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Controlling interfacial interaction of supramolecular assemblies by light-responsive overcrowded alkene

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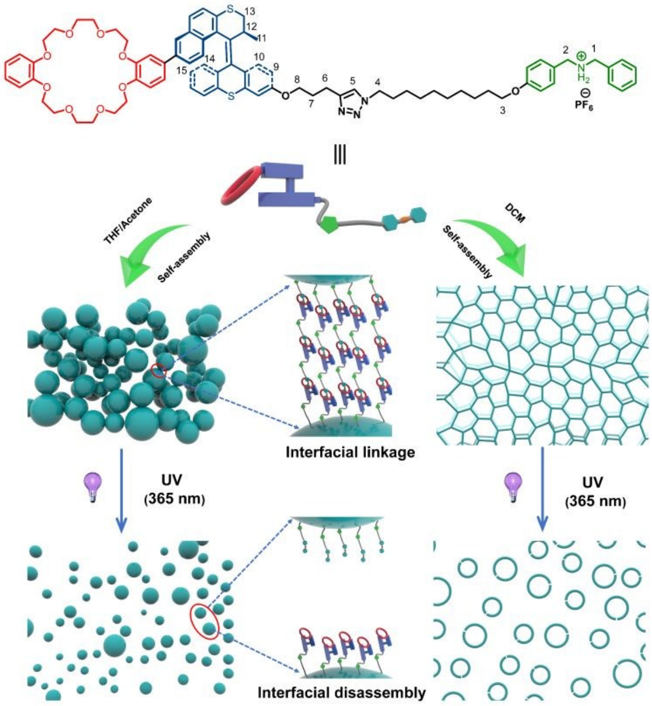
A light-responsive supramolecular polymer was constructed by a AB-type monomer containing a light-responsive overcrowded alkene. The primary assemblies of the supramolecular polymer can further undertake secondary self-assembly by interfacial host-guest connections, which can be manipulated by light stimuli to convert into discrete primary assemblies.

Self-assembly in nature creates a host of subtle supramolecular architectures exhibiting dynamic functions[1]. Inspired by these intriguing structures and functions, chemists have constructed a series of man-made supramolecular assemblies by non-covalent interactions, such as micelles[2], vesicles[3], polymers[4] and gels[5]. To mimic the intelligence of natural systems, stimuli-responsive units were introduced to manipulate these supramolecular systems in a dynamic and controllable way[6]. Light, owing to its remote stimuli, instant input/removal, and available source, is considered as the ideal manner to regulate the assembly manner[7]. Many successful examples have been achieved in the reversible light-responsive disassembly/reassembly of small building blocks, such as small molecules[8], inorganic nanoparticles[9], and polymeric networks[10], showing the tremendous promise of the light-responsive matter.

Although the light-controlled reversible disassembly/reassembly of supramolecular polymers have been widely investigated[11], one of the current major challenges locates on the fundamental question whether we can manipulate the secondary supramolecular interaction by external stimuli instead of the primary architectures[12]. Wang, et al. realized the interfacial secondary self-assembly of primary supramolecular spheres by anion-π interaction[13]. Stupp, et al. pioneeringly presented the reversible secondary self-assembly of the amphiphilic architectures by manipulating noncovalent interactions at interfaces[14]. These efforts presented the significance and complexity to explore the interfacial supramolecular self-assembly. However, such topic remains unfledged, especially in the light-controlled examples.



Scheme 1. The schematic representation of interfacial dissociation of *trans*-**8** in different solvents

The inner filtration effect exists as an intrinsic property in light-controlled molecular systems. Generally, the light irradiation would be filtered by the chromophores at superficial layers, while the inner chromophores would be inhibited from the light irradiation. In most cases, this intrinsic feature works as a negative issue for the design of light-controlled supramolecular polymers[15]. Here, our motivation rests on the interesting hypothesis whether the intrinsic inner filtration effect can be used to realize the interfacial self-assembly of supramolecular assemblies, which might provide an unprecedented

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strategy for the design and construction of light-controlled interfacial self-assembling systems.

The light-responsive supramolecular monomer was designed as *trans*-**8** (Scheme 1). Considering the strong non-covalent interactions between dibenzo-24-crown-8 (DB24C8) ring and dibenzylammonium (DBA) moieties, monomer *trans*-**8** could undertake intermolecular host-guest combination in low polar solvents, thus forming linear supramolecular polymers in concentrated solution. Additionally, a photo-responsive unit, the overcrowded alkene, was introduced and located nearby the host ring. The design of rigid linkage should allow the synergetic rotation of the DB24C8 macrocycle with the photoisomerization, thus enabling the effective manipulation of noncovalent connection at interfaces.

The detailed synthesis route of monomer *trans*-**8** was depicted in Scheme S1. Firstly, compound **5** and **6** were synthesized according to previous literatures[16], then the target molecular *trans*-**8** was obtained in a moderate yield (78%) by carrying out a copper(I)-catalyzed Huisgen 1,3-dipolarcycloaddition reaction between azide **5** and overcrowded alkene-based alkyne **6**. The reference compound *cis*-**8** was synthesized according to the similar method (Scheme S2). The chemical structure of *trans*-**8** and *cis*-**8** were characterized using ^{1}H NMR, ^{13}C NMR spectroscopies and high resolution electronic spray ionization (HR-ESI) mass spectrometry.

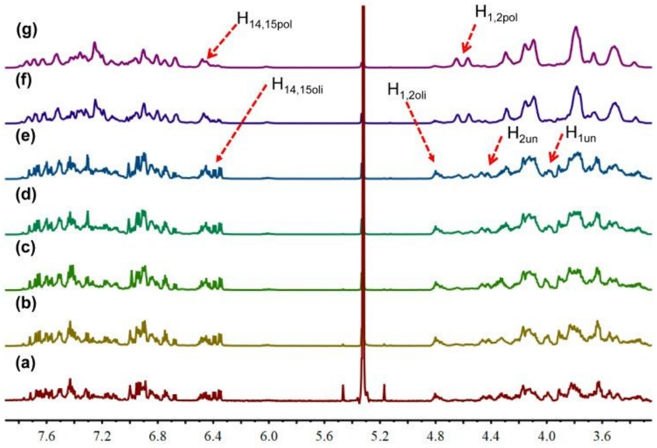

Figure 1. Partial ^{1}H NMR spectra of *trans*-**8** (400 MHz, CD_2Cl_2, 298 K) at various concentrations: a) 1 mM; b) 5 mM; c) 10 mM; d) 20 mM; e) 50 mM; f) 100 mM; g) 150 mM.

Concentration-variable ^{1}H NMR experiments were performed to monitor the self-assembly behaviors of *trans*-**8** (Fig. 1). At low concentration, the uncombined benzylic methylene protons (H_{1un}, H_{2un}) and cyclic oligomers signals ($H_{1,2oli}$, $H_{14,15oli}$) were observed in the ^{1}H NMR spectra. Meanwhile, no supramolecular polymer signals ($H_{1,2pol}$, $H_{14,15pol}$) were observed, the results represented a tendency to form oligomers. As the concentration increased, the uncombined protons signals of benzylic methylene (H_{1un}, H_{2un}) and oligomers ($H_{1,2oli}$, $H_{14,15oli}$) decreased gradually, while the polymers signals ($H_{1,2pol}$, $H_{14,15pol}$) appeared. Further increased concentration to 100 mM, the signals of protons H_{1un}, H_{2un}, $H_{1,2oli}$ and $H_{14,15oli}$ disappeared along with the appearance of $H_{1,2pol}$, $H_{14,15pol}$ peaks, and the whole broadening of resonance signals. All above results demonstrated the generation of supramolecular polymers, which were also in line with previous reports[17].

The photo- and thermal-isomerization behaviours were first detected using ^{1}H NMR spectra. Considering the *trans*-**8** polymerized at very low concentration in low polar solvent (Figure. S1, S2 and S3), polar solvent (DMSO-d_6) was selected as the solvent. The solution of *trans*-**8** was irradiated (365 nm, 298 K, 2 h) to reach the photostationary state (PSS), allowing the *trans*-**8** converted into *cis*-isomer. The proton H_{13} shifted upfield ($\Delta\delta$ = -0.34 ppm) and proton H_{11} shifted downfield ($\Delta\delta$ = 0.39 ppm) respectively due to conformation change of *trans*-**8**, meanwhile, the proton H_9 and H_{10} obviously shifted upfield as a result of shielding effect from the naphthalene (Fig. 2a and 2b). All above signal changes indicated that the *trans*-**8** transformed into *cis*-isomer. Subsequent thermal conversion was carried out in hot oil bath (333 K, 24 h), along with the recovery of the H_{11} and H_{13} signals (Fig. 2c).

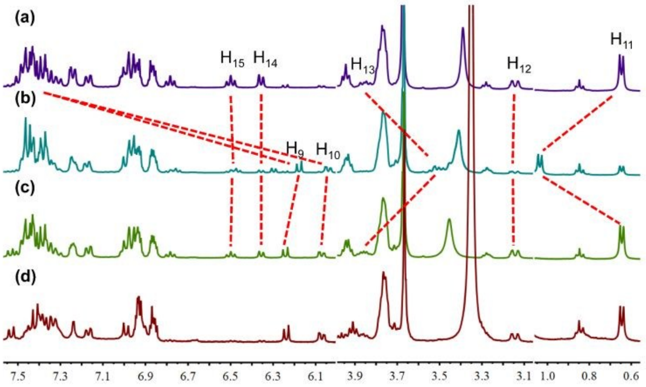

Figure 2. Partial ^{1}H NMR spectra (400 MHz, 20 mM, DMSO-d_6, 298 K). (a) *trans*-**8** before UV irradiation; (b) *trans*-**8** after UV irradiation (365 nm) for 2 h; (c) *trans*-**8** after UV irradiation (365 nm) for 2 h and then heated at 333 K for 24 h; (d) *cis*-**8** before UV irradiation.

The UV-vis spectroscopy was used to further confirm the photo- and thermal-isomerization processes. The diluted dimethylsulfoxide solution of *trans*-**8** was exposed to UV light (365 nm) for 2 h, the UV-vis spectra showed blue shift, suggesting the generation of high-energy *cis*-isomer[18]; then the solution was continuously heated for 24 h to undergo thermal conversion, the red shift of UV-vis spectra was observed (Fig. S4a). All of these results clearly confirmed that *trans*-**8** can undergo photo- and thermal-isomerization under light or heat stimuli.

Considering that the DB24C8 can bind DBA with different binding constants in various solvents[19], thus the self-assembly morphologies and subsequent photo-responsive behaviors of monomer *trans*-**8** were investigated in three different solvents (THF, acetone, DCM). Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to visualize the sizes and morphologies of supramolecular polymers. The specific self-assembly and disassembly processes were shown in scheme 1. As for THF solution of *trans*-**8**, interconnected nanospheres with an average diameter of 500 nm was observed (Fig. 3a and S5a). The reason for this interacted assemblies can be explained that *trans*-**8** first formed linear supramolecular polymers through the host-guest interaction between DB24C8 and DBA moieties; further intermolecular π-π stacking were induced by conjugated overcrowded alkene units, and form the spherical structure; subsequently, the uncombined host-guest moieties on the surface of nanospheres could function as velcro to link the nanospheres together[20]. The self-assembly morphology of *trans*-**8** in acetone is similar to the above THF solution, which showed the same spherical topology with average diameter of 50 nm (Figure. S6a). In addition, cross-linked networks instead of interconnected nanospheres were observed in DCM solution (Figure. 3c). A possible explanation is that the better solubility of *trans*-**8** in DCM (Table S1), which increased dispersity of the supramolecular polymers in solution and prevented the formation of nanosphere.

Photo-responsive experiments were performed with UV light (365 nm) under dark environment. The different solutions (THF, acetone, DCM) of *trans*-**8** were aged for 24 h and then exposed to UV light for 2 h, TEM and SEM measurements were used to monitor the morphologies. As shown in Fig. 3b and S5b, interestingly, the interconnected nanospheres in THF transformed into well-defined dispersed nanospheres with almost the same size. The similar conversion was observed in acetone solution (Figure. S6b). Meanwhile, the morphologies of *trans*-**8** in DCM transformed from cross-linked networks into dispersed nanorings after UV irradiation (Figure. 3d). The above phenomena can be attributed that the nanospheres or cross-linked networks are dense enough, which could prevent UV light penetrating, thus the main body of aggregates could maintain initial morphologies, but the overcrowded alkene units on the joint interfaces were exposed to UV light, and subsequent photoinduced isomerization could dissociate the host-guest interaction between DB24C8 and DBA, this caused the aggregated secondary structure to be dispersed.

To investigate whether the configuration change of *trans*-**8** had influence on the self-assembly morphologies, the control TEM and SEM experiments were performed by using reference compound *cis*-**8**. The THF was selected as solvent to study self-assembly processes and photo-responsive behaviors of *cis*-**8**. As shown in Fig. S7a and S7c, the similar interconnected nanospheres were observed in initial state; Upon the UV irradiation for 2 h, these interconnected nanospheres also converted into dispersed ones (Fig. S7b and S7d), these were almost in line with the above THF solution of *trans*-**8**. The results indicated that the configuration change of overcrowded alkene units was not the cause of aggregates dispersion, this further confirmed that the dispersion of aggregated supramolecular polymers was attributed to the dissociation of host-guest interactions which induced by the isomerization of overcrowded alkene.

Dynamic light scattering (DLS) measurement was performed to investigate the size distributions of *trans*-**8** in different solvents. After aging the THF solution of *trans*-**8** for 24 h, the DLS data were shown in Fig. S4b, in addition to few oligomers (2~3 nm) and monodispersed aggregates (500 nm), the very large aggregates with an average size of 5000 nm was observed, matching with the interconnected nanospheres. Importantly, upon UV irradiation for 2 h, the average size of large aggregates converted from 5000 nm to 1000 nm, indicating that interconnected nanospheres transformed into monodispersed ones. The similar transformations were also observed in acetone and DCM solution (Fig. S4c and S4d). These results were basically consistent with above TEM and SEM images, further evidenced the self-assembly and photo-responsive processes of *trans*-**8**.

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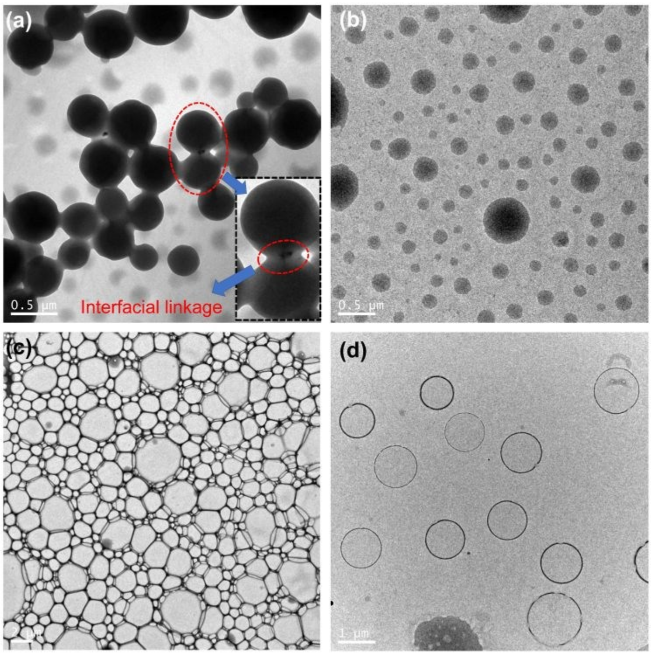

Figure 3. TEM images of *trans*-**8** aggregates in THF (c = 1×10^{-3} M): (a) before UV (365 nm) irradiation; (b) after UV (365 nm) irradiation for 2 h. TEM images of *trans*-**8** aggregates in DCM (c = 1×10^{-5} M): (c) before UV (365 nm) irradiation; (d) after UV (365 nm) irradiation for 2 h.

The pH-responsive behaviour of *trans*-**8** was detected using ^{1}H NMR (Fig. S8). After adding 1.0 equiv 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to dichloromethane-d_2 solution (20 mM) of *trans*-**8**, the proton signals of supramolecular polymers disappeared, meanwhile, most of initial broad peaks became sharp, demonstrating that supramolecular polymers had disassembled into the monomers, this is because that the deprotonation of DBA moieties by DBU could lead to the complete dissociation of the host-guest interactions. Besides, TEM measurements also gave further evidences for the disassembly of supramolecular polymers, no well-defined secondary topology was observed after adding DBU.

Conclusions

In summary, we have successfully synthesized a dual-modified monomer (*trans*-**8**) based on overcrowded alkene, which could self-assemble into interconnected nanospheres or cross-linked networks in different solvents through host-guest interactions. Upon exposed to UV light, the isomerization of overcrowded alkene units at joint interfaces could induce the dissociation of DB24C8 and DBA. As a result, monodispersed nanospheres or nanorings were formed. Furthermore, the effective disassembly of *trans*-**8** aggregates could be driven by adding DBU base. This work successfully controls the aggregation/dispersion of supramolecular polymers. We expect this work can provide a new strategy to design and fabricate stimuli-responsive supramolecular assemblies exhibiting dynamic features beyond primary architectures, which pushes the artificial molecular system towards some exciting biomimetic behaviours, such as micell adhesion, microtubule bundling, and cell aggregation.

Acknowledgments

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Conflicts of interest

There are no conflicts to declare.

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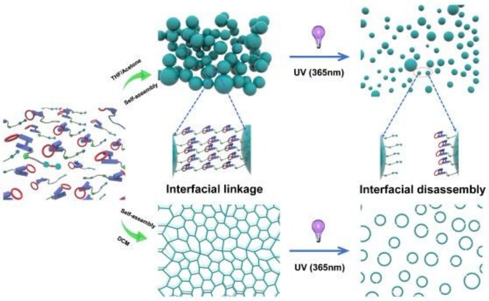

Controlled interfacial interaction of supramolecular assemblies is achieved by effective photo-isomerization of the overcrowded alkene units.