



Feature Article

Optical properties of amphiphilic copolymer-based self-assemblies



Wei Wang, Jiaping Lin*, Chunhua Cai, Shaoliang Lin*

Shanghai Key Laboratory of Advanced Polymeric Materials, State Key Laboratory of Bioreactor Engineering, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

Article history:

Received 3 November 2014

Received in revised form 12 January 2015

Accepted 14 January 2015

Available online 24 January 2015

Keywords:

Self-assembly

Amphiphilic copolymer

Aggregation-induced optical property

Photo-responsive property

Bioimaging

Drug delivery

ABSTRACT

As a promising technique for preparing polymeric materials with novel structures and properties, self-assembly is gaining increasing attentions. The applications of self-assemblies raise the claim of full expression of inherent functions and adequate stimuli-responsive features. Light is an excellent media for the realization of inherent functions, in favor of the communication with external environments. The aggregates self-assembled from polymers with optical functions can bring multifarious optical properties and promising applications. In the assemblies, the emission and fluorescence properties of polymers are dependent on both the aggregation type of the polymers and the aggregation-induced effects including planarization and specific intermolecular interactions. The aggregation-induced optical properties are influenced by external stimuli including pH and temperature, which confer various applications, such as in the areas of bioimaging and optical sensor. When photo-responsive groups with photochromism, photo-crosslink or photo-degradation properties are incorporated into polymers, self-assemblies are able to change their shape and inner structure under light irradiation. Such light triggered property is suitable in application for controllable release of loaded species from assemblies. We also discuss the challenges and developing directions regarding the studies and applications of self-assemblies from polymers with optical properties.

© 2015 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	113
2. Self-assembling polymers with optical properties	113
2.1. Polymers with optical properties	113

Abbreviations: AIEE, aggregation-induced emission enhancement; AIQ, aggregation-induced quenching; MCF-7, breast cancer cell; CLSM, confocal laser scanning microscopy; CPE, conjugated polyelectrolyte; NIH-3T3, fibroblast normal cell; FRET, fluorescence resonance energy transfer; FA, folic acid; LPL, linearly polarized light; MCTS, multicellular tumor spheroids; NIR, near infrared; NR, Nile Red; NLO, nonlinear optical; PL, photoluminescence; PDPA, poly(2-(diisopropylamino)ethyl methacrylate); PMPC, poly(2-(methacryloyloxy)ethyl phosphorylcholine); PFO, poly(9,9-dioctylfluorene); PAA, poly(acrylic acid); PEO, poly(ethylene oxide); PDMAEMA, poly(2-(dimethyl amino) ethyl methacrylate); PF-PE, poly(2,7-(9,9-dihexylfluorene)-alt-4,4'-phenylether); PMMAZO, poly(6-(4-methoxy-4'-oxy-azobenzene) hexyl methacrylate); PNIPAM, poly(*N*-isopropylacrylamide); PF, polyfluorene; PS, polystyrene; PUNB, polyurethane containing nitrobenzyl group; RhB, Rhodamine B; R6GEM, rhodamine-based monomer; SEM, scanning electron microscope; sPCHD, sulfonated poly(1, 3-cyclohexadiene); TP, tetraphenylthiophene; TPE, tetraphenylethene; TEM, transmission electron microscope; 2PA, two-photon absorption; UCNPs, upconverting nanoparticles.

* Corresponding authors. Tel.: +86 21 64253370.

E-mail addresses: jjlin@ecust.edu.cn (J. Lin), slin@ecust.edu.cn (S. Lin).<http://dx.doi.org/10.1016/j.eurpolymj.2015.01.023>

0014-3057/© 2015 Elsevier Ltd. All rights reserved.

2.2.	Self-assembly behaviors of polymers with optical properties	116
3.	Optical properties of aggregates self-assembled from polymers with optical groups	117
3.1.	Aggregation-induced optical properties	117
3.1.1.	Aggregation-induced emission change	117
3.1.2.	Stimuli-responsive emission change	119
3.2.	Photo-responsive properties	120
3.2.1.	Photo-induced deformation of aggregate shape	120
3.2.2.	Photo-induced transformation of aggregate structure	121
4.	Applications of self-assemblies with optical functions	122
4.1.	Controllable release of loaded species	122
4.2.	Bioimaging	124
4.3.	Optical sensors	125
5.	Summary and outlook	127
	Acknowledgements	128
	References	128

1. Introduction

Self-assembly, a powerful bottom-up strategy for fabrication of nano-materials with diversified structures, has attracted extensive scientific interests since it is potential in building advanced functional materials for applications in electronics, optics, biotechnology and environmental technology [1–4]. The self-assemblies are formed by the non-covalent interactions, involving hydrogen bonds, electrostatic interactions, hydrophobic effects, metal–ligand coordination, and host–guest interactions [5]. Since the interactions are dynamic, reversible and controllable, self-assembly systems exhibit tunable structures and properties, which are in favor of the achievement of functional applications [6]. However, the functional applications of self-assembled aggregates raise the claim of full expression of inherent functions and stimuli-responsive features. Light, as green and neat energy, is an excellent media for the realization of inherent functions, in favor of the communication with external environments. In addition, the use of light as a trigger is particularly attractive since its characteristics can be remotely and accurately controlled, quickly switched and easily focused on specific areas [7].

Through various chemical techniques, optical groups with luminous or photo-sensitive properties can be introduced into polymers [2,8]. The polymers with inherent or introduced optical functions can be further copolymerized with other polymers to form amphiphilic copolymers. Under the balance of hydrophobic and hydrophilic effects, these copolymers with optical properties are able to self-assemble into diversified aggregates in solution, including micelles, vesicles, rings, and tubes [9–12]. The polymeric aggregates can behave enhanced optical properties as more than the summation of their building parts, even bring completely new types of properties for special interests and more applications [13]. In addition, assemblies of biocompatible optical polymers in solution exhibit unique advantages in the biomedical applications [14]. Given the presence of various unique optical properties from these biocompatible self-assemblies, it is possible to develop new tools for bioimaging, diagnostics, drug delivery, and therapy [15,16].

However, most of the current interests in optical self-assemblies are directed to the preparation of functional films. The situations of the self-assembled aggregates in solution are less documented [17,18]. In this feature article, we emphasize the properties of aggregates self-assembled from polymers owning optical functions. The article is divided into four parts. The first one makes a brief introduction of both the structure and property of polymers owning luminous or photo-sensitive properties, along with the self-assembly behavior of amphiphilic copolymers consisting of these polymers. In the second part, the optical properties of aggregates self-assembled from the amphiphilic copolymers with optical functions are featured. Both the aggregation-induced optical properties and photo-responsive properties are referred. The applications of these self-assembled aggregates in the fields of biomedicine and optical sensor are summarized in the third section. Lastly, conclusions and outlook are presented.

2. Self-assembling polymers with optical properties

2.1. Polymers with optical properties

A variety of polymers bearing optical groups are capable to self-assemble into nano-sized aggregates in solution. These optical polymers typically include photochromic polymers, conjugated polymers, photo-crosslink polymers, photo-cleavage polymers, and coordination polymers. The unique optical properties are derived from their elaborate molecular structures as described below.

Photochromic polymers functionalized by photochromic moieties are the most common class, which can introduce diverse photo-responsive properties to their self-assemblies [18,19]. Photochromism refers to the reversible transition of a chemical species between two isomeric forms with different absorption spectra. These reversible transition processes are usually triggered by the irradiation of ultraviolet (UV) or visible light (Vis), as depicted in Fig. 1. For example, UV irradiation induces photochromic reaction of azobenzene proceeded by the conversion of the planar *trans* isomer to the bent *cis* isomeric form via the isomerization of a —N=N— bond (Fig. 1a). The

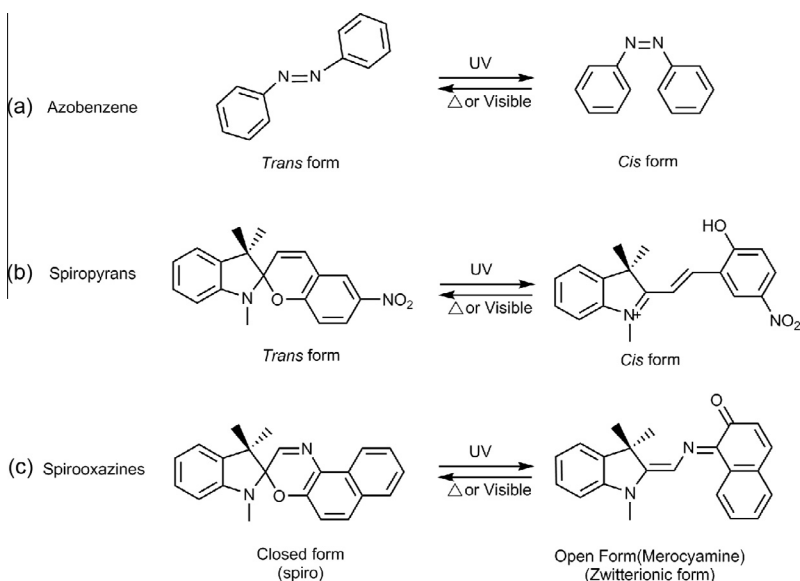


Fig. 1. Typical photochromic compounds used in polymeric systems. (a) azobenzene; (b) spiropyran; (c) spirooxazine.

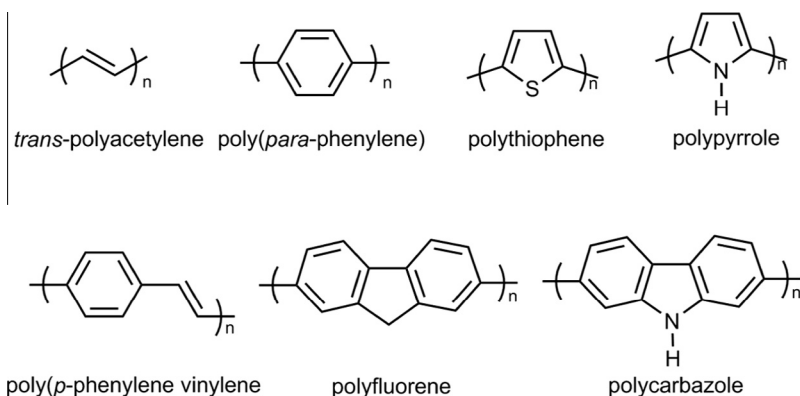


Fig. 2. Chemical structures of representative conjugated polymers.

absorption band is decreased in UV region but increased in Vis region after the *trans*–*cis* isomerization process. UV irradiation on spiropyran (Fig. 1b) or spirooxazine (Fig. 1c) stimulates electrocyclic ring opening reaction from spiro form to open and planar merocyanine form, which forms an extended conjugated system absorbing light strongly in the Vis region [20–23]. These transformation processes are all reversible after subsequent Vis irradiation or heating. In addition, the transformations also bring the changes of physical and chemical properties, such as the alterations in dipole moment, refractive index and geometrical structure. The assemblies formed by photochromic polymers should be able to capture optical signal and then convert it to a useful property change.

Conjugated polymers have been recognized of great importance since they provide a powerful route toward supramolecular objects with novel architectures, functions and physical properties [24]. As shown in Fig. 2, a variety of conjugated polymers have been reported including

polydiacetylene, polyfluorene, polyphenylene, polythiophene, polyquinolone, polypyrrole and so on [25–28]. Upon environmental perturbation, these conjugated polymers can undergo color and fluorescence transitions. The unique fluorescence and emission properties are derived from extensively delocalized π -electron networks and intrinsic conformational restrictions of the conjugated systems. The self-assembled structures of conjugated copolymers may lead to additional optical properties. Combined with the modifiable sensitivity, the assemblies of conjugated copolymers are suitable in optical sensors and bioimaging [2].

Other polymers owning the photo-crosslink and photo-cleavage properties such as coumarin-containing polymers are also reported [29,30]. The photo-dimerization of coumarin moieties at the irradiation wavelength of $\lambda > 310$ nm can result in interchain cross-linking, while irradiation at $\lambda < 260$ nm leads to the cleavage of these cross-linked bonds. By attaching coumarin groups to poly-

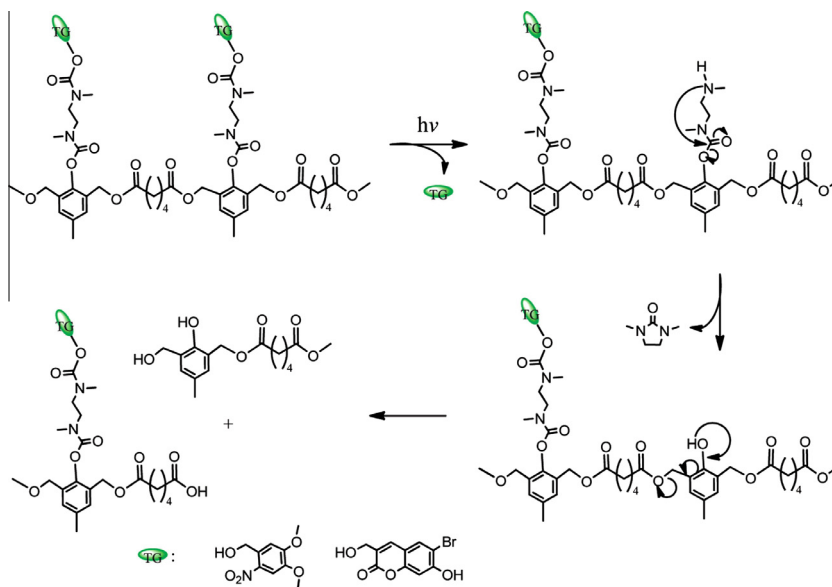


Fig. 3. Degradation mechanism of a light-sensitive polymer incorporating a quinone methide moiety. (Adapted with permission from [33]).

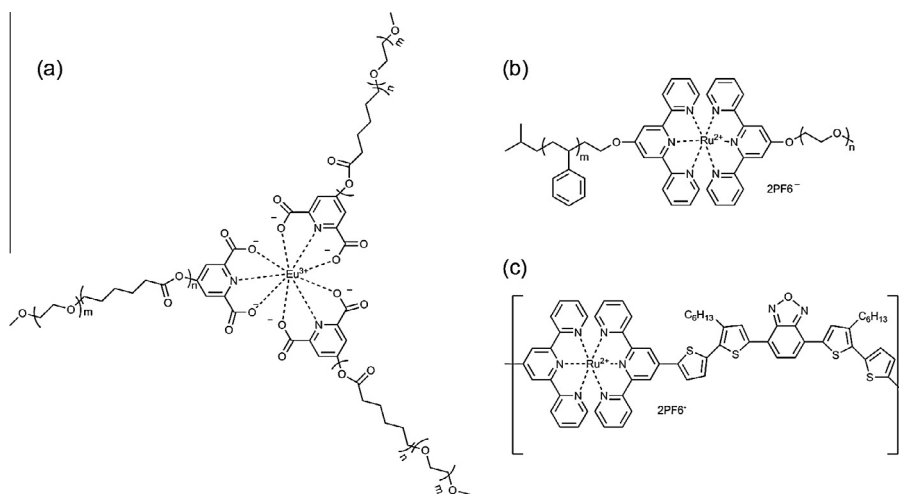


Fig. 4. Chemical structures of representative coordination polymers. (a) Eu-containing star-like coordination polymer; (b) Ru-containing block coordination copolymer; (c) Ru-containing linear coordination polymer.

mers, the polymers are able to be photo-crosslinked through the coumarin moieties to form insoluble networks where the light sensitivity is directly proportional to the degree of coumarin substitution [31]. This ability of reversible photo-dimerizing and subsequently photo-cleaving can be applied for controllable release of loaded species from micelles [32].

Recently, a new type of polymers named self-immolative polymers are synthesized for amplifying response output of photo-cleavage polymers [33]. As shown in Fig. 3, the polymer is composed of a self-immolative backbone and multiple pendant *N,N*-Dimethylethylene diamine groups protected with photo-cleavage triggering moieties such as coumarin and *o*-nitrobenzyl. The degradation starts when a triggering group is cleaved upon irradiation

with either UV or NIR light, releasing an amino group. And then *N,N*-Dimethylethylene diamine linker cyclizes, unmasking an unstable phenol. The subsequent quinone-methide rearrangement of the phenol results in the cleavage of the polymer backbone. This novel strategy allows the light signal to be amplified in a domino effect to fully degrade the polymer into small molecules [34,35]. In addition, the cascade degradation action can also be achieved on both dendrimers and linear polymers terminated with a single phototrigger [35,36]. Taking advantage of the high sensitivity to both UV and NIR light, self-assemblies of self-immolative polymers are promising in constructing sensors and drug delivery systems [37].

Incorporating metallic units into polymer chains by coordination bonds has emerged as a powerful and versa-

tile strategy for the construction of optical metallopolymers [38]. The resulting polymers possess rich functions derived both from their metallic elements and polymer chains. The architectures of coordination polymers rely on the metal–ligand bonds which link the two segments [39,40]. Several representative coordination polymers with different architectures are shown in Fig. 4. The presence of metal–ligand bonds also gives rise to unique optical properties. For example, ruthenium complexes possess extended absorption range along with high fluorescence intensity and color purity [41]. Lanthanide complexes allow the coordination polymers to offer unique optical properties including long excited state lifetimes, a large red shift between excitation and emission wavelengths, sharp emission lines and resistant to photo-bleaching [42]. In addition, the coordination bonds involved are substantially weaker than covalent bonds. Thus in many cases, the coordination bonds can be cleaved by environmental stimuli such as light, pH and temperature, providing the possibility of forming “switchable” systems [43,44]. Therefore, the coordination polymers may offer a new broad platform for the development of smart optical self-assemblies [41].

Various polymers with optical functions have been prepared so far. The elaborate molecular structures confer unique optical properties to these polymers. Above all, the diverse optical properties of above mentioned polymers can be transferred to their aggregates by self-assembly as depicted below.

2.2. Self-assembly behaviors of polymers with optical properties

Polymer self-assembly is a process in which polymers spontaneously form aggregates through intermolecular noncovalent interactions including van der Waals interactions, coulomb interactions, hydrophobic and hydrophilic effects, and π – π stacking [38]. In the scope of this feature article, the hydrophobic and hydrophilic effects are mainly considered. Therefore, an amphiphilic polymer system is necessary for the convenience of self-assembly. Due to the hydrophobic characters of chromophores which are responsible for light absorption and emission, the above

mentioned polymers should be combined with hydrophilic segments to form amphiphilic copolymers for the convenience of self-assembly. Main self-assembly approach referred in this feature article is the solvent removal method. The obtained amphiphilic copolymers are firstly dissolved in a specific solvent to form homogeneous solution. Self-assembly is subsequently performed by adding poor solvent (usually deionized water) as the precipitant to copolymer solution, followed by a dialysis process. Fig. 5 shows that diversified aggregates such as micelles, rods, vesicles, and tubes can be self-assembled from the amphiphilic copolymers. Meanwhile, unique optical properties including emission change and photo-responsive properties can be generated. In the self-assembly process, various factors have influence on the structure and morphology of final aggregates, including self-assembling temperature, solvent, polymer concentration, dropping speed and volume of deionized water, and so on. For example, variation of initial polymer concentration can induce the formation of vesicles at lower concentration but compound vesicles at higher concentration [45].

Azobenzene is a typical photochromic molecule. Various types of azobenzene-containing copolymers are prepared in our previous work [45–52], including AB type diblock copolymer [46], ABC type triblock copolymer [47,48], ABC 3-miktoarm star terpolymer [49], and ABC₂ type block copolymer [45]. As shown in Fig. 6, self-assembled structures of these azobenzene-containing copolymers change from spherical micelles to vesicles and tubes depending on the molecular structures. In addition, the photo-responsive properties such as photo-induced isomerization process are significantly influenced by formation of aggregates.

Conjugated polymers are always served as hydrophobic rod blocks. After copolymerizing the polymers with hydrophilic coil blocks, in addition to conventional spherical micelles and vesicles, unique self-assembled structures such as helices [53,54], ribbons [55], rings [56], and tubules [57,58] are frequently observed owing to ordered alignment of rigid rods [9]. In the aggregates, the packing style of conjugated rods can remarkably affect the final optical properties. Therefore, the self-assemblies of the rod–coil copolymers containing responsive coil blocks may display switchable optical characteristics by external stimuli.

Cooperative self-assembly of two polymers is a simple and efficient method to construct designed functional structures [59,60]. Zhang et al. demonstrated this efficient route for the fabrication of photo-responsive nanostructures by the cooperative self-assembly of diblock copolymers of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) and azobenzene-containing homopolymers [61]. The formed micelles and vesicles are photo-responsive and show reversible *trans*–*cis* photo-isomerization. Recently, we reported the cooperative self-assembly of azobenzene homopolymers with azobenzene-containing copolymers. The polymer mixtures can form photo-responsive spherical micelles with core–shell structures [47]. The addition of homopolymers not only increases the aggregate size but also has a significant influence on photo-responsive properties. In short, by transforming optical polymers to amphiphilic systems, self-assemblies with various

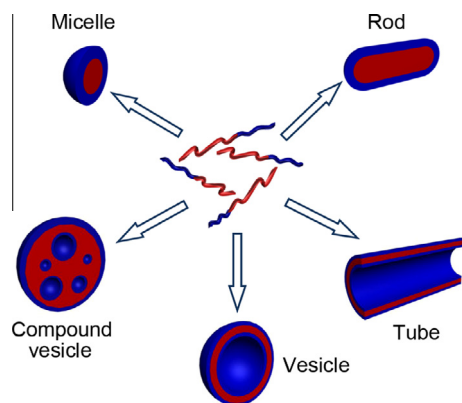


Fig. 5. Schematic aggregates formed through self-assembly of copolymers consisting of hydrophobic blocks (red chains) and hydrophilic blocks (blue chains). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

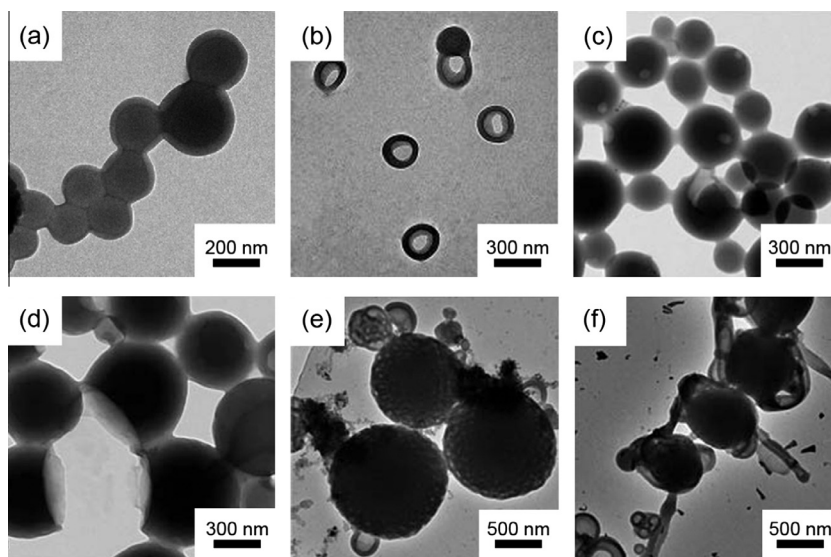


Fig. 6. Transmission electron microscope (TEM) images of typical aggregates self-assembled from azobenzene-containing copolymers. (a) micelles; (b) small vesicles; (c) large vesicles; (d) bowl-shaped vesicles; (e) compound vesicles; (f) twining tubes and compound vesicles. (Adapted with permission from [45,47–49]).

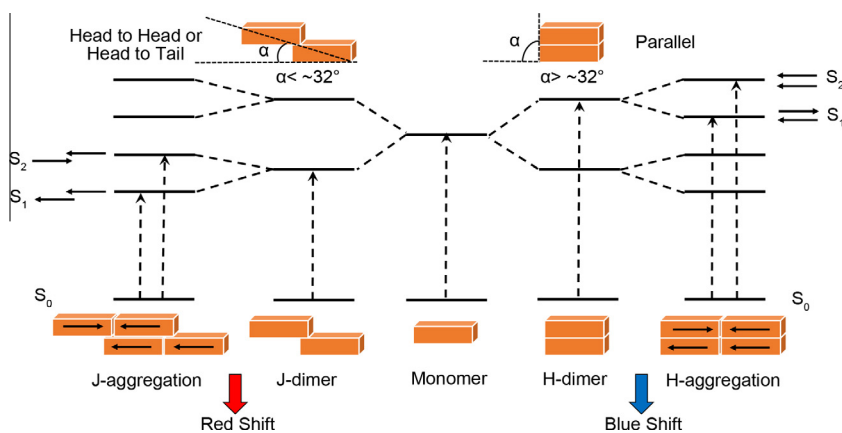


Fig. 7. Schematic illustration of the proposed H- and J-aggregated structures and their corresponding energy level diagram. (Adapted with permission from [2]).

structures can be constructed. Along with the formation of the aggregates, unique optical properties are generated. Such content will be depicted in the following section.

3. Optical properties of aggregates self-assembled from polymers with optical groups

For self-assemblies, a series of unique optical properties can be produced from the specific molecular architectures and self-assembled structures [62,63]. These optical properties of self-assemblies including aggregation-induced and photo-responsive properties are featured in the following sections.

3.1. Aggregation-induced optical properties

Polymers with fluorescent and emission functions have enormous advantages over their nonfluorescent analogues

[64,65]. The fluorescence and emission properties are derived from the inherent polymer structures, but these properties can be changed dramatically upon aggregation [13]. In addition, stimuli-responsive emission change properties are endowed along with the self-assembly process.

3.1.1. Aggregation-induced emission change

In nonselective solvent, polymers express their inherent absorption and emission properties under dissociative conditions. But for the polymer self-assemblies, the optical properties especially the emission properties are significantly influenced by the aggregation type of polymer segments with conjugated moieties. As shown in Fig. 7, H- and J-aggregation can be generated upon self-assembly of polymers [2]. H-aggregation refers to side-by-side oriented molecules with small displacement along the long molecular axis. The resulted H-aggregation absorption spectra are

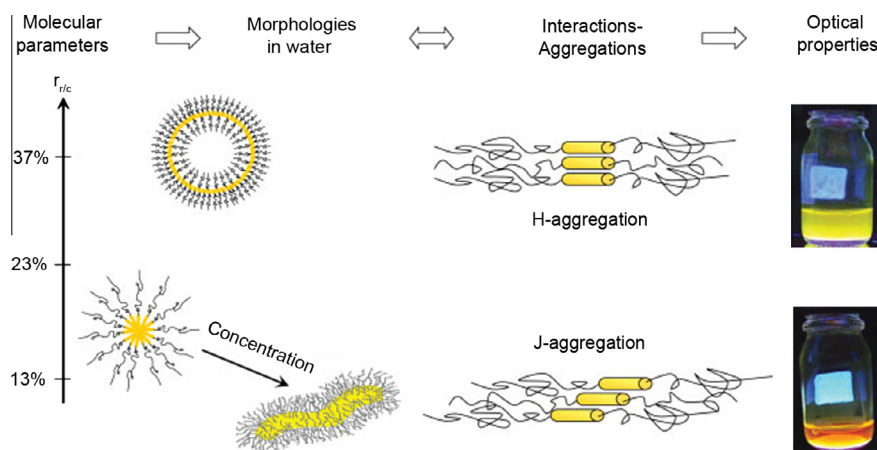


Fig. 8. Correlation between the weight percent of the conjugated part in the amphiphilic copolymers (r_{tc}), the self-assembly structures, and the optical properties. The vials of copolymers in water being placed under a UV lamp (365 nm). (Adapted with permission from [70]).

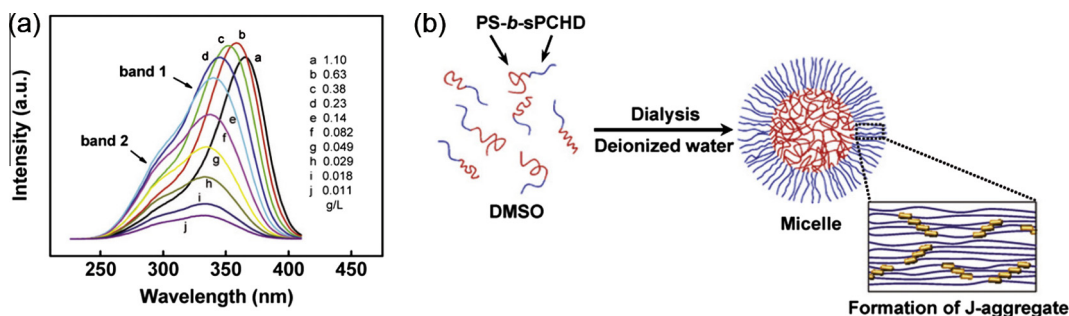


Fig. 9. (a) Typical fluorescence excitation spectra of PS-*b*-sPCHD in water at various copolymer concentrations; (b) schematic representation of the micellization and formation of J-aggregation. (Adapted with permission from [71]).

blue shifted against the solution and exhibit low radiative rate constants k_r due to the dipole-forbidden nature of the emitting state. H-aggregation may result in the aggregation-induced quenching (AIQ) effect, which is a thorny obstacle to high performance organic optoelectronic materials [66]. On the other hand, J-aggregation displays larger molecular displacement along the long molecular axis with higher k_r which usually induces a red shifted absorption spectrum and the formation of an aggregation-induced emission (AIEE) system [67,68]. In addition, the aggregation tendency of the conjugated polymers depends on the chemical structures as well as the environmental conditions, such as concentration, solvent polarity, and temperature [69].

Cloutet et al. synthesized a series of ABA type conjugated copolymers and examined the influence of molecular structure on self-assembly behaviors and optical properties. The coil-rod-coil triblock copolymer consist of a middle conjugated segment based on 3,4-ethylenedioxythiophene and two PEO chains linked with the middle segment by dihexylfluorene units [70]. The self-assembled morphologies depend on the volume fraction of each block. As illustrated in Fig. 8, in the case of short conjugated block (lower weight fraction), spherical and cylindrical micelles with J-aggregation of rod blocks are observed, accompanied by a 10 nm

red-shift of the absorption maximum. While for the polymers owning long conjugated block (higher weight fraction), vesicles with H-aggregation of rod blocks are formed, a significant blue shift of 105 nm occurs. Thus, the length of conjugated segment in the copolymers has an important influence on the optical properties of the assemblies.

In our previous report, AIEE system was achieved by the micellization of the block copolymer polystyrene-*block*-sulfonated poly(1,3-cyclohexadiene) (PS-*b*-sPCHD) [71]. Fluorescence spectroscopy studies suggest that the optical properties of the copolymer aqueous solution change substantially in the micellization process due to the facilitation of J-aggregation of the π -electron chromophores in sPCHD blocks. As shown in Fig. 9a, at lower concentrations, two peaks named bands 1 and 2 can be observed in the fluorescence excitation spectrum. The band 2 centered at 297 nm is taken as that of isolated chromophores. When the polymer concentration is increased, the micellization takes place. The hydrophobic PS blocks form the core and the hydrophilic sPCHD blocks form the corona of the micelles. Since sPCHD polymers are semirigid, they can align paralleled with each other within the corona, as schematically shown in Fig. 9b. As a result, the J-aggregation is significantly facilitated, giving rise to an intense band 1 of

the aggregates. Meanwhile, the band 1 shifts to longer wavelengths and its intensity is increased with the increase of the concentration, which is derived from the facilitated J-aggregation due to the increased order of sPCHD block alignment in compact spherical micelles.

In addition to the aggregation type, the aggregation-induced planarization and specific intermolecular interactions can also dramatically enhance emission upon aggregation due to the formation of the AIEE system [72,73]. Wu et al. synthesized a copolymer comprising a hydrophilic PEO block and a hydrophobic block of the AIEE-active 2-(1,2,3,4,5-pentaphenyl-1H-silol-1-yloxy)ethyl methacrylate [74]. Intense fluorescence was observed from micelles with emission peak at 503 nm when excited by the irradiation at 383 nm, while the polymer solutions in THF showed almost no emission. The quantum yields of the AIEE-active copolymer in mixed solvent (THF/water: $v/v = 1:9$) are as high as 13.8%. These AIEE properties are attributed to the confinement of optical materials in the hydrophobic cores of micelles, which restricts intramolecular rotation and shields AIEE moieties from interacting with polar solvent molecules.

3.1.2. Stimuli-responsive emission change

Due to the complex formation process of aggregation-induced emission change, the emission properties of self-assemblies can respond to environmental stimuli, including solvent, pH, and temperature, which modulate intermolecular interactions. Furthermore, through combining with a stimuli-responsive segment, stimuli-responsive copolymer with optical functions is generated. Thus, additional stimuli-responsive emission change properties can be produced from the aggregates self-assembled from these copolymers [75–78].

Hong et al. prepared an amphiphilic copolymer composed of two hydrophilic poly(*N*-isopropylacrylamide) (PNIPAM) block linked by an AIEE-active hydrophobic tetraphenylthiophene (TP) segment with ion bonds [78]. Dilute solution of ionic TP–PNIPAM in water is nonemissive. However, in the ethanol solvent, the solution exerts appreciable emission intensity due to the formation of

aggregated TP core of the micelles. If one changes the self-assembly conditions, such as the solvent environments, variations of optical properties can be observed. For example, addition of acetone can result in the shrinkage of micelles that shields the hydrophobic TPs from the acetone nonsolvent. Thus, molecular rotations of the TP luminogens are increasingly restricted in the shrunk core and increased fluorescence emission intensity is observed. In addition, when heating above the lower critical solution temperature of PNIPAM, the contracted PNIPAM chains in the shell of micelles led to a more compact TP core, resulting in an emission intensification due to the enhanced restriction on molecular rotation.

Chen et al. synthesized poly(2,7-(9,9-dihexylfluorene))-*block*-poly(2-(dimethylamino)ethyl methacrylate) (PF-*b*-PDMAEMA) rod-coil copolymers [56]. PDMAEMA is served as a typical smart polymer which can respond to both pH and temperature. As shown in Fig. 10a and b, the assemblies in water show reversible structure transformation between cylinder-bundles and spherical micelles over a heating-cooling cycle of 25–75 °C. Upon aggregation, a blue shift in the absorption maximum as well as dramatic fluorescence quenching are generated (see Fig. 10c), which due to the H-aggregation formed by parallel orientation of PF segments. In addition, photoluminescence (PL) intensity of the self-assemblies highly depends on environmental temperature, as shown in Fig. 10d. The PL intensity is reduced upon increasing temperature, and can be recovered by decreasing temperature. This thermo-responsive behavior can be attributed to the reversible formation of the intramolecular hydrogen bonds in PDMAEMA chains. Besides, the pH-responsive fluorescence intensity is switched from “off-on” to “on-off” profiles as the temperature is increased, which can be attributed to the temperature-induced dissolution state transition of the copolymers. This study suggests that the self-assemblies owning stimuli-responsive emission change properties are potential multifunctional sensory materials.

Through tuning chemical structure and self-assembly behavior of polymers, high quantum yields can be achieved in aggregates taking advantage of AIEE effect. In

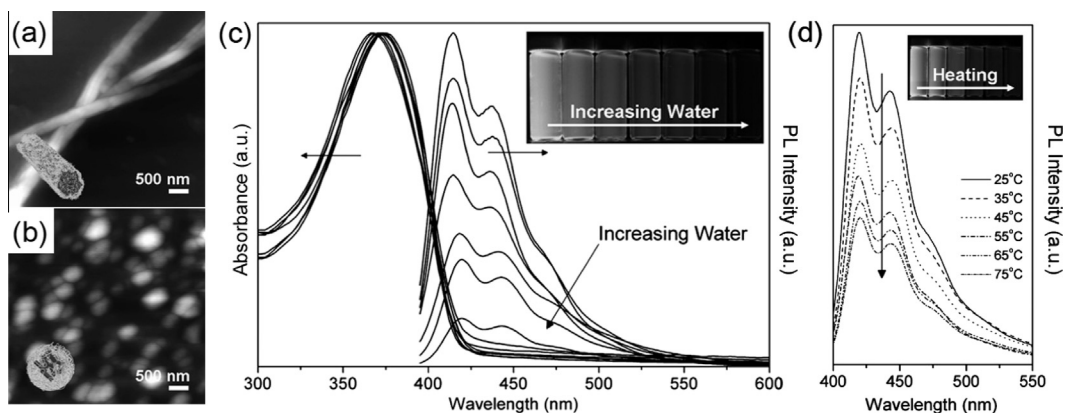


Fig. 10. Atomic force microscopy (AFM) images of PF-*b*-PDMAEMA aggregates in water at the temperature of (a) 25 °C, (b) 75 °C; (c) optical absorption and PL spectra of copolymer in 0–100 wt% water/THF solution; (d) PL spectra of aggregate aqueous solution in the heating process. (Adapted with permission from [56]).

addition, self-assemblies with stimuli-responsive emission change properties can also be constructed, conferring various applications in the area of smart materials. Further advancement in the multi-modality sensing systems and the combination with other medication processes such as controllable and targeted release could widen their applications including clinical diagnosis and therapeutic treatment. In addition to emission change, absorption and color change are also generated during the self-assembly process, which can be applied to construct chemosensors *in vitro*. Moreover, nonlinear optical (NLO) property is getting attention for its potential applications as optical computers and optical switches for ultrafast optical communications [79,80]. Two-photon absorption (2PA) is a typical nonlinear optical property that two photons are simultaneously absorbed to promote a molecule to the excited state by doubling the excitation energy. Introducing 2PA property to self-assembly system may find a variety of biomedical usages such as photodynamic therapy and drug delivery [36,81].

3.2. Photo-responsive properties

The stimuli-responsive property is defined as the ability of the system undergoing sharp responses to chemical changes or environmental changes such as pH, temperature, light, and redox [82–85]. Among the available stimuli, light has attracted special attention since it can be localized in time and space, and triggered from outside of the system [86]. Photo-responsive properties are always related to the photophysical configuration transformation of various photochromic moieties, as well as the photochemical reactions such as photo-crosslink and photo-degradation [87]. The incorporation of photo-responsive groups into polymers confers these properties

to the self-assembled aggregates. As a result, unique photo-responsive properties related to the self-assembled structures can be developed.

3.2.1. Photo-induced deformation of aggregate shape

So far lots of photo-induced shape deformation phenomena have been reported for aggregates constructed from amphiphilic azobenzene-containing copolymers [88–92]. Wang et al. prepared micelles by a copolymer composed of hydrophilic PEO block and hydrophobic acrylate-based block bearing azobenzene chromophores [93]. Upon irradiation by the incident linearly polarized light (LPL) for various time periods, these micelles were observed to be significantly elongated along the light polarization direction. In our recent work, the universality of this LPL-induced deformation approach is demonstrated and the deformation mechanism is attributed to photo-induced cooperative motion in molecule scale as well as photo-fluidization effect in microscale [19].

In another work of our group, the photo-induced deformation was observed for both vesicles and compound vesicles constructed from ABC₂ type azobenzene-containing copolymers [45]. As shown in Fig. 11, upon irradiation by LPL for 2 h, shape deformation from spheres to spindles was observed for all of the aggregates with elongation along the polarized direction. However, the morphology of aggregates have a great influence on the deformation degree. At higher initial concentration, the polymers self-assemble into large compound vesicles (see Fig. 9d and e). Compared with the nano-sized vesicles (see Fig. 9a and b) formed at lower concentration, these compound vesicles suffer a much significant elongation with an axial ratio up to 5.6. From this example, we learn that morphology of aggregates such as vesicles and compound vesicles can be manipulated by self-assembly process. Such

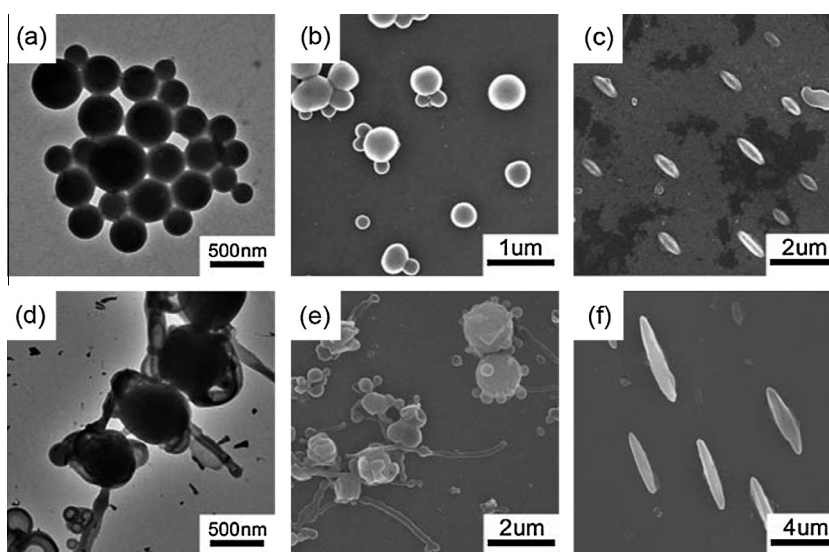


Fig. 11. Typical TEM and scanning electron microscope (SEM) images of aggregates. (a, b) TEM and SEM images at 0.05 g L⁻¹ before irradiation; (c) SEM images at 0.05 g L⁻¹ after irradiation for 2 h; (d, e) TEM and SEM images at 1 g L⁻¹ before irradiation; (f) SEM images at 1 g L⁻¹ after irradiation for 2 h. (Adapted with permission from [45]).

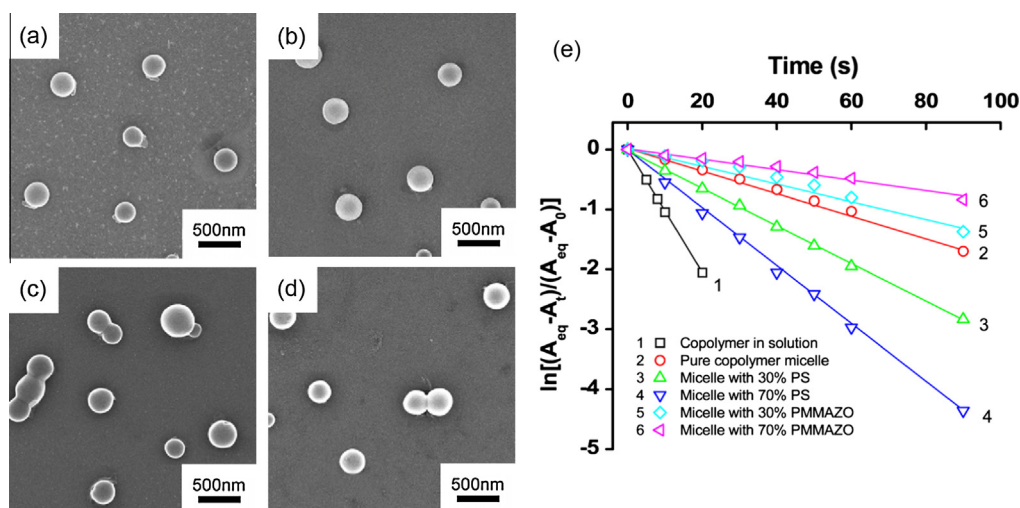


Fig. 12. SEM images of aggregates coassembled from a mixture containing various percentage of homopolymers and corresponding plots of the *trans*–*cis* photo-isomerization: (a) no homopolymers; (b) 30 wt% homo-PMMAZO; (c) 70 wt% homo-PMMAZO; (d) 70 wt% homo-PS. (e) Plots of the first-order *trans*–*cis* photo-isomerization of pure micelles and hybrid micelles. (Adapted with permission from [47]).

changes in micro-structure can generate different optical properties. In other words, the optical properties can be controlled by self-assembly process.

We also investigated the deformation behaviors of co-assembled micelles [47]. Spherical micelles are prepared from the azobenzene-containing triblock copolymers. As shown in Fig. 12, the addition of PS homopolymers or poly(6-(4-methoxy-4'-oxy-azobenzene) hexyl methacrylate) (PMMAZO) homopolymers can not only increase the aggregate sizes but also significantly influence the photo-responsive behavior of the micelles. The photo-isomerization rate ($\ln(A_{\infty} - A_t)/(A_{\infty} - A_0)$) of azobenzene chromophores increases when PS homopolymers are incorporated into micelles; while with the addition of PMMAZO homopolymers, it decreases (see Fig. 12e). In addition, the photo-induced deformation degree is increased with the weight fraction of azobenzene groups in the parent copolymers, as well as the PMMAZO content for the co-assembled micelles. These results can enrich our existing self-assembly knowledge of mixture polymers and their photo-responsive properties and provide useful information for design of photo devices [94].

3.2.2. Photo-induced transformation of aggregate structure

Various polymers with photo-responsive groups can be used for designing light sensitive self-assemblies [95]. In some cases, the self-assemblies can undergo dissociation upon irradiation at a specific wavelength light. Photochromic polymers with spiropyran or azobenzene chromophores have been used to achieve structure transformation upon illumination with UV/Vis or near infrared (NIR) light [96]. Zhao et al. synthesized a block copolymer composed of a hydrophilic block of poly (acrylic acid) (PAA) and a hydrophobic azobenzene polymethacrylate block [97]. The self-assembled micelles can be disrupted and reformed in solution upon alternating UV and visible light irradiation as a result of the reversible *trans*–*cis* photo-

isomerization of azobenzene groups in the core-forming hydrophobic block. In details, under UV light, the *trans*–*cis* isomerization induces order-to-disorder transition of chain packing of the azobenzene polymethacrylate blocks. The micelles are therefore mechanically unstable and then can be disrupted. However, azobenzene groups can regain the elongated *trans* isomer and the micelles are reformed under subsequent visible light.

Subsequently, Zhao et al. demonstrated a general, effective, and robust approach that allows polymer micelles to be disrupted by light. This method is achieved by incorporating photolabile chromophore onto the hydrophobic blocks which form the micelle core [98]. As shown in Fig. 13, upon UV light irradiation, the breakage of chemical bonds detach the chromophores and change the hydrophobic block to hydrophilic block, which leads to a thermodynamically unbalanced state and then disintegrates polymer micelles. This general strategy can readily be applied to many chromophores.

Another unique feature named photo-induced fusion was observed for vesicles self-assembled from azobenzene-containing copolymers [99–103]. Zhang et al. prepared polymer vesicles through self-assembly of an amphiphilic diblock copolymer composed of poly(*N*-isopropyl acrylamide) and polyacrylate with azobenzene pendant on the side-chains [100]. The vesicles can be observed directly under an optical microscope due to the giant micron scale. Upon irradiation of light at 365 nm, the real-time fusion processes are presented. Fusion of the vesicles is attributed to the thermodynamical instability caused by the configuration conversion of azobenzene groups during the photo-induced *trans*–*cis* isomerization. After fusion, the vesicles even enlarge to be about five times of their original size. This fusion system would be excellent model membranes for mimicking the dynamic and structural features of cellular processes, and disclosing the related mechanisms.

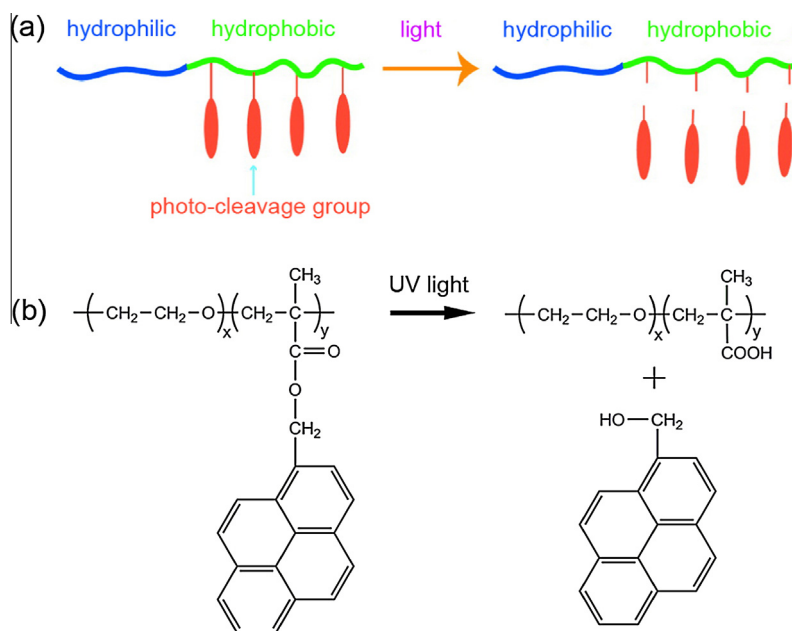


Fig. 13. (a) Schematic illustration of light-induced detachment of fluorescent pendant groups resulting in the hydrophobic-to-hydrophilic switch. (b) Chemical structure of the pyrene-containing amphiphilic diblock copolymer and its photosolvolysis under UV light irradiation. (Adapted with permission from [98]).

In short, numbers of research examples have demonstrated that the utilization of photo-responsive polymer to form self-assemblies is an excellent method to noninvasively manipulate the structure and function of aggregates [104]. Indeed, photo-processes usually start or stop when the light is switched on or off and they do not require particular reagents limiting byproducts. Moreover, a lot of parameters such as the intensity and the wavelength of light can be adjusted during the reaction time that enables good control over the reaction [19]. In other words, light signals can be directly translated to practical behaviors of self-assemblies including deformation, dissociation and fusion by a controllable photo-responsive process in self-assemblies. This light conversion process provides an approach for designing micro optical devices such as biomedical sensors. Non-contact and controllable release of loaded species in biocompatible aggregates is therefore accessible *in vivo*. The convenient light-control approach opens a door to practical usages, especially suitable for biomedical applications.

4. Applications of self-assemblies with optical functions

For self-assemblies formed by polymers with optical groups, unique optical properties can be generated in self-assembly process. These assemblies are applicable both *in vivo* and *in vitro* with great advantages including high emission intensity, hypersensitive and non-contact manipulation [9,105,106]. Representative applications of these self-assemblies, including controlled release, bio-imaging, and optical sensors are featured below.

4.1. Controllable release of loaded species

Recently, polymeric self-assemblies have attracted much attention for their applications in the controllable

release [107–109]. Growing interests in using light to remotely trigger the release of loaded species in polymeric aggregates are developed as light allows for spatiotemporal control of the polymer response in a precise and robust manner [110,111]. By incorporating appropriate photo-responsive moieties into polymers which form the self-assemblies, photochemical reactions such as *trans-cis* isomerization, molecular dimerization, and bond cleavage can lead to micellar disruption or changes of encapsulation capabilities, triggering the release process.

Based on the mechanism of photo-induced structure transformation, several approaches have been proposed for controlling the release of loaded species [112]. Photo-induced disruption of micelles or vesicles is an efficient method for the purpose of controllable release. Constructed by self-assembly of photo-cleavable polymers, aggregates can be disrupted upon irradiation with light, accompanied by the release of encapsulated target species. For instance, hydrophobic Nile Red (NR) is loaded in the core of micelles self-assembled from an amphiphilic ABA triblock copolymer, where the end block A is PEO and the middle block B is a hydrophobic polyurethane containing photo-cleavage nitrobenzyl group (PUNB) [113]. Upon a short time irradiation of 10 s, the emission intensity of NR loaded micelles drops to 30% by the fast photo-induced dissociation of core-forming PUNB blocks. Irradiating for additional 50 s can release the most loaded NR. Therefore, controllable and rapid release of loaded NR in aqueous solution is achieved.

Another approach allowing for photo-induced disruption of self-assemblies is incorporating photochromic groups onto the hydrophobic block. The photochromic reaction can increase the polarity of the block and thus shifts the hydrophilic-hydrophobic balance which renders

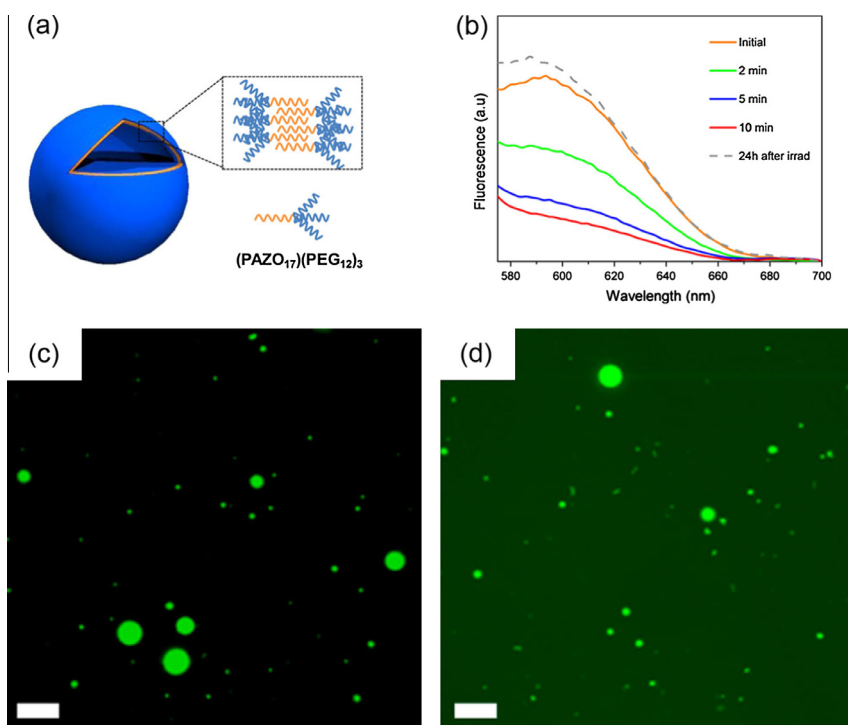


Fig. 14. (a) Schematic representation of a polymer vesicle; (b) emission spectra of the NR encapsulated micelles recorded for various irradiation time; fluorescence microscopy images of the water suspension of loaded vesicles before (c) and after (d) irradiation for 5 min. The length of the scale bar corresponds to 5 μm . (Adapted with permission from [114]).

the association of polymer chains to thermodynamically unstable state. Oriol et al. prepared a series of photochromic azobenzene-containing polymers for the study of photo-induced controllable release [114,115]. Representative example is the synthesis of miktoarm star polymer composed of a hydrophobic azobenzene-containing block and three hydrophilic PEO arms. This photochromic polymer forms stable polymeric vesicles in water, as schematically shown in Fig. 14a [114]. Firstly, NR is encapsulated in the vesicles to follow the reversible release and encapsulation process. Dramatical decrease of the NR fluorescence intensity was observed upon irradiation for 10 min (see Fig. 14b), indicating most NR are released from the membrane of vesicles to the aqueous solution due to the increase of polarity and shrinkage of vesicles. After subsequent 24 h in dark, the emission intensity almost recovers to its initial value for the re-encapsulation of the fluorescent probes. Secondly, Rhodamine B (RhB) is loaded in the vesicles to visualize the release process. As shown in Fig. 14c and d, after irradiation for 5 min, fluorescent dots are still visible by fluorescence microscopy. However, a fluorescent background can be observed, indicating large numbers of RhB are released from the interior of the vesicles to the aqueous solution.

The employment of photo-crosslinking is also a promising method. The introduction of these photosensitive moieties can regulate a reversible crosslinking process of the micelle cores or shells with light and tune the stability of the polymer nanostructure on demand. Through reversible dimerization of coumarin moieties incorporated in block

copolymers, micelles can be cross-linked and subsequently photocleaved by light illumination at two different wavelengths [29]. For example, Jiang et al. prepared NR-loaded micelles, and investigated the effect of photo-crosslinking on the release of NR from the hydrophobic core of micelles [30]. Core crosslinking slows down the release of loaded NR from the micelles, however, the rate of release can be increased by the following photo-cleavage. The results indicate that the release of loaded NR in micelle cores can be controlled by this reversible crosslinking-cleavage process.

The above examples clearly demonstrate that the use of light as a stimulus is particularly attractive for controllable release applications. But for biomedical practical applications in vivo, irradiation of short wavelength suffers high skin absorption and is detrimental to healthy cells. Longer-wavelength near-infrared light is more suitable for this purpose because it is less detrimental to healthy cells and has greater penetration depths (millimeters to centimeters) [116]. However, the photoreactions activated by 2PA effect of NIR light are generally slow and inefficient due to the typically low two-photon-absorbing cross sections of the chromophores. Moreover, the simultaneous absorption of two photons necessitates high laser power density and thus requires the use of a femtosecond pulse laser [117,118].

To surmount this obstacle, an appealing alternative has emerged for using NIR light based on lanthanide doped upconverting nanoparticles (UCNPs) [119,120]. UCNPs absorb NIR light and convert it to higher-energy photons

in the UV, visible, and NIR regions. In contrast to 2PA effect, the excitation of UCNPs by NIR light requires much lower power density [121]. Zhao et al. demonstrated this novel strategy based on NIR light-triggered dissociation of polymeric self-assemblies by taking advantage of UCNPs [122]. This strategy is very general and can be applied not only to self-assemblies but also to many other photosensitive polymeric materials of which the potential for applications is limited due to the wavelength issue.

Recent studies have led to significant progress in terms of the ability using light to control the release of loaded species in the nanocontainers formed by self-assembly [123]. Several strategies have been proposed to prepare various self-assembled aggregates aimed for photo-controllable release of loaded species. Benefiting from the photo-induced structure transformation which is non-contact and precisely controllable, these strategies are expected to be used in drug delivery in vivo [108]. However, the applicable wavelength region limits the practical usage of short wavelength light including UV and visible light. In addition, inaccessible 2PA of NIR light is an obstacle for practical applications of self-assemblies. Thus, researches toward novel mechanisms and new chemistries are needed. For instance, red light triggered producing of singlet oxygen and the following oxidation of selenium-containing polymers can surmount the obstacle of necessary short wavelength light and 2PA effect [124].

4.2. Bioimaging

Bioimaging has become a powerful tool in biological researches recently, because it offers a unique approach to visualize the morphological details of cells and tissues in vivo [125]. Self-assemblies owning optical properties are particularly suitable for bioimaging, as the encapsulated fluorescent probes are safe and sensitive [126,127]. However, most luminescent polymers undergo the well-known AIQ effect during the self-assembly process, which greatly limits the technological applications. To evading this obstacle, attempts to use the AIEE materials for bioimaging have been reported [128]. These fluorescent structures can be simply formed through self-assembly of polymers with fluorescent conjugated segments or polymers bearing AIEE-active molecules.

Liu et al. synthesized a PEG grafted conjugated polyelectrolyte (CPE) copolymer. And the copolymer was further modified with folic acid (FA) to form a cellular probe for targeted fluorescence cell imaging [129]. Uniform micelles with compact CPE cores and outer PEO shells are formed in aqueous solution. High intense emission at the range of NIR is achieved although the CPE is low-emissive. This is attributed to the dense PEO grafting chains in micelle shells which provide a hydrophobic microenvironment for the conjugated backbones against water invasion and inhibit the formation of low-emissive defects by π - π

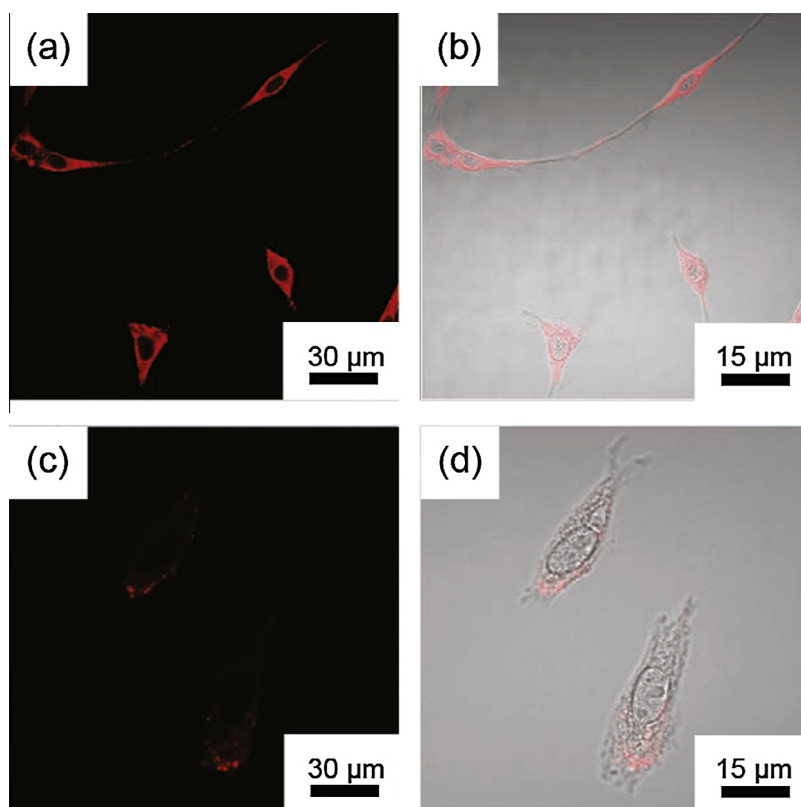


Fig. 15. Confocal laser scanning microscopy (CLSM) images stained by fluorescent micelles: (a) fluorescence and (b) fluorescence/transmission overlapped images of MCF-7 cells, and (c) fluorescence and (d) fluorescence/transmission overlapped images of NIH-3T3 cells. (Adapted with permission from [129]).

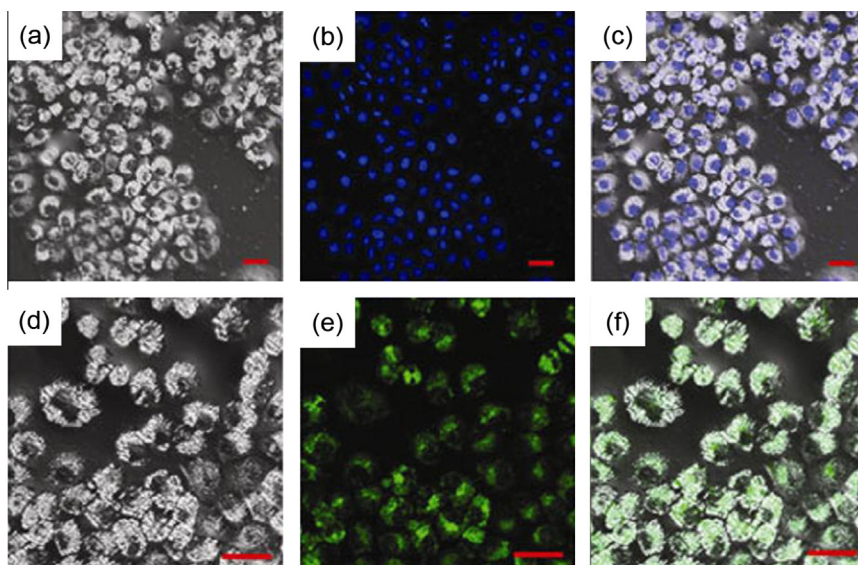


Fig. 16. CLSM images: (a–c) control: BCap37 cells, nuclei are stained with 4',6-diamidino-2-phenylindole; (d–e) BCap37 cells incubated with the micelles. Scale bars: 20 μm . (Adapted with permission from [131]).

stacking. Subsequently, breast cancer cells (MCF-7) and fibroblast normal cells (NIH-3T3) were tested in order to demonstrate the utility of fluorescent micelles in targeted cancer cell imaging. As shown in Fig. 15, strong fluorescence from the cellular cytoplasm was observed for MCF-7 cells while weak fluorescence with small staining area was observed for NIH-3T3 cells. This unique cell discrimination capability is derived from the FA groups which can be internalized by specific cancer cells based on receptor-mediated endocytosis. These results suggest that the micelles can behave as effective macromolecular probes for NIR targeted cancer cell imaging with good cellular specificity and high fluorescence contrast.

Tetraphenylethene (TPE) moieties possess attractive AIEE property [130]. Tang et al. found an amphiphilic copolymer bearing TPE moieties could self-assemble into size-tunable micelles with the hydrophobic moieties in the inner cores in DMF/H₂O mixtures [131]. The copolymer is virtually nonluminescent when molecularly dissolved in its good solvents but emits intensely when aggregated. The emissive micelles are nearly nontoxic to BCap37 cells and display great potential in bioimaging. As shown in Fig. 16, these micelles are suitable for cellular uptake without taking significant morphological change to BCap37 cells. The green emission particles can be accumulated in the cytosol rather than the nucleus and display distinguishable images of the cytosol and nucleus in cells. Therefore, this approach of constructing aggregates by the self-assembly of optical polymers bearing AIEE groups provides simple FL probes for bioimaging [132].

The self-assembly strategy has been proved to be simple and effective in transforming fluorescent molecules into aqueous media for various biological applications [15]. By encapsulating fluorescent groups into hydrophobic cores, high density of fluorescent groups as well as enhanced environmental stability are achieved. Recent advances of AIEE materials show great potential in con-

structing highly fluorescent aggregates taking advantage of the aggregation process. Thus, biocompatible self-assemblies with enhanced emission or fluorescence which are suitable for bioimaging can be obtained. In addition, molecules with specific recognition property can be anchored in copolymers to self-assemble into fluorescent aggregates which are applicable in the field of cell and tissue imaging with the advantages of extreme sensitivity and precise detection. Various signal amplification strategies, such as fluorescence resonance energy transfer (FRET) and metal-enhanced fluorescence, could be used to improve the brightness for fluorescence imaging further [133,134]. Much more smart fluorescent probes with practical usages based on polymeric aggregates would be developed to satisfy the requirements of selective and specific bioimaging in the future.

4.3. Optical sensors

The development of optical sensors for the detection of environmental and biological relevant species is currently of great interests due to their facile usage in solutions as well as their high sensitivity and selectivity for target species [135,136]. Traditional approaches for the design of new optical chemosensors or improvement of existing sensor systems are based on modification of dyes, which is time-consuming and costly. By simply encapsulating optical active species inside polymeric self-assemblies, enhancement of the sensing ability is generated [137]. This phenomenon can be attributed to significant enhanced communication between the encapsulated active component, which is significantly different from the properties of the individual components.

Both colorimetric and fluorescent properties are effective in the construction of optical sensors. For example, Liu et al. reported a dual fluorescent and colorimetric chemosensor for Fe³⁺ ions based on an amphiphilic

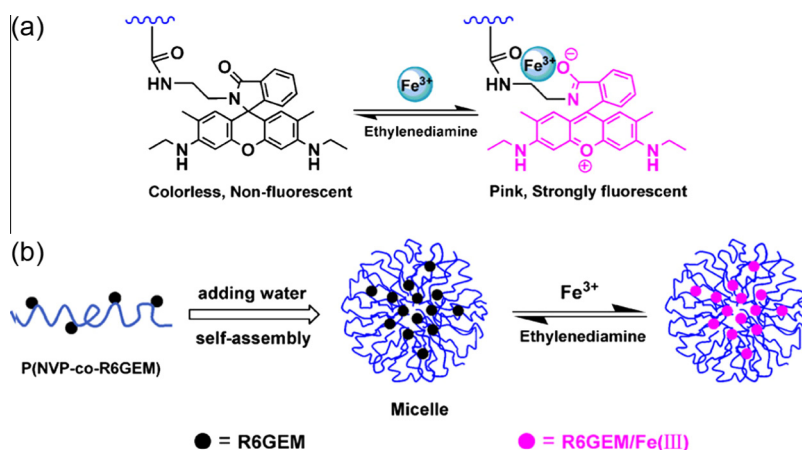


Fig. 17. Proposed ring-opening mechanism in the presence of Fe^{3+} (a) and a schematic illustration of the formation of the micelle and the Fe^{3+} sensing of the micelle in aqueous solution (b). (Adapted with permission from [138]).

random copolymer [138]. The copolymer composed of hydrophilic N-vinylpyrrolidone and hydrophobic rhodamine-based monomer R6GEM can self-assemble into micelles, which allow to be used as a chemosensor in aqueous solution. As shown in Fig. 17, the Fe^{3+} -recognizing R6GEM is colorless and under non-fluorescent ground state. Upon the addition of Fe^{3+} ions, the spirolactam moiety of the rhodamine group opens, resulting in appearance of a pink color and an orange fluorescence.

For the self-assembled fluorescent sensors, both receptors and hydrophobic fluorophores confined within the nano-sized aggregates are necessary. When analytes bind to the receptors, the proximity of the analytes to the fluorophore units result in the change of fluorescence, enabling optical detection of the analytes [137]. Recently, Huang et al. prepared a fluorescent conjugated polymer composed of poly(9,9-dioctylfluorene) (PFO) and poly(2,7-(9,9-dihexylfluorene)-alt-4,4'-phenylene ether) (PF-PE) as the fluorescence group [139]. Through cooperative self-assembling with the commercially available block copolymer F127, the formed fluorescent aggregates are easily dispersed in water. Obvious emission quench can be obtained when $5 \mu\text{M}$ of Sudan I is added and the PL of micelles can be completely quenched with the addition of $13.58 \mu\text{M}$ Sudan I. However, addition of other species such as capsanthin and β -carotene only slightly quenches the fluorescence of micelle aqueous solutions. Therefore, significantly enhanced sensitivity of the micelles is established toward trace amounts of Sudan I. The photochemical mechanism of amplified fluorescence quenching is revealed to be the charge transfer between copolymers and analytes as well as the enriching and collecting effect of aggregated structures.

Optical sensors formed by self-assembly possess promising prospect for biosensor applications [140,141]. Firstly, fluorescent moieties can be encapsulated in the aggregates, avoiding the incidental biotoxicity. Secondly, the biocompatible assemblies are much easier for the cellular uptake as an intracellular biosensor. In addition, self-assemblies owning fluorescence in range of NIR can significantly

improve the penetrability in the active tissues [142]. For example, Madsen et al. prepared a diblock copolymer poly(2-(methacryloyloxy)ethyl phosphorylcholine-*block*-2-(diisopropylamino)ethyl methacrylate) (PMPC-*b*-PDPA) to construct biosensor aggregates. The biomimetic PMPC block is known to facilitate rapid cell uptake for a wide range of cell lines, while the PDPA block composed of pH-responsive component enables facile self-assembly in aqueous solution [143]. Modified or unmodified Nile blue labels are then incorporated into the block copolymers to produce highly versatile dual capability probes. As shown in Fig. 18, copolymer chains are dissociative for the both protonated PDPA block and Nile Blue at lower pH. At higher pH between 5 and 6, deprotonation of the modified Nile Blue occurs, thus the copolymers exhibit a shift in both absorption and emission. While at physiological pH, all copolymers can self-assemble into biocompatible vesicles due to the deprotonated and hydrophobic PDPA blocks. These vesicles exhibit variable fluorescence emission depending on their environmental pH. When exposed to multicellular tumor spheroids (MCTS), these vesicles are dissociated and colorimetrically stain the interstitial tissue due to the lower pH. However, the vesicles can remain unchanged at around physiological pH in non-hypoxic tissue and be rapidly taken up by many cell lines to monitor intracellular compartments. Therefore, the self-assemblies can be utilized for imaging pH gradients within live tumor models and probing intracellular microenvironments.

Recently, chemosensors and biosensors are becoming highly demanded, facilitating opportunities to develop new techniques for the determination of target species presented in environmental and biological systems. Optical sensors have proven to be cost-effective devices and enable rather sophisticated multisensory functions. Optical sensors based on self-assemblies are becoming very popular due to their facile utilization in solution and their low requirement of preparation. For the progress of chemosensors, multiplexing detection capabilities for metal ions and environmental pollutants with usability both in solution and dry state are necessary. The properties in relation to

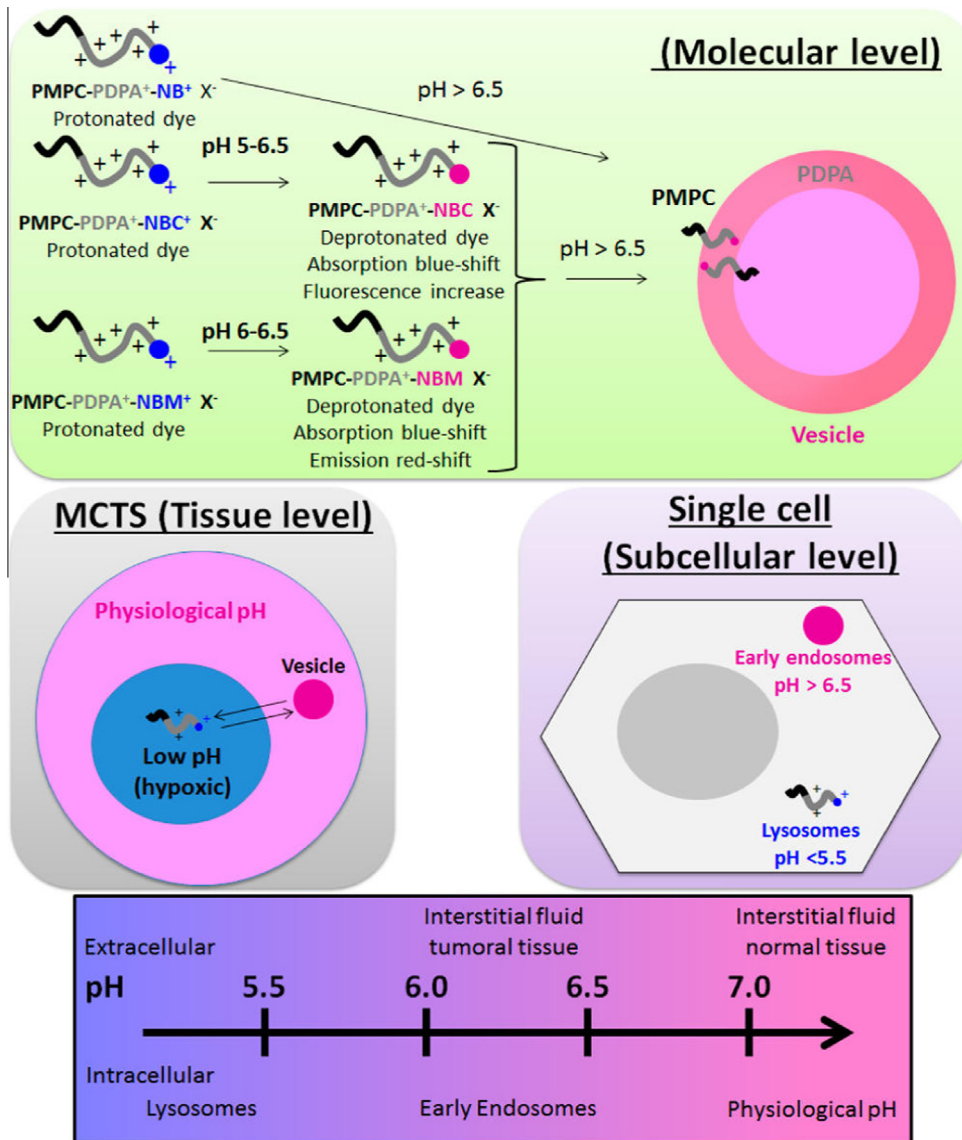


Fig. 18. Schematic representation of the basic principle for using Nile Blue-labeled copolymer vesicles as pH-sensitive probes at molecular, subcellular and tissue level, respectively. (Adapted with permission from [143]).

reproducibility and long-term stability of self-assemblies should be considered [14]. While for biosensors, higher selectivity and more pertinent detection are better, devising rationally designed polymeric receptors encapsulated in aggregates that have specificity toward a target analyte is essential [144].

5. Summary and outlook

So far lots of polymers owning optical functions have been applied to construct self-assembled aggregates. By the simple self-assembly process, polymeric aggregates owning various structures and optical properties are obtained. Optical properties of the aggregates are derived from the unique structures of polymers or the optical mol-

ecules anchored on the polymer chains. Significant variation in the emission and fluorescence properties of aggregates can be generated which is derived from the unique aggregation-induced packing type of conjugated polymer segments as well as the special enhanced intermolecular interactions. These aggregation-induced optical properties can be affected by environmental stimuli dramatically. In addition, the aggregates with photo-responsive properties can perceive light stimuli and change their structures accordingly. These enhanced optical properties by aggregation of polymers confer enormous advantages for practical usages, such as in biomedicine area and environmental detection.

When focused on aggregation-induced optical properties, AIEE is a property taking advantage of both the optical property and aggregated structure. Benefitting from AIEE

effect, self-assemblies with enhanced emission and stimuli-responsive properties are useful for optical imaging and optical sensors. Furthermore, the fluorescence intensity of aggregates can be improved by combining with other signal amplification strategies including fluorescence resonance energy transfer and metal-enhanced fluorescence. 2PA effect is a promising nonlinear optical property that can be applied to biomedical applications. However, inefficient photoreactions activated by 2PA effect of NIR light and the requirement of femtosecond pulse laser limit its practical application. In the near future, how to promote the usage of 2PA effect is needed to be addressed.

For aggregates with photo-responsive functions, however, their responsive mechanisms are not well addressed so far. This is challenging because the interrelated events on the molecular level should be investigated simultaneously. Besides, main photochromic fluorescent groups considered for the development and design of photo-responsive systems are confined to such species as azobenzenes, spiropyrans and diarylethenes. Efforts should be aimed at making further improvements to these available photo-responsive units with elaborate mechanical motions and large polarity. In addition, achieving multifunctional photo-responsive system is another promising research field. For instance, rapid response structure transformation can be achieved by combined utilization of multi photo-responsive properties such as large polarity change and photo-crosslinking. Moreover, combining light with other stimuli including pH and temperature offers possibilities to construct self-assemblies with high targeted sensitivity which can be widely applicable for complex conditions.

It should be noted that the optical properties of self-assemblies are significantly influenced by the morphology of aggregates. Since aggregate structures can be manipulated in self-assembly, it is a very appealing method to control over the final optical properties by tuning the self-assembly process. For instance, changing self-assembling temperature and initial concentration can manipulate the aggregate structure. Variation of the structures gives rise to different final optical properties. Thus, controllable optical properties are obtained.

Compared with aggregates in bulk, self-assemblies in solution have exceptional advantages for their applications in vivo due to their usability in aqueous solution. Promising applications such as photodynamic therapy have been proposed based on self-assemblies with optical properties [145]. In spite of this, many factors should be considered in practices. The biocompatibility and biotoxicity of these aggregates should be first evaluated. Although most aggregates are steady in suspension for several months even years, their stability in complex condition in vivo is not well known. An interesting option for improving the biocompatibility of self-assemblies may involve the use of self-destructive components owning optical properties, which could be degraded into unharmed products after the accomplishment of their purpose in vivo. In addition, the applicable wavelength region in biological tissue raises the requirement of enhanced optical property in the NIR region. Researches toward novel strategies of structure transformation are still needed to overcome the obstacle.

Moreover, the ability of high sensibility and targeted performance to the given species is necessary. Polymeric aggregates should be well-designed to meet the demands such as long circulation stabilization, low cytotoxicity, targeting and accumulating in tissues or cells.

Limited to the scope of this article, the hydrophobic and hydrophilic effects are mainly considered for the self-assembly behaviors. Other noncovalent interactions such as hydrogen bonds, π - π stacking and metal-ligand coordination can also be applied to construct self-assemblies. Combining use of these interactions would produce elaborate aggregate structure, along with enhanced photo-switchable optical properties and novel practical usages. The aggregates with multifarious optical properties generated from self-assembly of polymers would have more promising applications in the future.

Acknowledgements

This work is supported by National Natural Science Foundation of China (51103044, 21234002 and 51303055) and Research Fund for the Doctoral Program of Higher Education of China (20120074120001). Support from Projects of Shanghai Municipality (11QA1401600, 13ZZ041, 12JC1403102 and 12ZR1442500) and Fundamental Research Funds for the Central Universities (NCET-12-0857 and WD1213002) is also appreciated.

References

- [1] Lazzari M, Rodríguez-Abreu C, Rivas J, López-Quintela MA. Self-assembly: a minimalist route to the fabrication of nanomaterials. *J Nanosci Nanotechnol* 2006;6:892–905.
- [2] Liu C-L, Lin C-H, Kuo C-C, Lin S-T, Chen W-C. Conjugated rod-coil block copolymers: synthesis, morphology, photophysical properties, and stimuli-responsive applications. *Prog Polym Sci* 2011;36:603–37.
- [3] Cai C, Li Y, Lin J, Wang L, Lin S, Wang X-S, et al. Simulation-assisted self-assembly of multicomponent polymers into hierarchical assemblies with varied morphologies. *Angew Chem Int Ed* 2013; 52:7732–6.
- [4] Cai C, Lin J, Zhuang Z, Zhu W. Ordering of polypeptides in liquid crystals, gels and micelles. *Adv Polym Sci* 2013;259:159–99.
- [5] Wang A, Huang J, Yan Y. Hierarchical molecular self-assemblies: construction and advantages. *Soft Matter* 2014;10:3362–73.
- [6] Smith DK, Hirst AR, Love CS, Hardy JG, Brignell SV, Huang B. Self-assembly using dendritic building blocks—towards controllable nanomaterials. *Prog Polym Sci* 2005;30:220–93.
- [7] Yen H-C, Cabral H, Mi P, Toh K, Matsumoto Y, Liu X, Koori H, Kim A, Miyazaki K, Miura Y, Nishiyama N, Kataoka K. Light-induced cytosolic activation of reduction-sensitive camptothecin-loaded polymeric micelles for spatiotemporally controlled in vivo chemotherapy. *ACS Nano* 2014;8:11591–602.
- [8] Ercole F, Davis TP, Evans RA. Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond. *Polym Chem* 2010;1:37–54.
- [9] Zhang J, Chen X-F, Wei H-B, Wan X-H. Tunable assembly of amphiphilic rod-coil block copolymers in solution. *Chem Soc Rev* 2013;42:9127–54.
- [10] Li J, Li X, Ni D, Wang J, Tu G, Zhu J. Self-assembly of poly(3-hexyl thiophene)-*b*-poly(ethylene oxide) into cylindrical micelles in binary solvent mixtures. *J Appl Polym Sci* 2014;131:41186.
- [11] Jia L, Tong L, Liang Y, Petretic A, Guerin G, Manners I, Winnik MA. Templated fabrication of fiber-basket polymersomes via crystallization-driven block copolymer self-assembly. *J Am Chem Soc* 2014;136:16676–82.
- [12] Wang J, Wang X, Yang F, Shen H, You Y, Wu D. Self-assembly behavior of a linear-star supramolecular amphiphile based on host-guest complexation. *Langmuir* 2014;30:13014–20.

- [13] Ahn DJ, Lee S, Kim J-M. Rational design of conjugated polymer supramolecules with tunable colorimetric responses. *Adv Funct Mater* 2009;19:1483–96.
- [14] Canfarotta F, Whitcombe MJ, Piletsky SA. Polymeric nanoparticles for optical sensing. *Biotechnol Adv* 2013;31:1585–99.
- [15] Zhao Q, Wang Y, Yan Y, Huang J. Smart nanocarrier: self-assembly of bacteria-like vesicles with photoswitchable cilia. *ACS Nano* 2014;8:11341–9.
- [16] Xu H, Li Q, Wang L, He Y, Shi J, Tang B, Fan C. Nanoscale optical probes for cellular imaging. *Chem Soc Rev* 2014;43:2650–61.
- [17] Saibal B, Ashar AZ, Devi RN, Narayan KS, Asha SK. Nanostructured donor–acceptor self assembly with improved photoconductivity. *ACS Appl Mater Interfaces* 2014;6:19434–48.
- [18] Wang G, Zhang J. Photoresponsive molecular switches for biotechnology. *J Photochem Photobiol, C* 2012;13:299–309.
- [19] Wang W, Du C, Wang X, He X, Lin J, Li L, Lin S. Directional photomanipulation of breath figure arrays. *Angew Chem Int Ed* 2014;53:12116–9.
- [20] Yamamura M, Yamakawa K, Okazaki Y, Nabeshima T. Coordination-driven macrocyclization for locking of photo- and thermal cis-trans isomerization of azobenzene. *Chem – Eur J* 2014;20:16258–65.
- [21] Yildiz I, Deniz E, Raymo FM. Fluorescence modulation with photochromic switches in nanostructured constructs. *Chem Soc Rev* 2009;38:1859–67.
- [22] Harvey CP, Tovar JD. Main-chain photochromic conducting polymers. *Polym Chem* 2011;2:2699–706.
- [23] Zhu M-Q, Zhu L, Han JJ, Wu W, Hurst JK, Li ADQ. Spiropyran-based photochromic polymer nanoparticles with optically switchable luminescence. *J Am Chem Soc* 2006;128:4303–9.
- [24] de Cuendias A, Hiorns RC, Cloutet E, Vignau L, Cramail H. Conjugated rod–coil block copolymers and optoelectronic applications. *Polym Int* 2010;59:1452–76.
- [25] Kwon JH, Song JE, Yoon B, Kim JM, Cho EC. Role of gel to fluid transition temperatures of polydiacetylene vesicles with 10,12-pentacosadiynoic acid and cholesterol in their thermochromisms. *Bull Korean Chem Soc* 2014;35:1809–16.
- [26] Hui L, Bin Z, Ping S, Meixiu W, Songting T. Synthesis and electroluminescent properties of a polyfluorene grafted oligo (phenylenevinylene derivative with two triphenylamine side group). *Acta Polym Sin* 2010;501:7.
- [27] Navale ST, Mane AT, Khuspe GD, Chougule MA, Patil VB. Room temperature NO₂ sensing properties of polythiophene films. *Synth Met* 2014;195:228–33.
- [28] Liao J, Wu S, Yin Z, Huang S, Ning C, Tan G, Chu PK. Surface-dependent self-assembly of conducting polypyrrole nanotube arrays in template-free electrochemical polymerization. *ACS Appl Mater Interfaces* 2014;6:10946–51.
- [29] Seo HJ, Kim J-C. Characteristics and photo-responsive release property of liposome containing 7-acetoxy coumarin. *J Nanosci Nanotechnol* 2011;11:10262–70.
- [30] Jiang J, Qi B, Lepage M, Zhao Y. Polymer micelles stabilization on demand through reversible photo-cross-linking. *Macromolecules* 2007;40:790–2.
- [31] Kaur G, Johnston P, Saito K. Photo-reversible dimerisation reactions and their applications in polymeric systems. *Polym Chem* 2014;5:2171–86.
- [32] Yu H, Li J, Wu D, Qiu Z, Zhang Y. Chemistry and biological applications of photo-labile organic molecules. *Chem Soc Rev* 2010;39:464–73.
- [33] Fomina N, McFearnin CL, Sermsakdi M, Morachis JM, Almutairi A. Low power, biologically benign NIR light triggers polymer disassembly. *Macromolecules* 2011;44:8590–7.
- [34] Fomina N, McFearnin C, Sermsakdi M, Edigin O, Almutairi A. UV and Near-IR triggered release from polymeric nanoparticles. *J Am Chem Soc* 2010;132:9540–2.
- [35] de Gracia Lux C, McFearnin CL, Joshi-Barr S, Sankaranarayanan J, Fomina N, Almutairi A. Single UV or Near IR triggering event leads to polymer degradation into small molecules. *ACS Macro Lett* 2012;1:922–6.
- [36] Fomina N, McFearnin CL, Almutairi A. Increasing materials' response to two-photon NIR light via self-immolative dendritic scaffolds. *Chem Commun* 2012;48:9138–40.
- [37] Liu G, Wang X, Hu J, Zhang G, Liu S. Self-immolative polymersomes for high-efficiency triggered release and programmed enzymatic reactions. *J Am Chem Soc* 2014;136:7492–7.
- [38] Zhou Y, Yan D. Supramolecular self-assembly of amphiphilic hyperbranched polymers at all scales and dimensions: progress, characteristics and perspectives. *Chem Commun* 2009;1172–88.
- [39] Xu L, Feng L, Han Y, Jing Y, Xian Z, Liu Z, Huang J, Yan Y. Supramolecular self-assembly enhanced Europium (iii) luminescence under visible light. *Soft Matter* 2014;10:4686–93.
- [40] Padhy H, Sahu D, Chiang IH, Patra D, Kekuda D, Chu C-W, Lin H-C. Synthesis and applications of main-chain Ru(ii) metallo-polymers containing bis-terpyridyl ligands with various benzodiazole cores for solar cells. *J Mater Chem* 2011;21:1196–205.
- [41] Li Z, Ma R, An Y, Shi L. Micellization and luminescence of PEG-*b*-P4VP/Europium (III)/1,10-phenanthroline complex. *Colloid Polym Sci* 2010;288:1041–6.
- [42] Thévenaz DC, Monnier CA, Balog S, Fiore GL. Luminescent nanoparticles with lanthanide-containing poly(ethylene glycol)-poly(ϵ -caprolactone) block copolymers. *Biomacromolecules* 2014;15:3994–4001.
- [43] Chiper M, Winter A, Hoogenboom R, Egbe DAM, Wouters D, Hoepfner S, Fustin C-A, Gohy J-F, Schubert US. Synthesis and micellization of coil–rod–coil Ruthenium (II) terpyridine assemblies. *Macromolecules* 2008;41:8823–31.
- [44] Hofmeier H, Hoogenboom R, Wouters MEL, Schubert US. High molecular weight supramolecular polymers containing both terpyridine metal complexes and ureidopyrimidinone quadruple hydrogen-bonding units in the main chain. *J Am Chem Soc* 2005;127:2913–21.
- [45] Wang Y, Lin S, Zang M, Xing Y, He X, Lin J, Chen T. Self-assembly and photo-responsive behavior of novel ABC₂-type block copolymers containing azobenzene moieties. *Soft Matter* 2012;8:3131–8.
- [46] He X, Gao C, Sun W, Huang W, Lin S, Yan D. Synthesis and photoresponsive behavior of azobenzene-containing side-chain liquid crystalline diblock polymers with polypeptide block. *J Polym Sci, Part A: Polym Chem* 2013;51:1040–50.
- [47] Lin S, Wang Y, Cai C, Xing Y, Lin J, Chen T, He X. Tuning self-assembly and photo-responsive behavior of azobenzene-containing triblock copolymers by combining homopolymers. *Nanotechnology* 2013;24:085602.
- [48] Zang M, Li C, Sun W, He X, Lin S. Study on the synthesis, self-assembly and responsive behavior of triblock copolymers containing azobenzene moieties. *China Sciencepaper* 2014;6:648–53.
- [49] Sun W, He X, Gao C, Liao X, Xie M, Lin S, Yan D. Novel amphiphilic and photo-responsive ABC 3-miktoarm star terpolymers: synthesis, self-assembly and photo-responsive behavior. *Polym Chem* 2013;4:1939–49.
- [50] Xing Y, Lin S, Lin J. Synthesis, self-assembly and responsive properties of PEG-*b*-PDMAEMA-*b*-PMMAzo triblock copolymers. *Chin J Polym Sci* 2013;31:833–40.
- [51] Lin S, Lin J, Nose T, Iyoda T. Micellar structures of block-copolymers with ordered cores in dilute solution as studied by polarized and depolarized light scattering. *J Polym Sci, Part B: Polym Phys* 2007;45:1333–43.
- [52] Sun W, He X, Liao X, Lin S, Huang W, Xie M. Synthesis of azobenzene-containing side chain liquid crystalline diblock copolymers using RAFT polymerization and photo-responsive behavior. *J Appl Polym Sci* 2013;130:2165–75.
- [53] Yang Y, Zhang Y, Wei Z. Supramolecular helices: chirality transfer from conjugated molecules to structures. *Adv Mater* 2013;25:6039–49.
- [54] Huang Y-Q, Fan Q-L, Liu X-F, Fu N-N, Huang W. Solvent- and pH-induced self-assembly of cationic meta-linked poly(phenylene ethynylene): effects of helix formation on amplified fluorescence quenching and Förster resonance energy transfer. *Langmuir* 2010;26:19120–8.
- [55] Samorí P, Francke V, Müllen K, Rabe JP. Self-assembly of a conjugated polymer: from molecular rods to a nanoribbon architecture with molecular dimensions. *Chem – Eur J* 1999;5:2312–7.
- [56] Lin S-T, Tung Y-C, Chen W-C. Synthesis, structures and multifunctional sensory properties of poly[2,7-(9,9-dihexylfluorene)]-*block*-poly[2-(dimethylamino)ethyl methacrylate] rod–coil diblock copolymers. *J Mater Chem* 2008;18:3985–92.
- [57] ten Cate MGJ, Severin N, Börner HG. Self-assembling peptide–polymer conjugates comprising (D-alt-L)-cyclopeptides as aggregator domains. *Macromolecules* 2006;39:7831–8.
- [58] Cheng L, Zhang G, Zhu L, Chen D, Jiang M. Nanoscale tubular and sheetlike superstructures from hierarchical self-assembly of polymeric Janus particles. *Angew Chem Int Ed* 2008;120:10325–8.
- [59] Liu G, Ma R, Ren J, Li Z, Zhang H, Zhang Z, An Y, Shi L. A glucose-responsive complex polymeric micelle enabling repeated on–off release and insulin protection. *Soft Matter* 2013;9:1636–44.

- [60] Avestro A-J, Belowich ME, Stoddart JF. Cooperative self-assembly: producing synthetic polymers with precise and concise primary structures. *Chem Soc Rev* 2012;41:5881–95.
- [61] Wu S, Wang L, Kroeger A, Wu Y, Zhang Q, Bubeck C. Block copolymers of PS-*b*-PEO co-assembled with azobenzene-containing homopolymers and their photoresponsive properties. *Soft Matter* 2011;7:11535–45.
- [62] Zhang C, Jin S, Li S, Xue X, Liu J, Huang Y, Jiang Y, Chen W-Q, Zou G, Liang X-J. Imaging intracellular anticancer drug delivery by self-assembly micelles with aggregation-induced emission (AIE micelles). *ACS Appl Mater Interfaces* 2014;6:5212–20.
- [63] Jin C, Zhang T, Wang L, He M, Yuan T, Jiang B, Xiao D, Yin Q. Photoinduced deformation of hollow nanospheres formed by the self-assembly of amphiphilic random copolymers and small azo molecules. *RSC Adv* 2014;4:45890–4.
- [64] Deepak VD, Sundararajan PR. Solvent mixture induced self assembly of a terthiophene based rod-coil block co-oligomer. *J Phys Chem B* 2011;115:8458–64.
- [65] Jiang H, Zhang J, Sun J, Huang W. Novel amphiphilic photoluminescent copolymers containing fluorene, pyridine and thiophene moieties: synthesis, characterization and self-assembly. *Polymer* 2012;53:5684–90.
- [66] Shi C, Guo Z, Yan Y, Zhu S, Xie Y, Zhao YS, Zhu W, Tian H. Self-assembly solid-state enhanced red emission of quinolinemalononitrile: optical waveguides and stimuli response. *ACS Appl Mater Interfaces* 2012;5:192–8.
- [67] Wang M, Silva GL, Armitage BA. DNA-templated formation of a helical cyanine dye J-aggregate. *J Am Chem Soc* 2000;122:9977–86.
- [68] Zhang S, Qin A, Sun J, Tang B. Mechanism study of aggregation-induced emission. *Progr Chem* 2011;23:623–36.
- [69] Takagi K, Kawagita E, Kouchi R, Kawai J. Aggregation of polythiophene homopolymer and block copolymer in solution utilizing the characteristics of pyridine at the side chain. *J Polym Sci, Part A: Polym Chem* 2014;52:3383–9.
- [70] de Cuendias A, Ibarboure E, Lecommandoux S, Cloutet E, Cramail H. Synthesis and self-assembly in water of coil-rod-coil amphiphilic block copolymers with central π -conjugated sequence. *J Polym Sci, Part A: Polym Chem* 2008;46:4602–16.
- [71] Lin J, Ding W, Hong K, Mays JW, Xu Z, Yuan Y. Micellization coupled with facilitation of J-aggregation for poly(1,3-cyclohexadiene)-based amphiphilic block copolymers. *Soft Matter* 2008;4:1605–8.
- [72] Hong Y, Lam JWY, Tang BZ. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem Commun* 2009;29:4332–53.
- [73] Wang M, Zhang GX, Zhang DQ, Zhu DB, Tang B. Fluorescent bio/chemosensors based on silole and tetraphenylethene luminogens with aggregation-induced emission feature. *J Mater Chem* 2010;20:1858–67.
- [74] Chen J-I, Wu W-C. Fluorescent polymeric micelles with aggregation-induced emission properties for monitoring the encapsulation of doxorubicin. *Macromol Biosci* 2013;13:623–32.
- [75] Tu G, Li H, Forster M, Heiderhoff R, Balk LJ, Sigel R, Scherf U. Amphiphilic conjugated block copolymers: synthesis and solvent-selective photoluminescence quenching. *Small* 2007;3:1001–6.
- [76] Kew SJ, Hall EAH. PH response of carboxy-terminated colorimetric polydiacetylene vesicles. *Anal Chem* 2006;78:2231–8.
- [77] Chung CY-S, Yam VW-W. Dual pH- and temperature-responsive metallosupramolecular block copolymers with tunable critical micelle temperature by modulation of the self-assembly of NIR-emissive alkynylplatinum (II) complexes induced by changes in hydrophilicity and electrostatic effects. *Chem - Eur J* 2013;19:13182–92.
- [78] Yang C-M, Lai Y-W, Kuo S-W, Hong J-L. Complexation of fluorescent tetraphenylthiophene-derived ammonium chloride to poly(*N*-isopropylacrylamide) with sulfonate terminal: aggregation-induced emission, critical micelle concentration, and lower critical solution temperature. *Langmuir* 2012;28:15725–35.
- [79] Cho MJ, Choi DH, Sullivan PA, Akelaitis AJP, Dalton LR. Recent progress in second-order nonlinear optical polymers and dendrimers. *Prog Polym Sci* 2008;33:1013–58.
- [80] Ouyang CB, Liu HB, Song YL. Functionalized gold nanoparticles self-assemblies with efficient nonlinear optical properties. *J Nanosci Nanotechnol* 2012;12:2990–7.
- [81] Ji W, Li N, Chen D, Qi X, Sha W, Jiao Y, Xu Q, Lu J. Coumarin-containing photo-responsive nanocomposites for NIR light-triggered controlled drug release via a two-photon process. *J Mater Chem B* 2013;1:5942–9.
- [82] McKenzie TG, Wong EHH, Fu Q, Lam SJ, Dunstan DE, Qiao GG. Highly efficient and versatile formation of biocompatible star polymers in pure water and their stimuli-responsive self-assembly. *Macromolecules* 2014;47:7869–77.
- [83] Ulasan M, Yavuz E, Bagriaciak EU, Cengeloglu Y, Yavuz MS. Biocompatible thermoresponsive PEGMA nanoparticles crosslinked with cleavable disulfide-based crosslinker for dual drug release. *J Biomed Mater Res, Part A* 2015;103:243–51.
- [84] Yang P-C, Chen H-C, Wen H-W, Wu P-I. Preparation and self-assembly of stimuli-responsive azobenzene-containing diblock copolymers through microwave-assisted RAFT polymerization. *J Polym Sci, Part A: Polym Chem* 2014;52:3107–17.
- [85] Herzberger J, Kurzbach D, Werre M, Fischer K, Hinderberger D, Frey H. Stimuli-responsive tertiary amine functional PEGs based on *N,N*-Dialkylglycidylamines. *Macromolecules* 2014;47:7679–90.
- [86] Deloncle R, Caminade A-M. Stimuli-responsive dendritic structures: the case of light-driven azobenzene-containing dendrimers and dendrons. *J Photochem Photobiol, C* 2010;11:25–45.
- [87] Huang Y, Dong R, Zhu X, Yan D. Photo-responsive polymeric micelles. *Soft Matter* 2014;10:6121–38.
- [88] Wang D, Wang X. Amphiphilic azo polymers: molecular engineering, self-assembly and photoresponsive properties. *Prog Polym Sci* 2013;38:271–301.
- [89] Li Y, Deng Y, Tong X, Wang X. Formation of photoresponsive uniform colloidal spheres from an amphiphilic azobenzene-containing random copolymer. *Macromolecules* 2006;39:1108–15.
- [90] Liu J, He Y, Wang X. Azo polymer colloidal spheres containing different amounts of functional groups and their photoinduced deformation behavior. *Langmuir* 2008;24:678–82.
- [91] Li Y, He Y, Tong X, Wang X. Photoinduced deformation of amphiphilic azo polymer colloidal spheres. *J Am Chem Soc* 2005;127:2402–3.
- [92] Wang D, Liu J, Ye G, Wang X. Amphiphilic block copolymers bearing strong push-pull azo chromophores: synthesis, micelle formation and photoinduced shape deformation. *Polymer* 2009;50:418–27.
- [93] Wang D, Ye G, Zhu Y, Wang X. Photoinduced mass-migration behavior of two amphiphilic side-chain azo diblock copolymers with different length flexible spacers. *Macromolecules* 2009;42:2651–7.
- [94] Deng Y, Li N, He Y, Wang X. Hybrid colloids composed of two amphiphilic azo polymers: fabrication, characterization, and photoresponsive properties. *Macromolecules* 2007;40:6669–78.
- [95] Dai S, Ravi P, Tam KC. Thermo- and photo-responsive polymeric systems. *Soft Matter* 2009;5:2513–33.
- [96] Ye L, Liu X, Ito K, Feng Z. The preparation of an azo-substituted polyrotaxane end-capped with PNIPAAm and its dual stimuli-responsive behavior for drug delivery applications. *J Mater Chem B* 2014;2:5746–57.
- [97] Wang G, Tong X, Zhao Y. Preparation of azobenzene-containing amphiphilic diblock copolymers for light-responsive micellar aggregates. *Macromolecules* 2004;37:8911–7.
- [98] Jiang J, Tong X, Zhao Y. A new design for light-breakable polymer micelles. *J Am Chem Soc* 2005;127:8290–1.
- [99] Lin L, Yan Z, Gu J, Zhang Y, Feng Z, Yu Y. UV-responsive behavior of azopyridine-containing diblock copolymeric vesicles: photoinduced fusion, disintegration and rearrangement. *Macromol Rapid Commun* 2009;30:1089–93.
- [100] Su W, Luo Y, Yan Q, Wu S, Han K, Zhang Q, Gu Y, Li Y. Photoinduced fusion of micro-vesicles self-assembled from azobenzene-containing amphiphilic diblock copolymers. *Macromol Rapid Commun* 2007;28:1251–6.
- [101] Jin H, Zheng Y, Liu Y, Cheng H, Zhou Y, Yan D. Reversible and large-scale cytomimetic vesicle aggregation: light-responsive host-guest interactions. *Angew Chem Int Ed* 2011;50:10352–6.
- [102] Sun K, Chen K, Xue G, Cai J, Zou G, Li Y, Zhang Q. Near-infrared light induced fusion and fission of azobenzene-containing polymer vesicles. *RSC Adv* 2013;3:23997–4000.
- [103] Lin L, Feng Z, Yu Q, Yan Z, Yen C-C, Yu Y. Self-assembly and photoresponsive behavior of amphiphilic diblock copolymers containing azobenzene moieties. *Mol Cryst Liq Cryst* 2009;508:214/(576)–225/(587).
- [104] Kotharangannagar VK, Sánchez-Ferrer A, Ruokolainen J, Mezzenga R. Photoresponsive reversible aggregation and dissolution of rod-coil polypeptide diblock copolymers. *Macromolecules* 2011;44:4569–73.
- [105] Feng N, Dong J, Han G, Wang G. Polymer nanoparticles based on pyrene-functionalized poly(acrylic acid) for controlled release under photo and pH stimulation. *Macromol Rapid Commun* 2014;35:721–6.

- [106] Qin W, Ding D, Liu J, Yuan WZ, Hu Y, Liu B, Tang BZ. Biocompatible nanoparticles with aggregation-induced emission characteristics as far-red/near-infrared fluorescent bioprobes for in vitro and in vivo imaging applications. *Adv Funct Mater* 2012;22:771–9.
- [107] Zhang Q, Ko N Re, Oh JK. Recent advances in stimuli-responsive degradable block copolymer micelles: synthesis and controlled drug delivery applications. *Chem Commun* 2012;48:7542–52.
- [108] Li Y, Qian Y, Liu T, Zhang G, Liu S. Light-triggered concomitant enhancement of magnetic resonance imaging contrast performance and drug release rate of functionalized amphiphilic diblock copolymer micelles. *Biomacromolecules* 2012;13:3877–86.
- [109] Liu G, Dong C-M. Photoresponsive poly(s-(o-nitrobenzyl)-l-cysteine)-b-PEO from a l-cysteine N-carboxyanhydride monomer: synthesis, self-assembly, and phototriggered drug release. *Biomacromolecules* 2012;13:1573–83.
- [110] Cabane E, Malinova V, Menon S, Palivan CG, Meier W. Photoresponsive polymersomes as smart, triggerable nanocarriers. *Soft Matter* 2011;7:9167–76.
- [111] Kumar S, Allard J-F, Morris D, Dory YL, Lepage M, Zhao Y. Near-infrared light sensitive polypeptide block copolymer micelles for drug delivery. *J Mater Chem* 2012;22:7252–7.
- [112] Zhao Y. Photocontrollable block copolymer micelles: what can we control. *J Mater Chem* 2009;19:4887–95.
- [113] Han D, Tong X, Zhao Y. Fast photodegradable block copolymer micelles for burst release. *Macromolecules* 2011;44:437–9.
- [114] Blasco E, Schmidt BVKJ, Barner-Kowollik C, Piñol M, Oriol L. A novel photoresponsive azobenzene-containing miktoarm star polymer: self-assembly and photoresponse properties. *Macromolecules* 2014;47:3693–700.
- [115] Blasco E, Barrio Jd, Sanchez-Somolinos C, Pinol M, Oriol L. Light induced molecular release from vesicles based on amphiphilic linear-dendritic block copolymers. *Polym Chem* 2013;4:2246–54.
- [116] Sordillo LA, Pu Y, Prataveira S, Budansky Y, Alfano RR. Deep optical imaging of tissue using the second and third near-infrared spectral windows. *J Biomed Optics* 2014;19:056004.
- [117] Babin J, Pelletier M, Lepage M, Allard J-F, Morris D, Zhao Y. A new two-photon-sensitive block copolymer nanocarrier. *Angew Chem Int Ed* 2009;48:3329–32.
- [118] Wang C, Yeh AT. Two-photon excited fluorescence enhancement with broadband versus tunable femtosecond laser pulse excitation. *J Biomed Optics* 2012;17:0250031–38.
- [119] Wang F, Liu X. Upconversion multicolor fine-tuning: visible to near-infrared emission from lanthanide-doped NaYF₄ nanoparticles. *J Am Chem Soc* 2008;130:5642–3.
- [120] Jeong S, Won N, Lee J, Bang J, Yoo J, Kim SG, Chang JA, Kim J, Kim S. Multiplexed near-infrared in vivo imaging complementarily using quantum dots and upconverting NaYF₄:Yb³⁺, Tm³⁺ nanoparticles. *Chem Commun* 2011;47:8022–4.
- [121] Nyk M, Kumar R, Ohulchanskyy TY, Bergery EJ, Prasad PN. High contrast in vitro and in vivo photoluminescence bioimaging using near infrared to near infrared up-conversion in Tm³⁺ and Yb³⁺ doped fluoride nanophosphors. *Nano Lett* 2008;8:3834–8.
- [122] Yan B, Boyer J-C, Branda NR, Zhao Y. Near-infrared light-triggered dissociation of block copolymer micelles using upconverting nanoparticles. *J Am Chem Soc* 2011;133:19714–7.
- [123] Bédard MF, De Geest BG, Skirtach AG, Möhwald H, Sukhorukov GB. Polymeric microcapsules with light responsive properties for encapsulation and release. *Adv Colloid Interface Sci* 2010;158:2–14.
- [124] Han P, Li S, Cao W, Li Y, Sun Z, Wang Z, Xu H. Red light responsive diselenide-containing block copolymer micelles. *J Mater Chem B* 2013;1:740–3.
- [125] Kim J-H, Park K, Nam HY, Lee S, Kim K, Kwon IC. *Polym Bioimaging*. *Prog Polym Sci* 2007;32:1031–53.
- [126] Yu S, Dong R, Chen J, Chen F, Jiang W, Zhou Y, Zhu X, Yan D. Synthesis and self-assembly of amphiphilic aptamer-functionalized hyperbranched multiarm copolymers for targeted cancer imaging. *Biomacromolecules* 2014;15:1828–36.
- [127] He J, Huang X, Li Y-C, Liu Y, Babu T, Aronova MA, Wang S, Lu Z, Chen X, Nie Z. Self-assembly of amphiphilic plasmonic micelle-like nanoparticles in selective solvents. *J Am Chem Soc* 2013;135:7974–84.
- [128] Lu H, Su F, Mei Q, Zhou X, Tian Y, Tian W, Johnson RH, Meldrum DR. A series of poly[N-(2-hydroxypropyl)methacrylamide] copolymers with anthracene-derived fluorophores showing aggregation-induced emission properties for bioimaging. *J Polym Sci, Part A: Polym Chem* 2012;50:890–9.
- [129] Pu K-Y, Li K, Liu B. A molecular brush approach to enhance quantum yield and suppress nonspecific interactions of conjugated polyelectrolyte for targeted far-red/near-infrared fluorescence cell imaging. *Adv Funct Mater* 2010;20:2770–7.
- [130] Zhao Z, Chen B, Geng J, Chang Z, Aparicio-Ixta L, Nie H, Goh CC, Ng LG, Qin A, Ramos-Ortiz G, Liu B, Tang BZ. Red emissive biocompatible nanoparticles from tetraphenylethene-decorated BODIPY luminogens for two-photon excited fluorescence cellular imaging and mouse brain blood vascular visualization. *Part Part Syst Charact* 2014;31:481–91.
- [131] Qin A, Zhang Y, Han N, Mei J, Sun J, Fan W, Tang B. Preparation and self-assembly of amphiphilic polymer with aggregation-induced emission characteristics. *Sci China Chem* 2012;55:772–8.
- [132] Wu W-C, Chen C-Y, Tian Y, Jang S-H, Hong Y, Liu Y, Hu R, Tang BZ, Lee Y-T, Chen C-T, Chen W-C, Jen AKY. Enhancement of aggregation-induced emission in dye-encapsulating polymeric micelles for bioimaging. *Adv Funct Mater* 2010;20:1413–23.
- [133] Xu Z, Liao Q, Shi X, Li H, Zhang H, Fu H. Full-color tunable organic nanoparticles with FRET-assisted enhanced two-photon excited fluorescence for bio-imaging. *J Mater Chem B* 2013;1:6035–41.
- [134] Li A, Liu J, Liu G, Zhang J, Feng S. Design, synthesis of fluorescent core-shell nanoparticles with tunable lower critical solution temperature behavior and metal-enhanced fluorescence. *J Polym Sci, Part A: Polym Chem* 2014;52:87–95.
- [135] Nilsson KPR, Inganas O. Chip and solution detection of DNA hybridization using a luminescent zwitterionic polythiophene derivative. *Nat Mater* 2003;2:419–24.
- [136] Qazi HH, bin Mohammad AB, Akram M. Recent progress in optical chemical sensors. *Sensors* 2012;12:16522–56.
- [137] Bandyopadhyay P, Ghosh AK. Recent developments in micelle-induced fluorescent sensors. *Sens Lett* 2011;9:1249–64.
- [138] Wang Y, Wu H, Luo J, Liu X. Synthesis of an amphiphilic copolymer bearing rhodamine moieties and its self-assembly into micelles as chemosensors for Fe³⁺ in aqueous solution. *React Funct Polym* 2012;72:169–75.
- [139] Ye X, Zhang J, Chen H, Wang X, Huang F. Fluorescent nanomicelles for selective detection of sudan dye in pluronic F127 aqueous media. *ACS Appl Mater Interfaces* 2014;6:5113–21.
- [140] Monk D, Walt D. Optical fiber-based biosensors. *Anal Bioanal Chem* 2004;379:931–45.
- [141] Freeman R, Li Y, Tel-Vered R, Sharon E, Elbaz J, Willner I. Self-assembly of supramolecular aptamer structures for optical or electrochemical sensing. *Analyst* 2009;134:653–6.
- [142] McQuade DT, Pullen AE, Swager TM. Conjugated polymer-based chemical sensors. *Chem Rev* 2000;100:2537–74.
- [143] Madsen J, Canton I, Warren NJ, Themistou E, Blanz A, Ustbas B, Tian X, Pearson R, Battaglia G, Lewis AL, Armes SP. Nile blue-based nanosized pH sensors for simultaneous far-red and near-infrared live bioimaging. *J Am Chem Soc* 2013;135:14863–70.
- [144] Lee K, Povlich LK, Kim J. Recent advances in fluorescent and colorimetric conjugated polymer-based biosensors. *Analyst* 2010;135:2179–89.
- [145] Wang C, Cheng L, Liu Y, Wang X, Ma X, Deng Z, Li Y, Liu Z. Imaging-guided pH-sensitive photodynamic therapy using charge reversible upconversion nanoparticles under near-infrared light. *Adv Funct Mater* 2013;23:3077–86.