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Supramolecular Crosslinked Polymer for Efficient Organic Dye Removal from Aqueous Solution

*Xuan Wu, Yong Chen, and Yu Liu**

Removal of organic dyes from aqueous solution has attracted considerable attention in the field of environmental science and for industrial application. Herein, a crosslinked pillar[5]arene polymer (Ru-P5C) is synthesized by a click reaction between a hydrophobic azide-modified pillar[5]arene (N_3-P5) and a hydrophilic alkyne-modified Ru derivative. The synthesized material can efficiently remove various anionic organic dyes from aqueous solution upon irradiation at 450 nm in the air. The numerous positive charges on the nanoparticles facilitate adsorption of the dyes, and Ru-catalyzed photolysis, promoted by the hydrophobic environment of the nanoparticles, leads to their degradation. The removal efficiency after ≈25 min exceeds 95%, which is much higher than the removal efficiencies of TiO_2 (P25), BiOBr, and Ru(bipy)$_3$Cl$_2$. Moreover, the polymer not only exhibits good regeneration ability but also shows excellent performance for dye removal under irradiation from sunlight as well as in the wastewater system containing a number of dyes.

Macrocyclic molecules have been extensively investigated in the fields of molecular recognition and assembly owing to their excellent host–guest properties, symmetric structures, tunable molecular sizes, and easy modification.[1–4] Studies in this area have led to the construction of a large number of functional supramolecular assembly systems, such as supramolecular polymers,[5,6] supramolecular nanoparticles,[7–9] mechanical interlocked molecules,[10–12] artificial light-harvesting systems,[13,14] and other functional systems.[15–17] Recently, a considerable amount of research has been conducted on macrocyclic molecule-based crosslinked polymers for adsorption and separation processes. Macrocyclic molecules are used as crosslinkers because their symmetric nature allows for the formation of porous materials. Owing to the large Brunauer–Emmett–Teller (BET) surface areas (S_{BET}) of these crosslinked polymers and/or the 3D structures of macrocyclic molecules, they can efficiently remove pollutants from aqueous solutions.[18–21] For example, a crosslinked polymer formed by the reaction between the rigid linker tetrafluoroterephthalonitrile and β-cyclodextrin (CD) exhibited excellent performance for the removal of organic dyes from aqueous solutions.[19] Furthermore, by taking advantage of the size differences between α-, β-, and γ-CDs, researchers have constructed precise molecular sieving nanofilms via simple crosslinking reactions between CDs and trimesoyl chloride.[20,21] However, regeneration of this type of polymer requires the use of organic solvents to remove the adsorbed organic molecules, which results in secondary waste. Therefore, the development of self-cleaning crosslinked polymers is highly desirable. Particularly useful would be polymers that would permit chemical degradation of the adsorbed pollutant, for example, by photodegradation. To the best of our knowledge, few studies have been conducted to combine macrocyclic molecule-based crosslinked polymers and photosensitizers to generate self-cleaning materials for dye removal, especially nanosized assembly systems.

Ruthenium (Ru) complexes, which are well-known photosensitizers, have been widely used in the fields of photodynamic therapy,[22,23] synthetic chemistry,[24,25] and dye degradation.[26,27] These complexes can absorb light in the visible region to give stable, long-lived photoexcited states.[28–30] In particular, stable ground-state Ru complexes can be converted to redox-active species simply by irradiation with household light bulbs, and these species can induce unique and valuable processes.

Similar to CDs, pillar[*n*]arenes,[31,32] which exhibit total symmetry on both the upper and lower rims, have been used for the synthesis of crosslinked polymers. For example, Ma and co-workers recently reported a type of crosslinked polymer for the efficient removal of pollutants from aqueous solution, which was prepared by the reaction between tetrafluoroterephthalonitrile and the hydroxy groups on pillar[5]arene or pillar[6]arene.[33] In addition, Coskun and co-workers used Pd-catalyzed Sonogashira cross-coupling reactions between pillar[5]arenes and diynes to form rigid porous materials for the separation of propane and methane.[34] Considering the hydrophobicity of pillar[*n*]arenes, they can be expected to provide a hydrophobic environment in amphiphilic systems. This hydrophobic environment can increase the solubility of oxygen in water and/or extend the lifetime of singlet oxygen, both of which are

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Dr. X. Wu, Prof. Y. Chen, Prof. Y. Liu
College of Chemistry
State Key Laboratory of Elemento-Organic Chemistry
Nankai University
Tianjin 300071, China
E-mail: yuliu@nankai.edu.cn

Prof. Y. Chen, Prof. Y. Liu
Collaborative Innovation Center of Chemical Science
and Engineering (Tianjin)
Tianjin 300072, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adsu.201800165.

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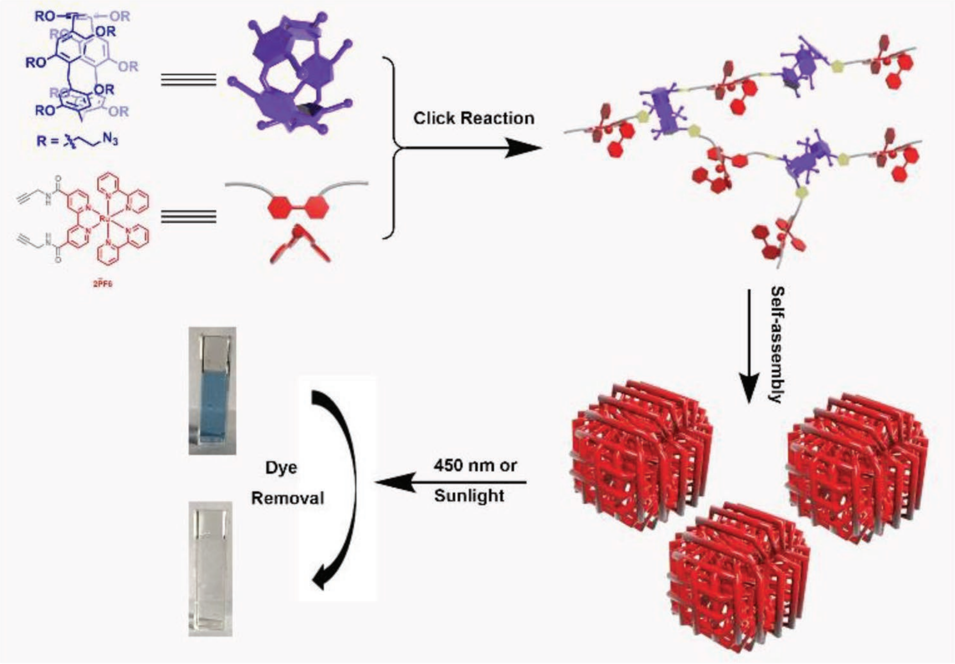

Scheme 1. Schematic illustration of a pillar[5]arene-based crosslinked polymer for dye removal.

essential to photodegradation processes.[35,36] In this study, we introduced a hydrophilic $[Ru(bipy)_3]^{2+}$ derivative into a pillar[5] arene-based crosslinked polymer by means of a click reaction, and the resulting crosslinked polymer could self-assemble into nanoparticles with a diameter of ≈2 µm. Then, we evaluated the activity of the resulting polymer as a heterogeneous catalyst for the removal of dyes from aqueous solution under irradiation under 450 nm or sunlight (**Scheme 1**). We found that the polymers removed dyes more efficiently than commercially available alternatives (TiO_2 (P25), BiOBr, and $Ru(bipy)_3Cl_2$). Moreover, the polymer not only exhibited good regeneration ability but also showed excellent performance in dye removal under irradiation of sunlight as well as in the wastewater system containing numbers of dyes.

The crosslinked polymer was synthesized in moderate yield by means of a click reaction between an azide-modified pillar[5]arene (**N_3-P5**)[37] and an alkyne-modified Ru complex (**Ru**). The azide-modified pillar[5]arene was synthesized according to the reported literature.[37] The alkyne-modified Ru complex was synthesized by the route shown in Scheme S2 in the Supporting Information. Briefly, the reaction of $RuCl_3\cdot 3H_2O$ and 2,2′-dipyridyl afforded *cis*-$[Ru(bipy)_2C1_2]$ occurred and the product was then allowed to react with dicarboxyl-modified 2,2′-dipyridyl. The resulting tripyridyl compound (**Ru-COOH**) was treated with 2-propynylamine to afford the target molecule (**Ru**). Finally, a copper(I)-catalyzed azide-alkyne cycloaddition reaction[38] was performed to form the crosslinked polymer, which underwent ion exchange upon being stirred in saturated NH_4Cl solution for 24 h. The resulting polymer was a dark red powder that was insoluble in most solvents, including dimethyl sulfoxide, *N,N*-dimethylformamide, dichloromethane, and water, thus having potential utility as a heterogeneous catalyst.

In the solid-state ^{13}C NMR spectrum of **N_3-P5** (Figure S9, Supporting Information), the peaks at 150, 127, and 113 ppm were assigned to the carbons of the phenyl rings of pillar[5] arene, and the peaks at 67, 51, and 30 ppm were assigned to the sp^3 carbons of pillar[5]arene. Most of these resonances were also observed in the spectrum of the crosslinked polymer (**Ru-P5C**; Figures S8 and S9, Supporting Information) but the signals were broadened. Moreover, the signal at 30 ppm in the spectrum of **N_3-P5** shifted to 36 ppm in the spectrum of **Ru-P5C**, and the latter showed a new signal at 140 ppm, which was assigned to the sp^2 carbons in **Ru**. These results indicated that the dark red powder was the product of the reaction between **N_3-P5** and **Ru**.

Furthermore, Fourier transform infrared spectroscopy results also confirmed the formation of a crosslinked polymer. As shown in Figure S10 in the Supporting Information, the spectrum of the polymer contained typical C—H stretching bands for benzene at 2933 and 2863 cm^{-1}, which were assigned to pillar[5]arene, and typical stretching bands for amides at 1690 and 1620 cm^{-1}, which were assigned to the **Ru**. Furthermore, the spectrum showed new peaks at 3136, 3079, 1601, and 1557 cm^{-1}, which were assigned to the C—H and C=N groups on the triazole units, indicating the occurrence of the click reaction. Finally, elemental analysis of the crosslinked polymer showed that it consisted of 16.75% N, 52.85% C, and 5.58% H.

The morphology of the polymer self-assembled in water was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images (**Figure 1**a,b) indicated that the crosslinked polymer self-assembled into nanoparticles with diameters of ≈2 µm, and this was confirmed by TEM. As shown in Figure 1c–e, the solid nanoparticles were observed with a narrow diameter distribution. In the energy-dispersive X-ray profile obtained by means

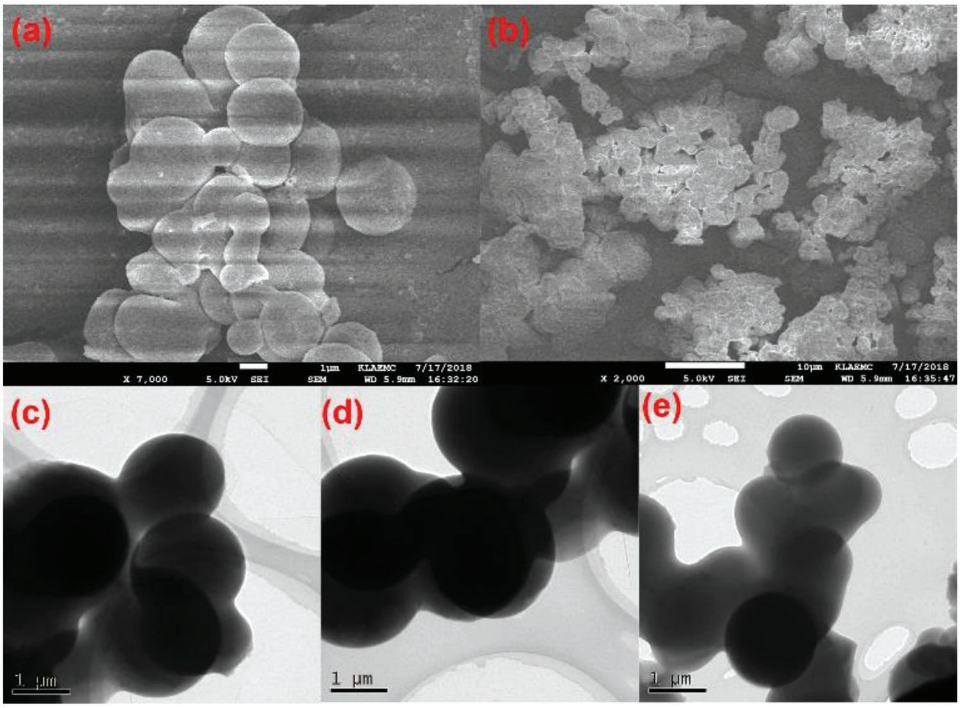

Figure 1. a,b) SEM images of **Ru-P5C** and c–e) TEM images of **Ru-P5C.**

of TEM (Figure S11, Supporting Information), a signal derived from Ru provided solid evidence that the crosslinked polymer existed in the observed nanoparticles. Zeta-potential analysis revealed that the nanoparticles had a positively charged surface (Figure S12, Supporting Information), with a zeta potential of +53 mV. This phenomenon might result from the introduction of the positively charged Ru complex into the crosslinked polymer. X-ray photoelectron spectroscopy revealed that Ru was partially distributed on the surface of the polymer; a characteristic signal for Ru 3d was observed at 284 eV (Figure S13, Supporting Information). Taken together, these characterization results indicated that the self-assembly morphology of the crosslinked polymer made it potentially useful for heterogeneous catalysis due to its spherical morphology and charged surface.

The BET analysis revealed that the BET surface area was 3.92 $m^2\ g^{-1}$ and the average pore size was 7.28 nm (Figure S15, Supporting Information). The low surface area might result from the spherical morphology of the formed nanoparticles, in which the hydrophobic region formed by pillar[5]arene can be expected to provide an environment that would increase the solubility of oxygen and/or extend the lifetime of singlet oxygen.[35,36] Thermogravimetric analysis under N_2 indicated that the polymer did not decompose at temperatures below 200 °C (Figure S16, Supporting Information). Moreover, the crosslinked polymer exhibited similar photochemical properties to **Ru** (Figure S14, Supporting Information). Both species showed a maximum emission at 650 nm, which indicated that incorporation of the Ru complex into the polymer had little effect on its photochemical properties. These results confirmed that the polymer had potential utility as a heterogeneous catalyst, owing to the presence of the Ru complex photosensitizer, the hydrophobic environment for singlet oxygen in the nanoparticles, and the thermostability of the polymer.

Having successfully constructed nanoparticles composed of Ru-loaded crosslinked polymers, we evaluated their ability to remove organic dyes from aqueous solutions using indigo carmine (IC, Figure S21, Supporting Information) as a model dye. First, we used UV–vis spectroscopy to investigate the stability of aqueous IC upon irradiation at 450 nm in air in the absence of the polymer over the course of 70 min (Figure S18, Supporting Information); the fact that we observed no obvious changes in the UV–vis spectra indicated the excellent stability of this dye.

Subsequently, we evaluated the dye removal efficiency when 5.00 mg **Ru-P5C** was added to 3 mL of the IC solution (1.00 mg mL^{-1}), again using UV–vis spectroscopy (**Figure 2**a). The absorption intensity decreased sharply with time; the removal efficiency was calculated to be 92% after 17 min, and dye removal was nearly complete after 35 min. Moreover, the solution changed from blue to colorless during irradiation (Figure 2b, insets), which gave visible proof of the removal of IC from the aqueous solution.

We also investigated the removal efficiencies of five additional dyes (Figure S21, Supporting Information): xylenol orange (XO), methyl orange (MO), orange I (OrI), brilliant crimson red (CR), and rhodamine B (RhB). After irradiation at 450 nm for 25 min, the dye solution became colorless, again providing visible proof of dye removal. The visual results were confirmed by UV–vis spectroscopy (**Figure 3**). The characteristic peaks of each of these dyes decreased sharply with irradiation time, indicating that the dye concentration in the solution decreased substantially. The removal efficiencies for all five dyes were calculated to exceed 95%. These results allowed us

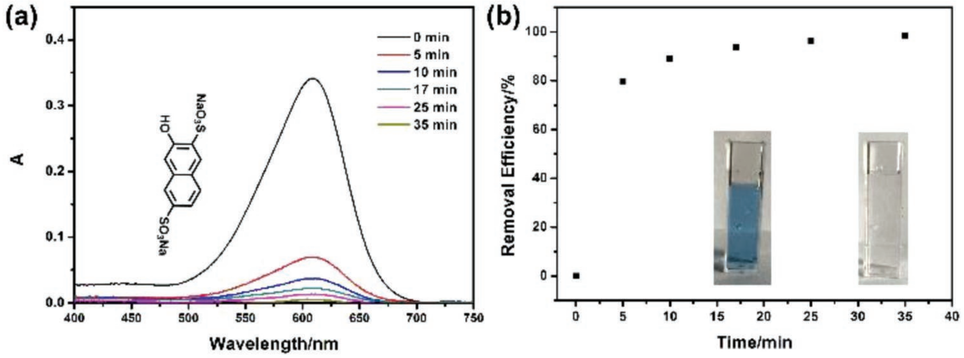

Figure 2. a) Time-dependent UV–vis spectra of IC solution upon irradiation at 450 nm in the presence of **Ru-P5C** and b) time dependence of IC removal efficiency. Insets in panel (b) are photos of the IC solution before and after irradiation. Initial conditions: [IC] = 1.00 mg mL^{-1}, V_{IC} = 3 mL, and $M_{\text{Ru-P5C}}$ = 5.00 mg; 50-µL aliquots were periodically removed and diluted with 3 mL of distilled water for analysis.

to conclude that the **Ru-P5C** polymer had the potential to be a versatile material for dye removal.

Next, we explored the dye removal mechanism. According to previous reports,[22–27] O_2 and light are necessary components in Ru-based photodynamic therapy systems and Ru-mediated photooxidation reactions. Therefore, it was vital that we determined whether O_2 and light participated in the dye removal process in this study. For this purpose, we again used IC as a model dye for two control experiments. Similar to the experiments described above, **Ru-P5C** (5.00 mg) was added to 3 mL of IC solution (1.00 mg mL^{-1}), and the mixture was allowed to stand in the dark in the presence of air or under N_2 in the light. At intervals, UV–vis spectra were recorded (**Figure 4**a,b). After inspection of the two sets of spectra, we concluded that the removal efficiencies under these two conditions were similar. In both cases, the absorption intensity decreased by ≈60% after 35 min (Figure 4c), and this decrease was smaller than that observed in the presence of both air and light.

It was also important to determine the role of the self-assembled morphology of the polymer in the removal process. For this purpose, we used Ru(bipy)$_3$Cl$_2$, which dissolved completely in the aqueous solution, as a reference compound. UV–vis spectra showed that only 8% of IC had been removed after irradiation for 25 min in the presence of Ru(bipy)$_3$Cl$_2$ (Figure S19, Supporting Information), which was much lower than the percentage removed after irradiation for the same time in the presence of **Ru-P5C**. This result indicated that the self-assembled nanoparticles of the polymer dramatically improved the dye

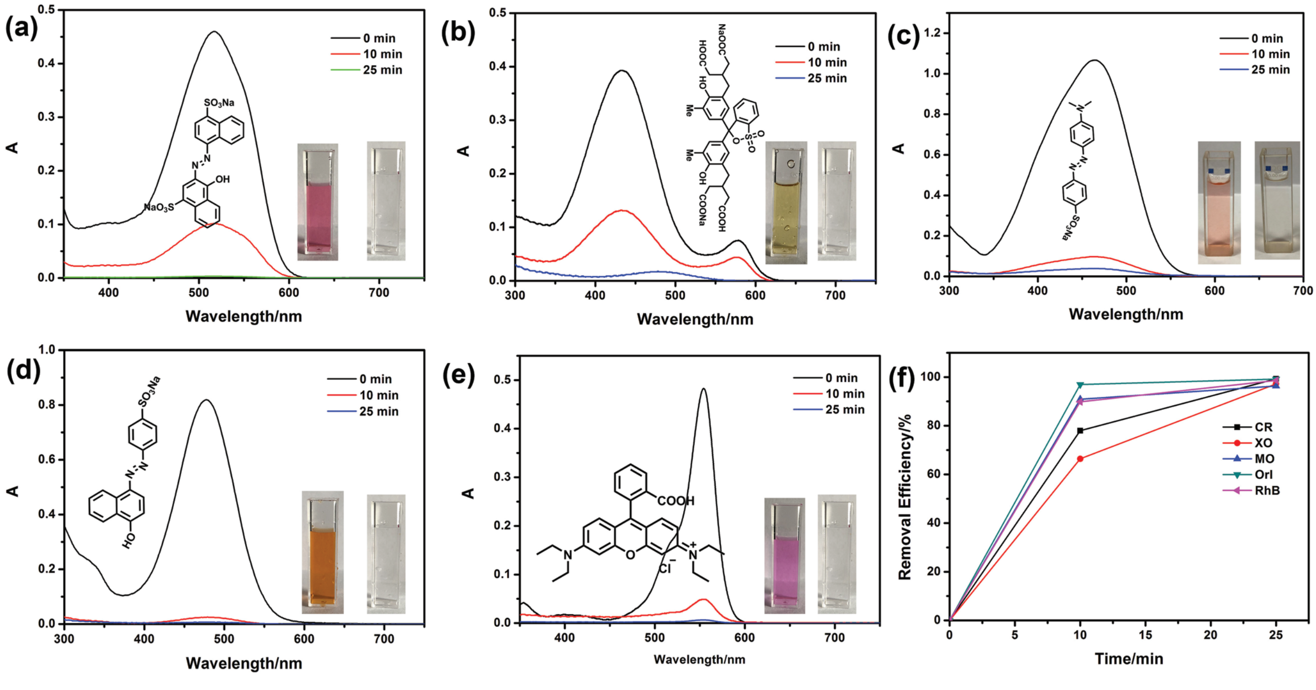

Figure 3. Time-dependent UV–vis spectra of a) carmine red, b) xylenol orange, c) methyl orange, d) orange I, and e) rhodamine B solutions during irradiation at 450 nm in the presence of **Ru-P5C** and f) time dependence of dye removal efficiency. The insets show photos of the dye solutions before and after irradiation. Initial conditions: [dye] = 1.00 mg mL^{-1}, V_{dye} = 3 mL, and $M_{\text{Ru-P5C}}$ = 5.00 mg; 50 µL aliquots were periodically removed and diluted with 3 mL of distilled water for analysis.

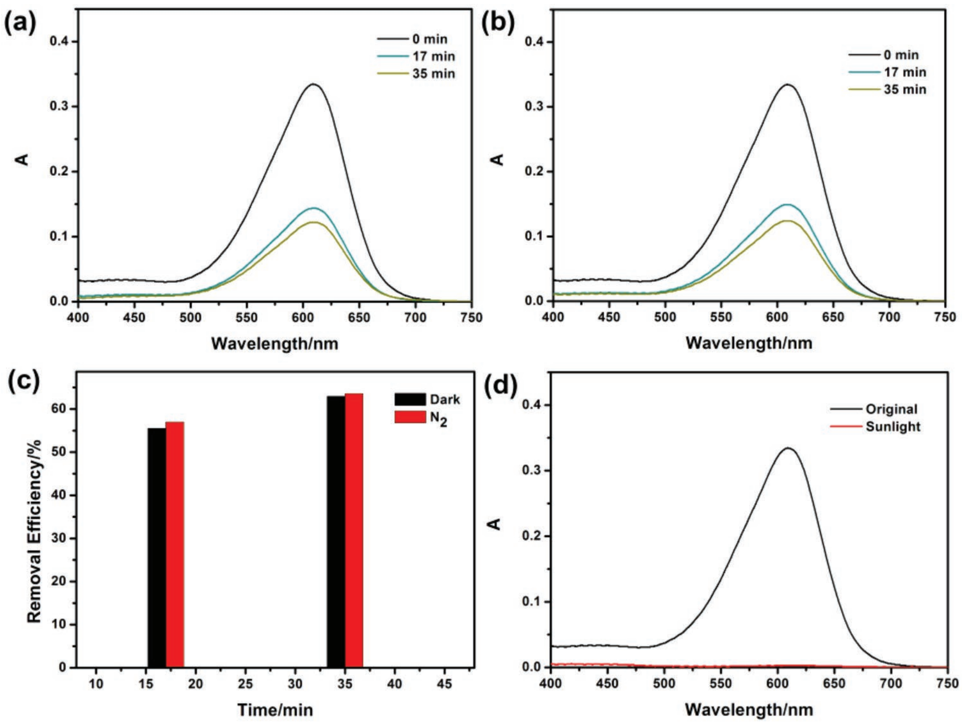

Figure 4. Time-dependent UV–vis spectra of indigo carmine (IC) solution kept a) in the dark in the presence of air and b) under N_2 in the light in the presence of **Ru-P5C**. c) Time dependence of dye removal efficiency by **Ru-P5C** in the dark in the presence of air and under N_2 in the light. d) UV–vis spectra of indigo carmine (IC) solution in the presence of **Ru-P5C** under irradiation with sunlight for 35 min. Initial conditions: [IC] = 1.00 mg mL^{-1}, V_{IC} = 3 mL, $M_{\text{Ru-P5C}}$ = 5.00 mg. 50 µL aliquots of the solution were diluted with 3 mL of distilled water for UV–vis spectroscopy.

removal efficiency. This improvement may result from the presence of a hydrophobic environment that could increase the solubility of oxygen and/or extend the lifetime of singlet oxygen as well as the electrostatic interaction between the anionic dyes and the positively charged surface of the nanoparticles. On the basis of these results, we concluded that the dye removal process involved two steps: 1) adsorption of the dye facilitated by electrostatic interactions and 2) Ru-induced photolysis.

We also investigated the ability to be regenerated for reuse. CR was used as the dye in these experiments. Specifically, the used **Ru-P5C** was filtered and washed in an ultrasonic cleaner and then dried under vacuum. The dried polymer (5.00 mg) was added to an aqueous dye solution (3 mL × 1.00 mg mL^{-1}), which was then subjected to the standard irradiation conditions. As shown in **Figure 5**, the dye removal efficiency was calculated to be 95% even after three cycles, indicating that **Ru-P5C** had been regenerated successfully.

The performance of the crosslinked polymer was compared with the performances of TiO_2 (P25) and BiOBr,[39–42] which are widely used for dye removal. The crosslinked polymer and

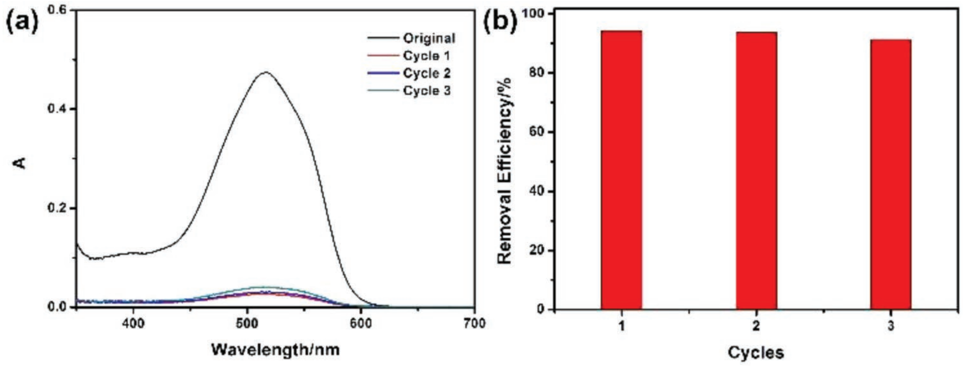

Figure 5. Evaluation of polymer regeneration with CR as a model dye: a) UV–vis spectra of CR solutions and b) removal efficiencies calculated on the basis of the decrease in adsorption intensity. Initial conditions: [CR] = 1.00 mg mL^{-1}, V_{CR} = 3 mL, and $M_{\text{Ru-P5C}}$ = 5.00 mg. 50 µL aliquots were periodically removed and diluted with 3 mL of distilled water for analysis.

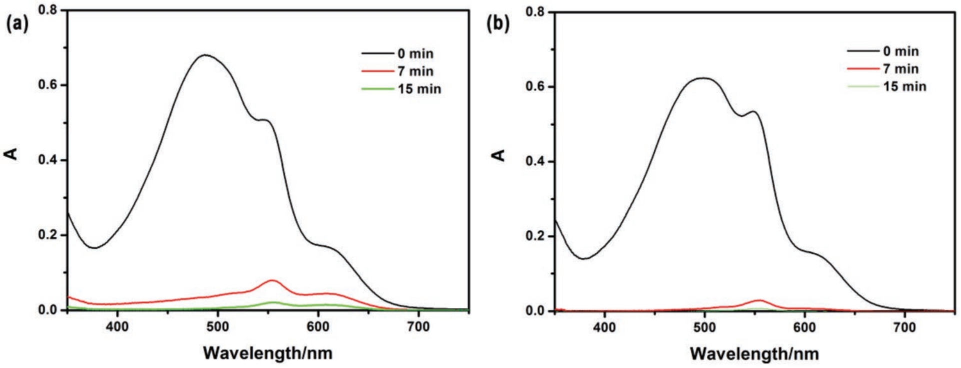

Figure 6. Time-dependent UV–vis spectra of mixed dye solutions in a) distilled water and b) sewage water from the city. Initial conditions: [IC] = [MO] = [ORI] = [CR] = [RhB] = 0.20 mg mL^{-1}, V = 3 mL, $M_{\mathbf{Ru\text{-}P5C}}$ = 5.00 mg. 120 µL aliquots of the solution were diluted with 3 mL of corresponding water for UV–vis spectroscopy.

each of the two reference compounds (5.00 mg in each case) were added to separate IC solutions (3 mL × 1.00 mg mL^{-1}). Then, the solutions were subjected to the usual irradiation conditions, and their UV–vis spectra were measured periodically (Figure S20, Supporting Information). We were encouraged to find that the removal efficiency of the crosslinked polymer was much higher than the efficiencies of TiO_2 or BiOBr, whose removal efficiencies after 17 min were 25% and 30%, respectively. The crosslinked polymer had removed nearly all of the dye after 17 min.

Finally, to evaluate the versatility of the crosslinked polymer, we also carried out experiments using sunlight as the irradiation source for dye removal (Figure 4d). We found that the characteristic absorption peak of IC decreased to nearly zero after exposure to sunlight for 35 min, indicating total removal of IC from the solution; this result was similar to that observed upon irradiation at 450 nm. Moreover, the obtained crosslinked polymer also exhibited excellent dye removal efficiency in relatively complex systems. First, a mixed dye solution containing five different dyes (IC, OrI, MO, CR, and RhB) was prepared and subjected to standard irradiation at 450 nm for 15 min. As shown in **Figure 6**a, the absorption peaks decreased sharply to near zero, indicating the excellent removal efficiency in the mixed solution. Then, to mimic a real wastewater system, sewage water from the city was used to prepare the mixed dye solution. Similar phenomena could be observed from Figure 6b, and the removal efficiency was more than 95% after being irradiated for 15 min. These results indicated that the obtained materials might have potential application in real waste-water treatment systems.

In this study, we synthesized a pillar[5]arene-based crosslinked polymer by means of a click reaction with a Ru complex. The polymer, which self-assembled into spherical nanoparticles with positively charged surfaces and photocatalytic ability, exhibited excellent performance for the removal of anionic dyes from aqueous solution upon irradiation at 450 nm in air. In addition, the polymer could be recycled and showed a better removal efficiency than commercially available TiO_2 (P25) and BiOBr. Moreover, the dye removal process could be carried out with sunlight as the irradiation source, and it was effective in treating a wastewater sample containing a number of dyes. The introduction of a photosensitizer into a crosslinked polymer to form a nanosized amphiphilic assembly represents a new strategy for the synthesis of self-cleaning heterogeneous materials for dye removal or other applications.

Experimental Section

The Calculation for the Dye Removal Efficiency: Five milligrams of **Ru-P5C** was added to 3 mL of dye solution (1.00 mg mL^{-1}). Next, the mixture was exposed to light sources (high-pressure mercury lamp with a power of 400 W or sunlight) and 50 µL aliquots were periodically removed and diluted with 3 mL of distilled water for UV–vis spectroscopy (light path = 1 cm, at 25 °C).

$$[\text{Removal efficiency}] = 1 - \frac{A}{A_0} \quad (1)$$

where A is the adsorption intensity of dye after irradiation and A_0 is the initial adsorption intensity of the dye solution.

Surface Parameters: Each sample (50 mg) was degassed at 80 °C for 24 h and then backfilled with N_2. Surface parameters were determined using multipoint BET and the pore size distribution was determined by means of the nonlocal density function theory (NLDFT) method.

Thermogravimetric Analysis: Thermogravimetric analysis of the sample (10 mg) was performed on an NETZSCH TG 209 instrument under a N_2 (15 mL min^{-1}) atmosphere in the range of 75–775 °C at a rate of 10 K min^{-1}.

TEM and SEM Spectroscopy: The sample (0.5 mg) was dispersed in water (10 mL) using the ultrasound method. Then, 5 µL of the solution was dropped and placed onto a carbon-coated copper grid or silicon slice and then air dried.

Zeta Potential and Dynamic Light Scattering (DLS): The sample (0.5 mg) was dispersed in water (10 mL) using the ultrasound method. Then, 1 mL of the solution was dropped and measured on a Zeta PALS+BI-90 instrument (Brookhaven Co., USA).

Polymer Regeneration: The polymers were separated by filtration and washed with pure water in an ultrasonic cleaner and then dried under vacuum at 65 °C overnight. Then, 5.00 mg **Ru-P5C** was added to 3 mL of dye solution (1.00 mg mL^{-1}) and the mixture was exposed to light sources (high-pressure mercury lamp with a power of 400 W or sunlight) for 35 min. Then, 50 µL aliquots were periodically removed and diluted with 3 mL of distilled water for UV–vis spectroscopy (light path = 1 cm, at 25 °C). The removal efficiency was calculated using the above equation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dye removal, pillar[5]arene, Ru complex, self-cleaning, supramolecular crosslinked polymers

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