Patchy Particle Self-Assembly via Metal Coordination

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S *Supporting Information*

ABSTRACT: Colloids with high-symmetry patches are functionalized with metal-coordination-based recognition units and assembled into larger chain architectures, demonstrating for the first time the use of metal coordination as a specific force in colloidal self-assembly. The cross-linked poly(styrene)-based patchy particles are fabricated by encapsulation of colloidal clusters following a two-stage swelling and polymerization methodology. The particle patches, containing carboxylic acid groups, are site-specifically functionalized either with a triblock copolymer (TBC), bearing primary alcohols, alkyl chains, and palladated pincer receptors, synthesized by ring-opening metathesis polymerization, or with a small molecule bearing a pyridine headgroup. Functionalizing with a TBC provides design flexibility for independently setting the range of the interaction and the recognition motif.

The self-assembly of colloidal particles into well-defined 3D structures is of great interest for potential applications in biomaterials, catalyst supports, and photonics.[1,2] Using spherical particles with isotropic attractions or repulsions, only a limited number of 3D structures can be obtained.[3−5] Incorporating anisotropy, through either particle shape[6−8] or surface functionality,[1,9] introduces bonding directionality and can thus extend the assemblies that can be realized to motifs as complex as those seen in atomic and molecular crystals.[2,9]

Numerous efforts have been devoted to the fabrication of anisotropic particles,[2] resulting in new techniques to engineer colloidal clusters,[10] Janus particles,[11] patchy particles,[9,12] branched particles,[13] and dimpled particles.[14,15] To take advantage of particle anisotropy to create highly directional bonds, interactions between particles should be relatively short ranged. Several bonding schemes meet this requirement and have been used for directional interactions in anisotropic colloidal systems. Hydrophobic interactions induced by short carbon chains have been utilized to drive triblock Janus particle (spherical particles with two patches located at the opposite poles) into a Kagome lattice.[1] Dimpled particles with a spherical cavity have been fabricated to bind by specific "lock and key" depletion interactions.[14] We have introduced a general method to functionalize patchy particles with well-defined symmetries with sticky-ended DNA, creating colloids with directional interactions; the "valence" is determined by the number of patches. Patch−patch attractions are realized by specific DNA hybridization, and the binding directionality is predetermined by the patch geometry.[9]

In this Communication, we describe an alternative bonding strategy that combines synthetic polymers with metal-coordination-based recognition units for the self-assembly of patchy particles. Supramolecular recognition units with high specificity and variable association constants (binding strength) have been developed and incorporated in synthetic polymers, yielding multifunctional polymeric structures.[16−19] Functionalizing colloids with supramolecular polymers permits the modulation of particle interactions, which significantly expands the tool set for anisotropic colloidal particle assembly.

We demonstrate this idea by synthesizing patchy particles that are functionalized with triblock copolymers. The colloidal particles have terminal carboxylic groups on the patches that serve as functional handles for polymer attachment. The copolymers, bearing a block of anchoring groups, a spacer block, and a block containing metal coordination complexes, are synthesized via ring-opening metathesis polymerization (ROMP). The particle patches can be site-specifically functionalized with these copolymers or pyridine containing small molecules. Using particles with two patches, we demonstrate that the functionalized colloids can self-assemble into larger architectures directed by metal coordination. The assembling/disassembling process can be triggered by the addition of small molecules, thus providing a modular strategy for anisotropic particle assembly and disassembly.

The use of a triblock copolymer is key to our research design as each block can be addressed in a modular fashion (Figure 1a). The first block is designed to contain the functional groups required to attach the block copolymer to the patchy particles. Primary alcohol groups ($-CH_2OH$, shown in blue, Figure 1a) can be attached to the colloid surface by an esterification reaction. The second block, consisting of an alkyl chain of eight carbons on each repeat unit ($-C_8H_{17}$, shown in red, Figure 1a), is designed to act as a spacer to (a) regulate the length scale of interparticle interactions and (b) separate the recognition motif from the patch surface. Other functionalities, such as fluorescent tags, can also be incorporated in this block. The final block contains the molecular recognition units as sticky ends. We use palladated pincer metal complexes as receptors (shown in green, Figure 1a), and, in our case, tridentate sulfur−carbon−sulfur pincer ligands coordinated to palladium(II). These are particularly useful molecular recognition units
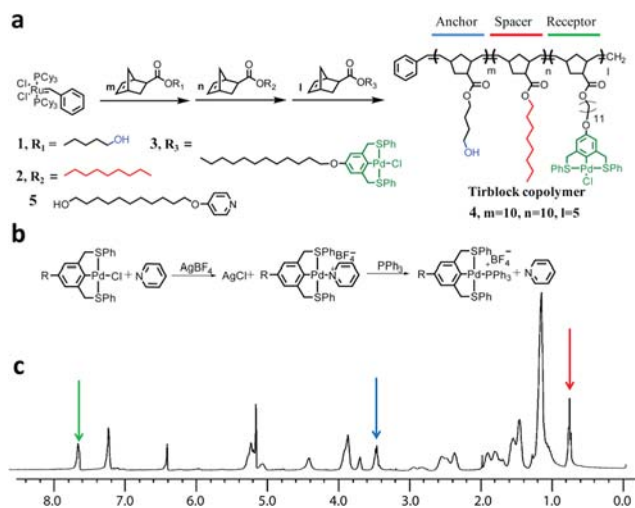
Figure 1. Triblock copolymer. (a) Scheme showing the synthesis of the triblock copolymer bearing different functional groups. (b) Palladated pincer–pyridine metal coordination and ligand exchange. (c) ^{1}H NMR spectrum of the triblock copolymer. Arrows indicate characteristic signals from each monomer.

Figure 2. SEM images of (a) two- and (b) three-patch particles (insets show the original clusters). (c) Bright-field image of a two-patch particle in THF, showing the contrast between the patch and anti-patch parts. (d) Confocal fluorescent images of two-patch particles. The anti-patch parts are fluorescently labeled and shown as green. Scale bar, 2 μm.

because they have only one open coordination site accessible and, upon triggering, can undergo specific, fast, and quantitative coordination with pyridine derivatives.[19−21] Stronger ligands, such as triphenylphosphine (PPh$_3$), can replace pyridine quantitatively (Figure 1b).[17]

To synthesize the triblock copolymers, we use ROMP of functionalized norbornene monomers **1**, **2**, and **3** (Figure 1a). ROMP is a living polymerization method that is fully functional group tolerant. Norbornene-based monomers have been shown to incorporate a wide variety of functional groups, including molecular recognition units such as hydrogen-bonding arrays and metal coordination complexes.[17]

Monomers **1**, **2**, and **3** are synthesized according to the literature.[21−23] The triblock copolymer is then synthesized using Grubbs' first-generation ruthenium catalyst (Figure 1a). The length of the polymer and the ratio of the different blocks (corresponding to the numbers for m, n, and l, Figure 1a) are tunable by varying the ratio of catalyst to monomers. The ^{1}H NMR spectrum of triblock copolymer **4** is shown in Figure 1c, with the characteristic signals for all three monomers pointed out by colored arrows, indicating successful incorporation of all monomers. The integration of the signals from each monomer agrees well with the feed ratio ($m = 10$, $n = 10$, $l = 5$). Copolymer **4** has a molecular weight of 6.3k and a polydispersity $M_w/M_n = 1.62$. Small molecule **5**, a pyridine derivative, is synthesized to act as the complementary part to the palladated pincer complex.

We fabricate carboxyl patchy particles following the "cluster-encapsulation" method previously reported[9] with some modifications. The carboxyl-modified poly(styrene) microspheres (620 nm in diameter, 3% divinylbenzene cross-linked) are synthesized via a surfactant-free emulsion polymerization.[24] 4,4′-Azobis(4-cyanopentanoic acid) is used as initiator, which provides the carboxylic acid groups on the colloid surface. Small clusters of the microspheres are formed using an "emulsion-evaporation" method.[10] Scanning electron microscope (SEM) images of clusters consisting of two and three microspheres are shown in the insets of Figure 2a,b. The clusters are then encapsulated by first swelling them with the desired amount of styrene followed by free radical polymerization, initiated by
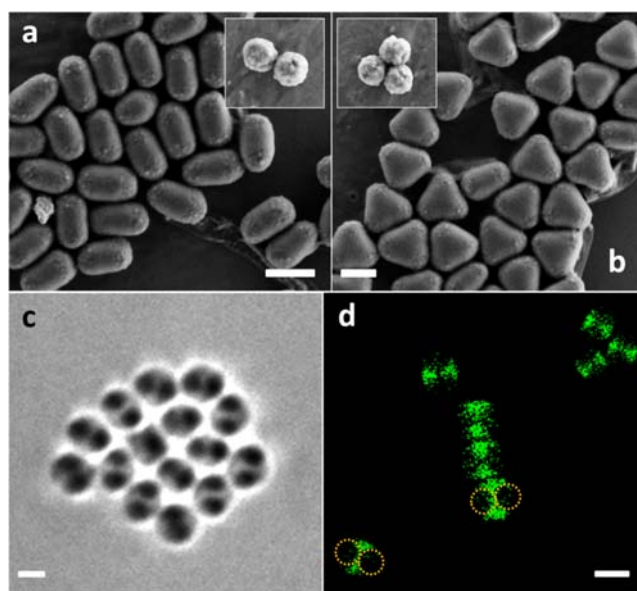
thermal degrading of benzoyl peroxide, to yield the carboxyl-containing patchy particles (carboxyl groups only on the patches). We copolymerize 5% divinylbenzene (DVB) with styrene to cross-link the shell, or "anti-patch", producing particles that can be dispersed in organic solvents such as tetrahydrofuran (THF) where metal coordination can take place (Supporting Information (SI), Figure S1). The introduction of the cross-links, which diminishes the degree of particle swelling and solubility, gives rise to particle aggregation during the encapsulation step. To avoid this, we add a non-ionic PEO-PPO-PEO surfactant (Pluronic 108) that embeds itself in the particle matrix, leading to more stable particles.[25] The particle patches can be clearly distinguished, as evidenced by SEM, optical microscope bright-field, and confocal fluorescence images.

Figure 2a,b shows SEM pictures of two- and three-patch particles purified by density gradient centrifugation. The anti-patch part encapsulates the majority of the core clusters. The "extremities" (i.e., vertices) of the clusters are exposed as patches. For comparison, SEM images of over-encapsulated clusters are shown in Figure S2, where the overall surface appears smooth with no patches. Bright-field microscopic images of patchy particles also display optical contrast between the core cluster, and the anti-patch shell arises from the difference in cross-linking density: the anti-patch (5% DVB) appears light gray while the core cluster (3% DVB) appears as dark dots (Figure 2c). Patchy particles of higher order can be seen in the SI (Figure S3 and Video 1).

To further verify that we have fabricated patchy particles, we fluorescently label the anti-patch part (SI Scheme 1 and Figure S4). Figure 2d shows a confocal fluorescent image of dye-labeled two-patch particles where the anti-patch can be seen as fluorescing green. The core clusters are invisible but depicted by the dotted line indicating the microsphere size. No

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dx.doi.org/10.1021/ja4075979 | *J. Am. Chem. Soc.* 2013, 135, 14064−14067

fluorescent signal is observed at or near the cluster particle extremities, confirming the patchiness of the particles.

The presence of the carboxylic acid groups on the patches provides a convenient way to covalently attach small molecules and polymers. We used N-(3-dimethylaminopropyl)-N'-ethyl-carbodiimide hydrochloride (EDC) as a coupling reagent to conjugate the carboxylic acids with primary alcohols in THF. The functionalization of the particles is visualized by fluorescence labeling. We synthesize a norbornene–coumarin monomer that is doped into the second block as a fluorescent tag during the formation of the triblock copolymer (SI Scheme 2 and Figures S5 and S6). We react the resulting triblock copolymer with two-patch particles in the presence of EDC. The block-copolymer-functionalized particles, after purification by centrifugation and redispersion in THF, show strong fluorescence (Figure 3a). We carry out a control experiment
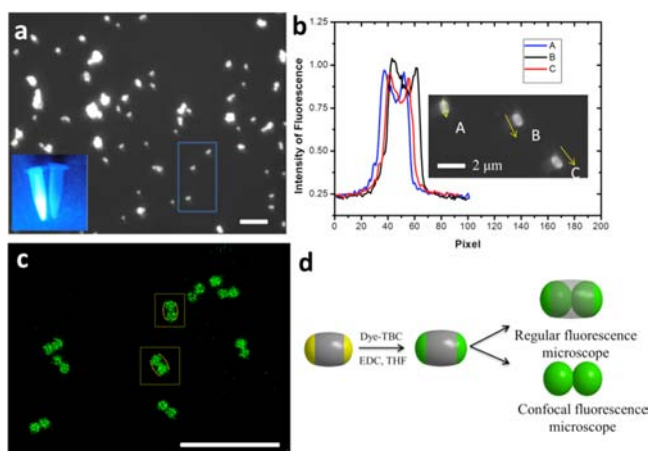

Figure 3. Patchy particle functionalization. (a) Fluorescent image of two-patch particles functionalized with triblock copolymer. Picture of the sample with control experiment under UV lamp (inset). (b) Fluorescent intensity measurement along the long axis of the two-patch particles. (c) Confocal fluorescent image of functionalized two-patch particles. (d) Schematic representation of patchy particle functionalization and expected results under regular and confocal microscope. Scale bars, 10 μm.

where we combine the patchy particles with the triblock copolymer but without the addition of EDC. In this case, no fluorescence is observed. Dispersions of the fluorescently labeled and the control samples are shown in Figure 3a inset. Only the functionalized particles display fluorescence under a UV lamp. Our result strongly suggests that in the presence of EDC, primary alcohols can be attached covalently to the particle patches through the formation of ester bonds.

Selective functionalization of the patches is essential to endow directionality to the self-assembly of patchy particles. We measure the fluorescence along the long axis of the elliptical two-patch particles and plot it as a function of pixels. Figure 3b shows that the patches are brighter than the anti-patch. The fluorescence intensity of the anti-patch, however, is not zero, which could be attributed to "over"-functionalization of the cluster. In THF, poly(styrene) particles swell and become porous. Small molecules as well as polymers might be able to diffuse through the anti-patch and react with carboxylic acids inside the particle matrix resulting in potential functionalization. We do not view this "over"-functionalization as a problem, as it will not jeopardize the directionality of the self-assembly. The

recognition units, though part of a polymer, are small enough that they should be buried beneath the surface of the anti-patch, except for those on the patch surfaces. In contrast, no acids groups are available on the anti-patch surface of the particles. This is evidenced by confocal fluorescence images of the patchy particles (Figure 3c) where the entire cluster is visible (functionalized), while the anti-patch (dotted line) does not show fluorescence at all (Figure 3d and SI Figure S3c).

Using this method, two-patch particles are functionalized with either **4**, designated as pincer particles, or **5**, designated as pyridine particles. Next, we investigate the self-assembly of these particles via palladated pincer–pyridine metal coordination. Because they are two-patch particles, we expect them to self-assemble into chain structures (Figure 4a, middle). First,
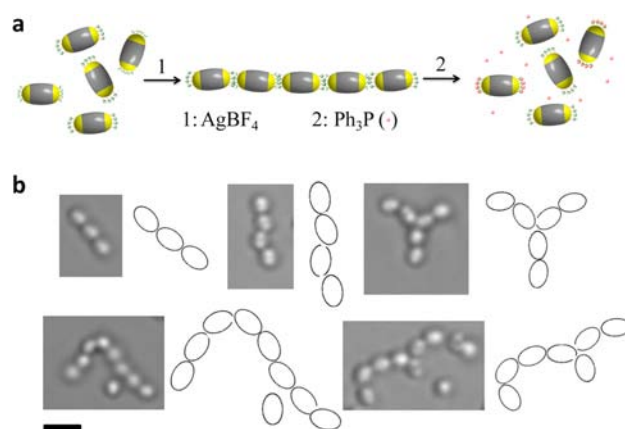

Figure 4. Self-assembly of two-patch particles via metal coordination. (a) Schematic representative showing the triggered assembling and disassembling process of the two-patch particles. (b) Snapshots of chain structures formed by the self-assembly of two-patch particles. Scale bar, 3 μm.

pincer and pyridine particles are combined in THF. We observe no assembled structures (Figure 4a, left); the oval-shaped particles are stable and well-dispersed (SI Figure S7a and Video 2). The metal coordination is triggered by adding AgBF$_4$ to the particle suspension (Figure 4a). Ag(I) activates the palladated pincer complex by removing the Cl ligand from the palladium, opening up a coordination site (Figure 1b). After the addition of AgBF$_4$, the particle mixture is agitated for 5 h at room temperature. The result is shown in SI Video 3 and Figure S7c–e. Most particles aggregate and form daisy chains consisting of different numbers of particles within each chain. Figure 4b shows snapshots of particle chains formed with different lengths. The number of particles per chain varies from 2 to 12, with some branched structures being observed (see Figure S8 for statistics). The oval-shaped particles linked together solely in a head-to-head configuration, suggesting the existence of the attraction interactions only between the patches. We carry out a series of control experiments in which single types of two-patch particles (pincer particle or pyridine particles) are mixed with AgBF$_4$. After agitation, the particle suspensions stay stable and no aggregation is found (SI Figure S7b).

We evaluate whether the assembled architectures can be disassembled. Triphenylphosphine (PPh$_3$) can serve as a competitive ligand for the palladium center and can displace quantitatively the pyridine ligand,[17] which can trigger the disassembling of patchy particles. Indeed, upon addition of

PPh_3 to the aggregates, the chain structures fall apart immediately (Figure 4a, right, and Figure S7f). This result strongly suggests that the metal coordination is the driving force for particle assembly.

In conclusion, this report describes the first use of metal coordination to direct the self-assembly of colloidal particles. In particular, we describe the self-assembly of patchy particles into larger chains. Our research strategy is based on a triblock copolymer containing multiple functionalities to functionalize the patches of the colloidal particles. Metal-coordination-driven assembly of the colloidal particles is highly directional and reversible. We view this strategy as a modular method which enables great advantages toward colloidal particle assembly including flexibility: polymer size (M_n), architecture, functionality, recognition units, and solvents can be adjusted easily to tune particle interactions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data for all new compounds, supplementary figures, and videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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