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Site-Selective Immobilization of Colloids on Au Substrates via a Noncovalent Supramolecular "Handcuff"

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We have examined hierarchical supramolecular structure in the formation of colloidal arrays by immobilizing monodispersed naphthalene-functionalized colloids onto Au substrates bearing viologen moieties using the macrocyclic host molecule cucurbit[8]uril as a supramolecular "handcuff". Naphthalene-functionalized poly(methyl methacrylate)- and polystyrene-based colloids were synthesized by soap-free emulsion polymerization and characterized by dynamic light scattering and scanning electron microscopy to realize the colloidal arrays and to facilitate direct macroscopic imaging. The formation of host-stabilized ternary complexes on the surface of naphthalene-functionalized microspheres in colloidal suspension was verified by titration of a preformed viologen−CB[8] complex and followed by zeta potential measurements. Patterned self-assembled monolayers of a viologen derivative on Au substrates were formed by backfilling viologen-modified thiols after spontaneous chemisorption of "protective" alkylthiols by microcontact printing. After the initial complexation of CB[8] onto the viologen derivative on the Au substrates, monolayers of colloids with both 1D and 2D patterns could be formed and characterized by contact angle measurement, optical microscopy, and scanning electron microscopy. Control experiments indicated that no colloids were attached to the Au substrate after moderate washing by water if (1) CB[8] was replaced by a smaller analogue of the macrocyclic host, CB[6] or CB[7], (2) colloids without naphthalene-functionalities on the periphery were employed, or (3) alkanethiol was used entirely instead of viologenthiol to protect the Au substrate. These results suggest that the supramolecular ternary complexes were key to successfully bind the colloids onto the Au substrates with the CB[8] acts as a supramolecular "handcuff". The fundamental expertise gained from the study of these materials is believed to facilitate progress in the field of smart materials and wet nanotechnology and lead to the preparation of controlled reversible architectures on surfaces.

Introduction

Recent efforts have been devoted to immobilization and manipulation of colloids on substrates with a predetermined arrangement of high accuracy. Well-defined colloidal arrays are of great interest for the possible integration of these building blocks into photonic devices,[1] high-density patterned media,[2,3] chemical and biological sensors,[4] and single molecule detectors.[5] A wide variety of methodologies, such as using physical confinement,[6] electrostatic and covalent interactions,[7−9] biological interactions,[10,11] and supramolecular interactions including contrast of hydrophilicity/hydrophobicity,[12] hydrogen-bonding interactions,[13] and host−guest interactions,[14,15] have been developed to noncovalently attach colloids and nanoparticles onto surfaces with feature patterns. Perfect colloidal patterns have been achieved by confining particles into physical templates with different shapes;[16] however, they have not yet been shown to exhibit high selectivity. Although the "expensive" biotin−avidin interaction also bears high specific noncovalent recognition attributes, it becomes much weaker in organic solvents or in high-temperature environments.

Most recently, host−guest chemistry has been employed as an alternative methodology to attach colloids onto substrates in a supramolecular fashion. Recognition-directed self-assembly serves as a more promising technique in that it can greatly improve the precision in position control by specifically and selectively recognizing and binding colloids to a substrate. Additionally, employing the noncovalent nature of supramolecular interactions provides a powerful tool to reversibly control the binding events which can lead to the realization of more complex functions. Fitzmaurice et al. have reported recognition-directed noncovalent self-organization of crown ether-modified nanoparticles onto cation-modified substrates by forming pseudorotaxanes.[14] More recently, Huskens et al. have employed cyclodextrin (CD) monolayers as "molecular printboards" on substrates on which 3D self-supported free-standing colloidal arrays were immobilized using adamantyl-functionalized dendrimers as a "supramolecular glue".[15,17−19]

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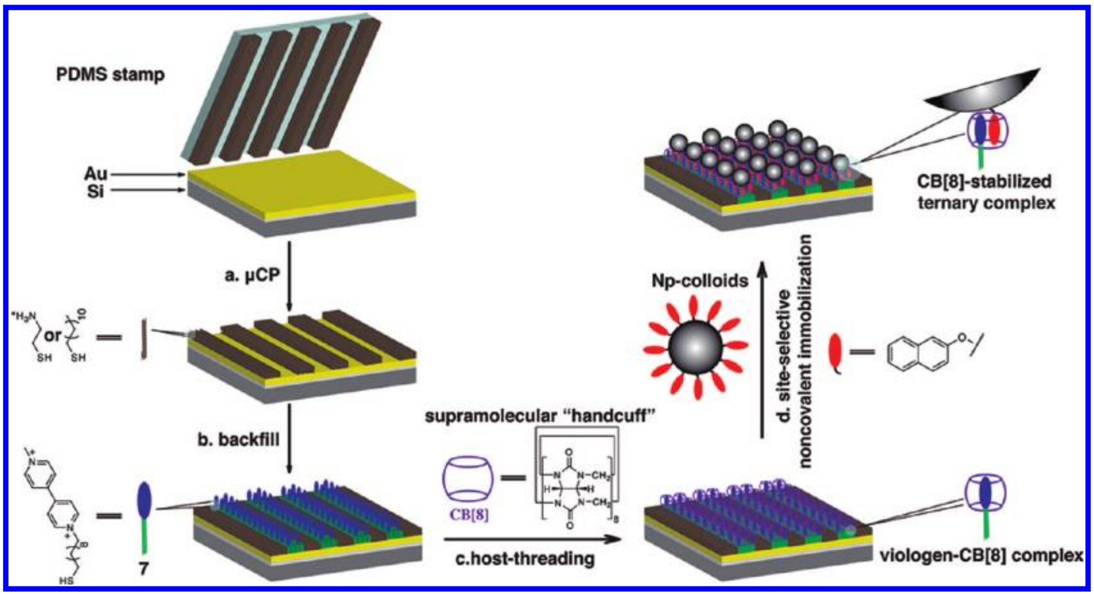
Scheme 1. Schematic Cartoon Illustration of Site-Selective Noncovalent Immobilization of Np-Colloids on a Micropatterned Viologen-Terminated Au Substrate in the Presence of CB[8][a]



[a] (a) Micro-contact printing a Au substrate by gently placing a PDMS stamp "inked" by protecting thiol for 30 s; (b) backfilling the viologendecanethiol by immersing the partially protected Au substrate in an EtOH solution of viologendecanethiol (**7**) for 2 min; (c) threading the macrocyclic host molecule as a supramolecular "handcuff" by immersing the Au substrate in a supersaturated CB[8] aqueous suspension for 5 min; (d) immobilizing the Np-colloids onto specific sites by immersing the Au substrate into an aqueous suspension of Np-colloids for 30 s. After each individual step, the resulting substrate was washed by a copious amount of the corresponding solvent and then dried under a stream of nitrogen if needed. Note that the density of the surface bound species has not yet been quantified.

Although cucurbit[*n*]uril (CB[*n*]) exhibits extraordinary host−guest properties[20−24] that are distinctly different from those of other host molecules, little attention has been paid to the CB[*n*]-mediated surface organization.[25,26] Different from smaller CB homologues, whose surface anchoring have been based on the direct chemical functionalization,[27,28] cucurbit[8]uril (CB[8]) specifically and selectively encapsulates two different guest molecules at the same time, an electron-deficient molecule (which serves as the first guest) and an electron-rich molecule (as the second guest), inside the cavity to form a stable 1:1:1 ternary complex. Ternary complex formation is driven by the hydrophobic effect and exhibits an enhanced charge-transfer (CT) interaction between the guest pair inside the hydrophobic cavity of CB[8].[23,29]

Based on its unique attributes, CB[8] was exploited herein as a supramolecular "handcuff" to lock second-guest functionalized polymeric colloids onto first-guest terminated Au substrates in a stepwise fashion by forming ternary complexes via specific host−guest interactions. This represents the first time that CB-[*n*]-based surface bound colloidal arrays with different feature patterns can be visualized. Furthermore, colloidal arrays have been achieved by using host−guest interactions, enhancing the accuracy of colloid positioning on substrates, increasing stability for nanofabrication, and introducing the opportunity to exploit controlled, reversible colloidal binding. Moreover, CB[8]-based ternary complexes were used instead of CD inclusion complexes to realize a higher selectivity of colloidal immobilization on a substrate. A scheme of site-selective noncovalent immobilization of naphthalene-functionalized colloids (Np-colloids) on micropatterned viologen-terminated Au substrates via CB[8]-stabilized host−guest interactions is shown in Scheme 1.

Table 1. Formulation of Preparation of Colloids via SFEP and Their Hydrodynamic Diameter and Size Distribution in Aqueous Environment[32,33]

colloids	monomers/g	DVB/g	NpMA/g	initiators[a]/mg	T/°C	D_h/nm[b]	PDI[c]
1	MMA/7.8	2	0.2	KPS/100	70	280	0.003
2	St/4	1		AIBA/155	60	222	0.007
3	St/3.8	1	0.2	AIBA/155	60	211	0.009
4	St/4	1		KPS/155	70	171	0.005
5	St/3.8	1	0.2	KPS/155	70	167	0.006
6	St/3.6	1	0.4	KPS/155	70	165	0.005

[a] KPS: potassium persulfate; AIBA: 2,2′-azobis(isobutyramidine) dihydrochloride. [b] D_h: hydrodynamic diameter, as determined by DLS. [c] PDI: polydispersity index, as determined by DLS.

Results and Discussion

Polymeric colloids were used in this study to investigate the interactions between soft matter and hard substrate, not only for their potential application in photonic device construction as well as colloidal template of photolithography but also because a wide variety of surface functionalities can be introduced as needed. Additionally, submicrometer polymeric colloids offer the advantage of direct macroscopic imaging of patterned self-organization of colloids immobilized on substrates. Monodispersed polystyrene (PS)- and poly(methyl methacrylate) (PMMA)-based Np-colloids with different Np-functionalities and surface charges

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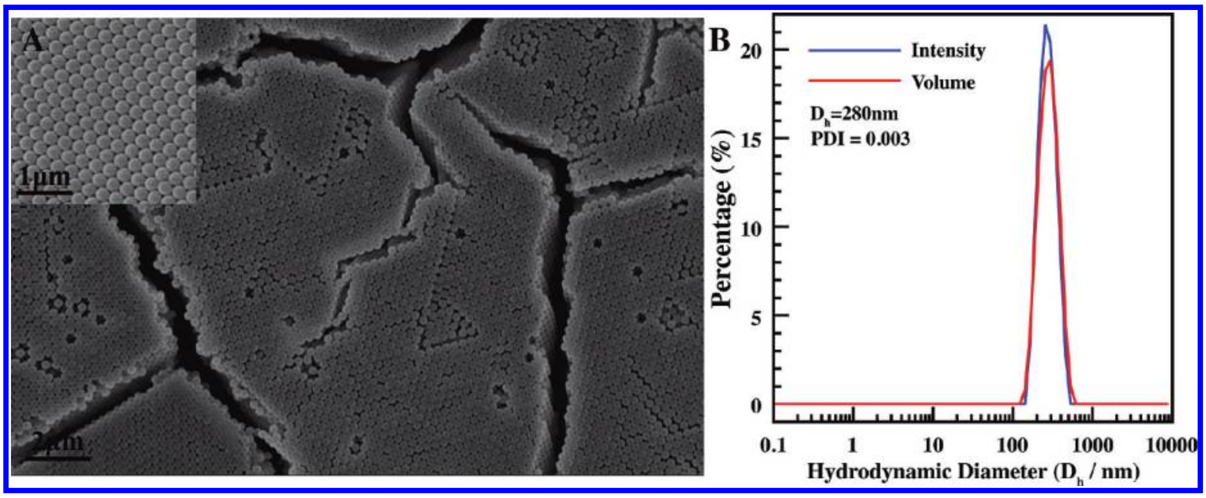

Figure 1. Size and distribution of colloid **1** from SFEP as shown by (A) scanning electron microscopy (SEM) of colloidal crystalline arrays after drying and (B) DLS in colloidal suspension.

were synthesized by soap-free emulsion polymerization (SFEP).[30,31] Styrene (St) or methyl methacrylate (MMA) was used as the bulk monomer and divinylbenzene (DVB) as the cross-linking agent. These colloids are themselves "inert" in terms of molecular recognition with CB[8] or a viologen patterned substrate. PMMA-based colloid **1** was prepared for the immobilization on Au substrates. PS-based colloids **2**−**5** were prepared for the zeta potential (ZP) titrations, which will be discussed in detail in the following section. Different initiators were used to obtain both negative-charge stabilized colloids as well as positive-charge stabilized colloids from the dissociation of potassium persulfate (KPS) and 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA), respectively. The feed ratio of the polymerization and hydrodynamic diameter and size distribution of the colloids after purification were characterized in an aqueous environment by dynamic light scattering (DLS) and summarized in Table 1.

All of the colloids obtained by SFEP in this study are monodispersed in water. As shown in Figure 1A, the size of colloid **1** measured by SEM is 275 ± 4.6 nm, which corresponds very well with the DLS result (Figure 1B) that shows the average hydrodynamic diameter is around 280 nm and with a very low PDI of 0.003. Colloid **1** is stabilized by negative charges from the dissociation of KPS and has a ZP of −57.9 ± 2.75 mV. Colloids **4**, **5**, and **6** are also negatively charged, which are chosen to follow the ZP change upon addition of first guest and host molecule. Colloids **2** and **3** are positively charge stabilized, from AIBA initiation for the same titration purpose.

Viologen derivatives (4,4′-bipyridium dications) are well-known as electron-deficient species and can readily form 1:1 inclusion complexes with CB[8] with a binding constant (K_a) of 1.1×10^5 M^{-1} in buffered water (0.1 M phosphate buffer). The viologen−CB[8] 1:1 inclusion complex can form a 1:1:1 ternary complex instantaneously upon addition of 1 equiv of a second, electron-rich species, which in our case are the Np-moieties. This ternary complex, which can be formed from both small molecules[23] and polymeric structures,[29] has been well-characterized in an aqueous environment with an overall binding constant up to 10^{10}−10^{11} M^{-2}. However, no previous report has shown that the ternary complexes are still capable of forming in a colloidal suspension when one of the components is covalently bound to a substrate.

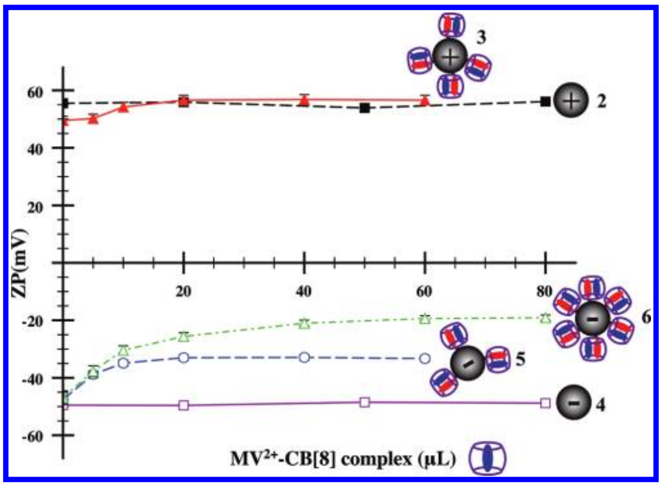

Figure 2. Change in ZP of colloids as a function of added MV^{2+}−CB[8] complex. The concentration of the titrated colloidal suspension was 1 mg/mL with a volume is 750 μL. The concentration of the titrant MV^{2+}−CB[8] complex in aqueous solution was 1 mM.

In order to verify whether the ternary complexes could form on the periphery of Np-functionalized colloids in an aqueous suspension, a solution containing 4,4′-methylviologen (MV^{2+})−CB[8] 1:1 preformed inclusion complex was added to a variety of aqueous suspensions of Np-colloids. Subsequently, ZP measurements were used to follow the change of surface charge on the Np-colloids upon addition of the MV^{2+}−CB[8] complex. As shown in Figure 2, the ZP of colloid **5** in an aqueous suspension (1 mg/mL) increased gradually from −47.6 to −32.9 mV upon the addition of the MV^{2+}−CB[8] complex. When colloid **4** without any Np-functionality was tested as a control, only a very slight change in ZP was detected, suggesting that the increase in ZP of colloid **5** indeed comes from the MV^{2+}−CB[8] complex recognizing Np-functionality and formation of the ternary complex. Upon titrating colloid **6**, which has twice the amount of the surface Np-functionality as colloid **5**, the increase in ZP is even more obvious from −46.9 to −19.4 mV, showing that the presence of Np-functionality is indeed key to the formation of the ternary complex on the colloid surface in an aqueous environment.

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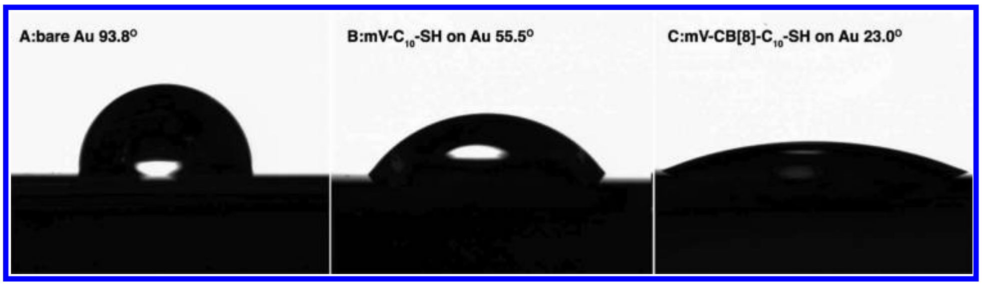

Figure 3. A water drop on (A) a bare Au substrate, (B) a viologendecanethiol-modified Au substrate, and (C) CB[8]-complexed viologendecanethiol-modified Au substrate, displaying enhanced hydrophilicity. The bare Au substrate was immersed in an ethanol solution (2 mM) for 30 s under nitrogen before drying. Then the resulting Au substrate was immersed in the CB[8] supersaturated aqueous solution for 5 min.

To eliminate the possibility of any electrostatic effect on the change of ZP of the negatively charged Np-colloids upon addition of the positively charged titrant, ZP measurements were also carried out on the positively charged Np-colloids **2** and **3**. No change in ZP was detected upon addition of the $MV^{2+}-CB[8]$ complex to the control colloid **2** due to the absence of Np-functionalities. However, the ZP of colloid **3** increased from 49.5 to 56.8 mV upon addition of the $MV^{2+}-CB[8]$ complex. This increase in ZP is more convincing, suggesting that the $MV^{2+}-CB[8]$ complex can overcome the electrostatic repulsion and form the ternary complexes on the surface of positively charged Np-colloids, thereby contributing to the increase of the surface charge.

The immobilization of colloids onto both nonpatterned and patterned assemblies was carried out in a stepwise fashion as the first guest was immobilized onto the Au substrate and the second guests onto the colloids. For the nonpatterned assembly, a viologen-terminated self-assembled monolayer (SAM) was first prepared by immersing a bare Au substrate into an ethanol solution (2 mM) of **7** for 30 s. After washing with ethanol and drying with a flow of nitrogen, the contact angle of a bare Au substrate changed from 93.8° (Figure 3A) to 55.5° (Figure 3B) on a viologen-terminated Au substrate. Then CB[8] was assembled onto the viologen motifs by immersing the viologen-terminated Au substrate into a supersaturated CB[8] aqueous suspension for 5 min. After washing with water and again drying under a flow of nitrogen, the contact angle of viologen-CB[8]-terminated Au substrates decreased further to 23.0° (Figure 3C). Figure 4A shows the SEM image of Np-colloids bound to a viologen-CB[8]-terminated Au substrate after dipping the viologen-CB[8]-terminated Au substrate into a colloidal suspension for 30 s. These surface-bound colloidal arrays are stable under slight sonication and maintain this arrangement in aerobic conditions even after 9 months.

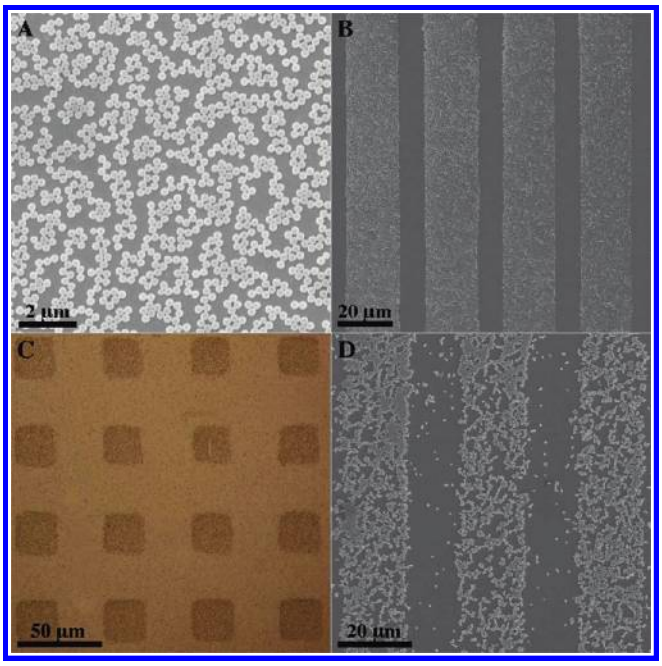

Figure 4. SEM images (A, B, and D) and optical microscopy image (C) of Np-colloids on viologen-terminated Au substrates in the presence of CB[8]: (A) nonpatterned monolayer colloidal immobilization; (B) 20 μm (line width) × 10 μm (interval width) linear colloidal arrays; (C) 50 μm (square length) × 50 μm (interval length) squared colloidal arrays; (D) 20 μm (line width) × 20 μm (interval width) linear colloidal arrays. No "protecting" thiol was used for (A). Dodecanethiol was used as the "protecting" species for the μCP of (B) and (C) and 2-aminoethanethiol hydrochloride for (D). Colloid **1** was used for (A), (B), and (C) while colloid **3** was used for (D).

Subsequently, patterned colloidal arrays were also prepared to illustrate that the colloids were only bound to areas of the surface capable of ternary complexation. Introduction of a feature pattern was accomplished by first protecting a portion of the Au substrate with an inert dodecanethiol via μCP and then backfilling the "bare" areas with **7**, thus forming a patterned SAM of viologen derivative on a Au substrate. After allowing CB[8] to form 1:1 complexes on the mixed thiol layer, Np-colloids were only found bound in the appropriate locations as evidenced by the linear patterns shown in Figure 4B. Furthermore, 2D square colloidal patterns were prepared through the same two-step thiol protection method by using a PDMS stamp with indented square areas for the μCP step and further confirms that the Np-colloids were bound onto the areas precoated by the viologen$-$CB[8] complex only rather than sitting on the protective layers. Finally, in an effort to rule out any possibility of simple electrostatic interactions between the colloids and the viologen covered Au substrates, positively charged colloid **3** was used to form a linear array (Figure 4D) on a Au substrate which had been first protected with 2-aminoethanethiol hydrochloride and then backfilled with **7**. Thus, the ternary complex "handcuff" structure serves as the driving force to immobilize the colloids onto the Au substrates, which must overcome electrostatic repulsion from like charges (accounting for the "negative" defects in the lines). The "positive" defects in between two viologen arrays are probably due to portal binding of CB[8] with the protonated amines of the protective layer used, which held the colloids by accommodating Np-functionality inside the cavity of CB[8].

A series of control experiments were further performed to reinforce the role of the CB[8]-stabilized ternary complexes in binding the colloids onto the substrates. When CB[8] was either removed completely from the procedure *or* replaced by smaller homologues, CB[6] and CB[7], there were no colloids remaining on the substrate after washing, as verified by both optical microscopy and SEM. Even if the extremely low binding constant of CB[6] with viologen ($K_a = 21\ M^{-1}$) could lead to a very small amount of CB[6]−viologen inclusion complexes on the substrate,[34] the cavity of CB[6] is incapable of binding a pair of molecules simultaneously.[21] When CB[7] was used, again access of the Np-functionalized colloids to substrate was not possible because the cavity of CB[7] is still not big enough to accommodate a pair of guest molecules.[35] Additionally, when colloid **4** (without any Np-moieties) was employed with CB[8], no colloids were detected after washing under a moderate flow of water. Furthermore, when the Au substrate was entirely covered by the "inert" alkanethiol after immersed the Au substrate in its ethanol solution (2 mM) for 72 h, no colloids were detected after moderate washing. It is worth noting that all successful immobilizations and patterns of Np-colloidal monolayers onto the Au substrates could be immediately identified by the naked eye as different colors could be seen by simply manipulating the substrates in a variety of angles upon reflection of sunlight by the colloidal arrays.

In this report, we have examined the utility of a supramolecular structure to immobilize and pattern functionalized monodispersed colloids onto viologen-functionalized Au substrates using CB[8] as a supramolecular "handcuff". Monodispersed functional colloids were prepared by soap-free emulsion polymerization to facilitate the direct imaging of the colloidal patterns. Stable and robust ternary complexes were formed by anchoring the viologen−CB[8] complexes onto an Au surface followed by addition of Np-functionalized colloids and were confirmed by ZP titrations as well as by SEM and optical microscopy. An efficient and convenient "dipping" methodology was developed to quickly immobilize and detect the patterned colloidal arrays on the substrates. Both 1D and 2D patterned colloidal arrays as well as control experiments demonstrated that the specific supramolecular ternary architecture was required for colloidal immobilization. The materials serve as a new class of building blocks to generate hierarchically self-assembled surface bound structures that are expected to exhibit interesting features valuable to areas ranging from condensed matter physics to photonics.

Experimental Section

Materials. All starting materials were purchased from Alfa Aesar and Sigma-Aldrich and used as received unless stated otherwise. CB[8] was prepared according to literature procedure.[36] Methyl methacrylate (MMA), styrene (St), and divinylbenzene (DVB) were passed through a basic alumina column to remove the inhibitor and stored over 4 Å molecular sieves, respectively. Triethylamine (TEA) was dried with potassium hydroxide and distilled before use. Potassium persulfate (KPS) was recrystallized twice from methanol.

Instrumentation. ^{1}H NMR (400 MHz) spectra was recorded using a Bruker Avance QNP 400. ^{13}C NMR (125 MHz) spectra was recorded using a Bruker Avance Cryobrobe ATM TCI DRX 500 or a Bruker Avance 500 BB-ATM. Optical microscopy was performed on Nikon Eclipse ME600L microscope using the DN100 capture system. Dynamic light scattering (DLS) and zeta potential (ZP) measurements were performed on Malvern Zetasizer NS90 instrument. Scanning electron microscopy (SEM) was performed on Leo 1530 VP FE-SEM. Contact angle measurements were performed on KSV Instruments KSV CAM 200 goniometer.

Synthesis of 2-Naphthyl Methacrylate (NpMA). NpMA was prepared by the condensation reaction of 2-naphthol (Np) and methacryloyl chloride in Et_2O in the presence of TEA to trap HCl. Np (10 g, 69.4 mmol) was dissolved in 150 mL of Et_2O in a 500 mL flask, to which TEA (14.5 mL, 104 mmol) was added. Methacryloyl chloride (8.056 mL, 83.2 mmol) in 100 mL of Et_2O was added dropwise to the solution for 1 h via a dropping funnel while the solution was kept at 0 °C. The reaction mixture was stirred for 24 h under room temperature. The resulting precipitate was filtered off, and the solvent was evaporated to give a white solid, which was dissolved in chloroform again. The residue was purified by column chromatography on silica gel in petroleum ether/EtOAc (30:1) as the solvent. A yield of 85% was obtained after purification. ^{1}H NMR ($CDCl_3$): δ 7.79−7.88 (m, 3H, ar), 7.60−7.61 (d, 1H, ar), 7.44−7.51 (m, 2H, ar), 7.25−7.28 (m, 1H, ar), 6.41 (d, 1H, $CH_2{-}C{-}CH_3$), 5.79 (t, 1H, $CH_2{-}C{-}CH_3$), 2.10 (t, 1H, $CH_2{-}C{-}CH_3$). ^{13}C NMR (d_6-DMSO): δ 129.3, 127.7, 127.6, 127.2, 126.4, 125.6, 121.1, 118.5, 18.4.

Soap-Free Emulsion Polymerization (SFEP). Polymeric colloids were synthesized by the SFEP technique. A typical procedure was as follows: MMA (or St), NpMA, and DVB were dispersed in water (100 g). The solution was placed into a 250 mL four-neck RBF with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer. Nitrogen was bubbled through the mixture of reagents for 1 h before elevating the temperature, and the nitrogen blanket was maintained throughout the polymerization. After stabilizing at 70 °C (for AIBA initiation, the temperature was set to 60 °C) for at least 30 min, polymerization was initiated by addition of a degassed aqueous solution of KPS (or AIBA). After 8 h polymerization, the product was washed by three cycles of centrifuge/redispersion using deionized water.

Synthesis of *N*-Methyl-4,4′-bipyridinium Iodide (MV^+). To a solution of 4,4′-bipyridine (1.0 g, 6.4 mmol) in 15 mL of DCM, methyl iodide (0.5 mL, 8.1 mmol) in DCM (5 mL) was added dropwise to the stirred solution. The mixture was left at room temperature for overnight. The yellow product was filtered off and purified by recrystallization from MeOH (1.544 g, 81%). ^{1}H NMR (d_3-MeCN): δ = 8.84 (d, 2H), 8.79 (d, 2H), 8.32 (d, 2H), 7.80 (d, 2H), 4.35 ppm (s, 3H). ^{13}C NMR (d_6-DMSO): δ = 152.3, 151.5, 146.6, 141.3, 125.4, 122.3, 48.0 ppm.

Synthesis of *N*-(10-Mercaptodecyl)-*N*′-methyl-4,4′-bipyridinium Chloride (7). MV^+ (2 g, 6.7 mmol) and 1,10-dibromodecane (1.76 g, 8.7 mmol) were refluxed in MeCN for 3 days. The precipitant **9** was filtered and washed with warm MeCN and dried under vacuum. Then **9** (4.4 g, 7.4 mmol) and potassium thioacetate (1.3 g, 11.1 mmol) were taken into EtOH (100 mL) and refluxed for several hours. The solution was added concentrated H_2SO_4 to obtain a pH = 1 solution under reflux for a further 24 h. The black precipitant was filtered off. To the water filtrate was added KPF_6 (2.6 g, 16 mmol), and the resulting white/yellow precipitate **8** was filtered off and washed with water and dried under vacuum. Then **8** (0.58 g, 0.91 mmol) was dissolved in 15 mL of acetone. To this solution, *n*-Bu_4NCl (1.06 g, 3.8 mmol) in 10 mL of acetone was added; the yellow/white precipitate (**7**, 299 mg, 79%) was collected by centrifuge, washed by acetone, and dried under vacuum. ^{1}H NMR (d_4-MeOD): δ = 8.42−9.28 (aromatic, 8H), 4.74 (t, 2H), 4.42 (s, 3H), 2.66 (t, 2H), 2.58 (t, 2H), 1.28−1.65 ppm (t, 14H).

Immobilization of Np-Colloids on Viologen-Terminated Au Substrate in the Presence of CB[8]. For μCP, PDMS stamps were wetted by a solution of dodecanethiol or 2-aminoethanethiol hydrochloride in EtOH (2 mM) and then placed onto a Au substrate for 30 s. After peeling away the PDMS stamp, the substrate was washed by EtOH and then immersed into a solution of **7** in EtOH (2 mM) for 5 min under a nitrogen atmosphere. The substrate was washed by EtOH and dried under

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nitrogen and immersed into a supersaturated CB[8] aqueous suspension, which was put onto a shaker with 200 rpm for 5 min. The resulting substrate was washed by a copious amount of water and dipped into the aqueous suspension of Np-colloids (0.5% w/v) for 30 s, washed by a copious amount of water, and dried under a stream of nitrogen.

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