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Light-controlled switching of the self-assembly of ill-defined amphiphilic SP-PAMAM

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Light-responsive amphiphilic spiropyrans-decorated polyamidoamine (SP-P3) with ill-defined structures was prepared by using 3.0G-PAMAM as scaffold and introducing of the spiropyrans to the periphery of it randomly. Under visible light illumination, the ill-defined structure SP-P3 could form adaptive amphiphilic macromolecule by rearranging dynamically the peripheral amino and SP groups on the surface of PAMAM. The resultant adaptive amphiphilic SP-P3 could hierarchically self-assemble into uniform macrorods with the size of about 800-1100nm in width and 50-80μm in length. When irradiated with UV light (365nm), hydrophobic SP-P3 would isomer into hydrophilic MC-P3, and induced the disassembly of rod-like aggregates. Irradiation with visible light transformed the MC-P3 back to the SP-P3 and then it could reself-assemble into the rod-like aggregates again. These results demonstrated that these macrorods could reversibly disassemble and reself-assembe in aqueous solution under alternative UV and visible light irradiation. Our experiments not only provide a novel strategy for preparing responsive dynamic materials, but also support the concept that ill-defined amphiphilic macromolecules could also self-assemble to form well-shaped supramolecular structures materials science.

Introduction

Molecular self-assembly has attracted extensive attention and become a hot issue in recent years[1-4]. A variety of molecules with well-defined structures have been designed and proposed for self-assembly in wide reports[5-8]. While, compared these well-defined molecules which are promised candidates for self-assembly, the self-assembly behaviors of the molecules with irregular structures have been neglected for a long time for which people held attitude towards that the molecules with irregular, random branched structures could not form regular supramolecular structures[9-10]. Nevertheless, there are many reports showing that well supramolecular structures could be assembled from these irregular macromolecules. For instance, Yan *et al.*[11] reported that an amphiphilic hyperbranched polymer with a hyperbranched hydrophobic core and ligated hydrophilic arms could self-assemble into macroscopic tubes in a selective solvent. At the same time, Tsukruk *et al.*[12-13] demonstraed that long, uniform nanofibers could be assembled from amphiphilic-functionalized hyperbranched molecules. Zhou and co-workers[14] synthesized a novel amphiphilic homopolymer HPHDP and realized it`s aqueous self-assembly to form various supramolecular structures including micelles, vesicles, tubes, fibers and films. The fact that ill-defined amphiphilic dendritic molecules can self-assemble to form uniform supramolecular structures provides a new way for development of supramolecular chemistry, and adds a new method for progressing materials science.

Though self-assembly of molecules with ill-structures has attracted gradually attention, few reports have been reported about construction of environment-stimuli responsive dynamic materials based on these ill-defined amphiphilic molecules. Dynamic materials have multiple advantages over their static counterparts: selected properties of interest can be reversibly turned "on'' and ''off '' at will and the ability to reconfigure these materials imparts upon them many uses[15]. Among different stimulations that can change the state of materials, light is one of good form of external inputs[16]. It has many advantages such as no chemical contaminants are introduced, closed systems can be actuated, and the light with specific wavelengths can be delivered[17]. Various photoswitchable molecules like azobenzenes, spiropyrans have been widely investigated and employ them or the construction of light-responsive systems and materials[18]. Spiropyrans (SPs) is a family of photosensitive molecules. It is well known that under the UV light irradiation, the hydrophobic SP can isomerize to the hydrophilic merocyanines (MC), and the MC form can revert to SP form again under the visible light irradiation[19]. Because of the large difference between SP and MC, various dynamic materials based on the SP have been explored. SPs have been investigated for optical memories, cell images, logic gates and so on[20-24]. For instance, the light-induced reversible formation of polymeric micelles has been reported[25]. Qu *et al.*[26] utilized spiropyrans conjugate-nanophosphors to successfully prepare NIR/visible light tuned interfacially active nanoparticles with reversible inversion properties. Meanwhile, using SP-functionalized dendrons to construct new photoswitchable supramolecular materials is also fantastic. For example, the light-triggered formation of nano or micrometer-size particles from SP-functionalized dendrons has been reported[27]. And light-responsive micelles of spiropyran initiated hyperbranched polyglycerol have been explored for smart drug delivery[28]. However, to the best of

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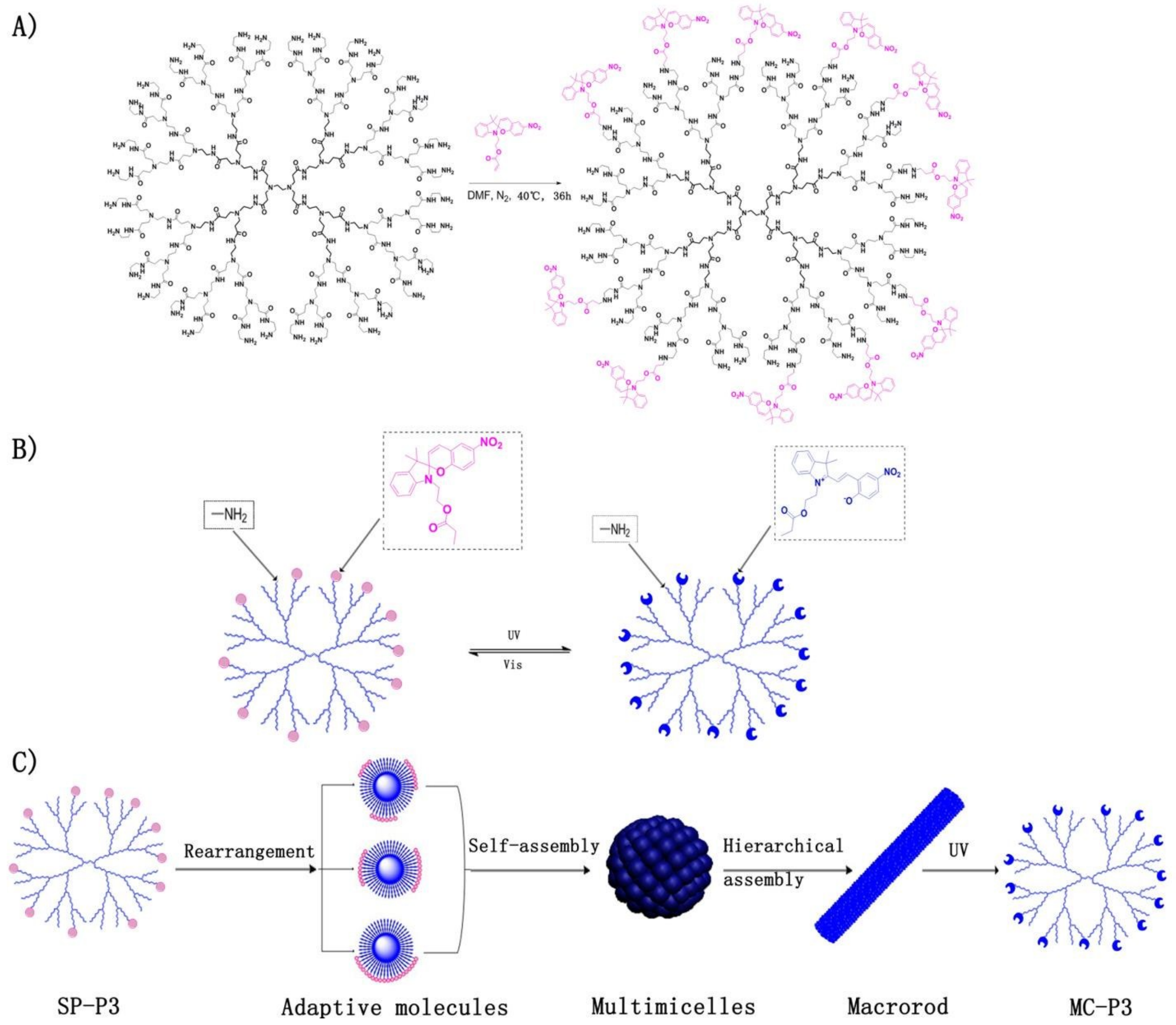
Electronic Supplementary Information (ESI) available: [synthesis schemes and characterization of new compounds, and spectroscopic studies (UV, NMR) and some images (TEM, SEM)]. See DOI: 10.1039/x0xx00000x



Scheme1. A) Synthesis of spiropyran conjugated 3.0G-PAMAM (SP-P3). B) Light-induced isomerization between SP-P3 and MC-P3 by UV (365nm) and visible light irradiation. C) The suggested hierarchical self-assembly of SP-P3 and light-induced distruption and regeneration of the self-assembly.

our knowledge, the reports concerning of using SP-functionalized dendrons to construct dynamic materials remain rarely.

Here, we present a new kind of SP-functionalized dendrons (SP-P3) with a percentage of the spir opyrans reaction on the periphery of the 3.0G-PAMAM randomly (Scheme 1A). 3.0G-PAMAM with 32 terminal amino groups around the surface was an optimal “soft nanoparticle” with a diameter of 4.0 nm and can be a good scaffold for self-assembly. SP-P3 was an amphiphilic macromolecule with ill-defined structure originally. On visible light illumination, it could form uniform macrorods by rearranging dynamically on the peripheral groups during their self-assembly from solution (Scheme 1C). Under UV light irradiation (365nm), the photoisomerization of hydrophobic SP-P3 to hydrophilic MC-P3 occurred (Scheme 1B), amphiphilic molecules lessened, resulting in the dissolution of self-assembly. Regeneration of self-assembly was observed as the result of irradiation with visible light for returning to its amphiphilic form as MC-P3 transformed to SP-P3 (Scheme 1B). These results provide new light-stimuli responsive dynamic materials and support the concept that ill-defined amphiphilic macromolecules could also self-assemble to form well-shaped supramolecular structures.

Experimental section

Materials

All the solvents were purchased from Beijing chemical plant. Dichloromethane (DCM), acetonitrile (MeCN), diethyl ether, chloroform ($CHCl_3$) and dimethyl formamide (DMF) were used with further purification. All the reagents were purchased from Energy Chemical plant.

Instruments

^{1}H-NMR spectra was measured by Bruker 510 spectrometer (500 MHz); DLS instrument was Malven Instrument zetasizer Nano Z. Optical microscopy images and fluorescence microscope images were charactersized by Olympus BX61. SEM images were recorded on scanning electron microscopy, JEOL JSM 6700F. TEM images were recorded on a JEM-2100F. UV/Vis spectrums were obtained from shimadzu 3100. Fluorescence spectrums were obtained from Fluorescence spectrophotometer (RF-5301PC). UV irradiation was carried out with a Xenon lamp (300 W; Asahi Spectra Co. Ltd.; MAX-302). Visible light irradiation was carried out with a fluoresce lamp.

Synthesis of 3.0G-PAMAM

The synthesis of 3.0G-PAMAM was carried out according to our previous work[29]. The ^{1}H-NMR spectrum of PAMAM is shown in figure S1. ^{1}H-NMR (500MHz, D_2O, 25°C, TMS): δ=2.43 (120H, -CC*H*$_2$CONH-), 2.62 (60H, -NC*H*2C*H*2N-, -NHCC*H*2N-), 2.72 (64H, -CC*H*$_2$NH$_2$), 2.82 (120H, -C*H*$_2$CCONH-), 3.24 (64H, -CONHC*H*$_2$CNH2), 3.29 (56H, -CONHC*H*$_2$CN-).

Synthesis of spiropyran (SP)

The SP was synthesized according to previous work[30] and shown in Scheme S1. During the synthesis, all the reaction vessels were wrapped in Aluminum foil to ensure the reaction was performed in the dark. A solution of 2, 3, 3-trimethyl-3H-indole (3.18g, 20.00mmol) and 2-bromoethanol (3.12g, 25.00mmol) in MeCN (20mL) was heated for 24h under reflux and N_2. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in Hexane (20mL) and the mixture was sonicated and filtered. The resulting solid was crystallized from $CHCl_3$ (30mL) to afford (1-(2-hydroxyethyl)-2, 3, 3-trimethyl-3H-indolium bromide (1) (4.19g, 73.70%). The solution of bromide (4.19g, 14.40mmol) and KOH (1.10g, 19.20mmol) in H_2O (60mL) was stirred at ambient temperature for 20 min, and then it was extracted with Et_2O (3×25mL). The organic phase was concentrated under reduced pressure to afford 9, 9, 9a-trimethyl-2, 3, 9, 9a-tetrahydro-oxzzo [3, 2-a] indole (2) (2.39g, 81.49%). The solution of 2 (2.39g, 11.76mmol) and 2-hydroxy-5-nitrobenzaldehyde (2.95g, 17.64mmol) in EtOH (15mL) was heated for 3h under reflux and N_2. The mixture was filtered after cooling down to room temperature. The resulting solid was washed with EtOH (3mL) and dried to afford SP (3) (3.47g, 83.82%). The ^{1}H-NMR spectrum of SP is shown in figure S2. ^{1}H-NMR (500MHz, DMSO, 25 °C, TMS): δ=1.22-1.32 (6H, -C(C*H*$_3$)$_2$), 3.34-3.52 (2H, -NC*H*$_2$CH$_2$-), 3.73-3.85 (2H, -OC*H*$_2$CH$_2$-), 5.90-6.0 and 6.69-6.71 (2H, -CC*H*CH-), 6.78-8.06(7H, -Ar*H*).

Synthesis of acryl-modified SP derivative (SPA)

The acryl-modified SP derivative (SPA) was synthesized according to the previous work[31]as shown in Scheme S2. SP (0.51g, 1.45mmol) was dissolved in CH_2Cl_2 (40mL). Acryloyl chloride (1mL, 12.46mmol) dissolved in CH_2Cl_2 (100mL) was added to the solution stirred at 0℃ and N_2 dropwise. Add finished, the system was stirred at 40 °C and N_2 for 4h. After cooling down to ambient temperature, The resulting solution was washed with 0.1 M HCl (3×25mL) and saturated $NaHCO_3$ solutions (3×25mL), dried over Na_2SO_4. Acryl-modified SP derivative (SPA) was afforded by reducing evaporation (0.32 g, 55.2 %). The ^{1}H-NMR spectrum of SPA is shown in figure S3. ^{1}H-NMR (500MHz, $CDCl_3$, 25 °C, TMS): δ=1.22-1.32 (6H, -C(C*H*$_3$)$_2$), 3.34-3.52 (2H, -NC*H*$_2$CH$_2$-), 3.73-3.85 (2H, -OC*H*$_2$CH$_2$-), 5.86 (1H, -C*H*CHH), 5.90 (1H, -CC*H*CH-), 6.00-6.10 (1H, -C*H*CH$_2$), 6.39-6.58 (1H, CHC*H*H), 6.66-6.75 (1H, -CCHC*H*-), 6.78-8.06 (7H, Ar*H*).

Synthesis of spiropyran conjugated 3.0G-PAMAM (SP-P3)

The spiropyrans conjugated 3.0G-PAMAM (SP-P3) was synthesized as shown in Scheme 1A. A solution of 3.0G-PAMAM (71mg, 0.01mmol) and triethylamine (1mL) in the unhydrous methanol was stirred at ambient temperature and N_2. SPA (110mg, 0.25mmol) dissolved in the DMF (10mL) was added to the solution dropwise. The system was stirred at 40 °C and N_2 for 36 hours, after the reaction finished. Cooling down to room temperature, the solution was rinsed with deionized water several times in order to remove unreacted SPA and other impurities to afford SP-P3 (100mg). The ^{1}H-NMR spectrum of SP-P3 is shown in Figure S4-1. ^{1}H-NMR (500MHz, DMSO, 25°C, TMS): δ= 2.10-2.40 (120H, -CC*H*$_2$CONH-), 3.10-3.30 (120H, - CONHC*H*$_2$CNH$_2$ and -CONHC*H*$_2$CN-), 6.90-8.06 (71H, Ar*H*)

We also synthesized series of SP-P3 with proper SP ratio 9%、18%、 25%、 50% and 63% accordance to the above method. ^{1}H-NMR spectrum of them was shown in supporting information from figureS4-2 to figureS4-6.

Results and discussion

The spiropyrans conjugated 3.0G-PAMAM (SP-P3) was synthesized by general addition reaction (Scheme 1A). We estimated from the ^{1}H-NMR spectrum that the number of SP conjugated to the surface of PAMAM was approximate 12. The number of peripheral amino after reaction (α) was about 20. The total number of peripheral groups (γ) was 32(α+β=32). The percentage of SP was about (δ) 38% (β/γ=12/32=38%). We should notice that the numbers present and discuss here should be considered as averaging for the ill-defined structure of the macromolecules. On the visible light, the SP-P3 had no visible absorption at 550-600nm wavelength. UV (365nm) irradiation of SP-P3 gave rise to the open-ring isomer (MC-P3) and it showed strong absorption at 550-600nm wavelength and intense emission band at 600-700nm. Compared with the MCA, the largest emission peak wavelength of MC-P3 did not change (Figure S5). It indicated that PAMAM had no effect on the property of SP including the photo-isomerization and ultraviolet spectrum.

Different quantities of SP-P3 was dispersed in deionized water (The solution pH valued between 7.0 and 8.0) and sonicated with water bath at 30 °C for 1 hour and let it stand for 1 day. We found that uniform structures can only be formed in the concentration range between 0.1mg/mL to 1.0mg/mL. Giant rod-like self-assembly aggregates of multiple-length scale were observed under a microscope (Figure 1A and 1C). Shown under UV irradiation 10s (Here, we irradiated the samples with 10s to induce small number of SP-P3 to isomer into MC-P3 which showed strong red

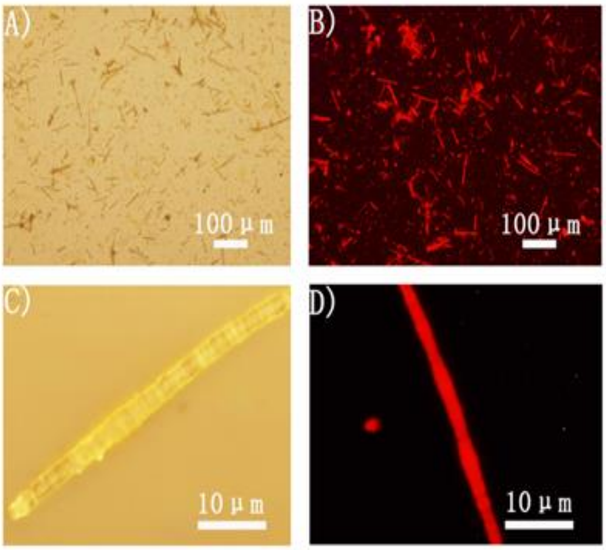


Figure1. Images of self-assembled aggregates generated from the solution (0.3mg/mL). A) and C) optical microscopy images B) and D) fluorescence microscope images(after exposure to UV light (365nm) for 10s). We should notice here A), B), C) and D) are the same samples. The samples were prepares by dropping the solutions on to a slide and air-dried.

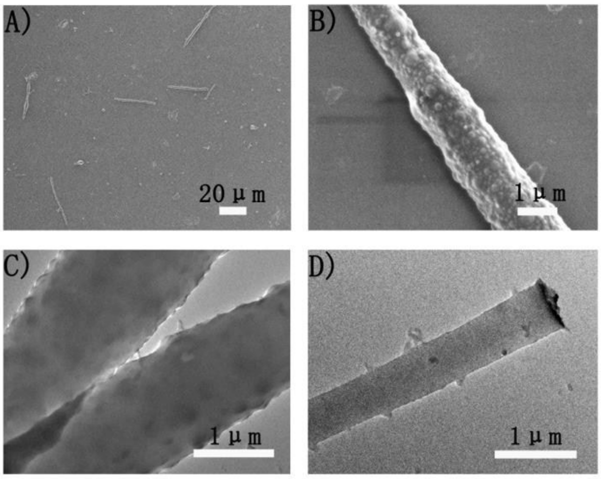


Figure2. Images of the self-assembly aggregates stemed from solution (0.3mg/mL). A) and B) scanning electron microscopy images. C) and D) Transmission electron microscopy images.

fluorescence. At the same time, we insured that the UV irradiation would not cause the disassembly of rods.), it was found that these aggregates showed strong red fluorescence with the observation of fluorescence microscope (shown in figure 1B and 1D). Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) analysis were used to investigate the morphology and characterization of the self-assembly aggregates(shown in Figure 1). From SEM images (Figure 2A and 2B), it was observed that these rod-like aggregates distributed with thickness and length unevenness and the surface was not smooth. And we calculated that the sizes of the rod-like aggregates were about 800-1100nm in width and 50-80μm in length. Transmission TEM analysis revealed that rod-like aggregates were huge micro-scale rods (Figure 2C and 2D). It clearly showed that the surface of them was not smooth though it has the tendency to grow smooth. To further illustrate the assembly, we designed a series of SP-P3 with percentage of SP about 10%、18%、25%、33%、50% and 63%. Under the same experimental environment and conditions, we found that 3.0G-PAMAM itself could not self-assemble (Figure S6A) and if high percentage of SP conjugated to the PAMAM (with 63% SP up), self-assembly neither came into being but only the aggregate of clutters (Figure S6B). Only could the assembly formation occur for SP-P3 with proper SP ratio of 18% to 50%. All the above experiments indicated that SP-P3 with irregular architecture self-assembled into supramolecular aggregates with uniform structures. These aggregates showed large scale and the surface of them was not smooth.

To understand the formation process and mechanism of self-assembly of SP-P3 thoroughly, we prepared the samples and continued to observe it during its assembly process. We used TEM analysis to observe the change of the sample every 4 hours. The TEM images under different time were shown in (Figure 3). We could see that multi-micelles about 300nm were formed at the beginning (Figure 3A), and we could clearly find that these multi-micelles were consist of small particles (Figure S7) after 8h; These multi-micelles aggregated to form rod-like micelles (Figure 3B and 3C) after 12h; Let it stand for a period of time, these large micelles hierarchically assembled to form these large scale rods (Figure 3D). Finally these rods grew more smoothly.

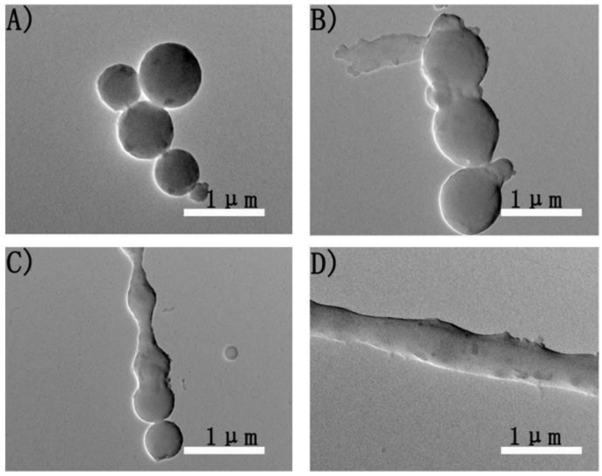


Figure3. Transmission electron microscopy images of self-assembly from solution (0.3mg/mL). A), B), C), D) were the same sample at different time. Every 4 hours, we observe the change of the sample. A) after 4h . B) after 8h. C) after 12h. D) after 16h.

All of the above experiments inspired us to suggest a proposal mechanism of macrorods formation shown in Scheme 1C. It was suggested that the self-assembly of SP-P3 was a multi-micelles aggregating process. And during the self-assembly process, the spontaneous organization into hydrophilic and hydrophobic domains at the surface of the PAMAM dendrimer, that was, the ability of ill-defined SP-P3 to flexibly rearrange its structure, played an essential role in the self-assembly process. SP could rearrange dynamically on the surface of PAMAM from solution to form hydrophobic "patches" (Scheme 1C) for its hydrophobic interactions distinguished from the hydrophility of peripheral amino and the flexibility of dendrimer. The adaptive amphiphilic macromolecules with the sizes of 4-5nm self-assembled gradually into multimicelles (Scheme 1C) with size about 300nm through H bonding and hydrophobic interaction. Then these micelles aggregated into large micelles. These large micelles further aggregated together to form finally rod-like self-assembly aggregates (Scheme 1C). Although the reason why these large scale micelles could aggregated together to form uniform rod-like aggregates remains unclear, we supposed that these multi-micelles maybe gradually fused together by weak interactions in one direction.

The photo-switch of disruption and regeneration of the macrorods were conducted by alternating irradiation of UV and visible light. When the assembly solution was exposed to 365nm UV light irradiation, the well-defined characteristic macrorods disappeared but the smaller particles with the size about 200-700nm formed (Figure 4A). We found that these smaller particles were ill-defined aggregate actually (Figure S8) and clusters. Then it was exposed to Vis light illumination for 24h, the macrorods with size about 700-900nm in width emerged (Figure 4B), which indicated the regeneration of the rod aggregates. The light-induced reversible formation of self-assembly was also demonstrated by fluorescence spectroscopy and dynamic light scattering (DLS) analysis. The initial self-assembly solution had no emission at 620nm (upon excitation at 550nm) (Figure 4C line1). The original size of aggregates was about 1100nm by the size distribution of volume with little small particles at 200nm (Figure S9 blue line). When the solution was irradiated with UV (365nm) light for 10min,

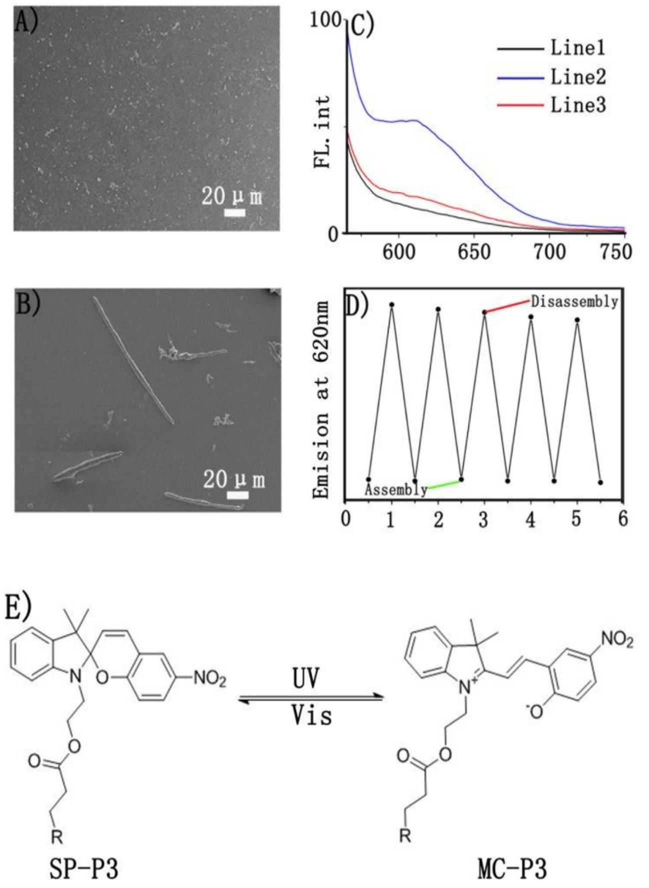


Figure4. A) and B) Scanning electron microscopy images; C) Fluorescent spectra with three different conditions, λexc=550nm. Line1 was original condition. Line2 was after UV irradiation condition. Line 3 was regeneration condition. D) Reversible fluorescence (lem = 620 nm) switching upon exposure to UV and Vis light (5 cycle). A), B), C) and D) the same sample (0.3mg/mL). E) Scheme of light-induced isomerization between SP-P3 and MC-P3 by UV (365nm) and visible light irradiation. R PAMAM.

an emission at 620nm appeared (Figure 4C line2), the aggregates decreased to 400nm (Figure S9 red line), which was characteristic of the disruption of the self-assembly form. Irradiation with visible light isomerized the MC-P3 form back to the SP-P3 form was confirmed by the spectra reverting to the original no emission profile after 24h (Figure 4C line3) and the system return to the initial aggregates size distribution (Figure S9 green line). After five UV–Vis cycles, the rod-like structures still remained though the reversible in fluorescent intensity showed a little decay (Figure 4D). By fluorescence spectroscopy analysis and dynamic light scattering analysis, we can also evidently find that the light switching exhibited excellent effect on the reversible disruption and regeneration of the self-assembly based on SP-P3 through controlling the transitions between the macrorods and small particles.

The light-induced disruption and regeneration behaviours of the macrorods should be attributed to the reversed isomerization of SP-P3 (see Figure 4E). On visible light illumination, SP-P3 was an ill-defined structure amphiphilic macromolecule originally and it could rearrange dynamically on the peripheral groups to form adaptive amphiphilic macromolecule by rearranging dynamically on the peripheral groups during their self-assembly from solution (Scheme 1B). The adaptive macromolecules could self-assemble into large scale supramolecular structures. Irradiated with UV light, hydrophobic SP-P3 would isomer into hydrophilic MC-P3 (Figure 4E), which induced the disassembly of rod-like aggregates (Scheme 1B). Irradiation with visible light transformed the MC-P3 back to the SP-P3 and then it self-assembled into the rod-like aggregates again.

Conclusions

In conclusion, we have described the synthesis, self-assembly and light-controlled switching of the self-assembly and disassembly of SP-P3. The results show that the SP-P3 with irregular structure could self-assemble to form uniform supramolecular structure by adapting the structure and rearrangement of the surface. These self-assembly structures were successfully characterized by optical microscopy, fluorescence microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis . In addition, we have shown that UV/Vis light could induce disruption and regeneration of the macrorods. These results not only support the opinion that ill-defined amphiphilic macromolecules can also self-assemble to form well-shaped supramolecular structures, but provide a new light-stimuli responsive dynamic material, which may have potential applications in light-stimuli responsive field.

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Table of Content

spiropyrans-decorated polyamidoamine (SP-P3) with ill-defined structures was successfully prepared for the construction of photocontrolled supramolecular macrorods.