Supramolecular Self-Assembly

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Photoresponsive Hybrid Raspberry-Like Colloids Based on Cucurbit[8]uril Host–Guest Interactions**

*Yang Lan, Yuchao Wu, Athan Karas, and Oren A. Scherman**

Abstract: *Hybrid raspberry-like colloids (HRCs) were prepared by employing cucurbit[8]uril (CB[8]) as a supramolecular linker to assemble functional polymeric nanoparticles onto a silica core. The formed HRCs are photoresponsive and can be reversibly disassembled upon light irradiation. This facile supramolecular approach provides a platform for the synthesis of colloids with sophisticated structures and properties.*

Research in the preparation of colloidal particles with topological complexity has grown substantially in recent years.[1–4] In particular, hybrid raspberry-like colloids (HRCs), which contain both organic and inorganic components and exhibit an hierarchical structure of a larger core particle decorated with smaller corona particles, have attracted great attention.[5–20] On account of their hybrid composition and unique morphology, HRCs have potential applications in many areas such as superhydrophobic surfaces,[7,8] optics,[9] and compartmentalized catalysis.[10] Generally, HRCs are prepared by coagulating corona particles onto the in situ prepared core particles.[13–20] This synthetic procedure, however, is dependent on a complicated interplay of experimental processes and parameters, making the design and synthesis of HRCs a black art.

Supramolecular methods have been applied in the preparation of various colloids.[21–25] These methods are normally straightforward and have advantages of good control over size, morphology and composition of the functional colloids. Cucurbit[8]uril (CB[8]) is a macrocyclic host molecule, which is capable of simultaneously encapsulating two guest molecules inside its cavity, forming a stable yet dynamic ternary complex.[26–28] Given its unique host–guest binding properties, CB[8] has recently been employed as a linking motif to prepare supramolecular polymers,[29–31] micelles,[32] dynamic hydrogels,[33] microcapsules,[34] and core–shell polymeric colloids.[25] However, little attention has been focused on the preparation of HRCs using any form of controllable host–guest supramolecular chemistry to date.

Herein, we report a facile route to prepare HRCs, whereby CB[8] is employed as a supramolecular linker to assemble functional polymeric nanoparticles of various sizes onto a silica core as shown in Figure 1. Moreover, the noncovalent nature of CB[8] host–guest interactions affords the supramolecular HRCs a novel property of reversible assembly controlled by light. This means that for the first time, HRCs can be assembled and disassembled in an efficient and controllable manner. In addition, this facile supramolecular synthetic method represents a potential platform for the synthesis of colloids with sophisticated structures and properties.

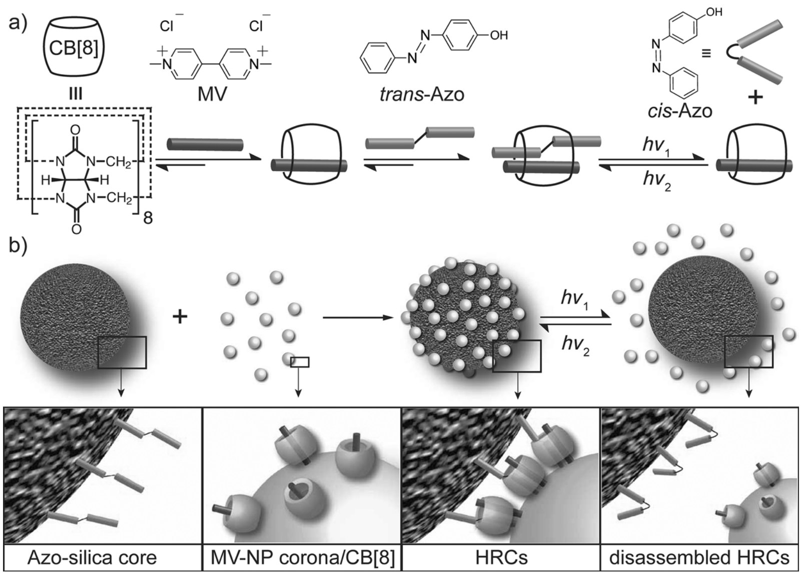

Figure 1. a) Stepwise formation of (MV/*trans*-Azo)@CB[8] ternary complex and light-driven reversible disassembly of the ternary complex. b) HRCs obtained by the formation of (MV/*trans*-Azo)@CB[8] ternary complexes and light-driven reversible disassembly of the HRCs.

As shown in Figure 1 a, methyl viologen (MV) and the *trans* isomer of 4-hydroxyazobenzene (*trans*-Azo) serve as good first and second guests for CB[8], leading to the

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[*] Y. Lan,[+] Y. Wu,[+] Dr. A. Karas, Prof. O. A. Scherman
Melville Laboratory for Polymer Synthesis
Department of Chemistry, University of Cambridge
Cambridge, CB2 1EW (UK)
E-mail: oas23@cam.ac.uk

[+] These authors contributed equally to this work.

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formation of a strong yet dynamic (MV/*trans*-Azo)@CB[8] ternary complex.[29,35] Here, 4-hydroxyazobenzene-functionalized silica microspheres (Azo-silica core) were chosen as the core of the HRCs (Figure 1b). The Azo-silica core was prepared by post-functionalization of preformed bare silica microspheres using 4-hydroxyazobenzene functional silane. The average diameter (D_{TEM}) and average hydrodynamic diameter (D_h) of the Azo-silica core obtained from TEM images (Figure 2a) and dynamic light scattering (DLS) measurements (Figure 2b) are 280 and 408 nm, respectively. MV-functionalized polymeric nanoparticles (MV-NP corona) were employed as the corona nanoparticles (Figure 2b). The MV-NP corona were synthesized using soap-free emulsion polymerization.[36] The D_{TEM} and D_h of the MV-NP corona are 42 (Figure 2c) and 50 nm (Figure 2d), respectively. It is perhaps noteworthy that the proposed HRCs are one of the few examples using silica microspheres as the core and polymeric nanoparticles as the corona. In comparison, most reported HRCs use polymeric microspheres as the core and silica nanoparticles as the corona.[13–20] The polymeric corona of HRCs reported here provides structural advantages for potential applications such as cargo loading and delivery.[37]

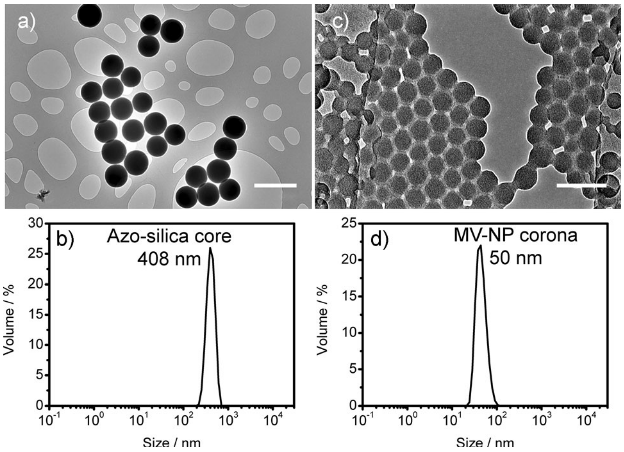

Figure 2. a) TEM image (the scale bar is 500 nm) and b) DLS result of Azo-silica core. c) TEM image (the scale bar is 100 nm) and d) DLS result of MV-NP corona.

The HRCs were then prepared simply by adding an aqueous dispersion of Azo-silica core into an aqueous dispersion of MV-NP corona precomplexed with CB[8] (MV-NP corona/CB[8]), and stirred at room temperature for 5 min.

To obtain HRCs with well-defined structure, the ratio between the Azo-silica core and MV-NP corona required optimization. An Azo-silica core dispersion (0.67 g$\,$L^{-1}, 0.010 mM Azo) was titrated into a 1.0 mL MV-NP corona/CB[8] dispersion (0.24 g$\,$L^{-1}, 0.015 mM MV, 0.1 mM CB[8]) and the assembly process was followed by DLS (Figure 3). Upon the addition of Azo-silica core, two peaks centered at 50 and 554 nm were observed in the DLS measurements (Figure 4a). The 554 nm peak represents the formation of the HRCs and the 50 nm peak indicates the presence of free MV-NP corona/CB[8] in the dispersion. Figure 3 depicts the volume percentage (VP) of the formed HRCs and the MV-NP corona/CB[8] in the dispersion obtained from DLS; it clearly shows that the VP of the MV-NP corona/CB[8] in the dispersion decreases gradually to 0% after the addition of 11 mL Azo-silica core dispersion. At this point, no free MV-NP corona remained in the dispersion as they were all grafted onto the Azo-silica core, forming the supramolecular HRCs. Consequently, the VP of the formed HRCs grew progressively upon addition of the Azo-silica core. However, the VP of the HRCs dropped suddenly to 19% after 11 mL of the Azo-silica core dispersion was added. This likely occurred on account of an excess of Azo-silica core leading to the aggregation of the formed HRCs. The DLS results (Figure 4a,b) confirmed this hypothesis. Compared with the DLS result after the addition

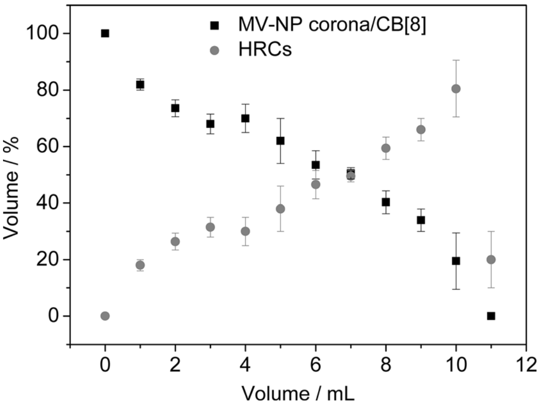

Figure 3. The variation of the volume percentage of the HRCs and MV-NP corona/CB[8] in the dispersion upon the addition of Azo-silica core.

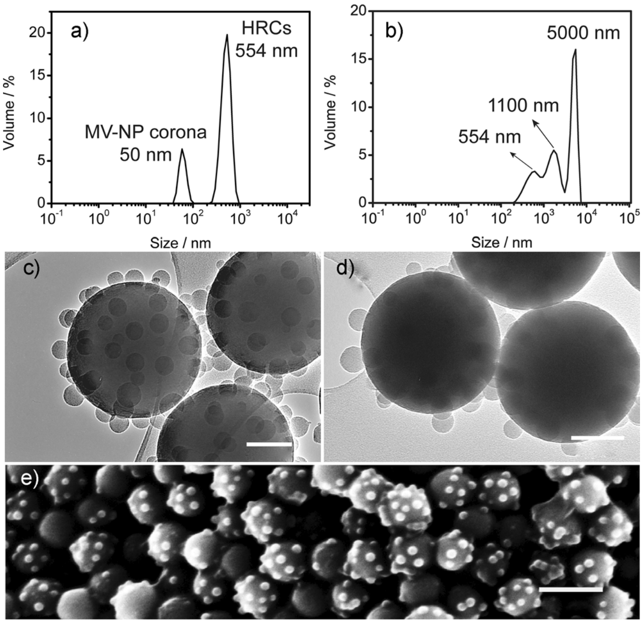

Figure 4. DLS results of a) 10 mL and b) 11 mL Azo-silica core dispersion added into 1 mL MV-NP corona dispersion. TEM images of c) HRCs$_{10\,\mathrm{mL}}$ (the scale bar is 100 nm) and d) HRCs$_{11\,\mathrm{mL}}$ (the scale bar is 100 nm). e) SEM image of HRCs$_{10\,\mathrm{mL}}$ (the scale bar is 400 nm).

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of 10 mL Azo-silica core (Figure 4a), no MV-nanoparticle/CB[8] peak (at about 50 nm) was observed in the DLS result after addition of 11 mL Azo-silica core (Figure 4b). Moreover, new peaks at 1100 and 5000 nm appeared, which indicated aggregation of the formed HRCs.

Figure 4c shows the TEM image of the formed HRCs ($HRCs_{10\,mL}$) when 10 mL Azo-silica core dispersion had been added into the MV-NP corona/CB[8] dispersion. Well-defined raspberry-like colloids with fully packed corona nanoparticles on the surface of the core microspheres can be clearly observed. Figure 4d shows the TEM image of the formed HRCs ($HRCs_{11\,mL}$) when 11 mL Azo-silica core dispersion had been added. The raspberry-like colloids can also be clearly distinguished. However, it is also clear that the Azo-silica core particles are significantly closer together and appear to "share" several MV-NP corona particles. The substantial differences in the DLS results and in the TEM images indicated that the binding between the MV-NP corona and the Azo-silica core is quite strong. SEM images were also taken to observe the surface structure of the prepared HRCs. Figure 4e shows the SEM image of $HRCs_{10\,mL}$, where raspberry-like structured colloids can be observed.

When CB[8] was either omitted from the procedure or replaced by the smaller homologue CB[7], which is only able to accommodate one MV molecule, flocculation of the particles occurred (see Figure S12 in the Supporting Information). Additionally, no HRCs can be observed from the TEM images (Figure S13). Experimentally the HRCs were exclusively formed by employing CB[8] as a supramolecular linking motif to bind together the MV-NP corona and Azo-silica core by the formation of (MV/*trans*-Azo)@CB[8] ternary complexes as shown in Figure 1. Moreover, the sizes of the core and corona of the HRCs could be readily altered using the same strategy by simply altering the synthetic protocol for each of the functionalized spherical units as shown in Figure S14 (see the Supporting Information).

Both the TEM and SEM images were obtained using predried samples. In order to observe the original morphology of HRCs in the dispersion and to prove that the formed HRCs are not a result of the drying process during the TEM and SEM sample preparation, "freezing" the bound MV-NP corona on the core in the dispersion was accomplished by coating a thin layer of SiO_2 onto the HRCs in the dispersion. Figure 5a shows the SiO_2-coated $HRCs_{10\,mL}$ in which raspberry-like colloids can be clearly observed. Consistent with the DLS results of $HRCs_{10\,mL}$ (Figure 4a), excess SiO_2-coated MV-NP corona are also observed in the TEM image. Furthermore, all SiO_2-coated HRCs are well-seperated from each other, which confirmed no aggregates were formed in the aqueous dispersion. Figure 5b depicts the TEM image of SiO_2 coated $HRCs_{11\,mL}$. Again, this is fully consistent with the TEM image (Figure 4d) and DLS result (Figure 4b) of the uncoated $HRCs_{11\,mL}$, whereby aggregated HRCs (indicated by the white arrow) can be readily observed. Figure 5c shows the SEM image of the SiO_2 coated $HRCs_{10\,mL}$, which clearly shows raspberry-like structured colloids. Interestingly, further manipulation of the SiO_2 coated HRCs could be carried out. Upon heating at 550 °C for 3 h, calcination of the SiO_2 occurred with concomitant removal of the polymeric corona particles leaving behind raspberry-like colloids with hollow SiO_2 nanospheres surrounding the central core SiO_2 microspheres (Figure 5d).

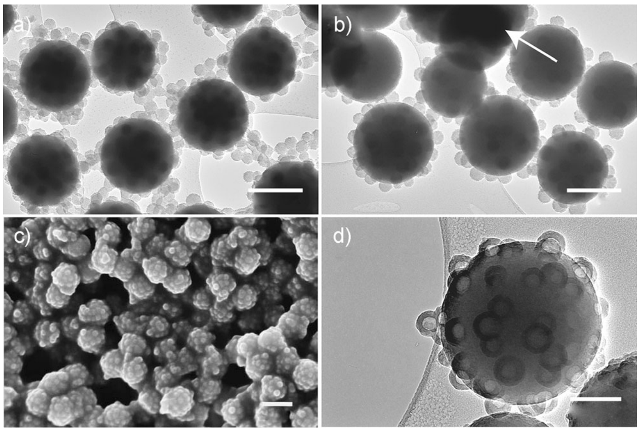

Figure 5. TEM images of SiO_2-coated a) $HRCs_{10\,mL}$ (the scale bar is 200 nm) and b) $HRCs_{11\,mL}$ (the scale bar is 200 nm). SEM images of c) SiO_2-coated $HRCs_{10\,mL}$ (the scale bar is 400 nm) and d) Raspberry-like colloids prepared by calcination of $HRCs_{10\,mL}$ (the scale bar is 100 nm).

The noncovalent nature of supramolecular interactions offers an opportunity to reversibly control complexation. As shown in Figure 1a, the (MV/*trans*-Azo)@CB[8] ternary complexes could be reversibly disassembled in a controlled manner.[35] Upon UV irradiation at 350 nm, the ternary complexes dissociated into MV@CB[8] binary complexes and free *cis*-Azo. The reverse process could be readily achieved by visible light irradiation at 420 nm. Since the HRCs are assembled through the formation of (MV/*trans*-Azo)@CB[8] ternary complexes, the photoresponsivity of the HRCs was tested. An aqueous dispersion of $HRCs_{10\,mL}$ was stirred under 350 nm UV irradiation for 10 minutes before taking DLS measurements. Two peaks centered at 50 and 400 nm, which represent the sizes of the MV-NP corona/CB[8] and the Azo-silica core, respectively, can be clearly observed (Figure 6a). No peak centered at 554 nm can be observed. The DLS result indicated that the HRCs were totally disassembled.

TEM images also confirmed the disassembly of $HRCs_{10\,mL}$. As shown in Figure 6c, free MV-NP corona and bare Azo-silica core particles can be observed in the TEM image. Consequently, the reverse process could also be performed by stirring the disassembled $HRCs_{10\,mL}$ dispersion with 420 nm irradiation for 10 minutes. The morphology of the reformed colloids (re-$HRCs_{10\,mL}$) was detected using TEM (Figure 6d), where raspberry-like colloids can be clearly observed. Compared to the original $HRCs_{10\,mL}$, the re-$HRCs_{10\,mL}$ contain slightly fewer MV-NP corona on the core. Moreover, the DLS result shows two peaks centered at 50 and 658 nm, respectively (Figure 6b). The 658 nm peak indicated the reformation of the HRCs with a small amount of aggregation and the 50 nm peak indicated that some free MV-NP corona remained in the dispersion. All these experimental results show that the HRCs prepared using the CB[8] host–guest supramolecular method are photoresponsive and the

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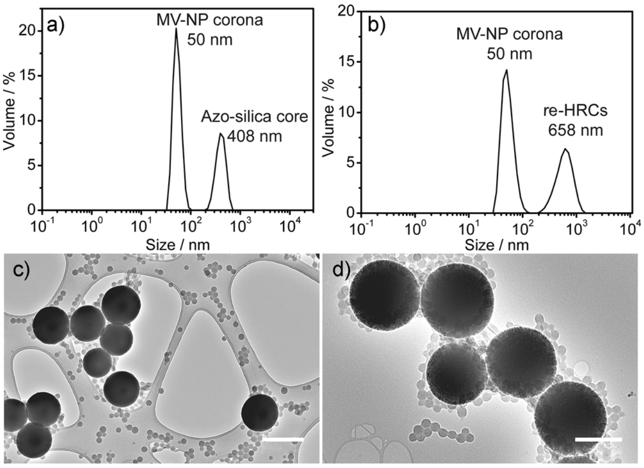

Figure 6. a) DLS result of the disassembled HRCs$_{10mL}$ upon UV irradiation at the wavelength of 350 nm for 10 minutes. b) DLS result of the re-HRCs$_{10mL}$ upon visible-light irradiation for 10 minutes. c) TEM images of the disassembled HRCs$_{10mL}$ (the scale bar is 300 nm) and d) of re-HRCs$_{10mL}$ (the scale bar is 200 nm).

HRCs can be reversibly disassembled in a controllable manner. As the (MV/*trans*-Azo)@CB[8] ternary complexes are also electrochemically responsive, the reversible assembly and disassembly of HRCs can be controlled by electrochemical potential as recently demonstrated.[35]

In summary, hybrid raspberry-like colloids (HRCs) bearing silica microspheres as the core and polymeric nanoparticles as the corona have been prepared by CB[8] host–guest complexation in water at room temperature. CB[8] was employed as the supramolecular linking agent to lock methyl viologen (MV) functionalized polymeric nanoparticles (MV-NP corona) onto 4-hydroxyazobenzene- (Azo-) functionalized silica microspheres (Azo-silica core) by forming the (MV/*trans*-Azo)@CB[8] ternary complexes. The formed HRCs are photoresponsive and can be reversibly disassembled upon light irradiation. This facile supramolecular approach provides a platform to prepare HRCs with sophisticated structures under mild conditions. Raspberry-like colloids with hollow corona nanoparticles were also prepared through calcination of the SiO$_2$-coated HRCs, which may prove useful in a number of potential applications including compartmentalized catalysis and cargo delivery.

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