

## Organic &amp; Supramolecular Chemistry

Photolysis Behaviors of Anthryl Derivative Aggregation Mediated by Sulfato- $\beta$ -CyclodextrinXuan Zhao,<sup>[a]</sup> Yong Chen,<sup>[a]</sup> Xin-Ran Guan,<sup>[a]</sup> Pei-Yu Li,<sup>[a]</sup> Wei-Lei Zhou,<sup>[a]</sup> and Yu Liu\*<sup>[a, b]</sup>

A photo-responsive supramolecular assembly was prepared using sulfato- $\beta$ -cyclodextrin (SCD) as the macrocyclic host and pyridinium-modified anthracene (Anpy) as the guest molecule, and its assembly and photolysis behaviors were fully investigated by mass spectrometry, UV-vis, dynamic light scattering, scanning electron microscopy, transmission electronic microscopy, Fourier transform infrared spectroscopy and powder X-ray diffraction, etc. Without SCD, the disruption of polycyclic aromatic structure in Anpy was relatively slow via a photo-oxidation reaction under UV irradiation at 365 nm. Interestingly, the photo-oxidation rate significantly increased 5.2 times after the supramolecular assembly of Anpy with SCD. This result will provide a supramolecular method for the efficient elimination of polycyclic aromatic hydrocarbons.

The organic pollution has already become a serious environmental issue currently, which will have long-term negative effects on the ecosystem and human health. Among the various persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs), generally produced via the incomplete combustion of oil, coal, garbage and other organic substances, have attracted more and more attention.<sup>[1]</sup> Nowadays the mostly used method for treating PAHs in soil is mainly the degradation by microorganisms to form intermediate metabolites such as epoxides and diketones, but this method also damages the ecological function of soil microorganisms.<sup>[2]</sup> On the other hand, PAHs possess the fairly low solubility in water and thus are difficult to be eliminated by microorganisms in water. Therefore, the photolysis is widely regarded as a significant method to eliminate PAHs in soil and water<sup>[3]</sup> because light is one of the most ideal means of eliminating organic pollutants owing to its cleanliness, high efficiency, low cost and so on.<sup>[4]</sup>

Supramolecular macrocyclic hosts are capable of providing well-defined rigid cavities to bind the substrate molecules and facilitating rapid and highly selective chemical reactions, especially photochemical reactions.<sup>[5]</sup> Amphiphilic self-assembly

using macrocyclic hosts is an attractive strategy for manufacturing nanostructures,<sup>[6]</sup> which has been widely used in drug delivery,<sup>[7]</sup> dye degradation,<sup>[8]</sup> photoelectric material<sup>[9]</sup> and pollutant treatment.<sup>[10]</sup> Yuan et al. reported that dialkoxanthracene-containing diblock copolymers self-assembled into a micellar structure in water and could be cut off by green visible light at 540 nm to induce the disassembly of self-assembled micelles.<sup>[11]</sup> Díaz-Urbe et al. reported that the incorporation of metal in the porphyrin ring significantly affected the photonic efficiency in the oxidation process and metal-free carboxyphenylporphyrin (TcPPH) had a 31% photonic efficiency in the anthracene photo-oxidation, which was higher than metal-carboxyphenylporphyrins (TcPP-M, M = Cu / Zn).<sup>[12]</sup> Wang et al. reported a bola-type supra-amphiphile assembled from a rod-coil guest molecule containing photoactive 9,10-dialkoxanthracene group and a water-soluble pillar[5]arene host, in which the photodecomposition rate of guest was remarkably promoted upon forming the supramolecular assembly.<sup>[13]</sup>

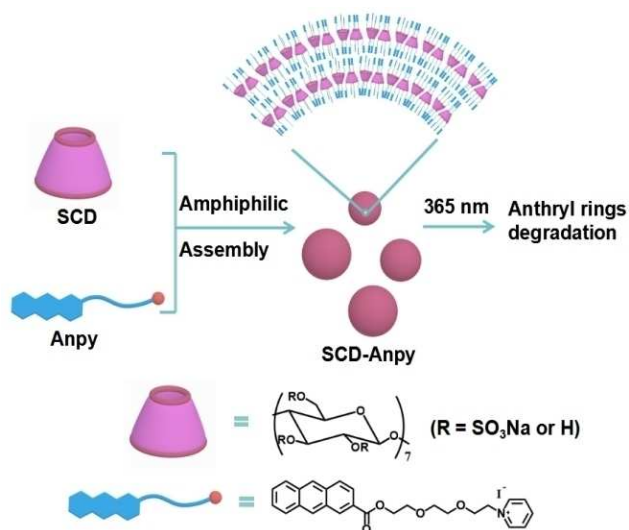
Recently, we constructed a photodegradable supramolecular assembly utilizing p-sulfonatocalix[4]arenes (SC4 A) and amphiphilic 9-alkoxy-substituted anthracene, and the results showed that the amphiphilic anthracene was highly photoreactive after aggregation induced by SC4 A in water.<sup>[14]</sup> Herein, a photodegradable supramolecular assembly was designed with sulfato- $\beta$ -cyclodextrin (SCD) as the host and 2-pyridinium alkoxy-substituted anthracene (Anpy) as the guest by molecular induced aggregation (Scheme 1). The inherent advantages of using SCD and anthracene derivative to construct such a supramolecular assembly are (1) SCD is a sulfonate-modified cyclic oligosaccharide linked by 7 glucose units by  $\alpha$ -1,4 glucosidic bonds, which is water-soluble, commercially available and environmental friendly;<sup>[15]</sup> (2) compared with porphyrin, calixarene or pillararene, the use of SCD cannot introduce new aromatic skeleton that may cause secondary pollution to environment in the process of PAHs degradation; (3) anthracene and its derivatives have high photoreactivity under illumination and are thus widely used as the important raw materials for polycyclic aromatic hydrocarbons in basic chemical researches and industrial applications.<sup>[16]</sup> As a result, the SCD-Anpy system shows a high photo-reactivity and elimination rate. It is our special interest to develop a clean and feasible supramolecular strategy for the elimination of polycyclic aromatic hydrocarbons.

Possessing a hydrophilic pyridinium head and a hydrophobic anthryl tail, the amphiphilic Anpy molecule has the tendency of self-aggregation in aqueous solution, and its critical aggregation concentrations (CAC) can be greatly

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Scheme 1. Schematic illustration of SCD-Anpy supramolecular assembly.

decreased in the presence of SCD. By monitoring the dependence of the optical transmittance on the concentration of Anpy at 475 nm, the CAC values of Anpy with and without SCD were measured.<sup>[17]</sup> As shown in Figure 1, the optical transmittance of free Anpy showed no appreciable change with concentrations increasing from 0.0005 to 0.5 mM, indicating that the individual guest could not self-aggregate in this concentration region. After the addition of SCD, the optical transmittance of Anpy at 475 nm decreased gradually with concentrations increasing. Moreover, an inflection point at 0.198 mM was observed on the plot of optical transmittance of SCD-Anpy at 475 nm (Figure 1c). This phenomenon indicated that SCD could greatly reduce the critical aggregation concentration of Anpy to 0.198 mM (Figure 1d), probably due to the SCD-induced aggregation of Anpy. In addition, the preferable mixing ratio of

the SCD-Anpy assembly was measured by gradually adding SCD to the Anpy solution at a fixed concentration of 0.2 mM. The optical transmittance at 475 nm decreased rapidly with the addition of SCD, and then gradually increased to a stable value (Figure S4, Supporting Information). The minimum was reached when the Anpy / SCD ratio was 20 : 1. A simple mixture of SCD with Anpy at the preferable molar ratio in water exhibited a strong Tyndall effect, indicating the existence of abundant aggregates (Figure S5, Supporting Information). There was no assembly when replacing SCD with D-gluconic acid sodium salt (GS) under comparable conditions (Figure S6, Supporting Information), which indicated the importance of the cyclic structure of SCD. A possible assembly mechanism may be that the negatively charged SCD cavity would be surrounded by the cationic pyridinium heads of Anpy through electrostatic attractions, and simultaneously the hydrophobic anthracene ring tails could stack with each other tightly through the  $\pi$ - $\pi$  interactions, which jointly led to the formation of multilayer assembly structure as illustrated in Scheme 1.

Subsequently, dynamic laser scattering (DLS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were employed to investigate the size distribution and morphology of the SCD-Anpy assembly as well as the molecular induced aggregation behaviors. Free Anpy showed no DLS signal, suggesting that Anpy could not form aggregates. However, the DLS data of SCD-Anpy assembly gave an average hydrodynamic diameter of 424 nm at a scattering angle of 90° (Figure S7, Supporting Information), indicating that Anpy and SCD could self-assemble into nano-scaled aggregates. TEM images (Figure 2a) and SEM images (Figure 2c) of SCD-Anpy also showed a lot of spherical nanostructures with diameters ranging from 300 to 500 nm, which was basically consistent with the corresponding values from DLS (Figure S8, Supporting Information). SCD exists as a mixture of CDs randomly substituted by sulfonate groups with an average degree of substitution of 13, so the resultant SCD-Anpy nanoparticles were inhomogeneous to some extent and were approximately classified as one type of spherical nanostructure.

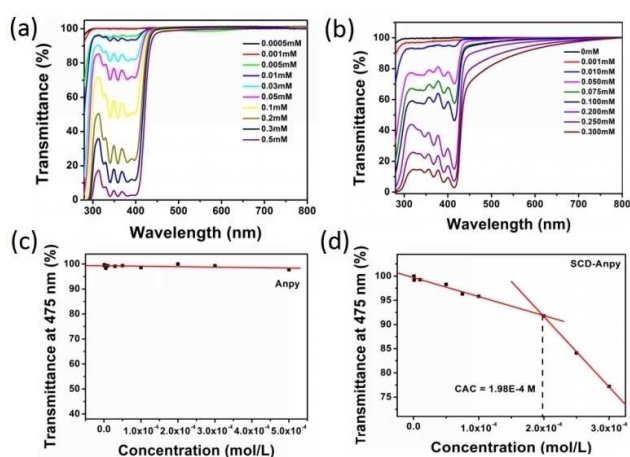


Figure 1. Optical transmittance of aqueous solutions of Anpy at different concentrations (a) without and (b) with SCD (0.03 mM) at 25 °C; Dependence of the optical transmittance on the concentration of Anpy at 475 nm (c) without and (d) with SCD (0.03 mM).

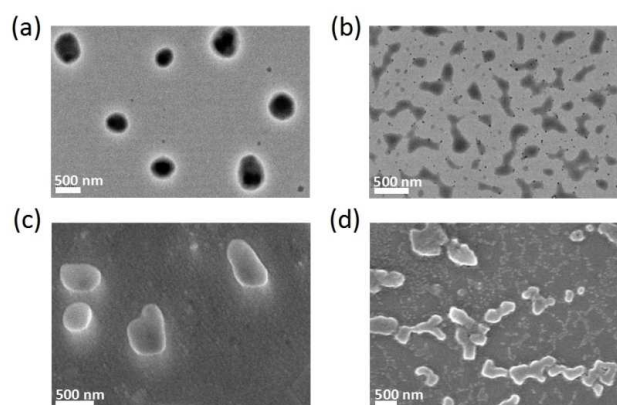


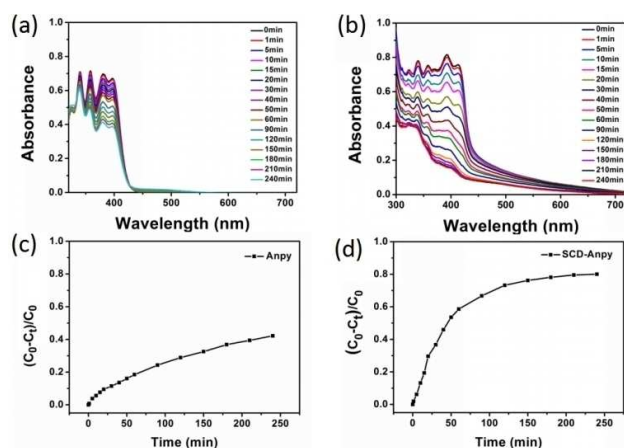
Figure 2. TEM images of SCD-Anpy assembly (a) before and (b) after UV irradiation (365 nm) for 240 minutes and SEM images of SCD-Anpy assembly (c) before and (d) after UV irradiation (365 nm) for 240 minutes.

These results further rationalize the assembly mechanism of SCD-Anpy as illustrated in Scheme 1. In addition, Fourier transform infrared (FTIR) spectroscopy was examined to understand the bonding nature between host-guest in the aggregates (Figure S9, Supporting Information). The FTIR spectrum of SCD-AnEA displayed that the characteristic absorption peaks of  $\text{—OH}$  from  $3400\text{ cm}^{-1}$  to  $3700\text{ cm}^{-1}$  has a red shift, and the characteristic absorption peaks of  $\text{O=S=O}$  in the sulfonate groups at  $992\text{ cm}^{-1}$  and  $1056\text{ cm}^{-1}$  has a certain blue shift to some extent, as compared with the FTIR spectrum of SCD. Also, powder X-ray diffraction (XRD) patterns of SCD-Anpy showed the appreciable changes as compared with those of Anpy and SCD, suggesting the certain crystallinity of the assembly (Figure S10, Supporting Information). These results indicated that the anthryl rings grappled by the SCD and pyridinium complexation were tightly aligned with each other via the hydrophobic and  $\pi$ - $\pi$  interactions. The synergistic effect of these non-covalent interactions led SCD-Anpy to assemble tightly and then bend to a large multi-layered spherical nanoparticles.<sup>[18]</sup>

Interestingly, the original spherical nanoparticles of SCD-Anpy turned into small amorphous structures after the UV irradiation at  $365\text{ nm}$  (Figure 2b, d). It is well known that two kinds of photolytic products of anthracene may be obtained upon excitation by UV irradiation. One is to form stable cyclic endoperoxids,<sup>[19]</sup> and the other is to produce anthraquinones after the rearrangement and further oxidation.<sup>[20]</sup> In addition, the photodimerization behavior of anthracene units may also occur under UV irradiation.<sup>[21]</sup> Before UV irradiation, the mass spectrum of Anpy gave a  $m/z$  peak at  $416.2$  (Figure S11a, Supporting Information), while a new peak appeared at  $446.2$  after UV irradiation at  $365\text{ nm}$  (Figure S11b, Supporting Information). Therefore, it was deduced that an anthraquinone structure was formed in the photo-reaction. It is noteworthy that the formation of anthraquinone structure decreased the hydrophobicity of the anthryl tail of Anpy and thus weakened the  $\pi$ - $\pi$  stacking of Anpy, which consequently led to the disassembly of SCD-Anpy, as illustrated in the TEM images.

Subsequently, UV-vis absorption and fluorescence spectroscopy were performed to investigate the effect of SCD on the photo-oxidation rate of Anpy (Figure 3a). After irradiation by UV light at  $365\text{ nm}$  for 240 minutes, the absorption intensity of free Anpy in the range of  $300\text{--}400\text{ nm}$  decreased slightly, accompanied by the slight change in fluorescence emission intensity (Figure S12, Supporting Information). In the control experiment, the photo-oxidation of Anpy was not significantly improved after the addition of D-gluconic acid sodium salt (Figure S13, Supporting Information). In contrast, the UV absorption and fluorescence emission of the anthracene moiety in the SCD-Anpy assembly greatly decreased (Figure 3b), indicating that the photo-oxidation of Anpy was significantly enhanced in the presence of SCD.

To quantitatively investigate the effect of SCD on Anpy photo-oxidation, the photo-oxidation rates with or without SCD were calculated according to the UV-vis absorption intensity, where the concentration of Anpy was fixed at  $0.2\text{ mM}$ . The results showed that only  $42.2\%$  of free Anpy was



**Figure 3.** UV-vis spectra of (a) Anpy ( $0.20\text{ mM}$ ) and (b) SCD-Anpy assembly ( $0.01\text{ mM} / 0.2\text{ mM}$ ) under UV irradiation ( $365\text{ nm}$ ) at different time within 240 minutes;  $(C_0 - C_t) / C_0$  as functions of degradation time (c) Anpy ( $0.2\text{ mM}$ ) and (d) SCD-Anpy assembly ( $0.01\text{ mM} / 0.2\text{ mM}$ ) corresponding to (a) Anpy and (b) SCD-Anpy assembly.

oxidized within 240 minutes in aqueous solution (Figure 3c), but this value significantly increased to  $80.1\%$  in the presence of SCD (Figure 3d). Moreover, the photo-oxidation processes of Anpy and SCD-Anpy were fitted by the first-order kinetics. The reaction rate constants ( $k$ ) were calculated to be  $0.0022\text{ min}^{-1}$  and  $0.01136\text{ min}^{-1}$  for Anpy and SCD-Anpy, and the corresponding half-life times ( $t_{1/2}$ ) of Anpy and SCD-Anpy were 315 minutes and 61 minutes respectively (Figure S14, Supporting Information). This indicated the photo-oxidation rate of Anpy enhanced 5.2 times in the presence of SCD. The possible reasons for the efficient improvement of SCD to the photo-oxidation of Anpy may be as follows: (1) Compared with the bulk water, the solubility of ground state oxygen and the lifetime of singlet oxygen are significantly improved in the hydrophobic environment provided by the SCD-Anpy supramolecular assembly;<sup>[22]</sup> (2) Since the efficiency of photosensitization is highly dependent on the distance between the sensitizers and targets,<sup>[23]</sup> the closely packed anthryl rings in the SCD-Anpy assembly promote the capture of singlet oxygen after illumination and ultimately lead to the improvement of oxidation rate.

In summary, a photodegradable supramolecular assembly was prepared utilizing the negatively charged macrocyclic host SCD and the amphiphilic guest Anpy via the electrostatic interactions. The resultant SCD-Anpy assembly provided a hydrophobic environment facilitating the closely packed anthryl rings to capture the singlet oxygen. Consequently, the photo-oxidation efficiency of Anpy was significantly improved by 5.2 times without the introduction of new aromatic structures, e.g. photosensitizer, to cause secondary environmental pollution. This work may provide an applicable supramolecular strategy for the construction of photo-responsive materials and the photolysis of polycyclic aromatic hydrocarbon pollutants.

## Supporting Information Summary

General experimental materials, methods and characterizations were attached in the Supporting information.

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