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Semiartificial Polysaccharide Can Provide a Unique Nanospace for the Construction of Supramolecular Dye-assembly

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We have revealed unique template effects of a semiartificial polysaccharide on the self-assembly of anionic cyanine dyes. The inner space of the polysaccharide acts not only as a nanotemplate for the dye assembly but also as a protective space from unfavorable photobleaching.

In nature, biopolymers frequently play roles as scaffolds for the construction of supramolecular nanoarchitectures which exert superior functionalities over their individual component molecules. For example, in LH1 and LH2 complexes of purple bacteria, bacteriochlorophylls (BChls) are regularly arranged in a cyclic manner with the aid of scaffold proteins, showing superior photophysical properties over individual BChl.[1] On the basis of this finding, utilization of biopolymers as promising scaffolds for the construction of supramolecular dye-assemblies has been attracting considerable attention.[2] So far, we have demonstrated that β-1,3-glucans, helix-forming natural polysaccharides, can act as a natural one-dimensional huge host for functional dye molecules such as porphyrins and azobenzene dyes to create unique supramolecular one-dimensional nanostructures.[3] Meanwhile, helical J-aggregates of cyanine dyes have also been a growing target of interest due to their unique photophysical properties including efficient excitation energy migration over many molecules, which allows us to provide prototype models for natural photosynthesis.[4] To self-organize achiral cyanine dyes into J-aggregate in a helical fashion, we have applied novel β-1,3-glucan polysaccharide hosting systems. Herein, we used cationic semiartificial curdlan (CUR-N$^+$) as a helical scaffold for an organization of merocyanine dye (MC540) bearing an anionic moiety (Figure 1). In the present system, one MC540 molecule would interact with one glucose unit along the CUR-N$^+$ chain mainly through electrostatic interaction to neutralize the opposite charges. Thus, one can expect that the creation of well regulated dye-assembly would be achieved under thermodynamic control.[5]

An aqueous solution containing MC540 was mixed with a CUR-N$^+$ aqueous solution changing the final [CUR-N$^+$]/[MC540] concentration ratios and UV–vis spectroscopic measurements were performed. In Figure 2a, one can recognize that aqueous MC540 solution, indicated as a red line, gives two peaks at 540 and 508 nm, which are assignable to MC540 monomer and its dimer, respectively.[6] This suggests that MC540 itself tends to form dimer in water probably due to dipole–dipole and π–π stacking interactions. Upon mixing with CUR-N$^+$ however, the original peak assignable to MC540 monomer at 540 nm disappeared and one broaden peak appeared at 508 nm. The significant blue-shift implies that most MC540 molecules form the dimeric species due to the hosting effect of CUR-N$^+$.[6,7] In Figure 2b, the absorption peak ratios (A_{508}/A_{540}), which show the preference of dimer formation over dissociated monomer, are plotted against the [trimethylammonium (in CUR-N$^+$)]/[sulfonate (in MC540)] ratios. The A_{508}/A_{540} ratios reached a maximum at 1.0 [trimethylammonium]/[sulfonate], supporting the view that the quantitative interaction between MC540 and CUR-N$^+$ is indeed taking place on the CUR-N$^+$ surface through electrostatic interaction, which further accelerates the MC540 dimer formation.[8] In Figure 2a, the shoulder peak around 580 nm would be ascribable to the dimer–dimer interaction.[7] Together with the stoichiometric interactions between MC540 and CUR-N$^+$, the supramolecular dye-assembly is further formed along the one-dimensional CUR-N$^+$ cavity, where MC540 dimers act as higher-stage building blocks. The positive role of CUR-N$^+$ for the self-assembling of MC540 was further evidenced by circular dichroism (CD). As shown in Figure 2a, an intense split induced CD (ICD) was observed, and importantly the cross-section point is largely consistent with the absorption maximum of MC540 dimer. These results indicate that MC540 dimers are incorporated into the CUR-N$^+$ cavity to

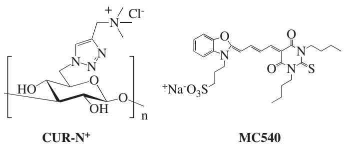

Figure 1. Chemical structures of CUR-N$^+$ and MC540.

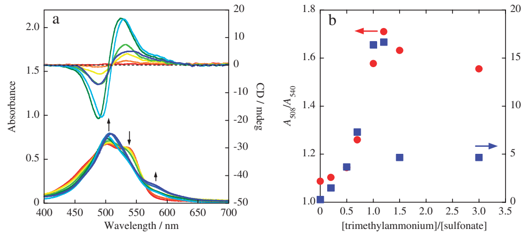

Figure 2. (a) UV–vis and CD spectral changes of MC540 in the presence of various concentrations of trimethylammonium unit in CUR-N$^+$: [sulfonate (in MC540)] = 1.3×10^{-5} M, [trimethylammonium (in CUR-N$^+$)] = 0–3.9×10^{-5} M, 25 °C, $d = 1.0$ cm. (b) The absorbance ratios (A_{508}/A_{540}) are plotted against the [trimethylammonium]/[sulfonate] ratios.

form one-dimensional supramolecular structures. In addition, the shape and sign of the ICD pattern are characteristic of a right-handed packing of MC540, reflecting the stereochemistry of CUR-N$^+$ which also tends to adopt a right-handed helical structure. Here, the size of MC540 dimer would be larger than the internal diameter of the CUR-N$^+$ cavity, implying that MC540 dimers are incorporated into the CUR-N$^+$ cavity in an induced-fit manner.[3] Upon addition of an excess amount of CUR-N$^+$, the intensity of ICD drastically decreases, as shown in Figure 2b, whereas the absorption peak ratios (A_{508}/A_{540}) only slightly decrease under the same conditions. This implies that the supramolecular MC540 fibrous structure is dissociated into dimeric MC540 species in the presence of excess CUR-N$^+$. Figure S1 shows the AFM image of the obtained composite with 0.5–0.8 nm high fibrous structures.[11] This image supports the view that the formation of the supramolecular MC540 fibrous structure is created along the CUR-N$^+$ cavity. It was also confirmed by AFM observation that neither CUR-N$^+$ nor MC540 gave any fibrous structure under the same conditions.

The IR spectrum of the obtained composite revealed that the weak interaction between MC540 and CUR-N$^+$, in addition to electrostatic interactions, plays a crucial role for the creation of the supramolecular dye-assembly. As shown in Figure S2, the OH stretching band of CUR-N$^+$ is significantly shifted from 3350 to 3410 cm^{-1} by 60 cm^{-1} after incorporation of MC540.[11] This significant shift suggests that intrapolymer hydrogen-bonding interactions among 2-OH groups along the CUR-N$^+$ main chain would be broken by accommodating MC540, where 2-OH groups, existing inside the helical cavity, directly interact with MC540.[9] It can be concluded from this reason that MC540 is incorporated into the helical cavity constructed by the CUR-N$^+$ main chain.

Although cyanine dyes exhibit excellent light harvest abilities, photobleaching under continuous photoirradiation frequently becomes a serious problem for practical applications. It is well accepted that saccharides have potential as a radical scavenger and act as a reductive agent for super-oxygen that is generated under photoirradiation in the presence of photosensitizer.[10] In the present system, as MC540 is incorporated into the cavity constructed by the saccharide chain, the dye-assembly thus obtained is expected to be effectively protected from unfavorable photobreaching. To clarify the effect of the saccharide chain, we first employed poly(diallyldimethylammonium chloride) (PDDA) as a template polymer, where MC540 also self-assembles into its dimer through electrostatic interactions. It can be recognized from Figures 3a, 3b, and S3[11] that photobleaching of PDDA/MC540 mixture rapidly occurs within 20 min. On the other hand, the decrease in absorption is effectively suppressed for the CUR-N$^+$/MC540 composite, as shown in Figure 3b, clearly demonstrating that MC540 entrapped in the CUR-N$^+$ is protected from photobleaching. The observed antiphotobleaching effect of MC540/CUR-N$^+$ composite undoubtedly arises from the regular MC540 arrangement inside the tailored nanospace constructed by polysaccharide.

In summary, we have demonstrated that novel supramolecular dye-assembly can be created through a unique template effect of semiartificial cationic polysaccharide. The incorporated dye-assembly is effectively protected from photobleaching due to the radical scavenger ability of saccharide. Advantageously, polysaccharide has no absorption band in the UV–vis range of most dyes. Therefore, the obtained composites are really useful for the construction of semiartificial light-harvesting systems.

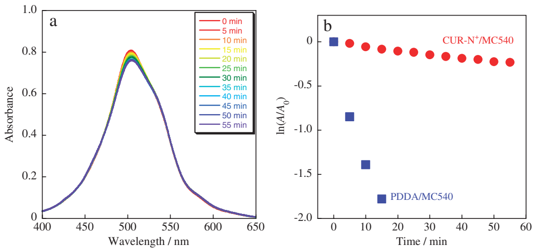

Figure 3. (a) Absorption spectra of CUR-N$^+$/MC540 complex after photoirradiation. (b) Plots of A_{500} vs. irradiation time: [sulfonate] $= 1.3 \times 10^{-5}$ M, [trimethylammonium] $= 1.6 \times 10^{-5}$ M, [quaternary amine in PDDA] $= 1.6 \times 10^{-5}$ M, 25 °C, $d = 1.0$ cm, $\lambda > 400$ nm.

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