

Structural Design and Application of Azo-based Supramolecular Polymer Systems

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Abstract This article presents a brief overview of recent advances in azo-containing supramolecular systems. In literature, it has been shown that azo supramolecular polymers and their composite materials exhibit fast and intelligent responses to various external stimuli, such as temperature, pH change, redox reagents, ligands, coupling reagents, *etc.* In applications, these systems are widely used for molecular motors, shape memory, liquid crystal, solar thermal energy storage, signal transmission, intelligent encryption, and other purposes. Furthermore, these systems can function as key components for device upgrade processing. However, the design and rules of azo supramolecular polymers are still not supported by an exact theory. Information about the relationship between the spatial structure and behavior is lacking, and new supramolecular materials cannot be designed by adding functional moieties to known azo polymers. Based on the current research status, this review mainly summarizes the structural design principles as well as structures and applications of known azo supramolecules; meanwhile, it highlights the emerging development fields, recent advances, and prospects in fabricating self-assembling intelligent supramolecular systems with azo supramolecular polymers as responsive units. The goal of this review is to bring new inspiration to researchers who want to optimize the chemical structure, steric conformation, electrostatic environment, and specific molecular functionalization.

Keywords Azo; Supramolecular; Structures; Application; Prospect

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INTRODUCTION

Design, manufacture, and application of functional materials based on non-covalent chemistry have become important topics in the research of material synthesis for many years. Supramolecular chemistry, as a new field, has attracted great attention from many researchers in the field of self-assembly for composite molecular design.^[1–3] In development, as one of the most effective strategies for constructing ordered nanostructures among various types of methods, supramolecular self-assembly has been successfully applied for energy storage,^[4,5] intelligent drive,^[6–8] and biomedicine^[9] purposes. Further, supramolecules have many unique and attractive features, such as networks that can be reshaped reversibly,^[10] low density and high free volume fluid properties,^[11] molecular density,^[12] excellent elasticity and machinability,^[13,14] and so on.

Azobenzene, a representative molecular model of *trans-cis* photo-responsive isomerization, is the most popularly used photo-responsive compound in many applications due to its

simple synthesis, rapid response, high efficiency isomerization, and photobleaching resistance.^[15–20] The photo-responsive isomerization of azobenzene was first discovered in 1937, nearly 32 years before the crown ether was found by Peterson.^[21] After years of research and development, scientists have discovered that azobenzene derivatives undergo significant structural changes through *trans-cis* isomerization under ultraviolet and visible light irradiation.^[22] Azobenzene and its derivatives are small molecules capable of reversible photochemical transformation between two different isomers under environmental changes. In order to improve the applicability and functional diversity of materials, azo units and polymers are often used in combination. Polymers not only can manipulate the movement of molecules, but also have a fast, gentle, and reversible effect.^[23] For example, researchers have developed azobenzene/ β -cyclodextrin (β -CD) supramolecular polymer materials, which could modulate the binding ability of β -CD.^[24] This is the first time that azo molecules have been used in supramolecular systems. It paved the way for the development of multi-type azo supramolecular materials, as well as the development of a variety of applications, such as liquid crystal (LCs) optical equipment, data storage, intelligent biomimetic polymers, and so on.^[25] Other polymers commonly include polymethacry-

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lates, peptides, polyisocyanates, etc.^[26,27]. An azo supramolecular polymer can be obtained by incorporating an azo unit having a photoresponsive function to a polymer. However, these polymers have relatively low T_g , and consequently, they are only used in some relatively soft special materials.

All applications are based on the special properties of photoisomerization and photo-reorientation of azo groups in polymer supramolecular chains. The introduction of photo-responsive compounds into supramolecular systems (supramolecular nanostructures) can effectively impart light-responsive behavior to materials and facilitate the fusion with other irritating responses.^[28] It has also been found that an ordered supramolecular material (structure) with a stimulating response can transform a signal, thus “amplifying” the photo-controlled isomerization and generating more complex functions. At this stage, azo-containing supramolecules have become a hot topic for researchers. Multiple applications of azo supramolecules are expanded, mainly including molecular motors, encoding and reading, shape memory devices, solar thermal energy storage, and signal sensors, etc.^[29,30] Similarly, functionalization of the azo structure on a graphene surface has also facilitated applications in energy storage and regulation of band gaps.^[31] Research directions and methods are developing rapidly, while the research results on azo supramolecules lack uniform design principles, mechanisms, and concepts in terms of materials. This brings great challenges to our design of materials and scientific research. Therefore, this paper summarizes the progress and viewpoints of the work from existing literature and further suggests a method for the design of azo supramolecules.

Herein, we mainly cover the molecular structure design principles, intermolecular forces, structures, and some recent applications of azo supramolecular systems. This review is structured as follows. Section 1 describes the design principles and reasons for supramolecules. In Section 2, we discuss three sorts of intermolecular interactions of supramolecular polymers, namely, host-guest interactions, hydrogen bonding (H-bonding), and electrostatic interactions. Section 3 concerns the molecular structures of azo supramolecular polymers, including main chains, side chains, and dendritic structures. Section 4 presents the recent applications and future development prospects, focusing on multi-function actuators, sensors, detectors, and energy storage. Finally, based on the results of our group and other research teams, the perspectives, development directions, and challenges in this area are suggested in Section 5.

AZO-BASED SUPRAMOLECULAR DESIGN

The development of azo supramolecular materials with multifunctional and structural properties should be based on rational design from multiple stimulating responses and application properties. Fig. 1 is the basic content of azo supramolecular material design. The multi-stimuli response application can be subdivided into physical and chemical stimulation. Physical stimuli usually include light, electricity, heat, and magnetism, while the chemical ones usually involve redox reactions, acid-base reactions, ion transport, and enzymes.^[32,33]

Supramolecular combinations of azo units and polymers can exert macroscopic effects by means of photoinduced molecular horizontal motion (photoisomerization), such as the photoelectric control of molecular alignment, self-assembly of block copolymer nanostructures, and photoinduced molecular patterning of polymers.^[34] The responsive application of azo supramolecules should be based on physicochemical properties, and then the appropriate structural design should be selected as needed. Many results have also proven that the design of supramolecular materials can be used as a guideline for the construction, performance optimization, and function regulation of photo-responsive azo-based polymers.^[1,3,34] In addition, the photophysical and chemical properties of the photo-responsive material systems can be well tuned by varying the type and strength of bonding between the polymer and azo units.^[35,36] In the following sections, we will review the research progress of azo supramolecules, and objectively comment on several common supramolecular design strategies: H-bonding, π - π interactions, ionic bonding, etc. The design of these photo-responsive supramolecular materials is simple and versatile, and the structural design of the following examples is convincing.

AZO-BASED SUPRAMOLECULAR INTERACTIONS

In recent decades, the field of azo supramolecular polymerization has been significantly developed, and polymer systems are constructed using (reversible) noncovalent interactions (H-bonding,^[37,38] ionic bonds,^[39] halogen bond ($D \cdots X-X$, $X = I, Br$),^[40,41] metal-ligand coordination,^[42] π - π stacking,^[43] etc.) between macro-monomer units (Fig. 2).

The first example of introducing H-bonding into the preparation of side chain azo supramolecular polymers was published in 2007.^[44] Subsequently, H-bonded azo supramolecular polymers have been greatly developed. Due to the stability, directionality, and saturation of H-bonding, intermolecular H-bonded interactions have received much attention in material science and life science, and are crucial in determining the properties of complexes and the design of novel complexes.^[37] Cui *et al.*^[45] synthesized an azopyridine side chain polymer, which can be easily converted into two H-bonding based supramolecular liquid crystal polymers (aliphatic or aromatic carboxylic acids) under appropriate conditions. Shibaev *et al.*^[46] reported a H-bonding based polymer composite material with a frozen cholesteric structure that can respond to pH variation, and they proved that the azopyridine small molecules are stably present under H-bonding. And when studying H-bonded type azo supramolecules, Zettsu *et al.*^[47] found that the r-junction (remoulding molecular binding sites) between the photoactive unit and the polymer matrix is a necessary prerequisite for the formation of surface relief structure of the azo supramolecular polymers in liquid crystals compared with nonbonded or poorly bonded mixtures. Similarly, some metal-ligand coordination, π - π stacking, and other related azo supramolecular polymers have been confirmed to exhibit a π - π stacking effect, such as graphene grafted with azobenzene, carbon nanotube/azo polymer composite, and others.^[48–50] In preparation, π - π

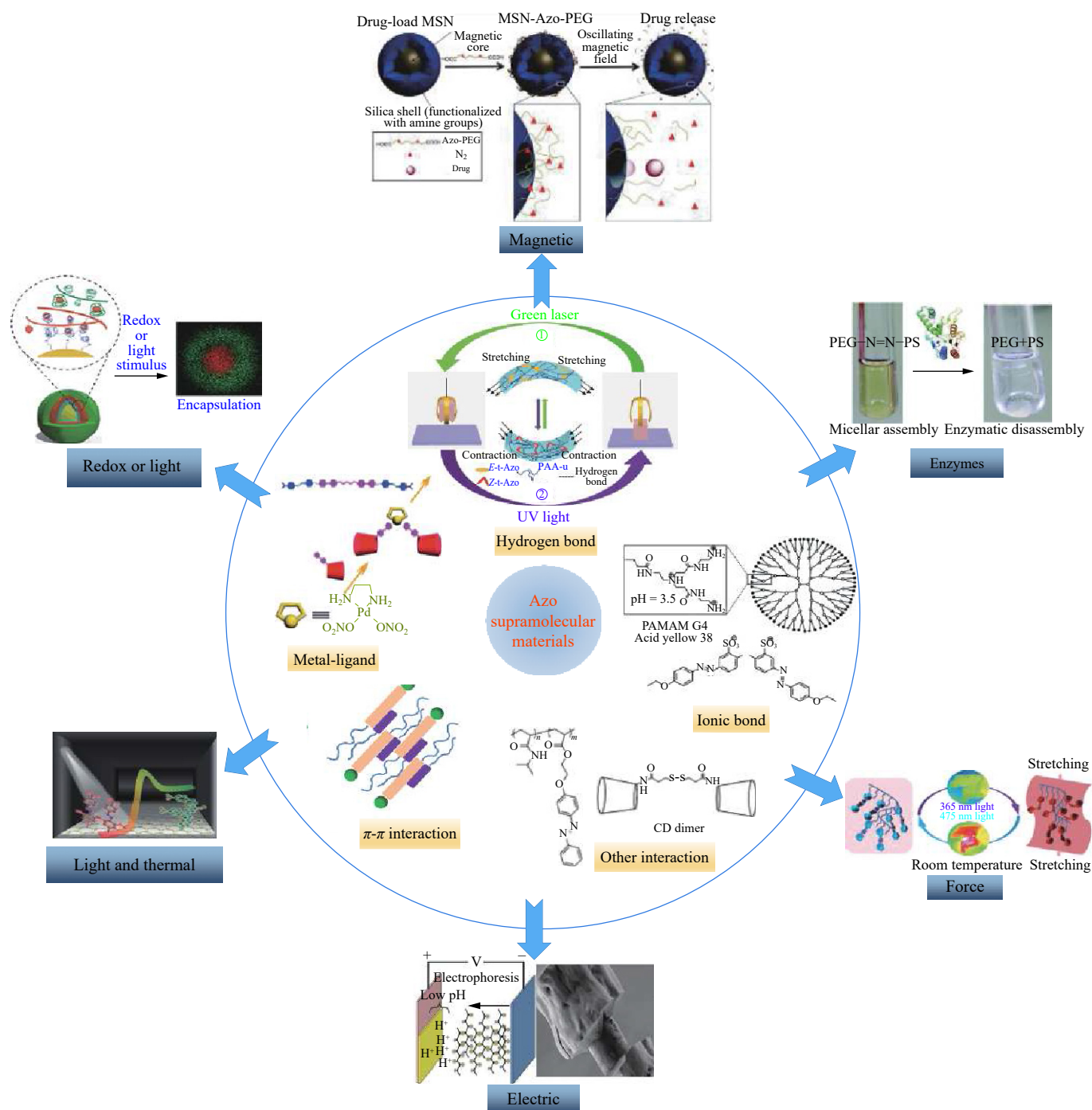


Fig. 1 Structural design and multi-stimulus response application of azo supramolecular materials (Reprinted with permission from Ref. [42]; Copyright (2015) The Royal Society of Chemistry) (Reprinted with permission from Ref. [43]; Copyright (2011) The Royal Society of Chemistry) (Reprinted with permission from Ref. [96]; Copyright (2019) Wiley) (Reprinted with permission from Ref. [100]; Copyright (2018) American Chemical Society) (Reprinted with permission from Ref. [112]; Copyright (2015) The Royal Society of Chemistry)

stacking effect materials require the selection of a suitable solvent, followed by simple mechanical mixing and then drying.^[51,52] The π - π interaction exists widely in the field of azo supramolecular. Due to the relatively complicated mechanism of action and limited experimental facts, the understanding of it is not comprehensive and thorough.

For ionic bonded supramolecular polymer materials, the preparation procedures are cumbersome, sometimes requiring modification of the molecular structure of the polymer

(e.g., quaternization) and typically the elimination of original counterions to drive the formation of the desired ionic bonding. The advantage of ionic bonding is that it can achieve high photoinduced anisotropy in the same materials and some of the products are water-soluble. However, the fabrication of ionic bonding supramolecular polymer materials requires more careful selection of a solvent compared to the one involving H-bonding.^[38,53] In recent years, halogen-bonded azo supramolecules have been developed and ap-

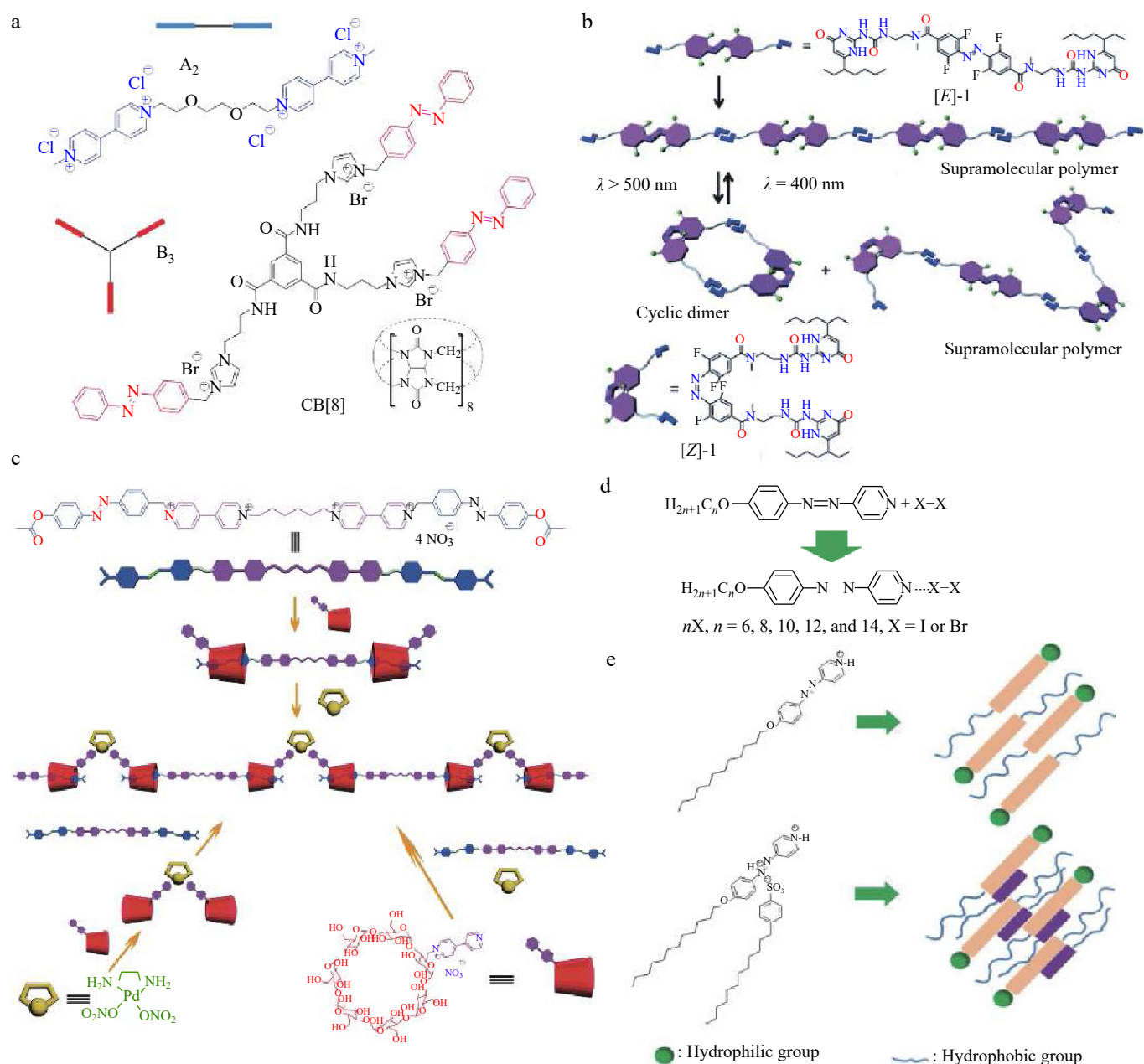


Fig. 2 The interactions of azo supramolecular polymers: (a) Molecular structure of ionic bonding by supramolecular polymers (Reprinted with permission from Ref. [39]; Copyright (2017) The Royal Society of Chemistry); (b) H-bonding based *ortho*-tetrafluorobenzene azobenzene supramolecular polymer structure (Reprinted with permission from Ref. [38]; Copyright (2017) The Royal Society of Chemistry); (c) Supramolecular polymer based on metal-ligand coordination (Reprinted with permission from Ref. [42]; Copyright (2015) The Royal Society of Chemistry); (d) Azo supramolecular polymer based on halogen bonding (Reprinted with permission from Ref. [41]; Copyright (2014) The Royal Society of Chemistry); (e) Azo supramolecules with $\pi-\pi$ interaction (Reprinted with permission from Ref. [43]; Copyright (2011) The Royal Society of Chemistry)

plied in liquid crystal materials.[41] It is easy to introduce and improve the interaction between supramolecules by changing halogen substitution. So, a series of halogen-bonded azo derivatives have been successfully synthesized, and the stability of mesophase and the interaction between molecules are significantly enhanced. Since the halogen bonding process is complicated and excessive heating or drying can reduce the content of azobenzene units, it is more straightforward to establish H-bonding with different degrees of complexing to realize the interactions between azo supra-

molecules.

Additionally, these supramolecular polymer materials can create a balance between high and low molecular weight materials, which sets a direction to develop a new matrix of properties. The balance ability to “calibrate” a system depends on the nature of the (macro)molecules of the high and low molecular weight materials, along with the structural properties determined during supramolecular polymer assembly.[54] For example, azo units are assembled with different types of polymers to give supramolecular polymers with

Table 1 The advantages and limitations for azo-based supramolecular interactions employing H-bonding, ionic bonding, halogen bonding, π - π stacking, and metal-ligand coordination

| Interaction type | Advantages | Limitations |
|---------------------------|--|---|
| H-bonding | Easy preparation; Moderate strength; Stability, directionality and saturation; Low chromophore content; Dynamics and reversibility; Easy elimination of azo molecules by selective solvation | Environmental sensitivity; Strict requirements for temperature, pH, <i>etc.</i> ; Decreased azo content under higher temperatures |
| Ionic bonding | High strength; High photoinduced anisotropy; Phase separation independent of the chromophore content; Partial water solubility | Molecular aggregation or phase separation at higher content of chromophore |
| Halogen bonding | Easy preparation; High strength; Enhanced stability of mesophase and intermolecular interaction | Complicated bonding process; Decreased azo content under high temperatures; Environmental sensitivity |
| π - π Stacking | Establishment of azo supramolecular skeleton; Easy interaction with two-dimensional material | Low strength; Low preparation efficiency; High demand for solvent applicability for azo supramolecules; Ineffective stacking and low structural stability |
| Metal-ligand coordination | Easy preparation; High strength; Directionality; Stability | High requirements for temperature, pH, <i>etc.</i> ; Environmental sensitivity |

different balance functions, such as beneficially irritating or environmentally sensitive “smart” materials.^[55–58] From another perspective, the establishment of the dynamic balance of azo supramolecular materials can lead to both self-assembly of nanostructures and stimulus responsiveness.^[59] These two unique properties are difficult to attain with standard covalent polymers, so they have been extensively studied in many fields. The stimulating response of nanostructures is a hot trend in recent research, and those responsive stimuli (temperature, chemistry, pressure, light, *etc.*) affect the dynamic balance of supramolecular polymers.^[60,61] For ease of understanding, Table 1 lists the advantages and disadvantages of different non-covalent bonds.

Of course, the response to external stimuli is a typical feature that has been applied to many traditional polymers, such as shape memory polymers, electroactive polymers, liquid crystal materials, phase change gels, and magnetorheological fluids.^[62–64] However, the sensitivity of conventional polymers to external stimuli varies widely, and they are not ideal stimuli-responsive materials. For self-assembly, any environmental stimuli can affect the interaction between the supramolecular polymer units, which in turn affects the degree of polymerization and the strength of polymer. Many results show that the supramolecular system can be heavily affected by the changes of temperature and molecule concentration.^[37,55,58] And the future research must be combined with the above factors.

AZO-BASED SUPRAMOLECULAR POLYMER STRUCTURE

Supramolecular polymers are referred to as “polymers beyond the molecule”, which are products of conformational polymers assembled by noncovalent interactions within a system. Similarly, azo supramolecular polymers can be described as polymer systems beyond molecules, and noncovalent interactions between molecules are used to identify their assembly forms and molecular conformations.^[65] The incorporation of azo-containing units into supramolecular polymer systems may endow the fabricated complexes with an optical response. The former can improve the mesophase stability, and the fluorination in the latter can enhance the

halogen-bonding interaction.^[40] If the description of supramolecules must take into account the structure of the supramolecules, it is known that azo supramolecular polymers can be roughly classified into three structures: main chain azo supramolecular polymers, side chain azo supramolecular polymers, and dendritic azo supramolecular polymers.

Main Chain Azo Supramolecular Polymers

In a main chain supramolecule, the polymer main chains are formed by noncovalent interactions, and thus the obtained supramolecular aggregates also have the characteristics of partial polymers. It mainly includes: (i) establishment of a balancing process between monomer, oligomer, and polymer under an ideal state; (ii) controlled aggregation of internal sequence coding by the synergistic effect of molecular subunits. In addition, the liquid azo supramolecules with mesomorphic units in the main chain have good thermal dimensional stability and are prone to molecular chain orientation in the external force field, but the disadvantage is that the main chain azo supramolecular has low viscosity and strong rigidity. So, compared with other structures, internal sequence and dynamically controlled azo supramolecules possess many special properties and functions. For example, part of the reversible photoisomerization of azo unit can destroy or repair the curvature of the main chain polymer segment, which can externally control the supramolecules' conformation. This property has been applied to optoelectronic devices, actuators (switches), and energy storage functions.^[66–68] Another property of the supramolecular structure in which the azo is located in the main chain is that the azo moiety has a relatively small geometry and can thus be filled with a plurality of macrocyclic cavity materials, such as photochromic compounds.^[69]

In other words, if the azobenzene and its derivatives are the guest molecules of a main chain supramolecular system, they will be the most important and effective tool for building photo-responsive supramolecular assemblies. In special main chain supramolecular polymer systems, the main macrocyclic compounds can “amplify” the *E/Z* isomerization of geometric structure to control some other properties, such as hydrophobic or hydrophilic conversion, circular dichroism (CD), and separation conversion.^[70] Bortolus *et al.*^[71] first

supramolecule. Similarly, Toh *et al.*^[76] synthesized a series of azopyridine-containing H-bonding acceptors with flexible spacers of oligo(methylene) (Fig. 3b). Rogness *et al.*^[77] fabricated a series of main chain liquid crystalline polymers through intermolecular using H-bonding between a functionalized bisazopyridine phenol and aromatic bisacids (Fig. 3c). In addition to using H-bonding to construct a backbone azo supramolecular polymer, Sun *et al.*^[78] prepared a photo-responsive azobenzene supramolecular polymer by recognition of host-guest molecules in water (Fig. 3d). Most of the complexes displayed reversible thermotropic nematic phase. Further, the characteristic that the main chain supramolecular polymer is reversible makes the main chain supramolecular polymer material a research hotspot and suggests many other new features.^[1,72,75] Although this research is very popular, and many examples and concepts have been reported in the past 30 years (such as stimulus response materials, nano-components, *etc.*), an actual application has not been realized.^[21,36,43]

Supramolecular Polymers with Azo Units in the Side Chains

The side chain type azo supramolecular polymer refers to a type of supramolecular polymer whose mesogenic units are located on the side chain of the polymers. The flexibility of a polymer is determined by the strength of side chain group structure interaction and steric hindrance effect. Compared

with the main chain type azo supramolecules, the properties of side chain azo supramolecular polymers depend to a large extent on the azo units, but are less affected by the properties of polymer main chain. The azobenzene side-chain polymer supramolecules have larger molecular weight than main-chain azo supramolecular polymer, and their structure is affected by the flexibility of amorphous chain; these features are conducive to achieving more effective light-driven mass transport in applications (Fig. 4a).^[79] To date, a large number of side chain azo supramolecules have been prepared. The side chain azo supramolecules can be divided into five categories according to their main chains: poly(methyl methacrylate), polyester, polystyrene, polyurethane, and polysiloxane.

According to our survey, many researchers have attempted to realize light-driven mass transfer in the host-guest system at this stage.^[50,79] The typical method is to embed azo dye molecules into the polymer film. However, surface unidulation of the system during *cis/trans* photoisomerization is very small (< 10 nm). More interestingly, the concentration of the dye is closely related to the ability of light to drive mass transfer (Fig. 4b).^[80] A low concentration makes it difficult to achieve practical results, which has great limitations for scientific research. Haque *et al.*^[81] believed that the functionalized side chain polymers can effectively improve the solubility of azo molecules by surface-initiated ring-opening double-decomposition polymerization of liquid crystalline

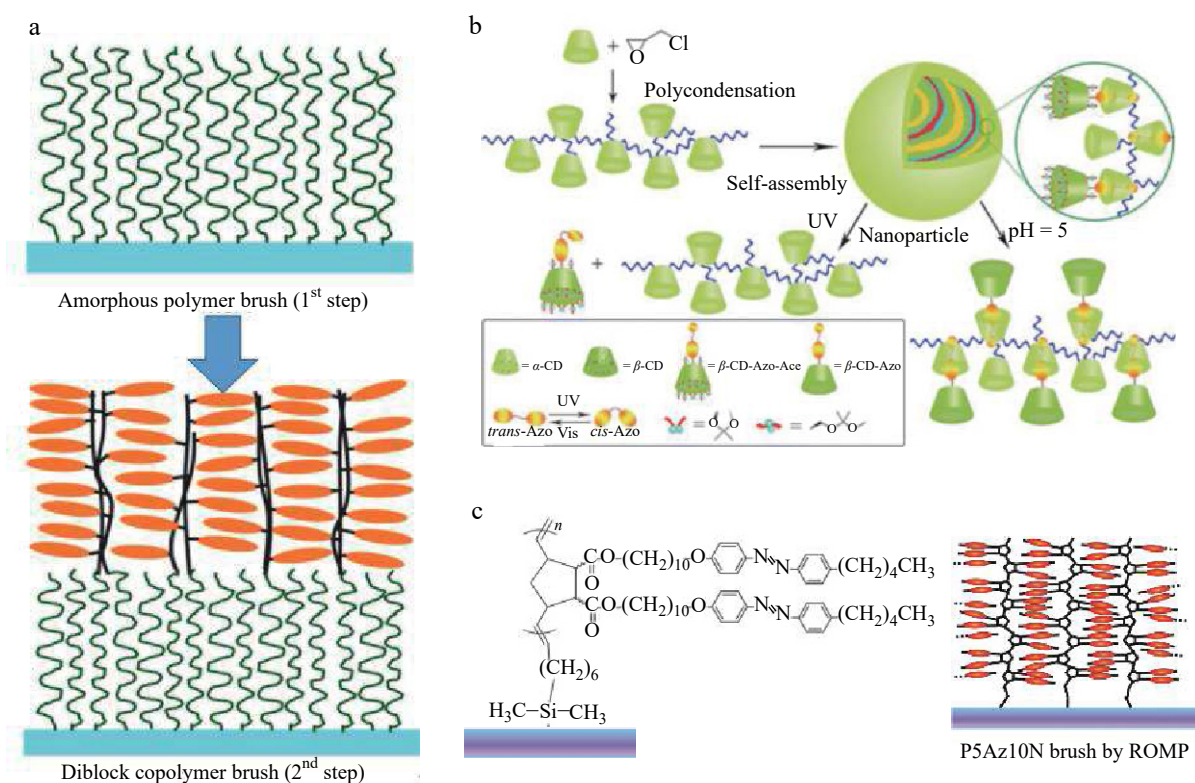


Fig. 4 Various side chain azo supramolecular design principles: (a) Azobenzene supramolecular structure influenced by the flexibility of the underlying amorphous chain (Reprinted with permission from Ref. [79]; Copyright (2013) American Chemical Society); (b) Dual stimulated supramolecular polymer based on poly(α -cyclodextrin) and acetal-modified β -cyclodextrin-azo (Reprinted with permission from Ref. [80]; Copyright (2018) Springer); (c) High-density liquid crystal azo polymer structure obtained by surface-initiated ring-opening metathesis polymerization (Reprinted with permission from Ref. [81]; Copyright (2013) American Chemical Society)

azo polymers in supramolecular systems (Fig. 4c). Capobianco *et al.*^[82] designed an azobenzene supramolecular material for lanthanide doped upconverting nanoparticles (Ln-UCNPs) and showed that NIR responsive $\text{LiYF}_4\text{:Tm}^{3+}/\text{Yb}^{3+}$ upconversion nanoparticles can induce a gel-sol transition in azobenzene/cyclodextrin supramolecular hydrogel systems. $\text{LiYF}_4\text{:Tm}^{3+}/\text{Yb}^{3+}$ Ln-UCNPs have good upconversion efficiency in the UV region and can be used to isomerize side chain azo supramolecules from *trans* to *cis*, as well as to induce dissociation of azo unit from the cyclodextrin cavity. In conclusion, the translation and rotation limits of side-chain azo supramolecular polymers are controllable, and one of the future research goals is to obtain side-chain azo supramolecules with the same behavior as corresponding small azo molecules.

Dendritic Azo Supramolecular Polymers

The dendritic azo supramolecular polymer is a special kind of dynamic polymer aggregate formed by self-assembly of non-covalent bonds between molecules. This type of assembly system has some special advantages because it can be controlled by changing temperature, pH, or other conditions and is dynamically reversible. The repeating unit of a dendritic azo supramolecular polymer consists of two parts: a linear main chain and a dendritic side group.^[82] Furthermore, dendrimers are a booming area in supramolecular chemistry.

As shown in Fig. 5(a), Stoffelen *et al.*^[65] prepared a molecular structure diagram of dual-stimulation self-assembled supramolecular nanoparticles. A dendritic ternary charge transfer complex between cucurbit[8] uril (CB), methyl viologen (MV), and azo moieties allowed supramolecular nanoparticles to be formed with controllable particle sizes. These nanosized azo supramolecular polymers have been developed for various applications, such as drug targeting, new materials, coolant additives, and conductive polymers. At this stage, many dendritic structures can initiate the formation of molecular hydrogel polymers under visible light to form space structures such as polyamines, polyphenyl ethers, polyamidoamines, carbosilanes, phosphorus-containing dendrimers, and polynuclear metal complexes (Fig. 5b).^[82] It is gratifying that some of these supramolecular systems have been commercialized and widely used in the fields of catalyst carriers, electronic materials, biosimulations, *etc.*^[83–85] The following will focus on some recent research efforts.

To demonstrate remote-controllable actuators, Kim *et al.*^[84] designed and synthesized a new dendritic supramolecular polymer with norbornene as the main body and azobenzene as the guest (Fig. 5c). Based on the ring-opening metathesis polymerization of azobenzene monomer, the uniaxially oriented polynorbornene serves as a skeleton, and the azobenzene molecules are side chains distributed parallel to the normal direction of the skeleton. The subtlety of this experiment is that the addition of azobenzene molecules helps to construct a layered superstructure with anisotropic and reversible photoisomerization fine adjustments. This experiment provides a great deal of reference for the design, development, and application of dendritic azo supramolecular polymers. Apart from this, Lee *et al.*^[83] designed self-assembly of tris(4-((*E*)-phenyldiazenyl)phenyl)-benzene-1,3,5-tricarboxamide (Azo-1) in aqueous organic solvent systems

(Fig. 5d). The results of this investigation show that the combination of supramolecular-favorable unit molecules and photoresponsive moieties (azobenzene) could serve as a foundation for the unique strategies for designing stimulus-responsive functional supramolecules.

Many types of heat-sensitive dendrimers have recently been reported, and most of them are constructed by attaching azo supramolecular thermal response units to the “surface” of these dendrimers.^[86] Their chemical molecular structures contain a linear backbone surrounded by a dense monodisperse and a linear skeleton surrounded by regular branch unit layers. These polymers could eventually develop into a variety of unprecedented thermally responsive materials with unique structures. Li *et al.*^[87] synthesized the first two generations of dendritic polymethacrylate (PMMA) derivatives with pendant oligoethylene glycol (OEG) groups, and their azo supramolecules displayed thermal responsivity. It was found that these polymers could dissolve completely in water at room temperature, and their solubility decreased at high temperatures. Roeser *et al.*^[88] also synthesized a series of azo supramolecular dendrimers with oligomeric (vinyloxy) peripheral branches. Liu *et al.*^[89] reported the preparation and thermoresponsive behaviors of two novel types of structural azo supramolecular dendronized polymers, which consisted of PMMA and dendritic side groups separated by linear hydrophobic alkyl or hydrophilic OEG units. These polymers showed fast transition and small hysteresis in performance. Their work also indicated that the phase transition temperature of the material ranged from 24 °C to 34 °C, independent of concentration. Moreover, in terms of polymer composition, both molecular weight and terminal groups of the side chains are affected by dendrimers with low critical solution temperatures. On the whole, the future research direction of dendritic azo supramolecules is the simple preparation of materials and the promotion and application of biological, energy, and intelligent materials.

RECENT APPLICATION

Azo molecules have two different photoswitchable molecular states that enable linear orientation and molecular transformation under UV or blue light induction.^[6,9,27,90] The azo supramolecular polymer has higher thermodynamic stability than the azo small molecule, and heating can change the *cis-trans* structure of azo.^[28,91,92] The molecules do not produce by-products during isomerization, and the supramolecular research is developing rapidly with many attractive and wide applications reported for azo supramolecules. In addition, due to the high spatial and temporal control in azo supramolecular systems, light shows a strong attraction and stimulation for energy storage, mechanical drives, medical equipment, and intelligent conduction applications. Now, based on the latest research results, we will highlight several applications in different fields and provide an outlook on their prospects.

Multi-functional Actuators

Scientific research shows that the photoisomerization of azo compounds is one of the cleanest photoreactions known; it has been intensively proven from experimental and theo-

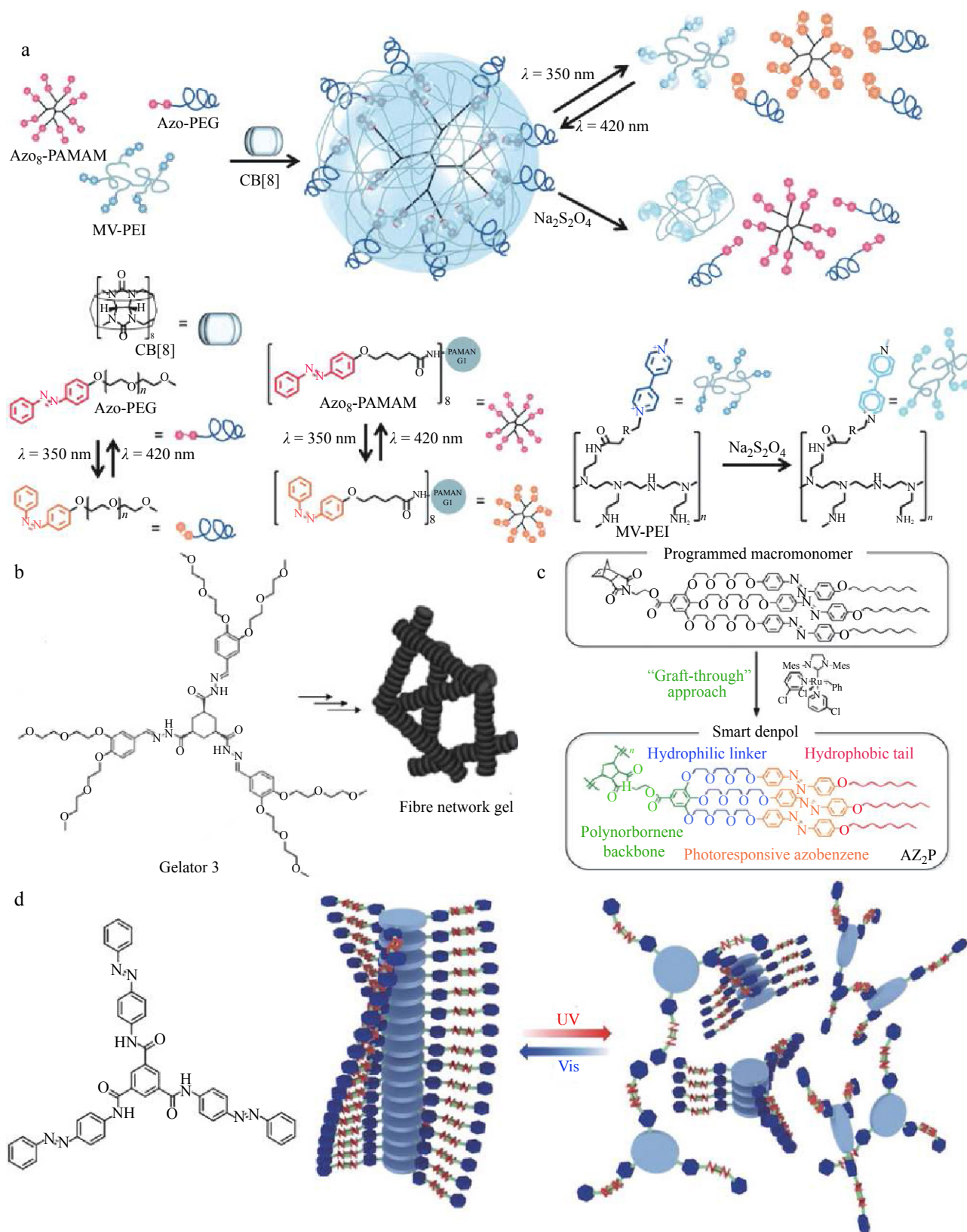


Fig. 5 Structure diagram of dendritic polymer azo supramolecular polymer: (a) Experimental flow and molecular structure diagram of dual-stimulation self-assembled supramolecular nanoparticles (Reprinted with permission from Ref. [65]; Copyright (2014) American Chemical Society); (b) Visible light-triggered spatial structure of superdendritic molecular hydrogel polymer (Reprinted with permission from Ref. [82]; Copyright (2015) Wiley); (c) Azo-based polynorbornene dendrimer (Reprinted with permission from Ref. [84]; Copyright (2017) Wiley Online Library); (d) Irritating response of azo supramolecular structure (Reprinted with permission from Ref. [83]; Copyright (2013) American Chemical Society)

retical point of views.^[93] As azo molecules can be easily and reversibly photo-isomerized, azo supramolecular polymer systems have been used to construct photo-switchable devices for many years. In 1996, Kato *et al.*^[93] demonstrated that the optical switch of azobenzene can drive the nematic-isotropic phase transition in hydrogen bonded azobenzene liquid crystals.

By practical application, Wiedbrauk showed that these systems undergo similar *E-Z* isomerization under light irradiation and have the ability to form host-guest complexes with macrocyclic compounds. At the same time, it can also be used as a photoresponsive unit in supramolecular self-assembly system, and the reversible cyclization/oxidation reaction occurs in the photolysis of *cis/trans* stilbene, so it is suitable for multicycle switching. Hemithioindigo is an emerging optical switch without much exploration to date.^[94] It is an asymmetric molecule containing thioindigo linked to the Astragalus fragment by a central double bond. The hemithioindigo has a central double bond that can be photo-isomerized under visible light at 400–410 nm (*Z-E*) and 480–490 nm (*E-Z*). Due to the relatively high energy barrier of the thermal *E/Z* isomerization (typically > 112.86 kJ/mol), thermal *E-Z* reversion is usually very slow. Although there are few studies on hemithioindigo in supramolecular self-assembly systems, its properties will certainly attract more attention in the future.^[95]

Fig. 6(a) shows the molecular structure unit of a cholesteric azo supramolecular polymer, which can exchange guest molecules at different light wavelengths. Moreover, the polymer molecule has been successfully applied to light-controlled intelligent switches (Fig. 6b).^[96] Chiral azo can be used as an optical switchable dopant to control the supramolecular helix. However, poor thermal stability of the *cis* isomers compromises the lifetime of the supramolecular helices generated by light. Huang *et al.*^[97] demonstrated a thermostable and axial chiral azobenzene switch that can be

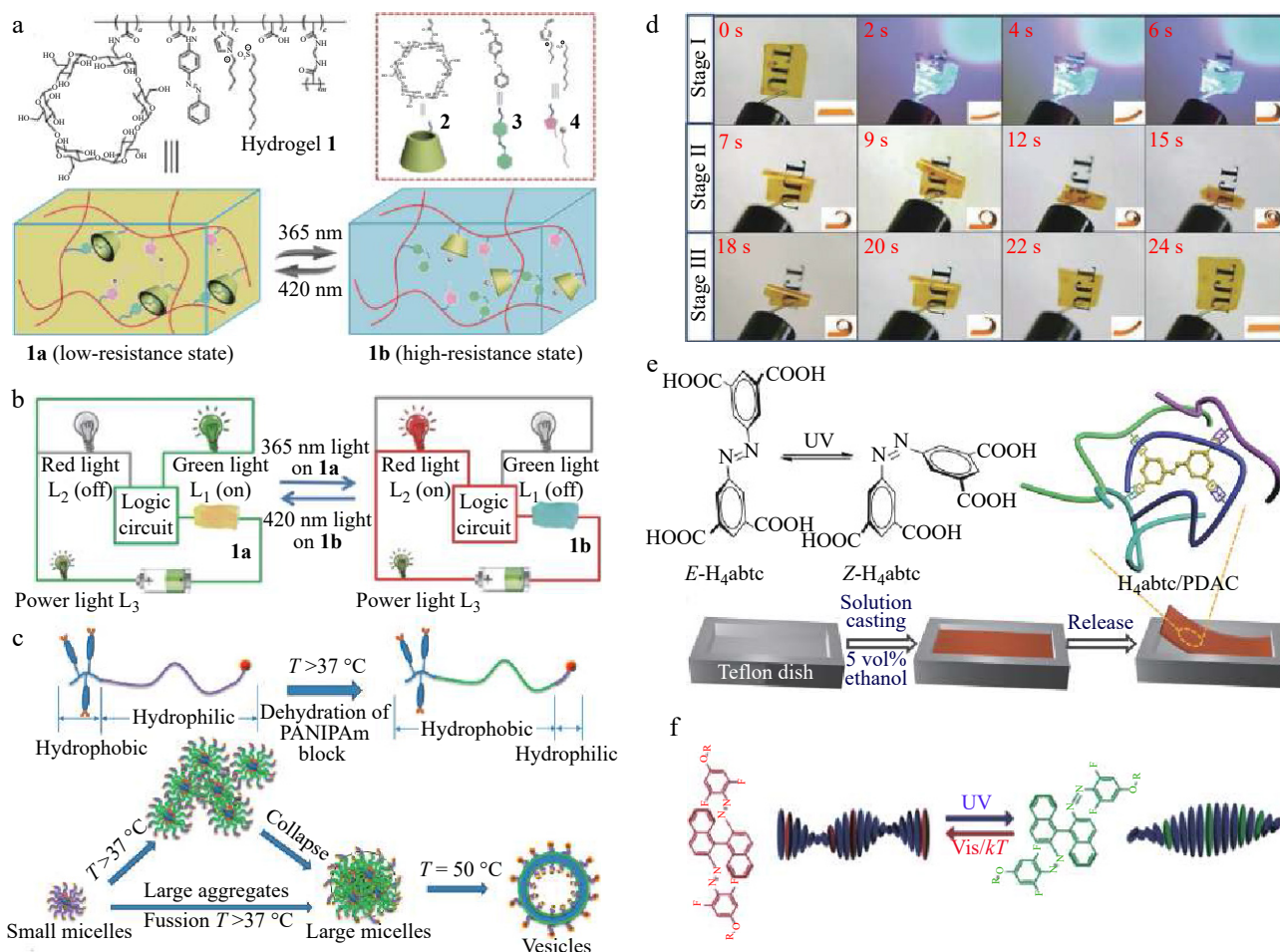


Fig. 6 (a) Application of azo supramolecular polymer in driving chemical structure of hydrogel **1** as well as molecular structural unit (**2**, **3**, and **4**), and diagram of guest molecule exchange in hydrogel **1** in different wavelengths of illumination; (b) Application in single ion supramolecular hydrogels (Reprinted with permission from Ref. [96]; Copyright (2019) Wiley); (c) Schematic diagram of the combined effect of hydrophilic-hydrophobic balance caused by vesicle transformation (Reprinted with permission from Ref. [98]; Copyright (2018) American Chemical Society); (d) High performance optical drive actuator film based on azobenzene/polymer supramolecular polymer (Reprinted with permission from Ref. [86]; Copyright (2015) The Royal Society of Chemistry); (e) Structure and film formation process of tetracarboxy azobenzene/polymer supramolecular assembly (Reprinted with permission from Ref. [101]; Copyright (2017) American Chemical Society); (f) Spiral supramolecular structure applied to fluorination lithography switch (Reprinted with permission from Ref. [97]; Copyright (2018) American Chemical Society)

used as a chiral dopant to produce supramolecular helices (Fig. 6f). Their *trans-cis* photoisomerization results in a 60% change in helical twisting force. These results indicate that the combination of *ortho*-fluorination and axial chirality in molecular optical switches constitutes an effective strategy for promoting long-lived helix states. In order to provide a new way for design of stimuli-responsive polymers, Ren *et al.*^[98] reported an unusual thermoresponsive behavior of a poly(*N*-isopropylacrylamide) based diblock copolymer containing carboxylic azo moieties, and it achieved a unique separation of microscopic dehydration and macroscopic phase transition (Fig. 6c). The uniqueness is that the ionized end-group prevented macroscopic phase separation of the block copolymer aqueous solution under basic conditions, leading to the absence of cloud point at high temperature.

Qin *et al.*^[86] noncovalently grafted an azobenzene chromophore (azo) with a disulfo group onto the side chain of the cationic polymer poly(diallyldimethylammonium chloride) (PDAC) by electrostatic interaction (Fig. 6d). The supramolecule of crosslinked azo/PDAC exhibited reversible isomerization by UV light and a good cycle stability. In addition, a variety of azo supramolecular materials have been developed, such as self-repairing azo supramolecular driving materials,^[83,99,100] azo/PDAC supramolecular film materials,^[101,102] *etc.* (Fig. 6e). Chu *et al.*^[8] first prepared a concentrated solution of A5/B8 functionalized 2.5 nm Au in water. Due to the different ligands, the hydrophobic azobenzene groups self-assembled into two different structures of supramolecular polymers. Azobenzene units adsorbed on the surface of inorganic nanoparticles (NPs) have better photoswitchability and are considered to be a better medical driving material.

Sensors

Since the first report by Goodman,^[103] optical induction of chiral supramolecules containing azo has been extensively studied. After irradiation with a certain wavelength of polarized light, portion of the azo is reoriented by reversible *trans-cis* photoisomerization. At the same time, under the interference of laser irradiation, surface relief grating (SRG) is formed on the azo polymer films, and different reliefs correspond to different incident light modes, which controls the properties such as intensity and polarization.^[47,104]

Researchers often use a one-step physical blending method to obtain commercial products, such as humidity memory materials. Another approach is to apply azo supramolecular materials to the surface of various objects, causing significant color changes. This color change is very intense, red to orange, but can be reversibly recovered as needed after moderate heating. Similarly, by using a red azo dye guest and a host polymer matrix to form a reversible supramolecular material, orange reversible dye aggregation can be made to turn red and used as a sensor.^[62,105] On this basis, much work has been done. Drotlef *et al.*^[106] invented a method for preparing novel and effective circularly polarized light (CPL)-induced chiral supramolecules to adjust the optical flow control media by using weak incoherent ultraviolet-visible light and multiple CPL lights. In principle, most researchers believe that designing and manufacturing supramolecular materials with single or double responsiveness is very simple.

However, for dual-responsive azo supramolecular materials, it is necessary to balance the structural and noncovalent interactions between polymers while maintaining the self-assembly ability between the azo-stimulated response portion and the polymer. In the application of optical induction, light-induced azo supramolecule chromophores undergo chiral orientation on amorphous polymer films. Many articles have suggested that chiral structure depends on the energy of the light, and chiral induction is caused by the gradual rotation of azo group under illumination.^[106–108] The future applications for azo supramolecular optics require a detailed understanding on the optically induced chiral upper structure and practical use of this very high optical rotation for chiral amplification.

Liquid Crystal Gel

Liquid crystalline polymers (LCPs) have been extensively studied as smart materials because of their excellent molecular synergy, anisotropy and elasticity of liquid crystalline networks, and reversible deformation under external stimuli.^[50,109] When a photoresponsive group (such as azobenzene and its derivatives) is introduced into the liquid crystal polymer, the photodeformation property can be imparted, and the light energy can be directly converted into mechanical energy. Through reasonable design of molecular structure and orientation, liquid crystal polymers can be subjected to various forms of photodeformation such as stretching, bending, twisting, vibration, *etc.*, and used for construction of various light-controlled flexible actuators.^[110–112] They possess unique advantages and broad application prospects in the fields of artificial muscles, micro-robots, and micro-liquid manipulation. Stimulus-responsive gel materials are popular candidates in sensors, actuators, and biomedical applications due to their dynamic and controllable properties. As a combination of the two, the multi-responsive azo supramolecular organogel is often used as a novel intelligent soft material because it can undergo significant phase transitions in response to external stimuli.

Chen *et al.*^[113] prepared a multi-response reversible liquid crystal gel with a carboxylic acid azo polymer (PM6Az-COOH) in dimethyl sulfoxide (DMSO), and the obtained gel showed multiple response behaviors to various stimuli (Fig. 7a). When heated, added with a less polar solvent, or irradiated with ultraviolet light, the responsive gel can be destroyed, but re-formed by a reverse process. In addition, it is difficult to construct a suitable crosslinking point in oil or organic materials due to the linear vinyl polymer for most purposes. By improvement, Ni *et al.* first prepared a mesogenic organogelling agent using a nitrogen-containing heteropyridine-based polymer and oleic acid by self-assembly (Fig. 7b).^[114] Oleic acid is an important component in the construction of mesogenic gels and also acts as a solvent embedded in the three-dimensional (3D) network gap of physical cross-linking. In performance, the azo supramolecular liquid crystal gel exhibited macroscopic gel-sol transitions and holographic grating switching upon external triggering of temperature, light, and organometallic ions. In order to obtain mesophase-stable liquid crystals, Du *et al.*^[40] and Chen *et al.*^[41] have successfully prepared a series of photosensitive halogen-bonded LCPs using molecular halogens and azo-

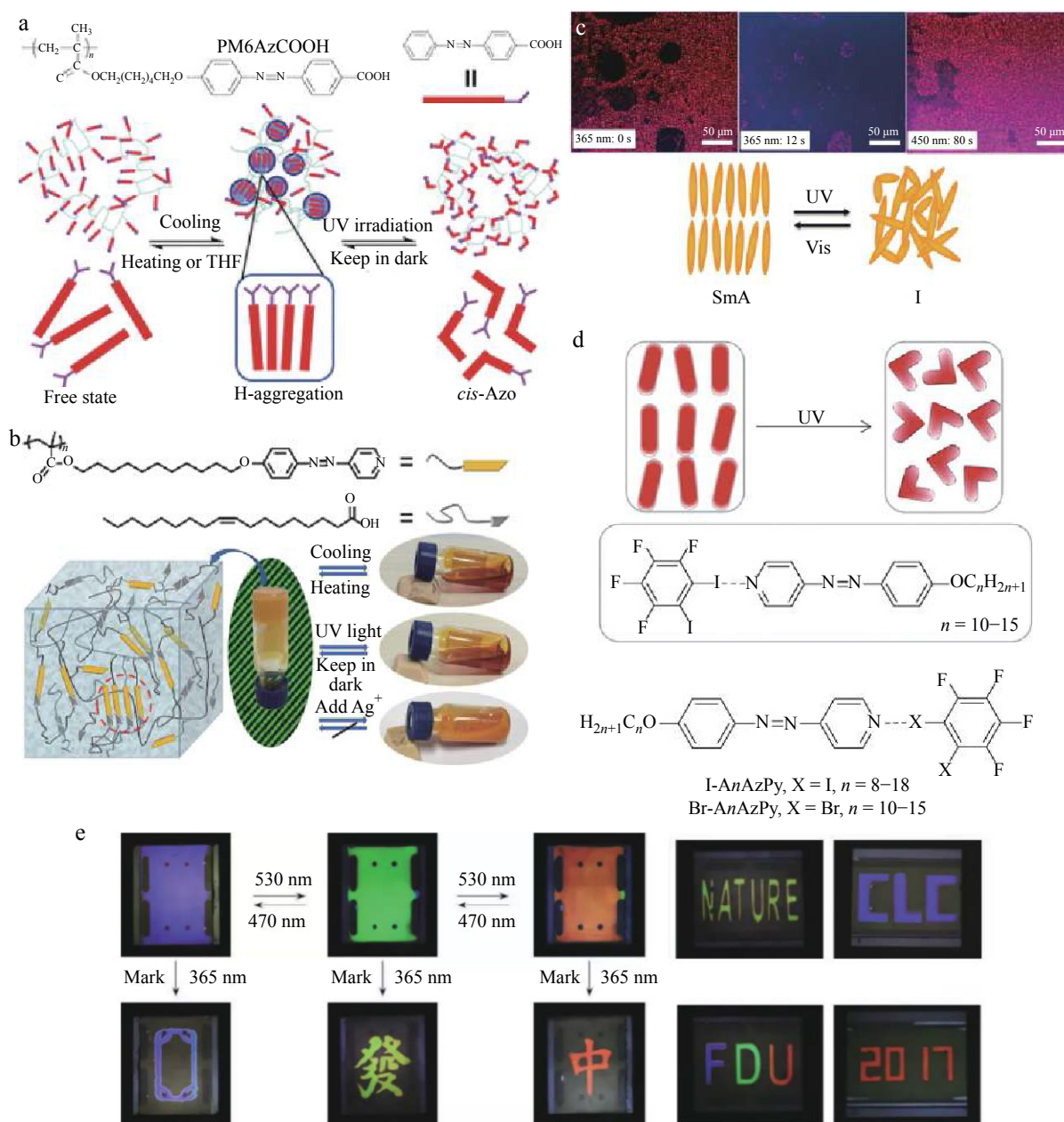


Fig. 7 Application of azo supramolecular polymer in liquid crystal gel: (a) An illustration of multiresponsive reversible gels formed with PM6AzCOOH in DMSO (Reprinted with permission from Ref. [113]; Copyright (2010) The Royal Society of Chemistry); (b) Azo supramolecular structure unit, photothermal response diagram, and physical diagram (Reprinted with permission from Ref. [114]; Copyright (2019) Americal Chemical Society); (c) The picture and process map obtained during and after 80 s of UV irradiation (Reprinted with permission from Ref. [41]; Copyright (2014) The Royal Society of Chemistry); (d) Light response behavior of compound I-A12AzPy in its liquid crystal phase and halogen bond linkages of azo supramolecules (Reprinted with permission from Ref. [40]; Copyright (2019) Taylor & Francis); (e) Color control of new cholesteric liquid crystals and their process of patterning (Reprinted with permission from Ref. [115]; Copyright (2017) Wiley)

pyridine compounds, which showed interesting properties of photoinduced phase transition under ultraviolet irradiation (Figs. 7c and 7d). Qin *et al.*^[115] have designed and developed a supramolecular material composed of novel piecewise controlled cholesteric liquid crystals. The photonic crystal of this material had a wide range of color control and could display different color patterns on a black background, even on the same background.

At present, most of the liquid crystalline supramolecular

organogels are composed of small molecules of gelation factor. For most linear polymers, they can usually be used as gelation factors of hydrogels, but it is difficult to form stable crosslinks or three-dimensional networks in organic solvents or oils. Therefore, the study of supramolecular organogels with linear polymers as gel factors is still limited and needs urgently. It is easier and easier to get them.

Photothermal Energy Storage

Azo supramolecular polymers have special photo-responsive

groups and have been continuously developed and applied in many fields. It has been found that dendritic azo supramolecular polymers can exhibit similar isomerization properties to azo monomers. Moreover, increasing the size of dendrimer and the number of azo groups has no effect on the space and yield of photoisomerization of the polymer. Archut *et al.*^[5] first attempted to use dendritic azo supramolecular polymers for holographic materials. They first prepared a polymer using a poly(propyleneimine) dendrimer and an *N*-hydroxysuccinimide ester, and then grew a cascade of 32 azo groups in the periphery. It has been found that the full *E* azo dendrimer unit can achieve a *Z*-form/*E*-form reversible conversion by light and radiation (heating) of a suitable wavelength. Moreover, when the diffraction efficiency is as high as 20%, the holographic grating can be completely recorded in the film of the azo dendrimer.

Solar thermal fuel can store the energy of radiation through structural and bond rearrangement of the photoactive material and then release the energy in the form of heat.^[109] Solar energy conversion and energy storage can be completed through reversible cycles in a single material system.^[109,116] Moreover, solar fuel has the advantages of no emissions, easy transportation, reproducibility, and control-

lability. As a new type of photo-responsive material, azobenzene and its derivatives have received great attention in solar energy storage. According to the survey, researchers have designed a variety of azo supramolecular materials for the solar thermal fuels.^[50,80,109–111,116] Among them are pure azo supramolecules, nanomaterialized azo supermolecules, and azo supramolecular polymers. In this section, we will present the applications of azo supramolecules in heat storage under different design schemes.

Azo supramolecules store solar energy by means of photochromism.^[117] Han *et al.*^[118] doped azo compound into the PCMs and changed the intermolecular kinetics by lowering their crystallization temperatures (T_c) to achieve heat storage at lower temperatures (Fig. 8a). Kolpak *et al.*^[119] have also developed azo supramolecular polymer materials by attaching azo chromophore to a nanotemplate as a solar thermal fuel, the high functional density, intermolecular H-bonding, and adjacently induced interactions generated by interplane binding can improve the storage capacity and lifetime (Fig. 8b). Scientists in Feng's group have designed a variety of nanotemplates for solar thermal fuels (Fig. 8c). The general measure is attaching the high-density azo molecules covalently to the surface of methoxy or carboxyl functionalized

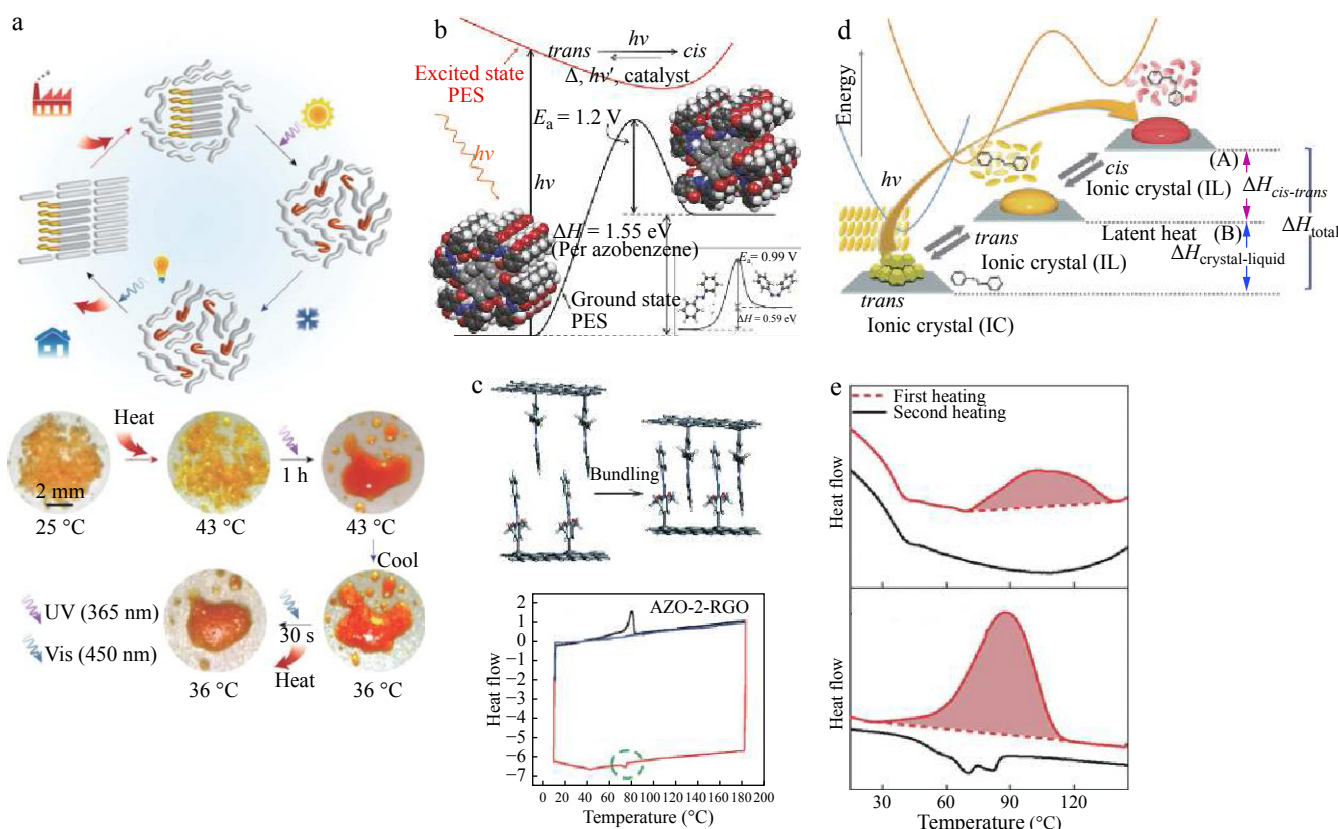


Fig. 8 Application examples of azo supramolecules in solar energy storage: (a) Optically controlled thermal energy storage and release mechanism and examples (Reprinted with permission from Ref. [118]; Copyright (2017) American Chemical Society); (b) Light-convertible azo supramolecules in different regions (Reprinted with permission from Ref. [119]; Copyright (2011) American Chemical Society); (c) Diazo/mixed template modular solar thermal fuel (Reprinted with permission from Ref. [121]; Copyright (2016) The Royal Society of Chemistry); (d) Solar energy storage capacity of self-assembled supramolecules (Reprinted with permission from Ref. [120]; Copyright (2016) American Chemical Society); (e) DSC curves for PmAzo (530 nm, 4 mW/cm², 40 min) and PAzo (365 nm, 2 mW/cm², 20 min) charged in solution that demonstrate heat release from *cis*-to-*trans* isomerization presented in the first heating (Reprinted with permission from Ref. [122]; Copyright (2016) The Royal Society of Chemistry)

nanosheets. The advantage is that the nanotemplate can generate intermolecular H-bonds to deal with the adjacently induced interactions, effectively increasing the storage capacity and storage life of the system (Fig. 8d).^[120] This bundling effect is critical to optimizing the thermal storage capacity and spatial coordination of azo supramolecular materials of the nanomaterial template. Feng *et al.*^[121] prepared a reduced graphene oxide/azo supramolecular material (RGO-bis azo) that shows a high energy density (~80 Wh/kg), with the maximum power density of approximately 2230 W/kg. In order to improve the effective energy storage of materials, Saydjari *et al.*^[122] developed an integrated device that could efficiently store both UV and visible light under full-spectrum solar irradiation (Fig. 8e). The equipment consisted of two different active layers, and the two active layers were different azopolymers. It comprised a UV (PAzo) absorbing polymer and a visible light (PmAzo) absorbing polymer, which could store energy by isomerization of the chromophores on the polymer side chains from the lower energy *trans* isomers to the higher energy *cis* isomers.

CONCLUSIONS AND PERSPECTIVES

We have reviewed recent papers on the design and related applications of azo supramolecular materials containing photochromic compounds. Azo supramolecular polymer materials have good photo-responsive properties, and many scientists are increasingly interested in these materials. Although many systems and concepts are still in their infancy, their applications have broad prospects. They can be used not only for traditional multi-functional actuators and solar thermal fuels, but also for biopharmaceutical delivery, functional surface modification, photoresponsive polymer smart gels, light control catalysts, and other aspects.

We consider the future aspects of processing, application, and development are as follows. First, in structural processing, future research on supramolecular polymers will focus on easy processing, high strength, and facile adjustment. The design of materials should be combined with multi-functional intermolecular forces to coordinate applications, and there are long-term research prospects in bioswitches, optical alignment, liquid crystal, and optomechanical drives. However, because traditionally bonded azo polymer materials cannot achieve reversible unbonded and aggregated behavioral transitions, the related research has been limited to soft-bonded supramolecular polymer systems. In the applications of smart sensing, a system that provides dynamic photo-responses, as reported in azo-containing organic gels, solvate discoloration, photochromism, catalysis, and humidity sensing, can be developed in the future.

Today's non-fossil energy development is getting faster and faster, and the research on solar energy is progressing rapidly. Azo supramolecular solar thermal storage and the efficient conversion of light into heat is an emerging field with great potential in practical applications. Unfortunately, its development is still hampered by low storage capacity and short storage lifetimes, and there are still many difficulties to be faced in future explorations and applications. Nevertheless, with the fast growing of computer science,

computer simulations combined with experimental and theoretical studies can lead to a better understanding of azo supramolecular systems and the development of more types of materials and applications. Although there are many studies on azo supramolecular polymers, we hope that this review will inspire more research innovations and experimental design ideas for more researchers.

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