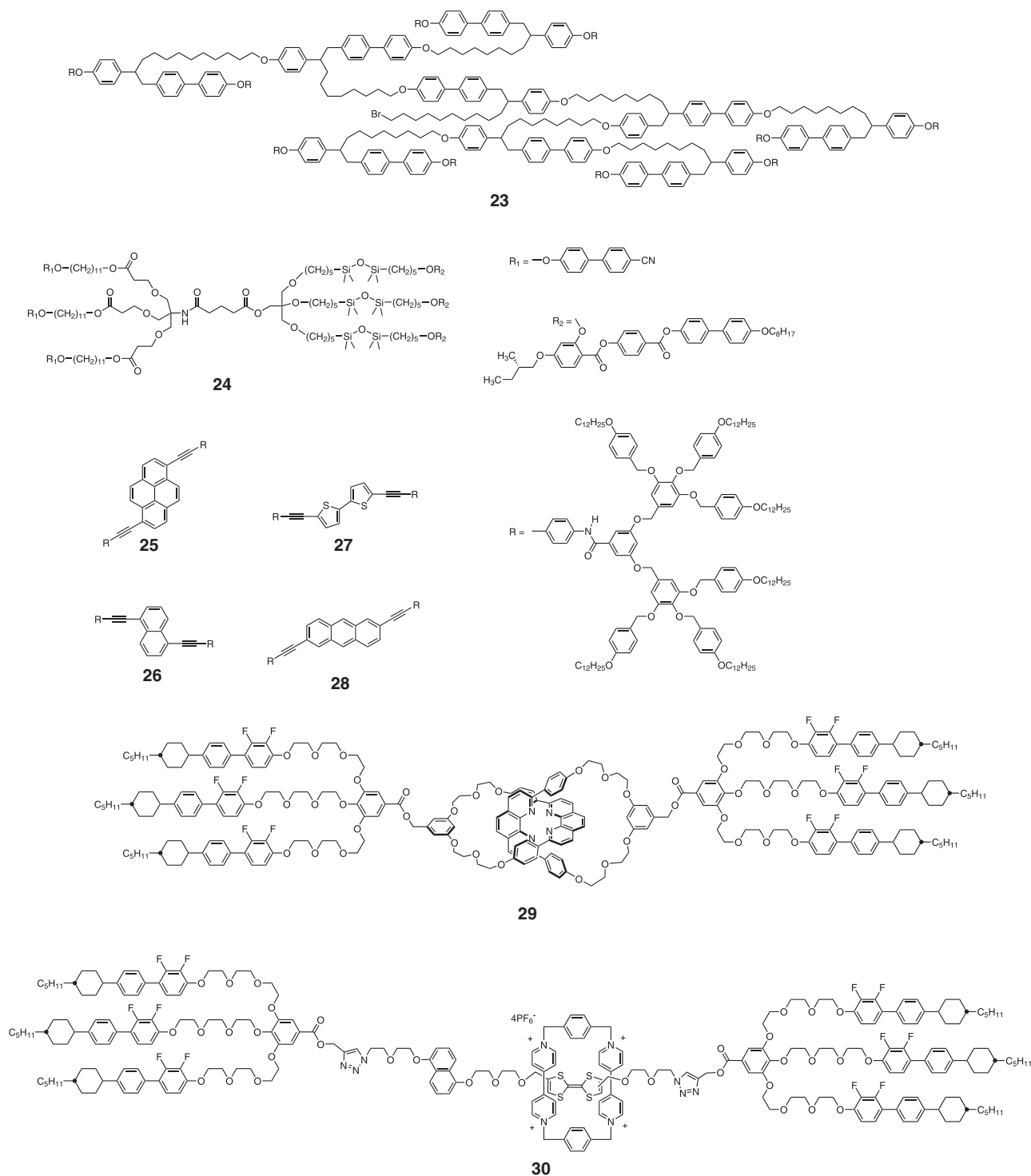


**Figure 6** Representative molecular structures of functional supramolecular LC polymers. LC, liquid crystalline.

Stimuli-responsive luminescent liquid crystals have been developed based on dendritic design.<sup>131–133</sup> Sagara and Kato reported mechanochromic liquid crystals consisting of  $\pi$ -conjugated organic molecules and dendritic side chains.<sup>134</sup> Pyrene,<sup>134</sup> naphthalene,<sup>135</sup> oligothiophene<sup>136,137</sup> and anthracene<sup>138–141</sup> derivatives have been used as the central luminescent cores of the dendritic molecules. For example, fan-shaped dendrons have been employed to prepare luminescent compounds 25–28. Bianthryl-based liquid crystals have also been obtained by attaching fork-like mesogens to the luminescent core moiety.<sup>142</sup> The photoluminescent color change is observed for these molecules upon shear-induced phase transition.<sup>133–139,142</sup> Some  $\pi$ -conjugated LC molecules with branched or dendritic side chains show unique mechanochromic properties such as reversible luminescent color change<sup>137</sup> and tricolored luminescence.<sup>139</sup> The type of LC phase transition depends on the molecular structures of dendritic moieties. Cubic-columnar phase transition is observed for the luminescent molecules with fan-shaped dendrons,<sup>133–136,138,139</sup> while

smectic-smectic phase transition is induced for those with fork-like mesogens<sup>143</sup> composed of rigid-rod mesogenic moieties.<sup>140,142</sup>

Metal-containing LC dendrimers show interesting functions such as luminescent, magnetic and redox properties.<sup>144</sup> The properties can be modulated by the design of dendritic ligands and metal centers. Dendritic ligands are often used to induce mesomorphic properties for discrete metal clusters such as polyoxometalates and metallic polyhedral clusters.<sup>145,146</sup> One approach for the preparation of LC clusters is to graft organic ligands on metal clusters through ionic interactions.<sup>146</sup> Self-assembly of ionic clusters and oppositely charged ligands provides dendritic and mesomorphic clusters. Another approach is to substitute mesogenic ligands for coordinating ligands that constitute the clusters.<sup>144,145</sup> Recently, the ligand exchange reaction has been utilized for the preparation of functional LC metal clusters.<sup>147–149</sup> Donnio reported mesomorphic dodecanuclear manganese complexes exhibiting magnetic properties through ligand exchange between dendritic benzoate ligands and acetate ligands of the



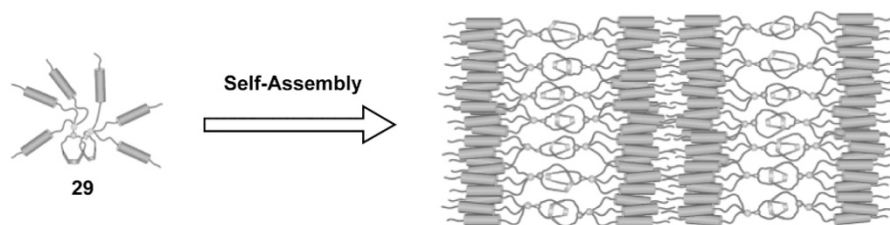
**Figure 7** Representative molecular structures of dendritic liquid crystals.

complexes.<sup>147,148</sup> In a similar manner, luminescent molybdenum octahedral clusters with dendritic structures have also been formed to exhibit LC smectic phases.<sup>149</sup>

LC dendrimers can be formed by attachment of mesogenic ligands on nanoparticles as the central scaffolds.<sup>150</sup> Major efforts have been made in the preparation of LC gold nanoparticles because control of their spatial arrangement has potential for the creation of

metamaterials.<sup>151</sup> The self-assembled structures of LC nanoparticles are controlled by the number, density and structures of ligands as well as particle size.<sup>150,151</sup> Calamitic,<sup>152</sup> discotic,<sup>153</sup> dendritic<sup>154,155</sup> and bent-core<sup>156</sup> moieties have been utilized as surrounding ligands of LC nanoparticles.

Introduction of dynamic and ordered states of liquid crystals into supramolecular complexes such as catenanes and rotaxanes has



**Figure 8** Schematic illustration of self-assembled structure of LC catenane. LC, liquid crystalline. Reproduced with permission from Wiley-VCH. A full color version of this figure is available at *Polymer Journal* online.

potential for the development of smart dynamic materials.<sup>80</sup> Dendritic structures are useful to organize such large-sized objects into LC nanostructures.<sup>80,144,150,151</sup> Fork-like mesogenic dendrons have been applied for the induction of smectic LC phases for supramolecular catenane **29** and rotaxane **30**.<sup>157–160</sup> For example, self-assembly of LC catenane **29** with fork-like mesogens into layered nanostructures is illustrated in Figure 8. LC rotaxane **30**, on the other hand, exhibits redox-switchable mechanical motion of a cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring accompanied by electrochromic behavior in the LC state.<sup>160</sup> Another example of supramolecular dendritic systems is formed by self-assembly of biomolecular derivatives.<sup>161–167</sup> Some of folic acid derivatives show ion-responsive phase transitions from smectic to columnar phases.<sup>161</sup> The design of these supramolecular assemblies has been extended to ion-conductive<sup>164,166</sup> and luminescent<sup>167</sup> materials.

### FUNCTIONAL LC POLYMERS AND NETWORKS

LC molecules consisting of two or more incompatible parts spontaneously form various nanosegregated structures, such as layered, cylindrical and globular structures.<sup>30,106</sup> Recently, growing attention has been paid to use of these nanosegregated liquid crystals as transport materials because of the formation of well-organized nanochannels structures.<sup>19,168–180</sup> These LC low-molecular weight molecules are easy to orient, and show one-dimensional, two-dimensional and three-dimensional (3D) transport features. However, they are in general soluble in organic solvents and exhibit poor mechanical properties that compromise their robustness and stability for being applied in devices or as functional coatings and membranes. One strategy to overcome this problem is polymerization and cross-linking of the self-organized LC molecules into LC networks with preserving the periodic nanostructures.<sup>30,49,181–187</sup> This process certainly reduces the mobility and dynamic nature of the LC arrays, but drastically improves the mechanical properties of the samples and their thermal stability.

There are some important processes for transforming nanosegregated liquid crystals into nanostructured LC networks (Figure 9): (1) introduction of polymerizable group into LC molecules; (2) spontaneous self-organization of the LC monomers; (3) alignment of LC domains in a macroscopic scale if necessary; and (4) *in situ* polymerization.

When one aims to construct LC networks with 1D, 2D and 3D nanochannels, the use of columnar, smectic and bicontinuous cubic LC monomers are required. Remarkably, the formation of the LC phases can be, in some extent, controlled by careful molecular engineering to obtain these LC phases.<sup>19,168–180</sup> The resulting phase is crucial because it determines the nature of the transport properties including their anisotropic properties.

Some representative LC monomers exhibiting thermotropic and lyotropic LC phases are shown in Figure 10. Compound **31** forms a

Col<sub>h</sub> phase from 20 to 50 °C.<sup>48</sup> Without special treatment, these columnar liquid crystals form a polydomain state. The creation of monodomain states with vertical and parallel alignment can be induced by chemical modification of the substrate of the surface and mechanical shearing, respectively. By performing photopolymerization process in the aligned states, self-standing polymer films with macroscopically oriented 1D ion channels have been successfully obtained. The formation of cross-linking network produces a decrease on the mobility of the component ions, which leads to the decrease of ionic conductivities. This drawback can be overcome by using supramolecular design of columnar liquid crystals. For example, the equimolar mixture of compound **32** and [bmim][Br] forms a Col phase from –10 to 41 °C.<sup>188</sup> The polymerization process has here a lower impact on the ionic conductivities than the previously described material.

For the alignment of columnar liquid crystals, various new techniques have been produced, such as applications of electric<sup>189,190</sup> and magnetic fields,<sup>191,192</sup> and other methods.<sup>193–196</sup> For compound **33a**, the macroscopic alignment of columns has been achieved by magnetic fields and the preservation of the 1D nanostructures has been also carried out.<sup>191,192</sup>

Nanostructured LC network design was also applied to the development of 2D ion transport polymer networks.<sup>20–22</sup> Kato and co-workers reported a series of rod-like mesogen bearing oligo (ethylene oxide) chains and polymerizable acrylate groups (compound **34**). These molecules form nanosegregated lamellar structures consisting of polar and non-polar layers. After addition of suitable inorganic salts, the polar layers constituted by the oligo (ethylene oxide) chains show ion transport features. The polymerization of the materials led to self-standing films with preserving the layered structures. These smectic phases were also aligned prior to their polymerization and the corresponding LC network films exhibited anisotropic ion transport. Broer and Schenning also prepared 2D ion channels by using LC mixtures of compound **35** and compound **36**.<sup>184</sup> Mixture of these compounds (10 wt% of compound **35**) forms a smectic phase that was photopolymerized forming thermally stable films. Interestingly, the resulting membranes could be swelled by cations upon uptake of alkaline water (NH<sub>4</sub>OH).

More recent efforts were directed toward the development of 3D ion channel networks based on Cub<sub>b</sub>i phases because these material does not require any alignment of LC domains in a macroscopic scale to optimize their transport efficiency.<sup>197–203</sup> In this regard, Gin and co-workers reported the wedge-shaped compound **33b** bearing acrylate polymerizable groups at the periphery of the three alkyl chains.<sup>198</sup> This molecule forms a lyotropic Cub<sub>b</sub>i phase (Q<sub>II</sub> phase) in the presence of lithium perchlorate and propylene carbonate. The photopolymerization of this mixture readily leads to thermally stable polymer films with a 3D structure exhibiting ionic conductivities in the order of 10<sup>–3</sup> S cm<sup>–1</sup>. Kato and colleagues<sup>199</sup> also achieved the



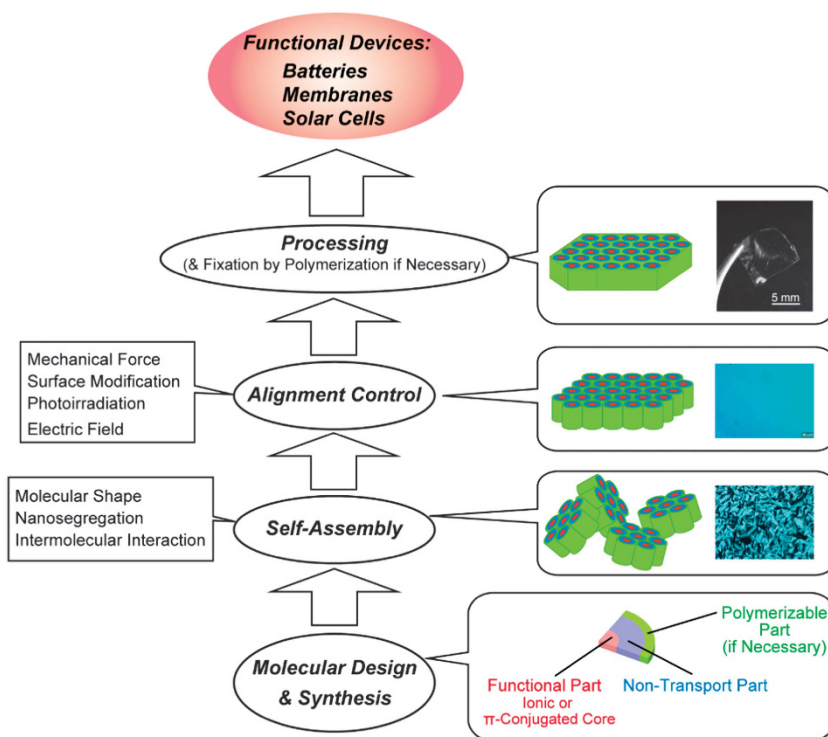


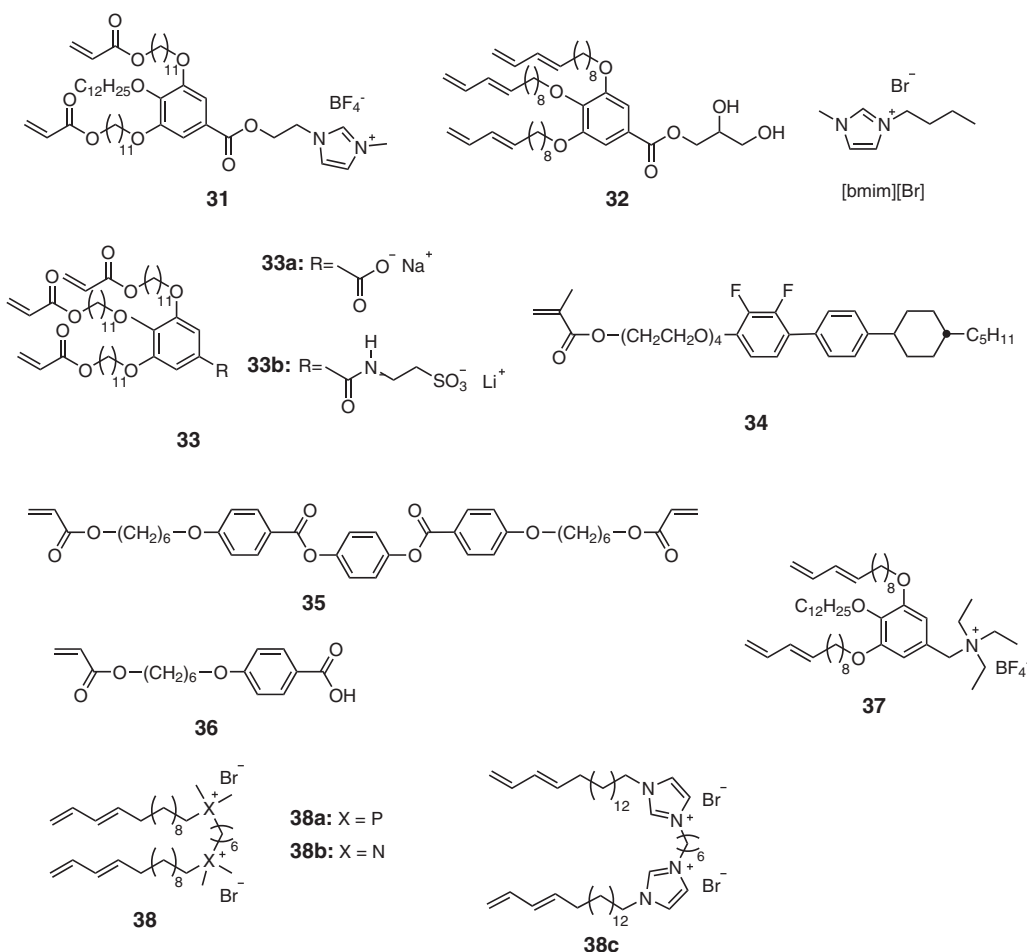
Figure 9 Design of nanostructured ion-conductive liquid-crystalline polymer films.

preparation of LC networks having 3D ionic nanochannels by designing ammonium-based thermotropic LC compound **37** that exhibits a  $Cub_{bi}$  phase from  $-5$  to  $19$  °C. The incorporation of  $LiBF_4$  to the 3D LC networks allowed the development of transparent lithium-ion conductor film (Figure 11).

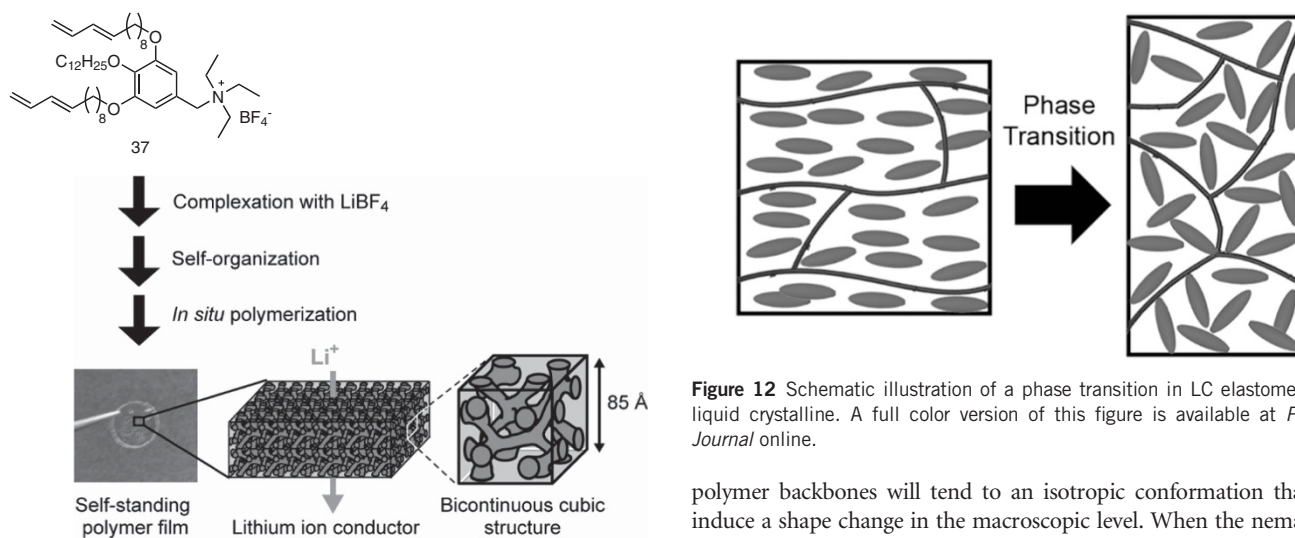
In the same vein, the polymerization of these nanostructured liquid crystals was employed to develop nano- and/or subnano-porous membranes for filtration and separation membranes.<sup>204–209</sup> For example, the 3D LC networks based on compound **37** have been used for separation membranes permeating selective ions. More recently, the application of these 3D LC networks for the rejection of virus has been also unveiled.<sup>205</sup> Gin and co-workers also successfully prepared 3D LC networks based on polymerized lyotropic liquid crystals for various applications, such as gas filtration and separation membranes.<sup>206–209</sup> For example, the sodium salt of acid compound **33a** was used to prepare composite membranes by employing polysulfone as support. The membrane showed selective filtration of anionic dyes from aqueous solutions. Gemini phosphonium, ammonium and imidazolium surfactants compound **38** were also applied to develop filtration membranes after polymerization of the lyotropic LC structures.<sup>207,209</sup> Compounds **38a** and **38b** form lyotropic bicontinuous cubic ( $Q_I$ ) phases ( $Pn3m$  or  $Ia3d$ ), which are normal-type lyotropic bicontinuous cubic phases, in the presence of water. These compounds were polymerized on porous substrates. Their ion rejection properties of the composite films were evaluated upon different aqueous solutions. Both compounds showed rejection as high as 90% for NaCl, KCl,  $MgCl_2$  and  $CaCl_2$  salts. In the case of compound **38c**,  $Q_I$  phases were prepared in the presence of glycerol instead of water, and the resulting membranes showed significant rejection properties of salts, but also of different small organic molecules such as sucrose and glucose.<sup>210</sup> These membranes seem to be operated by size exclusion. They exhibit well-defined structures of channels with homogenous size of pores, which allows the controlled selectivity.

While the covalent cross-linking of nanosegregated liquid crystals have been used to stabilize materials with transport functions, densely or fully covalent cross-linking of conventional nematic, cholesteric and smectic LC polymers have found other applications. For example, nematic LC networks have been widely investigated (Figure 1, right, bottom) and applied in display technologies, and in particular, in the confection of optical compensation films.<sup>211,212</sup> Dense cross-linked nematic and cholesteric materials still exhibit glass transitions (between 40 and 120 °C) that are also accompanied by shape deformations.<sup>45,184,213</sup> These properties have been exploited to prepare densely cross-linked nematic or cholesteric polymer networks with intriguing programmable stimuli-responsive properties after their careful alignment.<sup>46,47</sup> The orientation of the LC mixtures is typically induced prior their polymerization by different strategies such as patterned command surfaces or electric fields. In this regard, photopatterning has emerged as an efficient technique to prepare command surfaces for the development of exotic LC actuators.<sup>214–216</sup>

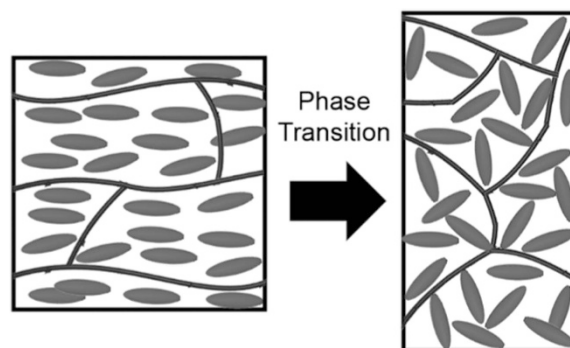
Introduction of densely cross-linked structures into liquid crystals induces stability and free-standing properties of the materials.<sup>50,67,184,217,218</sup> When partial cross-linked structure is introduced into polymers that exhibit LC phases (Figure 1, right, bottom), elastomeric properties emerge at ambient temperature.<sup>217–221</sup> Seminal studies of Finkelmann focused on the development of partially cross-linked side-chain LC polymers.<sup>222,223</sup> These polymers are self-standing materials that exhibit elastic properties and memory effects. Owing its properties, they are often described as LC elastomers.<sup>224</sup> These materials exhibit phase transitions that are often accompanied by shape deformations.<sup>45,217,218,225–227</sup> The basic principle behind the deformation in LC elastomers is depicted in Figure 12.<sup>217</sup> The polymer backbones experience an anisotropic environment in the presence of mesogenic groups. This provides certain order in the polymer chains that prevent the isotropic conformation. However, when the material experience a loss in the anisotropy (that is, isotropization), the



**Figure 10** Molecular structures of liquid-crystalline monomers.



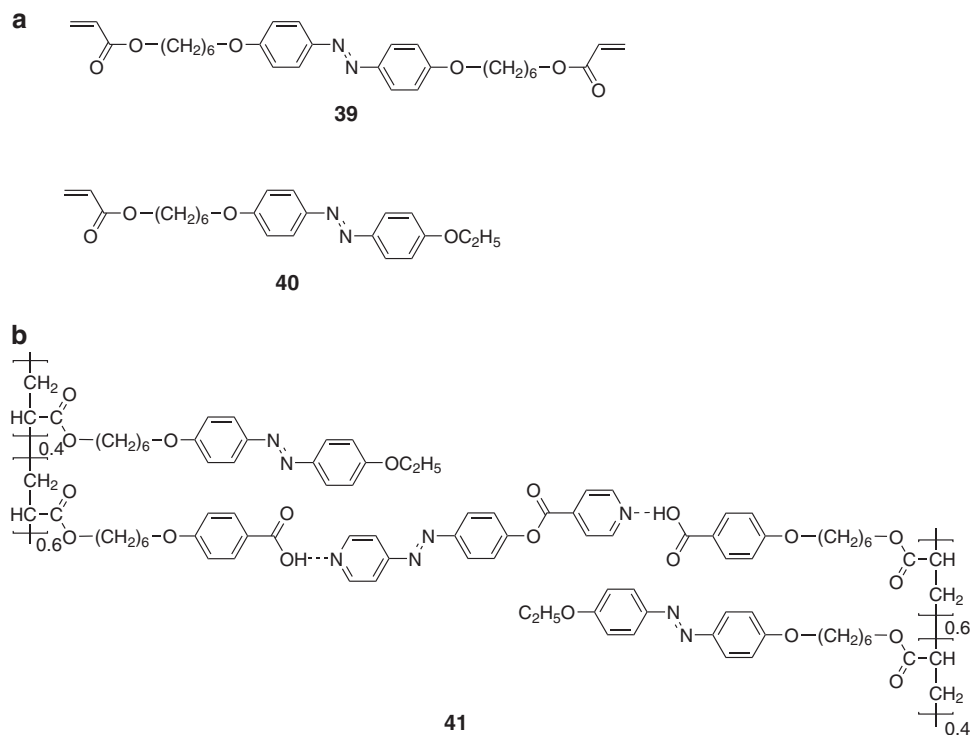
**Figure 11** Construction of self-standing densely cross-linked polymer films having 3D continuous ion nanochannel through polymerization of bicontinuous cubic liquid-crystalline compound **37**. Reproduced with permission from American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.



**Figure 12** Schematic illustration of a phase transition in LC elastomers. LC, liquid crystalline. A full color version of this figure is available at *Polymer Journal* online.

polymer backbones will tend to an isotropic conformation that will induce a shape change in the macroscopic level. When the nematic or smectic LC elastomers are macroscopically aligned, selective shrinkage strain along the director vector is observed during the LC-isotropic phase transitions.<sup>45,47,219–227</sup>

Light-induced deformations have been widely explored in cross-linked azobenzene-based LC networks.<sup>220,228</sup> The stimuli response of these materials rely on the light driven *cis-trans/trans-cis* photoisomerizations of azobenzene groups that act as photochromic molecules



**Figure 13** (a) Chemical structures of the azobenzene monomeric mesogens utilized for the preparation of photo-mobile cross-linked LC films and (b) chemical structures of the LC polymers and bispyridyl crosslinkers utilized for the preparation of supramolecularly cross-linked LC polymer networks. LC, liquid crystalline.

and as mesogens.<sup>229,230</sup> *Trans*-azobenzene stabilizes LC phases while the *cis*-form disturbs them. The photo-isomerization of azobenzene is controlled by ultraviolet or visible light or by heating the sample. Partially cross-linked LC networks with highly concentrated azobenzene moieties were prepared by using molecules **39** and **40** shown in Figure 13a.<sup>230</sup> When irradiated, the absorption mainly occurs in the exposed surface of the films, which produces a gradient in the contraction ratio between the surface and the bulk. When this gradient is sufficiently large, macroscopic bending of the film is observed. The reversible bending of the azobenzene-based LC polymer networks films by 366 nm light irradiation has been reported.<sup>230</sup> Selective bending is achieved by irradiating monodomains films with non-polarized light or either by irradiating linearly polarized light to polydomain films.

Ikeda also explored the use of hydrogen-bonding interactions to cross-link LC polymers containing azobenzene groups.<sup>100</sup> These materials **41** were prepared by mixing a side-chain LC polymer containing azobenzene and benzoic acid groups with bispyridyl derivatives (Figure 13b). Bispyridyl groups act as supramolecular crosslinkers between the side carboxylate groups<sup>50,67</sup> of the polymers. The resulting blends are free-standing, and show macroscopic bending and unbending upon irradiation due to the changes of the azobenzene groups at the microscopic level. The advantage to use supramolecular cross-linking is that, in contrast to covalently linked LC polymer networks, the supramolecular materials are soluble in organic solvents, and therefore can be recovered and recycled.

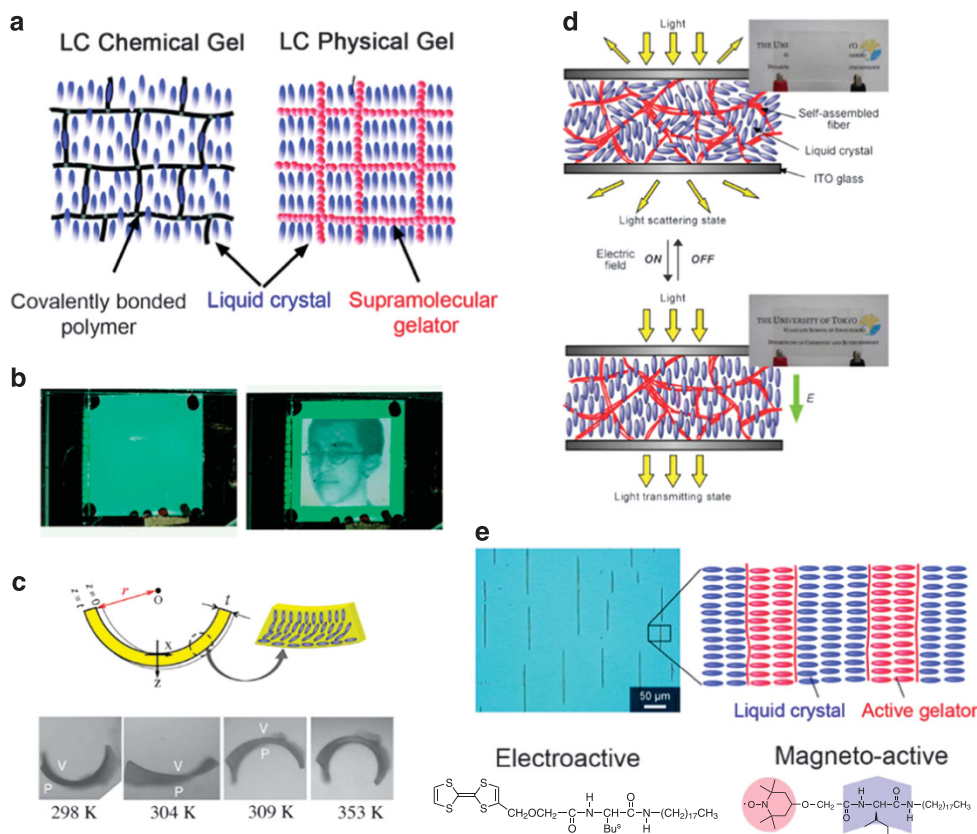
Thin films of nematic and cholesteric LC polymer networks can exhibit various types of deformations that strongly depends on the spatial configuration of the liquid crystal directors.<sup>47</sup> In general, selective contractions/elongations along the directors are observed in planarly aligned nematic and cholesteric phases. On the other hand,

the bending of films can be induced by splayed alignments of nematic LC films where the orientation of the local directors varies from planar to vertical in the direction of the thickness. More complex torsional deformations of films are induced by twist alignments along the thickness of the films. In addition, non-uniform deformations are achieved by creating hierarchical variations in the LC directors along the films surface.<sup>214</sup> Use of twisted nematic phases,<sup>214</sup> alignment layers with circular patterns<sup>215</sup> and alignment control within local volume elements (voxels)<sup>216</sup> have led to the development of films undergoing stimuli induced complex deformations.

Azobenzene mesogens have also been utilized to develop densely cross-linked LC polymer networks exhibiting programmed mechanical responses upon light irradiation.<sup>220,228</sup> For example, Broer group reported on photo-responsive artificial microstructured cilia that bend upon the appropriate light stimuli.<sup>231</sup> These cilia are composed of two parts that have distinct response to light. Each part can be stimulated independently and different mechanical responses can be induced by selecting the appropriate irradiation. Further works focused on the utilization of densely cross-linked LC polymers for the conversion of light into mechanical work.<sup>232–238</sup> In this regard, many researches focused on the development of azo-cantilever oscillators based on densely cross-linked polymer networks that work with artificial light or even with direct sunlight.<sup>232–236</sup>

## LC GELS

Two types of LC gels have been reported: LC chemical gels and LC physical gels (Figure 14a). While LC chemical gels are composed of conventional liquid crystals (liquid crystal solvent) and cross-linked LC polymers,<sup>239,240</sup> for LC physical gels, liquid crystals are mixed with low-molecular weight gelators that form self-assembled fibrous networks.<sup>241,242</sup> The resulting materials exhibit elastic mechanical



**Figure 14** (a) Schematic illustration of LC chemical and physical gels. (b) Pattern-wise LC chemical gel with off (left) and on (right) voltage. (c) Schematic for the bent LC gels with hybrid (splayed) alignment (top) and optical micrographs of the gel at different temperatures. (d) Schematic illustration of the OFF and ON modes of a light-scattering electro-optical switching device. Insets show the photographs of the cells filled with the LC physical gels. (e) Photomicrograph of an oriented LC physical gel and schematic illustration of the hierarchical structure (top). Chemical structures of an electro-active and a magneto-active gelators utilized to develop functional LC physical gels. LC, liquid crystalline. Reproduced with permission from The Royal Society of Chemistry, Springer Nature and American Chemical Society.

properties compared to conventional liquid crystals, but preserve the dynamics and stimuli-responsive properties of small molecules of liquid crystals.

In the LC chemical gels, the gelation is achieved by the *in situ* cross-linking of polymerizable mesogens dissolved in a LC solvent.<sup>239,240</sup> The presence of mesogenic groups attached to polymer networks provides the proper miscibility with the mesogens trapped by a 3D polymer network. Owing to their dynamic properties, LC chemical gels have been widely investigated for their application to optical devices.<sup>243,244</sup> For example, Hikmet<sup>243</sup> proposed nematic LC gels as alternative to conventional calamitic liquid crystals as components for informational displays. Some of these materials exhibited fast dynamics and low-threshold electric response. On the other hand, by utilizing cholesteric gels, more complex electro-switchable devices such as mirrors or patterned optical components have been developed (Figure 14b).<sup>245</sup> The formation of LC gels has also been applied to the preservation of exotic LC phases such as blue phases that have intriguing photonic functions.<sup>246–249</sup>

Remarkably, LC chemical gels also show shape variations in response to temperature and external fields.<sup>250–255</sup> Thermal actuation in LC chemical gels is often accompanied by volume variations.<sup>251,252</sup> Urayama and co-workers extensively studied the polymerized mixtures of mesogenic acrylates and diacrylates in LC solvents.<sup>250–253</sup> These materials exhibit temperature-induced dewelling and reswelling during nematic-isotropic transition. Here again the orientation of the local

director also has a key role on the deformation phenomena.<sup>250</sup> Figure 14c shows the optical micrographs of a LC gel film with planar-vertical orientation of the local directors at different temperatures.<sup>253</sup> Importantly, the curvature of the films appreciably depends on the temperature and it can be predicted on the basis of the lineal bending theory and the anisotropic Gaussian model.<sup>253</sup> Actuation in LC physical gels have been induced not only by temperature variations, but also by application of electric fields.<sup>254,255</sup>

LC physical gels are formed by micro-phase separation of liquid crystal solvents and supramolecular gelators forming fibrous aggregates.<sup>241,242</sup> Liquid crystals exhibiting nematic, cholesteric, smectic and columnar phases have been used to prepare LC gels. One of the most representative gelators is based on long alkyl chains bearing peptide sequences or urea groups and form long fibers via strong hydrogen-bonding interactions.<sup>256</sup> LC physical gels are obtained by cooling from isotropic liquid of a mixture of the liquid crystal and the supramolecular gelator (0.2–4%). Importantly, the nature and properties of the gels are dependent on the order of the isotropization temperature ( $T_{\text{iso}}$ ) of the liquid crystal and the sol-gel transition ( $T_{\text{sol-gel}}$ ) of the gelator.<sup>253</sup> For example, when  $T_{\text{sol-gel}} > T_{\text{iso}}$ , LC gels with randomly dispersed fibrous networks are formed. In contrast, when  $T_{\text{iso}} > T_{\text{sol-gel}}$ , the gelation is templated by the LC order, and therefore aligned fibers can be obtained by aligning the liquid crystals with command surfaces or external fields.<sup>241,242</sup>

Nematic LC physical gels showing electro-optical switching in the light-scattering mode have been reported.<sup>257–261</sup> As shown in Figure 14d, LC gels composed of randomly dispersed fibers and polydomain LC structures exhibit light scattering. However, after application of an electric field, the LC molecules reorient in the direction of the field forming a monodomain homeotropic alignment. This structural configuration permits the transmittance of the light. It should be noted that the LC gels recover their initial organization when the electric field is removed. Moreover, these structures can be covalently cross-linked by using gelators with polymerizable groups, leading to more stable materials.<sup>260,261</sup> Other functional LC physical gels have been prepared.<sup>241,242,262–266</sup> For example, a triphenylene columnar LC gel have been reported to show charge carrier transport.<sup>264</sup> Remarkably, the gelled columnar structure exhibits improved transport abilities compared to the pure discotic liquid crystal due to the repression of molecular fluctuations, which increases the columnar order and the hole mobilities. Another strategy to prepare functional LC gels consists of mixing active gelators with a nematic or smectic liquid crystal. By the alignment of the LC phase, the formation of anisotropic functional fibrous aggregates can be induced.<sup>257</sup> This approach has been applied to prepare conductive self-assembled fibers by using a gelator bearing an electro-active moiety such as tetrathiafulvalene (Figure 14e).<sup>265,266</sup> Similar approach has been used to prepare magneto-active fibers. In this case, gelators bearing 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) groups have been utilized.<sup>262,263</sup> Use of photofunctional gelators bearing azobenzene groups leads to the photoswitching of the LC gel structures.<sup>267,268</sup>

## CONCLUSIONS

An overview of the development of functional LC polymers are described in this review. A wide variety of molecular and supramolecular structures, and molecular self-assembled structures have been introduced into the materials design of the LC polymers. These LC polymers can exhibit ordered and anisotropic structures and properties. For further functionalization of the LC polymer materials, molecular orientation, defect control and domain formation should be more precisely controlled.<sup>269</sup> For example, new techniques<sup>44,270–273</sup> are proposed to control alignment using LC polymers. New materials will be used for the preparation of liquid crystals.<sup>274–276</sup> LC polymers may be more important in the field of energy, environment and biotechnology due to their unique nature.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## ACKNOWLEDGEMENTS

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