

Supramolecular gold nanoparticle–polymer composites formed in water with cucurbit[8]uril†‡

Roger J. Coulston, Samuel T. Jones, Tung-Chun Lee, Eric A. Appel and Oren A. Scherman*

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A gold nanoparticle–polymer composite material has been prepared in water using cucurbit[8]uril as a supramolecular “handcuff” to hold together viologen-functionalised gold nanoparticles and a naphthol-functionalised acrylamide copolymer.

Gold nanoparticles (AuNPs) have received a great deal of interest on account of their unique optical, electrical and chemical properties.¹ Incorporating nanoparticles into polymeric materials has potential for accessing a range of new composites² with interesting properties for applications ranging from polymeric photovoltaic devices to the control over polymer viscosity with nanoparticle crosslinks,³ however, controlling the formation of such dispersions remains a challenge.⁴ The ability to direct the self-assembly of AuNPs into networks and higher-order self-assembled structures^{5–7} allows them to be used as building blocks for the ‘bottom-up’ design⁸ of complex macroscopic materials. The surface modification of AuNPs with self-assembled monolayers (SAMs) consisting of organic ligands has allowed the chemical properties of such systems to be tailored.¹ Moreover, the size and shape of the organically modified AuNPs as well as the nature of the surface functionality play an important role in the binding interactions of these NPs.⁹ Currently, the SAM composition and subsequent properties of the AuNPs are determined by the covalently bound ligands, alternatively, AuNP surface functionality could be achieved from a SAM capable of ‘dynamic’ noncovalent chemistry thus gaining external control over the AuNP’s interactions with the surroundings.

A supramolecular approach could be achieved through the use of cucurbit[*n*]urils (CB[*n*], *n* = 5–8 of glycouril units) which are a class of barrel-shaped macrocyclic hosts with symmetric carbonyl-lined portals.¹⁰ CB[*n*]s are capable of forming inclusion complexes with appropriately sized guest compounds in water with high affinity ($K_a > 10^5 \text{ M}^{-1}$).^{10–12}

In particular, CB[8] can form stable 1:1:1 ternary complexes with an electron deficient and electron rich guest pair, such as a methyl viologen dication (MV^{2+}) and a naphthol (Np) derivative, leading to an overall binding constant (K_a) up to 10^{12} M^{-2} in aqueous buffer.¹³ This has been previously exploited for the noncovalent “handcuffing”

of dendrites,¹⁴ block copolymers,¹⁵ as well as peptides and proteins.^{16,17} Moreover, CB[8] has been used to affix both small and large molecules including Np-functionalised colloids onto an Au surface patterned with viologen-functionalised thiols.¹⁸ Utilising this supramolecular binding approach on NP surfaces dispersed within an aqueous environment would result in a versatile platform for appending a wide variety of motifs. Achieving this through a straightforward self-assembly process would have implications for the development of materials which could be used in biological^{9,19} and sensing applications²⁰ as well as in polymer based optoelectronic devices.³

As water solubility is a prerequisite for CB[8] ternary complexation, the AuNPs must be functionalised by a water-soluble SAM yet remain accessible for CB[8] host–guest binding. Therefore, a mixed self-assembled monolayer (*m*SAM) approach was employed to prepare water soluble functionalised-AuNP **3** with a neutral (major) ligand tri(ethylene glycol)-1-butanethiol ($\text{EG}_3\text{-C}_4\text{-SH}$; **1**) and a viologen-containing (minor) ligand, 1-methyl-4,4'-bipyridinium-dodecanethiol bisbromide ($[\text{MV}^{2+}\text{-C}_{12}\text{-SH}]\text{2Br}^-$; **2**). The functional ligand **2** was designed to extend the MV^{2+} recognition motif away from the secondary surface of the NP to allow for the formation of CB[8] ternary complexes. AuNPs with a diameter of roughly 5 nm were prepared following a modified literature procedure,²¹ and were functionalised with varying ligand mixtures of **1** and **2** leading to the AuNP **3** as depicted in Fig. 1a.

A NP control was prepared in the same manner with a SAM consisting of solely EG_3 ($\text{EG}_3\text{-AuNP}$ **4**). All AuNPs were characterised using dynamic light scattering (DLS). When no MV^{2+} functionality was present, the average hydrodynamic diameter (D_h) was 9 ± 2 nm while the D_h for all three MV^{2+} -AuNPs was 11 ± 2 nm. Moreover, zeta potential (ZP) measurements indicated that the surface of the MV^{2+} -AuNPs **3** had a positive charge of $38 \pm 13\text{mV}$, while the ZP for the $\text{EG}_3\text{-AuNP}$ **4** was below the minimum detection as expected for a neutral AuNP. This observation is consistent with the presence of MV^{2+} ligands on the surface of the AuNP **3**.

While the DLS data provided a clear indication of varying surface MV^{2+} -functionality and density, it was important to demonstrate that CB[8]-based ternary complexation remained viable on the NP surface. Unfortunately, optical spectroscopic techniques such as UV/vis and fluorescence were unable to provide any evidence for supramolecular ‘handcuff’ formation inside the CB[8]. Ternary complexation inside CB[8] typically leads to visible charge transfer (CT) bands in the UV/vis spectrum,^{15,22} however, all measurements carried out on the functionalised AuNPs masked such CT bands on account of

Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: oas23@cam.ac.uk; Fax: +44 (0)1223 334866; Tel: +44 (0)1223 334372

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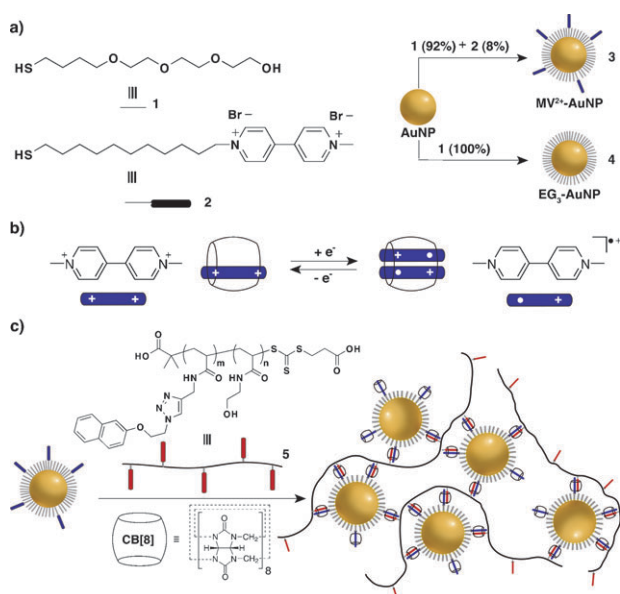


Fig. 1 Schematic representation of (a) preparation of MV²⁺-AuNP 3 and EG₃-AuNP 4, (b) formation of a 2:1 (MV^{+•})₂CB[8] inclusion complex upon reduction and (c) the noncovalent functionalisation of MV²⁺-AuNP 3 with CB[8] and multivalent Np-copolymers 5.

the surface plasmon resonance from the AuNPs which absorbs over a wide optical range (450–600 nm).

Nevertheless, viologen moieties can readily undergo one-electron reduction in the presence of either chemical or electrochemical stimuli yielding the radical cation form;²³ in the presence of CB[8], this leads to rapid generation of a 2:1 (MV^{+•})₂CB[8] inclusion complex (Fig. 1b). This redox control of the host-guest binding stoichiometry provided an opportunity to demonstrate the presence of MV functionality on the AuNP surface by interparticle aggregation of the MV²⁺-AuNPs in the presence of CB[8] upon addition of a suitable reductant. Addition of sodium dithionite (Na₂S₂O₄) to a solution of the MV²⁺-AuNP 3 with CB[8] in the absence of O₂ led to the complete precipitation of AuNPs from solution after 1 h as shown in Fig. 2c. On the other hand, aggregation was not observed for the reduced MV^{+•}-AuNPs in either the absence of any CB[*n*] (Fig. 2b)

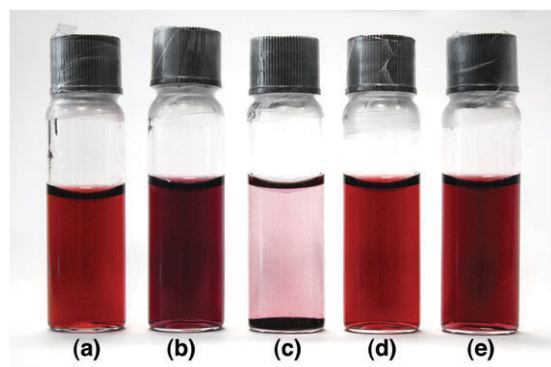


Fig. 2 Vials containing MV²⁺-AuNP 3 1 h after the addition of (a) H₂O, (b) Na₂S₂O₄, (c) CB[8] + Na₂S₂O₄, (d) CB[8] and (e) CB[7] + Na₂S₂O₄.

or in the presence of CB[7] (Fig. 2e), which is unable to form ternary complexes.¹¹

To demonstrate the versatility of the MV²⁺-AuNP 3 towards supramolecular self-assembly in aqueous solution, a functional copolymer, poly(2-hydroxyethyl acrylamide)-*co*-(naphtholtriazole acrylamide) (P(HEAm-*co*-NpTAM)), 5, bearing pendant Np second guest side chains was prepared. Addition of the multivalent Np-copolymer 5 to an aqueous solution of MV²⁺-AuNP 3 with CB[8] indicated a slight red shift in λ_{max} relative to the controls (3 + CB[7] + 5, 3 + 5, and 4 + CB[8] + 5) (for additional information see Fig. S5†), which taken alone does not provide conclusive evidence of aggregation in solution. We therefore turned to centrifugation in the presence of CB[8] to demonstrate the multivalent interactions between functionalised AuNPs and Np-copolymer 5. The small 5 nm size of the AuNPs prevents them from undergoing aggregation and precipitation from aqueous solution upon exposure to conventional centrifugal forces. However, precipitation was observed after centrifugation of the MV²⁺-AuNP 3 for 2 h at 12 100 g in the presence of CB[8] and 5 while nothing was observed when the EG₃-AuNP 4 was used.

In order to investigate this further, the AuNPs were treated with ultracentrifugation (290 000 g for 5 min) in a series of copolymer–AuNP mixtures, which included a control with the smaller homologue CB[7]. From this, only the samples which contained all three necessary components for formation of the ternary complexes: the MV²⁺-AuNP 3, CB[8] and the Np-copolymer 5, formed a pellet as shown in Fig. 3b (for 3). When either the smaller CB[7] homologue or no CB[*n*] was used with the AuNP 3 or when the AuNP 4 was employed, the concentrated regime was observed instead of a pellet. Both the conventional and ultracentrifugation experiments show that copolymer induced aggregation of the AuNPs was occurring in solution as a direct result of the supramolecular CB[8] ternary complexes (Fig. 1c).

To observe the level of control gained through the supramolecular aggregation of the AuNPs, transmission electron microscopic (TEM) images were taken on the composite formed from MV²⁺-AuNP 3, multivalent Np-copolymer 5 and CB[8] (Fig. 4a). Interestingly, the AuNPs were observed to form a single close packed layer and were completely dispersed within the thin film of the composite material that formed. A close up of the thin film boundary is shown in Fig. 4c, which

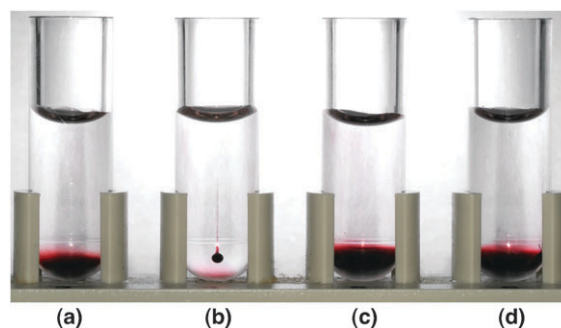


Fig. 3 Centrifuge tubes after 5 min at 290 000 g, containing 20 eq. of 5 and (a) CB[8] and EG₃-AuNP 4, (b) CB[8] and MV²⁺-AuNP 3, (c) CB[7] and MV²⁺-AuNP 3, and (d) MV²⁺-AuNP 3.

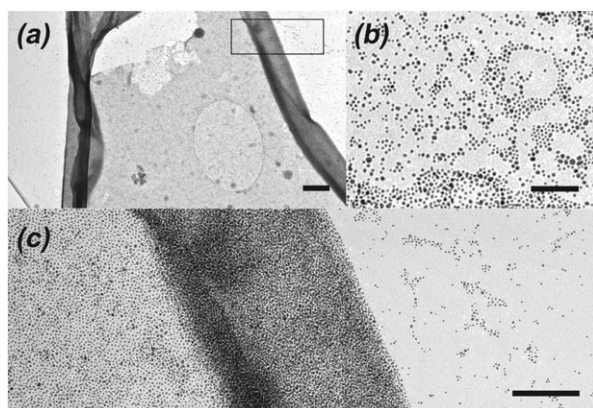


Fig. 4 TEM of (a) polymer film self assembled from **3**, **5** and CB[8], (b) mixture of **4**, **5** and CB[8], and (c) expansion of rectangle in (a); scale bars: (a) 500 nm, (b) 100 nm, (c) 200 nm.

consists of a single layer of close-packed AuNPs within the polymer matrix (left), a multilayer region of AuNPs where the thin film is “rolled” up (middle) and a sparse region of AuNPs supported on the carbon membrane of the TEM grid (right). Conversely, a controlled dispersion was not observed for EG₃-AuNP **4** (Fig. 4b) or other MV²⁺-AuNP controls. More importantly, no thin film formation was observed in any of the controls due to the lack of cross linking provided by the MV-functionalised AuNPs and CB[8].

In conclusion, we have synthesised AuNPs with a *m*SAM bearing MV²⁺ binding motifs and water soluble, non-functional co-ligands. Through reduction of the MV²⁺ moiety in the presence of CB[8] we have demonstrated that 2:1 (MV⁺•)₂:CB[8] inclusion complexation occurs, leading to interparticle aggregation in water and precipitation. Importantly, we have shown the versatility of the non-covalent attachment to the MV²⁺-AuNPs through ternary complexation with a Np-functionalised multivalent copolymer to form well-defined nanoparticle–polymer composites in the bulk. This work provides a platform for coupling water-based supramolecular chemistry with gold nanoparticle science using CB[8] host–guest complexation.

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