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Review Article

Transient self-assembly driven by chemical fuels

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ABSTRACT

Self-assembly has been extensively studied in chemistry, physics, biology, and materials engineering and has become an important "bottom-up" approach in creating intriguing structures for different applications. Using dissipative self-assembly to construct fuel-dependent, energy-consuming, and dynamic nonequilibrium systems is important for developing intelligent life-like materials. Furthermore, dissipative self-assembly has become a research hotspot in materials chemistry, biomedical science, environmental chemistry, and physical chemistry. An in-depth understanding of the process and mechanism provides useful insights to the researchers for developing materials using dissipative self-assembly and also helps guide future innovation in material fabrication. This critical review comprehensively analyzes various chemical fuel input and energy consumption mechanisms, supported by numerous illustrative examples. Versatile transient assemblies, including gels, vesicles, micelles, and nanoparticle aggregates, have been systematically studied in our and other laboratories. The relationship between the molecular structure of precursors and temporal assemblies in dissipative self-assemblies is discussed from the perspective of physical chemistry. Using dissipative self-assembly methods to construct functional assemblies provides important implications for constructing high-energy, nonequilibrium, and intelligent functional materials.

1. Introduction

The second law of thermodynamics states that spontaneous processes in isolated systems are consistently toward entropy increase. To reach a stable state with minimum free energy, a microscopic system must develop toward increasing disorder. However, most systems are not completely closed, and the building blocks can exchange energy or substances with the external environment, resulting in orderliness. From this perspective, self-assembly has been defined as the spontaneous process of disordered components transforming into ordered structures or patterns without external interference in living organisms or artificial systems [1]. Self-assembly allows scientists to create more new substances while creating infinite possibilities for constructing various functional materials [2]. Particularly, self-assembly with building blocks has become a reliable approach to fabricating ordered assemblies, which has become a research hotspot for constructing functional materials in the field of physical chemistry, material science and biomedicine science. Self-assembly is mainly divided into two categories, namely, static and dynamic self-assembly (also called dissipative self-assembly) [1]. The most substantial difference between them is whether energy dissipation is required. Static self-assembly can form thermodynamic equilibrium-assembled structures; however, it requires an external energy supply (such as heating and vibration). At the conceptual level, the property changes in static self-assemblies are passive. Classical stimuli-responsive systems require an external trigger to induce a one-way transition between thermodynamically stable states (such as assembly/disassembly), and the resulting state is infinitely stable. In contrast, dissipative self-assembly is a thermodynamic nonequilibrium process that requires dissipating energy [1]. Importantly, the assumed energy process is common in functional assemblies of living systems. Investigating dissipative self-assembly to synthesize highly complex and intelligent materials is crucial. Dissipative self-assembly is the synergetic operation of multiple fuel-activated precursors, relying on continuous external energy (fuel) to maintain transient building blocks accompanied by versatile self-assembled aggregates. Once energy is removed, the temporal self-assemblies reconvert to the original precursors (Fig. 1(a)) [3–6]. An in-depth understanding of the design principle of dissipative self-assembly is vital for creating more nonequilibrium assemblies [7–8].

Compared with thermodynamically stable systems, dissipative self-assembly systems exhibit more complex properties, such as programming controllability, spatiotemporal controllability, self-adaptability, self-healing capability, and energy dependence [4], endowing dissipative systems with more functionality and intelligence. These characteristics enable dissipative systems to be further applied in designing

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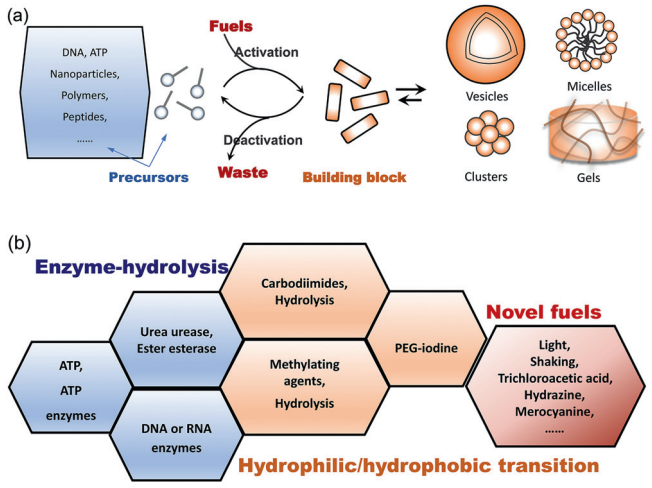

Fig. 1. (a) The self-assembly process from precursors to transient assemblies with energy activation and energy-consuming deactivation, and (b) the schematic summarizing the modes of fuel activation/energy consumption.

non-equilibrium photonic devices [9], time-programmed nanoreactors [10–11], smart biomimetic materials, fuel-driven drug-release carriers [12], movement-regulated molecular machines [13], and biocatalysis assemblies [10]. The design of various transient aggregates is essential for realizing the required functional materials in production and life. Two points should be noted: first, the structures and properties of temporal building blocks determine the final assembled structures, including vesicles [11,14–16], nanoparticle aggregates [17–19], micelles [20–22], gels [23–28], and more complex aggregates [10,29]; second, the building blocks are activated from precursors such as DNA [29–32], adenosine triphosphate (ATP) [10,33–35], nanoparticles [17,36], polymers [28,37–38], peptides [39], and other more complex structural molecules [13,15,26–27] (Fig. 1(a)). The selection and design of precursor structures are the primary requirements for fabricating dissipative self-assembly systems. However, in the absence of fuel, the simple self-assembly of precursor molecules produces thermodynamically stable assemblies. Therefore, introducing fuel into a self-assembled system is critical to build dynamic and thermodynamic nonequilibrium self-assembled systems. Meanwhile, integrating fuel input/energy depletion into precursors and activating building blocks are critical steps for successfully engineering a dissipative self-assembled system. The reported modes are mainly divided into two classes: i) The enzyme biocatalysis mechanism including ATP enzymes [10,33–35], urease [11,22], esterase [31], DNA enzymes [40], RNA enzymes, and lipase [41–42]; ii) The hydrophilic/hydrophobic transition mechanism fueled with I_2 [21,43], carbodiimides [17,26,28,44–47], and methylation reagent [38,48]. Notably, novel fuels such as shaking [25], trichloroacetic acid [13], hydrazine [18], light [49], and merocyanine molecules [19,50] will open new avenues for constructing more complex and functional dissipative self-assembled materials (Fig. 1(b)).

Although the structures and properties of the precursors are crucial, identifying the relationships among the versatile precursors, building blocks, and transient assemblies is challenging. In this review, we classify the precursors according to their fuel input/energy depletion modes. We emphatically discuss the activation mechanism of the precursors using the fuel and the noncovalent interactions between the fuel and precursors from the perspective of physical chemistry. On this basis, we summarize the principles of transient assemblies through precursors activated by several fuels, especially novel fuels, with innovative insights and significance. The applications of dissipative self-assembly systems have been summarized and elaborated upon. We believe that this review will provide important insights for researchers in life-like material construction and guide future developments and innovations.

2. Modes of chemical fuel activation/energy depletion

2.1. Enzyme biocatalysis mechanism

Biocatalysis is a pivotal biological regulatory mechanism that facilitates the spatiotemporal self-organization of complex structures and functions. Enzymes are integral in biocatalytic reactions and provide advanced control and regulatory functions for self-assembly. Enzymes can convert energy in biological systems using biocatalyzing fuels, making them excellent candidates in dissipative self-assembly systems. More importantly, enzymes induce energy dissipation, maintaining the self-assembly in a kinetically controlled state. Moreover, they enable the construction of soft matter materials with nonequilibrium, active, adaptive, and autonomous behaviors. Enzymes, including ATP enzymes, urease, esterase, DNA enzymes, RNA enzymes, and lipase, have been reported to promote dissipative self-assembly through site-specific reactions and selective regulation of reaction rates.

2.1.1. ATP/ATP enzymes

ATP is a high-energy compound composed of an adenine group, ribose with 1,2-cis-diols, and triphosphate ions (Fig. 2(a)). Owing to its structural characteristics, ATP exhibits self-assembly properties, enabling its utilization in developing other materials. On the one hand, phosphate ions can strongly bind to hydrogen donors, such as guanidinium groups [51] and protonated melamine groups [52], via the synergistic effect of electrostatic interactions and hydrogen bonding. For example, the polymers with ATP receptor units of the guanidine-cyclodextrin side can self-assemble with ATP to form the expansile micelles [53] and vesicles [54]. On the other hand, phosphate ions can interact with cationic substances such as surfactants [16,55], polymers [12,53,56], and small molecule compounds [35,57] via electrostatic interactions. Besides noncovalent interactions, 1,2-diol units of ATP can covalently bind with the boronic acid group [51]. These structural properties provide effective recognition sites for ATP to create functional assemblies or materials. However, enzymatic hydrolysis of ATP by enzymes directly destroys the phosphate-binding sites and alters the interaction modes. ATP enzymes include apyrase [33] (hydrolyzing ATP with a higher hydrolysis rate than that of adenosine diphosphate (ADP) hydrolysis and producing one adenosine monophosphate (AMP) and two phosphate molecules), alkaline phosphatase (hydrolyzing the phosphoanhydride bond for ATP, ADP, and AMP unselectively and yielding adenosine and three phosphate molecules) [16,33], and hexokinase (transferring a phosphate group from ATP to glucose and producing glucose-6-phosphate and ADP) [58]. In contrast, creatine phosphokinase transfers phosphate from phosphocreatine to ADP and generates ATP [33]. Apyrase and alkaline phosphatase can be employed to temporally control fuel switching from ATP to phosphates, whereas hexokinase and creatine phosphokinase can transiently control the fuel-waste transition between ATP and ADP.

The competition kinetics of ATP binding (fuel input) and enzymatic dissociation (energy depletion, ATP → AMP + two phosphates, or ATP → adenosine and three phosphates) will yield self-assemblies with precisely controlled dynamic behavior [16]. Based on this principle, a reciprocating division-fusion motion from micelles to smaller aggregates could be realized by ATP activation/enzyme deactivation. The micelles are formed by block copolymers containing 4,6-diamino-1,3,5-triazine moieties (PDAT; Fig. 2(b)), which can interact with ATP through multiple hydrogen bonds, coordination, and π–π stacking. PDAT micelles recognize ATP and form temporal ATP-fueled aggregates (PDAT/ATP). Enzymatic consumption of ATP by alkaline phosphatase induces the fusion of smaller PDAT/ATP aggregates into PDAT micelles [12]. Moreover, ATP activation/fuel depletion can also regulate a rhythmical contraction-expansion. A polymeric micelle bearing biguanidine-cyclodextrin side (Fig. 2(c)) as its ATP-binding receptor units has been manufactured. Increased hydrophobicity drives micel-

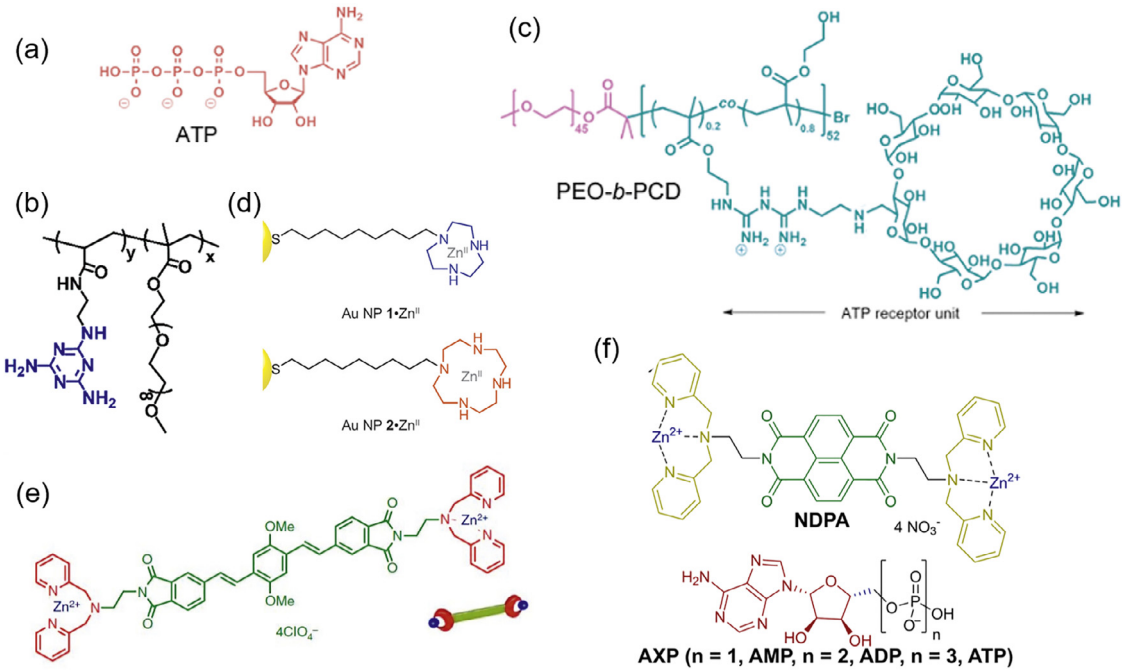

Fig. 2. (a) The structure of fuel adenosine triphosphate (ATP) molecules and the structures of the precursor containing an ATP receptor unit, including (b) block copolymers containing 4,6-diamino-1,3,5-triazine moieties (PDAT) [12], (c) amphiphilic block copolymer composed of a poly(ethylene oxide) block (PEO) and a functional block (PCD) appended with biguanidine-cyclodextrin side units [53], (d) Au nanoparticle (NP) with macrocyclic Zn^{2+}–1,4,7-triazacyclononane head group and Au NP with Zn^{2+}–1,4,7,10-tetraazacyclododecane (cyclen) head group [59], (e) dipicolylethylenediamine-Zn (Zn-DPA, precursor) [35], (f) naphthalene diimide derivative (NDPA) with Zn-DPA (precursor) [33].

lar expansion through ATP-fueled activation via electrostatic and host-guest interactions between ATP and biguanidine-cyclodextrin moieties. A deactivation process by apyrase hydrolysis increases the micellar hydrophilic ratio, leading to a contraction behavior for the micelle system [53]. Efficiently trapping ATP through specific ligand-receptor interactions and enzymatic catalysis are the primary reasons for their reversible assembled structure transformation. Therefore, by designing versatile precursors bearing ATP-binding receptor units, ATP and its associated enzymes can be employed as fuel input and depletion regulators to control various dissipative self-assembly systems. The reported precursors include Zn^{2+} (and Cu^{2+})-complexed surfactants with 1,4,7-triazacyclononane head groups (TACN·Zn^{2+} or TACN·Cu^{2+}) [16], Au nanoparticles (NPs) covered with TACN·Zn^{2+} or TACN·Cu^{2+} surfactants [57], Au NPs containing Zn^{2+}–1,4,7,10-tetraazacyclododecane (cyclen) head groups [59], block polymers containing PDAT moieties or biguanidine-cyclodextrin groups [53–54], and polylysine carrying stomatocyte assemblies [10]. For example, Au NPs carrying TACN·Zn^{2+} or TACN·Cu^{2+} surfactants recognize ATP via strong multivalent electrostatic interactions, resulting in the exchange of fluorescent probe molecules from the surface of Au NPs and subsequent fluorescent signal generation [60]. Under dissipative conditions, ATP fuel induces a fluorescent probe-displacement assay, thereby increasing fluorescence intensity. Apyrase irreversibly degrades ATP into weaker competitors (AMP and phosphate) and thus re-forms Au NP/probe complexes [57]. The affinity of ATP for Au NP TACN·Zn^{2+} via multivalent electrostatic interactions is the underlying reason for this signal production. However, Au NPs with macrocyclic Zn^{2+} surfactants can interact with nucleobases through coordination interactions and hydrogen bonds. To assess the fuel selectivity of different nucleotides XNP (X = A, T, C, G; N = M, D, T) under dissipative conditions, two constructs were synthesized: Au NP 1·Zn^{2+} (Fig. 2(d)) and a distinct macrocyclic Zn^{2+}-Au complex (Fig. 2(d)) referred to as Au NP 2·Zn^{2+}. The fuel-selective transient dislocation of a fluorescent probe from the Au NP leads to a temporal fluorescent signal [59].

In addition to the periodic switching of the self-assembled structures, ATP can also serve as a biologically relevant chiral auxiliary to fabricate chiral supramolecular polymers. The programmed hydrolysis of ATP (ATP → AMP + two phosphates) endows chiral supramolecular polymers with dynamically tunable properties. The reported precursors are chromophores functionalized with ATP receptors, such as oligo(*p*-phenylenevinylene) derivatives with dipicolylethylenediamine-Zn (Zn-DPA) (Fig. 2(e)) [35], naphthalene diimide derivatives (NDPA) with Zn-DPA (Fig. 2(f)) [33], and porphyrin with cationic primary amine groups [61]. The helical supramolecular polymerization mainly depends on the π–π interaction between adjacent chromophores, electrostatic interaction between ATP and receptors of precursors, as well as additional hydrophobic interaction, hydrogen bonding, and π–π interaction between the adenine base and ribose sugar. For example, the intermolecular hydrogen bonds in ATP-bound stacks bring precursors (Fig. 2(e)), oligo(p-phenylenevinylene) derivatives with Zn-DPA receptors closer to each other, resulting in an increased π–π interaction of the oligo(p-phenylenevinylene) derivatives. This ultimately results in the formation of temporary supramolecular chiral assemblies. Furthermore, the temporal supramolecular chiral assemblies are completely selective to ATP rather than other adenosine phosphates (ADP and AMP) and triphosphates (GTP, UTP, and CTP) [35]. Conversely, NDPA, which includes a Zn-DPA receptor (Fig. 2(f)), can achieve the selection and adoption of opposite helical conformations in adenosine phosphate. Specifically, binding with ATP forms a P-helix, whereas binding with ADP forms an M-helix. Two complementary phosphoryl transferases, hexokinase (ATP → ADP) and creatine phosphokinase (ADP → ATP), can temporally control conformational switching between the P- and M-helices [58]. NDPA with the Zn-DPA receptor can form multi-chiral supramolecular self-assemblies with ATP, ADP, and AMP. These enzymes, including alkaline phosphatase (ATP → adenosine + three phosphate molecules), apyrase (ATP → AMP + two phosphate molecules), and creatine phosphokinase (ADP → ATP), are used to realize temporally programmed conformational transitions [33].

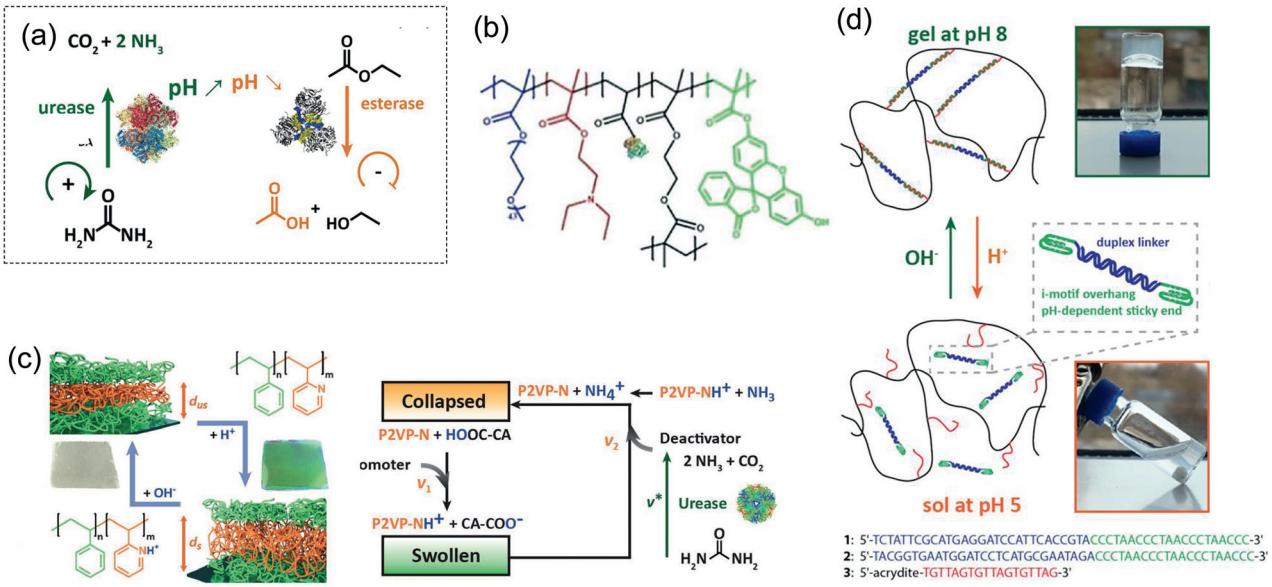

Fig. 3. (a) The pH increase caused by urease hydrolysis of urea and the pH decrease through esterase hydrolysis of ethyl acetate [31]. (b) The copolymer containing DEAEMA moieties; the protonated/deprotonated units can be controlled from urease hydrolysis and pH change [34]. (c) Protonation of the pyridine group and swelling of P2VP in a PS-*b*-P2VP photonic film, presenting a reflective color (transient assemblies); slow urease catalysis results in the deswelling of the P2VP layer with a transparent appearance [9]. (d) In alkaline pH, the duplex linker can self-assemble with DNA-containing polyacrylamide copolymers, whereas in acidic pH, the cross-linker forms i-motif duplex DNA, leading to a disassembly process [31].

As a biofuel carrying energy in living systems, ATP provides an interesting bioinspired method for constructing life-like materials using ATP-hydrolyzing enzymes. ATP enzymes possess high selectivity and efficiency in ATP production or consumption. ATP enzymes endow the corresponding ATP self-assemblies with dynamic, responsive, nonequilibrium, and periodic properties, allowing them to successfully construct dissipative self-assemblies with biomimetic, life-like, and nature-mimetic characteristics, producing functional assemblies such as programmed microseparators [54,56], temporally controlled drug carriers [12,53], life-like supramolecular polymers [33], and nature-mimetic signal generation probes. ATP also imposes restrictions on the structure of the precursors. ATP receptor motifs, such as positively charged units, guanidine-cyclodextrin side [53], guanidinium, and boronic groups [51] are a precondition for precursors to interact with ATP through electrostatic interactions, host-guest interactions, hydrogen bonding, and borate covalent bonding. This inevitably requires the complex synthesis of precursor molecules. When using ATP/ATP enzymes in a dissipative self-assembly system, certain considerations need to be taken into account. These include storing the ATP enzyme powder at −20 °C, avoiding freeze-thaw cycles for the ATP enzyme solution, and assessing whether the addition of ATP/ATP enzyme would impact the pH of the solution and subsequently affect the precursors [57].

2.1.2. Urease and esterase

Urease exhibits efficient catalytic activity in converting urea into NH_3 and CO_2, leading to a pH increase toward basic values. Its activity follows a bell-shaped curve within the pH range of 4–9, with the maximum turnover rate observed around pH = 7 (Fig. 3(a)). Once the pH increases to a basic level after urea catalysis, the activity of urease returns to its dormant state. Urease-catalyzed hydrolysis of urea facilitates an autonomous pH cycle and forms various pH-switchable temporary self-assemblies, including gels [62], microgels [34], vesicles [11], and films [9]. Typically, urease catalysis can be utilized for pH-switchable polymers containing protonated/deprotonated units [9,11]. For example, poly-[(diethylamino)ethyl methacrylate] (DEAEMA) with a pK_a of approximately 7.3, is water-soluble at pH < 7.0 owing to the protonated aminoethyl, whereas turns into insoluble at pH > 7.0 [63–65]. A polymer nanoreactor consists of pH-responsive DEAEMA copolymers. In a basic buffer, the nanoreactor shrinks (OFF state) owing to the deprotonation of DEAEMA. The addition of HCl and urea as chemical fuels causes a rapid pH decrease, thereby increasing the size of the nanoreactors (ON state) owing to the protonation of DEAEMA. Over time, a slow increase in the pH due to urease catalysis results in the deprotonation of DEAEMA. The nanoreactor then returns to its shrunken state (OFF state). An ingenious design of DEAEMA and urea shows a temporal biocatalysis of horseradish peroxidase (HRP), empowering the functional polymersome nanoreactors with size-increased/permeability-enhanced properties [11]. Remarkably, the DEAEMA shown in Fig. 3(b) also acts as the pH-responsive part of the microgel, where urea and HCl are the fuel sources. The fast protonation of DEAEMA and the slow urea depletion synergistically control the "breathing" of the microgel [34]. In addition to DEAEMA [65], several other functional groups, such as (dimethyl amino)ethyl methacrylate [65], (diisopropyl-amino)ethyl methacrylate (pK_a ≈ 6) [65], methacrylic acid (pK_a ≈ 5.4) [64,66], pyridine (pK_a ≈ 5.2) [9], 4-vinylpyridine (pK_a ≈ 5) [67–68], 2-vinylpyridine (pK_a ≈ 3) [67–68], *para*-mercaptophenol (pK_a ≈ 8.3) [69–70], and carboxylate group (pH ≈ 7) [22] are typical pH-responsive units in polymers that facilitate a selective hydrophobic/hydrophilic change owing to their responsive ionization behavior. For example, Walther et al. created lamellar structures from the copolymer polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP), which can be used as a photonic film. The addition of acid and urea (pH < 3.2) to the photonic film causes protonation of pyridine and swelling of P2VP, responsible for the macroscopic reflective color. The slow urease catalysis results in the deswelling of the hydrophilic layer, accompanied by a transparent appearance (Fig. 3(c)) [9]. In addition to the protonation of pH-responsive polymers, urease can also effectively catalyze other substances with pH-responsive ionization behaviors, especially peptides with $-NH_2$ or −COOH. The pH increase caused by urease catalysis further changes the protonation of amino/carboxyl groups. The sol-gel switching behavior of certain peptides, such as Fmoc-leucine-OH peptide (sol-gel transition at pH = 5.8) [62] and naphthalene-phenylalanine-phenylalanine peptide (sol-gel transition at pH = 4.1, pK_a ≈ 5.7) [24], is controlled by the fast protonation of amino/carboxyl groups in acidic conditions and the slow deprotonation during urea depletion; these processes contribute to the transient sol-gel transitions observed in these systems.

Esterase catalyzes the formation of alcohols and acids from ethyl acetate, which is accompanied by a decrease in pH (Fig. 3(a)). Researchers have combined urease and esterase to produce an antagonistic pH-modulating effect in a feedback-controlled biocatalytic reaction network [31]. A DNA hydrogel was formed using polyacrylamide copolymers containing DNA and an i-motif duplex as a cross-linker. Cytosine-rich DNA sequences are important pH-responsive molecules. Under acidic conditions, the cross-linker folds into the four-stranded intercalated DNA structures of i-motifs via hemi-protonated cytosine$^+$-H-cytosine base pairs [71]. This i-motif duplex can serve as a pH-responsive cross-linking unit for pH-dependent polymer hydrogels. At alkaline pH, oligonucleotides (1 and 2 in Fig. 3(d)) are partially hybridized into a duplex (blue) with a single-stranded 5′-end polyacrylamide copolymer (red, Fig. 3(d)), leading to a polyacrylamide gel. At an acidic pH, the crosslinkers of oligonucleotides 1 and 2 formed an i-motif tetraplex (green, Fig. 3(d)), leading to a sol state. The combination of urease and esterase produces an antagonistic pH-modulating effect. Coupling it to the pH-responsive DNA hydrogels realizes a programmable sol-gel-sol translation process (Fig. 3(d)) [31]. Similarly, through sequence-specific parallel Hoogsteen interactions (T-A-T and C-G-C), pH-sensitive single-strand DNA on gold nanorods can bind to DNA origami templates via forming a triplex DNA (pH < pK_a, pK_a = 7.2 or 6.6 according to different TAT/CGC contents), generating active chiral plasmonic metamolecules (L state or R state). Regulating the pH (pH > pK_a) by integrating urea/urease leads to the disassembly of the chiral tetrahedron-shaped DNA origami. By setting a programmable pH change in the urea-urease/acid buffer, the kinetically temporal self-assembly of chiral plasmonic metamolecules can be constructed by introducing transient formation and dissociation of the DNA triplex [29]. Importantly, urease and esterase regulate the pH during biological catalysis. In fact, without esterase, esters including methyl formate (pK_a = 3.77) [69], D-(+)-glucoronic acid γ-lactone (pK_a = 3.77) [69], D-(+)-gluconic acid δ-lactone (pK_a = 3.70) [69], methyl formate (pK_a = 3.77) [69], ε-caprolactone (pK_a = 4.88) [69], β-butyrolactone (pK_a = 4.41) [72], and methylene glycol-sulfite [73], have autocatalytic properties to produce acid. Therefore, programmable pH controllability can be achieved by utilizing a urease/acidic buffer, urease/ester, urease/esterase, and ester/basic buffer, which serve as pH modulators mastering the kinetic framework for a programmable transient pH.

This mode has two major advantages: First, molecules with pH-responsive motifs are potential precursors to engineering transient self-assemblies via urea/urease or ester/esterase. By integrating urea/urease and ester/esterase with versatile pH-responsive precursors, further transient self-assemblies can be created for complex applications. Second, the antagonizing pH-switching effects of urease and esterase result in a feedback loop conducive to manufacturing more complex nonequilibrium structures in space and time.

2.1.3. DNA or RNA/DNA or RNA enzymes

DNA is a biomacromolecule that consists of linearly linked 2-deoxyribose, phosphate groups, and nitrogenous heterocyclic nucleobases. In nature, four nucleobases are present in DNA: the pyrimidines adenine (A) and guanine (G) and the purines thymine (T) and cytosine (C). DNA has a unique structure and properties, including good biocompatibility, remarkable molecular self-assembly capabilities, and unique structural motifs [74]. Versatile noncovalent interactions, including electrostatic interactions [75], π–π stacking, hydrogen bonding (Watson-Crick pairing G: C and A: T) [76], and metal-base coordination [77] can drive DNA nanoassembly formation. Notably, DNA is an effective building block in self-assembly, demonstrating great applicability in bioprobes, chemical detection, drug delivery, bionic structures, cancer therapy, and more.

DNA is ideally suited for dissipative self-assembly owing to its enzymatic responsiveness. Versatile DNA (or RNA) enzymes, including deoxyribonuclease [40,78], endoribonuclease [30,79], and DNA ligase [32], facilitate different controls over the activation site for DNA (or RNA) in terms of selectivity and affinity. Deoxyribonuclease I (DNase I) can enzymatically hydrolyze the DNA backbone, breaking it into smaller fragments [78]. For example, a fluorescent DNA nanoassembly composed of DNA and TQA-TPE (containing aggregation-induced emission AIEgen with cationic chains) is constructed by multiple electrostatic interactions. The hydrolysis of DNA by DNase I reduces the binding sites between TQA-TPE and DNA, further leading to the spontaneous disassembly of DNA fluorescent assemblies accompanied by fluorescence quenching (Fig. 4(a)) [40]. In contrast to DNase I, the endoribonuclease enzyme RNase H shows better selectivity and affinity as an endonuclease, facilitating highly selective RNA consumption; it can bind to the RNA/DNA heteroduplex formed between the DNA loop and RNA and selectively hydrolyzes the RNA strand. For example, a triplex DNA structure is formed by clamp-like receptor DNA (gray/blue strand) and cargo DNA (orange) through Watson-Crick (A-T and C-G) and Hoogsteen interactions (T-A-T and C-G-C). Fuel RNA strands bind to the DNA receptor loop. This process causes a conformational change resulting in triplex DNA opening and the release of cargo DNA. RNA cleavage by RNase H restores the formation of the triplex DNA structure. The transient loading/release of cargo DNA can be realized using RNase H (Fig. 4(b)) [79]. Integrating specific targets of aptamers [80] and the specific responsiveness of enzymes further improves the programmability, predictability, functionality, and controllability of dissipative DNA assemblies. Nucleic acid aptamers are single-stranded oligonucleotides with unique intramolecular conformations and specific cognate target recognition abilities. Allosteric DNA-based nanodevices for the transient loading and release of ATP are realized by aptamer-induced conformational changes. A DNA sequence contains two ATP-binding aptamer sequences connected by a linker DNA, serving as an allosteric site. An allosteric inhibitor of the fuel DNA binds to the linker domain, causing a conformational change that negatively affects the affinity of the aptamer for ATP. Thus, the enzyme Nt.BsmAI can specifically recognize and cut the double strands-DNA (dsDNA) sequence of the linker DNA and DNA allosteric inhibitor, restoring the original affinity of the ATP-binding aptamer (Fig. 4(c)) [30].

T4 DNA ligase enables the formation of DNA phosphodiester bonds via ATP-fueled enzymatic activation. However, antagonistic BamHI restriction enzymes cut dsDNA strands via hydrolytic cleavage of the phosphodiester bond. Combining T4 DNA ligase (in the presence of ATP) and the antagonistic restriction enzyme BamHI builds dynamic DNA covalent bonds by joining and cutting the phosphodiester bond. This antagonistic enzymatic reaction network of concurrent ligation and cleavage results in a transient dynamization of covalent DNA bonds (Fig. 4(d)) [32]. A new catalytic DNA circuit was developed by introducing a nickel-assisted reactant-recycling strategy to create an entropy-driven DNA circuit. Duplex gate components (generated from the last circuit reaction) can revert to their original active states with the aid of nicking enzyme digestion. The newly nicked gate component can then participate in the next circuit reaction [81]. Notably, studying temporal assemblies containing DNA molecules is of interest, as it covers a wide range of versatile dissipative self-assemblies fabricated by DNA with surfactants, polymers, nanoparticles, carbon materials, and quantum dots. Studying the multiple synergetic noncovalent interactions in transient DNA nanoassemblies contributes to analyzing the energy depletion process. Moreover, integrating aptamers and DNA enzymes into DNA nanoassemblies has numerous functions in dissipative self-assemblies.

2.1.4. Other enzymes

In addition to these enzymes, a range of enzymatic reaction networks has been fabricated based on controlled enzyme-mediated consumption. Various oxidases, including glucose, choline, urate, and sarcosine oxidases, using glucose, choline, uric acid, and sarcosine as substrates, respectively, yield a strong oxidizing agent (H_2O_2) after an enzymatic hydrolysis process [82]. For example, glucose oxidase catalyzes substrates of glucose and oxygen to produce H_2O_2 and gluconic acid [37]. This redox strategy allows for the generation of transient recon-

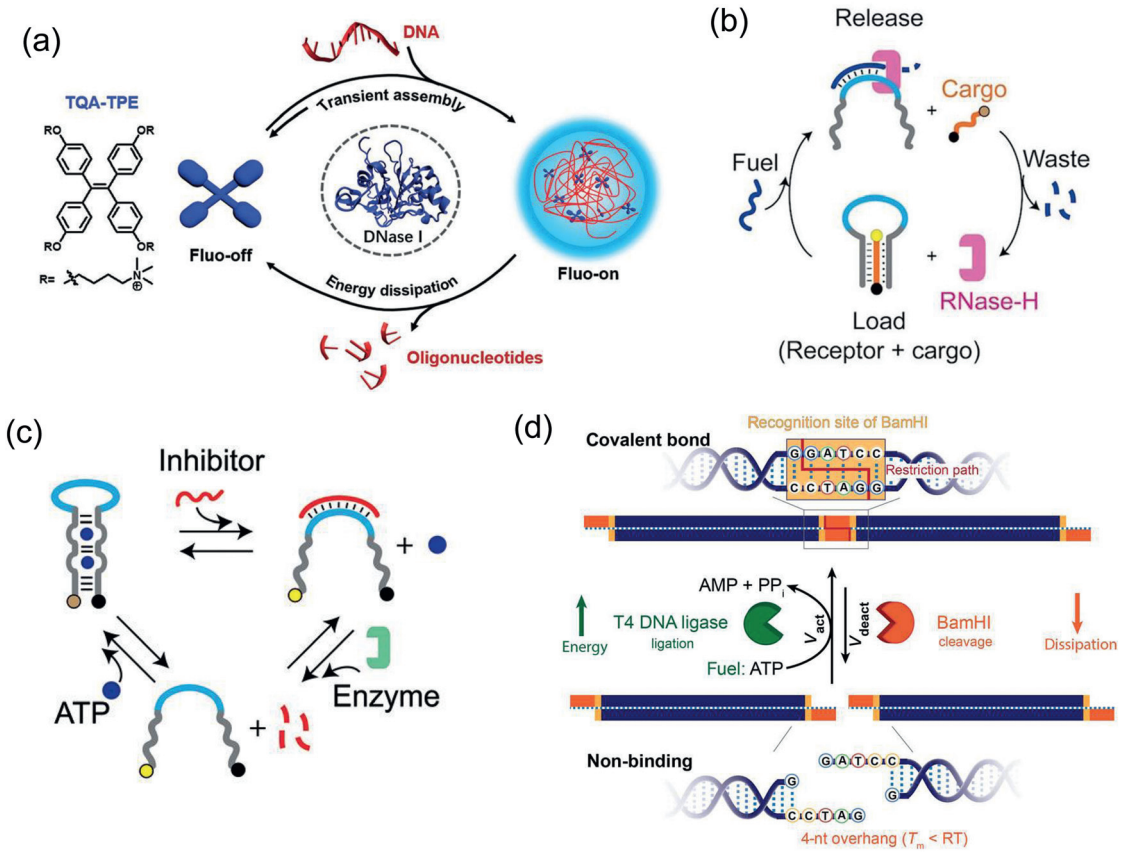

Fig. 4. (a) Fuel DNA can interact with cationic TQA-TPE, whereas the DNase I induces a hydrolysis process [40]. (b) Fuel RNA binds with DNA loop and forms a triplex DNA structure, leading to a conformational change and cargo release; however, endoribonuclease enzyme RNase H can recapture cargo [79]. (c) RNA causes an allosteric switching for releasing ATP and enzyme Nt.BsmAI restores the ATP binding capability [30]. (d) The combination of T4 DNA ligase (in the presence of ATP) and antagonistic BamHI restriction enzyme builds on dynamic DNA covalent bonds by joining and cutting the phosphodiester bond [32].

figuration in the charge-transfer molecular system [83]; it can also be applied to H_2O_2-reactive molecular systems, such as peptides containing an H_2O_2-reactive boronoarylmethoxycarbonyl group [82]. Lipase has a high degradation efficiency for triglyceride into acetic acid and glycerol, which can be applied in generating lipase-based mesoporous silica nanoparticles and oil-in-water emulsion droplets [41–42]. The enzymes trypsin and chymotrypsin can cleave peptide Z-phenylalanine-arginine-AMC (AMC: 7-amino-4-methylcoumarin) at different cleavage sites: trypsin preferably cleaves amide bonds at the C-terminal end of positively charged amino acids, yielding Z-phenylalanine-arginine-OH and fluorescent AMC. However, chymotrypsin enables the cleavage of amide bonds after hydrophobic and aromatic amino acids, producing Z-phenylalanine-OH and nonfluorescent H-arginine-AMC. Trypsin activates chymotrypsinogen by generating a fluorescent output; however, activated chymotrypsin counteracts trypsin. The dual activity of these enzymes eventually produces a pulse-like fluorescent signal [84]. Moreover, α-chymotrypsin catalyzes a fast transacylation of aspartyl-phenylalanine-methyl ester into transient tripeptide, further forming fibers. However, the amide bond is thermodynamically disfavored and slowly hydrolyzes into aspartyl-phenylalanine. This biocatalytic pathway controls the assembly and disassembly of transient tripeptide nanostructures [85].

2.2. Hydrophilic/hydrophobic switching of precursors

Surfactants are amphiphilic molecules containing hydrophilic heads and hydrophobic alkyl chains. Their hydrophilic and hydrophobic properties enable them to form various aggregates through hydrophobic interactions. Inspired by surfactants, a hydrophilic precursor can be fuel-driven into amphiphilic building blocks and further self-assembled into versatile temporal assemblies. Once the energy is removed, the building blocks become completely hydrophilic, leading to disassembly. Hence, controlling the hydrophilic/hydrophobic balance of precursors is an effective way to complete the nonequilibrium cycle of high-energy self-assembly and low-energy-state precursors. The carboxylate group in the precursor can undergo hydrophilic/hydrophobic switching via esterification induced by carbodiimides or alkylating agents.

2.2.1. Carbodiimides

Carbodiimides are a class of substances with N=C=N functional groups that are mainly utilized to activate carboxyl groups and promote the formation of amides and esters. Carbodiimides mainly include 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), dicyclohexylcarbodiimide (CMC), N, N-dicyclohexylcarbodiimide (DIC) (Fig. 5(a), fuel R_1), and other derivatives (Fig. 5(a), fuel R_2). EDC is the most commonly used carbodiimide for dissipative self-assembly. Carbodiimides interact with the carboxylate in the precursor to form metastable O-acylisourea and form a building block; the direct hydrolysis of O-acylisourea into the original precursor accomplishes the disassembly process.

In the presence of fuel EDC, the chemical reaction network can convert the precursors of dicarboxylates [45–47] and carboxylates [17,26,47] into metastable building blocks, including intramolecular anhydrides (Fig. 5(a)) [45–47], intermolecular anhydrides [47], and esters [17,26]. The increased hydrophobicity of the metastable products further induces the self-assembly process. Once the chemical reaction network runs out of fuel, the unstable anhydride or ester product is rapidly hydrolyzed back to its original precursor. For example, in the dissipative self-assembly of silicon nanocrystals (SiNCs) reported by

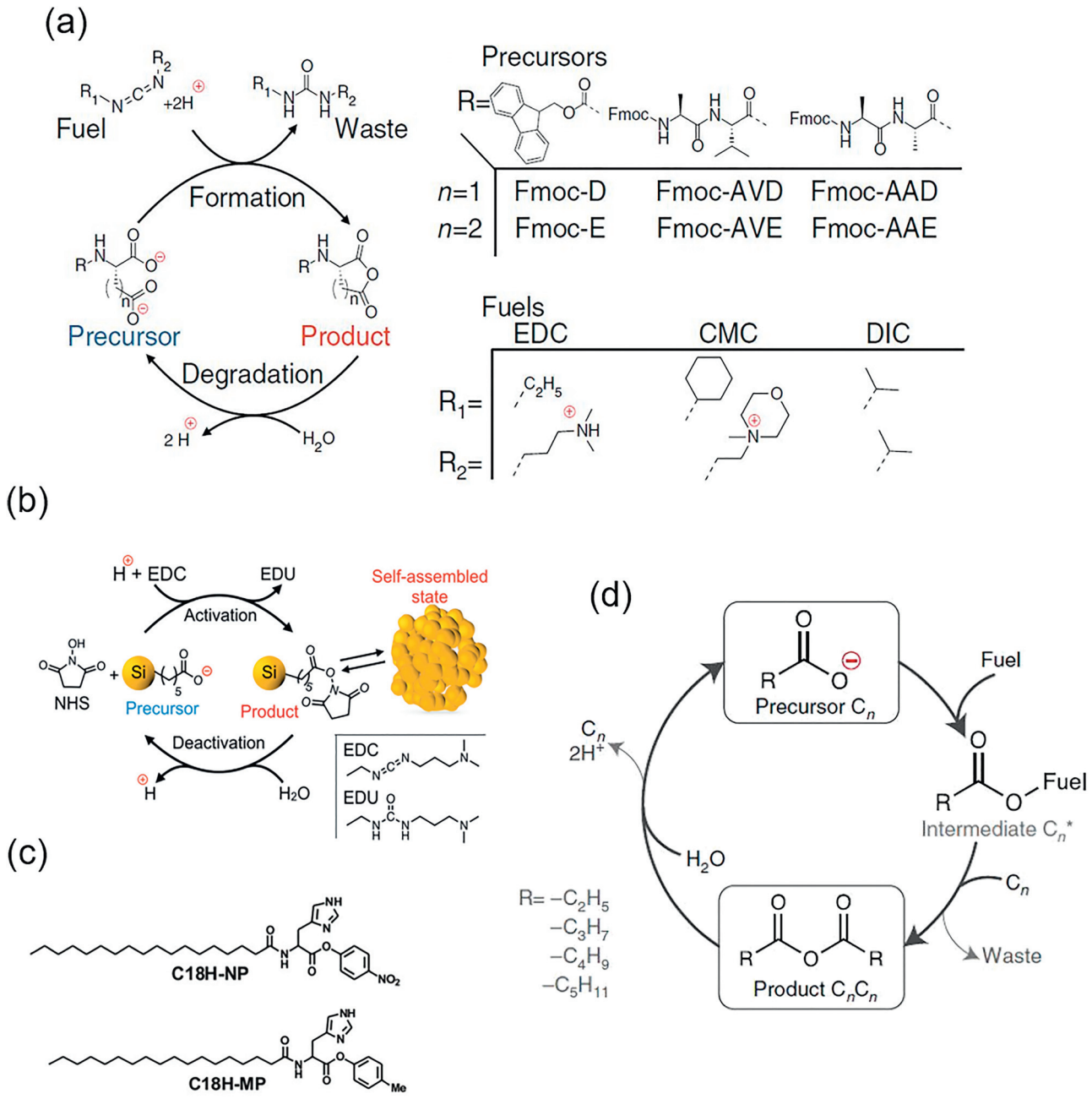

Fig. 5. (a) Schematic representation of the chemical reaction network for carbodiimide driven by a transient anhydride bond and structures of precursors and carbodiimides [46]. (b) Carboxylate silicon nanocrystals (SiNCs) (precursor) with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) activation (fuel) to form hydrophobic N-hydroxysuccinimide (NHS) ester and further self-assembled into SiNC clusters (transient assemblies) [17]. (c) The structures of $C_{18}H$–NP and $C_{18}H$-MP (building block) formed by $C_{18}H$ with 4-NP and 4-MP [26]. (d) Aliphatic carboxylic acid precursors (C_n) are activated by EDC (fuel). The activated intermediate (C_n^*) can react with a second precursor molecule to form a transient anhydride product (C_nC_n). The network operates in water, and the product thus rapidly hydrolyzes to the original precursor [44].

Boekhoven et al., the fuel EDC activates the interaction of SiNCs with 5-hexenoic acid and N-hydroxysuccinimide (NHS). The carboxylate ligands are then converted into NHS-esters, inducing the self-assembly of SiNCs and forming clusters. The NHS-esters hydrolyze back into the original carboxylate state, completing the deactivation process (Fig. 5(b)) [17]. Excluding carboxylic acid-functionalized SiNCs, precursors of carboxylates contain carboxylic acid derivatives of potassium sulfobenzoic acid, methoxyethoxy acetic acid [47], peptides with a large hydrophobic protecting group of fluoren-9-ylmethoxycarbonyl (Fmoc-peptide) [46] and amphiphile molecule of stearoylation with histidine [26]. They can interact with EDC and form metastable anhydrides or esters. The fuel EDC endows the chemical reaction network with time programmability and nonequilibrium properties. Moreover, CMC and DIC (Fig. 5(a)) can interact with precursors and facilitate metastable bonds in the building blocks [46].

In EDC-activated dissipative self-assembly, one of the key aspects to emphasize is the formation of metastable anhydrides or esters. These intermediates can be hydrolyzed back into their original precursors in a controllable manner. This requirement ensures the reversible nature of the self-assembly process and allows for dynamic changes and reconfiguration. Once the yielded anhydrides or esters stabilize, the chemical reaction network does not revert to the state of the original precursor.

For example, in the case of the nucleophile 4-nitrophenol (4-NP), a high-energy ester bond is formed between the 4-NP and the amphiphile during stearoylation with histidine ($C_{18}H$). Hydrolysis of the metastable ester bond ($C_{18}NP$) results in rapid ester formation-hydrolysis switching. However, when 4-methylphenol (4-MP) serves as the nucleophile of $C_{18}H$, a less hydrolyzable ester ($C_{18}MP$) is obtained owing to the replacement of the electron-withdrawing group $-NO_2$ with a positive inductive effect promoting the methyl group, resulting in a stable ester compound for 3 days (Fig. 5(c)) [26]. Therefore, when using EDC to activate the precursor, the interaction between precursors and co-factors should be carefully considered and verified. The ratio and concentration of EDC and NHS have been reported to significantly influence the final assemblies [86]. Hence, using the different hydrolysis rates for metastable anhydrides could realize the self-selection of dissipating assemblies through phase separation. In the presence of EDC, the precursors (C_n, n = 3, 4, 5, and 6) form transient symmetric anhydrides of C_nC_n, which are subsequently hydrolyzed into the original C_n. However, metastable anhydride products with higher carbon numbers (C_5C_5 and C_6C_6) are separated into droplets that protect C_5C_5 and C_6C_6 from hydrolysis, accomplishing the selection of nonequilibrium products (Fig. 5(d)) [44].

Notably, carbodiimides can regulate the tunable lifetime of metastable anhydrides and esters in dissipative self-assemblies. However, for the EDC activation/O-acylisourea hydrolysis process, the structure of the precursors and the interaction between the precursors and fuels play an important role in constructing various transient assemblies. Using the EDC activation process, transient anhydrides are formed from Fmoc-D and Fmoc-E, which further assemble into spherulites and colloids, respectively. Nevertheless, transient anhydrides of Fmoc-AAD, Fmoc-AVD, Fmoc-AAE, and Fmoc-AVE assemble into anisotropic fibers, (D, aspartate; E, glutamate; A, alanine; V, valine). These different assemblies exhibit distinct properties and functions, including transparent-turbid change (Fmoc-D), rhythmical contraction switch (Fmoc-E), and sol-gel transition (Fmoc-AAD). The resulting structures offer diverse capabilities and applications (Fig. 5(a)) [46]. The versatile modes of non-covalent interactions between temporal anhydrides and esters are the driving forces that induce various self-assemblies. By incorporating carbodiimide activation/energy consumption, chemical reaction networks have been successfully applied in creating self-erasing inks [46], releasing dyes [46], delaying the cellular uptake of SiNCs [17], and establishing supramolecular hosts of cationic guests [47].

In summary, there are various types of carbodiimides, including EDC, CMC, and DIC (Fig. 5(a)), among which EDC is the most studied fuel; however, under specific conditions, EDC, CMC and DIC can serve as alternative fuel sources owing to their distinct physicochemical properties. EDC is water-soluble, whereas CMC and DIC are insoluble in water. CMC and DIC are typically used in polypeptide synthesis, whereas DIC is applied in solid-phase synthesis. These properties and the diversity of carbodiimide molecules provide more possibilities for hydrophobic precursors and produce abundant metastable building blocks and temporal assemblies via dissipative self-assembly.

2.2.2. Methylating agents

Methylation is a common organic reaction in which a methyl group ($-CH_3$) replaces the hydrogen in an organic compound. Utilizing methylation, the carboxylate group can be transferred to hydrophobic methyl esters via the replacement of H by CH_3. The formed methyl esters can undergo base-catalyzed hydrolysis, leading to the regeneration of the original carboxylate. Based on this, methylating agents, including methyl iodide (CH_3I) [48] and dimethyl sulfate ($(CH_3)_2SO_4$) [38], can convert hydrophilic precursors with carboxylate groups into amphipathic building blocks with methyl esters. The loss of electrostatic stabilization increases the hydrophobicity of the carboxylate, resulting in transient self-assembly while accomplishing energy depletion through the hydrolysis of methyl esters into precursors. These carboxylates can be moieties in peptides, polypeptide derivatives [48], polymers [38], and ligands on

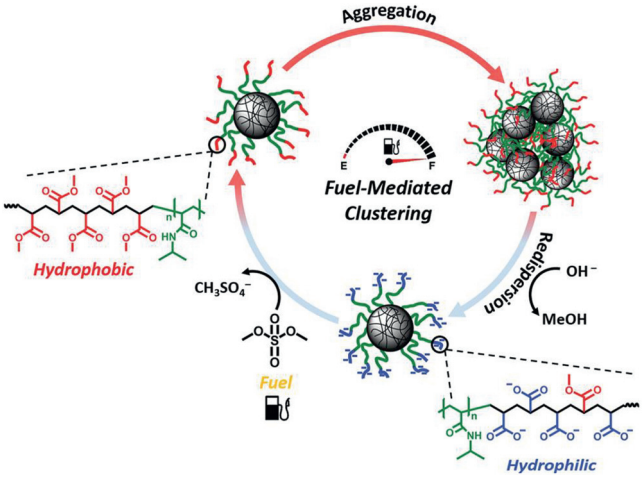

Fig. 6. The self-assembly/disassembly of a polymer containing carboxylic acids (precursor) mediated via esterification (fuel is $(CH_3)_2SO_4$) and hydrolysis processes [38].

nanoparticles. For example, $(CH_3)_2SO_4$ can convert the charged carboxylic acids of a polymer to hydrophobic methyl esters, which further self-assemble into temporal micelles. With the hydrolysis of the ester, electrostatic repulsion eventually disassembles the assemblies (Fig. 6) [38]. Two important aspects should be noted: first, in dissipative self-assembly, the ester formation should be faster than its hydrolysis; hence, the pH and temperature are important requirements for controlling the reaction rate. Second, hydrolysis of the ester consumes hydroxide ions and produces MeOH, releasing highly acidic protons; hence, a basic buffered environment and higher fuel concentrations (after consecutive cycles) are required [38,48].

2.2.3. PEG-iodine

The coordination between polyethylene glycol (PEG) and iodine can greatly improve the hydrophobicity of PEG [87–89]. As shown in Fig. 7(a), the reduction of $NaIO_3$ produces I_2. Polymers containing PEG segments can self-assemble into transient micelles owing to the increased hydrophobicity resulting from the coordination between PEG and I_2. Once I_2 is reduced to I^- by thiourea, the PEG segment becomes hydrophilic again, further resulting in the disassembly of the micelles (Fig. 7(a)). Reversible micelle formation/disassembly can be regulated by fuel iodine, which is a transient product generated from the chemical oscillator of IO_3^--SO_3^{2-}-thiourea (Fig. 7(a)) [21] or IO_3^--NH_3OH^+-OH^- (Fig. 7(b)) [43].

2.2.4. New chemical fuels

Charge transfer interactions play a crucial role in governing the behavior of amphiphilic foldamers, allowing for temporal control over their switchable conformation. This control can be achieved through redox-reduction processes and enzymatic pathways [90]. Recent studies have explored various novel fuels for dissipative self-assembly, such as shaking [25], trichloroacetic acid [13]. Hydrazine [18], and merocyanine molecules [19,50]. These new fuel options hold the potential to enhance dissipative self-assembly and enable the development of functional materials with life-like properties (Fig. 1(b)). The factors involved in dissipative self-assembly, including precursors, fuels, activated building blocks, transient assemblies, and their corresponding applications are summarized in Table 1.

PDAT:4,6-diamino-1,3,5-triazine moieties; NDPA: naphthalene diimide derivative; Zn-DPA: Zn^{2+}-dipicolylethylenediamine; C_{16}TACN·Zn^{2+}: Surfactant containing a polar C_{16} chain and 1,4,7-triazcyclononane·Zn^{2+}; Au NP 1·Zn^{2+}: Au NPs with C_9-alkanethiolates bearing a 1,4,7-triazacyclononane head group; Au NP 2·Zn^{2+}: Au NPs with C_9-alkanethiolates bearing a 1,4,7,10-tetraaza-cyclododecane

Table 1
Versatile modes of fuel input/energy depletion in dissipative self-assembly systems for different substrates, switching processes, and applications.

Fuel activation/energy consumption mode	Fuel, (cofactors); energy depletion factor	Precursors	Transient switching process	Interaction of transient self-assemblies	Application	Ref.
Enzyme bio-catalysis mechanism (ATP enzymes)	ATP; alkaline phosphatase	Micelles of PDAT block copolymer	Micelle-smaller complex switching	Hydrogen bonding and electrostatic interactions	Smart drug carrier	[12]
	ATP; apyrase	Vesicle of block copolymer with biguanidine-cyclodextrin side	Reversible expansion-contraction for vesicle	Ligand-receptor interactions	Programmed micro-separators	[54]
	ATP; apyrase	Micelles of block copolymer with biguanidine-cyclodextrin side	Reversible expansion-contraction for micelle	Ligand-receptor interactions	Smart drug carrier	[53]
	ATP, ADP, AMP, Pi; enzymes (alkaline Phosphatase, apyrase, creatine phosphokinase)	NDPA with Zn-DPA receptor	NDPA chiral Supra-molecule	Electrostatic, hydrophobic, π–π stacking and hydrogen bonding	Supramolecular polymer with transient helicity	[33,58]
	ATP/apyrase	Oligo(*p*-phenylenevinylene) derivative with Zn-DPA receptor	Chiral Supra-molecule	Mainly electrostatic and π–π stacking	Supramolecular polymer with transient helicity	[35]
	ATP/apyrase	Surfactant C_{16}TACN·Zn^{2+}	Transient vesicle	Electrostatic and hydrophobic interactions	Vesicular nanoreactor	[16]
	ATP/apyrase	Au NP 1·Zn^{2+}	Transient signal generation	Stronger electrostatic interactions	Nanosystem for signal generation	[57]
	ATP/apyrase	Bowl-shaped polymer vesicles with polylysine	Reversible open-closed state	–	Nanoreactor and nanomotor	[10]
	nucleotides NDP and NTP (N = A, T, G, C)/alkaline phosphatase	Au NP 1·Zn^{2+}, Au NP 2·Zn^{2+}	Transient signal generation	Stronger electrostatic interactions	Nanosystem for signal generation	[59]
	ATP/ creatine phosphokinase	Cationic porphyrin derivative	Temporal double-helical supramolecular structure	π–π stacking and electrostatic interaction	–	[61]
Enzyme bio-catalysis mechanism (Urease and esterase)	$CO(NH_2)_2$, citric acid-trisodium citrate buffer; urease	PS-*b*-P2VP deblock copolymer	Collapsed–swollen–collapsed switch for photonic films	–	Photonic devices	[9]
	Urea, acidic buffer; urease	Copolymer of PEG and PDEAEMA	Reversible shrinking-expansion for vesicle	Protonation of polymer	Self-adaptive nanoreactor	[11]
	Urea, acidic buffer; urease	pH-responsive microgel	Reversible shrinking-expansion for microgel	–	–	[34]
	Urea; urease/methyl formate; esterase	Fmoc-dipeptide	Sol-gel-sol transition	Deprotonation and noncovalent interaction	Supramolecular gels	[23]
	Urea; urease/Ethyl acetate; esterase	DNA i-motif as the linker	Reversible sol-gel transition	Formation of i-motif, (hemiprotonated cytosine$^+$-H-cytosine base pairs)	DNA hydrogel	[31]
	Urea, acid buffer; urease	DNA origami and Au NPs	Reversible assembly/disassembly to DNA origami immobilized Au NPs	Formation of a pH responsive DNA duplex	–	[29]
	Urea; urease Ester of polymer; base	ETTMP and PEGDA	Reversible sol-gel transition	Base-catalyzed thiol-Michael addition reaction	Temporal gelation and polymerization	[91]
	Urea; Urease	Complex coacervate core micelles of CPF and DBP	Programmed disassembly and reassembly of micelles	Protonation/deprotonation of carboxylated side chains	Fluorescence sensor and release/recapture of cargo	[22]
	Urea; Urease	Peptide	Gel-sol-gel transition	–	Creating gel-sol with pre-determined switchable time	[24]
Enzyme bio-catalysis mechanism (DNA or RNA enzymes)	DNA; DNase I	TQA-TPE	Reversible fluorescence "ON-OFF"	Electrostatic interaction	–	[40]
	RNA; RNase H restriction enzyme	Triplex DNA with cargo DNA	Reversible duplex and triplex DNA	Watson-Crick (A-T and C-G)	Reversible cargo capture and release	[79]
	RNA; Nt.BsmAI restriction enzyme	ATP (or cocaine) aptamers connected by linker DNA	Reversible allosteric DNA nanodevices	Watson-Crick (A-T and C-G)	Capture and release of ATP and cocaine	[30]
	DNA monomer; T4 DNA ligase (with ATP), BamHI restriction enzyme	DNA monomer	Dynamic covalent polymerization of DNA chain	Formation and cleavage of phosphodiester bond	–	[32]

(*continued on next page*)

Table 1 (*continued*)

Fuel activation/energy consumption mode	Fuel, (cofactors); energy depletion factor	Precursors	Transient switching process	Interaction of transient self-assemblies	Application	Ref.
Hydrophilic/hydrophobic switching of substrates (EDC)	EDC (H^+); Hydrolysis of esters	SiNCs with 5-hexenoic acid	Reversible SiNCs and clusters	Formation of NHS-esters	Delaying the cell uptake of SiNCs	[17]
	EDC (H^+); Hydrolysis of anhydrides	Derivatives of aspartic or glutamic acid	Reversible precursor-micelles	Formation of anhydrides	–	[45]
	EDC (H^+); Hydrolysis of anhydrides (pyridine)	KSB-Ac or MEA-Ac or TEG-Ac or PEG-Ac	Reversible carboxylic acid and anhydride	Formation of anhydrides	Supramolecular hosts of cationic guests	[47]
	EDC; Hydrolysis of $C_{18}H$-NP	$C_{18}H$ and 4-NP	Reversible sol-gel transition	Formation of $C_{18}H$–NP	–	[26]
	EDC or CMC or DIC	Fmoc-D or Fmoc-E, Fmoc-AVD or Fmoc-AVE, Fmoc-AAD or Fmoc-AAE	Reversible sol-gel transition, turbid-transparent solution change, expansion-contraction for colloids	Formation of anhydride bond	Self-erasing inks, releasing of dyes	[46]
	EDC; Hydrolysis; (Inhibition via phase separation)	C_n, n = 3, 4, 5, 6	C_nC_n-C_n translation (n = 3, 4); (C_nC_n oil droplet for C_5C_5 and C_6C_6)	Formation of anhydride bond	Self-selection of dissipative assemblies	[44]
Hydrophilic/hydrophobic switching of substrates (Methylation)	Methyl iodide; Base-catalyzed hydrolysis of ester	Dibenzoyl-(L)-cystine	Reversible sol-gel transition	Intermolecular hydrogen bonds and hydrophobic interaction	–	[48]
	Dimethyl sulfate; Base-catalyzed hydrolysis of ester	Polymer brush containing PMMA	Reversible assembly-disassembly of micelle	Mainly hydrophobic interaction	–	[38]
Hydrophilic/hydrophobic switching of substrates (I_2)	I_2 (IO_3^--SO_3^{2-}-thiourea); I_2 depletion	Polymer PEG_m-$PLKC_n$	Reversible assembly-disassembly of micelle	Coordination of PEG and I_2 and hydrophobic interaction	Removing impurity (with modified MCNTs)	[21]
	I_2 (IO_3^--NH_3OH^+-OH^-); I_2 depletion	Polymer PEG_m-$PLKC_n$	Reversible assembly-disassembly of micelle	Coordination of PEG and I_2 and hydrophobic interaction	–	[43]
Hydrophilic/hydrophobic switching of substrates (Charge transfer)	Reduction of sodium dithionite; Enzymatic glucose oxidase	PV-VN foldamer	Reversible sheet-vesicle translation	Hydrophilic-hydrophobic transition by charge transfer	–	[90]

(cyclen) head group; PS-*b*-P2PV: polystyrene-*b*-poly(2-vinyl pyridine); DEAEMA: poly(diethylaminoethyl methacrylate); PEG: poly(ethylene glycol); PDEAEMA: poly[2-(diethylamino) ethyl methacrylate]; ETTMP: ethoxylated trimethylolpropane tri(3-mercaptopropionate); PEGDA: poly(ethylene glycol) diacrylate; DNase I: deoxyribonuclease; CPF: poly[9,9´-bis(3´-propanoate)fluoren-2,7-yl] sodium salt (CPF); DBP: poly(N-methyl-2-vinylpyridinium)$_{29}$-*b*-poly(ethylene oxide)$_{204}$; TQA-TPE: tetraphenylethylene-based AIEgen with cationic side chains. EDC:1-ethyl-3-(3-dimethylaminopropyl) carbodiimide; SiNCs: silicon nanocrystals; NHS: N-hydroxysuccinimide; KSB-Ac: potassium sulfobenzoic acid; MEA-Ac: methoxyethoxyacetic acid; TEG-Ac: tetraethylene glycol diacids; PEG-Ac: pentaethylene glycol diacids; $C_{18}H$: stearoylation of histidine; 4-NP: 4-nitrophenol; Fmoc: fluoren-9-ylmethoxyacrbonyl (D: aspartate; E: glutamate; A: alanine; V: valine.) PMMA, polymerization of methyl methacrylate; PEG, polyethylene glycol; PLKC, poly(L-lysine hydrochloride); MCNTs, multiwalled carbon nanotubes; PN-VN, pyranine and viologen foldamer.

(1) There are notable limitations to enzyme biocatalysis. After several cycles of the enzyme-catalyzed reaction, the gradual accumulation of waste products significantly decreases the cycle number and affects the formation of transient assemblies. Furthermore, special attention should be paid to enzyme activity during the experimental process. In addition, the structure of the precursors has some limitations. i) For ATP/ATP enzymes, precursors should contain ATP-binding re-

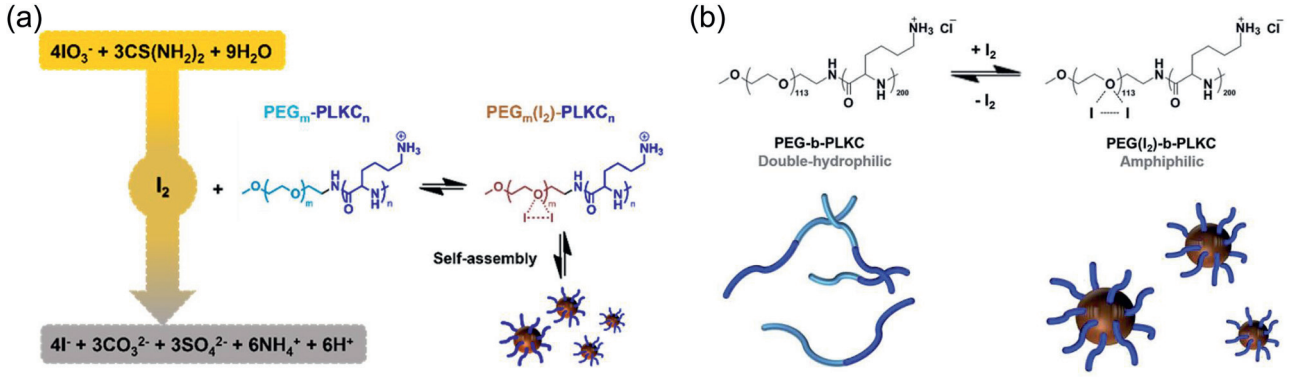

Fig. 7. (a) The process of I_2 producing (fuel) with an oscillator of IO_3^--SO_3^{2-}-thiourea and the self-assembly of the PEG copolymer (precursor) into temporal micelles. The disassembly process is induced by the reduction of I_2 [21]. (b) The self-assembly/disassembly of the PEG copolymer regulated by I_2 from the oscillator IO_3^--NH_3OH^+-OH^- [43].

ceptor units such as guanidinium and melamine groups. Thus, complex precursors with ATP receptors are required to be designed and synthesized. ii) Urease induces a pH increase after catalysis, whereas esterase causes a pH decrease. Temporal assemblies are activated by pH-switchable precursors. iii) For DNA or RNA enzymes, dynamic DNA (or RNA) assemblies that are temporally controlled by enzymes (nickases, ligases, or endonucleases), and DNAzymes require well-designed DNA sequences or modified functional molecules (such as fluorophores, quenchers, and azobenzenes). (2) In dissipative self-assemblies, challenges such as waste accumulation and limitations on the structure of the precursors are faced during the hydrophilic/hydrophobic switching process. When EDC or methylating agents serve as fuels, precursors with carboxylate groups are required; moreover, the precursors should contain PEG segments with I_2. In summary, more complex dissipative self-assembly systems require well-designed precursors and the corresponding fuels.

3. Transient self-assembly from precursors

3.1. Transient supramolecular gel

Gels are spatial network structures formed by the linking of colloidal particles or organic molecules under specific conditions; these unique colloidal dispersions exhibit properties of both liquids and solids, containing substantial amounts of liquid while behaving as solids. Permanent gels are solid-like materials with an inverted immobility. Owing to their good biocompatibility and multilevel sol-gel transition, permanent gels have been extensively applied in cosmetics, environmental engineering, and biological medicine. However, the current artificial control of the sol-gel transition is not advanced enough to meet the complex and functional requirements of various production and life applications. Using dissipative self-assembly to set a controllable lifetime for the sol-gel-sol transition has several advantages, including self-regulation, time programming, self-adaptation, and dynamic properties. Transient gels hold significant potential for various applications under specific conditions. For example, they can be utilized to create a temporary gel for storage that can be switched to a sol state for injection [24]. Moreover, they enable time-controlled gelation with programmable self-degradation, thereby offering versatile functionality. The main differences between transient and permanent gels lie in their temporal behavior and rheological properties, as transient gels exhibit reversible gel-sol transitions, whereas permanent gels, characterized by high viscosity and elasticity, maintain a stable solid-like state indefinitely. Within a certain oscillation frequency range, the storage modulus (G') and loss modulus (G'') are nearly constant with frequency. G' is significantly larger than G'' over a large frequency range within the linear viscoelastic region [92]. Temporal gels exhibit a time-dependent behavior where the values of G' and G'' initially increase to a maximum and then decrease over time [23–24]. In permanent gels, the platform of G' can indicate their mechanical strength; however, G' in dissipative self-assembly systems increases first with gel formation and then decreases slowly, accompanied by gel collapse.

Based on the molecular weights of the gelators, transient gels can be divided into polymer and supramolecular gels. In contrast to polymer gels, supramolecular gels [93–94] present highly controllable self-assembly/disassembly behavior because their driving forces are noncovalent interactions. Thus, supramolecular gel materials can easily respond to various stimuli, enabling sol-gel switching. Peptide-based molecules serve as precursors in temporal supramolecular gel formation. Peptide-based supramolecular gels have attracted considerable attention owing to their versatility, biocompatibility, biodegradability, and wide range of applications. Peptides are the most promising gelators owing to their versatility in amino acid sequences, charges, pK_a, hydrophobicity, and size [95–96]. Furthermore, responsive peptides can alter their properties, such as pH, temperature, enzyme, and redox, which require various functions. Peptides [23,62,85], peptides derivative [27], and amino acid surfactants [26] can be used to construct metastable supramolecular gels [39]. Strictly, some gelators in transient gels are amino acid derivatives rather than peptides. They are typically functionalized with hydrophobic benzyl-, naphthyl-, fluorenyl-, or perylene-based groups to facilitate gel formation. Four energy input/depletion methods can be introduced into supramolecular gel systems by regulating the hydrophilic/hydrophobic transition of peptides (and derivatives). First, carbodiimide (EDC, CMC, and DIC) can convert the -COOH groups in Fmoc-alanine-alanine-aspartate [46] and Fmoc-alanine-alanine-glutamate [46] or histidine-based surfactant [26] into metastable anhydrides or esters, inducing a transient gel. Once the chemical reaction network runs out of fuel, the anhydride or ester product becomes unstable and rapidly hydrolyzes back to the original sol. In addition to the noncovalent interactions such as electrostatic interactions and hydrogen bonding involving amino acid groups, the presence of large hydrophobic protecting groups (such as Fmoc), as well as hydrophobic interactions facilitated by alkyl chains, collectively contribute to the self-assembly of peptides into dense fiber networks and the formation of supramolecular gels [26,46]. Second, by removing electrostatic repulsion, the change in hydrophilic/hydrophobic equilibrium and hydrogen bonding and pH further facilitates the formation of gels. For example, the pH triggers of urease/methyl formate enable a pH increase followed by a gradual pH decrease, facilitating a programmable sol-gel-sol transition of Fmoc derivatives. This transition occurs through the deprotonation switching of amine groups and leads to gelation at pH = 8.5–8.6 [23]. In contrast, the protonation of the carboxyl group facilitates gelation. A sharp rise in pH of the acidic buffer and a slower pH decrease of urea/urease generate a highly controllable sol-gel-sol switching for Fmoc-leucine-glycine-OH (gelation at pH = 5.8) [62]. In addition to urease catalysis and counter trigger (acidic buffer and ester hydrolysis), yeast can convert fuel sucrose into ethanol and CO_2 accompanied by a pH decrease process ($CO_2 + H_2O \rightarrow HCO_3^- + H^+$). By setting a base/$CO_2$ production/CO_2 slow elimination trigger, peptide-based surfactants with a free carboxylate undergo a temmporal sol-gel transition by protonation switching of the carboxyl group [97]. Third, some peptides are receptors or enzyme substrates; thus, biocatalytic enzymes will contribute to the formation of temporal hydrogelators and transient peptide gels. α-Chymotrypsin catalyzes the transacylation of aspartyl-phenylalanine-methyl ester and amino acid amides to form a temporary tripeptide hydrogelator [85]. Fourth, redox-controlled gelator molecules must be elaborately designed and synthesized. Oxidase-catalyzed oxidation to produce hydrogen peroxide is a powerful tool for addressing peptide gels. For example, H_2O_2 can trigger the cleavage of the boronophenyl methoxycarbonyl (BPmoc) group and produce *p*-quinone methide, boric acid, and CO_2. The tripeptide of the phenylalanine-bearing BPmoc unit realizes a gel-sol transition via an oxidation/elimination reaction triggered by H_2O_2. Thus, oxidases such as glucose, choline, urate, and sarcosine oxidases in peptide matrices generate H_2O_2 in situ and further construct an enzyme-responsive transient gel system [82]. The use of a peptide, including pH-switchable glutamic acid and the redox-responsive methionine amino acid, results in a multi-stimuli-responsive peptide gel. The glucose oxidase-catalyzed, and glucose-fueled release of protons coupled with H_2O_2 production controls a programmable sol-gel-sol transition [98]. In addition to the oxidation process, reducing disulfide bonds by a phosphine-based reducing agent is another strategy employed in transient peptide gels. The competition between the pH activator and the reducing agent deactivator enables a sol-gel-sol cycle in the transient gel composed of N, N′-dibenzoyl-L-cystine [27].

Synthesis of novel gelators, exploration of novel energy input/depletion modes, and discovery of new self-assembly methods are significant challenges in developing functional metastable gel materials. According to a comprehensive study, the pseudopolyrotaxane molecular tubes (Fig. 8(a)), featuring nitrogen atoms marked in blue, can be threaded by PEG chains (with oxygen atoms marked in red). These PEG chains then intrachain-coordinate with Cu^{2+} ions, leading to the for-

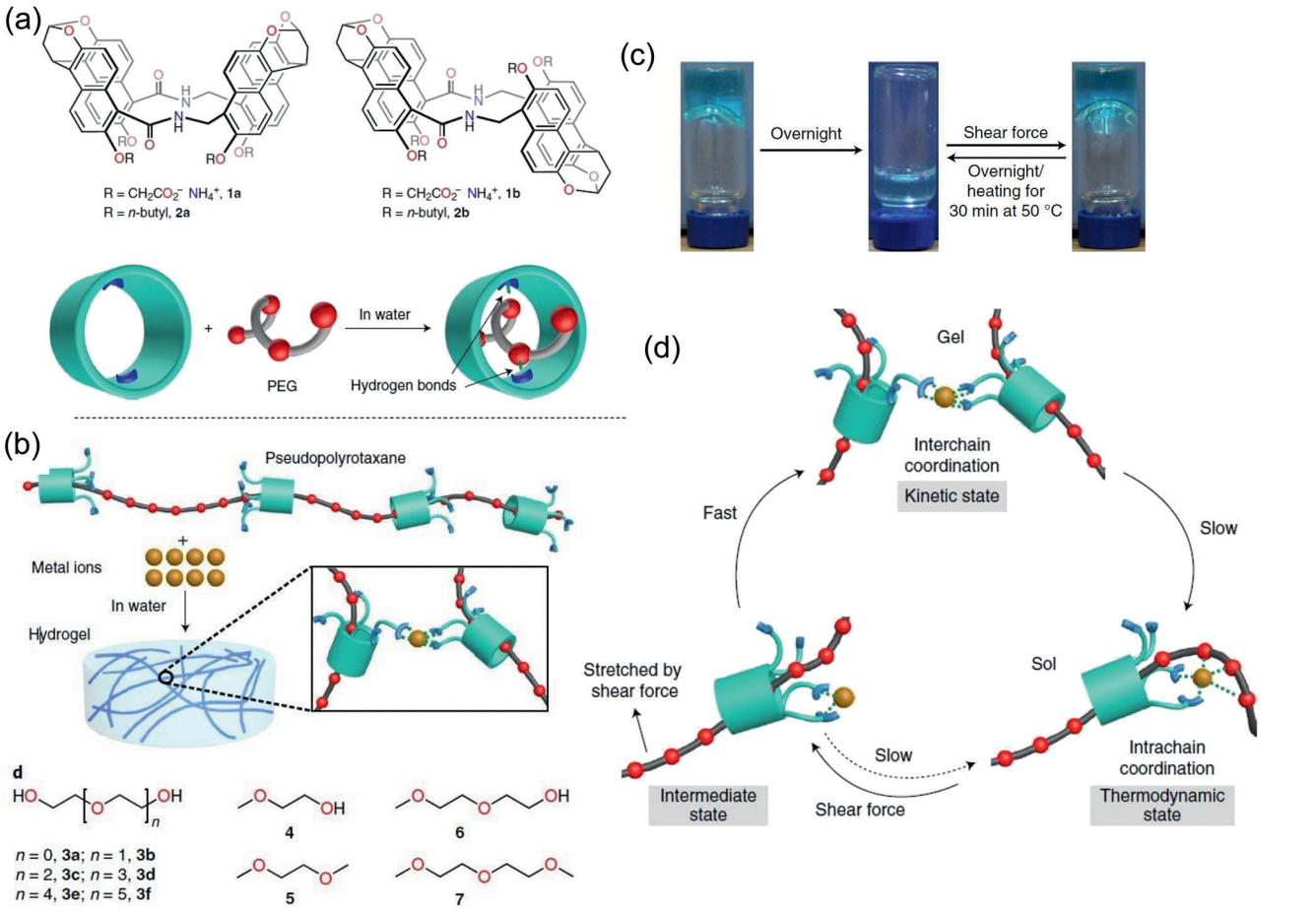

Fig. 8. The self-assembly and disassembly of shear-induced gelation. (a) Chemical structures of molecular tubes. The possible intermolecular-hydrogen bonding between molecular tubes (with nitrogen atoms marked in blue) and PEG chains (with oxygen atoms marked in red). (b) The Cu^{2+}-based hydrogel reverts to a sol state overnight but converts to gel under shear force. (c) The mechanism of shear-induced gelation and thermal relaxation. (d) Proposed mechanism for shear-induced gelation and thermal relaxation [25].

mation of a sol state (Fig. 8(b)). Fuel shaking transforms the sol into a highly stretchable gel through the interchain coordination of Cu^{2+} and carboxylates on different pseudopolyrotaxane strands. Subsequently, the interchain coordination complexes gradually return to intrachain complexes after thermal relaxation, exhibiting a sol–gel–sol transition (Figs. 8(c)(d)). Notably, the shear force may not destroy the interchain coordination because the PEG polymer can slide freely through the tube molecules. Thus, shaking destroys intrachain coordination and simultaneously forms interchain coordination. This shear-induced transient gel combines shear-thickening properties and high stretchability, which are important for constructing energy-dissipative mechano-responsive materials [25]. In addition, utilizing seeded self-assembly of multicomponent gelators is another efficient method for constructing metastable supramolecular gels [99].

Transient supramolecular gels are formed via noncovalent self-assembly (physical cross-linking). However, temporal polymer gels are formed via polymerization accompanied by covalent crosslinking or noncovalent self-assembly (chemical or physical crosslinking), and polymerization is the main reason for temporal gelation. Therefore, transient polymer gels generally possess stronger G', tensile strength, and mechanical strength than those of temporal supramolecular gels based on noncovalent self-assembly. Polymerization is the first step in the formation of transient polymer gels, and dynamic chemical or physical crosslinking is the second step in the formation of temporal gels. For example, reversible addition-fragmentation chain transfer polymerization has been used to prepare an acrylamide oligomer with a pendant carboxylic acid. Fuel EDC converts carboxylic acids into transient anhydrides, resulting in the covalent crosslinking of polymer gels [28]. The base-catalyzed thiol-Michael addition reaction of the monomers ethoxylates trimethylolpropane tri(3-mercapto-propionate) and poly(ethylene glycol) diacrylate. Using urease-catalyzed urea and base-catalyzed ester hydrolysis provides temporal control over sol-gel-sol switching for this thiol-acrylate polymerization [91]. In contrast to covalent crosslinking, DNA is an ingenious noncovalent crosslinker for hydrogelation owing to its base complementary pairing. DNA-containing polyacrylamide is produced by free-radical copolymerization and forms gels by adding a complementary i-motif DNA. The antagonistic enzymes, urease, and esterase, regulate the programmed gel-sol-gel transition [31].

3.2. *Transient micelles and vesicles*

Self-assembly has provided researchers with the necessary tools to construct micelles and vesicular bilayer structures, which are promising for various applications in micro-reactors, biosensors, and biomimetic strategies [100]. Typical micelles and vesicles consist of amphiphiles, including high molecular weight polymers, [101] and low molecular weight surfactants [102–105] and phospholipids. Recently, nanoparticles [106–107], quantum dot [78,108], nanoclusters [109], and polyoxometalates [110–111] have been shown to self-assemble into micelles and bilayer vesicular structures through ligand-ligand interactions. However, the current artificial micelles and vesicles often lack the complexities and functionalities exhibited by lifelike materials. The out-of-equilibrium process is ubiquitous and often characterized by adaptive and transient behaviors. Dissipative self-assemblies are essential

for creating artificial architectures, biomimetic systems, and complex microreactors. Constructing transient micelles or vesicles with time-programmed controllability of their morphology, size, and permeability poses a significant challenge and remains a crucial step in expanding their application fields. Increasing research has focused on manufacturing micelles and vesicles that are responsive to stimuli such as light, temperature, pH, and CO_2. Utilizing dissipative and self-assembled elements as energy bridges transforms traditional micelles and vesicles into dissipative micelles.

The chemical and physical properties of transient micelles or vesicles depend highly on the amphiphile structure. Based on their molecular weights, amphiphiles in transient micelles and vesicles can be divided into polymers and surfactants. Polymers are copolymers comprising hydrophilic and hydrophobic blocks. The properties of each block, as well as the overall polymer chains, including the hydrophilic/hydrophobic volume ratio, molecular weight, and dispersity, have a considerable influence on transient micelles and vesicles. pH-responsive polymers can be obtained using pH-sensitive blocks in the copolymer chains. For instance, DEAEMA is water-soluble but becomes insoluble at pH > 7.0, and its protonation regulates the hydrophilic/hydrophobic ratio of blocks in copolymers, changing the morphology, size, and permeability of micelles and vesicles. An amphiphilic copolymer consisting of PEG-PDEAEMA-poly[2--hydroxy-4-(methacryloyloxy) benzophenone] was self-assembled into pH-responsive vesicles. Acid/urea-urease triggers regulated programmable pH transitions, changing the permeability and size of transient vesicles [11]. In addition, through designing block structures and molecular weights in copolymers, transiently spherical micelles, and vesicles are derived from poly(ethylene oxide)$_{114}$-*b*-DEAEMA$_{99}$ (M_n = 26000 g/mol) and poly(oligo-ethylene oxide methacrylate)$_9$-*b*-DEAEMA$_{22}$ (M_n = 46000 g/mol), respectively. Alkaline buffer/ester hydrolysis sets a self-regulated assembly/disassembly of transient micelles and vesicles [69]. Turning the hydrophilic-hydrophobic balance into a controllable time domain is the primary driver behind the dissipative self-assembly of micelles and vesicles. To achieve time-programmability, transient micelles can be constructed by reversibly regulating the hydrophilic/hydrophobic switching of the PEG block with coordinated I_2, in which I_2 is an intermediate product from the IO_3^--SO_3^{2-}-thiourea. The hydrophilic copolymer methoxy-PEG$_m$-*b*-poly(L-lysine hydrochloride)$_n$ is converted into a supra-amphiphile by coupling PEG and I_2 [38,43]. Although these transient micelles and vesicles have been applied in cyclic dye removal [21], programmed cargo release [15,112], and nanoreactors [11], the exploitation of novel functions remains a significant problem for micelles and vesicles in dissipative systems.

In addition to using a single polymer to fabricate transient micelles and vesicles, electrostatic self-assembly of oppositely charged polymers is another brilliant method for forming micelles and vesicles with more functional groups and structural properties. Strong polyelectrolyte blocks, including cationic poly[(dimethyl-amino)ethyl methacrylate] [113], cationic poly(N-methyl-2-vinylpyridinium) [22], negatively charged poly(vinyl sulfonate) block [113], and anionic poly[9,9-bis(3-propanoate)fluoren-2,7-yl] polyelectrolytes [22], are alternative building blocks for the formation of complex polymeric micelles and vesicles. These polyelectrolytes can increase the responsiveness and function of the micelles in transient assemblies. Introducing this responsive co-assembly into dissipative systems and utilizing it for the controlled accumulation and release of energy is a promising research subject. As shown in Fig. 9(a), cationic copolymer poly(N-methyl-2-vinylpyridinium)$_{29}$-*b*-poly(ethylene oxide)$_{204}$ (DBP) and anionic poly[9,9-bis(3-propanoate)fluoren-2,7-yl] poly-electrolyte (CPF) constitute pH-responsive polymeric micelles (formation at pH ≈ 7). Above pH = 7, the deprotonation of the carboxylate side chain is sufficient to provide solubility, resulting in a loss of coassembly capability with the cationic polyelectrolyte. Thus, the programmable assembly-disassembly-assembly process can be modulated using a urease-catalyzed feedback system. π-conjugated polyfluorene and cargo doxorubicin HCl can be used for polymeric micelle assembly/disassembly accompanied by binding-induced fluorescence quenching, exhibiting a comprehensive output in cargo release and fluorescence sensing (Fig. 9(b)) [22]. Another interpolyelectrolyte complex micelle was manufactured using oppositely charged PEO-*b*-PDAEMA and poly(N-isopropylacrylamide)-*b*-poly(vinyl sulfonate). Poly(N-isopropylacrylamide) (PNIPAM) has a lower critical solution temperature (LCST) of approximately 32 ˚C, enabling a hydrophilic-hydrophobic balance of micellar structures by controlling the temperature. Based on the thermoresponsiveness of PNIPAM, these interpolyelectrolyte micelles are spherical at T < LCST and have higher-order structures at T > LCST in the presence of 0.3 M NaCl. Reducing the NaCl content or adding salt results in micellar structures with cycles of nonequilibrium/equilibrium transitions [113].

Surfactants are amphiphiles that participate in a micelle or vesicle fabrication. In addition to fabricating micelles or vesicles using cationic-anionic polymers, catanionic surfactants are potential molecules for engineering micelles or vesicles. A transient catanionic vesicle is formed via a cationic ammonium surfactant with an ester linker (O-lauroylethanolamine) (OLEA) and the negatively charged surfactant sodium dodecyl benzene sulfonate (SDBS), in which O-lauroylethanolamine undergoes O-acyl to N-acyl migration, shifts the pK_a by 2.0–2.5. Control experiments with lauryloxyethanamine (LEA) and lauryl amine (LA) do not yield acyl chain migration because they are devoid of carbonyl groups (Fig. 10(a)) [112]. The aggregates in the solution can be predicted by the critical packing parameter P, which is defined as $P = v_0/al_0$, where v_0 and l_0 are the volume and length of the hydrophobic tail, respectively, and a refers to the hydrophobic-hydrophilic interfacial area. According to the packing parameter theory, micelles and vesicles generally have different P values: spherical micelles for $P < 1/3$, ellipsoid and cylinder micelles for $1/3 < P < 1/2$, and vesicles for $1/2 < P < 1$ (strictly, $1/2 < P < 1$ for bilayers) [114]. Changing the v_0 for surfactants might be an effective method for controlling the assembly/disassembly transitions of micelles and vesicles. Introducing dynamic covalent bonds into surfactants provides a controllable way to regulate v_0, further determining the aggregate morphology and assembly/disassembly processes. Versatile dynamic association/dissociation of cross-links responsive to external stimuli can be realized by dynamic phenylboronate esters, disulfide bonds, imine bonds, acylhydrazone bonds, reversible radical reactions, and Diels-Alder reactions [115], providing a perspective on the construction of transient micelles and vesicles. Amine-containing lysosphingomyelin reacts chemoselectively with long-chain aldehydes to form imines with double alkyl chains, resulting in increased v_0 (Fig. 10(b)). The reversibility of imines is utilized to fabricate vesicles that are responsive to external stimuli. This biomimetic liposome plays an important role in the formation of dynamic phospholipid vesicles and the development of vesicle carriers [15].

Supramolecular polymerization is an alternative approach for fabricating transient micelles or vesicles. One of the supramolecular polymers is formed by a high degree of polymerization of charge-transfer noncovalent amphiphile with a high association constant as the donor-acceptor monomers. Donors are generally chromophoric molecules, including coronene slats [116–117], pyranine [90], and core-substituted naphthalene diimide [83], whereas the acceptors include amphiphilic methyl viologen [90,116–117]. The chromophoric molecules integrate with the redox-reduction reaction as well as charge-transfer interactions, forming transient reconfigurations related to micelles or vesicles. For example, ethoxy core-substituted naphthalene diimide derivatives bis-functionalized with β-alanine methyl ester groups at the imide positions (cNDI) self-assemble into vesicles. The reduction of cNDI into its radical anion ($cNDI^{\bullet -}$) and dianion ($cNDI^{2-}$) with the strong reducing agent sodium dithionite SDT ($Na_2S_2O_4 \rightarrow S_2O_3^{2-} + HSO_4^-$) lead to a vesicle-sheet transition. A redox-mediated transient reconfiguration of vesicles into sheets was constructed by exploiting the fast reduction of SDT and slower oxidation by oxygen [83].

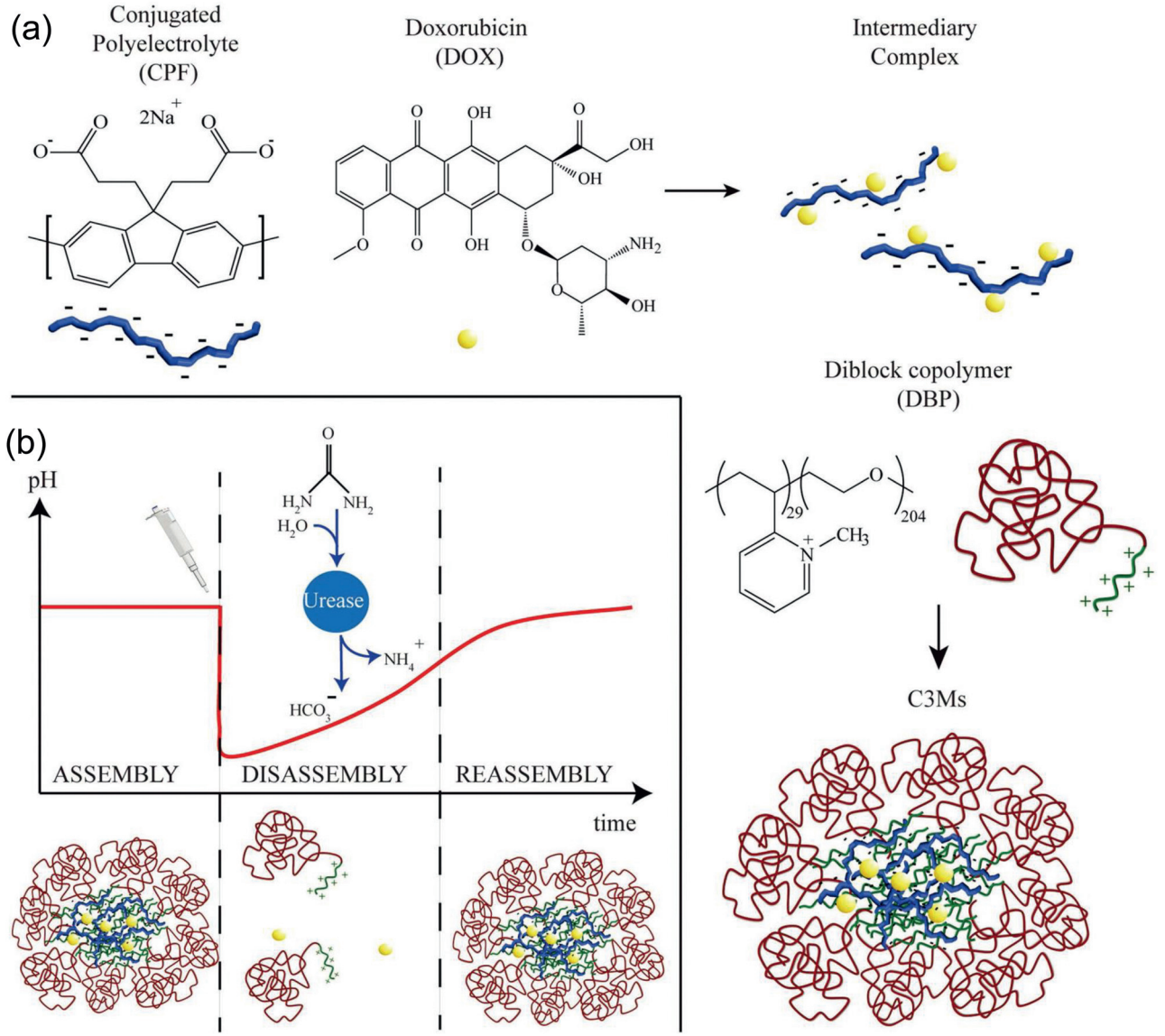

Fig. 9. (a) Schematic of the pH-responsive polymeric micelles formed using carboxylated polyfluorene, cationic doxorubicin, and neutral-cationic diblock copolymers. (b) Programmable regulation of the assembly and disassembly of polymer micelles via a citrate buffer as an acidic activator (fast pH decrease) and urea/urease as a basic activator (slow pH increase) [22].

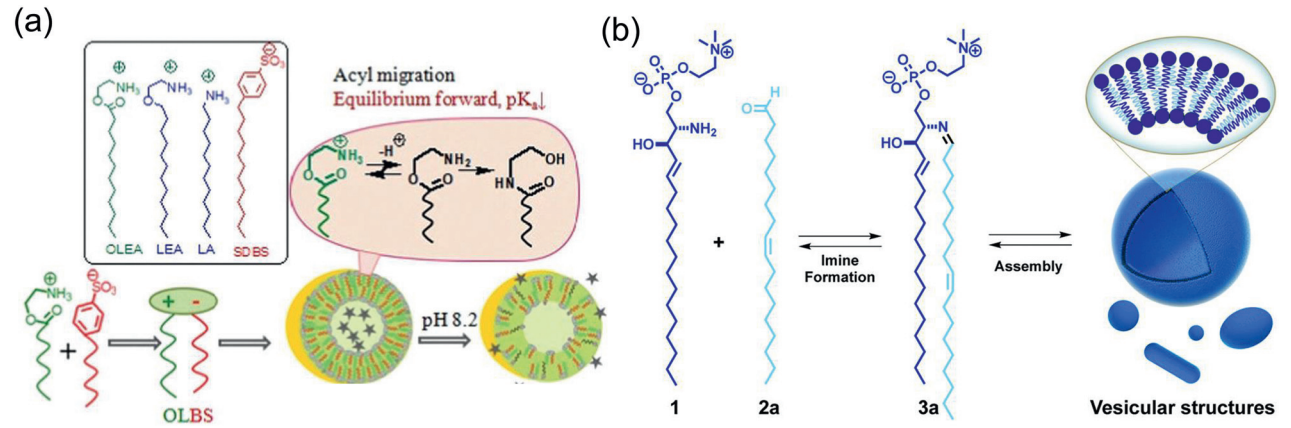

Fig. 10. (a) The structures of O-lauroylethanolamine (OLEA), lauryloxyethanamine (LEA), lauryl amine (LA), and sodium dodecyl benzene sulfonate (SDBS), as well as the catanionic vesicle formed by SDBS and OLEA. The vesicle fabrication and rupture at pH = 8.2 perturb the pK_a via acyl chain migration [112]. (b) Biomimetic assembly of the vesicular structure by a reversible imine linkage represented by amine-containing lysosphingomyelin and aliphatic aldehydes [15].

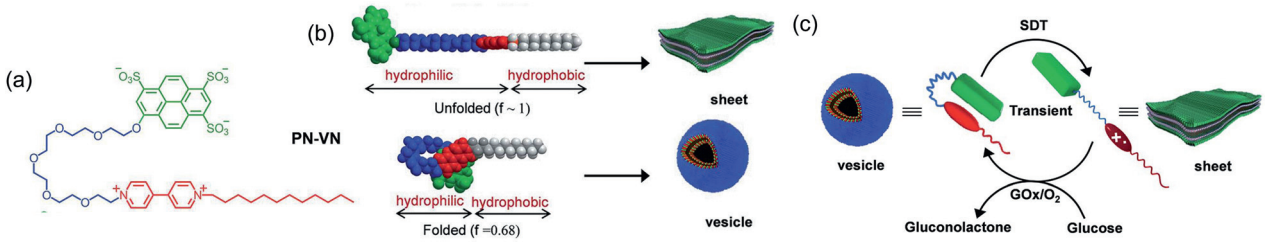

Fig. 11. (a) Molecular structure of the pyranine-viologen (PN-VN) amphiphilic foldamer. (b) Molecular models of the unfolded and folded conformations of PN-VN with different packing factors (*f*), forming a sheet and vesicle, respectively. (c) Schematic representation for the transient conformational response of the foldamer driven by a chemical fuel and mediated via an enzymatic pathway [90].

As shown in Fig. 11(a), an amphiphilic foldamer contains an electron donor, pyranine (PN, green), connected to hydrophilic hexamethylene glycol (blue), and an electron acceptor, viologen (VN, red). The hydrophilic-hydrophobic switching of this foldamer is affected by conformational control, resulting in unique assemblies: unfolded PN-VN with packing factor (f) ~ 1 forms a sheet; conversely, folded PN-VN with f= 0.68 forms a vesicle through charge-transfer interactions (Fig. 11(b)). Adding fuel sodium dithionite (SDT) into the vesicle of the folded PN-VN reduces the viologen dication (VN^{2+}) to the radical cation ($VN^{\bullet+}$), decreasing the acceptor strength of VN. Owing to the weakened charge transfer interaction, PN-$VN^{\bullet+}$ unfolds, thus forming a sheet. A programmed sheet-vesicle transition was realized by the slow oxidation of glucose oxidase (GO_x) and fast reduction of SDT (Fig. 11(c)). Cylindrical micellar aggregates can also be formed from a charge-transfer-based supramolecular polymer of potassium coronene slat-dodecyl methyl viologen. The disassembly of the micellar aggregates is mediated by the rapid reduction of SDT. A controlled assembly-disassembly mechanism of micelles can be achieved by coupling the slow oxidation process catalyzed by glucose oxidase [116]. Notably, these cylindrical micellar aggregates can further self-assemble into multidimensional and multilayered gels, presenting a higher viscoelasticity and yield stress. Redox fuel can drive a programmable sol-gel-sol switching of coronene slat-dodecyl methyl viologen [116]. Hence, there are no explicit boundaries for micelles, vesicles, sheets, liquid crystals, nanofibers, and gels.

3.3. Transient assemblies of nanoparticles

Ligand-protected inorganic NPs are particularly attractive building blocks for self-assembly. NPs of diverse sizes, shapes, ligands, charges, and pK_a values exhibit various properties and functions. The self-assembly (or aggregation) of nanoparticles into nanoarchitectures is a promising approach for constructing multifunctional smart materials [118]. Importing responsiveness into nanoarchitectures produces emerging collective properties and functions [106]. The most studied nanoparticles in self-assembly are Au NPs (increased localized surface plasmon resonance [119], photo-thermal conversion properties [120]), Fe_3O_4 NPs, and nanoclusters [121–122] (aggregation-induced emission). Owing to remarkable advances in dissipative self-assembly, fuel-driven temporal nanoassemblies are expected to facilitate innovative applications in nanotechnology. Ligand molecules on the nanoparticles induce self-assembly/disassembly behavior. pK_a, hydrophilicity/hydrophobicity, and functional groups are crucial for aggregation transition. In particular, nanoparticles containing −COOH groups such as Au NPs [73] and SiNCs [17], form transient assemblies by introducing dissipative modes including EDC/NHS ester hydrolysis [17], methylene glycol-sulfite/lactone hydrolysis [73], and BrO_3^--SO_3^{2-}/HSO_3^- pH oscillation [123]. For example, in the presence of a BrO_3^--SO_3^{2-}/HSO_3^- pH oscillator (oscillation range from pH = 4 to 7 and cycle period of 40 min), Au NPs protected with 12-meraptododecanoic acid (pK_a = 5) have a rapid assembly process with a gradual red-shift in the localized surface plasmon resonance and a slow disassembling process with blue-shift [123]. The controllable switching of Au NPs induced by dynamic changes in the interparticle distance has great potential for applications in bioanalytical nanosystems, nanosensors, switchable catalysts, and bright coloring switchers. In addition to a single mode, the dispersion/aggregation of pH-responsive Au NPs can be controlled by double modes of transient pH regulation in the time domain. This is achieved by combining the methylene glycol-sulfite clock reaction coupled to lactone hydrolysis. Reaction of methylene glycol-sulfite generates a fast pH spike owing to its autocatalytic nature, while the hydrolysis of D(+) gluconic acid δ-lactone or δ-valerolactone gradually decreases the pH back to the acidic range [73].

In the process of dissipative self-assembly, NPs serve as fuel-activated building blocks and promote their assembly into aggregates. The activated state is metastable and decays to the original precursor, thus reversing the assembly. Under certain conditions, the NPs can assemble permanently in a kinetically trapped state, resulting in aggregation rather than returning to the original nanoparticles. For example, the transient assembly of Au-COOH NPs can only be realized at an EDC of ~ 0.5 equivalents (eq.) The carboxylic acid groups on the Au NPs form metastable NHS-esters after EDC activation, serving as building blocks for aggregate formation, whereas NHS-ester hydrolysis converts to the original dispersive nanoparticle. However, the Au NPs almost do not assemble when the EDC is < 0.5 eq. Conversely, they are assembled permanently in kinetically trapped aggregates (resulting in an insoluble precipitate) when the EDC exceeds 0.8 eq. (Fig. 12(a)). The kinetically trapped Au NPs exclude all the water from the assemblies, inhibiting NHS-ester hydrolysis and further influencing the disassembly process. Alternatively, a high fuel concentration facilitates the formation of Au assemblies via stronger noncovalent interactions, making the energy barrier for disassembly too high to overcome. To address this issue, one strategy involves adding 0.9 eq. of EDC in three separate batches of 0.3 eq. (or two batches of 0.45 eq.) during the preparation of transient Au aggregations. This multi-step addition ensures successful disassembly, as a one-time addition of 0.90 eq. of EDC would result in the NPs remaining in a kinetically trapped state (Fig. 12(b)) [36]. Investigating the pathway complexity is expected to greatly improve the possibility of developing temporal nanoparticles. In addition to nanoparticles with −COOH ligands, surfactants, amino acids, proteins, and organic molecules are well-researched ligand molecules for nanoparticles. Further exploration of the influence of ligands is crucial in understanding the energy-dissipative mode. This investigation will pave the way for novel pathways in achieving transient aggregation of NPs, offering conceptually distinct approaches. For instance, based on a seed-mediated approach, 10 nm Au NPs were obtained by reducing $HAuCl_4$ with an excess of hydrazine in the presence of 6 nm Au NPs seeds ($4Au^{III} + 3N_2H_4 \rightarrow 4Au^0 + 3N_2 + 12H^+$). This reaction was performed using didodecyldimethylammonium bromide and dodecylamine; dodecylamine stabilized the Au NPs with a monolayer coating. The reductant hydrazine (fuel) induced the growth of Au NPs, accompanied by a high local concentration of dodecylamine, forming a bilayer on the Au nanoparticles, leading to transient nanoparticle aggregates through solvophobic interactions. Subsequently, superabundant dodecylamine was released into the water with disassembly of Au NPs (Fig. 12(c))

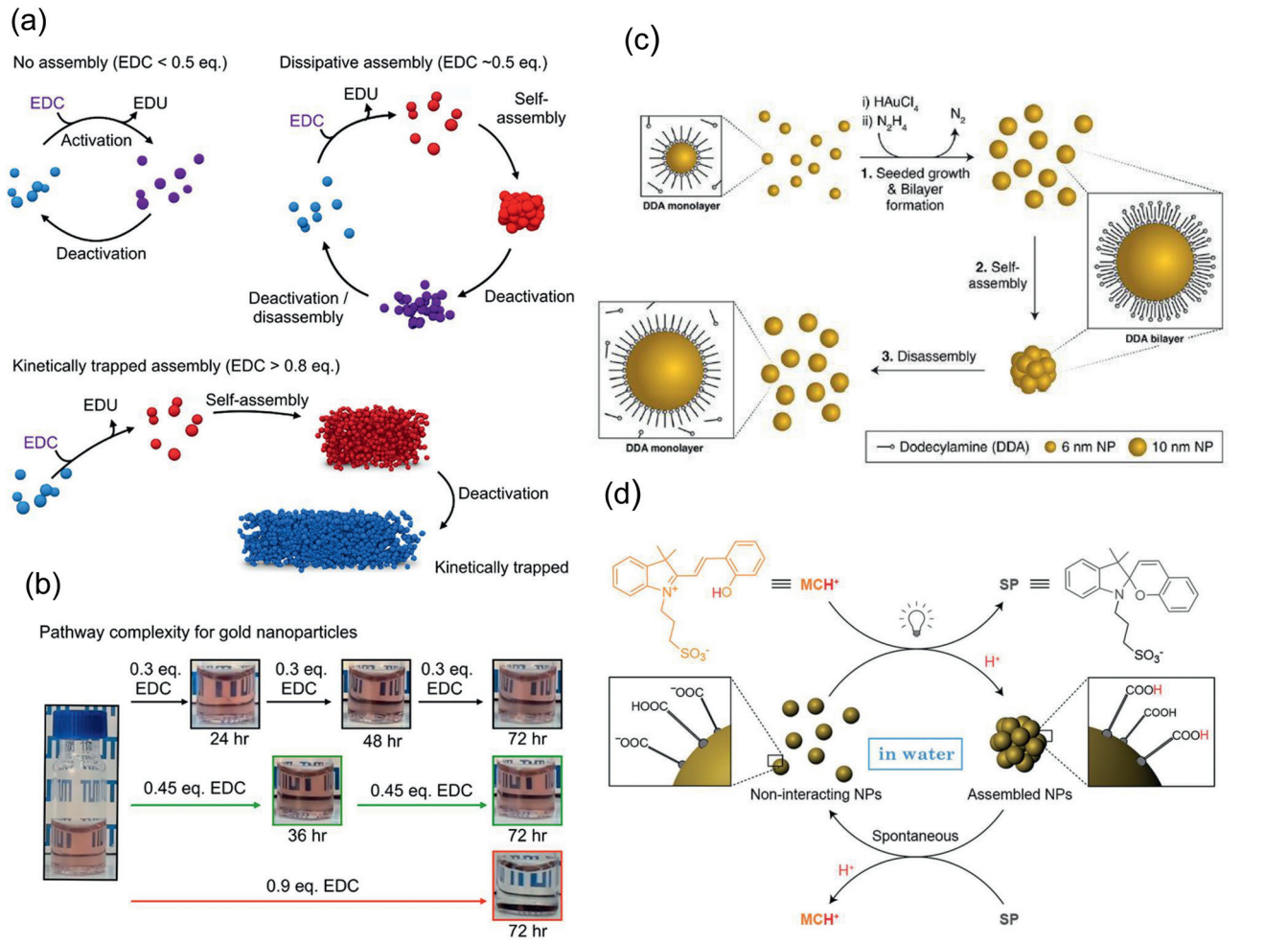

Fig. 12. (a) The self-assembly pathway depends on the fuel: no assembly, dissipative assembly, and kinetically trapped assembly driven by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). (b) Pathway complexity of Au NPs regulated by EDC [36]. (c) The proposed process of forming out-of-equilibrium Au NPs aggregates fueled by N_2H_2 [18]. (d) Light-induced out-of-equilibrium aggregation of carboxylic acid decorated Au NPs in the presence of photoacid MCH^+ [19].

[18]. This protocol can potentially expand the possibilities of obtaining diverse temporal assemblies, encompassing materials such as Fe_3O_4, Cu, Ag, and SiO_2.

Another attractive method to fabricate transient nanoparticle assemblies is to exploit light as fuel [124]; however, the light-controlled self-assembly requires the anchoring of light-responsive ligands, including azobenzene (hydrophobic trans-azobenzene to more polar cis-azobenzene upon exposure to UV light) [125], and spiropyran (hydrophobic closed-ring spiropyran to hydrophilic open-ring merocyanine upon irradiation with UV light) [126] on nanoparticles. For instance, NPs decorated with *trans*-azobenzene are soluble in nonpolar solvents. Upon exposure to UV light, azobenzene isomerizes into a more polar cis-isomer, resulting in attractive interparticle interactions. NP aggregates are metastable and can disintegrate in the dark [125]. However, complex synthesis poses a bottleneck for obtaining various transient assemblies of nanoparticles. Recently, a novel methodology using photoacid molecules as a light source has been developed [19,50]; which does not require nanoparticles to function with photoswitchable molecules. A protonated merocyanine exposed to visible light undergoes a ring-closing reaction with spiropyran and transiently releases H ions [127]. Under the influence of light-driven protonation, 6-mercaptohexanoic acid-functionalized nanoparticles can undergo self-assembly into metastable aggregates by protonating the COO^- groups in an aqueous environment. Upon turning off the light, the closed-ring isomer of the switch functions as a base, capturing H ions and initiating the disassembly process (Fig. 12(d)) [19]. In contrast to the photoacid molecules, malachite green as a photo-based molecule produces OH^- under UV light irradiation [128]. The light-responsive behavior of nanoparticle assemblies enables them to be triggered by photo acids or bases. This is advantageous because these molecules can regulate solution pH upon light exposure without producing byproducts such as water or salt, typically associated with traditional chemical stimuli of acids or bases. The presence of byproducts in dissipative self-assembly processes is a common challenge, as it decreases the cycle index.

4. Application of dissipative self-assemblies

Dissipative self-assembly is an energy storage and consumption process that exhibits a dynamic self-assembly behavior similar to that of the energy metabolism of living organisms. Thus, the use of dissipative self-assembly to create functional materials can mimic and even surpass living organisms. Fully understanding and utilizing dissipative self-assembly properties, functionalized groups in precursors, and energy-dissipative mechanisms are useful for creating versatile, functional materials. The reported application of dissipative self-assemblies follows the rule of “Tao follows nature”, meaning the application research should learn from nature. Dissipative self-assembly enables properties such as self-healing, self-replication behavior (Fig. 13), adaptivity, out-of-equilibrium, dynamic features, and energy dependence in the construction of biomimetic materials, photonic devices, controllable molec-

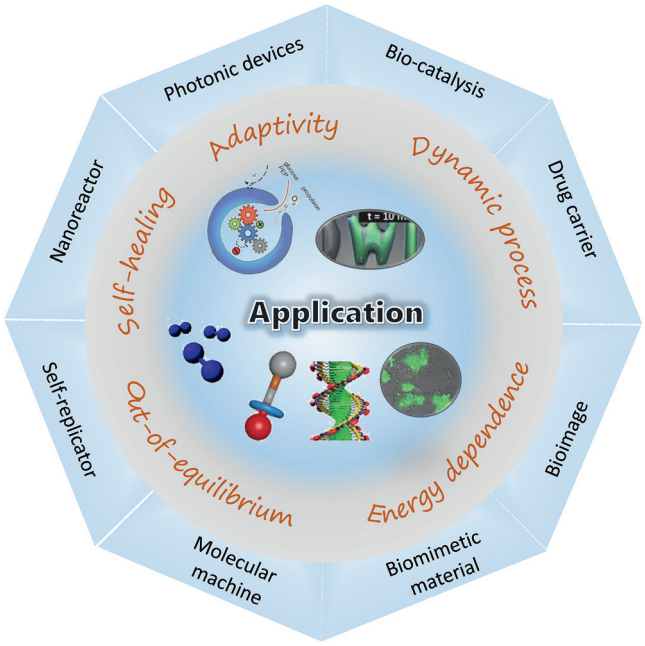

Fig. 13. Schematic diagram of the properties and applications of dissipative self-assemblies.

ular machines, and nanoreactors; furthermore, it facilitates applications in biological imaging, catalysis, and drug delivery.

4.1. Biomimetic materials

Functional self-assemblies in living organisms are not in thermodynamic equilibrium and are accompanied by energy depletion. Dissipative self-assemblies perfectly accord with the principles of nature, making them effective methods for biomimicry studies. Taking inspiration from natural systems, such as cytoskeleton proteins and transmembrane proteins, the ATP-fueled bioinspired approach is an effective way to achieve supramolecular polymers with transient helical conformational switching [58] or multiple transient states [33]. To obtain biomimetic phospholipid membranes, a dynamic covalent bond is introduced into dissipative assemblies owing to dynamic reversibility and then successfully applied in the biomimetic generation and remodeling of phospholipid membranes. Phospholipid vesicles are generated by dynamic imines constructed from lysosphingomyelin and different aldehydes, which can respond to temperature changes by shifting their composition. This result is analogous to that of cells that change their membrane composition in response to an external temperature. Moreover, the addition of a salicylaldehyde derivative to the iminophospholipid of lysosphingomyelin and (Z)−9-octadecenal induces a remodeling phenomenon in the phospholipid membrane, resembling the Land's cycle observed in cellular membranes [15]. Taking inspiration from the rhythmic contraction and expansion observed in heartbeats, biomimetic materials with similar behavior have been developed. Examples include self-regulated microgels mediated by urea/urease [34], "breathing" polymersomes controlled by urea/urease [11], and pulsating polymer micelles regulated by ATP/ATPase [12,53], demonstrating potential applications in creating dynamic and responsive materials. The rhythmic behavior observed in dissipative self-assembly systems enables the control of size and membrane permeability. The pulsation periodicity and size change can be precisely tuned by adjusting the concentration of the fuel molecule. For example, in polymer micelles mediated by ATP as the fuel, increasing the ATP concentration from 50 to 100 to 200 μM leads to a decrease in pulsating periodicity from 148 to 95 to 60 min, while the sizes of the micelles increase from 33 to 54 to 68 nm [53]. The high maneuverability and programmability for dissipative self-assembly provide convenience for creating biomimetic materials. Notably, more complex and functional dissipative assemblies should be created to imitate living tissue. Understanding the basic principles of living systems is the first step toward creating synthetic life-like materials. The investigation of dissipative self-assemblies offers a valuable approach to replicating biological systems in a laboratory setting and serves as a physical model for studying fundamental properties that are typically observed within living systems.

4.2. Materials nanoreactors and cargo carriers

To transport the substrate across the nanoreactor membrane barrier or release the cargo in a controlled manner, diverse stimuli-responsive elements have been introduced into designed assemblies. Dissipative self-assembly can bring more perspective to these nanoreactors or cargo carriers by controlling their size, membrane permeability, conformation, and assembly/disassembly behavior. Recently, versatile assemblies with cargo- or enzyme-packaging capabilities have been created from transient self-assemblies, such as stomatocyte-like assemblies [10], "breathing" polymersomes [11], pulsating polymer vesicles [54], DNA receptors [30,79], polymeric micelles [12], and catanionic vesicles [112]. Fuel-mediated nanoreactors demonstrate remarkable self-regulation and time-programming capabilities, enabling controlled access or separation of substrates and catalysts. This capability allows for accelerated or reduced catalytic activity within the nanoreactors. For example, a self-adaptive nanoreactor incorporates enzymes, such as horseradish peroxidase (HRP). HRP catalyzes the oxidation of 3,3′-dimethoxybenzidine (DMB), and the product can be monitored by a gradual increase in absorbance at 492 nm. Stomatocyte-like assemblies are decorated with polylysine (Fig. 14(a)). The interaction of fuel ATP and polylysine realizes the "nanoreactor OFF" state and stops catalyzing DMB. Conversely, apyrase effectively promotes the "nanoreactor ON" state (Figs. 14(b)(c)). Furthermore, the nanoreactor can function as a nanomotor by encapsulating Pt nanoparticles. The Pt nanoparticles decompose H_2O_2 into O_2, driving the movement of the nanomotor. ATP and apyrase control the switching of the OFF/ON mode (Figs. 14(d)(e)) [10]. The transient "ON" or "OFF" state of HRP enzymatic catalysis can also be realized in a "breathing" polymersome nanoreactor containing a pH-responsive DEAEMA block; a fast pH decrease induced by HCl causes swelling and permeable change of the nanoreactor, facilitating a temporal "ON" controllability. Subsequently, urease catalysis induces a slow pH increase, promoting an "OFF" state with shrinking behavior [11].

For cargo carriers, the noncovalent interaction strength between carriers and cargo can be strengthened or weakened by performing energy input/energy depletion to realize high loading and controllable release. Dissipative self-assembly improves cargo release efficiency, carrier recycling, and periodic cargo release. Time-programmable assembly or disassembly of vesicles is a promising idea. For a catanionic vesicle with OLEA and SDBS, acyl chain migration perturbs the acid-base equilibrium within a proper range. The formation and rupture of vesicles have a critical pH of 8.2, and the addition of external OLEA can further drag the dynamic equilibrium toward disruption (or disassembly). This promotes cargo release through two mechanisms: (1) pH-induced release triggered by alkaline conditions and (2) release facilitated by the addition of OLEA [112]. Similarly, short-chain salicylaldehyde displaces the long aliphatic tail in the iminophospholipid of vesicles, resulting in disassembly and the release of cargo encapsulated in carriers [15]. The expansion-contraction of micelles or vesicles, as well as their structure switching, are alternative approaches to encapsulate cargo and release profiles. Regular pulsation enables controlled and periodic cargo release in ATP-mediated micelles or vesicles, leading to prolonged circulation and enhanced functionality of the carriers. After interacting with ATP, the highly expanded surface of the micelles enhances membrane permeability, leading to an abrupt cargo release from 6.5% to 95%. ATP endows the carriers with recycling [53]. For other polymeric micelles

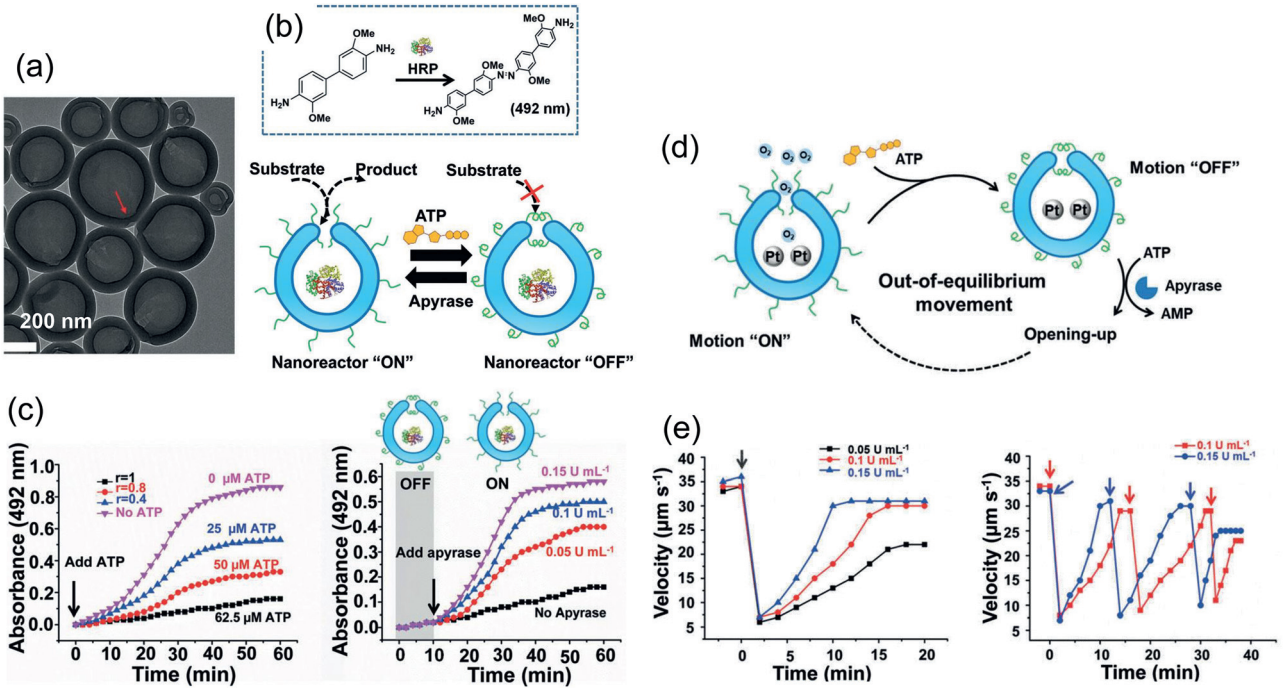

Fig. 14. (a) TEM image of polylysine-modified bowl-shaped polymer vesicles. (b) The polymer vesicles serve as nanoreactors to encapsulate HRP, where ATP and apyrase regulate the open/closed state of the nanoreactor. (c) The UV absorbance at 492 nm of 3,3′-dimethoxybenzidine (DMB) was utilized to evaluate the closed state by ATP and the open state via apyrase. (d) ATP-regulated Pt nanoparticle-loaded nanomotors, in which apyrase controls the open state. (e) Velocity of the Pt nanoparticle-loaded nanomotors with ATP and different concentrations of apyrase [10].

with ATP-receptor, interaction with fuel ATP induces a structural transition from micelles to smaller structures with loose cores. This process directly causes an enhanced cargo release from 8% (without ATP) to 20% (4 mM ATP) to 34.1% (10 mM ATP) after 24 h incubation [12]. DNA-based nanoassemblies provide precise control of the cargo loading and release through cyclic, switchable, and allosteric conformational change or highly efficient and specific catalysis. DNA-based receptors can load specific cargo DNA and form a triplex structure. Fuel causes a transient release of cargo DNA; however, the RNA endonuclease restores the capacity of the DNA receptor to load cargo [79]. The allosteric DNA serve as nanodevices, allowing for flexible loading of ATP and cocaine upon the addition of a chemical trigger under dissipative self-assembly [30].

4.3. Optical materials

Fluorescence techniques have attracted increasing attention because of their low cost, high sensitivity, real-time, and noninvasive monitoring capabilities. The self-assembly process generally induces changes in the molecular configuration of building blocks, accompanied by aggregation-induced emission (AIE) or aggregation-caused quenching (ACQ). Hence, fluorescent materials have the advantages of direct visualization and real-time monitoring of dissipative self-assembly processes. For example, fuel ATP induces gradual fluorescence quenching owing to the formation of a double helix with a porphyrin derivative. The ATP enzyme causes fluorescence recovery and distinct solution color change [61]. The fluorescent approach can also be utilized for π-conjugated molecules such as dipicolylethylenediamine derivatives [35], polyfluorene-based conjugated polyelectrolytes [22], cationic AIEgens [40], as well as silicon nanocrystals [17]. The autonomously dynamic and self-regulating behavior in dissipative self-assemblies enables the creation of remotely controlled signal propagation and sensing by forming transient photonic materials. Acid/urease catalysis control the expansion-collapse switching of photonic materials based on poly(2-vinyl pyridine) copolymers, resulting in a macroscopic reflective color. This out-of-equilibrium photonic device can be useful for sensing, computation, and communication [9]. Transient assemblies with tunable fluorescence offer promising opportunities for biomedical applications, extending beyond material science. For example, single SiNCs are readily taken up by cells, showing notable fluorescence within COS-7 fibroblast-like cells (Fig. 15(b)). The process of dissipative self-assembly poses a challenge to delay the passive uptake of temporal SiNCs by cells; the activation of EDC and form transient NHS ester leads to the formation of temporal Si clusters, hindering their cellular entry even after 4.5 h of incubation. After a slow NHS-ester hydrolysis process, the Si clusters gradually disassemble into dispersed SiNCs. These smaller SiNCs are then able to be taken up by passive diffusion within 9 h, as shown in Figs. 15(a)(c). The addition of EDC can drastically increase the percentage of the take-up cells (Fig. 15(e)), which is confirmed by the higher mean fluorescence intensity of the cell nucleus compared to that of the cell uptake in the absence of EDC (Fig. 15(d)) [17].

The remarkable color change observed in the assembled Au NPs is attributed to the plasmonic coupling effect [106], which makes them highly promising for applications in dissipative self-assemblies with programmable optical behavior. The design and realization of dynamic assemblies of Au NPs are important for storing information, sensing, and spatiotemporal catalysis. Dissipative self-assembly sets a time-programming aggregation and disaggregation for Au, where aggregation leads to a redshift in surface plasma resonance, and redispersion results in a blueshift in surface plasma resonance. The Au NPs undergo time programming in the blue-red color change through several elements that facilitate energy input and depletion, such as light/azobenzene [125], light/spiropyran [19,127], hydrazine [18], methylene glycol-sulfite clock reaction, and lactone hydrolysis.

4.4. Self-erasing materials

The autonomous appearance and consecutive disappearance of the pattern are the most notable characteristics of self-erasing materials. Dissipative self-assembly offers temporal control over the autonomous life-

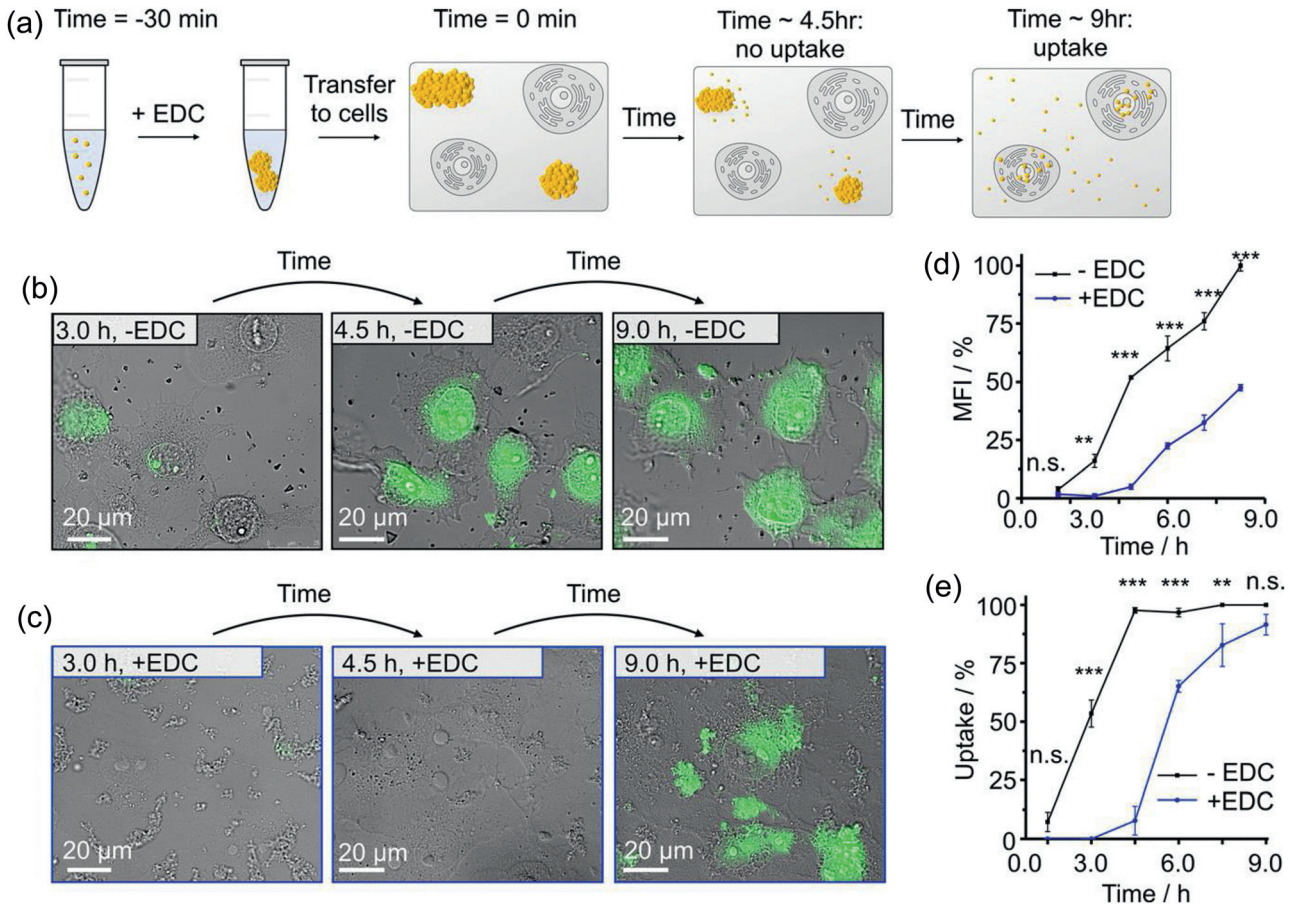

Fig. 15. (a) Schematic of the delayed uptake of EDC-driven transient SiNCs aggregates. Fluorescence images of cells incubated with SiNCs (b) without and (c) with EDC. (d) Mean fluorescence intensity of nucleus cell and nucleus incubated with Si nanocrystal without and with EDC. (e) Percentage of taken-up cells without and with EDC [17].

time of transient assemblies, providing numerous achievable elements for patterned displays and erasing. Through energy input and depletion, changes such as sol-gel transition [37,116], transparent-turbid appearances [46], and color change [116] can be encoded in a programmable and self-erasing manner. For example, a charge-transfer supramolecular polymer of coronene salt-dodecyl methyl viologen can form red-colored gels. Adding the reducing agent $Na_2S_2O_2$ induces transient disassembly and violet sol, further reforming the gel state mediated by the oxidation of glucose oxidase. After forming a red hydrogel writing matrix, the $Na_2S_2O_2$ ink causes an instantaneous color change from red to violet and a gel-sol transition. Subsequently, oxidation induces the violet color to disappear, along with the erasure of the temporary message [116]. In addition to color, transient turbidity is another carrier for a temporary message. The fuel ink of the EDC can drive Fmoc-D to form Fmoc-D anhydride with a size of hundreds of nanometers, showing a clear-turbid transion. The turbid part in pattern mode displays part of the information. With the hydrolysis of Fmoc-D anhydride, this turbid pattern gradually became transparent over a set time, completing the full message expression and erasing process [46]. It is noteworthy that the encoding time can be regulated by fuel concentration, enriching the encoded information in materials. Moreover, the self-erasing materials can be subjected to multiple cycles.

4.5. *Transient self-healing materials*

Self-healing materials have attracted considerable attention in recent years, and the exploitation of dynamic covalent bonds [115] and supramolecular interactions has become a reliable approach for realizing the self-healing properties of materials. However, conventional self-healing materials generally have difficuty in balance of kinetic stability and intrinsic healability (Fig. 16(a)), limiting their application as self-healing materials. However, conventional kinetically stable materials cannot heal on their own (Fig. 16(a)). Constructing a material with high kinetic stability and intrinsic self-healing ability is important. Dissipative self-assembly endows materials with transient structures, properties, and aggregates within controlled time ranges. With fuel addition, kinetically inert materials can be transformed into temporally kinetically unstable materials with self-healing capability. Once the fuel is depleted, these transient self-healing materials recover their high-stability state (Fig. 16(a)). For example, a hydrogel is generated from the dynamic acylhydrazone bonds of an acrylamide-co-diacetone acrylamide polymer and adipic acid dihydrazide [129]. Dynamic acylhydrazone bonds are reversible under acidic conditions but stable in basic environments [115]. The addition of a urea-containing acid buffer to the damaged hydrogels triggers a rapid localized decrease in pH, activating the acylhydrazone bonds and resulting in a self-repairing behavior of the damaged hydrogels. With the slow urease enzymatic generation of the base, dynamic acylhydrazone bonds are locked, and the healable hydrogels recover to their stable state (Fig. 16(b)) [129]. Besides dynamic covalent bonds, the coordinated metallosupermolecular hydrogel of the histidine-modified polymer and Co^{3+} also possess transient healability by adding fuels. The coordination of Co^{3+} and histidine-based polymers forms gels; however, Co^{2+} tends to form kinetically labile coordination bonds with ligands and produces viscoelastic liquids. For damaged Co^{3+}-histide-based metallosupramolecular hydrogels, fast reductive ascorbic acid produces Co^{2+}-based viscoelastic liquids, endowing the gels with

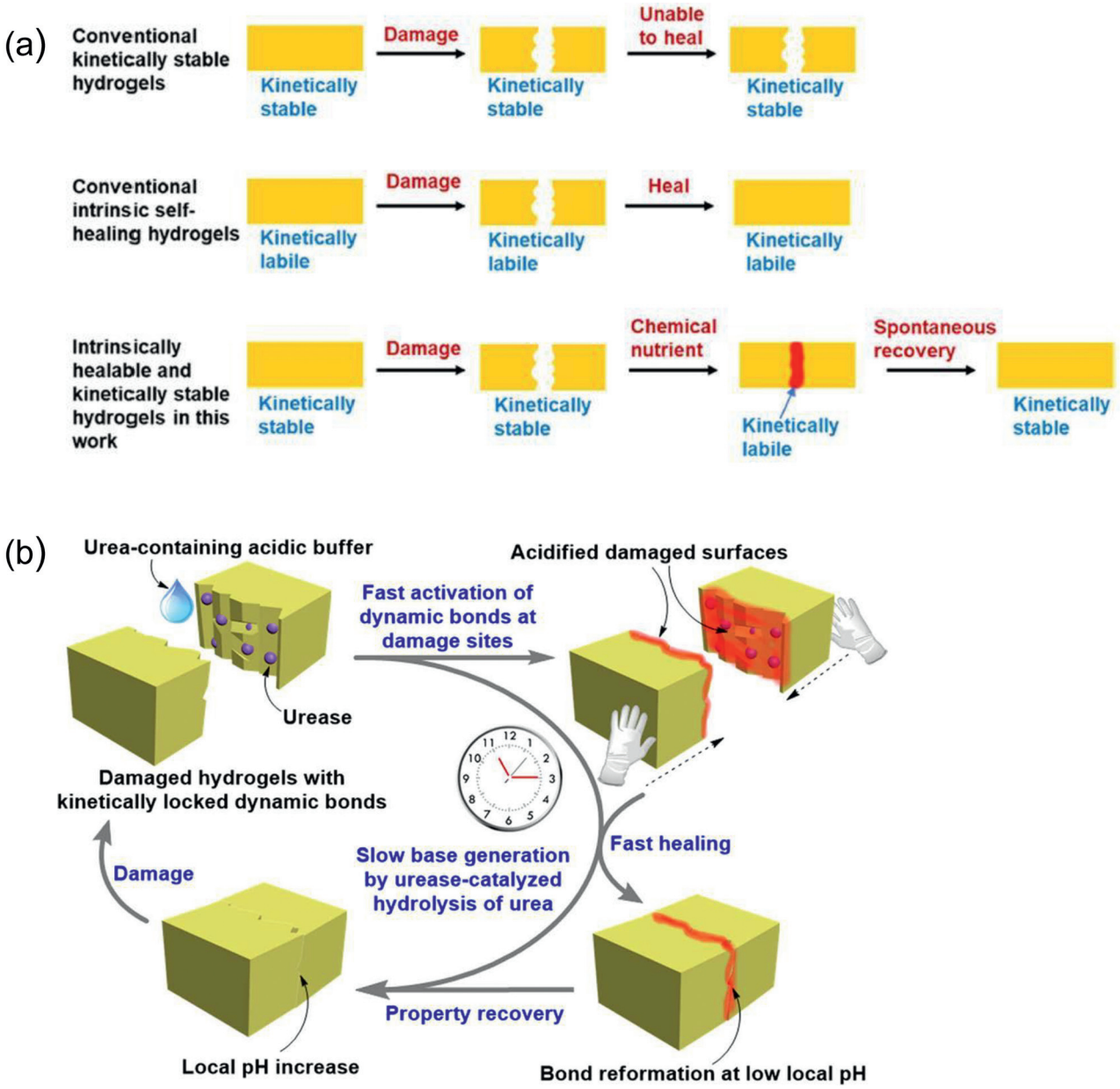

Fig. 16. (a) Performance of different materials after mechanical damages: conventional kinetically stable hydrogels cannot heal themselves; conventional intrinsic self-healing hydrogels can heal themselves but are kinetically stable; transient self-healing hydrogels with high kinetic stability. (b) Schematic of temporally self-healing hydrogels; their transient healability is realized by adding a fast acidic buffer with a slow base generation from urease hydrolysis [129].

temporal self-healing capability. Slow enzymatic generation of H_2O_2 further recovers kinetically stable Co^{3+}-based gels [130]. Fast sol generation at the cutting face and slow gel formation in situ are the precedent conditions for transient self-healing gels.

4.6. Other applications

The structures and functions of the simplest living organisms serve as valuable resources to draw inspiration from and emulate. The behavior of biological systems inspires the formation of artificial functional molecules or materials via dissipative self-assembly. Owing to the self-replication behavior of chromosomes or cells, various surfactant replicators are produced by two-phase-separated reactants using an alkene metathesis catalyst and micelle-mediated self-replication [20,131]. This nonbiological self-replication of dynamically metastable replicators will help us understand the biological self-replication process and further create intelligent functional materials. Further research involves utilizing the phase-separation method for the self-selection of carboxylate replicators [44]. Although the functions of synthesized dissipative assemblies draw inspiration from living systems, further efforts are needed to surpass and enhance the capabilities of the original systems. Based on thermodynamic and kinetic molecular machines with trajectory and cycle [132–133], a transient molecular machine was constructed using rotaxane molecular shuttles threaded by molecules containing secondary ammonium/amine and thiourea stations. It had a ratcheted directional motion behavior driven by the chemical fuel of trichloroacetic acid [134], producing high controllability of catalytically active and inactive states [13]. According to a recent theoretical analysis, the fuel–waste conversion in nature is commonly catalyzed by building blocks; this inherent fuel conversion is more efficient in the assembled state [5]. More-

over, substrate-induced assemblies of TACN·Zn^{2+} and 2-hydroxypropyl *p*-nitrophenyl phosphate (HPNPP) accelerate the catalysis of HPNPP [14].

5. Concluding remarks

Dissipative self-assembly enables the development of fuel-dependent materials that hold significant value in creating life-like materials capable of energy-consuming processes. By drawing inspiration from living systems, researchers gain motivation and insights to design nonequilibrium chemical systems. Key energy sources such as light, electricity, magnetism, and biological and chemical substances play crucial roles in driving dissipative self-assembly systems, offering opportunities to engineer dynamic and functional materials that mimic the complexity and functionality observed in living systems. In this review, we summarize several fuel input/energy depletion mechanisms, including the enzyme-responsive and hydrophilic/hydrophobic switching modes. Versatile transient self-assemblies, including gels, vesicles, micelles, and nanoparticle clusters, have also been discussed.

Although many dissipative self-assembly systems have been reported, they remain a significant and challenging research focus. Four important issues must be solved: i) dissipative self-assembly requires regular guidance for the design, construction, and prediction of the aggregates, properties, and functions; ii) versatile fuels carrying energy should be synthesized; correspondingly, the modes of the fuel input/energy depletion mechanism need to be enriched and expanded. Stimulating factors such as pH, light, temperature, enzymes, redox agents, gas, magnetism, and electrochemistry show tremendous potential in dissipative self-assembly systems, which will greatly enrich the nonequilibrium chemical reaction network. iii) More functional precursors with complex structures and multiple responsive motifs should be designed to serve as building blocks for dissipative self-assembly studies. Fuel input/energy depletion modes affect the structures of transient self-assemblies, interactions, and other properties. iv) The removal of waste should be considered: the efficiency of fuel in reinducing transient assemblies and the number of cycles decreases, presumably owing to the accumulation of waste products in the closed reaction system; thus, the removal of waste is necessary. Hermans et al. extended transient self-assembly using a dialysis membrane set up to control the influx of fuel and the outflux of waste to obtain nonequilibrium steady states. Dialysis membranes facilitate continuous fuel/waste exchange and compartmentalization. Dialysis membranes maintain the nonequilibrium steady states for a long time as long as fuel influx and waste outflux are constant [135]. Moreover, light can be applied as a novel fuel because it is clean, noninvasive, remotely controlled, and without waste [136]. v) Factors including application, availability, price, and complexity are important issues that should be considered. By leveraging interdisciplinary approaches, we can harness novel inspiration and motivation, leading to the exploration of entirely new precursors or fuels. This interdisciplinary advantage enables the investigation of unconventional fuels such as shaking [25], hydrazine [18], and merocyanine molecules [19,50], which have the potential to enrich dissipative self-assembly and unlock the development of more functional and lifelike materials. An in-depth study should be performed using self-assembly strategies such as supramolecular chemistry [33,58,117] and host-guest chemistry [13,25,117]. Self-assembly and disassembly are tightly driven by the structures and properties of activated precursors. Thus, rationally and purposefully designing precursors with responsive functional groups are expected to yield predictable cycles and lifetimes for nonequilibrium chemical reaction networks. One promising avenue for advancing the field of dissipative self-assembly is incorporating dynamic covalent bonds into the interactions between ligands and NPs. This innovative approach holds the potential to provide new insights and ideas for the development of dynamic and responsive materials. As dissipative self-assembly continues to gain significance in the preparation of functional and complex materials, this review serves to contribute to our understanding of the field and offers strategies for addressing some of the challenges associated with it.

Declaration of Competing Interest

Jingcheng Hao is an associate editor for ChemPhysMater and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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