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Adaptive Soft Molecular Self-Assemblies

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ABSTRACT: Adaptive molecular self-assemblies provides possibility to construct smart and functional materials in a non-covalent bottom-up manner. Exploiting the intrinsic property of responsiveness of the 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 enzyme, CO_2, metal ions, redox agents, explosives, biomolecules; (3) Field adaptiveness, including self-assembled materials that are able to be adaptive 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 associate 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 chorus of multiple non-covalent bonds can still construct robust systems[18]. Moreover, the dynamic nature of the non-covalent interactions can be exploited to design adaptive systems, since the environmental sensitivity of non-covalent bonds make the systems willingly to respond to external stimuli [19]. These finally result in changes both in structure and function for 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 materials[20] in various fields such as controlled-delivery[21-23], sensors[24-26], self-healing materials[27-30], piezoelectronic devices[31], mechanochroism[32, 33], or stimuli responsive devices[34].

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 membrane structure and function changes correspondingly when a signal arrives. For artificial materials, the general idea for 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 potentials [35]. In this review, we briefly summarize recent progress in fabrication of advanced materials or molecular devices that are adaptive to environments, special chemicals, and external stimulus.

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 ‘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 adaptive to environmental changes to lead to potential applications.

1.1 pH adaptiveness

Nature and biological systems employ pH variation to reach their functions. For instance, the seasoning change of colour for leaves can be attributed to the variation of pH in cell liquid; 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 vesicle to micelle transition 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 are emerged 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 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, they [42] utilized a dynamic covalent bond to fabricate a bola-form superamphiphile from 1-(10-(4-formylphenoxy)decyl)pyridinium (FDP) and 1-(10-(4-(ammoniomethyl)phenoxy)decyl)pyridinium (AMDP). At basic conditions, the two molecules can be connected by a dynamic benzoic imine bond to form a bola-like superamphiphile with a hydrophilic – hydrophobic – hydrophilic structure. 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.

Similar strategy was also adopted by them to fabricate a toothbrush-type SA[43]. In this approach, methoxy-poly(ethyleneglycol)114–block–poly(L-lysine hydrochloride)200 (PEG–b–PLKC) and 4-(decyloxy)benzaldehyde (DBA) was chosen to be the two components of the supramolecular building block which was also connected by 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 micelles[46] based on dynamic surfactant are also obtained by J. H. van Esch and coworkers. In their progress, 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 Gemini surfactant that looks like the dimmers 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. (Figure 1).

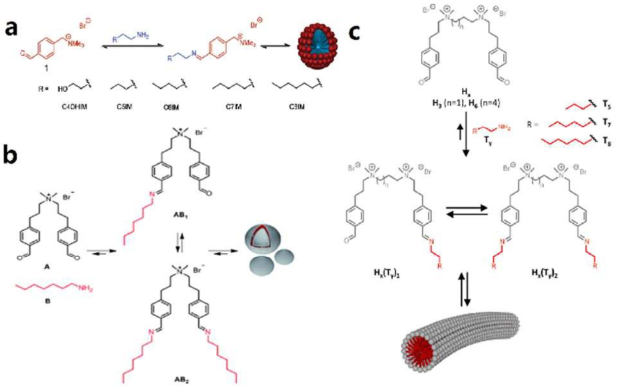

Figure 1. pH-responsive dynamic amphiphiles. (A)Micelle formation. (B)Vesicle formation. (C) Wormlike micelles formed by dynamic gemini surfactants. Adapted with permission from ref. [44-46]. Copyright © 2009 and 2012, American Chemical Society[44, 46] and © 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim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

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-workers[51] reported an example of pH-responsive multifunctional three-layered nanoparticles (3LNPs). The 3LNPs have a poly (e-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 a core-layer-layer structure. As a nanocarrier, 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 is blocked by 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. (Figure 2) Using elegantly designed molecules, Feng et al is 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 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 formation of pseudo Gemini surfactants, which displays extremely pH adaptiveness compared with conventional Gemini ones.[53]

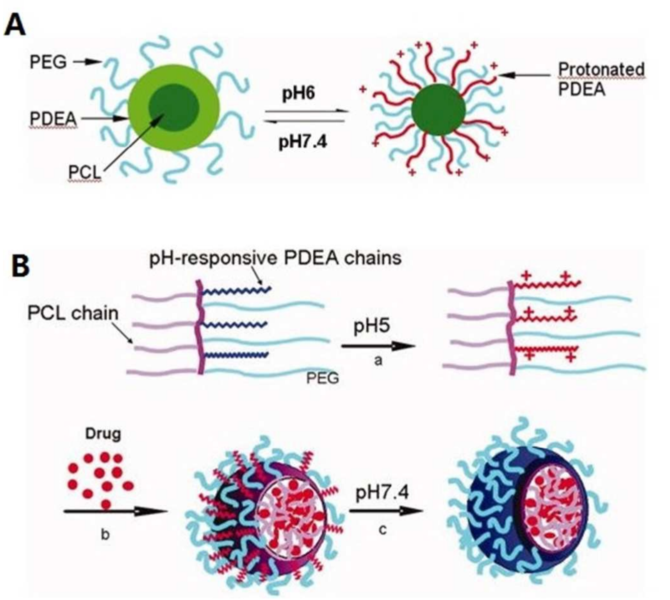

Figure 2. 3LNPs. (A) pH adaptive 3LNPs. (B) The drug release process of the drug-loaded system. Adapted with permission from ref. [51]. Copyright © 2008, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim [51].

pH responsiveness not only produces structural differences to materials, it can also be smartly related to the functions. For instance, Zhou and Zhu et al.[54] have 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 (Figure 3). The vesicles exhibit "breathing" property which is a size change accompanied by corresponding changes in light-emitting triggered by variation of pH.

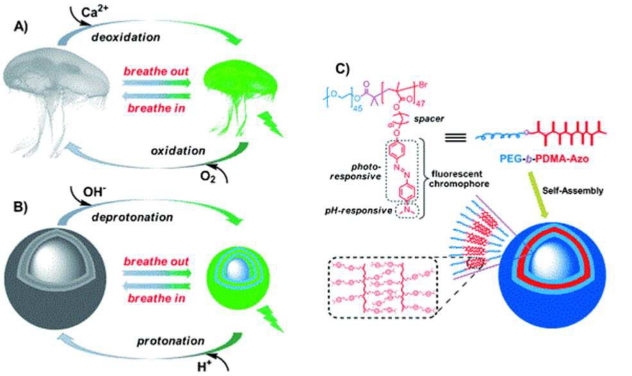

Figure 3. "Breathing" Vesicles. (A) Breathing process of the jellyfish. (B) pH-promoted "breathing" process of the vesicles. (C) .Schematic representation of the amphiphilic copolymer and the structure of the vesicle. Adapted with permission from Ref. [54] Copyright: 2012 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim [54].

1.1.3 pH responsiveness facilitated by small molecules

Except designing complicated molecules, Huang and coworkers[55] 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 switched between a gel-like state and a water-like state within a narrow pH range. Raghavan and co-workers[56] have developed similar method to impart pH-responsive properties to gels of biopolymers by embedding fatty-acid-based pH-adaptive vesicles into the gels. The nanosized vesicles contained in the gels exhibit a pH-responsive vesicle-micelle transformation. This enables capability of pH-dependent controlled release of the vesicle-loaded gels.

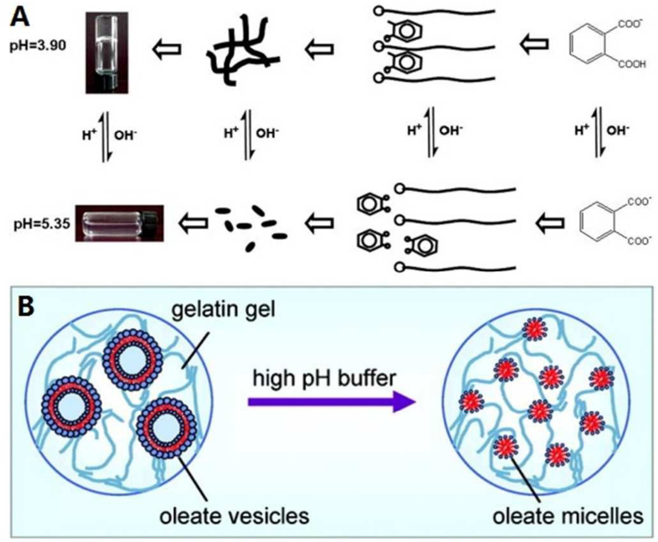

Figure 4. Examples of pH responsiveness facilitated by small molecules: (A) pH-responsive viscoelastic wormlike micelles based on commercial compounds by J. Huang et al. (B) pH-responsive vesicle-micelle transformation which enables capability of pH-dependent controlled release of the vesicle-loaded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

1.2 Thermo adaptiveness

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, the heat accompanied with temperature change can be a convenient and efficient source of external energy, which may drive 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 its 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 dimmers in toluene. The hydrogen bonding groups are associated with multi-functional molecules and finally form supramolecular polymers with high degrees of polymerization (Figure 5). Heating this supramolecular polymer resulted in the breaking of hydrogen bonding which depolymerize the structure. A reverse process was realized upon cooling.

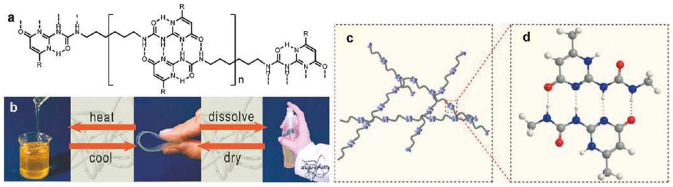

Figure 5. Thermoreversible supramolecular polymer rely on quadruple hydrogen bonds[65]. Copyright © 2008, Nature Publishing Group.

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 bonds. 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 easily to be re-used and recycled (Figure 6).

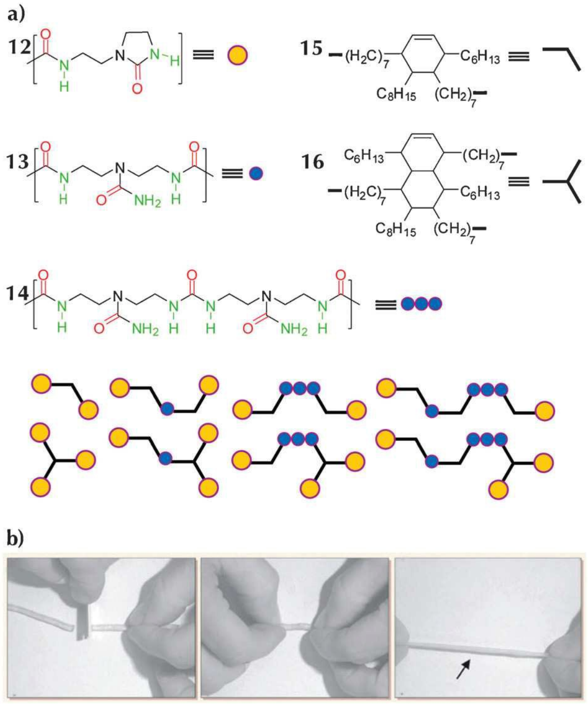

Figure 6. Self-healable and thermoreversible supramolecular rubbers[27]. Copyright © 2008, Nature Publishing Group.

1.2.2. Thermo-responsive colour change

The response of hydrogen bonds also leads to change of the electronic structure of the materials[64, 67]. An interesting example can be found in the photo-functional nanomaterials made with polystyrene-block-poly(4-vinylpyridinium methanesulphonate), (P4VP(MSA)) and 3-n-pentadecylphenol (PDP)[68]. P4VP(MSA) and PDP associated by hydrogen bonds forms highly ordered arrays which has a long lamellar period. This material is green at room temperature due to the photonic band-gap brought by the periodic structure. Upon heating, the breaking of hydrogen bonds leads to a sharp and reversible transition to uncoloured material due to the destruction of the lamellar structure. This adaptive nanomaterial is potentially useful for creating sensors and thermo-responsive materials.

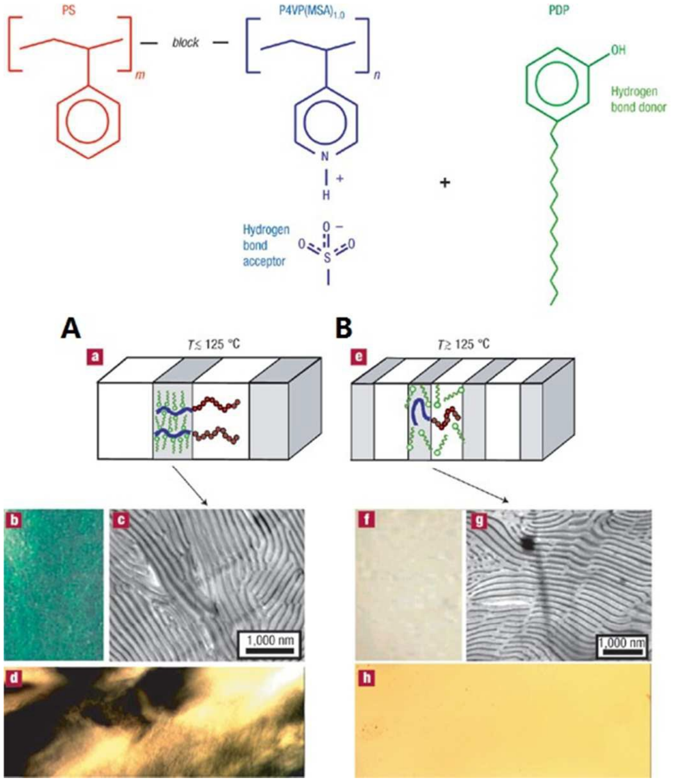

Figure 7. Thermo-responsive color change of the P4VP(MSA) and PDP system. (A) Green material with periodic structure. (B) uncolored material due to the destruction of the lamellar structure. Adapted from Ref[68]. Copyright © 2004, Nature Publishing Group.

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 of the self-assembly of beta-cyclodextrins (beta-CD) and amphiphic molecules[69-73], a temperature-controlled transition between SDS@2beta-CD microtubes and vesicles[74] has been developed, which provides us with a new prospective of stimuli-adaptive chemistry in inclusion complexes based on CDs. Moreover, the CD-amphiphiles inclusion system can be used to assemble colloidal spheres thermo-reversibly[75]. In this approach, the co-assembly of spherical colloids and surfactant-cyclodextrin microtubes yields a library of dynamic colloid-in-tube structures including helices (Figure 8), while de-assemble can be achieved simply by heating the system.

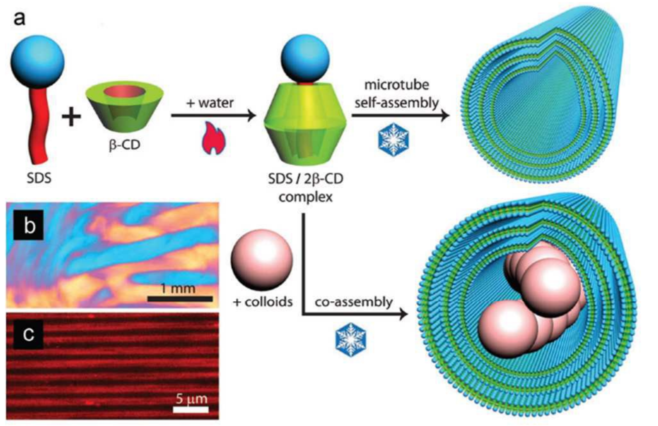

Figure 8. Thermo-reversible co-assembly of microtubes and colloids.[75] Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Heat induced nanostructure transition also leads to change in the bulk materials. In 2011, Huang and coworkers[76] has 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 gel the water. Upon increasing the temperature, both the width and length of these one dimensional structures increase, which enhances the stiffness of the hydrogel. Similar principle was also found in the thermal induced gelation of palmitylamidosulfobetaine by feng et al [77]. Micellar growth from globular aggregates to entangled worms upon heating is responsible for the thermal gelation.

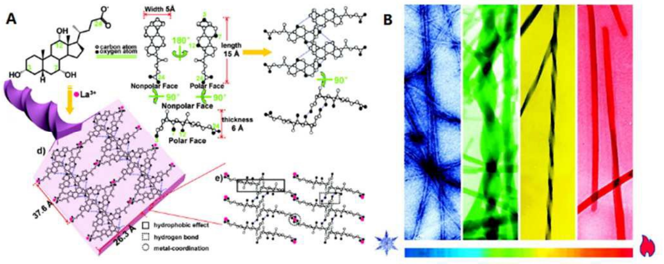

Figure 9. Temperature-dependent one dimensional architectures. (A) The scheme of the twisted nanoribbon. (B) Representative Scheme of Temperature-Dependent Nanostrucutural Evoluation of the Hydrogel. Adapted from ref[76]. Copyright © 2010, American Chemical Society.

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 of cracks.

1.3.1 Moisture responsive layer-by-layer (LBL) films

The first case of moisture responsive materials is probably reported by South and Lyon who demonstrated a hydrogel thin film[78] which could undergo a rapid healing process responsive to water exposure. 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 results in rupture of polyanion-polycation interactions. The dissociation leaves the particles excess positive charges and makes the films to be heterogeneous in terms of overall charge. After resolvation, the increased polymer mobility promotes redistribution of the charges in order to lower 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 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 exhibited high flow ability therefore allows repairing 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. Typical examples in 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 were protected and bridged together by the water soluble B block to from neutral hydrogel at charge balancing ratio. As a result, any damage to this hydrogel has to detach one A block from the neutral coacervate domain, which leads to separation of the positive and negative charges. Upon addition of water, the increased chain mobility immediately allows re-combination of the 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-group as guest moieties were synthesized in this approach. When putting pieces of host-gels and guest-gels together in water, they are proven to adhere to one another by molecular recognition between three kinds of cyclodextrin and three different hydrocarbon groups. By this way different gels can be assembled and sorted into macroscopic-sized structures selectively by microscopic interactions. (Figure 10)

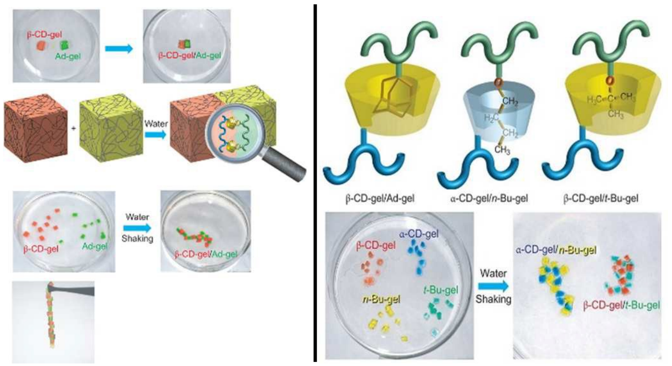

Figure 10. Macroscopic self-assembly of gels and selectivity. Adapt from Ref.[81] Copyright © 2010 Nature Publishing Group.

1.4 Pressure adaptiveness

Changing the pressure may bring a series of influence 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 the 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

The Pressurization exerts upon the assemblies makes 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 low pressure region the HPS molecules show a unique effect of pressurization-enhanced emission phenomenon. However, keep increasing the pressure leads to slow decrease of the emission. The mechanism explained by authors refered that the imposed pressure brings dye molecules closer which enhanced the RIR (Restricted Intramolecular Rotation) process as well as boosted molecular interactions. The latter promoted the formation of excimer which underlined the strength of light emission.

Except direct pressure imposed to a liquid of gas system, mechanical force may produce 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 brought by grinding has an explicit influence on the aggregation behaviour and accumulation mode of the molecules, thus promotes the change on luminescence. Jia et al.[87] have reported a dipeptide-based multicolored-switching solid material. The material was fabricated from peptides functionalized with pyrene group and rhodamine B group, respectively. Multiluminescent colours from blue to green, and finally red can be switched in one such sample, which was based on the transformation in the molecular assemblies and chemical structure of the peptides together (Figure 11).

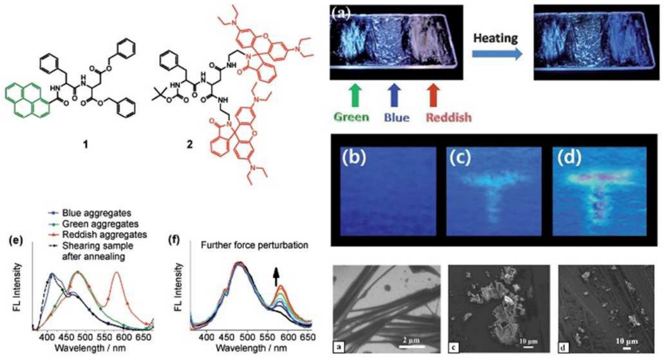

Figure. 11 Dipeptide-based multicolored-switching solid material. MC-1/2 on a filter paper with (b)blue lumminescence, (c) force-induced green luminescence, (d) force-induced reddish luminescence pattern and three different emission colors in one paper. Adapted from ref[87]. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1.4.2. Pressure adaptive molecular self-assemblies

Super critical fluid has been verified a wonderful media for self-assembly to occur[88-91]. In these systems CO_2 molecules may be pressed into the amphiphlic region in the self-assembled structures, which will lead to a structural change to the system. A typical case was reported by Han et al regarding the reversible switch between lamellar liquid crystal phase and micellar solution in compressed CO_2.[92] Upon tuning the pressure of CO_2 the sodium bis-2-ethylhexylsulfosuccinate (AOT)/water system undergoes a transition from high viscosity condition at low pressure to transparent fluid without viscoelasticity above the optimum value of CO_2 pressure. Providing appropriate pressure, CO_2 can be inserted into the surfactant bilayer and change the structure of the bilayers. Increasing the pressure of the gas resulted in disruption of the ordered structure and promoted the formation of more thermodynamiclly stable micelles. Similarly, Liu et al. reported a pressure responsive assembling system of L-proline in compressed or supercritical CO_2 [93]. In this work, high pressure may compress CO_2 into the hydrophobic domain of the self-assembled structures. This enabled amphiphilic proline behave as organocatalyst for the asymmetric aldol reaction. The size of the assemblies can be tuned by compressed CO_2 dynamically which effect explicitly on the catalyst activity and selectivity. (Figure 12) [94].

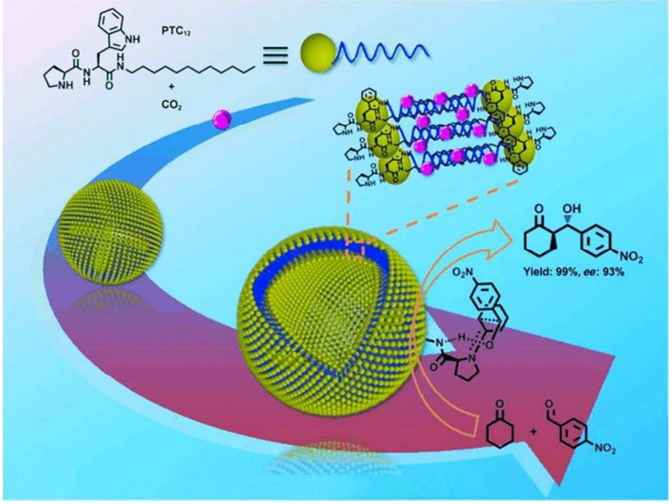

Figure 12. The compressed CO2-regulated self-assembly and catalyzation of the asymetric aldol reaction. Adapt from ref. [94]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2. Special chemical adaptivities

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

2.1 Enzyme adaptiveness

Enzymes have recently emerged to be promising triggers of the adaptive systems[95, 96] as enzyme-catalyzed reactions are highly selective and efficient, requiring only mild condition. 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 with 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 agents[103] at specific sites where the target enzyme is located.

2.1.1 Enzyme responsive component as 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 supramolecular vesicle[104] (Figure 13). The vesicle disassembled upon 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 the Alzheimer’s disease.

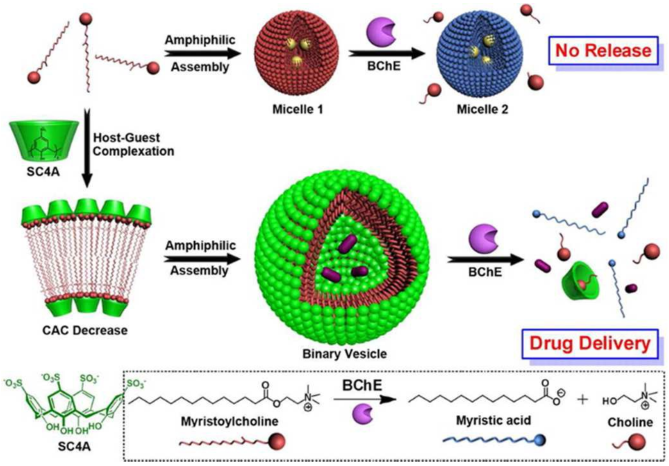

Figure 13. Myristoylcholine-SC4A supra-amphiphiles, its aggreagtes, and drug release. Adapted with permission from ref.[104]. Copyright © 2012, American Chemical Society.

Myristoylcholine was also employed by Xing et al. to from 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 addition of acetylcholinesterase which can split ester linkage of the myristoylcholine chloride, the loaded drug was released. In a similar way, Zhang et al. constructed enzyme-responsive polymeric systems with Adenosine Triphosphate (ATP) utilizing electrostatic interactions[106]. As shown in Figure 14, a double hydrophilic block copolymer methoxy-poly(ethyleneglycol)$_{114}$-block-poly(L-lysinehydrochloride)$_{200}$ (PEG-b-PLKC), and ATP were associated together by electrostatic interaction to form a polymeric micelle[40, 41]. When phosphatase was added, ATP was hydrolyzed so that the micelle was disassembled. In analogy, pyridoxal phosphate was employed to form compartment micelles with PEG-b-PLKC[107] which are responsive to pH and enzyme.

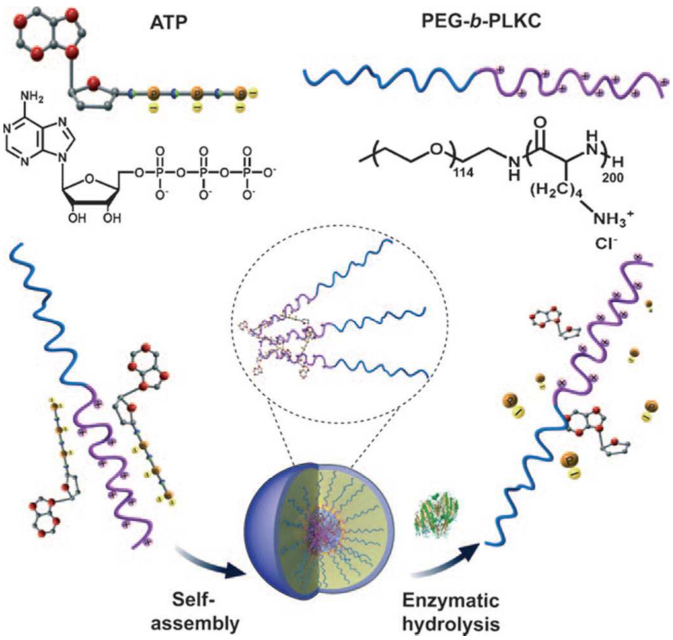

Figure 14. Self-assembly and enzyme-catalyzed disassembly of the superamphiphile aggregates. Adapted with permission from ref.[106]. Copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Huang and coworkers[108] have 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 with surfactant and β-CD (Figure 15). After the addition of alpha-amylase, the central components for 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.

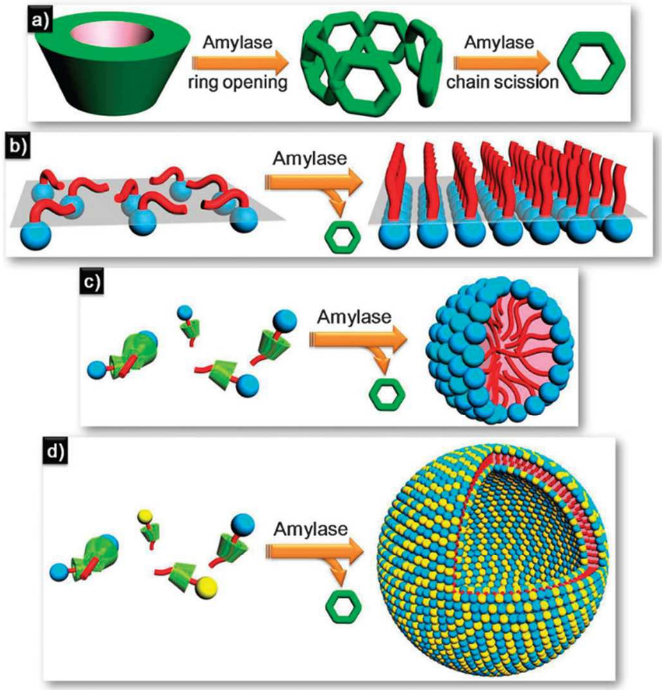

Figure 15. Degradation of beta-CD by alpha-amylase(a), enzyme-triggered monolayer formation(b), enzyme-triggered micellization(c), enzyme-triggered vesicle formation(d). Adapted with permission from ref. [108]. Copyright © 2012 Royal Society of Chemistry.

2.1.2 Enzyme responsive components as triggers.

If the above examples can be categorized as the 'direct' approach which use enzyme-responsive moieties to directly construct the self-assembled structures, Liu et al have reported an 'indirect' way to build enzyme responsive self-assembly where enzyme was not involved in the formation of the self-assembled structure but to generate a component which may affect the structure[109]. They synthesized CGPs (charge generation polymer)[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] (Figure 16). The fluorescence can only occur when charges were generated by H_2O_2 which is produced by the combination of Gox-glucose and AP-Gox-D-glucose 6-phosphate, since the later allows the GCP to transform into cationic polyelectrolyte. The combination of newly generated positively charged polymer and TPE-COOH4 allows formation of nanoparticles, which effectively turn on the fluorescence via AIE process and thus become an effective sensor system.

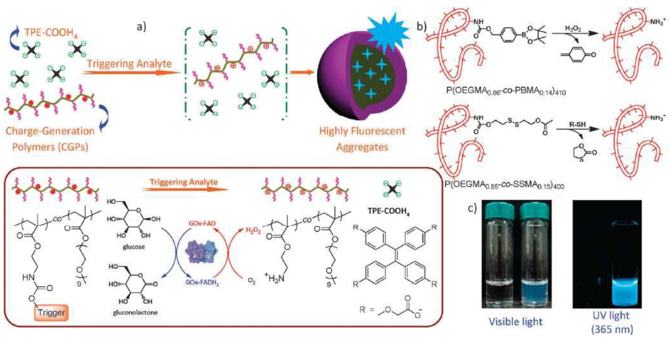

Figure 16. Construction of fluorogenic sensors from negetively charged AIE molecule and positively charged CGPs. Adapted with permission from ref. [109]. Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2 CO_2 Adaptiveness

CO_2 is a small gas molecule which plays a crucial role both in metabolization[112] and climate revolution[113, 114]. Exploiting CO_2 as a stimulus to regulate the shape and property of self-assembled aggregates might be very promising in understanding many mysteries of nature. As an advance, Zhao and coworkers[115] have reported a CO_2-stimulated diversiform polymer assemblies recently. The system containing copolymers composed of outer hydrophilic poly(ethylene oxide), middle hydrophobic poly(styrene), and CO_2-responsive interior poly((2-diethylamino)ethyl methacrylate) flank. This series of copolymers can assemble into different types of aggregates like micelles, vesicles, and one-dimensional worm-like micelles. Upon pressing 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 with N_2. Thus the reversible deformations of vesicles looks very like the lysosomes' endocytosis behaviour when giant sac is compartmentalized into dozens of smaller irregular vacuoles by CO_2 stimuli. (Figure 17)

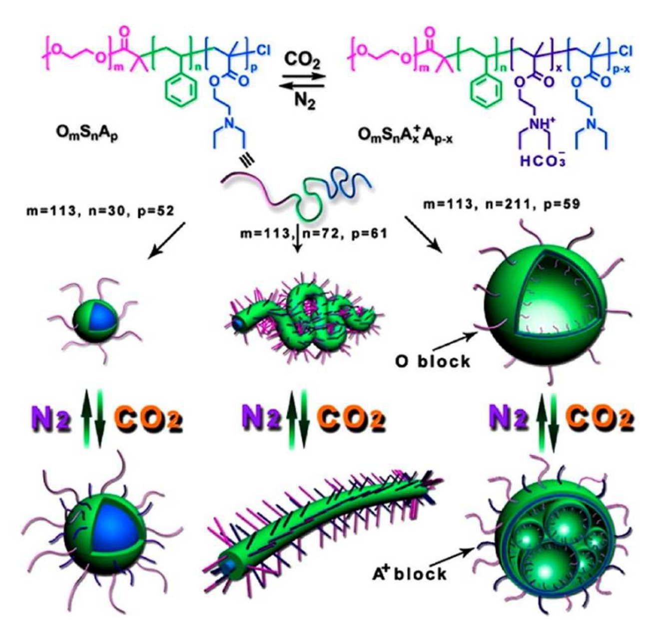

Figure 17. Construction of CO2-stimulated diversiform polymer assemblies. Adapted with permission from ref. [115]. Copyright © 2013, American Chemical Society.

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 they explicit reversibility. After introduced this amidine switchable group into the polymer, the diblock copolymer PEO-b-PAD (poly(ethylene oxide) – b – poly((N-amidino)dodecyl acrylamide)) forms vesicles in water which expand as CO_2 is pressed into the solution. This breathing polymersome was further utilized as size-selective nanoseparators where the membrane permeability and the scale of membrane nanochannels can be regulated by CO_2 via controlling the vesicular expansion and contraction. [117] (Figure 18)

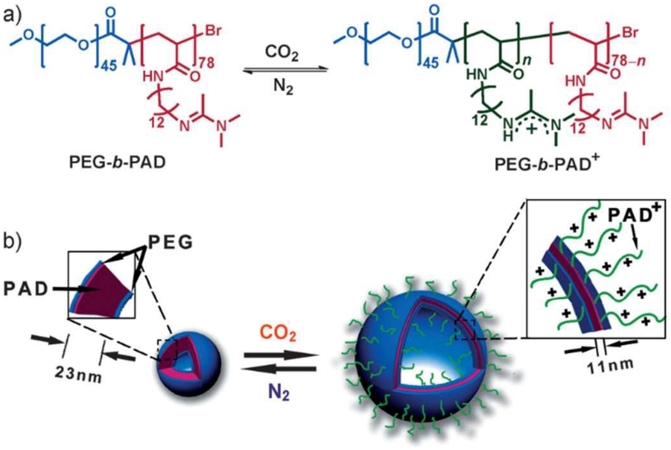

Figure 18. CO2 controlled breathing vesicles. Adapted with permission from Ref. [117]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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-assembled 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. Similar strategy was adopted by these authors to create CO_2-eesponsive "smart" single-walled carbon nanotubes. They wrap the carbon nanotubes with a polymer which contains quaternizable nitrogen. Upon pressing CO_2, the nitrogen is charged which disperse 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 usage 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 to create sensors for metal ion detection. Many self-assembled sensors are developed for detection of metal ions, such as Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} , Zn^{2+} , etc.

Porphyrin-based self-assembly systems is of special interest for sensing heavy metal ions in aqueous solutions since prominent fluorescence quenching often occurs when metalloporphyrins 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 detection of mercury ions in water[126]. Upon coordination with Hg^{2+} ions, the fluorescence of porphyrin was quenched dramatically. This allows detection of Hg^{2+} with a high selectivity over other metal ions.

Fluorescent nanoparticles can provide versatile choices in metal ions detection. Arduini et al. utilized silica nanoparticles doped with fluorenscent dyes to achieve rationmetric Pb^{2+} detection[127]. The thiol groups were grafted on 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 which buried far enough in the core of the nanoparticles were unaffected. With this unaffected fluorescence as the reference signal, this self-organized system exhibits ability of ratiometric detection.

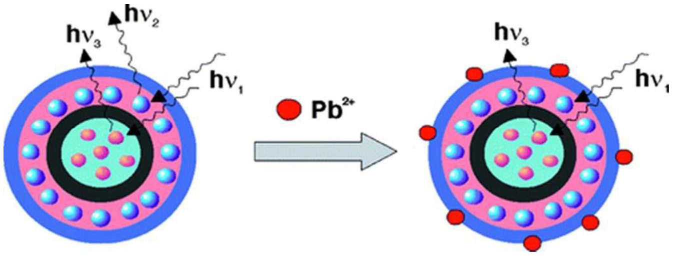

Figure 19. Self-organized ratiometric nanosensor for Pb2+ ions. Adapted with permission from ref.[127] Copyright © 2007, American Chemical Society.

Aggregation induced emission (AIE) has been verified a very efficient way to detect metal ions. AIE dyes are very crucial in this approach. For instance, Sanji and co-workers[128] attached azide group to the famous AIE dye of tetraphenylethene (TPE). Upon addition of Cu^{2+} ions in the mixed solution of azide modified TPE and diethylene glycol dipropiolate, click reaction may occur to form intermolecular cross-linked products, which displays an intense emission because of restriction of the intramolecular rotations. (Figure20). In this way, a fluorometric sensor for Cu^{2+} detection was invented. In another example of Sun and co-workers[129], TPE compound is exploited to create a Zn^{2+} fluorescence turn-on sensor and then successfully used for intracellular Zn^{2+} imaging.

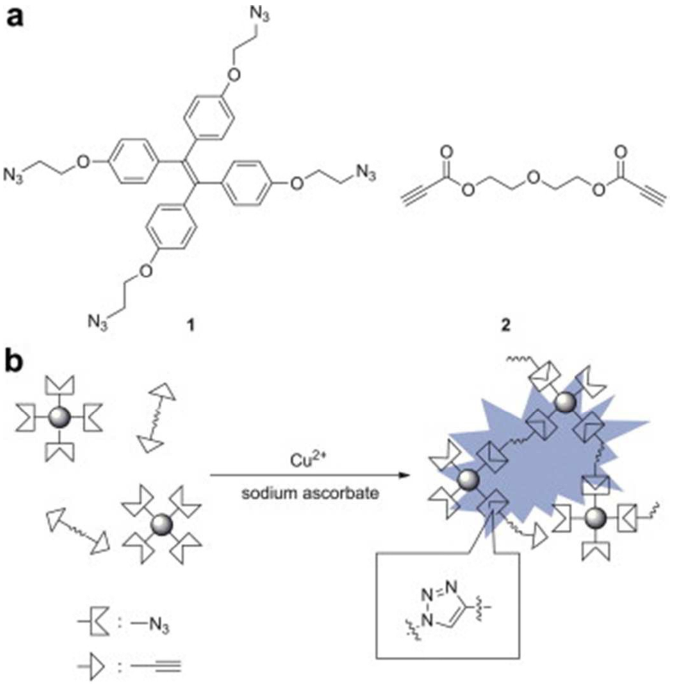

Figure 20. Fluorescence 'turn-on' detection of Cu2+ ions based on click chemistry. Adapted from an open access ref. [128]

2.4 Redox responsiveness

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

2.4.1. Redox based on ferrocenyl

Organic amphiphiles that contain iron is one of the easiest starting points to build redox responsive self-assemblies. For this reason, amphiphiles containing the ferrocenyl group were widely investigated[130-134]. Manners and coworkers[135](Figure 21) constructed a redox responsive self-assembly using polystyrene$_n$-b-poly(ferrocenylphenylmethylsilane)$_m$ diblock copolymers. When more than half of the ferrocenyl units undergo oxidation, spherical micelles with a PFS-PS core-corona structure were obtained. When the polymer blocks were replaced by semicrystalline poly(ferrocenyldimethylsilane) (PFDMS) segments, the oxidized systems form ribbon-like micelles instead.

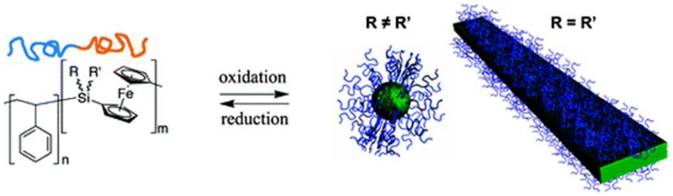

Figure 21. Redox controlled micellization of polyferrocenylsilane copolymers. Adapted from Ref. [135]. Copyright © 2011, American Chemical Society.

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 24h. While providing oxidants, the healing process is blocked and no healing is observed after 24h. Otherwise, by spreading reductants to the oxidized cut surface the healing between two cut pieces is observed after 24h. The oxidized ferrocenium gel is selectively adhered to the gel formed out of styrene sulfonic acid sodium salt by ionic interaction. Thus, an ABC-type macroscopic self-assembly of three sorts of gels (CD gel, Fc gel, and SSNa gel) through two discrete noncovalent interaction 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, 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]. (Figure 22) Other examples on redox endowed by metal ions in the molecular self-assembled systems can also be found from time to time[139]. Royal and coworkers has developed a metallo-supramolecular polymer system that show a gel-sol transition upon redox-induced changing 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 $Co(ClO_4)_2$ 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. Self-assembled redox-responsive metallogel based on the copper(II) complex of quinolinol-substituted L-glutamide with reversible gel-sol transition property was also reported[142].

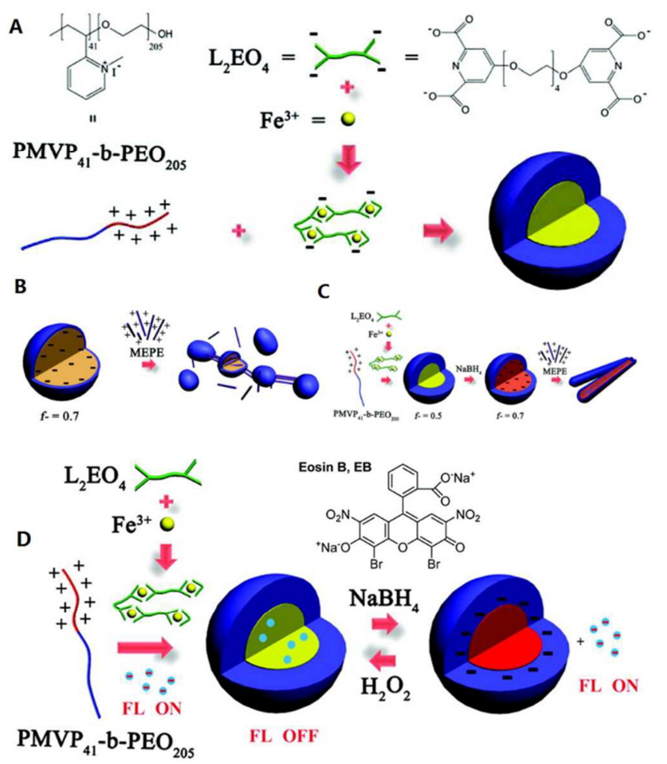

Figure 22. Uptake and release L_2EO_4-Fe^{3+} system. (A)(B)(C) Adapted with permission from ref[137]. (D) Adapted with permission from ref[138]. Copyright © 2012, American Chemical Society.

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 reason is the mild redox chemistry of selenium may endows the relating self-assembly or materials desired redox adaptivity[143, 144]. Selenium can be covalently incorporated into the backbone of an amphiphile. Upon oxidation, the selenium will transform into the hydrophilic form of S=O. This greatly alters the self-assembling 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 displayed catalytic activity, and this performance can be reversibly regulated by the redox stimuli couples of hydrogen peroxide/ vitamin C[148]. The redox switchable nature of selenium also endows the change of self-assembled structure by Feng et al, which can be used to regulated the gel-solution phase transition. [149]

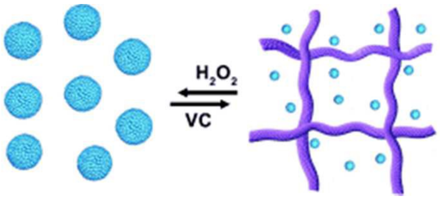

Figure 23. Reversible formation of the nanostructures of the selenium-containing peptides. Adapted with permission from ref.[148] Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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 of luminescence signal is often employed in various explosive detections. The dominant mechanism of detection is static quenching process which occurred through 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 explosive detections[155-158]. These dyes show luminescence when their rotation is restricted, either by fixing to a solid material or entrapment in a molecular self-assembly. Tang et al. has reported an approach of superadaptive detection of explosives by AIE luminogen-functionalized mesoporous materials[159]. In their work, mesoporous silica SBA-15 and the AIE luminogen tetraphenylethene (TPE) are connected via covalent chemical bonding. This TPE-functionalized mesoporous materials exhibit strong fluorescence, yet the fluorescence can be quenched drastically by trace amount 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 solution process[160]. As the nanostructure 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 coworkers[161] 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 fluorescence increase has been achieved in the explosive vapor detection. Similarly, Liao et al also reported a size tunable fluorescent sensor based on oligotriphenylene nanofibers. The sensor can be used as of detection of the nitro-based explosives such as nitromethane, nitrobenzene, and 2, 4, 6-trinitrophenol both in dispersions or oligotriphenylene/polysulfone composite films with satisfied selectivity and sensitivity.sensors [162].

Proper self-assembled structures also allows selectively detect explosives. As an example, Wang et al. has introduced a facile and versatile method to selectively detect trinitrophenol (TNP) among other explosive molecules such as TNT and DNT [163].(Figure 24) 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 addition TNP into the aqueous solution of the 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.

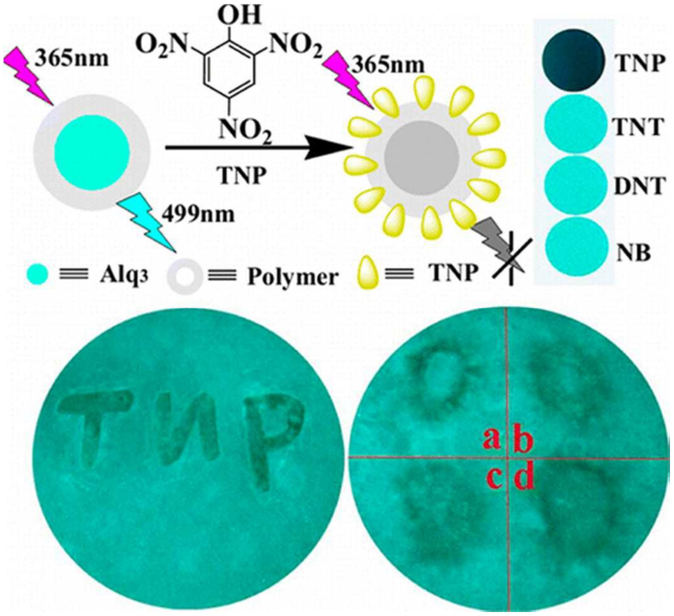

Figure 24. Composite nanospheres with bluish green fluorescent that can detect TNP selectively. Adapted with permission from ref. [163]. Copyright © 2012, American Chemical Society.

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 neurotrarnsmitter 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 may be completely different[166, 167] and thus 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 detect dopamine in phosphate buffered saline solution selectively, with 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. (Figure 25)

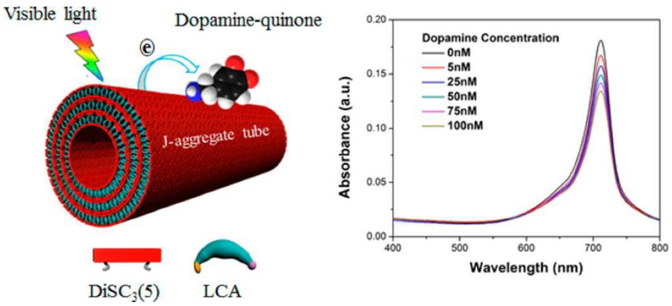

Figure 25. J-Aggregate nanotube and sensing dopamine. Adapt with permission from ref. [168] Copyright © 2014, American Chemical Society.

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 the tetraphenylethene-cored diboronic acid they synthesized is greatly boosted. The enhancement of emission relate to restriction of the intramolecular rotations of the TPE molecule by 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 oligomerize process occurred.

Other biomolecules can also be detected using adapative self-assembly methods. For instance, the detection of protein[170-174], nucleic acids[175-177], etc. have been widely reported as well. Like the enzyme responsive self-assemblies, self-assembled materials which are able to respond to certain biomolecules are expected to have great potential in disease treatment.

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 the materials is inevitably affected by the external fields. Developing materials response to various fields then has apparent significance in different applications.

3.1 Light adaptiveness

Light is a facile approach to provide energy and external stimuli into a microscopic system 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 responsiveness 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 the light responsiveness, this section is to be discussed in the following three parts.

3.1.1 Adaptiveness triggered by photo responsive bond-cleavage

Light induced bond-cleavage may change the self-assembling behaviour of the mother molecules. Spiropyran group is often employed to reach this goal [178-180]. The spiropyran 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[181].(Figure 26) The MC form forms disk-like spherical aggregates when adsorbed on a flat silica plate while the more hydrophobic SP forms larger aggregates. The 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.

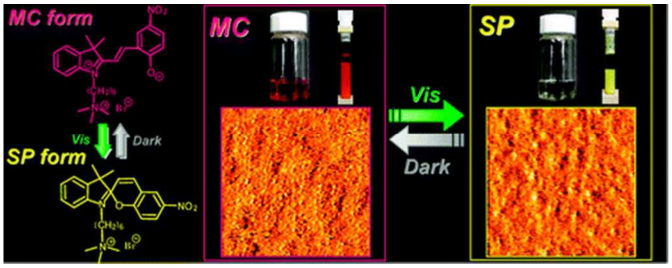

Figure 26. Photoreisomerization surfactant system. Adapted with permission form ref[181]. Copyright © 2010, American Chemical Society.

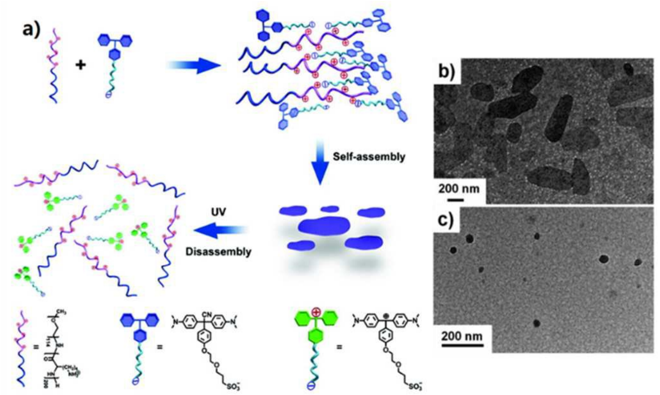

Figure 27. Photoresponsive SA system. (A) Scheme of the photoresponsive system. (B) TEM image of the SA system with charge rations of 1:1. (C) TEM image after UV. Adapted with permission from ref[187]. Copyright © 2011, American Chemical Society.

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 metal conterions is promoted by excitation of the ligand-to-metal charge transfer (LMCT) band in the photoreactive surfactant. This led to generation of metal and metal-oxide nanoparticles inside the reversed micelles. The photoractive surfactants are then exploited as precursors to obtain nearly monodispersed 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 isomerizations belong to this category. The change of molecular conformations may affect their packing in the self-assembly so that lead to a different structure[190-194]. Using this strategy, Raghavan et al. have developed a class of photoresponsive system based on the mixed self-assembling system of a cationic surfactant and a photoisomerizable o-mehtoxycinnamic 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, the 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 property[195]. UV light triggered desorption of OMCA from EDAB micelles which enabled the wormlike micelles grew longer and entangled to form network which gels the solvent.

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

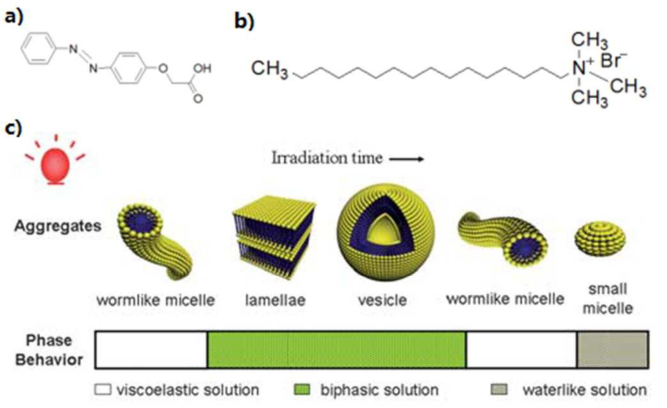

Figure 28. Structural evolution and phase behavior in the solution of AzoNa system varied with UV irradiation time. [197]. Copyright © 2010, Royal Society of Chemistry.

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. utilize the photo triggered trans-cis isomezation of the butyl izobenezene amphiphile which contains a pseudo-sugar head group (C4AG) achieved vesicles with cilia[205]. The callia were developed upon exposure of the normal vesicles to UV light. They found that this unique structural deformation is originated from the disassembly of C4AG from CD as the azo-benzene group underwent trans-cis isomerization. Since this photoreaction is reversible, the calia also displayed on-off behaviour, which just likes the stretching of contracting of the calia of lived virus. The calia has been verified actually double helixes of CD-cis-C4AG, which looks very alike as those helices formed by trans-C4AG in their previous work. [206, 207]

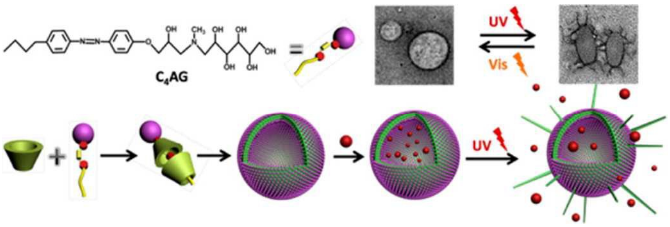

Figure 29. Scheme of the self-assembly of bacteria-like vesicles with photoswitchable cilia as smart nanocarriers. Adapted with permission from ref[205]. Copyright © 2014, American Chemical Society.

3.1.3 Photo triggered bond reformation- self-healing system

As an external stimulus, light not only provide necessary energy for bond-cleavage of bond-rotation, it also produces heat in case the energy doesn't match that required for the bond changes [29, 30]. Burnworth et al. smartly employed the heat produced by light to create a optical healable supramolecular polymer[208](Figure 30). They synthesized a series of metallosupramolecular polymer 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 into heat in the metal-ligand motifs, which causes temporary disengagement of the motifs and thereby allowing 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.

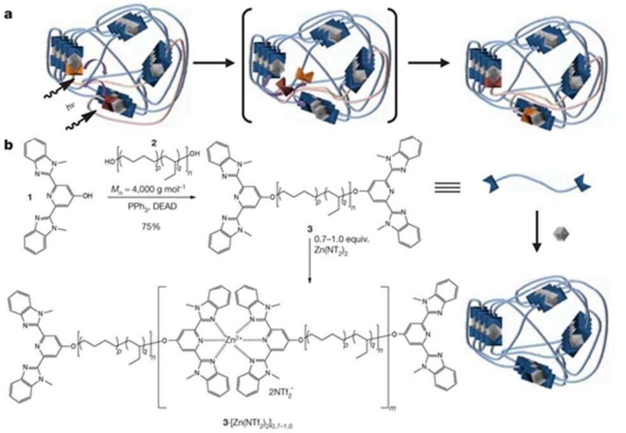

Figure 30. Mechanism and synthesis of photohealable metallosupramolecular polymers. Adapted with permission form ref[208]. Copyright © 2011, Nature Publishing Group.

3.2 Adaptiveness to magnetic field

Magnetic field has been found affect the growth, morphology, and self-assembly of many nanoparticles and electric materials [209-213]. Vilfan and co-workers[214] have introduced an advancement of artificial biomimetic cilia which are constructed from spherical superparamagnetic colloidal particles. These particles self-assembled in an external magnetic field into flexible and stable long chains and mimic a ciliated surface with imitations of motions to generate fluid flow. Either by individually trapped the superparamagnetic beads by optical tweezers or just let the particles 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. By Switch on and off the external magnetic field enables disassembly or reassembly of the cilia.

Klajn et al. have developed dual-responsive nanoparticles both adaptive to light and magnetic stimulis[215]. The nanoparticles are designed to receive magnetic interactions between each other by the superparamagnetic Fe_3O_4 cores and response 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 toluenes induced by the electric dipole interactions between *cis* azobenzenes. When exposed to UV light the initially aggregates assemble together to form larger aggregates which show reversibility in UV-vis cycles. (Figure 31A). Moreover, the AC-NPs formed one-dimensional assemblies when exposed to both light and magnetic field.

Xu and coworkers have 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, 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 by the effect of the magnetic field.

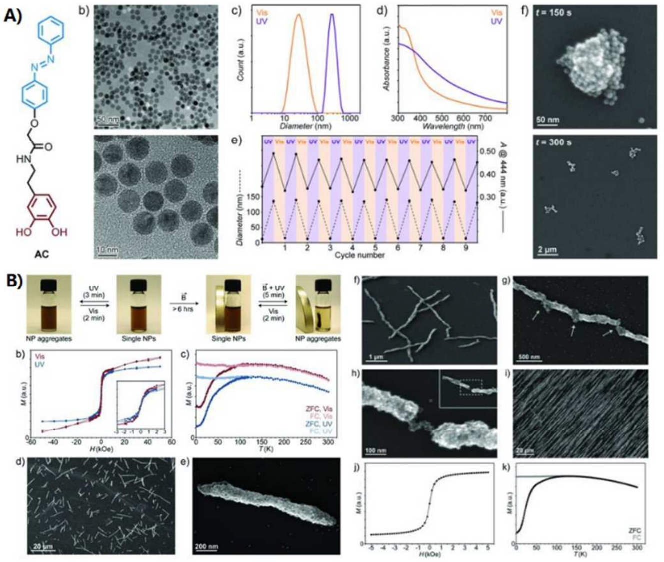

Figure 31 (A)Light-induced self-assembly of magnetite NPs (B) Assemblies when both exposed to light and magnetic field. Adapted with permission from ref. [215]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Christianen et al. have reported self-assembled nanocapsules that exhibited property of deformation in 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 the ability of magnetic forces as an ideal method of supramolecular assemblies in solution with a contact-free and noninvasive manner.

3.3 Adaptiveness to electric fields

Electric field can be a versatile tool to direct the assembly of colloidal nanoparticles by inducing interactions or taken as a stimuli to the specific responsive systems[217-219]. For instance, a novel temperature and electric field dual-stimulus responsive nanoparticle system for programmed drug delivery is 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. have developed voltage-responsive vesicles based on 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-assembly process (firstly form 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 assembly or disassembly of the vesicles. (Figure 32)

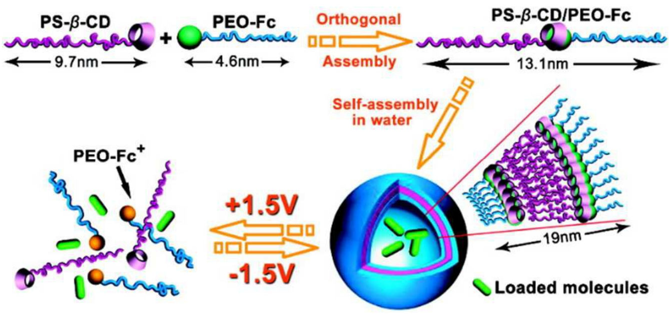

Figure 32. Electric fields-controlled assembly and disassembly of a supramolecular vesicles. Adapt from ref. [220]. Copyright © 2010, American Chemical Society.

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 the viscosity can be retained without shear force[224]. For example, shear thinning hydrogels[225] which exhibit rapid recovery after the cessation of shear are attractive materials for application such as injectable biomaterials. The physical essence behind this macroscopic phenomenon is actually the transition of the self-assembled structures under shear.

The influence of shear force on self-assembled structures is mainly systematically studied by Hoffmann et al.[226-230] He found that the self-assembled structure in the charged tetradecyl dimetyl ammonium oxide (C14DMAO) and Long chain alcohol (CnOH) system is flattened layers if the charging process is achieved by releasing protons to the system via a chemical reaction, where the system is not stirred of shaken, namely without any shear. However, if the system was shaken by hand, one will only get spherical vesicles. This is for the first time to experimentally prove that shear force have significant effect on the self-assembled structures.

In fact, in words of fluid, shear induced fluidity changes is well-known with a long history. The most famous phenomena include shear thinning or shear-thickening. Nevertheless, shear induced micro-structural change is the origin 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 injectable state and stiffened state. In this work, thermoresponsive block copolymers are utilized to form a second reinforcing network inside the protein-based hydrogels. PNIPAM was conjugated to the protein and produce a triblock copolymer. Thus two independent networks were formed from a single molecule by the hydrophobically association of the PNIPAM blocks and specific interactions of the coiled-coil of the middle protein block orthogonally. At low temperature, the hydrogel is soft and fragile with shear thinning property, while a gel-gel transition makes the gel reinforced and tougher at physiological temperatures(Figure 33).

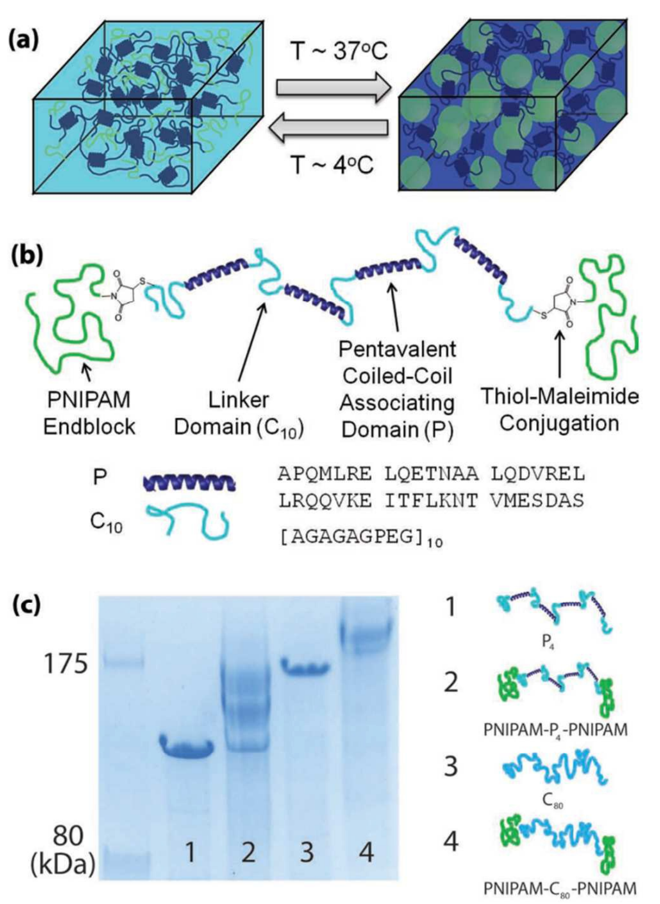

Figure 33. Responsive self-aseembly of PNIPAM within a physically associating protein gel to reinforce the shear thinning gels. Adapt with permission from ref. [231]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Polymers can also be made into colloidal particles so that 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 property as the network destroyed when under shear stress. After removal of the shear force, the networks self-healed spontaneously which enables modify of the gels.(Figure 34)

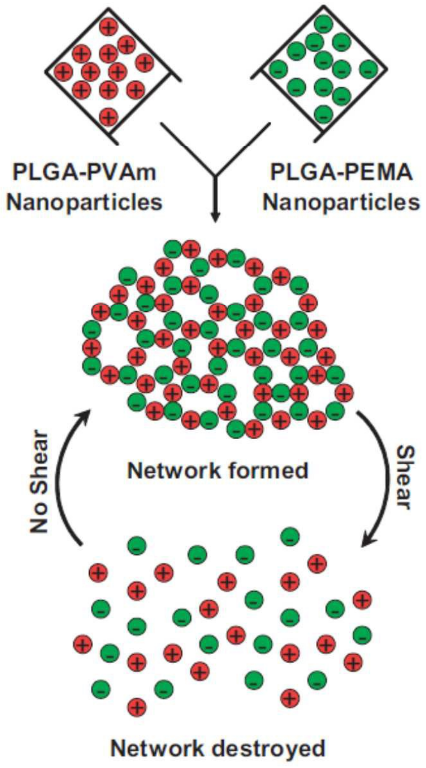

Figure 34. Shear responsive colloidal gels prepared from oppositely charged nanoparticles. Adapt with permission from ref. [232]. Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Conclusion and Perspectives

Soft materials based on various molecular self-assemblies have already exhibited significant advantages toward traditional covalent counterparts and showed great potentials 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 are emerged in this area, only a small amount 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 upon structural construction and their functions are highly demanded. How to get more precise control on the non-covalent interactions and how to manipulate them to get them act in a desirable way? It should admit that while providing highly responsive and dynamic properties, non-covalent interactions also make the soft materials based on them lack of robustness generally. To construct molecular self-organized systems with satisfying robustness meanwhile retain their intrinsic adaptivity is still remaining as a challenging problem.

The achievement 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 material science. Many problems still remains 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 are still very limited. In recent days, Mann et al[233-240] are devoting to create much advanced self-assembling systems that may have more intelligible performance, yet there is still a long way to go for the systematic design and construction of the complicated systems. It envisages that delicate designs which embody the wisdom from different fields, especially those from biology and material science in a manner of cooperation with chemistry, are required to push revolutionary progress in this field.

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Notes and references

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TOC graph for

Adaptive Soft Molecular Self-Assemblies

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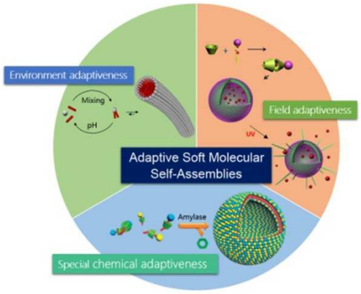

Adaptive molecular self-assemblies provide possibility to construct smart and functional materials owing to their adaptiveness to environments, chemicals, and fields.