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REVIEW

Recent progress in photoinduced transitions between the solid, glass, and liquid states based on molecular photoswitches

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Abstract

Photoinduced transitions between the solid, glass, and liquid states based on molecular photoswitches promise a wide variety of applications. Photoswitchable adhesives are representative examples and are expected to contribute to material recycling for a sustainable future in the era of composite materials due to strong bonding and on-demand photo-induced debonding with minimal damage to the adherends. Only a few molecular photoswitches are known to undergo these transitions, but recent progress, mainly with azobenzene, has been remarkable. Here, we review the photoinduced transitions of small molecules and polymers over approximately a decade and systematically discuss the molecular designs, mechanisms, applications, merits and demerits, and future challenges in each photoswitch and the whole field. We hope this review provides useful information, inspiration, and ideas for the development of this field and the expansion of its applications.

Introduction

Transitions between solids (crystals and some elastomers with crystalline or glassy regions), glasses (frozen liquids), and flowing liquids at room temperature induced by photoirradiation and resulting changes in the melting points (T_ms) and glass transition temperatures (T_gs) [1–4] have attracted considerable attention in various fields and are considered for applications such as photoswitchable adhesives [5, 6], energy storage and release [7–13], photolithography [14], actuators [15], healable materials, and gas separations (Fig. 1a). Unlike conventional temperature control to induce the transitions, isothermal photostimulation is fascinating because of the high spatiotemporal resolution, easy and precise regulation of the wavelength and intensity, and no generation of chemical waste. In particular, photoswitchable adhesives are expected to contribute to material recycling for a sustainable future as complex architectures composed of dissimilar materials are being developed in diverse fields [16–20], because they enable both robust bonding during use and on-demand debonding after use with minimal damage to the adherends due to the advantages of light. In addition to photoinduced transitions, polarity changes [21–26] and bond formation and dissociation [27–36] (and resulting liquid crystal–liquid transitions [37]) have enabled the photocontrol of adhesion [5]. The photoinduced transitions of small molecules and polymers have been achieved with molecular photoswitches, which are (thermo)reversibly isomerized between at least two thermodynamically (meta)stable states with photoirradiation [38–42]. Although a huge variety of molecular photoswitches are known and widely used, to the best of our knowledge, only five of them have been demonstrated to show photoinduced transitions, and these are azobenzene (AB), spiropyran (SP), hydrazone, diarylethene (DAE), and 1,2-diketone (Fig. 1b), since the first paper using AB was reported in 2011 [43]. Moreover, the previously published papers were predominantly on AB. The progress realized primarily with AB small molecules and polymers has been summarized in excellent reviews [1–4]. In this article, we highlight recent progress in photoinduced transitions based on AB and other photoswitches. Transitory liquefaction induced by the photothermal effect or continuous photoisomerization cycles and photoinduced transitions of liquid crystals [44–54], between sols and gels, and between liquids and elastomers without crystalline or

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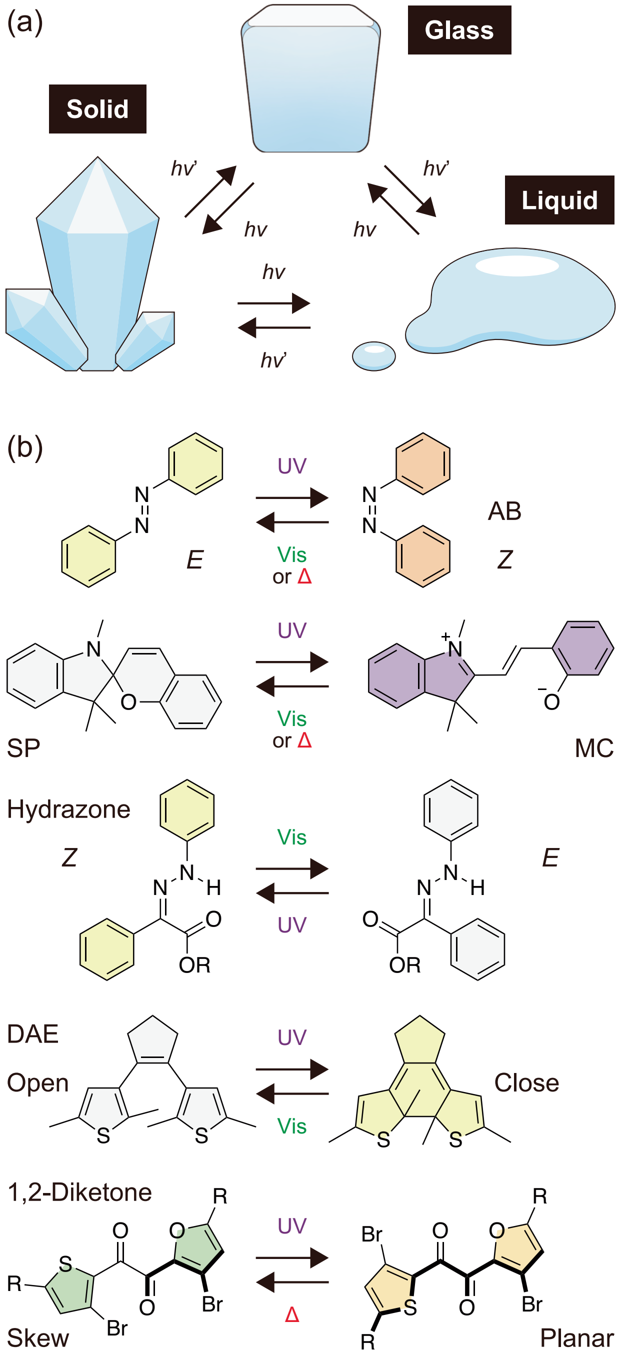
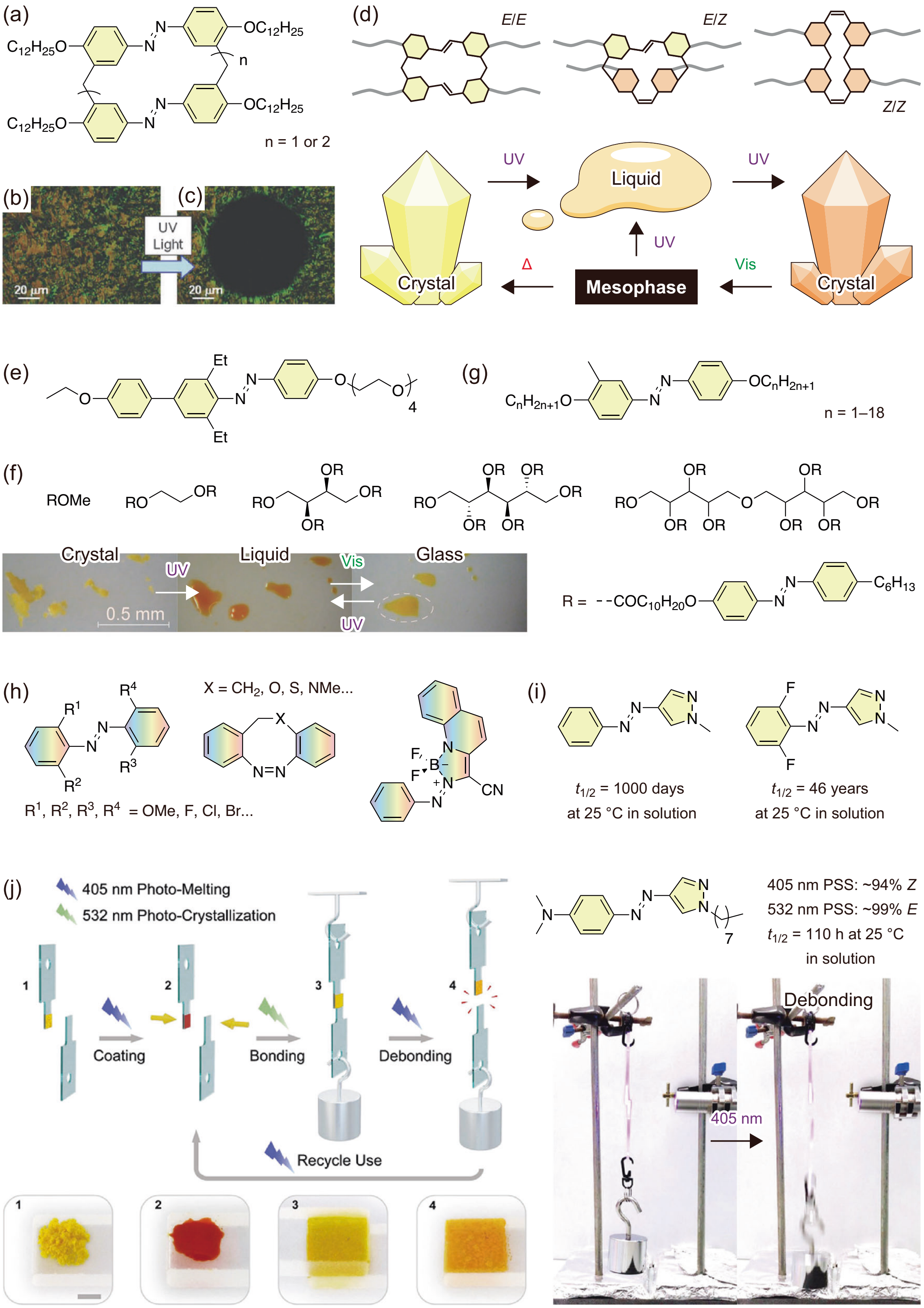


Fig. 1 **a** Illustration of photoinduced transitions between solid, glass, and liquid states. **b** Photoswitches previously reported to show photoinduced transitions

glassy regions are beyond the scope of this review. Here, previous studies on photoinduced transitions between solids, glasses, and liquids are divided into eight sections based on the kinds of photoswitches and molecular weights, i.e., small molecules or polymers including monodisperse oligomers and dendrimers, and discussed separately in terms of the molecular designs, mechanisms, applications, merits and demerits, and future challenges. Finally, we also suggest future challenges for the whole field.

Azobenzene small molecules

The photoinduced transitions based on AB are described in the other remarkable reviews [1–4]. Here, we will describe and discuss only the essence of the previous studies. AB is definitely the most commonly used molecular photoswitch and is characterized by large motions generated during isomerization between the thermodynamically stable *E* isomer and the metastable *Z* isomer during irradiation with UV and visible light (Fig. 1b) [55, 56]. Macrocyclic AB molecules with long alkyl chains were discovered for the first time to show photoinduced solid–liquid phase transitions at room temperature (Fig. 2a) [43]. Both the dimer and trimer macrocycles, in which all incorporated ABs were the *E* isomers, were isothermally changed from the crystalline to the isotropic phase by UV light (Fig. 2b, c). The trimer changed more slowly than the dimer, and the corresponding macrocycles without long alkyl chains did not undergo these photoinduced transitions. The phase transitions were highly sensitive to light and induced even by the generation of a small *Z* fraction. One reason for the high sensitivity is that *E*/*Z* mixtures generally have much lower T_ms than the pure *E* and *Z* isomers, as observed with the parent AB [57, 58], which is significantly different from unidirectional T_g changes in AB-containing polymers as a function of the *E*/*Z* ratio. Subsequent work demonstrated that the macrocyclic *E*/*E* dimer isomerized to the *E*/*Z* isomer to the *Z*/*Z* isomer under UV irradiation and underwent transitions from crystalline to liquid to another crystalline phase, which were reversibly induced with visible light exposure and heating (Fig. 2d) [59]. The photoinduced liquefaction mechanism was also elucidated by X-ray crystallography under UV irradiation at different temperatures [60]. After the first paper, photoinduced transitions from a crystal to a liquid and between crystals, glasses, and liquids were reported for an asymmetric *ortho*-alkylated AB [61] and sugar alcohol derivatives with multiple ABs [62], respectively (Fig. 2e, f). Although the asymmetric AB has not been studied subsequently, a systematic study on a series of multi-AB sugar alcohol derivatives was conducted and found that those with one or two ABs did not isomerize and liquefy upon UV irradiation, probably due to the high crystallinity and absence of available free volume for isomerization [63–65]. On the other hand, the syntheses and isolation of these AB derivatives were relatively difficult. Therefore, since then, most of the molecular structures have been simple but asymmetric and composed of one AB and one or more long alkyl chains. A typical example is shown in Fig. 2g [66–70]. Two alkyl chains were added at the (*para*) 4- and 4’-



positions of AB, and one methyl group was introduced at the (*meta*) 3-position. Generally, long alkyl chains prompt easy *E*-AB aggregation and make *Z*-AB a liquid due to the large free volume [65]. The methyl group broke the molecular symmetry, disrupted crystal packing, destabilized the crystal structures, provided enough free volume for

◀ **Fig. 2** **a** Macrocyclic AB molecules reported in the first paper. Photoinduced transition from **b** crystal to **c** liquid states of macrocyclic AB ($n = 1$) and **d** the details. Reproduced with permission from Norikane et al. [43]. Copyright 2011, the Royal Society of Chemistry. **e** An asymmetric *ortho*-alkylated AB, **f** sugar alcohol derivatives with multiple ABs, and **g** a typical example of simple asymmetric ABs that show photoinduced transitions between crystal, glass, and liquid states. Reproduced with permission from Akiyama and Yoshida [62]. Copyright 2012, John Wiley & Sons. **h** Visible and NIR light-responsive *ortho*-substituted, coordinated, and bridged ABs. **i** Representative thermally stable azoheteroarenes. **j** A photoswitchable azoheteroarene adhesive. Reproduced with permission from Huang et al. [120]. Copyright 2022, American Chemical Society

photoisomerization, and enabled photoinduced crystal–liquid transitions. The corresponding symmetric AB derivatives without the methyl group or with two methyl groups at the 3- and 3’-positions underwent no photoinduced transitions. In addition to these AB small molecules, a wide variety of ABs have shown photoinduced crystal–liquid transitions, including an amphiphile [71], ionic crystals and liquids [72–74], star-shaped tetramers [75, 76], simple ABs with one or two small substituents such as methyl and methoxy groups [77–83], and others [84–87].

The simple AB skeleton was employed in all molecules described above but has two fatal drawbacks for some applications, i.e., UV excitation is required for *E*-to-*Z* isomerization, and the *Z* isomer has a short half-life ($t_{1/2}$) of approximately 1 day [55, 56]. UV light causes damage to organic and polymeric materials and biological components, although the high spatiotemporal resolution of the light can minimize the effect. The *Z* isomer formed the liquid state with high molecular mobility and therefore could not maintain the state due to the short $t_{1/2}$ in the photoinduced transitions described above. To broaden the application range, the excitation wavelength has been redshifted to the visible and near infrared (NIR) regions mainly by *ortho*-substitution, coordination, and bridging of the two phenyl rings (Fig. 2h) [88–103], and the thermal stability of the *Z* isomer has been improved to provide $t_{1/2}$ values of up to several decades (at 25 °C in solution) for *ortho*-substituted ABs and azoheteroarenes (Fig. 2i) [104–112]. Recently, some of them have been demonstrated to show crystal–liquid transitions with only visible light [113, 114] and by photoisomerization with a thermally stable *Z* isomer [106, 115–122]. Photoinduced transitions between liquid *E*-AB and solid (crystalline) *Z*-AB would suppress thermal isomerization by restricting the molecular mobility of the *Z* isomer as approached in polymers (Fig. 3c), but this has not been reported. The *Z* isomer of the parent AB has a higher T_m (ca. 71 °C) than the *E* isomer (ca. 68 °C) [3, 4, 123], but modification of the AB skeleton reverses the original T_ms. The reason is still unknown [3].

To date, photoinduced transitions of AB small molecules have been used for switching fluorescence [61] and enzymatic degradation of a biodegradable polymer [68], switchable adhesives [62–65, 67, 115, 120, 122], photoresists for simple photolithography without harsh conditions [66, 74, 119], a remote-controllable light shutter [71], energy storage and release [72, 74, 76, 80, 82–84, 86, 87, 113, 114, 116–118, 121], gas separation [75], moving crystals on glass and water surfaces [77–79, 81], an actuator [69], and shape memory [70]. A representative example of photoswitchable adhesives is shown in Fig. 2j. An azoheteroarene with a $t_{1/2}$ of several days and almost quantitative photoisomerization yields in both *E*–*Z* directions was used as the adhesive and showed reversible bonding via solidification and debonding via liquefaction induced by visible and UV irradiation, respectively. Photoisomerization was clearly confirmed by the color changes. Nevertheless, incorporation of the system in polymers is desired because commercial adhesives are mainly composed of polymers. In energy storage and release, blending small ABs with photoinactive phase-change materials [124–130] or solely unliquefiable ABs [131] is a powerful strategy.

Azobenzene polymers

Photoinduced transitions between solid, glass, and liquid states of polymers were independently reported for the first time in 2017 by two research groups [132, 133]. Both pioneering studies demonstrated that glassy linear polyacrylates with *E*-AB in the side chains were converted to flowing liquids with T_gs below room temperature upon UV irradiation and the consequent *E*-to-*Z* isomerization and returned to glasses by visible irradiation and *Z*-to-*E* isomerization (Fig. 3a, b). The T_gs monotonically decreased with increasing *Z* ratios [132], which was completely different from the dependence of T_ms on the *E*/*Z* ratios in AB small molecules. The effect of molecular weight on photoliquefaction was also investigated [132, 134]. Interestingly, all polyacrylate linear homopolymers of AB ($R^1 = H$, $m = 6$, $R^2 = CH_3$ in Fig. 3a) with different molecular weights ranging from 5×10^3 g mol^{-1} to 10^5 g mol^{-1} were photoliquefied. The changes in T_gs between the original *E* polymer and a photostationary state (PSS) in the *E*-to-*Z* isomerization (ΔT_g) were similar. Rather, the ΔT_g in the 10^5 g mol^{-1} polymer (ca. 70 °C) was larger than that with a molecular weight of 10^4 g mol^{-1} (ca. 60 °C), although the higher molecular weight resulted in increased T_gs for both isomers (*E*: from 48 °C to 80 °C, *Z*: from −10 °C to 7 °C). A high molecular weight also generated bulk physical properties such as free-standing and stretchable capabilities. Regarding the polymer structure, the length of the alkyl chain spacer, by which AB was connected to the main

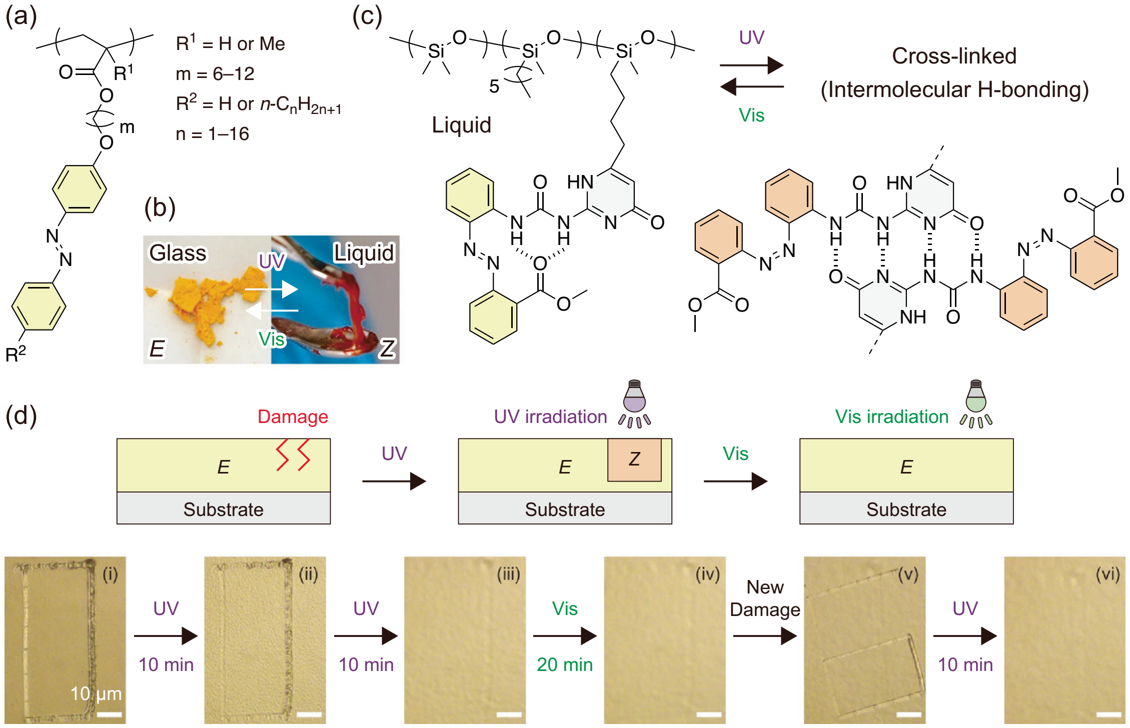


Fig. 3 **a** Representative poly(meth)acrylate linear homopolymers of AB that show photoinduced transitions between glass and liquid states. **b** Photoinduced glass–liquid transitions of an AB homopolymer ($R^1 = H$, $m = 6$, $R^2 = CH_3$). **c** Photoinduced transitions between the liquid *E* isomer and the physically cross-linked solid-like *Z* isomer using an AB monomer fused with a quadruple hydrogen bonding ureidopyrimidinone moiety. **d** Healing of the AB homopolymer bulk material with UV and visible light irradiation ($R^1 = H$, $m = 6$, $R^2 = CH_3$). Reproduced with permission from Zhou et al. [132]. Copyright 2017, Springer Nature

chain, should not be too short or too long [135]. Short and long spacers failed to induce phototransitions due to the restricted molecular mobility of AB and the crystalline natures of long alkyl chains such as n-$C_{20}H_{40}$, respectively. Similarly, the length of the alkyl chain at the side chain end significantly affected the photoinduced transitions [136]. Longer tails up to n-$C_{16}H_{33}$ resulted in higher T_gs for both isomers but larger ΔT_g and lower viscosity for the *Z* isomers. Moreover, polyacrylate was more appropriate than polymethacrylate as the main chain backbone for photoinduced glass–flowing liquid transitions due to its higher flexibility [137, 138]. In addition to the side chains of these poly(meth)acrylate linear homopolymers [122, 132–147], AB has been incorporated into a variety of polymers and positions to enable photoinduced transitions between solids, glasses, and liquids, including side chains of other linear homopolymers (poly(vinyl ether) and polynorbornene) [148, 149], linear statistical copolymers [150, 151], and linear and star block copolymers [152–155], main chains of linear polymers [156–160], both chain ends of linear oligomers [161, 162], one end of a linear polymer [163], cross-linked polymers [164, 165], and the peripheries of dendrimers [166].

Photoinduced transitions were also demonstrated for azoheteroarenes [122, 141], with only visible light [157], and for crystalline polymers [140, 147, 148, 155–158, 161–163]. Furthermore, photoinduced transitions between a stable liquid *E* isomer and a physically cross-linked solid-like metastable *Z* isomer were achieved by fusing AB with a quadruple hydrogen-bonding ureidopyrimidinone moiety and incorporating it into the side chains of liquid polysiloxanes (Fig. 3c) [151]. The reverse direction to the common transitions using AB could solve the thermal isomerization and back transition occurring at room temperature by restricting the molecular mobility of the *Z* isomer, which has never been addressed in AB small molecules and promises to broaden the applications. Meanwhile, the intrinsic instability of *Z*-AB was not improved ($t_{1/2}$ = ca. 8 h at 25 °C in solution), and this system may be excluded from the scope of this review because the T_ms and T_gs were not determined.

The number of papers on photoinduced transitions of AB-containing polymers is still small compared to that of low-molecular-weight ABs. In particular, the use of upgraded ABs [88–103] and azoheteroarenes [104–112] is rare but needed. In terms of practical use, blending AB small molecules into photoinactive polymers is an effective strategy to realize photoinduced transitions of the polymeric materials [167–172]. To date, photoinduced transitions of polymers have been considered for applications including healable materials (Fig. 3d) [132, 134–136, 138, 160, 163, 166, 170], switchable adhesives [122, 133, 137, 139, 148, 150–154, 159–161, 166, 168, 169], actuators [134, 157, 158, 164, 165], switching thermal conductivity [140, 147] and fluorescence [172], fabrication of micro- and nanopatterns (lithography) [142, 144, 149, 155, 160], information encryption and smart windows [163], shape memory [165], and energy storage and release [166].

Spiropyran small molecule

Noncharged SP isomerizes to the metastable zwitterionic merocyanine (MC) under UV irradiation and spontaneously reverts back to SP at room temperature and more rapidly with heating or visible irradiation (Fig. 1) [173, 174]. The large polarity changes are intriguing and have been utilized in various applications [21, 22, 24–26, 175]. To date, only one SP small molecule has been reported to show photoinduced solid–liquid transitions [176]. An SP derivative with two long alkyl chains was a liquid but changed to a solid upon UV light exposure and subsequent thermal treatment (Fig. 4a, b). The J-aggregate of MC and blue crystals were formed by heating at 30 °C, while the H-aggregate and red crystals were generated by heating at 35–55 °C. Heating above the estimated T_ms of the crystals (>60 °C) or visible light exposure resulted in liquefaction and color fading. In contrast to the photoinduced transitions based on AB, the thermally unstable MC isomer formed a solid. Therefore, both crystals were stable, and no thermal isomerization to SP was observed in the dark at room temperature.

Spiropyran polymers

Switching of T_gs by SP–MC photoisomerization has been achieved with linear polymers and a cross-linked polymer [177, 178], although photoinduced transitions between glasses and flowing liquids have not been demonstrated at room temperature. The T_gs of the linear statistical copolymers of an SP methacrylate and di(ethylene glycol)methyl ether methacrylate with different compositions were increased by up to ca. 20 °C upon UV irradiation, probably due to the high polarity of the generated MC isomer and consequent enhanced intermolecular interactions (Fig. 4c) [178]. The direction of the T_g changes was opposite to that of AB polymers and similar to the T_m changes in the SP small molecule. However, unlike the small SP, the MC form in the bulk reverted back to the SP form at room temperature over a period of 2–3 h. In the cross-linked polymer, the T_g increase seen during UV light exposure was ca. 10 °C and smaller than those of the linear polymers, but some fraction of the MC form was maintained for several months in the dark [177]. Photoinduced glass–liquid transitions at room temperature will be possible by optimization of the compositions in both systems.

Hydrazone small molecules

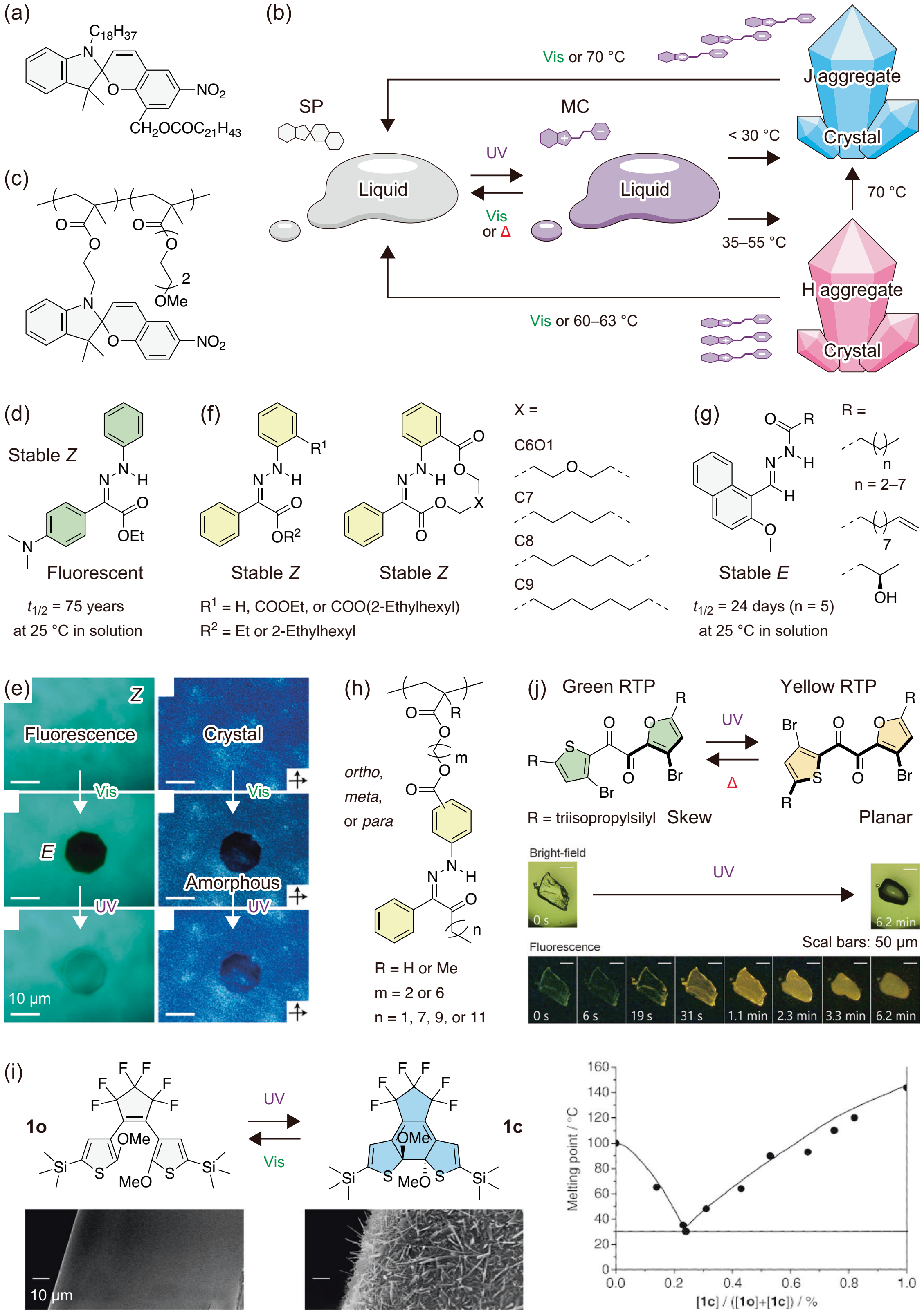
Recently, hydrazone photoswitches with extremely high thermal stabilities have been developed [179–184]. The $t_{1/2}$s of the relatively unstable E or Z isomers, which changed depending on the chemical structure, were up to ten thousand years at 25 °C in solution and in the bulk [185], although the thermal isomerization strongly depended on the polarity of the media. Photoinduced crystal–isotropic transitions of a hydrazone small molecule were discovered in 2018 [186]. The crystalline Z isomer of a hydrazone derivative with a dimethyl amino group changed to isotropic with fluorescence quenching upon blue light irradiation because the E isomer was noncrystalline and nonfluorescent (Fig. 4d, e). The crystal and fluorescence were partially restored by UV exposure. Similarly, photoinduced crystal–liquid transitions were observed in macrocyclic hydrazones (X = C8 and C9 in Fig. 4f) and used for energy storage and release [185]. Although such transitions did not occur at room temperature, photoinduced T_m changes ($\Delta T_m < 60$ °C) were possible with other acyclic and cyclic hydrazone molecules (Fig. 4f, g) [185, 187]. Interestingly, the E isomers of the macrocycles with short alkyl linkers (X = C6O1 and C7) had higher T_ms than the corresponding Z isomers, which indicates that the opposite direction, i.e., transitions between liquid Z isomers and solid E isomers, will be also possible in hydrazone small molecules by optimizing the modification.

Hydrazone polymers

Linear poly(meth)acrylate homopolymers of hydrazone changed their T_gs upon light irradiation (Fig. 4h) [188]. Purple light irradiation of the stable Z isomers produced the metastable E isomers and increased the T_gs by up to 22 °C. The effects of the side chain spacer (m) and tail (n) lengths, substitution position (*ortho*, *meta*, or *para*), and main chain backbone (acrylate or methacrylate) were investigated. Finally, the T_gs of both isomers were tuned to around room temperature (20–37 °C) with ΔT_g of 15 or 16 °C (*para*, R = H, $m = 2$, $n = 9$ or 11).

Diarylethene small molecule

Isomerization between the thermally stable open and closed forms of DAE proceeds via UV and visible irradiation, and



the conjugation changes have attracted considerable interest (Fig. 1) [189, 190]. Although the small structural changes are considered unsuitable, photoinduced crystal-to-liquid transitions were found for a DAE derivative (Fig. 4i) [191]. The open-ring and closed-ring isomers were crystalline at room temperature with T_ms of ca. 100 °C and ca. 140 °C,

◀ **Fig. 4** **a** An SP small molecule that shows photoinduced solid–liquid transitions and **b** the details. **c** Linear statistical copolymers containing SP with photoswitchable T_gs. **d** A fluorescent hydrazone and **e** its photoinduced crystal–isotropic transitions (left: fluorescence images, right: polarizing images). Reproduced with permission from Shao et al. [186]. Copyright 2018, American Chemical Society. **f, g** Acyclic and cyclic hydrazones that change their T_ms upon light exposure. **h** Linear homopolymers of hydrazone that show photoinduced T_g changes. **i** Formation and disappearance of microfibrils on DAE crystals via photoinduced crystal-to-liquid transitions. Reproduced with permission from Uchida et al. [191]. Copyright 2006, John Wiley and Sons. **j** Photoinduced crystal-to-liquid transition of an asymmetric heteroaromatic 1,2-diketone. Reproduced with permission from Komura et al. [193]. Copyright 2023, the Royal Society of Chemistry

respectively, while the T_m of their mixture decreased to approximately 30 °C. UV light exposure of the open-ring crystals generated the closed-ring isomer and caused liquefaction of the surface due to the lowered T_m of the mixture. Microfibrils of the closed-ring isomer formed on the surface over 24 h in the dark and disappeared during visible light irradiation.

1,2-Diketone small molecule

An asymmetric heteroaromatic 1,2-diketone consisting of thiophene and furan rings exhibited room-temperature phosphorescence (RTP) in the crystalline and supercooled liquid states (Fig. 4j) [192]. The diketone mainly exists in the stable skew and metastable planar conformations. While the skew conformer forms the crystals and produces feeble green RTP, the planar conformer is more stable in the excited state and yields strong yellow RTP in the liquid state. Very recently, the diketone was reported to show a photoinduced crystal-to-liquid transition at room temperature with RTP changes [193]. UV irradiation macroscopically melted the crystals into a liquid after disappearance of the initial green RTP and emergence of the yellow RTP (Fig. 4j). The mechanism was elucidated with real-time monitoring of the RTP changes, single crystal X-ray structural analyzes at different temperatures and after UV light irradiation, and density functional theory calculations with comparisons to the corresponding symmetric heteroaromatic 1,2-diketones [194–196]. A symmetric diketone composed of two furan rings also changed from crystals to a liquid without luminescence upon UV exposure. Although recrystallization from the liquid asymmetric diketone was extremely slow and required several months [192], spontaneous and quick liquid-to-crystal transitions after photoinduced melting and on-demand liquid-to-crystal transitions caused by an external stimulus will be possible after modification of the chemical structure based on the elucidated mechanism. Additionally, photoinduced transitions of polymers with diketones will be fascinating [197].

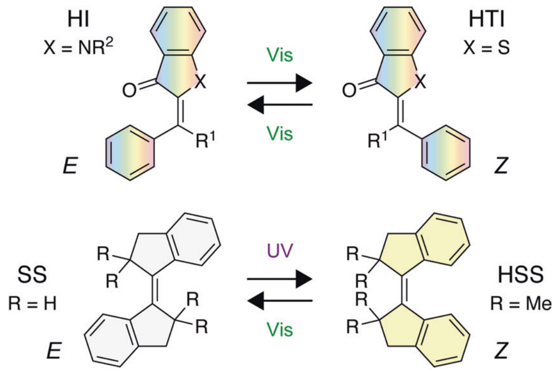


Fig. 5 Photoswitches that are thermally stable but have not been reported to show photoinduced transitions

Conclusion

In this article, we reviewed the recent progress made with photoinduced transitions of small molecules and polymers between the solid, glass, and liquid states based on molecular photoswitches. Only a few photoswitches were found to undergo photoinduced transitions, and those based on AB have been intensively studied for approximately a decade. Therefore, the mechanisms and structural requirements for the transitions are poorly understood. Additionally, AB is unsuitable for some applications due to the thermal instability and high polarity of the *Z* isomer. Photoinduced transitions should be studied with a wide variety of photoswitches. In particular, thermally stable photoswitches such as hydrazone [179–188], DAE [189–191], hemiindigo (HI) [198], hemithioindigo (HTI) [198, 199], stiff stilbene (SS) [200], and sterically hindered SS (HSS) [201, 202] (Fig. 5) and visible and NIR light-responsive switches [203, 204] are promising. HI and HTI combine both thermal stability and two-way isomerization induced by visible light. SS and HSS have already been reported to show largely different T_ms in the *E* and *Z* isomers [203]. We believe that future studies on these photoinduced transitions will completely elucidate the mechanisms, establish design guidelines, broaden the use, and accelerate practical applications.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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