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Hindrance of photodimerization of coumarin derivative induced by pillar[5]arene-based molecular recognition in water†

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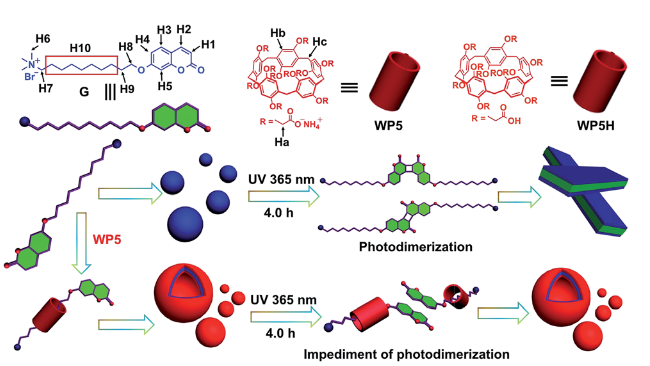
In this paper, an unprecedented method for hindrance of the photodimerization of coumarin derivative induced by pillar[5]arene-based molecular recognition in water is reported.

Photophysical and photochemical behavior of coumarin derivatives have attracted much interest by scientists in recent years.[1] After ultraviolet (UV) irradiation at wavelengths greater than 310 nm, a coumarin moiety will undergo dimerization through [2π + 2π] cycloaddition.[2] In addition, coumarin and its derivatives have been widely used in designing photosensitive polymeric materials and have been investigated for use as lasers and antenna models of artificial photosynthesis because of their high quantum yield. For example, Zhang *et al.* reported a photocontrollable supramolecular gel, which is achieved by incorporating photoactive coumarin moieties into a tribranched monomer and then self-assembly with cyclodextrin (CD) followed by noncovalent–covalent switchover.[3] Although there are so many applications relating to the photodimerization of coumarin derivatives, studies of the hindrance of photodimerization of coumarin derivatives have rarely been reported. This greatly impedes the development of applications of coumarin derivatives. Therefore, studies of the hindrance of photodimerization of coumarin derivatives are needed.

Pillar[*n*]arenes are a new class of supramolecular hosts similar to crown ethers,[4] CDs,[5] calixarenes[6] and cucurbiturils[7] and they were discovered in 2008.[8] Their syntheses, functionalizations, host–guest properties, conformations and the applications in different fields have been actively studied.[9] Their unique structure and easy functionalization properties give them superior properties in host–guest recognition. However, most of these studies have been focused on the cyclic dimers, supramolecular polymers, chemosensors, drug delivery systems, transmembrane channels and use as a cell glue. In sharp contrast, only a few efforts have been made to explore their application in the control of organic reactions. The lack of such applications may greatly impede the use of pillararenes in the field of supramolecular chemistry. Therefore, it is important and necessary to explore the application of the control of organic reactions based on pillararene-based molecular recognition. Thus, the unprecedented hindrance of the photodimerization of coumarin induced by pillar[5]arene-based molecular recognition in water is reported in this paper. Furthermore, this host–guest system can successfully be used in supra-amphiphile self-assembly in water. In particular, this is the first time that pillararene-based molecular recognition was used for the hindrance of the photodimerization of coumarin and which was then used further for supra-amphiphile self-assembly in water.

Firstly, a water-soluble coumarin derivative (G, Scheme 1) was designed and synthesized, which contained one trimethylammonium group and a coumarin unit. Because G contains a coumarin group, the possibility of whether G could undergo dimerization through [2π + 2π] cycloaddition under UV light (365 nm) in water was investigated. In order to confirm this, the photodimerization behavior was first studied using proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. According to the ^{1}H-NMR spectrum of an aqueous solution of G, the photodimerization can be observed after UV irradiation (365 nm, 4.0 h) in water on the ^{1}H-NMR timescale (Fig. 1). Peaks related to protons H_1–H_2 on G, were shifted upfield after UV



Scheme 1 Schematic representation of the hindrance of photodimerization and the self-assembly process of G and WP5⊃G in water.

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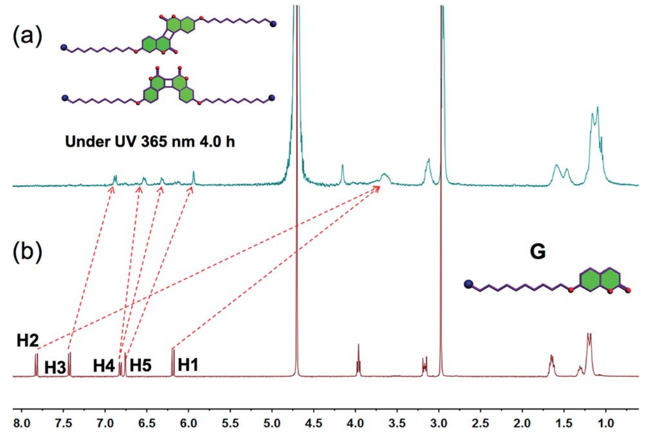

Fig. 1 ^{1}H-NMR spectra (400 MHz, deuterium oxide [D_2O], 298 K) of G (10.0 M): (a) before UV irradiation; (b) after UV irradiation for 4.0 h (365 nm).

irradiation. Meanwhile, peaks related to protons H_3–H_5 on G were also shifted upfield. These results indicated that G could undergo dimerization through [2π + 2π] cycloaddition under UV light (365 nm) in water. In addition, the self-assembly behavior of molecule G before and after UV irradiation in water was also investigated. Amphiphilic G self-assembles into nanoparticles in water before UV irradiation (Scheme 1). After irradiation under 365 nm UV light for 4.0 h, these nanoparticles will transform into nanosheets because of the photodimerization of molecule G (Scheme 1). The conductivities of the solutions as functions of the concentrations of G before and after UV irradiation were measured to determine the critical aggregation concentrations (CAC). The two linear segments in the curve and a sudden reduction of the slope indicate that the CAC value of G before UV irradiation is approximately 1.45×10^{-4} M (Fig. S6a, ESI†) and the CAC value of G after UV irradiation is approximately 1.72×10^{-4} M (Fig. S6b, ESI†). The self-assembly behaviour of G before and after UV irradiation was subsequently investigated in water using transmission electron microscopy (TEM). TEM experiments helped in the visualization of the self-assembled nanostructures from G before and after UV irradiation. Fig. 2a shows TEM micrographs of G aggregates before UV irradiation. Spherical assemblies of about 50 nm in diameter were obtained before UV irradiation and sheet assemblies were obtained after UV irradiation (365 nm, 4.0 h) (Fig. 2b). The dynamic light scattering (DLS) result (Fig. 2c) showed that the aggregates of G before UV irradiation have an average diameter of ~50 nm with a narrow size distribution, which supports the TEM result.

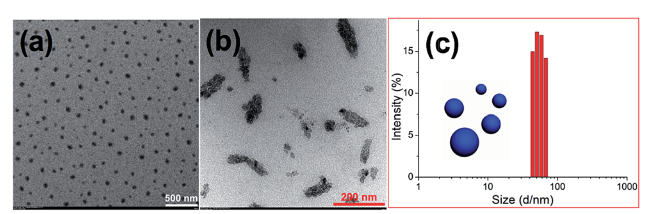

Fig. 2 (a) TEM image of the nanoparticle aggregates of G before UV irradiation (1.00×10^{-3} M); (b) TEM image of the nanosheet aggregates of G after UV irradiation (1.00×10^{-3} M); (c) DLS study the nanoparticle assemblies of G before UV irradiation (1.00×10^{-3} M).

It has been well established that pillararenes can complex with positively charged guests.[10] Because G contains a trimethylammonium group, an investigation was carried out to determine whether G could complex with WP5 to form a pseudorotaxane and further hinder the photodimerization of G. In order to confirm this, the host–guest complexation between WP5 and G was first studied using ^{1}H-NMR. According to the ^{1}H-NMR spectrum of an equimolar (10.0 mM) aqueous solution of WP5 and G, the complexation rapidly exchanges on the ^{1}H-NMR timescale (Fig. 3). Peaks related to protons H_8–H_{10} on G shifted upfield after complexation. As can be seen in Fig. 3, the chemical shift of H_9 slightly shifted upfield while that of H_8 shifted greatly upfield. This is abnormal because H_9 is closer to WP5 than H_8. Meanwhile, peaks related to protons Ha–c on WP5 shifted downfield. Furthermore, a two-dimensional (2D) nuclear Overhauser effect spectroscopy (NOESY) NMR study of the aqueous solution of G and WP5 was performed to investigate the relative spatial positions of protons in this host–guest complex (Fig. S7, ESI†). Correlation signals were observed between protons H_8–H_{10} on G and protons Ha–c on WP5. These results indicated that the positively charged trimethylammonium head of G was threaded into the cavity of the cyclic host WP5 to form a pseudorotaxane.

After the WP5⊃G recognition motif was established, an investigation was carried to determine whether the photodimerization behavior of G could be hindered by the host–guest interaction between WP5 and G in water. Several experiments were performed to confirm that the hindrance of photodimerization of G was induced by pillar[5]arene-based molecular recognition in water. Firstly, the hindrance of photodimerization behavior induced by pillar[5]arene-based molecular recognition was studied using ^{1}H-NMR. As shown in Fig. 4, after the UV irradiation (365 nm) for 4.0 h, peaks related to protons on G showed no changes. So, the

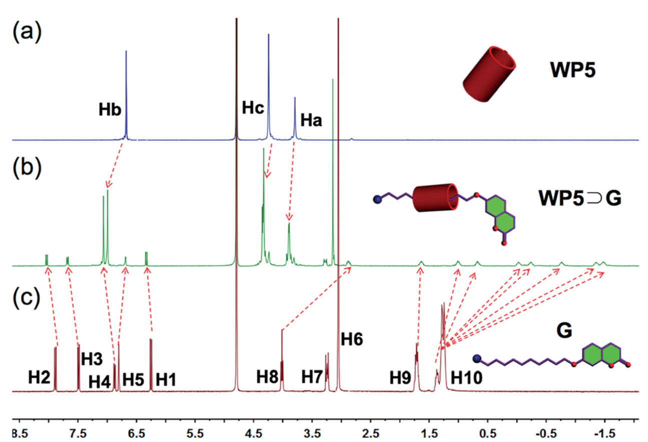

Fig. 3 Partial ^{1}H-NMR (400 Hz, D_2O, 293 K) spectra: (a) WP5 (10.0 mM); (b) WP5 (10.0 mM) and G (10.0 mM); (c) guest molecule G (10.0 mM).

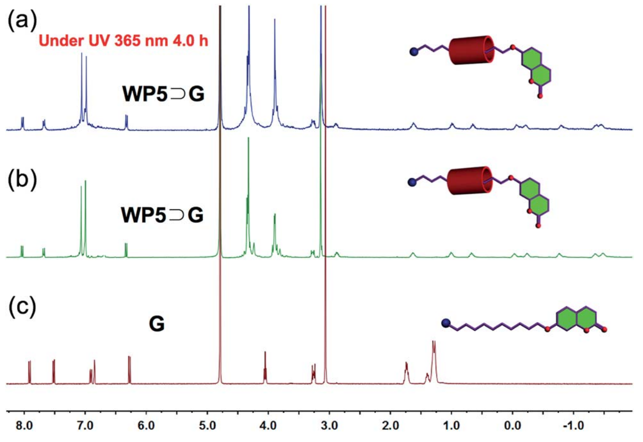

Fig. 4 ^{1}H-NMR (400 Hz, D_2O, 293 K) spectra: (a) WP5⊃G (10.0 mM) after UV irradiation 4.0 h (365 nm) (10.0 mM); (b) WP5⊃G (10.0 mM) before UV irradiation (10.0 mM); (c) guest molecule G (10.0 mM).

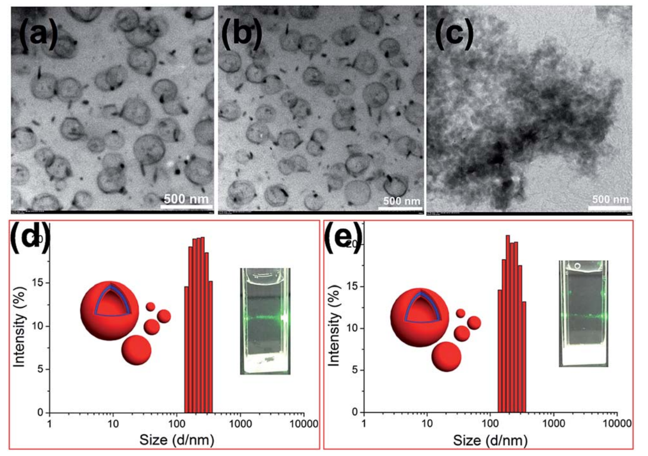

Fig. 5 (a) TEM image of the vesicle aggregates of WP5⊃G before UV irradiation (1.00×10^{-3} M); (b) TEM image of the vesicle aggregates of WP5⊃G after UV irradiation 4.0 h (365 nm) (1.00×10^{-3} M); (c) TEM image of WP5⊃G complex after the addition of H^+ in pure water (1.00×10^{-3} M); (d) DLS study of the vesicle assemblies of WP5⊃G before UV irradiation (1.00×10^{-3} M); (e) DLS study the vesicle assemblies of WP5⊃G after UV irradiation 4.0 h (365 nm) (1.00×10^{-3} M).

photodimerization behavior of the guest molecule G can be successfully hindered by the host–guest interaction between WP5 and G in water. According to the results shown in Fig. 3, 4 and S7 (ESIref E * MERGEFORMAT †), because H_9 and H_8 are closed to WP5 in the WP5⊃G complex, the steric hindrance of WP5⊃G can successfully hinder the photodimerization behavior of the guest molecule G.

Furthermore, the self-assembly behavior of the host–guest complex WP5⊃G before and after UV irradiation was investigated in water. The conductivities of the solutions as a function of the concentrations of WP5⊃G before and after UV irradiation were measured to determine the CAC. The two linear segments in the curve and a sudden reduction of the slope indicate that the CAC value of WP5⊃G before UV irradiation was approximately 5.2×10^{-5} M (Fig. S8a, ESI†) and the CAC value of WP5⊃G after UV irradiation was approximately 5.0×10^{-5} M (Fig. S8b, ESI†). There is no obvious changes of the CAC value of WP5⊃G before and after UV irradiation. The self-assembly behaviour of WP5⊃G before and after UV irradiation was subsequently investigated in water using TEM. The results of the TEM experiments helped in the visualization of the self-assembled nanostructures from WP5⊃G before and after UV irradiation. Fig. 5 shows TEM micrographs of WP5⊃G aggregates before and after UV irradiation. Vesicles of about 200 nm in diameter were obtained with WP5⊃G both before and after UV irradiation (365 nm, 4.0 h). Tyndall effects (Fig. 5d and e) were observed for the solutions of WP5⊃G before and after UV irradiation, indicating the formation of the nanostructures of WP5⊃G before and after UV irradiation. DLS results (Fig. 5d and e) showed that the aggregates of WP5⊃G before and after UV irradiation have an average diameter of 200 nm with a narrow size distribution, which supports the TEM results. These results provided direct evidence that the photodimerization behavior of the guest molecule G was successfully hindered by the host–guest interaction between WP5 and G in water.

From previous work,[11] it was known that the complex WP5⊃G can be easily destroyed by acid, because acid protonates the carboxylate groups to convert WP5 to WP5H (Scheme 1), resulting in WP5H precipitation from the aqueous solution. So, when the pH of the aqueous solution of WP5 and G decreased to 2.00, the self-assembly morphology of WP5⊃G changed from nanoparticles to irregular aggregates because the complex WP5⊃G was destroyed (Fig. 5c). These results indicated that this supramolecular amphiphile had pH responsiveness.

In conclusion, a previously unknown method for the hindrance of the photodimerization of coumarin induced by pillar[5]arene-based molecular recognition in water has been found. Several experiments were performed to confirm the hindrance of photodimerization of G induced by pillar[5]arene-based molecular recognition in water. Furthermore, this host–guest system can be successfully used in supra-amphiphile self-assembly in water. Amphiphilic G self-assembles into nanoparticles in water before UV irradiation. After irradiation under 365 nm UV light for 4.0 h, these nanoparticles will transform into nanosheets because of the photodimerization of molecule G. Furthermore, the host–guest complex WP5⊃G can self-assemble into vesicles before UV irradiation. Because of the hindrance of photodimerization of G induced by pillar[5]arene-based molecular recognition, the host–guest complex WP5⊃G can still self-assemble into vesicles after UV irradiation (365 nm, 4.0 h). And, this host–guest complex WP5⊃G has very good pH responsiveness. Finally, the present study provided a new and simple method to hinder the photodimerization of the coumarin derivative, which may be of high importance for the development of novel functional materials and molecular devices in the future.

Acknowledgements

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