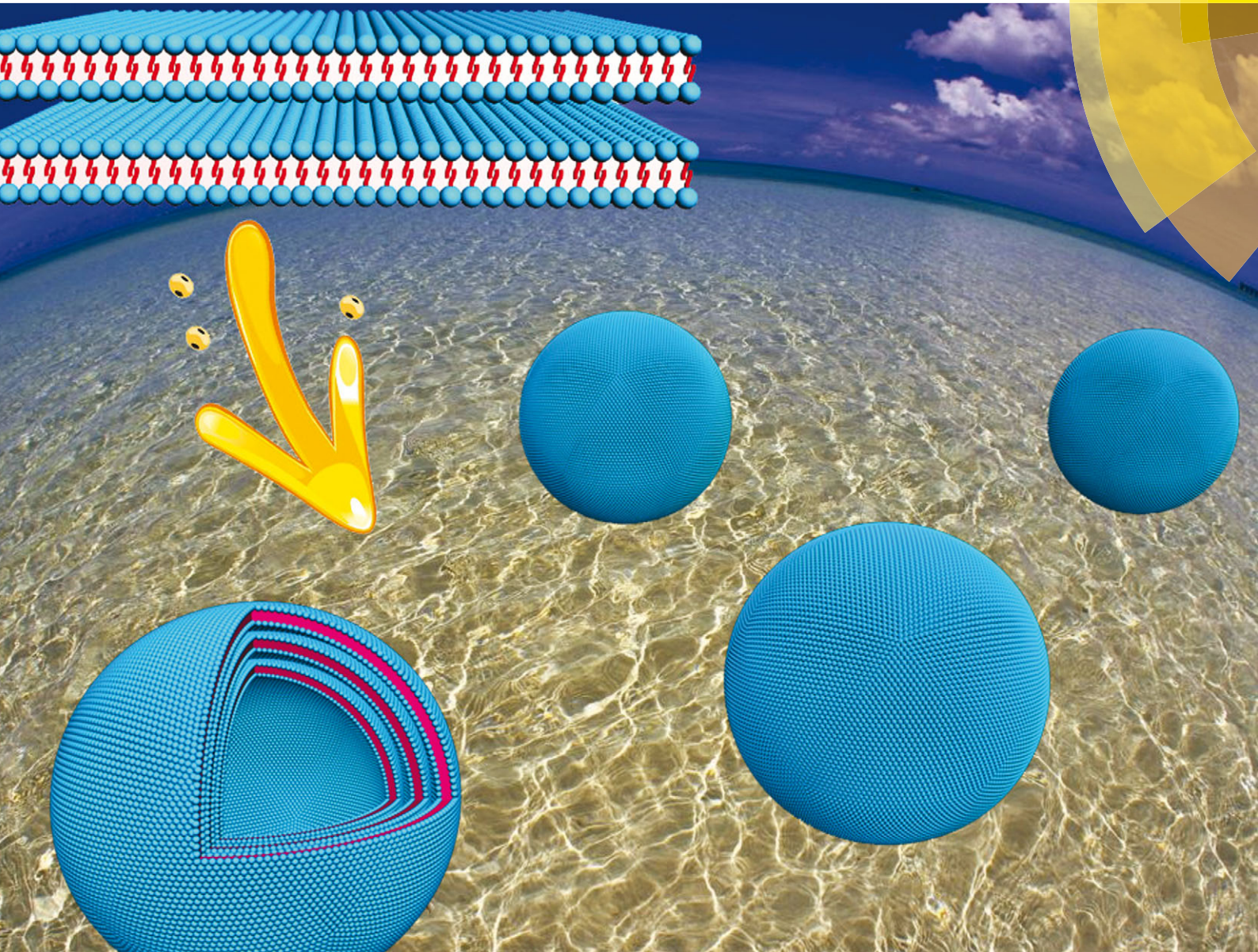


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Adaptive soft molecular self-assemblies

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Adaptive soft molecular self-assemblies

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Adaptive molecular self-assemblies provide possibility of constructing smart and functional materials in a non-covalent bottom-up manner. Exploiting the intrinsic properties of responsiveness of non-covalent interactions, a great number of fancy self-assemblies have been achieved. In this review, we try to highlight the recent advances in this field. The following contents are focused: (1) environmental adaptiveness, including smart self-assemblies adaptive to pH, temperature, pressure, and moisture; (2) special chemical adaptiveness, including nanostructures adaptive to important chemicals, such as enzymes, CO₂, metal ions, redox agents, explosives, biomolecules; (3) field adaptiveness, including self-assembled materials that are capable of adapting to external fields such as magnetic field, electric field, light irradiation, and shear forces.

Introduction

The bottom-up method of soft molecular self-assembly^{1–4} is becoming a powerful technique to construct complicated nanostructures with relatively simple ingredients.⁵ Driven by a variety of inter-molecular non-covalent interactions such as hydrophobic effect,⁶ hydrogen bonding,^{7–9} host–guest recognition,¹⁰ electrostatic interaction,¹¹ aromatic stacking,^{12,13} or metal–ligand coordination,^{14–16} molecules can assemble spontaneously into structurally well-defined, highly-ordered, and most important, functional nano- or meso-scaled structures.¹⁷ Although single

non-covalent interaction may not be as robust as covalent ones, the group of multiple non-covalent bonds can still construct robust systems.¹⁸ Moreover, the dynamic nature of non-covalent interactions can be exploited to design adaptive systems, since the environmental sensitivity of non-covalent bonds make the systems to respond willingly to external stimuli.¹⁹ These finally result in changes both in structure and function of the supramolecular materials and automatically bring the system to a state that is adaptive to the environment. In contrast with their covalent counterparts, the non-covalent molecular self-assemblies also have unique and fascinating properties such as facility in fabrication and reversibility. These advantages make them very competitive candidates for developing smart materials²⁰ in various fields such as controlled-delivery,^{21–23} sensors,^{24–26} self-healing materials,^{27–30} piezoelectric devices,³¹ mechanochromism,^{32,33} or stimuli responsive devices.³⁴

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Actually, adaptive self-assembling systems are playing significant roles both in natural and artificial materials.^{1,4,5} Most life activities are realized through the adaptive behaviours of cells to biological stimuli. The structure and function of the membrane change correspondingly when a signal arrives. For artificial materials, the general idea for the construction of adaptive architectures is (1) to ingeniously design building blocks which may respond to external stimuli and (2) to produce self-assembly of these building blocks through multiple non-covalent interactions. The building blocks and the non-covalent interactions run together to allow the whole system to respond to different types of external stimuli. The orthogonal combination of the two aspects is expected to produce artificial adaptive self-assembled materials with fascinating potential.³⁵ In this review, we briefly summarize recent progress in the fabrication of advanced materials or molecular devices that are adaptive to environments, special chemicals, and external stimuli.

1. Environment adaptive self-assemblies

Environmental factors often affect the performance of many materials. Strictly speaking, any factor that is not involved in the self-assembled structures is the 'environmental factor'. However, considering the mode of interaction, factors that don't have special selectivity in acting on the self-assembling systems, such as pH, temperature, pressure, and moisture, are classified as environmental factors in this review. Then it is highly desired to understand how these factors affect a certain system and to employ these influences to design smart

materials that may adapt to environmental changes to lead to potential applications.

1.1 pH adaptiveness

Nature and biological systems employ pH variation to achieve their functions. For instance, the seasonal change in the colour of leaves can be attributed to the variation of pH in cell liquid components; tumour tissues usually have a lower pH than the normal ones. Artificial pH adaptive architectures either contain protonable groups or pH cleavable chemical bonds. The most simple pH adaptive molecular self-assemblies are the vesicles formed by fatty acids.^{36,37} These amphiphilic compounds dissolve slightly at neutral and acidic pH but self-assemble into micelles in extremely basic solutions. Vesicles can be formed only at pH in between these two extreme conditions. The pH at which the vesicle to micelle transition occur can be made the same or very close to that of the biological environment by tuning the number and structure of protonable groups.^{38,39} Such vesicles are ideal vehicles for controlled drug delivery. In addition to tuning the structure of protonable groups to design pH responsive vesicles, novel ideas should be explored to create advanced soft smart materials that exhibit pH adaptiveness. In this section, we briefly summarize some recent advances in this aspect.

1.1.1 pH responsiveness endowed by supramphiphiles. Specially designed pH responsive self-assemblies are usually formed by rather complicated molecules. The invention of supramphiphiles (SA) by Zhang *et al.*^{40,41} greatly simplified the synthetic procedure toward this goal. For instance, they⁴² utilized a dynamic covalent bond to fabricate a bola-form superamphiphile from 1-(10-(4-formylphenoxy)decyl)pyridinium (FDP) and



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Professor Jianbin Huang obtained his bachelor (1987), master (1990), and PhD (1993) degrees all at Peking University, China. After a postdoctoral study at the same university, he was nominated as an associate professor in 1995, as a full professor in 2001, and was awarded "Outstanding Young Scientist of China" in 2004. His main research interests include soft self-assembly of amphiphiles and one dimensional nanomaterials that are synthesized using soft

templates. He is currently the senior editor of Soft Matter, and also the member of the editorial board of Langmuir.



Yun Yan

Professor Yun Yan earned her bachelor degree at Northeast Normal University (1997) and the PhD degree at Peking University (2003), China. After two post-doctoral studies in Bayreuth University (Germany, with professor Hoffmann) and Wageningen University (the Netherlands, with professor Martien A. Cohen Stuart) in colloid science, she joined Peking University as an associate professor in 2008. She was selected in the New Century Training Program for

the Talents by the State Education Commission of China in 2009, and was awarded "Outstanding Young Professor of Colloid Science of China" in 2013, Teaching Award of Peking University (2013), winner of Outstanding Youth Science Foundation, Natural Science Foundation of China (NSFC, 2014), Excellent doctoral thesis instructor of Peking University (2014). Her current interest is solution based functional molecular self-assemblies, especially control over the functions of the self-assembled materials through the rational design of a self-assembling method.

1-(10-(4-(ammoniomethyl)phenoxy)decyl)pyridinium (AMDP). Under basic conditions, the two molecules can be connected by a dynamic benzoic imine bond to form a bola-like super-amphiphile with a hydrophilic–hydrophobic–hydrophilic structure. A spherical micellar nano-structure was formed by hydrophobic interactions. As the pH was switched to slightly acidic values, the benzoic imine bond was hydrolyzed, thus the SA dissociated and resulted in disassembly of the micelles.

A similar strategy was also adopted by them to fabricate a toothbrush-type SA.⁴³ In this approach, methoxy-poly(ethylene-glycol)114-*block*-poly(L-lysine hydrochloride)200 (PEG-*b*-PLKC) and 4-(decyloxy)benzaldehyde (DBA) were chosen to be the two components of the supramolecular building block which was also connected by a benzoic imine bond. This SA is able to form spherical aggregates in water, which disassemble reversibly under mild acidic conditions. In the same way, pH-responsive micelles,⁴⁴ vesicles,⁴⁵ and wormlike micelles⁴⁶ based on a dynamic surfactant are also obtained by van Esch and coworkers. In their progress, the dynamic imine bond was exploited to connect two non-surface-active precursors to form diverse forms of classical surfactants, such as classical single chained or double chained ones, or the Gemini surfactant that looks like the dimers of the classical single chained one. The addition of acid can cause the dissociation of these supramolecular surfactants, which leads to pH responsive aggregates with diverse morphologies (Fig. 1).

1.1.2 pH responsiveness endowed by specially designed covalent compounds. Molecular structure is very crucial in creating various responsive nanostructures; this is also true for advanced pH responsive materials.^{47–50} For instance, Shen and co-workers⁵¹ reported pH-responsive multifunctional three-layered nanoparticles (3LNPs). The 3LNPs have a poly(ϵ -caprolactone) (PCL) core, a pH-responsive poly[2-(*N,N*-diethylamino)ethyl methacrylate] (PDEA) middle layer and a polyethylene glycol (PEG) outer layer which consisted of a core-layer-layer structure. As a nano-carrier, hydrophobic drugs can be loaded in the core, but the releasing performance can be controlled by the solubility of the PDEA layer which is pH dependent. When the pH value is above 7 (approximately at physiological pH), the drug release process

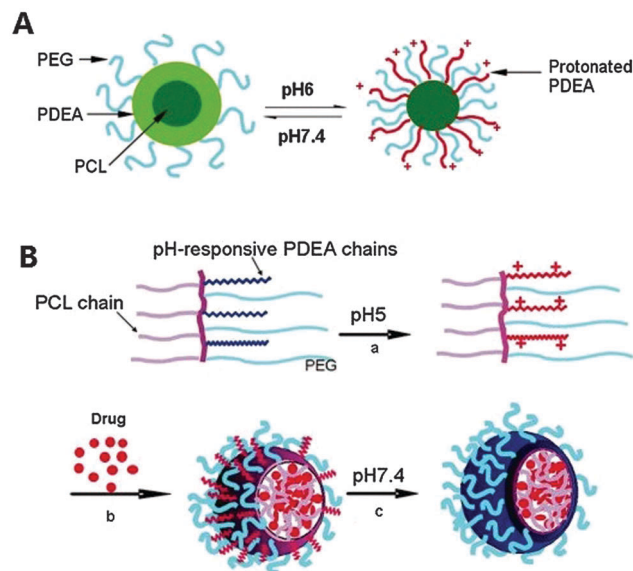


Fig. 2 3LNPs. (A) pH adaptive 3LNPs. (B) The drug release process of the drug-loaded system. Adapted with permission from ref. 51. Copyright © 2008, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.⁵¹

is blocked by the PDEA layer which covers the core. As the pH value drops below 6.5, the positively charged middle layer becomes soluble, which enables the drug release process. (Fig. 2) Using elegantly designed molecules, Feng *et al.* were able to create a pH switchable worm-like micelle. The system was composed of the mixture of *N*-erucamidopropyl-*N,N*-dimethylamine and maleic acid with a molar ratio of 2:1. The viscosity of the micellar solution is switchable *via* tuning the pH. Such a system possesses the characteristics of a facile, rapid, cost-effective reversible process and recyclable cheaper materials.⁵² This combination also allows the formation of pseudo Gemini surfactants, which display extreme pH adaptiveness compared with conventional Gemini ones.⁵³

pH responsiveness not only results in structural differences in materials, but can also be smartly related to the functions. For instance, Zhou and Zhu *et al.*⁵⁴ designed a “breathing” vesicle with jellyfish-like on-off switchable fluorescence. An amphiphilic diblock copolymer containing dimethylaminoazobenzene groups as fluorescent chromophores is used in the preparation of the polymeric vesicle through aqueous self-assembly (Fig. 3). The vesicles exhibit “breathing” properties, which are a change in size accompanied by corresponding changes in light emission triggered by variation of pH.

1.1.3 pH responsiveness facilitated by small molecules. Except designing complicated molecules, Huang and coworkers⁵⁵ aimed to construct pH-adaptive self-assembly by introducing a pH adaptive small molecule into an amphiphilic system. For instance, they obtained pH-responsive viscoelastic wormlike micelles based on commercial compounds. According to this route, pH-adaptive viscoelastic fluids can be easily obtained by introducing a pH-responsive hydrotrope into a surfactant solution. The pH-adaptive fluid of the mixed system of cetyltrimethylammonium bromide and potassium phthalic acid can be

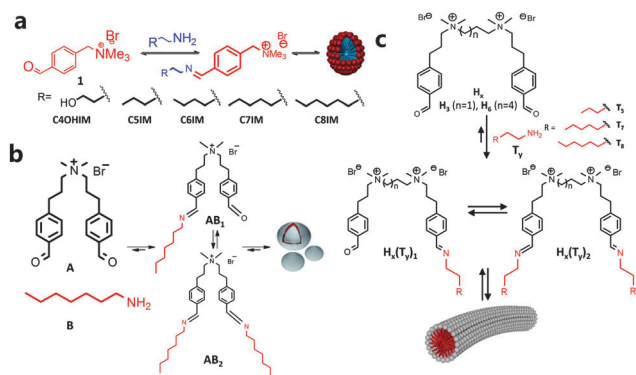


Fig. 1 pH-responsive dynamic amphiphiles. (A) Micelle formation. (B) Vesicle formation. (C) Wormlike micelles formed by dynamic gemini surfactants. Adapted with permission from ref. 44–46. Copyright © 2009 and 2012, American Chemical Society^{44,46} and © 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.⁴⁵

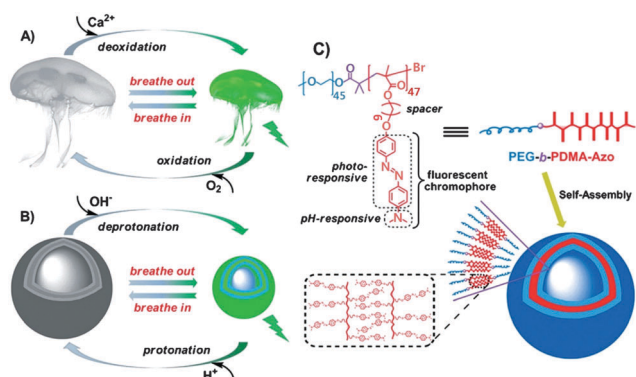


Fig. 3 “Breathing” vesicles. (A) Breathing process of jellyfish. (B) pH-promoted “breathing” process of the vesicles. (C) Schematic representation of the amphiphilic copolymer and the structure of the vesicle. Adapted with permission from ref. 54. Copyright: 2012 © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.⁵⁴

switched between a gel-like state and a water-like state within a narrow pH range (Fig. 4A). Raghavan and co-workers⁵⁶ developed a similar method to impart pH-responsive properties to gels of biopolymers by embedding fatty-acid-based pH-adaptive vesicles into the gels (Fig. 4B). The nanosized vesicles contained in the gels exhibit a pH-responsive vesicle-micelle transformation. This enables the pH-dependent controlled release of the vesicle-loaded gels.

1.2 Thermoadaptiveness

One of the most common environmental factors that control the conformation and process of self-assembly is temperature.⁵⁷ Temperature has great effect on the solubility of molecules, extent of bond vibration, and strength of hydrogen bonding. For these reasons, heat accompanied with the change in

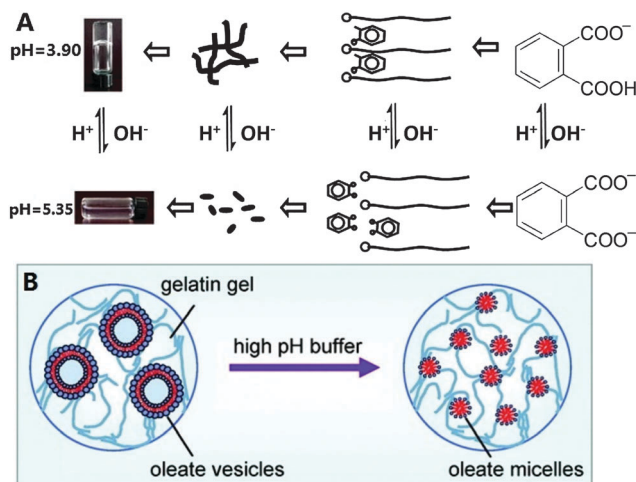


Fig. 4 Examples of pH responsiveness facilitated by small molecules: (A) pH-responsive viscoelastic wormlike micelles based on commercial compounds by J. Huang *et al.* (B) pH-responsive vesicle-micelle transformation which enables capability of pH-dependent controlled release of the vesicle-loaded gels by Raghavan *et al.* Adapted with permission from ref. 55 and 56. Copyright © 2009, American Chemical Society.⁵⁶

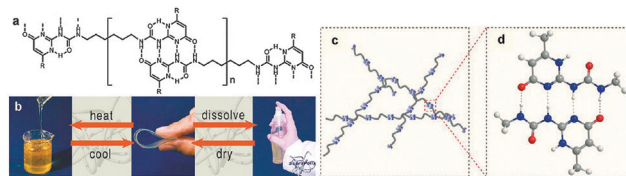


Fig. 5 Thermoreversible supramolecular polymer rely on quadruple hydrogen bonds.⁶⁵ Copyright © 2008, Nature Publishing Group.

temperature can be a convenient and efficient source of external energy, which may lead to many desired changes, such as self-healing,^{58–60} thermo-responsive,^{61,62} and thermo-chromic processes,^{63,64} which are required for smart adaptive materials.

1.2.1 Thermo-reversible self-healing. Self-assembled supramolecular entities built with hydrogen bonds are likely to be affected by thermo-stimuli and show their adaptive abilities. One versatile example is the self-complementary array of 2-ureido-4-pyrimidone,^{65,66} in which strong quadruple hydrogen bonding held the units together to form dimers in toluene. The hydrogen bonding groups are associated with multi-functional molecules and finally form supramolecular polymers with high degrees of polymerization (Fig. 5). Heating this supramolecular polymer resulted in the breaking of hydrogen bonding which depolymerized the structure. A reverse process was realized upon cooling.

Hydrogen bonding was also employed by Leibler *et al.*²⁷ to produce self-healing and thermo-reversible rubbers from supramolecular assembly in 2008. The molecules they designed and synthesized can associate together and form cross-links and chains *via* intermolecular hydrogen bonding. These cross-linking systems can be simply self-repaired by bringing fractured surfaces together at room temperature. Moreover, the break-and-repair process can be repeated for many times, which makes the materials easy to be re-used and recycled (Fig. 6).

1.2.2 Thermo-responsive colour change. The response of hydrogen bonds also leads to a change in the electronic structure of the materials.^{64,67} An interesting example can be found in the photo-functional nanomaterials made by polystyrene-*block*-poly(4-vinylpyridinium methanesulphonate), (P4VP(MSA)) and 3-*n*-pentadecylphenol (PDP).⁶⁸ P4VP(MSA) and PDP combined by hydrogen bonds form highly ordered arrays which have a long lamellar period. These materials are green at room temperature due to the photonic band-gap brought about by the periodic structure. Upon heating, the breaking of hydrogen bonds leads to a sharp and reversible transition to uncoloured materials due to the destruction of the lamellar structure. These adaptive nanomaterials are potentially useful for creating sensors and thermo-responsive materials (Fig. 7).

1.2.3 Thermo-responsive nanostructures. Heat-induced breaking of hydrogen bonds can be utilized to create thermo-responsive nanostructures. As a successive work of Huang *et al.* on the self-assembly of beta-cyclodextrins (beta-CD) and amphiphilic molecules,^{69–73} a temperature-controlled transition between SDS@2beta-CD microtubes and vesicles⁷⁴ has been developed, which provides us with a new prospective of stimuli-adaptive chemistry in inclusion complexes based on CDs.

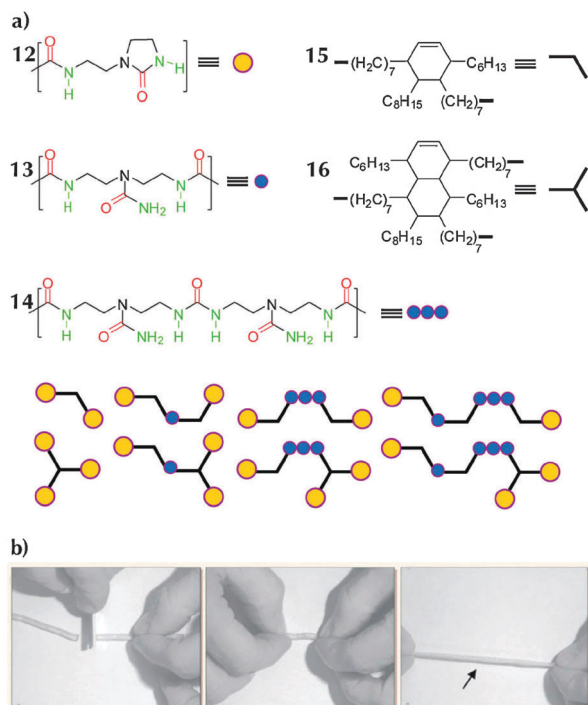


Fig. 6 Self-healable and thermoreversible supramolecular rubbers.²⁷ Copyright © 2008, Nature Publishing Group.

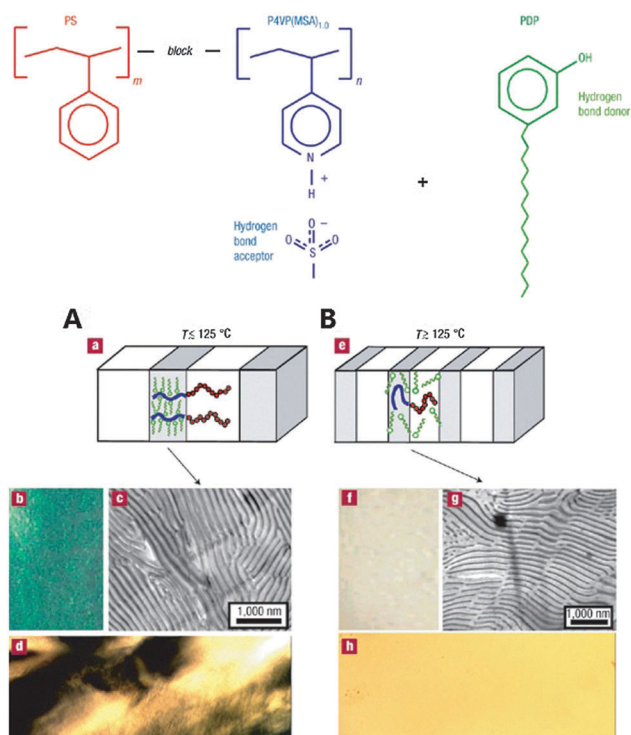


Fig. 7 Thermo-responsive color change of the P4VP(MSA) and PDP system. (A) Green material with periodic structure. (B) uncolored material due to the destruction of the lamellar structure. Adapted from ref. 68. Copyright © 2004, Nature Publishing Group.

Moreover, the CD-amphiphile inclusion system can be used to assemble colloidal spheres thermo-reversibly.⁷⁵ In this

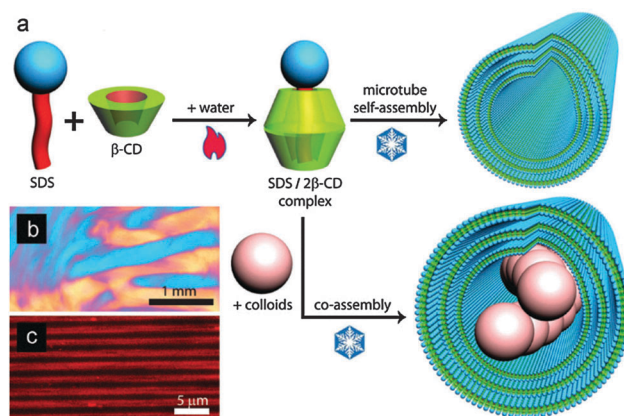


Fig. 8 Thermo-reversible co-assembly of microtubes and colloids.⁷⁵ Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

approach, the co-assembly of spherical colloids and surfactant-cyclodextrin microtubes yields a library of dynamic colloid-in-tube structures including helices (Fig. 8), while disassembly can be achieved simply by heating the system.

Heat induced nanostructure transition also leads to a change in bulk materials. In 2011, Huang and coworkers⁷⁶ reported a unique temperature-dependent supramolecular self-assembly transition. In this approach, hierarchical one dimensional architectures including nanotubes, coiled-coil rope-like structures, nanohelices, and nanoribbons are created *via* lanthanum-cholate supramolecular self-assembly. These one-dimensional nanostructures form networks in the system which results in gelation of water. Upon increasing the temperature, both the width and the length of these one-dimensional structures increase, which enhances the stiffness of the hydrogel. A similar principle was also found in the thermally induced gelation of palmitylamidulosulfobetaine by Feng *et al.*⁷⁷ Micellar growth from globular aggregates to entangled worms upon heating is responsible for thermal gelation (Fig. 9).

1.3 Moisture adaptiveness

Moisture resulting from water is ubiquitous in everyday life. For materials composed of water-soluble molecules, increasing the environmental moisture may increase the molecular mobility which finally leads to self-healing of the scratches or cracks.

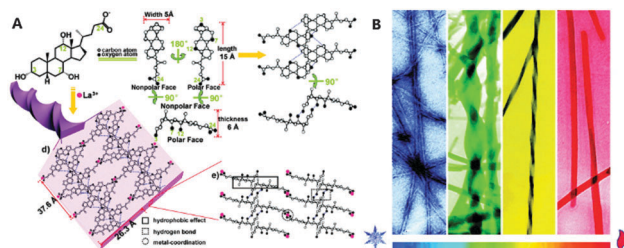


Fig. 9 Temperature-dependent one dimensional architectures. (A) The scheme of the twisted nanoribbon. (B) Representative scheme of temperature-dependent nanostructural evolution of the hydrogel. Adapted from ref. 76. Copyright © 2010, American Chemical Society.

1.3.1 Moisture responsive layer-by-layer (LbL) films. The first case of moisture responsive materials was probably reported by South and Lyon who demonstrated a hydrogel thin film⁷⁸ which could undergo a rapid healing process responsive to exposure to water. The continuous and multilayered films are fabricated by a LbL procedure which employed spherical, sub-micrometer-sized hydrogel particles composed of *N*-isopropylacrylamide, acrylic acid and the cross-linker poly(ethylene glycol)diacrylate as the main building blocks. The films were then constructed on an elastomeric substrate (poly(dimethylsiloxane), PDMS) which exhibited repeatable healing behaviour upon multiple mechanical deformations when solvated with water. The self-healing property is attributed to the Columbic forces that hold the films together. Stress-induced folding or cracking which deforms the elastomeric substrate and subsequently transmits to films leads to the disruption of polyanion–polycation interactions. The dissociation leads to the particles with excess positive charges and makes the films heterogeneous in terms of the overall charge. After resolution, the increase in polymer mobility promotes redistribution of the charges in order to decrease the energy by reformation of anion–cation pairs.

A similar case is the LbL assembled polyelectrolyte multilayer reported by Sun *et al.*⁷⁹ In this approach, intrinsic self-healing polyelectrolyte multilayer (PEM) coatings were fabricated rapidly by the LbL technique. The PEM coatings are mechanically robust but softened in the presence of water owing to the unfolding of the chain. The softened PEM exhibits high flow ability therefore allows repairing of severe damages. This self-healing process can be repeated multiple times in the same area.

1.3.2 Moisture responsive self-healing hydrogel. Many self-healable materials are driven by recognition effect, such as charge recognition or host–guest inclusion. A typical example of the former class is the self-healable supramolecular luminescent hydrogel constructed by Zhang *et al.*⁸⁰ This hydrogel is prepared from negatively charged POMs (polyoxometalates) and ABA triblock copolymers with two cationic A blocks. The negatively charged POMs interact with positively charged A blocks of the polymers to form coacervates. Many such coacervate domains are protected and bridged together by the water soluble B block to form neutral hydrogel at a charge balancing ratio. As a result, any damage to this hydrogel results in the detachment of one A block from the neutral coacervate domain, which leads to separation of positive and negative charges. Upon addition of water, the increase in chain mobility immediately allows re-combination of charges, and ‘self-healing’ of the hydrogel occurs.

Supramolecular materials based on host–guest interaction also exhibit moisture responsive self-healing behavior. For instance, Harada *et al.*⁸¹ have constructed a hydrogel based on the host–guest interaction between cyclodextrin (host) and hydrocarbon-groups (guest). Acrylamide-based gels functionalized with cyclodextrin as host moieties or hydrocarbon-groups as guest moieties were synthesized in this approach. When putting pieces of host-gels and guest-gels together in water, they are proved to adhere to one another by molecular recognition between three kinds of cyclodextrins and three different hydrocarbon groups.

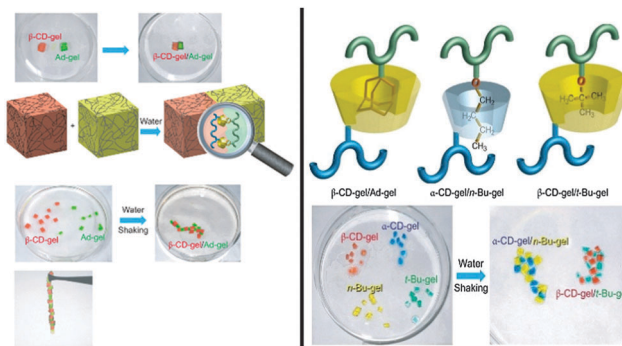


Fig. 10 Macroscopic self-assembly of gels and selectivity. Adapted from ref. 81. Copyright © 2010 Nature Publishing Group.

By this way different gels can be assembled and sorted into macroscopic-sized structures selectively by microscopic interactions (Fig. 10).

1.4 Pressure adaptiveness

Changing the pressure may bring a series of effects to the system. For solutions, pressure may affect the solubility, partial molar volume, and mobility of the solute. For solid materials, pressure may lead to the change of molecular packing, or even breaking of some weak interactions. These changes may be reflected on the bulk properties.⁸² Therefore, adaptive materials that respond to pressurization are also obtained by the efforts of chemists.

1.4.1 Pressure adaptive luminescence. Pressure exerted on the assemblies makes the molecules inside closer to each other or restricts their motion, which finally leads to responsiveness. In an aggregation induced emission system discovered by Tang *et al.*,^{83,84} this perspective is clearly shown. In a low pressure region the HPS molecules show a unique effect of the pressurization-enhanced emission phenomenon. However, a continuous increase in pressure leads to a slow decrease of emission. The mechanism explained by authors shows that the imposed pressure brings dye molecules closer, which enhances the RIR (Restricted Intramolecular Rotation) process as well as boosted molecular interactions. The latter promoted the formation of excimers which underline the strength of light emission.

Except direct pressure imposed to a liquid of the gas system, mechanical force may exert pressure on solid materials. Tang *et al.* achieved emission transformation of diphenyldibenzofulvenes from green to yellow by grinding.^{85,86} The change of colour was proved reversible, which is attributed to the grinding–heating imposed transformation between amorphization and crystallization of dye molecules. The pressure due to grinding has an explicit influence on the aggregation behaviour and accumulation mode of the molecules, thus promotes the change in luminescence. Jia *et al.*⁸⁷ reported a dipeptide-based multicolored-switching solid material. The material was fabricated from peptides functionalized with a pyrene group and a rhodamine B group, respectively. Multiluminescent colours from blue to green, and finally red can be switched in one such sample, which is based on the transformation in both the

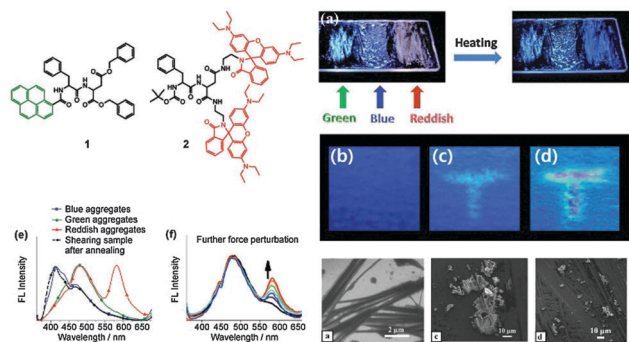


Fig. 11 (a) MC-1/2 aggregates showing different emission colors under force perturbation (irradiated by 365 nm UV light) and their color restoration by heating, (b) blue luminescence, (c) force-induced green luminescence, (d) force-induced reddish luminescence pattern and three different emission colors in one paper. The three TEM images at the bottom right corner are the aggregates corresponding to the emissions. Adapted from ref. 87. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

molecular assemblies and the chemical structure of the peptides (Fig. 11).

1.4.2 Pressure adaptive molecular self-assemblies. Supercritical fluid has been verified to be wonderful media for the occurrence of self-assembly.^{88–91} In these systems CO₂ molecules may be pressed into the amphiphilic region in the self-assembled structures, which would lead to a structural change in the system. A typical case was reported by Han *et al.* regarding the reversible switch between the lamellar liquid crystal phase and the micellar solution with compressed CO₂.⁹² Upon tuning the pressure of CO₂ the sodium bis-2-ethylhexylsulfosuccinate (AOT)/water system undergoes a transition from high viscosity conditions at low pressure to transparent fluid without viscoelasticity above the optimum value of CO₂ pressure. Upon providing appropriate pressure, CO₂ can be inserted into the surfactant bilayer, which could change the structure of the bilayers. Increasing the pressure of gas resulted in disruption of the ordered structure

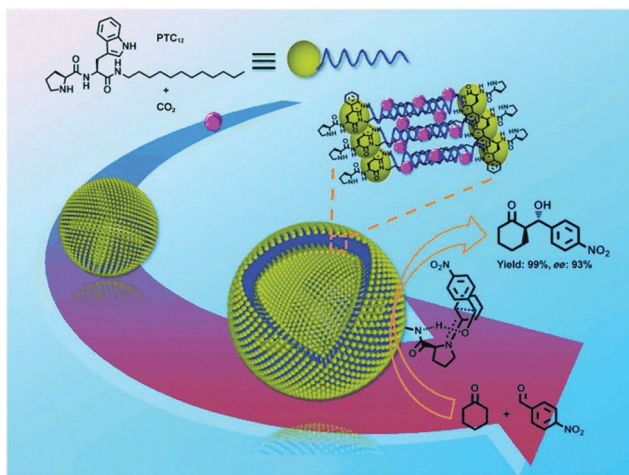


Fig. 12 The compressed CO₂-regulated self-assembly and catalysis of the asymmetric aldol reaction. Adapted from ref. 94. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

and promoted the formation of more thermodynamically stable micelles. Similarly, Liu *et al.* reported a pressure responsive assembling system of L-proline in compressed or supercritical CO₂.⁹³ In this work, high pressure may compress CO₂ into the hydrophobic domain of the self-assembled structures. This enabled amphiphilic proline to behave as an organocatalyst for the asymmetric aldol reaction. The size of the assemblies can be tuned by dynamically compressed CO₂ which explicitly affects the catalyst activity and selectivity (Fig. 12).⁹⁴

2. Special chemical adaptivities

One of the important aims in developing smart materials is to detect certain chemicals which are very relevant to the environment, medical, food, disease, and biological processes. For this reason, the adaptive self-assembled system that responds to specific chemicals such as enzymes, various metal ions, and biomolecules are very attractive for practical applications.

2.1 Enzyme adaptiveness

Enzymes have recently emerged as promising triggers of the adaptive systems^{95,96} as enzyme-catalyzed reactions are highly selective and efficient, requiring only mild conditions. In addition, enzymes are closely related to many biological processes. The abnormal level of enzymes often characterizes a specific disease. For instance, Alzheimer's disease,^{97,98} Parkinson's disease,^{99,100} and diabetes^{101,102} are all related to enzymes. Therefore, enzyme-responsive, amphiphilic self-assembly represents one of the increasingly significant topics in biomaterials research and finds feasible applications to the controlled release of therapeutic agents¹⁰³ at specific sites where the target enzyme is located.

2.1.1 Enzyme responsive component as a building block.

The main approach to build enzyme responsive self-assemblies is to employ enzyme responsive components as building blocks. For instance, Liu *et al.* utilized myristoylcholine and the biocompatible *p*-sulfonatocalix[4]arene (SC4A) to fabricate a supra-molecular vesicle¹⁰⁴ (Fig. 13). The vesicle disassembled upon the addition of cholinesterase, which finally led to drug release. As cholinesterase is a key protein overexpressed in Alzheimer's disease, the self-assembled system may have potential for the delivery of drugs for Alzheimer's disease.

Myristoylcholine was also employed by Xing *et al.* to form a drug delivery vehicle with poly(ethylene glycol)-*block*-poly(acrylic acid).¹⁰⁵ Simply by mixing these two components in water, spherical aggregates were obtained. Hydrophobic drugs may be stored in the hydrophobic interior of these aggregates. Upon the addition of acetylcholinesterase, which can split the ester linkage of myristoylcholine chloride, the loaded drug was released. In a similar way, Zhang *et al.* constructed enzyme-responsive polymeric systems with Adenosine Triphosphate (ATP) by utilizing electrostatic interactions.¹⁰⁶ As shown in Fig. 14, a double hydrophilic block copolymer methoxy-poly(ethyleneglycol)₁₁₄-*block*-poly(L-lysinehydrochloride)₂₀₀ (PEG-*b*-PLKC), and ATP were combined together by electrostatic interaction to form a

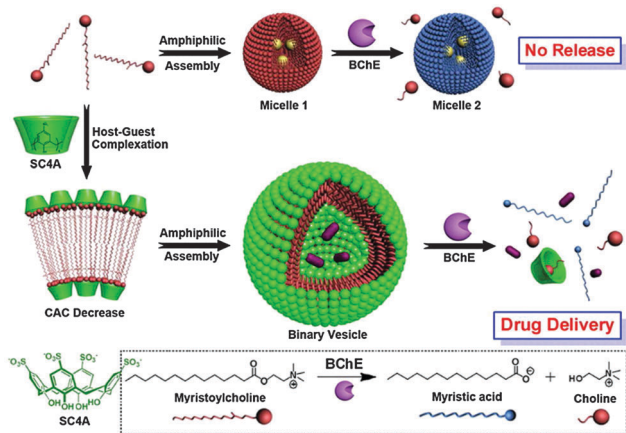


Fig. 13 Myristoylcholine-SC4A supra-amphiphiles, its aggregates, and drug release. Adapted with permission from ref. 104. Copyright © 2012, American Chemical Society.

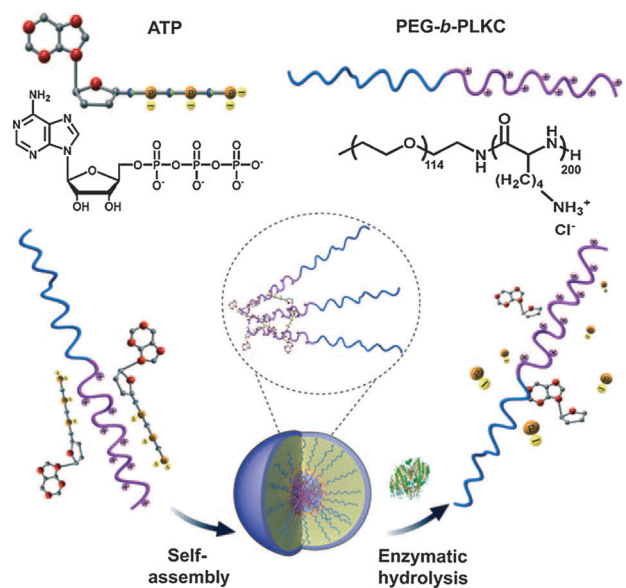


Fig. 14 Self-assembly and enzyme-catalyzed disassembly of the super-amphiphile aggregates. Adapted with permission from ref. 106. Copyright © 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

polymeric micelle.^{40,41} When phosphatase was added, ATP was hydrolyzed to disassemble the micelle. In analogy, pyridoxal phosphate was employed to form compartment micelles with PEG-*b*-PLKC,¹⁰⁷ which are responsive to pH and enzymes.

Huang and coworkers¹⁰⁸ developed a host-guest approach to construct enzyme-triggered self-assembling systems. In their work, they established a family of enzyme-responsive self-assembled structures including monolayers, micelles, and vesicles on the basis of the inclusion complexes formed by the surfactant and β -CD (Fig. 15). After the addition of alpha-amylase, the central components of these structures, the surfactant- β -CD inclusion complexes, are destroyed due to the degradation of β -CD, which results in the disassembly of all the self-assembled structures.

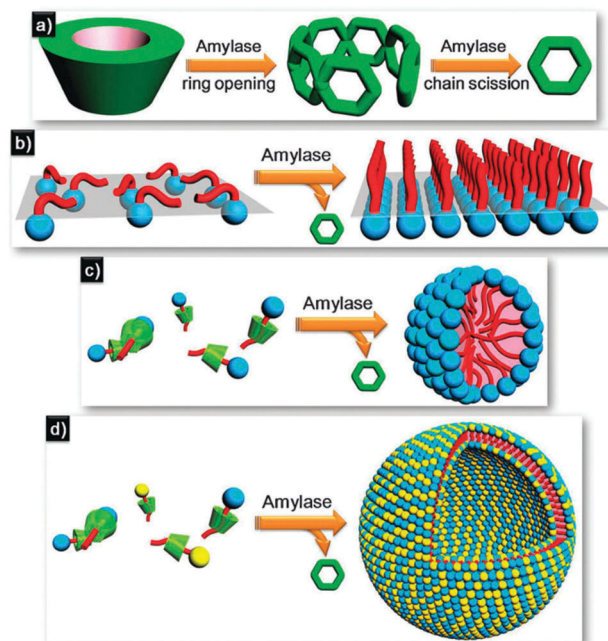


Fig. 15 Degradation of beta-CD by alpha-amylase (a), enzyme-triggered monolayer formation (b), enzyme-triggered micellization (c), enzyme-triggered vesicle formation (d). Adapted with permission from ref. 108. Copyright © 2012 Royal Society of Chemistry.

2.1.2 Enzyme responsive components as triggers. If the above-mentioned examples can be categorized as the 'direct' approach which uses enzyme-responsive moieties to directly construct the self-assembled structures, Liu *et al.* reported an 'indirect' way to build enzyme responsive self-assembly where enzymes were not involved in the formation of the self-assembled structure but in the generation of a component which may affect the structure.¹⁰⁹ They synthesized CGPs (charge generation polymers)¹¹⁰ containing hydrogen peroxide-reactive caged primary amine moieties and integrated CGPs with negatively charged TPE-COOH4 which is a fluorogen exhibiting aggregation induced emission (AIE)¹¹¹ (Fig. 16). Fluorescence can only occur when charges are generated by H_2O_2 , which is produced by the combination of Gox-glucose and AP-Gox-D-glucose 6-phosphate, since the latter allows the GCP to transform into a cationic polyelectrolyte. The combination of a newly generated positively charged polymer and TPE-COOH4 allows the formation of nanoparticles, which effectively turns on fluorescence *via* the AIE process and thus becomes an effective sensor system.

2.2 CO₂ adaptiveness

CO₂ is a small gas molecule which plays a crucial role both in metabolism¹¹² and climate revolution.^{113,114} Exploiting CO₂ as a stimulus to regulate the shape and properties of self-assembled aggregates might be very promising in understanding many mysteries of nature. As an advance, Zhao and coworkers¹¹⁵ recently reported CO₂-stimulated diversiform polymer assemblies. The system containing copolymers composed of outer hydrophilic poly(ethylene oxide), middle hydrophobic poly(styrene), and interior CO₂-responsive poly((2-diethylamino)ethyl methacrylate) flanks.

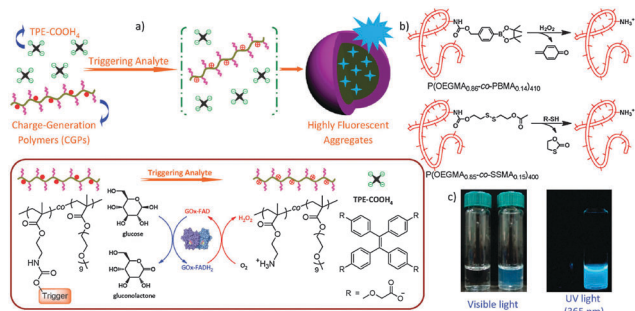


Fig. 16 Construction of fluorogenic sensors from negatively charged AIE molecules and positively charged CGPs. Adapted with permission from ref. 109. Copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

This series of copolymers can assemble into different types of aggregates like micelles, vesicles, and one-dimensional worm-like micelles. Upon compressing CO_2 into the solution, the size, shape, and morphology of aggregates are all changed dramatically. This process can be reversed by degassing CO_2 using N_2 . Thus the reversible deformations of vesicles seem very similar to the endocytosis behaviour of lysosomes when a giant sac is compartmentalized into dozens of smaller irregular vacuoles by CO_2 stimuli (Fig. 17).

Another interesting bio-mimicking CO_2 -stimulated system is the 'breathing vesicles' reported by Yan *et al.*^{116,117} A specific amidine-containing block copolymer is utilized to fabricate the vesicles. The amidine group can transform into a charged amidinium species upon reaction with CO_2 , and upon exposure to argon it exhibits reversibility. After introducing this amidine switchable group into the polymer, the diblock copolymer PEO-*b*-PAD (poly(ethylene oxide)-*b*-poly((*N*-amidino)dodecyl acrylamide))

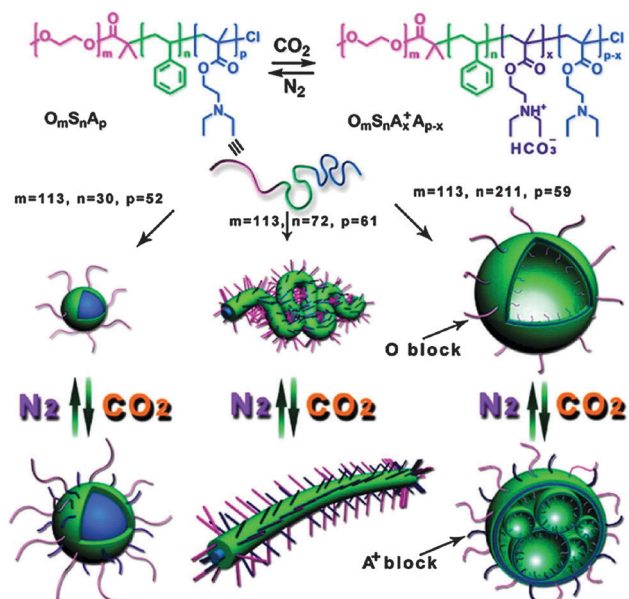


Fig. 17 Construction of CO_2 -stimulated diversiform polymer assemblies. Adapted with permission from ref. 115. Copyright © 2013, American Chemical Society.

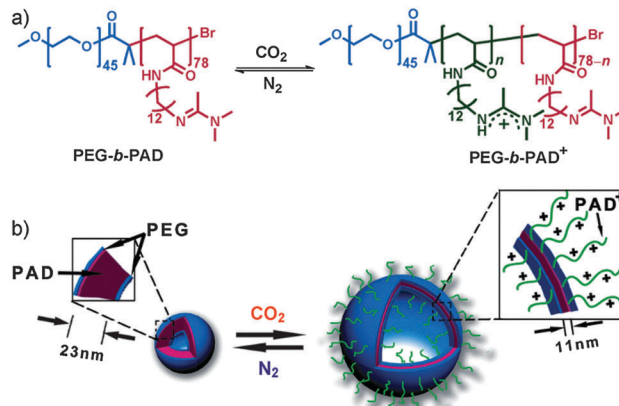


Fig. 18 CO_2 controlled breathing vesicles. Adapted with permission from ref. 117. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

forms vesicles in water which expand as CO_2 is compressed into the solution. This breathing polymersome was further utilized as a size-selective nanoseparator in which the membrane permeability and the scale of membrane nanochannels can be regulated by CO_2 *via* controlling the vesicular expansion and contraction (Fig. 18).¹¹⁷

In addition to bio-mimicking systems, other CO_2 responsive self-assemblies which aim at advanced materials are also developed.^{118–124} One example of CO_2 -switchable worm-like micelles was reported by Feng *et al.*¹¹⁹ The wormlike micelles are based on sodium dodecyl sulfate (SDS) and tetramethylpropanediamine (TMPDA) at a molar ratio of 2 : 1. Pressing CO_2 into the mixed system makes the TMPDA molecules protonated and thus promotes electrostatic interaction between TMPDA and SDS. This supramolecular Gemini-like building block subsequently self-assembles into viscoelastic wormlike micelles. The removal of CO_2 resulted in deprotonation of TMPDA molecules which dissociated the supramolecular Gemini structure. As a result, the worm-like micelles are disassembled and the system becomes water-like fluid. A similar strategy was adopted by these authors to create CO_2 -responsive "smart" single-walled carbon nanotubes. They wrapped carbon nanotubes with a polymer which contains quaternizable nitrogen. Upon pressing CO_2 , nitrogen is charged, which disperses the carbon nanotubes into water.¹²⁴

2.3 Responsiveness to metal ions

The content of metal ions is crucial both for drinking water and biological systems. Therefore, materials that may report the abnormal level of metal ions are of practical use in many areas. Driven by coordination interactions or electrostatic interactions, self-assembling systems are easily designed rationally to interact with metal ions. The adaptivity to metal ions provides possibilities of creating sensors for metal ion detection. Many self-assembled sensors are developed for the detection of metal ions, such as Hg^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , *etc.*

Porphyrin-based self-assembly systems are of special interest for sensing heavy metal ions in aqueous solutions since prominent fluorescence quenching often occurs when metalloporphyrins

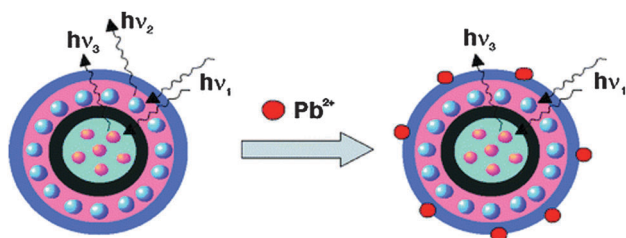


Fig. 19 Self-organized ratiometric nanosensor for Pb^{2+} ions. Adapted with permission from ref. 127. Copyright © 2007, American Chemical Society.

are formed.¹²⁵ For instance, the film of cationic 5,15-(*p*-(9,9-bis(6-trimethylammoniumhexyl)fluorenylethynyl) phenyl)porphyrin tetrabromide can be used for the detection of mercury ions in water.¹²⁶ Upon coordination with Hg^{2+} ions, the fluorescence of porphyrin was quenched dramatically. This allows the detection of Hg^{2+} with a high selectivity over other metal ions.

Fluorescent nanoparticles can provide versatile choices for metal ion detection. Arduini *et al.* utilized silica nanoparticles doped with fluorescent dyes to achieve ratiometric Pb^{2+} detection.¹²⁷ The thiol groups were grafted onto the nanoparticles which provide analyte binding sites for the Pb^{2+} ions while the reporting dyes concentrated in the external shells of the nanoparticles. Upon binding Pb^{2+} ions, the fluorescence of the reporting dyes is quenched while the second dye buried far enough in the core of the nanoparticles was unaffected. With this unaffected fluorescence as the reference signal, this self-organized system exhibits the ability of ratiometric detection (Fig. 19).

Aggregation induced emission (AIE) has been verified as a very efficient way to detect metal ions. AIE dyes are very crucial in this approach. For instance, Sanji and co-workers¹²⁸ attached an azide group to the famous AIE dye of tetraphenylethene (TPE). Upon the addition of Cu^{2+} ions in the mixed solution of azide modified TPE and diethylene glycol dipropionate, click reaction may occur to form intermolecular cross-linked products, which display an intense emission because of restriction of intramolecular rotations (Fig. 20). In this way, a fluorometric sensor for Cu^{2+} detection was invented. In another example of Sun and co-workers,¹²⁹ the TPE compound is exploited to create a Zn^{2+} fluorescent turn-on sensor and then successfully used for intracellular Zn^{2+} imaging.

2.4 Redox responsiveness

Redox responsiveness plays significant roles in biosystems, and has various promising applications in materials science. Thus, the design, synthesis, and modulation of redox responsive self-assemblies have attracted wide interest. Usually, a redox adaptive group should be involved in the materials. Then upon adding an oxidant or a reducing agent, the group changes accordingly, which triggers a change in the structure or properties of the material. So far, many redox responsive self-assembled structures have been reported, here we only briefly review some studies using inorganic elements as redox active centres.

2.4.1 Redox based on ferrocenyl. Organic amphiphiles that contain iron are one of the easiest starting points to build redox

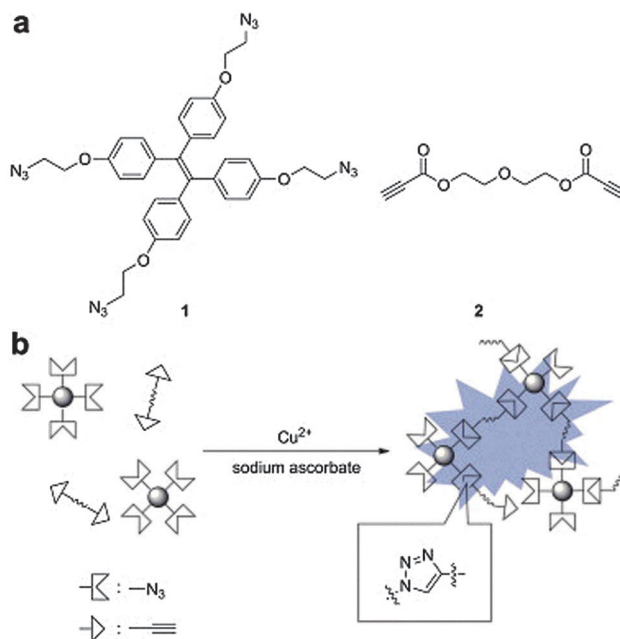


Fig. 20 Fluorescence 'turn-on' detection of Cu^{2+} ions based on click chemistry. Adapted from an open access ref. 128.

responsive self-assemblies. For this reason, amphiphiles containing the ferrocenyl group were widely investigated.^{130–134} Manners and coworkers¹³⁵ (Fig. 21) constructed a redox responsive self-assembly using polystyrene-*b*-poly(ferrocenylphenylmethylsilane)_m diblock copolymers. When more than half of the ferrocenyl units underwent oxidation, spherical micelles with a PFS-PS core-corona structure were obtained. When the polymer blocks were replaced by semicrystalline poly(ferrocenyl-dimethylsilane) (PFDMS) segments, the oxidized systems form ribbon-like micelles instead.

Utilizing the different host-guest behavior of ferrocene with CD, Harada *et al.*²⁸ developed redox-adaptive self-healing materials. Reversible sol-gel switching by redox was realized in the poly(acrylic acid)-cyclodextrins (pAA-CD) and poly(acrylic acid)-ferrocene (pAA-Fc) host-guest system. The hydrogel system then exhibits self-healing capability. Two cut pieces rejoin and form one gel after standing for 24 h. While providing oxidants, the healing process is blocked and no healing is observed after 24 h. Otherwise, by spreading reductants on the oxidized cut surface healing between two cut pieces is observed after 24 h. The oxidized ferrocenium gel is selectively adhered to the gel formed out of styrene sulfonic acid sodium salt by ionic interaction.

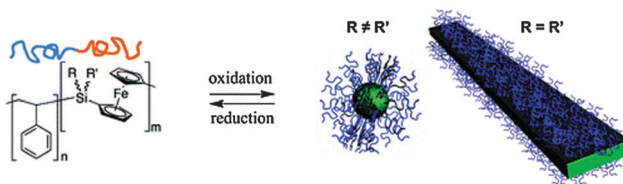


Fig. 21 Redox controlled micellization of polyferrocenylsilane copolymers. Adapted from ref. 135. Copyright © 2011, American Chemical Society.

Thus, an ABC-type macroscopic self-assembly of three sorts of gels (CD gel, Fc gel, and SSNa gel) through two discrete noncovalent interactions is achieved.¹³⁶

2.4.2 Redox based on metal ions. When metal ions on their own are the crucial component for the self-assembled systems, the redox chemistry of the metal ions may affect the self-assembled structures. For instance, when coordination polymers made with iron ions form electrostatic micelles with oppositely charged block polyelectrolytes, a redox stimulus may change the net charges carried by the coordinating centre, which affect the charge balance and the structure of the electrostatic micelles.¹³⁷ Such micelles are envisaged to have potential applications in redox-gated uptake and release systems.¹³⁸ (Fig. 22) Other examples on redox provided by metal ions in the molecular self-assembled systems can also be found from time to time.¹³⁹ Royal and coworkers developed a metallo-supramolecular polymer system that shows a gel–sol transition upon redox-induced change of the valence of the cobalt ions.^{140,141} They used a polytopic ligand cyclam-bis-terpyridine which has two terpyridine units and metal ions as linkages to prepare the coordination polymer. The ligands and $\text{Co}(\text{ClO}_4)_2$ form red gels in DMF with a molar ratio of 1 : 2. The oxidation of the Co^{2+} ions incorporated in the supramolecular polymers caused a transition from the red gel to a green solution, which is reversible. The transition is attributed to the increased positive charges in the polymer after oxidation, which affects the solubility and destabilizes the gels. A self-assembled redox-responsive metallogel based on the copper(II) complex of

quinolinol-substituted L-glutamide with reversible gel–sol transition properties was also reported.¹⁴²

2.4.3 Redox based on selenium-containing amphiphiles.

Recently, the self-assemblies based on selenium-amphiphiles have drawn considerable attention. One of the important reasons is that the mild redox chemistry of selenium may provide the related self-assembly or materials desired for redox adaptivity.^{143,144} Selenium can be covalently incorporated into the backbone of an amphiphile. Upon oxidation, the selenium transforms into the hydrophilic form of $\text{S}=\text{O}$. This greatly alters the self-assembly behaviour of the system, so that redox may trigger desired response in the selenium containing systems. Xu and Zhang *et al.* have done excellent work in this field.¹⁴⁵ For instance, the micelles formed out of a selenium-containing surfactant and a block copolymer PEG-*b*-PAA can be disassembled when subjected to mild oxidative conditions with 0.1% hydrogen peroxide.¹⁴⁶ This strategy can be transmitted to many molecular structures. For instance, if the selenium was incorporated into the side-chain of an amphiphilic block copolymer, redox responsive polymeric micelles can be generated.¹⁴⁷ Alternatively, if the selenium is put into peptide, the self-assembled nanostructures display catalytic activity, and this performance can be reversibly regulated by the redox stimuli couples of hydrogen peroxide/vitamin C (Fig. 23).¹⁴⁸ The redox switchable nature of selenium also provides the change in the self-assembled structure by Feng *et al.*, which can be used to regulate the gel-solution phase transition.¹⁴⁹

2.5 Explosive detection by adaptive self-assembly

The detection of explosive chemicals including compounds like nitro-organics and nitramines attracts wide attention for homeland security and public safety.^{150,151} For this reason various chromic self-assembled structures that are responsive to the explosive targets have been developed. For the convenience of application, the change in the luminescence signal is often employed in various explosive detections. The dominant mechanism of detection is the static quenching process which occurs through the formation of the charge-transfer complex between the fluorophores and the electron-deficient explosive molecules.^{152–154} The mechanism was proved by fluorescence lifetime, UV-vis absorption measurement, and molecular dynamic simulations.

Dyes containing AIE groups have been widely employed recently in the detection of explosives.^{155–158} These dyes show

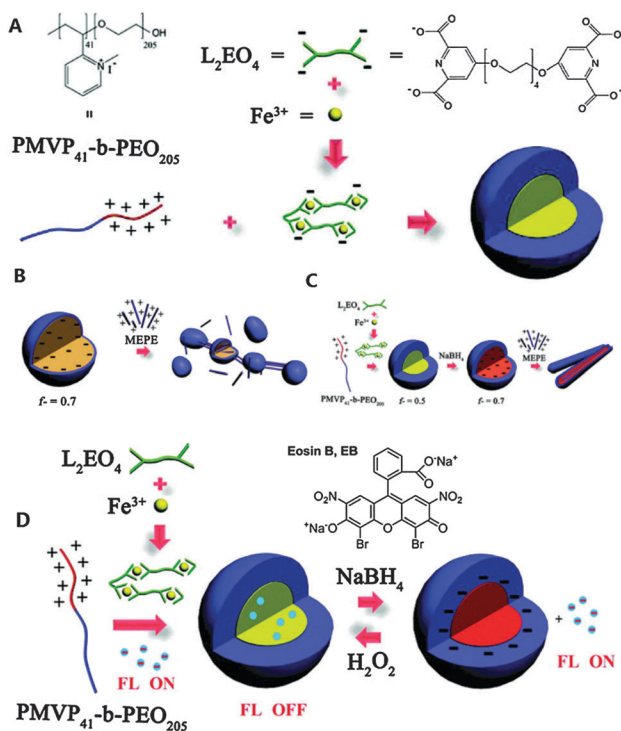


Fig. 22 Uptake and release $\text{L}_2\text{EO}_4\text{-Fe}^{3+}$ system. (A)–(C) Adapted with permission from ref. 137 (D) Adapted with permission from ref. 138. Copyright © 2012, American Chemical Society.

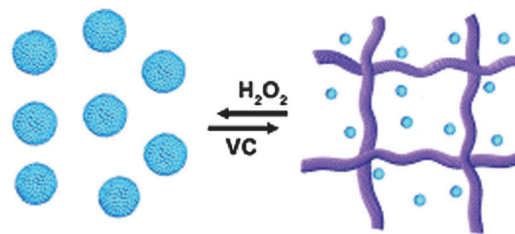


Fig. 23 Reversible formation of the nanostructures of the selenium-containing peptides. Adapted with permission from ref. 148. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

luminescence when their rotation is restricted, either by fixing to a solid material or entrapment in a molecular self-assembly. Tang *et al.* reported the superadaptive detection of explosives by AIE luminogen-functionalized mesoporous materials.¹⁵⁹ In their work, mesoporous silica SBA-15 and AIE luminogen tetraphenylethene (TPE) are connected *via* covalent chemical bonding. These TPE-functionalized mesoporous materials exhibit strong fluorescence, yet fluorescence can be quenched drastically by trace amounts of picric acid. Pei *et al.* found that when the AIE dyes self-assemble into nanostructures, control over the self-assembled structure may become an approach to tune the detection limits. In their work, an oligoarene derivative may self-assemble into 1D microbelts and flowerlike supernanostructures *via* the solution process.¹⁶⁰ As the nanostructure can be transformed from the one-dimensional microbelts to the flowerlike structures, the detection speed for dinitrophenol (DNT) and TNT can be enhanced 700 times. In analogy, Takeuchi and coworkers¹⁶¹ synthesized a fluorescent organic molecule consisting of binaphthyl functionalized with donor-acceptor stilbenes. As the self-assembled structure changed to entangled fibrous structures, nearly 9-folds increase in fluorescence was achieved in the detection of explosive vapor. Similarly, Liao *et al.* also reported a size tunable fluorescent sensor based on oligotriphenylene nanofibers. The sensor can be used for the detection of nitro-based explosives such as nitromethane, nitrobenzene, and 2,4,6-trinitrophenol both in dispersions or oligotriphenylene/polysulfone composite films with satisfactory selectivity and sensitivity.¹⁶²

Appropriate self-assembled structures also allow selective detection of explosives. As an example, Wang *et al.* introduced a facile and versatile method to selectively detect trinitrophenol (TNP) among other explosive molecules such as TNT and DNT (Fig. 24).¹⁶³ They constructed a composite nanosphere with bluish green fluorescence based on 8-hydroxyquinoline aluminium. This molecule self-assembled under stirring and ultrasonic treatment. Dramatic fluorescence quenching can be observed only upon the addition of TNP into the aqueous solution of nanocomposites, rather than the addition of other explosives such as TNT and DNT, which finally becomes a convenient and rapid selective paper sensor for TNP detection.

2.6 Adaptivity to other biological components

Other than examples listed above, adaptive self-assembly systems that are responsive to important biological compounds also developed in virtue of medical desires.

Dopamine (DA) is an important neurotransmitter in mammalian central nervous systems.^{164,165} The concentration of DA in biological fluids for healthy people and patients with disease such as Parkinson's disease may be completely different^{166,167} and thus the detection of DA may offer important information for diagnosis and therapy. A J-aggregate nanotube is fabricated by means of self-assembly from lithocholic acid and 3,3'-dipropylthiadicarbocyanine iodide in water.¹⁶⁸ The J-aggregate nanotube can then be used as a probe to selectively detect dopamine in phosphate buffered saline solution, with a

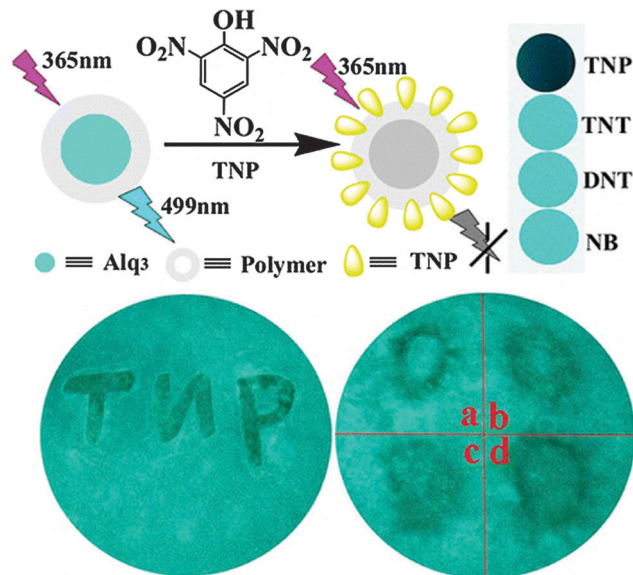


Fig. 24 Composite nanospheres with bluish green fluorescence that can detect TNP selectively. Adapted with permission from ref. 163. Copyright © 2012, American Chemical Society.

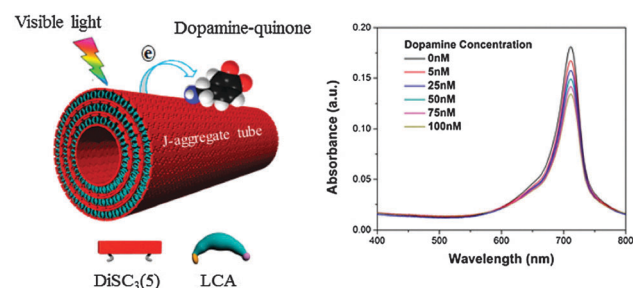


Fig. 25 J-Aggregate nanotube and sensing dopamine. Adapted with permission from ref. 168. Copyright © 2014, American Chemical Society.

detection limit of ~ 0.4 nM by observing the intensity change of the J-band, which attributes to the efficient photoinduced electron transfer process between the nanotubes and the adsorbed DA (Fig. 25).

The specific detection of D-glucose can be realized by a tetraphenylethene-based fluorescent sensor developed by Tang *et al.*¹⁶⁹ When oligomerized with Glu, the emission of tetraphenylethene-cored diboronic acid they synthesized is greatly boosted. The enhancement of emission is related to restriction of the intramolecular rotations of the TPE molecule by the formation of the oligomer. Otherwise when the TPE cored acid was mixed with D-fructose, D-galactose, or D-mannose, little change of the emission intensity was observed as no oligomerization occurred.

Other biomolecules can also be detected using adaptive self-assembly methods. For instance, the detection of proteins,^{170–174} nucleic acids,^{175–177} *etc.* has also been widely reported. Like the enzyme responsive self-assemblies, self-assembled materials which are able to respond to certain biomolecules are expected to have great potential in the treatment of disease.

3. Field adaptiveness

Materials in practical applications are always subjected to certain external physical fields such as light irradiation, shear forces, electric fields, or magnetic fields. This means that the performance of materials is inevitably affected by external fields. Developing materials response to various fields then has an apparent significance in different applications.

3.1 Light adaptiveness

Light provides energy and external stimuli to a microscopic system facilely *via* macroscopic means.¹¹ Materials that are adaptive to light may have many practical applications such as remote control, sensing, self-healing, *etc.* In order to create a material that is adaptive to light, a molecule that contains photo-responsive portion should be employed. The responses can be *trans-cis* isomerization, bond cleavage, or transcription. These structural changes triggered by light further leads to change in microstructures thus bulk properties. According to the molecular mechanism of light responsiveness, this section is discussed in the following three parts.

3.1.1 Adaptiveness triggered by photo-responsive bond-cleavage. Light induced bond-cleavage may change the self-assembly behaviour of the mother molecules. The spirocyan group is often employed to achieve this goal.^{178–180} The spirocyan surfactant SP-Me-6 has two reversible forms, namely, merocyanine (MC) and spiro (SP), which are stable under visible light and in the dark, respectively (Fig. 26).¹⁸¹ The MC form forms disk-like spherical aggregates when adsorbed on a flat silica plate while the more hydrophobic SP forms larger aggregates. Photoisomerization occurs reversibly and is expected to be applied in smart surface coatings. So far light-induced bond-cleavage has been employed as an efficient approach to fabricate smart materials.^{182–186} For instance, Zhang *et al.*¹⁸⁷ utilized the photoreactive malachite green derivative to form SA with the block copolymer PEG-*b*-PLKC. This SA further self-assembled into sheet-like structures (Fig. 27). Under UV irradiation, the malachite green derivative transformed into ionic species, thus lead to disassembly of the aggregates.

Light induced bond-cleavage may also be utilized to fabricate nanoparticles. Eastoe *et al.* reported a photoreactive surfactant cobalt 2-ethylhexanoate^{188,189} which can form reverse micelles in a hydrocarbon solvent. It can also form mixed reversed micelles with AOT. Electron transfer from the surfactant to the associated

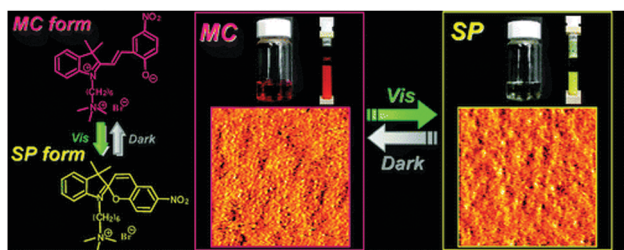


Fig. 26 Photoreisomerization surfactant system. Adapted with permission from ref. 181 Copyright © 2010, American Chemical Society.

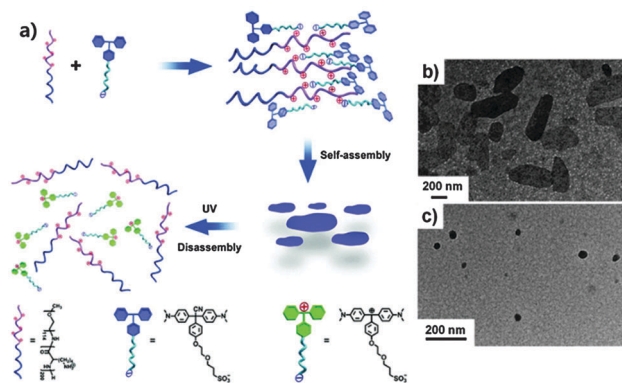


Fig. 27 Photoresponsive SA system. (A) Scheme of the photoresponsive system. (B) TEM image of the SA system with charge ratios of 1:1. (C) TEM image after UV. Adapted with permission from ref. 187. Copyright © 2011, American Chemical Society.

metal counterions is promoted by excitation of the ligand-to-metal charge transfer (LMCT) band in the photoreactive surfactant. This led to the generation of metal and metal-oxide nanoparticles inside the reversed micelles. The photoreactive surfactants are then exploited as precursors to obtain nearly monodisperse inorganic nanoparticles. This approach was expected to be a new straightforward route to the generation of nanomaterials.

3.1.2 Photo-triggered isomerization. In many photo-reactions, the bond doesn't cleave but only rotates to a different configuration. Photo-triggered isomerization belongs to this category. The change of molecular conformations may affect their packing in the self-assembly, which lead to a different structure.^{190–194} Using this strategy, Raghavan *et al.* developed a class of photoresponsive systems based on the mixed self-assembly system of a cationic surfactant and photoisomerizable *o*-methoxycinnamic acid (OMCA).^{195,196} In their work, aqueous mixtures of cetyl trimethyl acid bromide (CTAB) and OMCA self-assemble into long, wormlike micelles in basic solution. Upon UV irradiation, OMCA underwent *trans* to *cis* isomerization which altered the molecular packing in the micelles and resulted in the transformation from wormlike micelles to much shorter entities. This led to a sharp decrease in viscosity by more than 4 orders of magnitude. As the surfactant CTAB is replaced by erucyl dimethyl amidopropyl betaine (EDAB), the system displayed photo-gelling properties.¹⁹⁵ UV light triggered desorption of OMCA from EDAB micelles enabled the wormlike micelles to grow longer and entangled to form a network which resulted in the gelation of the solvent.

Using the photoisomerization of the azobenzene group, Huang *et al.* achieved self-assembly transition in multi-scale.¹⁹⁷ They introduced sodium (4-phenylazo-phenoxy)-acetate (AzoNa) to the aqueous solution of CTAB (Fig. 28). The *trans* and *cis* binary state of the azobenzene group induced the formation of multi-state nanostructures including wormlike micelles, vesicles, lamellae, and oblate micelles depending on the irradiation time. Correspondingly, the system appears as viscoelastic, biphasic, and water-like solution. This approach clearly demonstrated that the change in molecular scale affects structures in meso- and macroscopic scale.

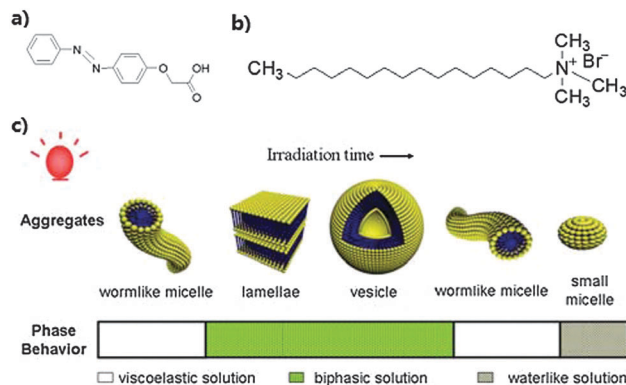


Fig. 28 Structural evolution and phase behavior in the solution of AzoNa system varied with UV irradiation time.¹⁹⁷ Copyright © 2010, Royal Society of Chemistry.

The *trans*-*cis* isomerization of azo-benzene derivatives has been employed in a large variety photo-responsive self-assemblies and materials, such as photo-responsive surfaces,^{198–201} photo-responsive machines,^{202–204} *etc.* Recently Huang *et al.* utilized the photo-triggered *trans*-*cis* isomerization of the butyl azobenzene amphiphile which contains a pseudo-sugar head group (C4AG) and achieved vesicles with cilia.²⁰⁵ The cilia were developed upon exposure of the normal vesicles to UV light. They found that this unique structural deformation originated from the disassembly of C4AG from CD as the azobenzene group underwent *trans*-*cis* isomerization. Since this photo-reaction is reversible, the cilia also displayed on-off behaviour, which stretch and contract just like the cilia of living virus. The cilia have been verified actually as double helices of CD-*cis*-C4AG, which seem very similar to the helices formed by *trans*-C4AG in their previous work (Fig. 29).^{206,207}

3.1.3 Photo-triggered bond reformation – a self-healing system. As an external stimulus, light not only provides necessary energy for bond-cleavage or bond-rotation, but also produces heat in case the energy doesn't meet the requirement to cause changes in bonds.^{29,30} Burnworth *et al.* smartly employed the heat produced by light to create an optically healable supramolecular polymer²⁰⁸ (Fig. 30). They synthesized a series of metallosupramolecular polymers that can be mended through exposure to light. The supramolecular polymers are telechelic, rubbery, low-molecular-mass polymers with ligand end groups that are non-covalently associated with coordination bonds. The energy brought by ultraviolet light is absorbed and converted

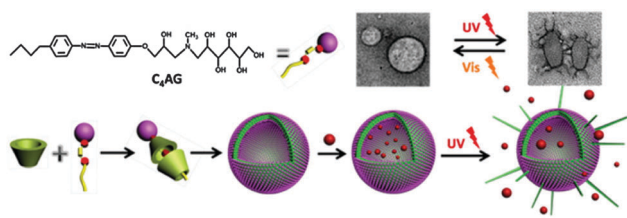


Fig. 29 Scheme of the self-assembly of bacteria-like vesicles with photo-switchable cilia as smart nanocarriers. Adapted with permission from ref. 205. Copyright © 2014, American Chemical Society.

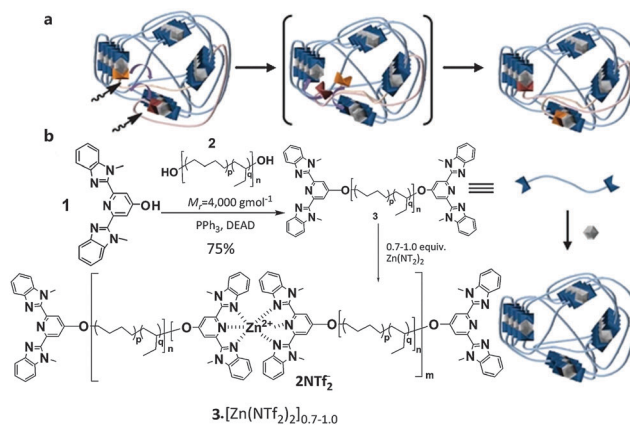


Fig. 30 Mechanism and synthesis of photohealable metallosupramolecular polymers. Adapted with permission from ref. 208. Copyright © 2011, Nature Publishing Group.

into heat in the metal-ligand motifs, which causes temporary disengagement of the motifs and thereby allowing a quick and efficient self-repairing process. As light can be applied locally to the damaged places, this optical healable system shows possibility of exclusively exposing and healing the damaged region.

3.2 Adaptiveness to the magnetic field

The magnetic field has been found to affect the growth, morphology, and self-assembly of many nanoparticles and electrical materials.^{209–213} Vilfan and co-workers²¹⁴ introduced an advancement of artificial biomimetic cilia which are constructed from spherical superparamagnetic colloidal particles. These particles self-assemble in an external magnetic field into flexible and stable long chains and mimic a ciliated surface with limitations of motion due to the generation of fluid flow. Either by individually trapping the superparamagnetic beads by optical tweezers or just letting the particles to self-assemble by themselves in the external field, arrays of long chains of the particle beads are obtained with self-healing ability to repair shorter cilia with beads presented in the surrounding fluid. Switching on and off the external magnetic field enables the disassembly or reassembly of the cilia.

Klajn *et al.* developed dual-responsive nanoparticles adaptive to both light and magnetic stimulus.²¹⁵ The nanoparticles are designed to achieve magnetic interactions between each other by the superparamagnetic Fe₃O₄ cores and respond to light stimuli by exploiting the photoresponsive ligands, azobenzene-catechol (AC), attached to the surface of the cores. The nanoparticles (NPs) form spherical aggregates in toluene induced by the electric dipole interactions between *cis* azobenzenes. When exposed to UV light the initial aggregates assemble together to form larger aggregates which show reversibility in UV-vis cycles. (Fig. 31A). Moreover, the AC-NPs formed one-dimensional assemblies when exposed to both light and the magnetic field.

Xu and coworkers designed an interfacially active and magnetically responsive nanoparticle which can be used for multiphase separation applications. Created from bromoesterified ethyl cellulose and amino-functionalized magnetite nanoparticles,

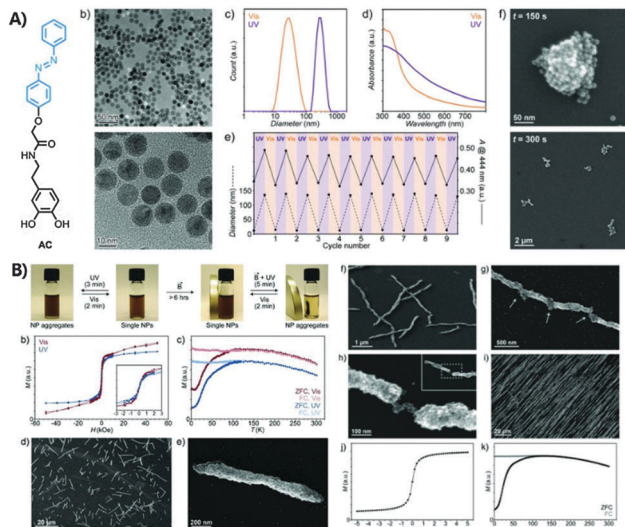


Fig. 31 (A) Light-induced self-assembly of magnetite NPs (B) Assemblies when both exposed to light and magnetic field. Adapted with permission from ref. 215. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

the magnetically responsive nanoparticles at the interface oil/water can tune the interfacial properties by the external magnetic field. The nanoparticles can occupy the interface and thus allow separation of water from emulsions due to the effect of the magnetic field.

Christianen *et al.* reported self-assembled nanocapsules that exhibited the properties of deformation in the magnetic field.²¹⁶ The spherical nanocapsules were self-assembled from bolaamphiphilic sexithiophene molecules and these spheroids can deform in magnetic fields in organogels. This result shows that the magnetic forces are ideal for supramolecular assemblies in solution in a contact-free and noninvasive manner.

3.3 Adaptiveness to electric fields

The electric field can be a versatile tool to direct the assembly of colloidal nanoparticles by inducing interactions or can be used as a stimulus for the specific responsive systems.^{217–219} For instance, a novel temperature and electric field dual-stimulus responsive nanoparticle system for programmed drug delivery was developed by Zare *et al.*²¹⁷ The nanoparticles are prepared from a conducting polymer, polypyrrole. Loaded with therapeutic pharmaceuticals and localized *in vivo* with a hydrogel PLGA-PEG-PLGA, the conductive nanoparticles can be controlled by a weak external DC electric field to perform a drug release process. The mechanism of this electric field-induced drug release is explained to involve a synergistic process of electrochemical reduction/oxidation and electric-field-driven movement of charged molecules.

The application of electric fields can also be employed to modulate the fabrication of aggregates. Yuan *et al.* developed voltage-responsive vesicles based on the orthogonal assembly of two homopolymers.²²⁰ Two end-decorated homopolymers, poly(styrene)- β -cyclodextrin and poly(ethylene oxide)-ferrocene, form vesicles in aqueous solution by a hierarchical self-

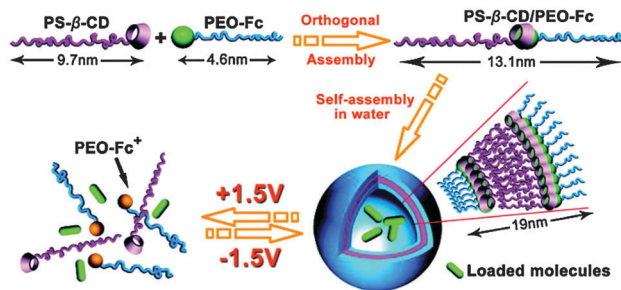


Fig. 32 Electric field-controlled assembly and disassembly of a supra-molecular vesicles. Adapted from ref. 220. Copyright © 2010, American Chemical Society.

assembly process (firstly form a supramolecular diblock copolymer by host-guest interaction, then vesicles). The aggregation behaviors are controlled to switch by application of voltage, which affects association and disassociation of the connection of the two polymers that finally end up with the assembly or disassembly of the vesicles (Fig. 32).

3.4 Shear force adaptive materials

Self-assembled materials which are adaptive to shear force may exhibit changes in viscosity.^{221–223} This property is extraordinarily important in applications because the decreased viscosity makes it possible to transport the materials easily while viscosity can be retained without shear force.²²⁴ For example, shear thinning hydrogels²²⁵ which exhibit rapid recovery after the cessation of shear are attractive materials for use as injectable biomaterials. The physical essence behind this macroscopic phenomenon is actually the transition of self-assembled structures under shear.

The influence of shear force on self-assembled structures is mainly systematically studied by Hoffmann *et al.*^{226–230} They found that the self-assembled structures in the charged tetradecyl dimethyl ammonium oxide (C14DMAO) and the long chain alcohol (CnOH) system is flat layers if the charging process is achieved by releasing protons to the system *via* a chemical reaction, where the system is not stirred or shaken, namely without any shear. However, if the system were shaken by hand, one would only get spherical vesicles. This investigation has been done for the first time to experimentally prove that shear force have significant effect on the self-assembled structures.

In fact, in terms of fluid, shear induced fluidity changes are well known and have a long history. The most famous phenomena include shear thinning or shear thickening. Nevertheless, a shear induced micro-structural change is the basis of these phenomena. Nowadays people are able to utilize this principle to design shear responsive materials, for instance, shear thinning artificially engineered protein gels reinforced by self-assembled polymer networks from inside developed by Glassman *et al.*²³¹ The gels exhibit a responsive transformation between the injectable state and the stiffened state. In this work, thermoresponsive block copolymers are utilized to form a second reinforcing network inside the protein-based hydrogels. PNIPAM was

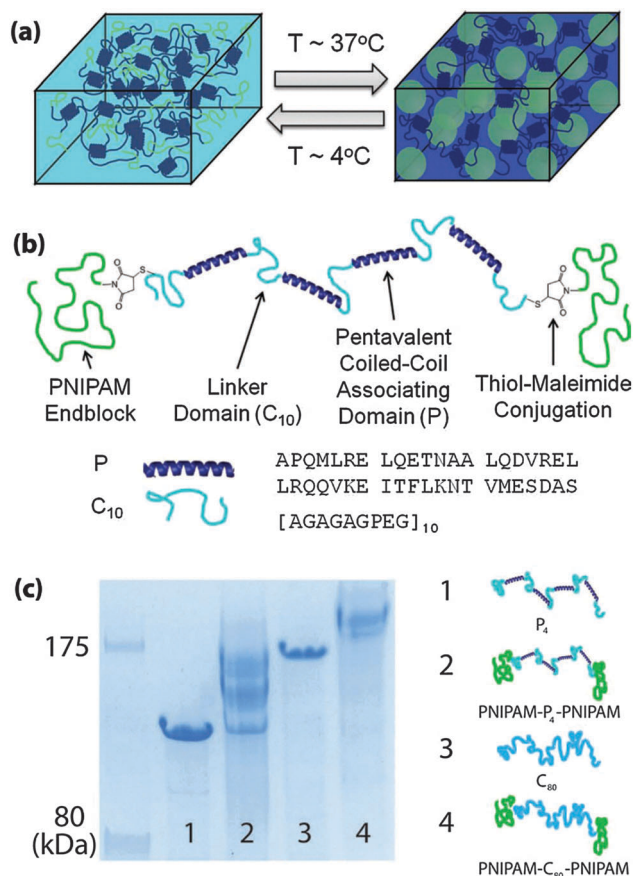


Fig. 33 Responsive self-assembly of PNIPAM within a physically associating protein gel to reinforce the shear thinning gels. Adapted with permission from ref. 231. Copyright © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

conjugated to the protein and produce a triblock copolymer. Thus two independent networks were formed from a single molecule by the hydrophobic association of the PNIPAM blocks and the specific interactions of the coiled-coil of the middle protein block orthogonally. At low temperature, the hydrogel is soft and fragile with shear thinning properties, while a gel-gel transition makes the gel reinforced and tougher at physiological temperatures (Fig. 33).

Polymers can also be transformed into colloidal particles to produce shear responsive colloidal gels.²³² For instance, a colloidal gel was prepared from two oppositely charged nanoparticles of poly(D,L-lactic-co-glycolic acid) (PLGA), one is coated with positively charged polyvinylamine, while the other is coated with negatively charged poly(ethylene-co-maleic acid).¹⁸⁵ The two nanoparticles self-assemble, driven by electrostatic attraction, and form interconnected ring-like structures. The colloidal gels show shear thinning properties as the network is destroyed when under shear stress. After the removal of the shear force, the networks self-healed spontaneously which enables the modification of gels (Fig. 34).

4. Conclusion and perspectives

Soft materials based on various molecular self-assemblies have already exhibited significant advantages compared to their

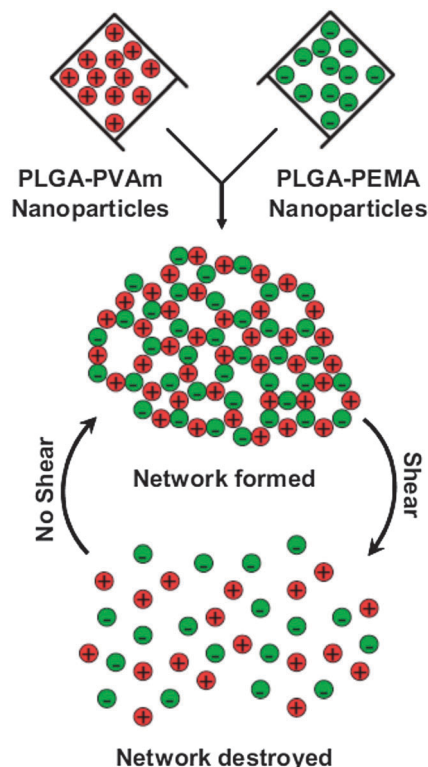


Fig. 34 Shear responsive colloidal gels prepared from oppositely charged nanoparticles. Adapted with permission from ref. 232. Copyright © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

traditional covalent counterparts and have shown great potential for application in smart and functional materials. The unique properties such as reversibility and responsiveness brought by non-covalent interactions are intrinsic for adaptive self-assemblies. While a great number of fancy ideas and implementations have emerged in this area, only a small number of approaches of adaptive molecular self-assembly are included in this review, but we hope these examples may provide the general principle in designing various self-assembled materials and reflect current situation about this blooming field.

For future advances in this field, more accurate control on their structural construction and functions is highly demanded. How to get more precise control on the non-covalent interactions and how to manipulate them to make them act in a desirable way? We should admit that while providing highly responsive and dynamic properties, non-covalent interactions also form soft materials generally due to the lack of robustness. To construct molecular self-organized systems with satisfactory robustness meanwhile retain their intrinsic adaptivity is still a challenging problem.

The achievements on adaptive molecular self-assembled materials so far are fascinating and very impressive, but all these contributions are only at the earlier stage in terms of real materials science. Many issues still remain unsolved, such as increasing the recycling life, allowing adaptiveness to a wide spectrum of stimuli, enabling smart on-off behaviours, improving the sensitivity to stimuli, and so on. Any way, compared

with biological reactions toward an external stimulus, the responsiveness achieved by artificial self-assembled materials is still very limited. In recent days, Mann *et al.*^{233–240} are devoted to create much advanced self-assembly systems that may exhibit more effective performance, yet there is still a long way to go to systematically design and construct the complicated systems. It envisages that delicate designs which embody the wisdom from different fields, especially those from biology and materials science in combination with chemistry, are required to push revolutionary progress in this field.

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