**REVIEW ARTICLE** 

# **R**esponsive materials Wiley

# **Responsive molecular liquid materials**

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#### Abstract

This review focuses on solvent-free molecular liquid materials that exhibit changes in response to stimuli. Along with the recent development of soft functional materials, research on functional liquids possessing free deformability and ease of molding is becoming a new trend. A typical method for designing functional molecular liquids (FMLs) introduces flexible alkyl side-chains around a  $\pi$ -conjugation unit at the center of the molecule. As a result, the aggregation between  $\pi$ -conjugated units is inhibited, and an entropy-rich room temperature liquid is obtained. FMLs designed in this way can exhibit unique and exciting stimulus responses due to the high density of functional units and fluidity. Such notable features include electrochromism, phase transitions, and dynamic changes in the nanostructure. In addition, some stimulus responses are reversible and thanks to the fluidity, return to their initial state under relatively mild conditions, such as room temperature or slight heating. To elicit such effective stimulus responses, selecting an optimal  $\pi$ -core, and modifying it with the appropriate alkyl side-chains (length, branching, and substitution position) is essential. A deep understanding of the alkyl- $\pi$  molecular design will enable the creation of more attractive stimuliresponsive FMLs, which are of high value in advanced fields such as healthcare, security, sensors, soft electronics, and robotics.

#### Keywords

alkyl-n engineering, functional molecular liquids, soft materials, stimuli responses

## **1** | INTRODUCTION

Thanks to progress in advanced science and technology, various high-performance devices have become increasingly familiar.<sup>[1–5]</sup> In the IoT society of the future, the types and number of sensors in the world are expected to increase explosively. In addition, the number of people and opportunities for wearing elastic optoelectronic devices, small and lightweight devices, and small sensors for medical purposes will likely increase. Since the human body is a soft material that is flexible and elastic, it is essential to develop adaptable devices and sensors that can freely deform using soft materials that follow the movements of the human body and demonstrate advanced performance.<sup>[6–8]</sup> Against this

background, the development of soft materials with new functions, such as liquid crystals,<sup>[9,10]</sup> gels,<sup>[11–13]</sup> and elastomers,<sup>[14,15]</sup> is being actively pursued.

Among advanced soft materials, solvent-free functional molecular liquids (FMLs) are attracting particular attention due to their unique characteristics such as fluidity, free deformation, low environmental impact owing to solvent-free handling, and solvent-like functions of dissolving other molecules or nanomaterials.<sup>[16,17]</sup> In functional organic solid materials, subtle differences in the number of crystal defects and molecular orientation can significantly affect the material properties.<sup>[18]</sup> In addition, highly oriented solids and film materials cannot maintain their structure against free deformation such as tension, bending, and torsion. On the

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other hand, liquids do not cause defects thanks to their fluidity, and isotropic liquids do not require consideration of molecular orientation; therefore, FMLs can exhibit stable performance with a simple molding process. In addition to such ease of handling, fluids with densely packed functional cores have unique properties not seen in solids or solutions, such as molecular diffusion and dynamic intermolecular interactions. The development of new functions is expected to produce an attractive liquid that retains these properties.

FMLs are defined as solvent-free liquids at room temperature with advanced functions originating from a functional molecular core unit. One of the standard methods for designing FMLs is to attach flexible and fluid molecular chains to a rigid and aggregation-prone functional  $\pi$ -conjugated unit or framework to weaken the interaction between functional cores.<sup>[16,17,19]</sup> This is distinctly different from ionic liquids, which are designed to be liquid at room temperature through strategies that weaken ionic interactions by tuning the ionic radius or symmetry.<sup>[20,21]</sup> There are reports of introducing functional moieties into ionic liquids<sup>[22–26]</sup>: however, restrictions on liquefaction conditions often limit the introduction of various functions into ionic molecules. The development of ionic liquids with large  $\pi$ -units requires the introduction of large ions with bulky alkyl chains to weaken  $\pi - \pi$  interactions and ionic interactions.<sup>[24,27–31]</sup> In contrast, FMLs have been reported to introduce different functional moieties owing to their simple molecular design strategy. In addition, ionic liquids have ionic conductivity, and their application to electrochemical devices has been extensively studied, whereas FMLs have low polarity and can be applied to applications where conductivity is a hindrance, such as semiconductors<sup>[32-34]</sup> and electret devices.<sup>[35,36]</sup> Furthermore, the photostability of FML containing dye moieties was found to be approximately 10fold higher than the original unmodified dyes.<sup>[37]</sup> In contrast, the photostability of ionic liquids containing dye moieties has not been fully considered. [29-31] Table 1 summarizes the differences in the characteristics of FMLs, ionic liquids, and low-molecular-weight organic solvents.

There are several types of FMLs depending on the unit used as the functional core, including liquids with  $\pi$ -conjugated dyes, porous units,<sup>[38,39]</sup> proteins,<sup>[40,41]</sup> and inorganic nanoparticles.<sup>[42–44]</sup> Several types of flexible molecular chains have also been reported. Particularly, alkyl chains,<sup>[45]</sup> oligo or poly(ethylene oxide) chains,<sup>[46]</sup> and siloxane

chains<sup>[47,48]</sup> are frequently employed. In the following, as a typical example, FMLs composed of a  $\pi$ -conjugated core with alkyl side-chains are described in more detail. It is possible to create molecular liquids with various optical functions by selecting functional  $\pi$ -conjugated cores such as those with full-color luminescence,<sup>[37,49]</sup> room-temperature phospho-rescence,<sup>[50,51]</sup> and upconversion.<sup>[52]</sup> A remarkable point in such a molecular design is that the fluidity in a solvent-free liquid state and the strength of the interaction between functional cores can be controlled by the length, the degree of branching, and the substitution position of the flexible molecular chains.<sup>[53–59]</sup> For example, in a study using alkylated liquid pyrenes as the model molecule,<sup>[60]</sup> when only one side of the pyrene core was modified with alkyl chains so that the pyrene core was not fully covered, the luminescence was delivered from the excimer formation between the pyrene cores. In this case, van der Waals and  $\pi$ - $\pi$  interactions acted between the molecules (Figure 1a). On the other hand, when the alkyl chains were modified to wrap around the entire pyrene core, almost no excimer emission was observed, and optical properties peculiar to the isolated core were exhibited. Only van der Waals interactions acted between the molecules in such a molecular design (Figure 1b). Molecular dynamics calculations of these molecules suggested that pyrene units partially shielded by alkyl chains form local  $\pi$ - $\pi$  stacking columnar structures in the fluids, whereas structure is hardly formed when pyrene units are effectively shielded by multiple alkyl side-chains.<sup>[61]</sup> The difference in intermolecular interactions significantly affected the stimulus responses. Therefore, understanding the effects of such a molecular structure on intermolecular interactions is crucial in designing FMLs that show the desired stimulus responses. Appropriate control of intermolecular interactions enables tuning and switching of functions of FMLs for more advanced applications.

In this review, we focus on stimuli-responsive FMLs. Electricity, chemical molecules, light, heat, and mechanical forces are attracting attention as stimuli that change the functions of liquid materials. These stimuli are generally known to have the following effects on material properties.

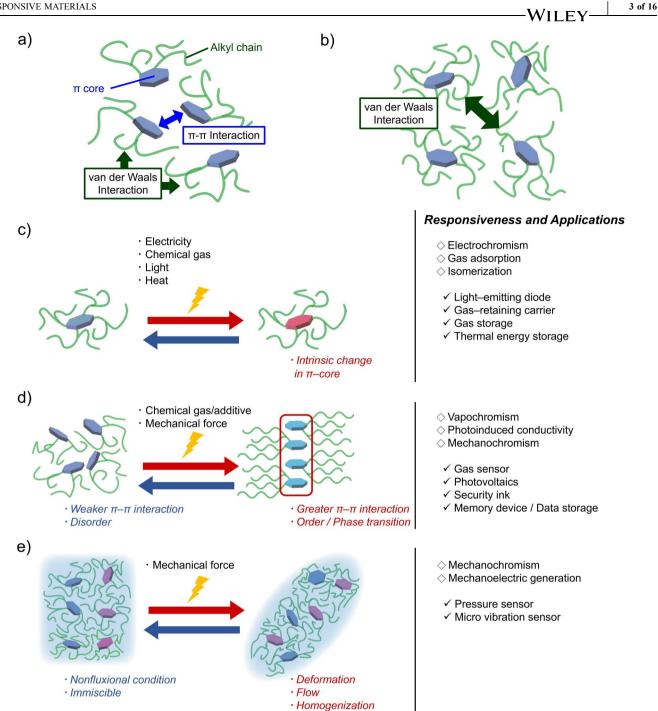
i) *Electrical stimuli* Electrical stimulation can excite electrons in materials by injecting them. The resulting response contains a system of light-emitting diodes (LEDs). Regarding soft materials, polymers,<sup>[62]</sup> and

TABLE 1 Properties of FMLs, ionic liquids, and low-molecular-weight organic solvents.

	FMLs	Ionic liquids	Organic solvents <sup>a</sup>
Viscosity	Moderate-high	Low-moderate	Low
Volatility	Low	Low	High
Polarity	Low	Moderate-high	Low-high
Optoelectronic functions	Wide variety	Limited functions	No functions

Abbreviation: FMLs, functional molecular liquids.

<sup>a</sup>Methanol, diethyl ether, chloroform, toluene, and hexane are assumed here as representative organic solvents.



Illustrations of molecular designs that affect intermolecular interactions and various reversible stimuli responses of solvent-free functional FIGURE 1 molecular liquids as well as their responsiveness and applications. Red arrows indicate response to stimuli and blue arrows indicate restoration to the original state under mild conditions. (a) When only part of the *n*-core is covered with alkyl side chains, both van der Waals and *n*-*n* interactions act between the molecules. (b) Only van der Waals interactions act between the molecules if the  $\pi$ -core is entirely wrapped with alkyl side chains. (c) Electricity, light, and heat alter the intrinsic properties of the  $\pi$ -core independently of the alkyl side chains, leading to changes such as chromism and structural isomerization. Due to the core characteristics, adsorption and desorption of gas molecules also occur independently of the alkyl side chains. (d) Molecular arrangements change when mechanical forces such as shear or chemical additives affect intermolecular interactions. Polarity changes due to gas stimulation or structural isomerization also cause molecular ordering. Increased  $\pi$ - $\pi$  interactions can alter the optical or electronic properties due to the order. (e) Mechanical forces, such as surface scratching and vibration, can deform and flow liquids. When mixing several different liquid molecules, the mechanical force can homogenize them.

polymer gels<sup>[63]</sup> are reported to be applied as lightemitting layers of LEDs. Electricity can also induce electrochemical redox reactions that change the structure and electronic state of organic compounds. The

color of the material changes under potential control, which is known as electrochromism, and has been demonstrated in soft materials in polymers<sup>[64]</sup> and metal supramolecular polymers.<sup>[65]</sup>

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- ii) Chemical stimuli Examples of changes in the properties of matter due to chemical stimulation can be divided into two cases. One is when polar molecules, for example, gaseous molecules, act to change the electronic state and polarity of the matter. The other is when the guest molecule acts on the host material to induce molecular order. For example, a host–guest reaction of pillar[5]arene with *n*-hexane to form supramolecular polymers has been reported.<sup>[66]</sup> Porous materials can also adsorb and possibly release trapped gaseous molecules. In organic materials, gas adsorption/desorption has been reported in covalent organic frameworks (COFs)<sup>[67,68]</sup> and hydrogen-bonded organic frameworks (HOFs).<sup>[69,70]</sup>
- iii) Photo stimuli Light can excite electrons in insulators and semiconductors, resulting in photo-induced conductivity switching. Light also excites electrons in double bonds in certain types of molecules, which makes them rotatable and triggers photoisomerization to metastable isomers. Azobenzene moiety is a prime example of such photo-isomerization.<sup>[71]</sup> Several attempts have been made to induce dynamic changes through photoisomerization by introducing azobenzene into soft materials.<sup>[72,73]</sup> For example, when a polymer film containing azobenzene is irradiated with light, its shape changes.<sup>[74]</sup> Azobenzene has also been used as a cross-linking point for hydrogels and induces a sol–gel transition triggered by the photo-isomerization of azobenzene.<sup>[75]</sup>
- iv) Thermal stimuli Heat can restore the thermodynamically stable state of chemicals that are metastable due to other stimuli. Furthermore, heat facilitates the diffusion of molecules. Therefore, it is often used to restore materials to their initial state in response to reversible thermal stimuli. For example, heat can reverse the above-described azobenzene isomerization from the *cis* form to the *trans* form. Some materials exhibit thermo-chromism, in which the molecular structure and electronic state change depending on the temperature and the color changes.<sup>[76]</sup>
- v) Mechanical force stimuli Mechanical forces can affect the intermolecular interactions of organic molecules and sometimes change the molecular arrangement. Therefore, phase transitions and changes in optical properties can be induced. Mechanochromism<sup>[77,78]</sup> and crystal structure transition<sup>[79]</sup> in organic crystalline materials have been reported. In addition, shear-induced phase transition and accompanying color change have been reported in liquid crystals<sup>[80–82]</sup> and supramolecular assemblies.<sup>[83,84]</sup>

Some of the responses to these stimuli in FMLs are derived from the intrinsic functions of  $\pi$ -conjugated units isolated by bulky yet flexible alkyl side chains, such as changes in absorption and fluorescence features upon stimulation (Figure 1c). Other responses induce changes in the nanostructures, optoelectronic properties, and phase transitions caused by stimuli that alter the balance between

intermolecular interactions of the functional cores and van der Waals interactions among the alkyl chains (Figure 1d). Such stimuli responses often show more intense changes in the case of liquid materials than in solids and solutions originating from the fluidity of solvent-free liquids and the high density of functional cores. In addition, since liquids can be freely deformed, flowed, or mixed by mechanical force, chromism due to changes in the state of phase separation and applications to vibration-responsive electret devices can be expected (Figure 1e). Stimulus responses in solvent-free liquids are reversible in many cases, returning to their original state under mild conditions such as room temperature or slight heating thanks to the fluidity of liquids. These features highlight the importance of solvent-free FMLs in developing stimuliresponsive materials. Furthermore, an overview of the molecular design and functions of recently reported responsive solvent-free liquid materials should help create more attractive and highly functional responsive soft materials.

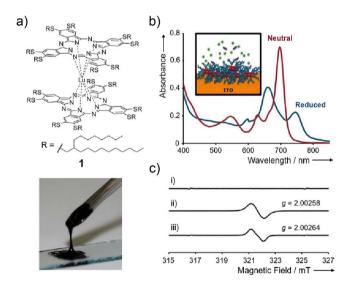
## 2 | ELECTRICAL STIMULI

Electroluminescence is one of the responses to electrical stimuli. As an example of electroluminescence in non-solvent liquid materials, Adachi et al. reported an organic lightemitting diode (OLED) utilizing 9-(2-ethylhexyl) carbazole as a neat liquid host of the active layer in which 1.0 wt.% 5,6,11,12-tetraphenylnapthacene was doped as the guest emitter.<sup>[46,85–88]</sup> Using liquid luminescent materials has advantages in fabricating flexible devices. For instance, Mizuno et al. proposed a microfluidic OLED for manufacturing a precisely arranged light-emitting device through integration while taking advantage of its flexibility.<sup>[89,90]</sup>

Recently, isomerization of FMLs by electrical stimulation has also been reported. As explained in Section 5 below, the isomerization of FMLs triggered by light or heat has been studied for application in thermal fuels.<sup>[91,92]</sup> Arylazopyrazole derivatives bearing flexible molecular chains are one of the room temperature functional liquids that can be applied for thermal fuels.<sup>[93]</sup> Fuchter et al. reported that the arylazopyrazole liquids were isomerized by light and could be reverse isomerized to their original state by electric current.<sup>[94]</sup> Electrocatalytic isomerization was applied to molecular liquids; introducing organic ionic moieties proceeded isomerization more efficiently. Utilizing such an electrocatalytic reaction is advantageous as a thermal fuel because isomerization can be efficiently induced in the liquid condensed phase with less energy.

Another response to electrical stimuli is electrochromism, which is a change in color. The double-decker lutetium (III) phthalocyanine ( $Pc_2Lu$ ) is known for its spin-active, paramagnetic, and electrochromic properties.<sup>[95–97]</sup>  $Pc_2Lu$  modified with branched alkyl side chains (1) exists in a liquid state at room temperature, and this liquid exhibits electrochromic functions similar to those of the original  $Pc_2Lu$ .<sup>[98]</sup> The electrochromic properties of 1 were evaluated in the neat film on an indium tin oxide coated glass (ITO) electrode in an aqueous tetrabutylammonium chloride solution. The change in UV-Vis spectra during the reduction process from the neutral form was monitored under an applied potential of -0.6 V versus the reference Ag/AgCl/KCl electrode (Figure 2b). In this process, the absorption peak at 699 nm decreased while two new absorption peaks at 744 and 661 nm increased, similar to 1 in dichloromethane. This change in the neat film state occurred faster than in the solution state, demonstrating the advantage of the thin diffusion layer of the liquid film. Furthermore, 1 also showed a spin-active nature similar to that of Pc<sub>2</sub>Lu. Electron spin resonance (ESR) spectra in a dichloromethane  $(10^{-4} \text{ M})$  solution of 1 and neat thin film of neutral 1 at room temperature exhibited an ESR signal at  $g = 2.0027 \pm 0.0002$  and wide peak widths of about  $0.9 \pm 0.1$  mT. On the other hand, the neat thin film of the oneelectron-reduced species of 1 did not exhibit any remarkable ESR signals (Figure 2c). This result means that the spin-active nature of 1 can be switched by an electrical stimulus. Such spin-active and optical-active liquids pave the way for new applications, such as memory devices.

As a material design concept that makes full use of the electric stimulus response of functional liquids, in addition to a molecular design that effectively utilizes the electronic functions unique to the  $\pi$ -conjugated core moiety, it is also essential to have a device design that takes advantage of the liquid fluidity. In the future, it will be interesting to combine device designs that do not impair the fluidity of liquids, such as the microfluidics presented here, <sup>[89,90]</sup> with the functions of luminescence and multicolor chromism. In addition to



**FIGURE 2** (a) Chemical structure and photo image of **1**. (b) Changes in UV-Vis spectra of a thin film of **1** pasted on an ITO working electrode in an aqueous tetrabutylammonium chloride (0.5 M) during the electrochemical reduction at 0 V (red line) and -0.6 V (blue lines). The inset shows the scheme of the environment surrounding the Pc<sub>2</sub>Lu molecules. (c) ESR spectra of (i) thin film of one-electron-reduced species of **1**, (ii) thin film of neutral **1**, and (iii) dichloromethane solution of **1** ( $10^{-4}$  M). Reproduced with permission.<sup>[98]</sup> Copyright 2018 John Wiley and Sons. ESR, electron spin resonance; ITO, indium tin oxide coated glass.

### **3** | CHEMICAL GAS STIMULI

The electrochromism described above was induced by a change in the oxidation state of Pc<sub>2</sub>Lu through a redox reaction. Another effective method is to modulate the oxidation state with acid gas molecules. Examples of gas-responsive liquid systems are alkylated N-heteroacene liquids, which show vapochromism by hydrochloric acid (HCl) gas. Isoda et al. reported that a N-heteroacene derivative with branched alkoxy chains and thiophene moieties (2) (Figure 3a) exists in a liquid state at room temperature ( $T_g = -29.0^{\circ}$ C) and changed color from pale yellow to dark yellow upon adsorption of HCl vapor.<sup>[100]</sup> In the same operation, the emission color changed from blue to yellow under ultraviolet irradiation (Figure 3b). This is because the lone pair of imino nitrogen can act as a Lewis base and interact with Lewis acids such as protons. Such protonation causes changes in the absorption and emission spectra due to two effects: change in electronic properties and change in molecular alignment. The electronic properties were evaluated by cyclic voltammetry and theoretical calculations, and the results suggested that the protonation stabilizes the lowest unoccupied molecular orbital (LUMO) level. X-ray diffractometry (XRD) characterized the change in molecular alignment, which showed new diffraction peaks by protonation. This alignment change is likely due to an increase in the dipole moment and the formation of an excimer. HCl can be desorbed from the protonated 2 by leaving it in the air for 1 h. Therefore, this vapochromism is reversible. By changing the design of the alkylated  $\pi$ -conjugated liquid system containing N-heteroacene, Isoda et al. succeeded in changing the emission color after the adsorption of HCl or simultaneously causing the change in the emission color and the formation of the crystal structure.<sup>[103,104]</sup>

Furthermore, attaching a chiral alkyl chain to *N*-heteroacene produces liquids that show circularly polarized luminescence (CPL) triggered by the adsorption of HCl.<sup>[101]</sup> The *R*-form and *S*-form of alkylated *N*-heteroacene (**3a** and **3b**, Figure **3c**) did not show any CPL because these molecules were disordered in the neat liquid state. Nevertheless, exposure to HCl increased the dipole moment of the molecules. It enhanced the intermolecular dipole–dipole interactions of **3a** and **3b**, which formed a helical self-assembled structure under the influence of the chiral alkyl chain. As a result, the CPL derived from the helical assembly could be observed after the exposure to HCl, and the sign of CPL was opposite for the *R*- and *S*-forms (Figure **3d**). This study is the first report on a stimuli-responsive CPL on/off liquid material.

Another example of stimuli-responsive liquids using gas molecules is phase transition by means of host-guest

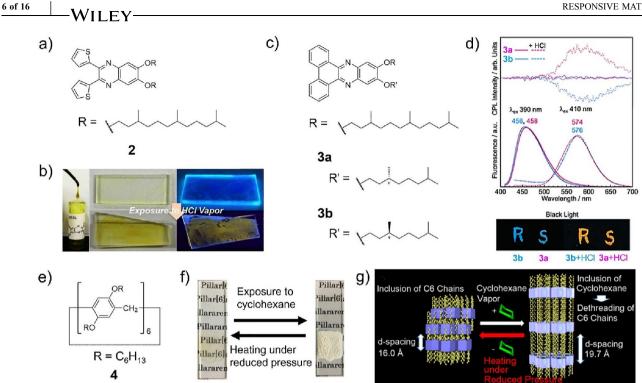
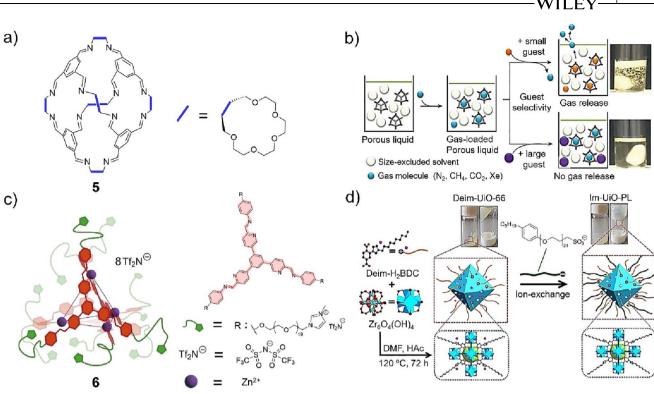


FIGURE 3 (a) Chemical structure of 2. (b) Photo images of 2 and coated films of 2 under room light and 365 nm light, and 2 before and after exposure to HCl vapor. Adapted with permission.<sup>[100]</sup> Copyright 2017 John Wiley and Sons. (c) Chemical structure of **3a** and **3b**. (d) CPL and FL spectra, photos of 3a, 3b, 3a-HCl, and 3b-HCl. Photos were taken under 365 nm black light. Reproduced with permission.<sup>[101]</sup> Copyright 2021 American Chemical Society. (e) Chemical structure of 4. (f) Photos of cast film of 4 before and after exposure to cyclohexane guest vapor. (g) Schematic illustration showing the change in 4 caused by the host-guest reaction with cyclohexane vapor. Adapted with permission.<sup>[102]</sup> Copyright 2019 American Chemical Society. HCl, hydrochloric acid.

interaction. Ogoshi et al. synthesized a pillar[6]arene modified with *n*-hexyl groups (4, Figure 3e), a transparent liquid at room temperature.<sup>[102]</sup> This liquid transitioned to a solid and became turbid when exposed to cyclohexane vapor (Figure 3f). <sup>1</sup>H NMR measurements and the sorption isotherms of 4 revealed that the cyclohexane guest was brought into the pillar[6]arene cavity owing to their similar size. Since this host-guest reaction caused crystallization, an apparent change in the XRD peaks was observed, and the packing structure after crystallization was determined, as shown in Figure 3g. When heated to 80°C under reduced pressure, the cyclohexane was removed, and the film of 4 returned to a transparent liquid state. Therefore, this transition between a liquid and a solid induced by cyclohexane vapor is reversible.

In addition to such host-guest reactions, other responses to gas stimuli include the trapping of gas molecules in the pores. Porous liquids are widely studied as liquid adsorbing gas molecules.<sup>[105–107]</sup> Porous materials have characteristics such as high specific surface area and selectivity due to the size of the pores and can be applied to the adsorption/separation of molecules and catalyst carriers. Porous materials are generally solids, which limits their use to applications such as pelletizing or fixed-bed systems. In industrial handling, liquids have several advantages over solids, including the ability to be pressurized or pumped. If porous liquid materials are put to practical use, new industrial processes, such as circulating gas adsorption systems that use their fluidity, are expected to be developed. Conventional liquids can only form temporary voids between molecules. In contrast, permanent pores could be created in liquids by incorporating a rigid porous structure, as proposed by James et al.<sup>[108]</sup> Methods for imparting fluidity to porous materials include dispersing rigid organic cages or porous structures in a solvent or modifying them with flexible molecular chains such as polyethylene glycol (PEG) chains to liquefy them without a solvent.

Based on this idea, James et al. reported for the first time a porous liquid in which an organic molecular cage composed of imines modified with cyclic ethers (5) was dispersed in crown ether (15-crown-5).<sup>[109]</sup> In this material, the inside of the organic cages acts as a pore and can adsorb  $N_2$ ,  $CH_4$ ,  $CO_2$ , and Xe. Furthermore, as shown in Figure 4b, when chloroform is added as a guest molecule to a solution of 5, which adsorbs Xe, the cage interior is rapidly replaced by chloroform, and Xe is released. On the other hand, the addition of 1*t*-butyl-3.5-dimethylbenzene, which is a large molecule, does not release Xe. Initially, James et al. attempted to modify organic imine cages with alkyl chains to obtain porous liquids.<sup>[110]</sup> However, although the liquid was porous at a lowtemperature solid state, it was not porous at the temperature where it existed in a liquid state because the alkyl chains penetrated the cages and blocked the pores. According to this result, it is necessary to devise ways to prevent the fluid molecules and molecular chains from clogging the pores



**FIGURE 4** (a) Chemical structure of **5**. (b) Schematic of gas capture and release image in cages of **5** in 15-crown-5 solution. Reproduced with permission.<sup>[109]</sup> Copyright 2015 Springer Nature Publishing AG. (c) Chemical structure of **6**. (d) Synthesis scheme of liquid UiO-66 attached with PEG chains. Reproduced with permission.<sup>[39]</sup> Copyright 2021 John Wiley and Sons. PEG, polyethylene glycol.

when designing porous liquids. In example **5**, since the cyclic ether is sufficiently larger than the pore size, fluid units do not enter the pores and they remain porous even in the liquid state. Although this report is not an example of non-solvent molecular liquids, it is essential to clarify the guidelines for designing porous liquids.

Adsorption/desorption of  $O_2$  by a water-dispersing porous framework<sup>[111]</sup> is also a noteworthy example of the liquid dispersion of such porous units. In this example, silicalite and a metal-organic framework (MOF) with hydrophilic surfaces were colloidally dispersed in water. Because the inside pores were hydrophobic, water could not enter the pores, and the porosity was maintained. Due to its function of  $O_2$  adsorption/desorption, it has been proposed as a medium for artificial blood and the preservation of organs and body tissue.

On the other hand, solvent-free porous liquids have also been reported, such as PEG chain-modified organic cages terminated with ionic liquid moieties (6).<sup>[112]</sup> In this structure, PEG chains could not enter the organic cages due to the bulky anions of the ionic liquid moieties at the end of the chains. The porosity was maintained even in the liquid state. The porosity of the neat liquid cage was confirmed by positron annihilation lifetime spectroscopy. If the PEG chain is not long enough, it exists in a solid state. Therefore, although this example is a type of ionic liquid, the policy of designing 6 has similarities to the design of FMLs. It was demonstrated that 6 adsorbed ozone-depleting and climate-warming chlorofluorocarbon gas into the cage, as confirmed by changes in the chemical shift of <sup>1</sup>H NMR and <sup>19</sup>F NMR. Thus, this material may be helpful for applications in environmental conservation.

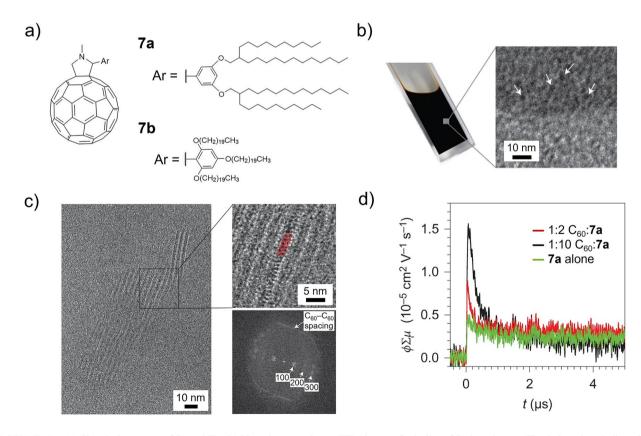
As another example of the adsorption of gas molecules in solvent-free porous liquids, Cao et al. reported UIO-66<sup>[113]</sup> (MOF composed of tetrahedra and octahedra of a  $Zr_4O_6(OH)_6$ cluster and terephthalic acid), the surface of which was modified with PEG chains (Figure 4d).<sup>[39]</sup> To fabricate MOFbased porous liquids, lowering their melting point and preventing the functional groups or guest molecules from blocking the pores are two key issues. Since imidazoliumfunctionalized UiO-66 is cationic, anionic PEG-tailed sulfonate PEG chains can be introduced using the ion exchange method. This porous liquid showed CO<sub>2</sub> adsorption approximately 14 times larger than pure PEGs owing to physical adsorption into the UIO-66 pores. Furthermore, a cycloaddition reaction between epichlorohydrin and the CO<sub>2</sub> adsorbed in this liquid was demonstrated. The reaction proceeded by exposing the epichlorohydrin and tetrabutylammonium bromide to the UIO-66 porous liquid adsorbing CO<sub>2</sub> at 120°C in an autoclave. This system gave a high yield of chloropropene carbonate products. Such porous absorbency has advantages in industrial applications due to its fluidity compared to conventional porous solid catalysts. Therefore, it is expected to be applied to new catalytic reaction systems. In addition to these porous liquids, liquefied proteins are attracting attention as gas-responsive liquids because they can adsorb and release O<sub>2</sub>.<sup>[40]</sup>

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The development of porous liquids is one of the stimuliresponsive liquids currently attracting the most attention.<sup>[105-107]</sup> The quest for applications as a new gasretaining carrier with fluidity and gas storage capacity and its utilization as an oxygen carrier in the medical field is essential. In addition to gas adsorption and desorption, researchers are also interested in modifying the molecular functions of liquids, such as chemically reacting with gas molecules<sup>[100,103,104]</sup> as well as capturing and interacting with them.<sup>[102]</sup> The design of the core moiety that interacts with the gas molecules tends to be the focus of attention, but if the modification of the molecular side chains can improve the diffusivity and selectivity of the gas molecules, research in this field will become even more active. The future may see advances in development, such as a new catalyst flow system that combines liquid flow and catalytic functionality.

## 4 | CHEMICAL ADDITIVE STIMULI

As discussed in gas-responsive liquids, interactions and reactions with small gas molecules can change the liquid at the molecular level, resulting in changes in their nanostructures and aggregate structures. Nanostructural changes due to the addition of chemicals also occur in liquid fullerenes. Since fullerene-C<sub>60</sub> is known to be an n-type semiconductor with excellent electron-accepting properties, methods to control their nanostructures are important in device fabrication.<sup>[114–117]</sup> Branched alkyl chains attached to  $C_{60}$  (7a) produce a liquid at room temperature.<sup>[118,119]</sup> This molecule comprises immiscible  $\pi$ -conjugated moieties and alkyl chains, thus forming interesting nanostructures depending on the additives. For example, mixing 7a with n-decane formed a micelle with an average diameter of  $2.5 \pm 0.3$  nm, confirmed by cryogenic transmission electron microscopy (cryo-TEM, Figure 5b), small-angle X-ray scattering (SAXS), and smallangle neutron scattering (SANS). On the other hand, adding a C<sub>60</sub> molecule at a 1:10 molecular ratio formed a lamellar structure in a viscoelastic liquid state, observed by cryo-TEM (Figure 5c), XRD, and polarized optical microscopy (POM). No peaks were attributed to the face-centered cubic phase of  $C_{60}$  in XRD, suggesting that  $C_{60}$  is mainly incorporated into the lamellar structure. A cryo-TEM image shows that the  $C_{60}$ units are interdigitated; fast Fourier transform indicates that the *d*-spacings of the lamellar structure and  $C_{60}$ - $C_{60}$  are 3.6 and 1.1 nm, respectively. Therefore, in this lamellar structure, nanosheets of C<sub>60</sub> are insulated by the alkyl chain layers. In contrast, a mixture of C<sub>60</sub> molecules and liquid 7a at a 1:2 molecular ratio showed a liquid crystalline-like behavior. It exhibited smaller lamellar spacing and a reduced persistence



**FIGURE 5** (a) Chemical structure of **7a** and **7b**. (b) Photo image and cryo-TEM image of micelles of **7a** in *n*-decane. The dark regions indicated by white arrows are the C<sub>60</sub>-rich cores of the micelles. (c) TEM images and fast Fourier transform of a lamellar structure formed by mixing C<sub>60</sub> and **7a** at a 1:10 molar ratio at room temperature. (d) FP-TRMC results for neat **7a** and mixture of **7a** with C<sub>60</sub> under solvent-free conditions ( $\lambda_{ex} = 355$  nm). Reproduced under terms of the CC-BY license.<sup>[118]</sup> Copyright 2014, T. Nakanishi et al., published by Springer Nature Publishing AG. FP-TRMC, flash-photolysis time-resolved microwave conductivity; TEM, transmission electron microscopy.

length of the lamellar structure compared to the 1:10 mixture as determined by XRD. These differences in the assembled structure can be understood by considering the hydrophobic amphipathic properties coming from the  $\pi$ -conjugated moieties and alkyl chains. Such alkyl chains attached to  $C_{60}$ showed photoconductivity as confirmed by flash-photolysis time-resolved microwave conductivity, and the conductivity was different depending on the persistence length of the  $C_{60}$ assembly. The photoconductivity of the 1:10 mixture of  $C_{60}$ and 7a increased significantly compared to 7a alone; however, increasing the  $C_{60}$  ratio up to 1:2 resulted in a decrease in the conductivity (Figure 5d). Alkylated  $C_{60}$  7b was also liquid at room temperature and showed photoconductivity, which suggests interactions with  $C_{60}$  to some extent.<sup>[120-122]</sup> In short, alkylated fullerenes exhibit photoconductivity depending on the persistence length of  $C_{60}$  aggregates, and conductivity varied by molecular design and chemical additives.

Other examples of structure and optical properties change due to interactions between liquids and guest molecules, which have been reported.<sup>[123]</sup> Kimizuka et al. obtained dihydrophenazine (DHP) derivatives modified with branched alkyl chains as isotropic liquids at room temperature. Adding 7,7,8,8-tetracyanoguinodimethane (TCNO), a strong acceptor, to a liquid DHP donor caused supramolecular alternating copolymerization and the formation of ionic charge-transfer complexes, leading to columnar liquid crystalline mesophases with alternating molecular alignment.<sup>[124]</sup> Isoda et al. synthesized an electron-accepting pyromellitic diimide (PMDI) modified with branched alkyl chains. This liquid dissolved the electron-donating solid naphthalene, triggering the formation of exciplex of PMDI and naphthalene. As a result, the blue photoluminescence of the neat liquid PMDI changed to green.<sup>[125]</sup>

As described in this and the next session, a small  $\pi$ conjugated molecule can be a solute of FMLs, which induces complex formation, phase transition, and energy transfer. Mixing a solid with a liquid is inspired by the function of the liquid as a solvent.<sup>[37,38,126]</sup> Selecting appropriate additives can effectively tune or switch the functions. However, in the case of alkyl $-\pi$  molecular liquids, for example, the solubility of  $\pi$ -conjugated molecules as a solute is not high.<sup>[127]</sup> On the other hand, if the  $\pi$ -conjugated moiety of the alkyl- $\pi$  molecules can interact with the solute of the  $\pi$ -conjugated molecules, the liquid can be transformed from a disordered state to an ordered state with enhanced optoelectronic properties.<sup>[118]</sup> The point of the molecular design here is to only partially cover the  $\pi$ -conjugated moiety with alkyl side chains. For example, partially exposed  $\pi$ -conjugated moieties can form donor-acceptor (D-A) and charge-transfer (CT) type complexes with added  $\pi$ -conjugated guest molecules.<sup>[124,125,128,129]</sup> Other effective interactions can be assumed, such as hydrogen bonding and coordination bonding. Therefore, when we consider the function of the liquid as a solvent, various functional soft materials with phase and morphology changes can be created by a precise molecular design of the core site and appropriate selection of guest molecules.

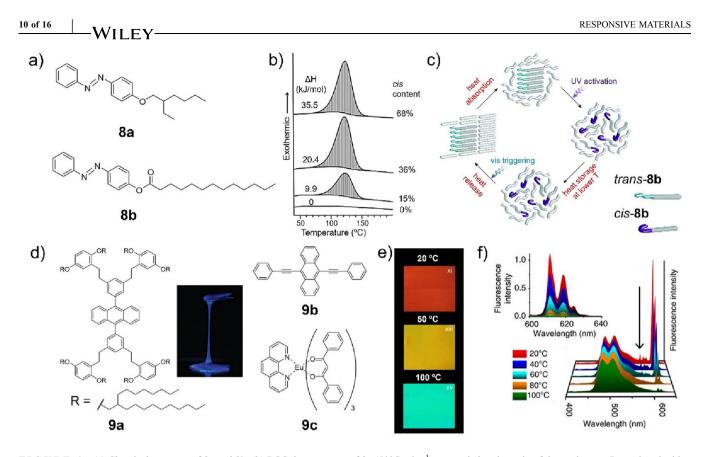
#### 5 | PHOTO AND THERMAL STIMULI

Photoisomerization of azobenzene moiety shows attractive responses to light. One example of this application is materials that reversibly change phase between the solid and liquid state in response to light. Norikane et al. reported a reversible photoinduced isothermal phase transition between a crystal and an isotropic liquid of macrocyclic azobenzene modified with long alkyl chains.<sup>[130]</sup> By irradiating linearly polarized light to the isotropic liquid state macrocyclic azobenzene derivatives, the orientation of the crystal could be controlled.<sup>[131]</sup> Macrocyclic azobenzene without alkyl chains was solid and did not show such photoinduced phase transition to a liquid; thus, alkyl chains play an essential role in forming an isotropic liquid phase in this system. The reversible photoinduced phase transition of azobenzenederived liquids has also been investigated for its application to photocurable and detachable adhesives.<sup>[132]</sup>

Thermal fuels also utilize the photoisomerization of azobenzene exciplex, which combines the response to photo and thermal stimuli. Therefore, developing the technology for effectively using solar energy is an important issue. The development of a method for storing light energy has been promoted as one such technology. Studies focusing on the photoisomerization of liquid-state azobenzene modified with an alkyl chain are gathering attention in this research field. The trans form of azobenzene photoisomerizes to the metastable cis form by UV irradiation, which releases heat when it returns to the stable trans form. Therefore, alkylated azobenzene can store solar energy in the form of heat. However, energy storage and release by isomerization are not efficient in the crystalline state because of the dense packing of the molecules, and the energy density is low in the solution state. Therefore, liquefied azobenzene by attaching alkyl chains has advantages in thermal fuel applications compared to the crystal and solution of azobenzene derivatives.

Kimizuka et al. reported such a liquid azobenzene thermal fuel system for the first time.<sup>[91,92]</sup> The *trans* form of the azobenzene derivative **8a** (Figure 6a) was liquid at room temperature ( $T_g = -63$ °C) due to the effect of the branched alkyl chains on weakening the intermolecular interaction, and it isomerized to the *cis* form upon irradiation of UV light. Figure 6b shows differential scanning calorimetry (DSC) thermograms of **8a** at different photoisomerization degrees determined from <sup>1</sup>H NMR. The  $\Delta H$  values calculated from the DSC thermograms were consistent with the isomerization enthalpy of unsubstituted cis-azobenzene.<sup>[91]</sup> Therefore, it has been demonstrated that liquid azobenzene is a promising optical energy storage material.

Moreover, Han et al. reported the ability to store heat at low temperatures for 10 h or more in a material in which alkylated azobenzene (**8b**) was added as a trigger to aliphatic phase-change materials (PCMs) that can store thermal energy.<sup>[133–135]</sup> The scheme is shown in Figure 6c. The PCMs had a melting point between 10 and 70°C depending on the alkyl chain length and they melted by absorbing heat, whereas the *trans* form of **8b** had a melting point at 73°C



**FIGURE** 6 (a) Chemical structure of **8a** and **8b**. (b) DSC thermograms of **8a** ( $50^{\circ}$ C min<sup>-1</sup>) at a varied molar ratio of the *cis*-isomer. Reproduced with permission.<sup>[91]</sup> Copyright 2014, Royal Society of Chemistry. (c) Schematic image of heat storage and release cycle in the composite of phase-change materials and **8b**. Reproduced with permission.<sup>[133]</sup> Copyright 2018, Royal Society of Chemistry. (d) Photos of **9a** under 365 nm UV light and chemical structure of **9a**, **9b**, and **9c**. (e) Photos of **9a** films containing **9b** and **9c** showing the luminescence color modulation depending on the temperature (20, 50, and 100°C). (f) Thermo-reversible luminescence spectral changes of the composite of **9a**, **9b**, and **9c** supported on a quartz plate ( $\lambda_{ex} = 375$  nm) upon heating. Inset shows an enlarged view between 600 and 640 nm. Reproduced under terms of the CC-BY license.<sup>[37]</sup> Copyright 2013, T. Nakanishi et al., published by Springer Nature Publishing AG. DSC, differential scanning calorimetry.

and dispersed in liquid PCMs in an aggregated state. When UV light was irradiated to this mixture, the *trans* form **8b** isomerized to the bulkier and more polar *cis* form, which stabilized the liquid phase of the PCMs at lower temperatures. The heat stored in this way was released by visible light irradiation causing the *cis* form **8b** to return to the *trans* form and the crystallization of the PCMs.<sup>[133]</sup> This system has attracted attention because the addition of **8b** enables the storage of heat at a temperature lower than the pure-phase crystallization point and the easy control of heat extraction due to employing a visible light trigger.

In addition to thermal fuels, changes in the fluorescence color have been reported as another response to temperature changes. It has been reported in liquefied anthracene (**9a**) systems.<sup>[37]</sup> When **9b** and **9c** were added as dopants to **9a** (Figure 6d), which was liquid at room temperature due to the flexibility of the branched alkyl chains, the fluorescent color was changed by energy transfer from the donor liquid to the acceptor dopant while the liquid state was maintained. Generally, europium complexes are well known for their temperature dependence on the emission color. Regarding this system, reversible luminescence modulation according to temperature was observed (Figure 6e). The fluorescence spectra showed a temperature-dependent change in the

fluorescence intensity between 600 and 640 nm as derived from 9c (Figure 6f). This example is another report that mixing additives to FMLs as a solvent modulates the functions.

When light or heat is used as a stimulus, it is necessary to apply energy that exceeds their threshold. Also, the key to obtaining such a stimulus-responsive material is how the metastable state can be stably maintained. Considering the many molecules that are known, such as photo-responsive molecules and molecules associated with thermal bonding and dissociation, there are high expectations for creating functional liquid materials that can reversibly control two or more states.

## 6 | MECHANICAL FORCE STIMULI

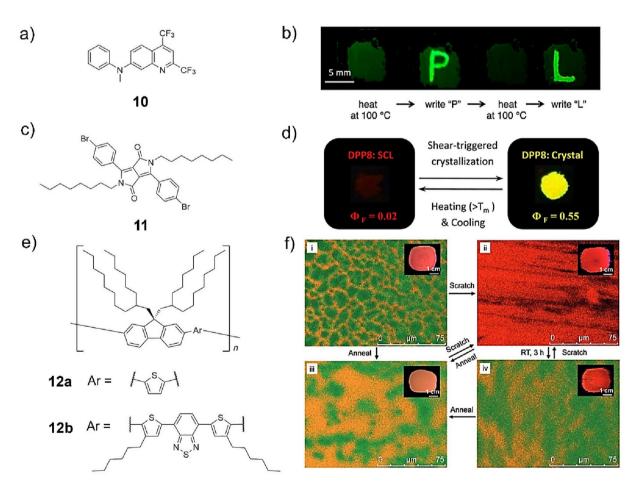
Mechanical force is often used as a stimulus to change the assembled phase structure to a different phase structure, and in recent years, mechanoluminescent materials have attracted attention.<sup>[136]</sup> Phase transition behavior is also caused by applying mechanical force to the supercooled liquid state. Although the supercooled liquid state is precarious in general liquids, it is relatively stable in some highly viscous

liquids.<sup>[51,53,137,138]</sup> The molecular structure and stability of the supercooled state have been studied in detail utilizing a series of anthracenes with branched alkyl chains as model molecules.<sup>[137]</sup> If the alkyl chain is too short relative to the size of the  $\pi$ -conjugated unit, the compound becomes solid at room temperature because the  $\pi$ - $\pi$  interactions are not sufficiently hindered. On the other hand, anthracene with long branched alkyl chains exists as a supercooled liquid at room temperature. It crystallizes over time or by triggers generating crystal nuclei because of increased van der Waals interactions. Furthermore, making the  $\pi$ -conjugated unit bulkier and lowering the symmetry by introducing bromine atoms to the anthracene unit improves the stability of the liquid state. These results suggest that the ratio of alkyl chains to the  $\pi$ -conjugated unit and the bulkiness and symmetry of the  $\pi$ -conjugated unit affect the supercooling behavior.

Sometimes, such metastable supercooled liquids show a phase transition in response to mechanical force. Koga et al. reported the phase transition and change in fluorescence intensity of supercooled N,N-(R)-phenyl-7-amino-2,4-

trifluoromethylquinoline derivatives (10, Figure 7a) induced by scratching.<sup>[138]</sup> Although the  $T_m$  of 10 determined from DSC was 98°C, it could form a supercooled state at room temperature, which was maintained for over a week. According to the XRD results, the supercooled state of 10 was amorphous (liquid). However, a clear peak appeared after scratching, which suggests crystallization from the supercooled liquid state. Therefore, 10 in the crystal state can be returned to the supercooling state by heating at 100°C to transform it into an isotropic liquid and then cooling at 25°C. Since the fluorescence intensity in the crystal state was much higher than that in the supercooled liquid state, writing and erasing letters on the film of 10 was possible (Figure 7b).

Kim et al. found that diketopyrrolopyrrole derivatives modified with octyl chains (**11**, Figure 7c) exist as a metastable supercooled liquid at room temperature and crystallize upon the application of shear stress above 0.90 kPa.<sup>[139]</sup> The fluorescence quantum yield increased significantly from 0.02 to 0.55 upon crystallization, and the color changed from dim orange-red to bright greenish yellow (Figure 7d). In addition to shearing, ultrasonic waves and adding sea sand are practical



**FIGURE** 7 (a) Chemical structure of **10**. (b) Photo images of **10** film under the conditions of heating at 100°C and cooling at 25°C, and the letters "P" and "L" written by scratching with a fine wire on the film. Adapted with permission.<sup>[138]</sup> Copyright 2014 American Chemical Society. (c) Chemical structure of **11**. (d) Photo images of a cast film of **11** showing reversible phase transformation with optical property change caused by shear and heat treatment. Adapted under terms of the CC-BY license.<sup>[139]</sup> Copyright 2015, J. Kim et al., published by American Chemical Society. (e) Chemical structure of **12a** and **12b**. (f) Fluorescence microscopy images of the blend of **12a** (green region) and **12b** (red region); (i) as-cast film, (ii) after scratching, (iii) heat treatment for 1 h at 100°C, and (iv) scratched film after 3 h at room temperature. Adapted with permission.<sup>[140]</sup> Copyright 2019 John Wiley and Sons.

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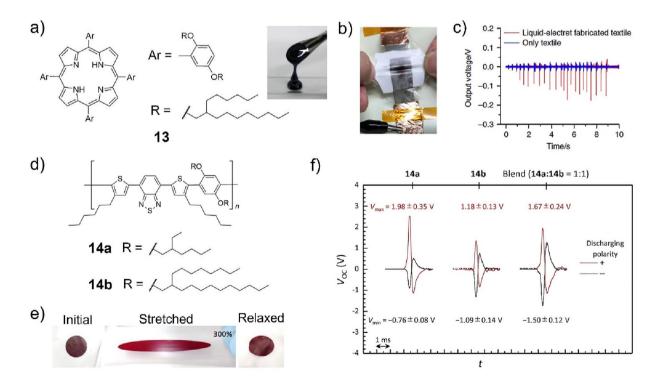
triggers for crystallizing supercooled liquids because they can generate crystal nuclei. Similar to other examples, the phase transition of a supercooled liquid induced by mechanical force has been reported in *N*-heteroacene derivatives<sup>[141]</sup> and cyanostilbene derivatives.<sup>[142]</sup>

Another attempt at a response to mechanical force is mechanically induced fluorescence color changes (MIFCs) derived from microscale phase separation.  $\pi$ -Conjugated polymers modified with branched alkyl chains (12a, 12b, Figure 7e) showed fluidic viscoelastic properties.<sup>[140]</sup> The 1:1 (w/w) blend film of 12a and 12b showed clear phase separation when observed under 365 nm UV light using a fluorescence microscope (Figure 7f, i). Since this material was viscoelastic, it could retain a miscible mixed state to some extent when mixed by mechanical scratching (Figure 7f, ii). In the miscible mixed condition, the donor fluorescence was quenched by fluorescence resonance energy transfer (FRET), resulting in a red emission that was similar to the emission color of pure **12b**. The miscible mixed state spontaneously returned to a phase-separated state when left at room temperature (Figure 7f, iv); the time for the half-restoration was approximately 50 min. Therefore, the MIFCs of this material were reversible. Conventional materials exhibit MIFCs that need stimuli such as heat or light for recovery. Compared to such traditional MIFC systems, recovering under mild conditions owing to its fluidity is an advantage of this viscoelastic  $\pi$ -conjugated polymer blend. Heat and solvent vapors

facilitate this restoration (Figure 7f, iii). Such materials with unique optical and fluidic properties have potential applications in sensing, memory, and security systems.

The most recent discovery is liquid molecules that can store an electrostatic charge and generate an electric current in response to vibration/pressure, that is, liquid electrets. Conventional electrets are known to be made of inorganic solids or non-flexible polymers.<sup>[143]</sup> In contrast, electrets made of softer and more deformable materials are expected to be applied in the medical and healthcare fields as stretchable/deformable devices.<sup>[143-146]</sup> Porphyrin modified with branched alkyl chains (13, Figure 8a) is a viscous liquid at room temperature under solvent-free conditions.<sup>[35]</sup> This liquid can retain electrostatic charges owing to the molecular structure of the charge-storing  $\pi$ -unit isolated by insulating alkyl chains. The surface potential of 13 after poling by corona charging was measured at -330 V. Due to its fluidity, 13 could penetrate a stretchable textile, which enabled the fabrication of a flexible electret device (Figure 8b). This device produced voltage pulses of around -0.1 V in response to finger pressure (Figure 8c).

Stretchable/deformable electret devices have also been fabricated with  $\pi$ -conjugated polymer fluids modified with branched alkyl chains. A  $\pi$ -conjugated polymer with branched ethylhexyl chains (**14a**) was glass at room temperature ( $T_g = 29^{\circ}$ C); on the other hand, a  $\pi$ -conjugated polymer with branched octyldodecyl chains (**14b**) was a



**FIGURE 8** (a) Chemical structure and photo image of **13**. (b) Photo images of a flexible device utilizing **13** as an electret. (c) Output voltage characteristics of the liquid-electret device in the presence and absence of **13**. Adapted under terms of the CC-BY license.<sup>[35]</sup> Copyright 2019, T. Nakanishi et al., published by Springer Nature Publishing AG. (d) Chemical structure of **14a** and **14b**. (e) Photo images of **14a** and **14b** blended film laminated on polyurethane in the initial, stretched, and relaxed state. (f) Open circuit voltages generated by the stretchable device utilizing neat **14a**, **14b**, and 1:1 blend of **14a** and **14b** as an electret. The devices were placed on a wooden plate, and a rigid sphere weighing 1.57 g was dropped onto the device from a height of 100 mm. Reproduced under terms of the CC-BY license.<sup>[36]</sup> Copyright 2023, T. Nakanishi et al., published by Springer Nature Publishing AG.

liquid ( $T_g = -29^{\circ}$ C, Figure 8d).<sup>[36]</sup> These were miscible to each other, and the modulus of the blend could be controlled depending on the ratio of 14a and 14b. The equimass blended film transferred onto polyurethane showed 300% stretchable properties without the film cracking or the polymer bleeding (Figure 8e). This film could retain the charge by positive or negative poling by corona discharge. A stretchable electret device was fabricated by inserting the charged film with a porous separator between the Ag fiber and polyurethane stretchable electrodes. When a circuit was made using this device, an electric current and voltage were generated in response to vibration or impact (Figure 8f). Thanks to the flexibility of the materials, this device could withstand deformation such as stretching, twisting, and folding. Such flexible devices based on fluidic materials are expected to be helpful in soft sensing and robotics.

## 7 | CONCLUSION AND PERSPECTIVES

This review summarized recent studies of liquid materials that respond to stimuli such as electricity, chemical gas/additives, light, heat, and mechanical forces. These stimuli trigger changes in the absorption and fluorescence features due to changes in the intrinsic electronic state of the liquid molecules. They also transform the intermolecular interactions and the nanostructures that enable phase transitions, changes in photoconductivity, and adsorption/emission of gas molecules. In addition, mechanical forces affecting the distance between the charged molecular liquid and the electrode induce responses that generate currents and voltages, which can be employed as a liquid-electret-based deformable mechanoelectric generator.

One method for designing such stimuli-responsive liquid molecules is to attach bulky yet flexible alkyl chains or PEG chains to rigid functional  $\pi$ -conjugated units to prevent aggregation through  $\pi$ - $\pi$  interactions. This results in a material that behaves as a liquid while retaining the optoelectronic properties inherent in the  $\pi$ -conjugated unit. The mechanisms by which these FMLs exhibit stimuli responses differ depending on the type of stimulus and response. For example, changes in the electronic state caused by electricity or light related to changes in absorption and photoluminescence spectra come from the intrinsic properties of the  $\pi$ -conjugated unit. In addition, by utilizing porous materials and organic cages as rigid functional parts, it becomes a liquid with a gas storage function. Intermolecular interactions and nanostructure changes are induced by changes in the balance between  $\pi$ - $\pi$  interactions and van der Waals interactions triggered by chemical molecules or mechanical force stimuli. The electret function is due to the effective combination of charge-storing  $\pi$ -conjugated units and insulating alkyl chains. In a liquid material system in which two or more moieties playing different roles are hybridized, a deep understanding of the role of each unit and how to hybridize them is crucial for obtaining materials expressing the desired functions and stimuli responsiveness.

There are several well-accepted challenges for FML materials. For example, mass production of FMLs can be difficult; if one expects a more substantial function in the functional core unit and sets a complex molecule, the number of synthesis steps will increase. Highly functional FMLs tend to have a large molecular size and molecular weight and simultaneously are highly viscous. Therefore, if liquids' fluidity is positively utilized in applications, the key is finding an appropriate molecular design to lower the viscosity.<sup>[21,61]</sup> In the field of  $\pi$ -conjugated dye glasses, a method of suppressing crystallinity by mixing different molecules for increasing entropy has been reported recently.<sup>[58,147]</sup> This mixing technique has the potential of a new technique for lowering the melting point or viscosity of FMLs. Although most of the current development directions of alkyl- $\pi$  FMLs rely on the optoelectronic functions from the  $\pi$ -unit, as for perspectives of FMLs, there are several challenges in this research area. It is necessary to create the following advanced technologies, such as device architectures that act simultaneously on the liquid fluidity or free deformation and specific stimulus responsiveness. The utilization of microfluidics<sup>[148,149]</sup> would be a powerful and useful tool in this direction. Developing liquid catalyst systems in which the functional core and side chains act effectively and selectively on gases is also essential. It is interesting not only to adsorb and desorb gas molecules and guest molecules in FMLs but also to induce specific catalytic reactions with functional core units and release reaction products by stimuli while circulating liquids. Furthermore, liquid materials with two or more states that can be controlled precisely and reversibly by chemicals, heat, or light will expand the range of applications. Thanks to such progress in research, stimuli-responsive liquid materials are expected to be practically used in various technologies and research fields, such as healthcare, security, sensors, soft electronics, and robotics.

#### AUTHOR CONTRIBUTIONS

Akito Tateyama: Conceptualization (Supporting); Writing – original draft (Lead); Writing – review & editing (Supporting). Takashi Nakanishi: Conceptualization (Lead); Supervision (Lead); Writing – original draft (Supporting); Writing – review & editing (Lead).

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

### DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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