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Photolysis of a bola-type supra-amphiphile promoted by watersoluble pillar[5]arene-induced assembly Shuwen Guo, Xin Liu, Chenhao Yao, Chengxi Lu, Qingxin Chen, Xiao-Yu Hu,* Leyong Wang*

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A bola-type supra-amphiphile assembled from a water-soluble pillar[5]arene host (WP5) and a rod-coil guest molecule (G) containing photoactive 9,10-dialkoxyanthracene group was successfully constructed, which could further assemble into monolayer supramolecular vesicle. Interestingly, the photodecomposition rate of G was remarkably promoted after its aggregation with WP5, accompanied by the disassembly of the formed supramolecular vesicle, especially with the coassembly of a photosensitizer eosin Y, which holds potential applications in phototherapy.

Light is an efficient external physical stimulus for regulating microscopic structures and relevant physicochemical properties of molecular assembly.1 Therefore, noninvasive light stimulus is often used as an effective strategy to regulate responsive materials, which has been applied in many research fields, such as separation technology,² photodynamic therapy,^{3a} and photolithography.^{3a,b} Among various photoresponsive materials, photodegradable materials that can be irreversibly decomposed after irradiation have attracted much attention due to their wide applications in controlled drug release and tissue engineering research,⁴ particularly those photodegradable materials constructed by supramolecular assembly that can be easily regulated due to the weak and reversible noncovalent interactions, resulting in the disassembly of aggregates and generating small fragments after light stimulus.⁵ So far, although photoresponsive supramolecular assemblies have been well-studied, there are only a few reports on the construction of photodegradable supramolecular assemblies with high photolysis efficiency.⁶ Therefore, it is essential and importance to develop an efficient way supramolecular assemblies to construct with high photodecomposition efficiency.

Pillararenes, as a new type of macrocyclic hosts with unique symmetric pillar frameworks and π -rich cavities, are capable of being easily modified to construct various functional supramolecular materials, such as supramolecular polymers, transmembrane channels, metal-organic frameworks, and supra-amphiphiles.⁷ Due to their excellent pH-responsiveness and good biocompatibility, water-

soluble pillar[6]arene (**WP6**) and pillar[5]arene (**WP5**) have been widely used to construct supramolecular assemblies in aqueous solution for biological and pharmaceutical applications.⁸ For example, Huang and co-workers have elaborately designed a pillararene-based ternary drug delivery system for photocontrolled anticancer drug release.^{8h} However, pillararene-based supramolecular assemblies with high photolysis efficiency promoted by water-soluble pillar[5]arene-induced assembly have never been reported, which might hold potential applications in drug delivery.

Herein, we demonstrate a novel strategy for developing a photodegradable bola-type supra-amphiphile, whose photolysis efficiency can be remarkably promoted based on the **WP5**-induced aggregation. It is well-known that anthracene can efficiently trap singlet oxygen and form relatively stable endoperoxides, which can be used for singlet oxygen detection and delivery; however, applications in developing photodegradable supramolecular assembly have not yet been fully studied.⁹ Moreover, trimethylammonium derivatives have been confirmed to have strong binding affinity with **WP5** and can form stable inclusion complex.^{8e} Accordingly, a rod-coil molecule (**G**) containing both photoactive 9,10-dialkoxyanthracene group and trimethylammonium terminals



Scheme 1. Schematic illustration of the photolyzable supramolecular amphiphilic assembly.

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was designed and used for further assembling to form supramolecular complex with **WP5**, and then the photolysis behaviors of which were further investigated. Based on the above design, a bola-type supra-amphiphile was successfully fabricated based on the host-guest interaction between **WP5** and **G** (Scheme 1). After assembly, the fluorescence of **G** was significantly quenched, which was adverse for photosensitization.¹⁰ However, it was found that the photodecomposition rate of the assembled **G** was remarkably promoted, which is in contrast with the previous work reported by Liu and co-workers, where the constructed photolysis system kept retaining photosensitivity.¹¹ Moreover, we found that the obtained **WP5-G** aggregates after coassembling with an exogenous photosensitizer (eosin Y, ESY) could be efficiently disassembled under visible light irradiation, which holds potential applications in phototherapy.

WP5 was synthesized according to the reported literature,^{8c} and photoactive guest molecule G was obtained by using anthraquinone as the starting material. Similar to other bola-type amphiphilic molecules reported before,^{8g, 12} G could form large higher-order assemblies in the presence of WP5. And the best molar ratio of G with WP5 for the formation of supramolecular aggregate was measured by monitoring the dependence of the optical transmittance at 600 nm on the concentration of WP5.13 Since G can dissolve readily in water, the optical transmittance of which at 600 nm showed no discernible change with its concentration increasing from 0.01 mM to 0.20 mM (Fig. S5, ESI⁺). Whereas, the transmittance of G at 600 nm underwent a sharp decrease and then an inverse increase upon gradually adding WP5, and an inflection point was observed in the plot of the optical transmittance at 600 nm versus WP5 concentration (Fig. 1a and Fig. S6), which indicated that the best molar ratio of G and WP5 for such aggregation was 6:1 ([G]/[WP5]). Based on this best molar ratio, the critical aggregation concentration (CAC) for WP5-G assembly was determined to be 0.01 mM (Fig. 1b and Fig. S7).



Fig. 1 (a) Dependence of the optical transmittance at 600 nm on the WP5 concentration (0 – 0.10 mM) with a fixed G concentration (0.10 mM) in water at 25 °C. (b) Concentration-dependent optical transmittance at 600 nm of the WP5-G aggregates at a fixed molar ratio of [WP5]/[G] = 1 : 6. (c) DLS data of the WP5-G aggregates. Inset: Photo showing of the Tyndall effect of WP5-G aggregates. (d) TEM image of the WP5-G aggregates.

The solution of **WP5** and **G** at the best molar ratio exhibited a clear Tyndall effect (inset of Fig. 3c), indicating the existence of abundant nanoparticles. Furthermore, the morphology and size of the formed aggregates were investigated by dynamic light scattering (DLS) and transmission electron microscopy (TEM) experiments. DLS result showed that the **WP5-G** complex formed spectacular

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aggregates with a narrow size distribution, giving an everage diameter of 212 nm (Fig. 3c); whereas, nooDLSisignal could be observed for free G (Fig. S8, ESI⁺). Moreover, TEM image showed the hollow spherical morphology with an average diameter ~155 nm (Fig. 1d), convincingly indicating the formation of vesicular structure. It is reasonable that the diameter of vesicles measured by DLS is larger than that observed by TEM, because DLS and TEM showed the swollen and solid vesicles, respectively.9c The thickness of the vesicle membrane was measured to be about 4.0 nm from the TEM image (Fig. 1d), which is corresponded to the extended length (3.2 nm) of molecule **G** calculated by Gaussian 09 program (Fig. S9, ESI[†]), suggesting that the obtained vesicles have monolayer structure. Moreover, ζ -potential experiment suggested that the nanoparticles held a relatively large negative ζ -potential (-28.6 mV, Fig. S10, ESI[†]), indicating the existence of repulsive forces among vesicles which can obviously enhance the stability of the obtained vesicles.

Subsequently, ¹H NMR was performed to investigate the detailed complex structure of the formed supra-amphiphile. Since it has been confirmed that WP5 can efficiently bind trimethylammonium with high binding affinity $(5.67 \times 10^3 \text{ M}^{-1})$,^{8e} we first investigated the stoichiometry of complexation between WP5 and G, and found that **WP5** and **G** could form a $(WP5)_2 \supset G$ supramolecular complex with a 2:1 stoichiometry based on the Job's plot experiment (Fig. S11, ESI[†]). Then, a mixture of [WP5]/[G] = 2:1 was studied for comparison with the WP5-G aggregates formed at a molar ratio of [WP5]/[G] = 1:2, since the signals of the aggregates formed at the best molar ratio broadened severely and was unidentifiable and/or undetectable. Upon adding 2 equiv. of WP5 into the G solution, the signals of H_{b-e} on G shifted upfield remarkably due to the shielding effect of the electron-rich cavity of WP5 (Fig. 2b), reflecting the inclusion of the alkyl chain of G into the hydrophobic WP5 cavity.8e Meanwhile, the signals of anthracene group shifted downfield, which might be due to the deshielding effect of the aromatic ring of WP5 after inclusion with G. However, when only 0.5 equiv. of WP5 was added into G solution, the threaded signals of H_{b-e} on G could also be detected, and the signals of anthracene group became more broad and complicated due to the π - π stacking effect (Fig. 2c), indicating the occurrence of WP5-induced aggregation process.



Fig. 2 ¹H NMR spectra of (a) **G**, (b) **WP5** + **G** ([**WP5**]/[**G**] = 2/1), (c) the assembly formed by **WP5** and **G** ([**WP5**]/[**G**] = 1/2), and (d) the **WP5-G** aggregates after UV irradiation (365 nm) for 20 min in D_2O ([**G**] = 2.0 mM).

It is well known that anthracene can trap singlet oxygen $({}^{1}O_{2})$ and form stable endoperoxides upon UV irradiation, whereas, the endoperoxides formed by of 9,10-dialkoxy-substituted anthracene derivatives would decompose and generate anthraquinone and

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relevant alkanols.¹⁴ The typical absorption peak of anthracene group at 300 - 420 nm slightly decreased after irradiation at 365 nm for 30 min, indicating that only a very small amount of G was decomposed (Fig. S12, ESI[†]). In contrast to G, a redshift (6 nm) could be observed from the absorption spectra of WP5-G aggregates, which could be ascribed to the π - π stacking and charge-transfer interactions.13b Moreover, this spectrum decreased sharply upon UV irradiation at 365 nm for the same time (Fig. S12, ESI⁺), accompanying with the formation of yellow precipitate (Fig. S13, ESI \dagger), which implied that **G** in its aggregated form could be significantly cleaved under UV irradiation. ¹H NMR and mass spectrometry (MS) were then performed to identify the photolytic product. As show in Fig. 2d, after the WP5-G aggregates were irradiated, the signals of anthracene group disappeared largely and the signals of the methylene groups that threaded into the cavity of **WP5** increased obviously, since these signals did not broaden any more after the aggregates collapsed. Meanwhile, new signals at $\delta =$ 3.45 ppm appeared, which could be assigned to the methylene group adjacent to the generated hydroxyl group after decomposition. Moreover, an indicative peak corresponding to 8-hydroxy-N,N,Ntrimethyloctan-1-aminium at m/z 188.2 was clearly observed in the MS spectrum (Fig. S14, ESI⁺), and the signals for anthraquinone could also be detected when the precipitate obtained from the irradiated solution was analyzed by ¹H NMR (Fig. S15, ESI[†]). Furthermore, it was found that the aggregates formed at the best molar ratio exhibited similar phenomena as mentioned above. On the basis of the above mentioned results, we could infer that G in its aggregated form with WP5 showed photodegradable property and into anthraquinone decomposed and 8-hydroxy-N,N,Ntrimethyloctan-1-aminium as illustrated in Scheme S3.

Furthermore, the photolysis rates of free G and assembled G were investigated with UV-Vis spectra. Free G showed moderate photocleavage rate at a concentration of 0.01 mM upon irradiation at 365 nm for 60 min, which possibly due to the amount of the produced singlet oxygen was excessive relative to G with low concentration. However, the photocleavage rate of G was gradually slowed down as its concentration increased, and less than 10% of G was cleaved when G (with high concentration, ≥ 0.1 mM) was irradiated for 60 min (Fig. 3a). In sharp contrast with free G, the assembled G (0.1 mM) was cleaved quickly, indicating that the photocleavage rate of G was significantly promoted in the assembled structure. Moreover, it should be note that when irradiation was performed under air, the photocleavage process of G could be restricted by the limited concentration of oxygen (about 0.25 mM). However, when argon or oxygen was pumped for 15 min before irradiation, the cleavage rate was slowed down or accelerated, respectively. But the absorbance of G showed no change when the aggregates were irradiated at 455 nm, indicating that photoactivation is crucial for cleaving G in the assembled structure (Fig. 3b). When



Fig. 3 (a) Normalized absorbance at 386 nm of G upon irradiation with UV light at 365 nm for different time. (b) Normalized absorbance at 386 nm of the WP5-G aggregates upon irradiation at 365 nm (or 455 nm) for different time.

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G was cleaved into insoluble anthraquinone and hydrophilic alkanol, the formed WP5-G aggregates also disassembled/owhich 59 was confirmed by the DLS and TEM results (Fig. S16, ESI[†]).

In order to further understand the mechanism of the aggregationpromoted photolysis, fluorescence spectra were performed to investigate the photophysical properties of WP5-G aggregates. Compared with free G, the emission intensity of the aggregates decreased significantly (Fig. S17, ESI⁺), which was mainly due to the π - π stacking and enhanced charge-transfer interactions after its binding with WP5.¹⁵ Although the WP5-G aggregates showed relatively weaker fluorescence than free G, the photocleavage rate of the aggregates was accelerated. Moreover, the fluorescence of G with excessive amount of WP5 was also quenched to the level of the **WP5-G** aggregates,^{15b, 15d} and the photocleavage rate of which was similar to that of free G, indicating that WP5 itself could not promote the photocleavage reaction (Fig. S17, ESI[†]). It should be noted that Liu and co-workers have reported an aggregationprompted photolysis system with retained photosensitivity of the illuminophore (or photosensitizer),¹¹ which was completely different with our reduced photosensitivity but prompted photolysis system. Therefore, we presumed that the enhanced photolysis might be possibly due to (i) prolonged lifetime of singlet oxygen in the hydrophobic assembly layer;¹⁶ and (ii) when the reactive 9,10dialkoxyanthracenes were packed, they could interact with singlet oxygen more conveniently.¹⁷

Subsequently, we further tested the photolysis of the WP5-G aggregates under visible light with ESY (a green light absorbing sensitizer) coassembling. The absorption spectra of ESY were broadened and showed slight red shift in the presence of G or WP5-G aggregates due to strong π - π stacking effect between ESY and anthracene group (Fig. 4a).^{11, 18} The size of the WP5-G aggregates with ESY coassembling showed no manifest changes, indicating only a small amount of ESY could not affect the assembly of WP5 with G and the stability of the aggregates (Fig. S18, ESI[†]). Upon green light irradiation, the ESY-coassembled aggregates cleaved significantly, while the WP5-G aggregates without ESY coassembling decomposed slightly and free G in the presence of ESY also showed almost no decomposition, confirming that the stabilized single oxygen in the aggregates facilitates the photolysis process (Fig. 4b and Fig. S19).



Fig. 4 (a) UV-vis absorption spectra of ESY (0.003 mM), G (0.1 mM) with eosin (0.003 mM), WP5-G aggregates with ESY (0.003 mM) (containing 0.5% DMSO). (b) Absorbance at 386 nm of the WP5-G aggregate and the WP5-G aggregates with ESY (0.003 mM) upon irradiation at 525 nm for different time.

Finally, since the WP5-G aggregates with ESY coassembling is visible light-responsive, and combining with the fact that WP5based supra-amphiphile is pH-responsive, the obtained WP5-G aggregates was further studied as a possible medium for controlled drug release. Hydrophilic drug mitoxantrone (MTZ) was successfully encapsulated into the WP5-G aggregates with ESY coassembling, which was demonstrated by UV-Vis spectra, DLS and TEM experiments (Fig. 5). As show in Fig. 6, under neutral

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Fig 5. (a) UV–Vis absorption spectra of the solution of ESY, MTZ, unloaded **WP5-G** vesicles, ESY-loaded **WP5-G** vesicles, and both ESY- and MTZ-loaded **WP5-G** vesicles at 25 °C in water. (b) DLS data of the both ESY- and MTZ-loaded vesicles. (c-e) TEM images of the both ESY- and MTZ-loaded vesicles.

conditions (pH = 7.0), almost no release of MTZ could be observed, while a sudden release (> 90% within 30 min) was observed upon green light irradiation due to photolysis of the aggregates. Moreover, when the solution pH was adjusted to 6.0, 42% of MTZ was released without irradiation, while a burst release in a shorter time could be observed upon green light-stimuli because of the quick disaggregation of vesicles. Since visible light is harmless to tissues, these pH- and visible light-responsive vesicles might hold potential applications in phototherapy.



Fig. 6 MTZ-release profiles of the MTZ-loaded vesicles (a) and MTZ-loaded vesicles upon irradiation at 525 nm (b) in the release media with different pH values.

Conclusions

In summary, we have successfully constructed a bola-type photodegradable supra-amphiphile based on the host-guest interactions between **WP5** and photo-decomposable guest **G**. Upon UV light irradiation, the 9,10-dialkoxyanthracenecontaining guest **G** could slowly decompose into anthraquinone and alkanol, but its photodecomposition rate was remarkably promoted after its assembled with **WP5**, and accompanied by the disassembly of the obtained monolayer supramolecular vesicles. The **WP5-G** vesicles also exhibited pH- and visible light-responsiveness after coassembling with an exogenous photosensitizer ESY, which holds potential applications in phototherapy.

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