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Light-controlled reversible self-assembly of nanorod suprastructures†

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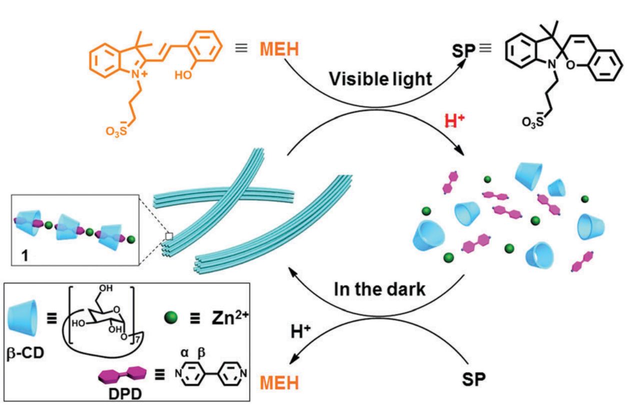
Nanorod suprastructures constructed by the coordination of zinc ions with the inclusion complex of 4,4′-dipyridine in β-cyclodextrin can dissociate and rebuild repeatedly *via* alternate visible light irradiation in the presence of photoacid merocyanine in aqueous solution.

Supramolecular smart materials are currently intensively studied for their potential applications in drug delivery, self-healing materials, controllable catalysis, and tissue engineering. In designing and fabricating new supramolecular smart materials, one of the crucial features is their reversibility. There are lots of reports on smart materials showing reversible responses to pH,[1] competitive binding,[2] redox stimuli/inputs,[3] light,[4] and enzymes.[5] Of these the pH adjustment is intensively investigated for existing plentiful easy protonation groups in supramolecular assembly units. However, the operation induced by acid and base would produce waste products, which would stop the operation. In sharp contrast, the light response is particularly attractive, because it not only can carry out remote control, but there are also no additional chemical species to be introduced into systems. If those smart materials with pH-responsive groups could be activated by light instead of acid and base, it will facilitate reversibility of supramolecular smart materials. Photoacids have an excited electronic state pK_a much lower than that in their ground state, so they have proven useful in operating molecular switches and logic gates by pH change.[6] On the other hand, 4,4′-bipyridine (DPD) has been extensively investigated in coordination and supramolecular chemistry.[7] Its neutral and rigid N-donor site makes DPD an excellent candidate which can be used as a bridging linker for two- and three-dimensional supramolecular architectures.[8] We previously investigated the inclusion complexation of DPD with β-cyclodextrin (β-CD) and the subsequent coordination of the inclusion complex DPD⊂β-CD with Ni^{2+},[9] and prepared a series of polypseudorotaxanes with different morphological nanoarchitectures by coordinating Co^{2+} or Zn^{2+} ions with the N-donor of DPD in the inclusion complex DPD⊂β-CD.[10] Herein, we report the light-controlled reversible self-assembly of nanorod suprastructures formed from the polypseudorotaxane (**1**) of the inclusion complex DPD⊂β-CD with Zn^{2+} in aqueous solution containing the protonated merocyanine (MEH). Using NMR, UV-vis, FT-IR, dynamic light scattering (DLS), and transmission electron microscopy (TEM) studies, we will show that both the monomer DPD and the included DPD in DPD⊂β-CD can be protonated and deprotonated[11] induced by MEH with light, and the nanorod suprastructures formed by Zn^{2+} ions with DPD⊂β-CD can dissociate and re-form *via* the reversible transition of the photoacid. Our particular interest is to regulate nano-suprastructures containing pH only-responsive groups activated by light instead of acid and base. The illustration of the formation/dissociation of nanorod suprastructures is shown in Scheme 1.

It is well demonstrated that the host–guest interactions between β-CD and DPD are attributed to hydrophobic interactions,



Scheme 1 Schematic representation of light-controlled reversible self-assembly of nanorod suprastructures based on polypseudorotaxane **1**.

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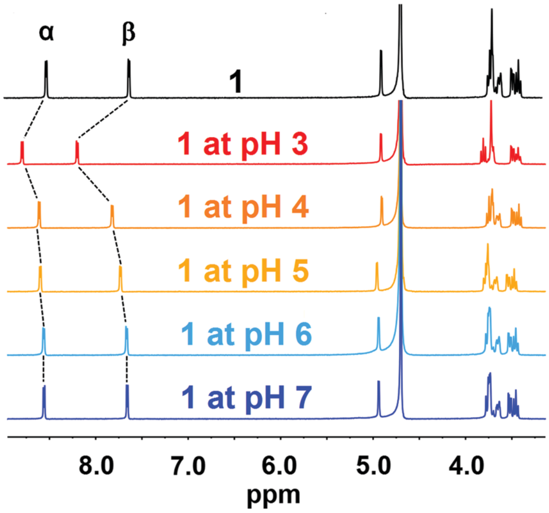

Fig. 1 Partial ^1H NMR spectra (400 MHz, D_2O, 25 °C) of polypseudorotaxane **1** (2.0×10^{-4} M) at different pHs upon the sequential addition of HCl and NaOH.

and DPD in its mono/double-protonated form interacts with β-CD more weakly than its initial unprotonated form, which occupy a large proportion below pH 5.[12] Therefore, we first investigated the influence of pH on the protonation of DPD in polypseudorotaxane **1**. As can be seen from Fig. 1, both meta and ortho protons of DPD exhibit slightly downfield shifts at pH 4–6, and an obvious shift is observed at a pH value of 3. This observation indicates that DPD should be in its double-protonated form when the pH value reaches *ca.* 3. And then, we measured the pH values of MEH at different concentrations with irradiation. When the aqueous solution of MEH was irradiated by visible light of 420 nm, MEH underwent a light-induced ring-closing reaction to the SP with the release of a proton to the environment.[13] After the light was turned off, the SP reverted back to the MEH in *ca.* 5 minutes. As expected, the pH value of MEH exhibits no significant change when the concentration of MEH increased gradually from 1.0×10^{-4} M to 6.0×10^{-4} M (Fig. 2a). However, after irradiation with visible light at 420 nm for 5 min, the extent of pH variation of MEH shows clear concentration dependency. The pH value decreases (by about 1.2 units) to pH 4.9 at 1.0×10^{-4} M, but (2.6 units) to pH 3.4 at 6.0×10^{-4} M. When the light was removed, the pH value of MEH gradually comes back to its initial value. However, upon irradiation of the mixed solution containing **1** (2.0×10^{-4} M) and MEH with 420 nm light for 5 min, the corresponding changes of the pH values are smaller than those of free MEH (Fig. 2b). One reasonable explanation is that the N-atom of DPD in **1** may undergo a protonation process with the protons released from the ring-closing reaction of MEH to SP, leading to a small change in the pH value.

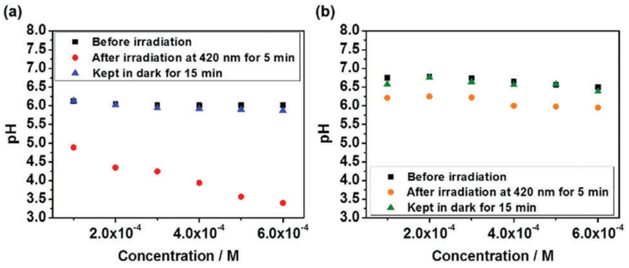

Fig. 2 The pH values of (a) MEH before irradiation (black "■"), after irradiation at 420 nm for 5 min (red "●"), and when kept in the dark for 15 min (blue "▲") at different MEH concentrations, and (b) **1** (2.0×10^{-4} M) + MEH before irradiation (black "■"), after irradiation at 420 nm for 5 min (orange "●"), and when kept in the dark for 15 min (green "▲") at different MEH concentrations.

Detailed information about the morphology of assemblies formed from polypseudorotaxane **1** was obtained from their TEM experiments. As expected,[10] nanorod suprastructures were observed in the absence of MEH (Fig. 3a). When the pH value of the solution of **1** was adjusted to 3 with HCl, a lot of smaller nanorods were observed with a length of about 30 nm in the TEM image (Fig. S8b, ESI†). This observation should be attributed to the protonation of DPD in **1** at low pH, leading to the dissociation of the coordination bond between Zn^{2+} and the N-atom in DPD. When we further adjusted the pH value to 7 with NaOH, the original rod-like structures were observed again (Fig. S8c, ESI†). To visualize the impact of pH on the dissociation and reforming processes of polypseudorotaxane **1**, a series of TEM measurements was performed at three different pH values (from 4 to 6). As can be seen from Fig. S9 (ESI†), the pH value of the solution has a significant impact on its dissociation and reforming processes;[11] there is a similar phenomenon observed for the solution at pH 4 compared to those above pH 3, but the TEM images at pH values of 5 and 6 still show nanorod suprastructures.

When an aqueous solution of **1** (1.0×10^{-5} M) was mixed with MEH (6×10^{-4} M), no evidence for dissociation was obtained by TEM observations (Fig. 3b). However, after the mixture was irradiated at 420 nm for 5 min, a light-induced transition from the aggregated to dispersed state was observed (Fig. 3c). Keeping the solution in the dark leads to the re-formation of nanorod suprastructures (Fig. 3d).

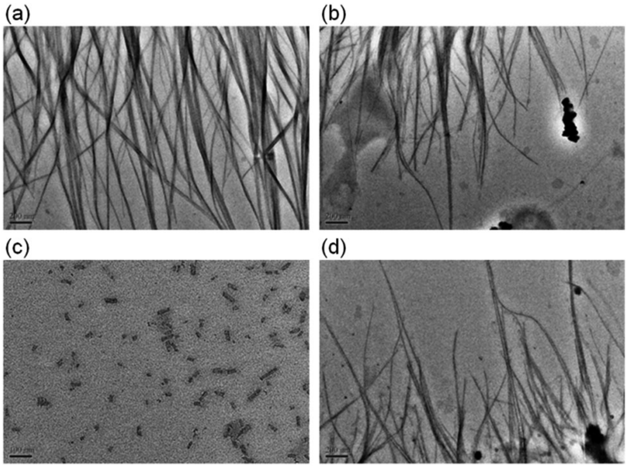

Fig. 3 TEM images of (a) **1** (1.0×10^{-5} M), (b) **1** (1.0×10^{-5} M) + MEH (6×10^{-4} M), (c) **1** (1.0×10^{-5} M) + MEH (6×10^{-4} M) after irradiation at 420 nm for 5 min, and (d) **1** (1.0×10^{-5} M) + MEH (6×10^{-4} M) after being irradiated at 420 nm for 5 min and kept in the dark.

We further used DLS to confirm the reversible dissociation and re-formation processes of assemblies formed from polypseudorotaxane **1** in aqueous solution. For a mixed solution containing **1** and MEH, the DLS results show that polypseudorotaxane **1** forms assemblies with a size distribution of 2.76 μm (Fig. 4a). After irradiation at 420 nm for 5 min, the size distribution of the assemblies falls into two categories: one is from 0.84 to 0.62 μm, and the other is from 3.71 to 2.49 μm. The former should belong to smaller nanorods due to the dissociation of the original assemblies, and the latter still belongs to undissociated assemblies (Fig. 4b). When the sample was placed in the dark for 15 min, the size distribution returns to 4.29 μm (Fig. 4c). Similar observations were also found in control experiments with HCl/NaOH instead of MEH (Fig. S10, ESI†).

UV-vis spectroscopy was further performed to investigate the reversibility of the assembly process of nanorod suprastructures. As can be seen from Fig. 5, the aqueous solution containing **1** and MEH is yellow with an absorption band at $\lambda_{\max}$ = 423 nm, which can be attributed to the protonated MEH as illustrated in Scheme 1. After being irradiated by visible light at 420 nm for 5 min, the solution becomes pale yellow accompanied by a decrease of the absorption intensity at $\lambda_{\max}$ = 423 nm. This observation is due to the isomerization of MEH to SP. When keeping the solution in the dark, the representative absorption band of MEH at 423 nm quickly appears, suggesting reversion of SP to MEH.

Once the first cycle is complete, the dissociation–reforming sequence can be repeated. To evaluate the reversibility of the system, we repeatedly switched the system. Fig. 6 shows five cycles, in which the pH value of the mixture of **1** and MEH can be reversibly switched between *ca.* 6.5 and *ca.* 5.7 just by turning the visible light on and off. We observed no significant changes in the samples, indicating that the switching process is fully reversible. Because of the good reproducibility of the protonation and deprotonation processes of DPD, the photoinduced dissociation and reforming processes of polypseudorotaxane **1** could be repeated many times without appreciable degradation at room temperature.

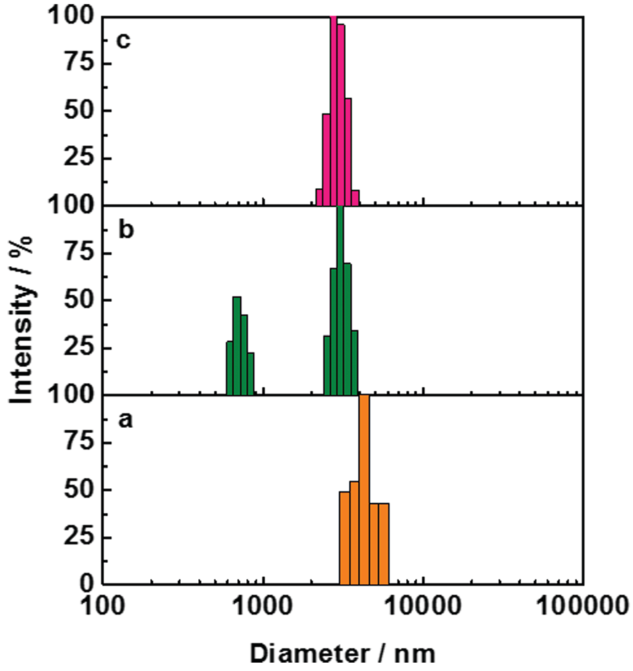

Fig. 4 DLS of (a) **1** (2.0 × 10^{-4} M) + MEH (6 × 10^{-4} M), (b) **1** (2.0 × 10^{-4} M) + MEH (6 × 10^{-4} M) after irradiation at 420 nm for 5 min, and (c) **1** (2.0 × 10^{-4} M) + MEH (6 × 10^{-4} M) kept in the dark for 15 min after being irradiated at 420 nm for 5 min.

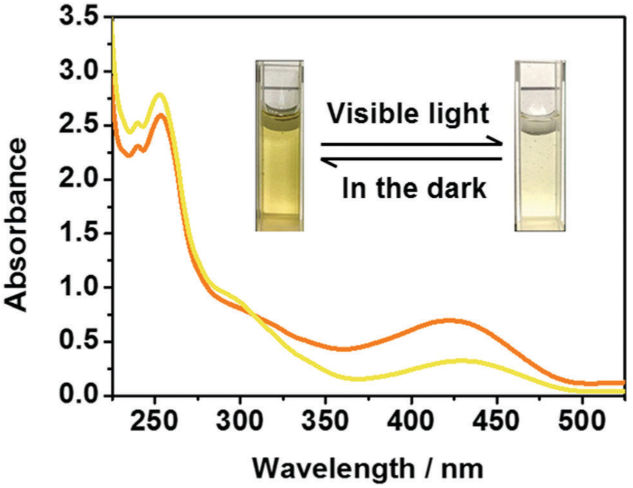

Fig. 5 UV-vis absorption of MEH (2 × 10^{-4} M) + 1 (2 × 10^{-6} M) before (orange) and 2 min after irradiation (yellow) (inset figures show colour changes of **1** (2.0 × 10^{-4} M) + MEH before and after irradiation at 420 nm for 5 min).

In summary, we have demonstrated a method to regulate the self-assembly of nanoscale materials containing pH only-responsive groups activated by light instead of acid and base. We first constructed nanorod suprastructures by the coordination of the inclusion complex DPD$\subset$β-CD with Zn^{2+} in the presence of

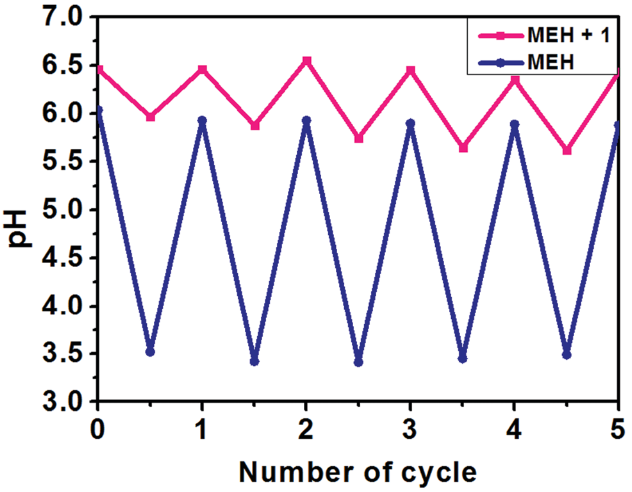

Fig. 6 Cycles of pH change under irradiation and in the dark. For each cycle, the solution of **1** (2.0 × 10^{-4} M) + MEH (6.0 × 10^{-4} M) (red) and MEH (2.0 × 10^{-4} M) (blue) were irradiated at 420 nm for 5 min and kept in the dark for 15 min.

photoacid MEH, and found that the nanorod suprastructures can dissociate and re-form repeatedly *via* alternate visible light irradiation. From NMR and UV-vis studies, we elucidated that there is a perfect match of the pH changes between the protonation of DPD and the ring-closing/opening reaction of MEH. The present results may open the way toward the effective development of new strategies in light-controlled soft nanotechnology.

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