

Supramolecular alignment of gold nanorods *via* cucurbit[8]uril ternary complex formation†

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We have shown, for the first time, that a three component system is capable of aligning gold nanorods (AuNRs) through supramolecular host-guest interactions leading to control over AuNR end-to-end assembly. Viologen end-functionalised AuNRs were prepared that were capable of selectively binding to a cucurbit[8]uril (CB[8]) macrocyclic host molecule. These end-functionalised AuNRs could participate in 1 : 1 : 1 ternary complexation with synthesised telechelic linker molecules bearing second guest moieties, in the presence of CB[8]. When the linker length was long and flexible aggregation and precipitation of AuNRs were readily observed, but with no control over the AuNR conformation. On the other hand, when the linker length was shortened thereby imparting a more rigid connection between neighboring gold nanorods, the end-to-end assembly of AuNRs was achieved. We also note that in the presence of a molecule capable of occupying the entirety of the CB[8] cavity, end-to-end assembly is not observed as the system's ability to form a 1 : 1 : 1 ternary complex is halted. Thus, the end-to-end assembly relies upon both having a relatively short and rigid linker as well as the specific, yet tuneable supramolecular 1 : 1 : 1 ternary complexation between the three components.

Metal nanoparticles (NPs) have received a great deal of interest on account of their unique electronic, chemical and optical properties. Specifically, noble metals show interesting optical properties when the particle size is smaller than the incident wavelength of light.¹ Incident light induces collective oscillations of the particles' conduction electrons giving rise to surface plasmon resonances (SPR). The wavelengths of noble-metal nanoparticle SPR bands are known to be highly dependant on the size, shape and composition of the NPs.^{2,3}

Gold nanorods (AuNRs) are of interest on account of their anisotropic shape and tuneable aspect ratio, which can allow the SPR bands to be tuned over a wider range than those of non-anisotropic noble-metal NPs.⁴

When AuNRs are assembled, the observed SPR bands of individual rods can couple, leading to changes in the absorbance wavelength.^{4,5} In recent years, the aggregation and kinetics of AuNR assembly has been studied in great detail, with self-assembly techniques proving to be the most versatile.^{4,6,7} Due to the unique optical coupling effects achieved by end-to-end assembly of AuNRs, the ability to control such assembly is of particular importance in areas such as sensing.^{8,9} Additionally, there is much interest in the use of controlled assembly of nanoparticles for nano-electronic applications.¹⁰

Previous reports on supramolecular end-to-end AuNR alignment have focused on two main approaches. The first being the direct self-assembly of end-functionalised AuNRs *via* solvent induced aggregation of ligands bound to the ends of AuNRs.^{11–14} The second approach links AuNRs through two-component systems where rods are functionalised with ligands capable of binding a bridging component such as metal salts^{15,16} or biological motifs.^{7,17} For the first time, we report here a three-component system, comprising of functional AuNRs, a ditopic linker molecule, and an unique macrocycle, exploiting specific host-guest interactions. This novel approach enables greater control over the AuNR linear assembly and may allow for the formation of hierarchical assemblies that go beyond simple chains, towards elaborate structures such as hexagonal arrays of AuNRs yet unattainable using previously published techniques.

Our approach to controlling both the end-to-end alignment and the spacing between the AuNRs relies on the use of cucurbit [*n*]urils (CB[*n*], *n* = 5–8 of glycouril units), which are a class of rigid, barrel-shaped macrocyclic hosts with symmetric carbonyl-lined portals.¹⁸ CB[*n*]s are capable of forming inclusion complexes with appropriately sized guest compounds in water with high affinity ($K_{eq} \geq 10^{15} \text{ M}^{-1}$).^{18–20} The larger CB[*n*] homologues can accommodate multiple guests inside their cavity simultaneously. In particular, CB[8] can form stable

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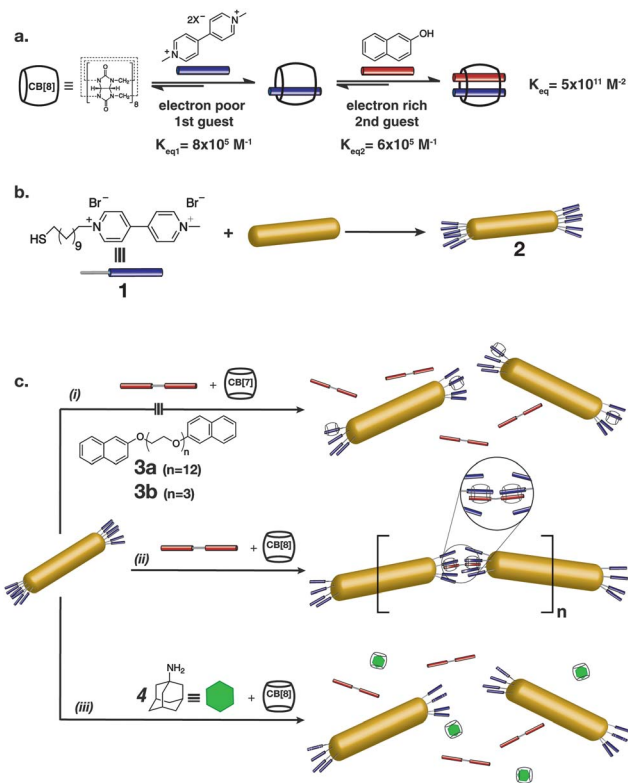


Fig. 1 (a) Formation of a ternary complex between methyl viologen, 2-naphthol and CB[8], (b) functionalisation of AuNRs with methyl viologen moieties **1** to produce MV²⁺-AuNRs **2**, and (c) addition of either ditopic naphthol linker (**3a** or **3b**) (i) with CB[7], (ii) with CB[8], or (iii) with CB[8] in the presence of **4**.

1 : 1 : 1 ternary complexes with an electron deficient and electron rich guest pair, such as methyl viologen (MV²⁺) and naphthoxy (Np) derivatives, leading to extremely high overall binding constants (K_{eq}) of up to 10^{12} M^{-2} in water as illustrated in Fig. 1a. This has been previously exploited in the non-covalent “handcuffing” together of supramolecular polymers and block copolymers,^{21–23} as well as peptides and proteins.^{24–26}

Recently, we demonstrated that CB[8] could also be used to form hybrid materials holding together gold nanoparticle–polymer composites, which could be assembled into hollow microcapsules through microfluidic techniques, highlighting the versatility and strength of this supramolecular approach towards NP assembly.^{27,28}

In order to exploit CB[8] ternary complexation in the alignment of nanorods, AuNRs were prepared with functional moieties only at their ends. It has been shown that exclusive end-functionalisation of AuNRs is possible with the use of cetyltrimethylammonium bromide (CTAB) as a stabilising ligand, on account of strong preferential binding of CTAB molecules to the {100} side facets of the long face of AuNRs and comparatively weak binding to the curved {111} ends of the nanorods.⁶ The parent AuNRs were synthesised by a previously reported seed-mediated technique producing nanorods with an aspect ratio of 4 (40 nm × 10 nm) and coated with CTAB.²⁹

A MV²⁺ (first guest) containing ligand (**1**) capable of AuNR binding through a terminal thiol group was synthesised. This ligand was then mixed with the CTAB-coated AuNRs to yield end-functionalised AuNR-MV²⁺ (**2**) as shown in Fig. 1b. These MV²⁺-functionalised nanorods were characterised by UV-vis spectroscopy without any changes observed in the characteristic absorbances, suggesting that no undesired aggregation of **2** took place in aqueous solution. Once functionalisation with MV²⁺ had been achieved, two telechelic, ditopic linker molecules with naphthol moieties at each end, but with different linker lengths (**3a**: $n = 12$ and **3b**: $n = 3$), were prepared (see ESI†). As depicted in Fig. 1c, this allows for the alignment of the functionalised AuNRs through the formation of CB[8] ternary complexes between the MV²⁺ termini of two adjacent AuNRs and **3a** or **3b**. To ensure water solubility, which is critical for CB[n] binding, a linker with twelve ethylene glycol repeat units (**3a**) was designed and prepared using a bidirectional elongation route.³⁰

Upon purification **3a** was mixed with **2** in the presence of CB[8] (1 : 1 : 1) in an aqueous solution; precipitation occurred almost immediately, eventually forming a black precipitate and

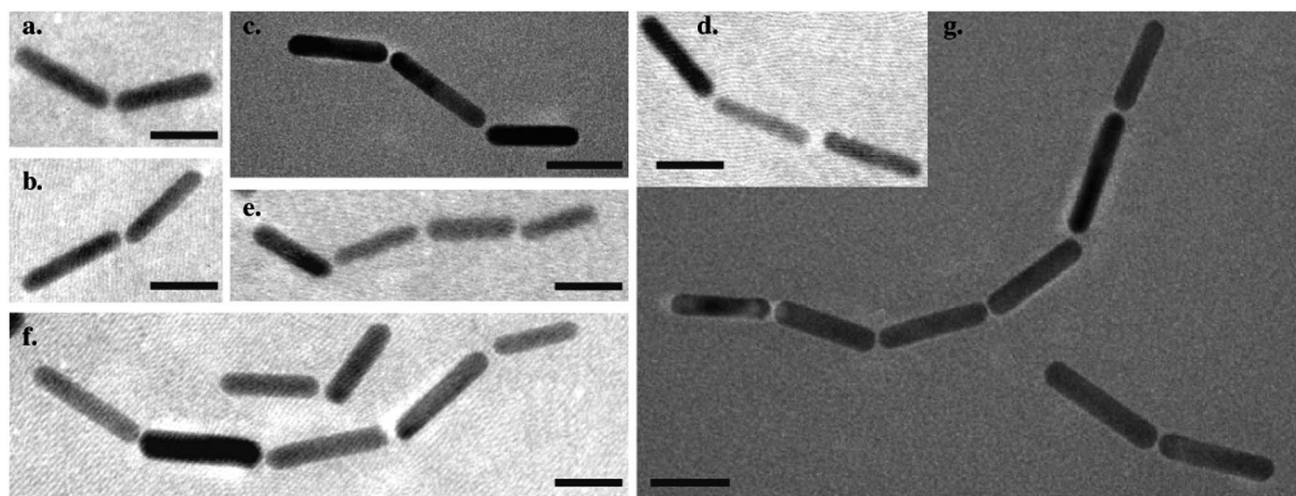


Fig. 2 TEM images depicting the alignment of AuNRs (**2**) with **3b** via CB[8] ternary complex formation. (a and b) Dimers of AuNRs, (c and d) trimers of AuNRs, (e) tetramer of AuNRs, (f) pentamer and dimer of AuNRs and (g) hexamer and dimer of AuNRs. Scale bars = 25 nm.



clear solution. Analysis of the black precipitate was conducted by transmission electron microscopy (TEM), which showed large aggregates of AuNRs with no control over rod conformation. Although **3a** shows high water solubility and clearly aggregates **2** in the presence of CB[8], it is unable to provide enough rigidity to the system, leading to large aggregates of AuNR rather than the desired controlled end-to-end assembly of AuNRs (Fig. 4b). As the points of attachment are only at the rod ends, reducing the flexibility of the ditopic linker should promote controlled end-to-end assembly of the AuNRs.

By reducing the length of the linker molecule it is possible to still ensure a degree of water solubility whilst decreasing the overall flexibility of the linker. In order to achieve this a triethylene glycol spacer was chosen as the hydrophilic linker between the two hydrophobic naphthoxy units (**3b**). Commercially available tri(ethylene glycol) di(*p*-toluenesulfonate) was reacted with two equivalents of 2-naphthol in the presence of anhydrous K_2CO_3 to arrive at **3b** in 54% yield.

Upon mixing all components, **2**, **3b** and CB[8] (1 : 1 : 1) in water, no immediate change in absorbance was observed in the UV/vis spectrum; however, this is consistent with both previous observations of supramolecular AuNR alignment⁷ and CB[8] ternary complexation at the surface of a nanoparticle.²⁷ To observe the formation of AuNR chains, TEM was carried out by drying the 1 : 1 : 1 ternary mixture onto copper TEM grids over a few minutes. As the aqueous solution dried, the local concentration of all components increased, leading to the formation of AuNR chains, which can be seen in Fig. 2. A varying number of AuNRs per chain is observed over the whole sample with dimers (Fig. 2a and b) being most predominant and trimers (Fig. 2c and d), tetramers (Fig. 2c), pentamers (Fig. 2f) and hexamers (Fig. 2g) each being observed but to lesser degrees. It should be noted that the drying period does appear to influence the number and length of chains with longer drying times leading to samples containing more aligned AuNRs, although quantification of this trend has not yet been achieved.

In order to confirm that the AuNR alignment is indeed due to the formation of a CB[8] ternary complex between end-functionalised **2** and ditopic linker **3b**, a control experiment with CB[7] was performed. CB[7] has a smaller annulus than CB[8] and as such is incapable of forming ternary complexes between MV^{2+} and Np guests.¹⁸ It can be seen that when CB[7] is used in place of CB[8] in the mixture of **2** and **3b**, the AuNRs show no alignment (Fig. 4a). This observation was further verified by analysis of the TEM images (*vide infra*) (Fig. 3).

Alignment of AuNRs through a supramolecular ternary complex allows for additional control over the observed morphology. The system can be disrupted *via* the use of a competitive guest for the CB[8] cavity, such as adamantaneamine (**4**). Molecule **4** has a strong binding affinity for CB[8] and is capable of displacing both the MV^{2+} and Np guests, inhibiting the formation of a ternary complex as shown in Fig. 1c. When **4** is added to a solution of **2**, **3b** and CB[8] and analysed *via* TEM, the alignment of **2** is inhibited (Fig. 4c). Additionally, it should be noted that in this control a large proportion of the AuNRs were seen to be aggregated side-to-side. As the CB[8] cavity is occupied by **4**, it is no longer able to encapsulate the Np moieties present

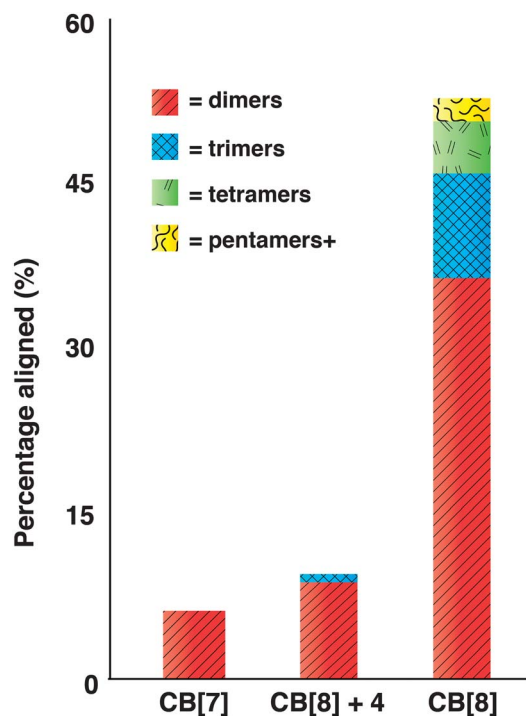


Fig. 3 Statistical analysis of TEM images showing percentage of AuNRs aligned.

on the linker molecule **3b**. It has been shown previously that these Np moieties are capable of incorporation into the CTAB bilayer present on the side faces of the AuNRs.³¹ In the presence of a ditopic Np linker (**3b**) and with the CB[8] cavity occupied by **4** the AuNRs are aggregated side-to-side (Fig. 4c).

Statistical analysis of TEM images was undertaken to clearly show that end-to-end alignment of AuNRs is on account of CB[8] ternary complex formation between **2** and **3b** and not an artifact of drying (3). From an analysis of TEM images it can be

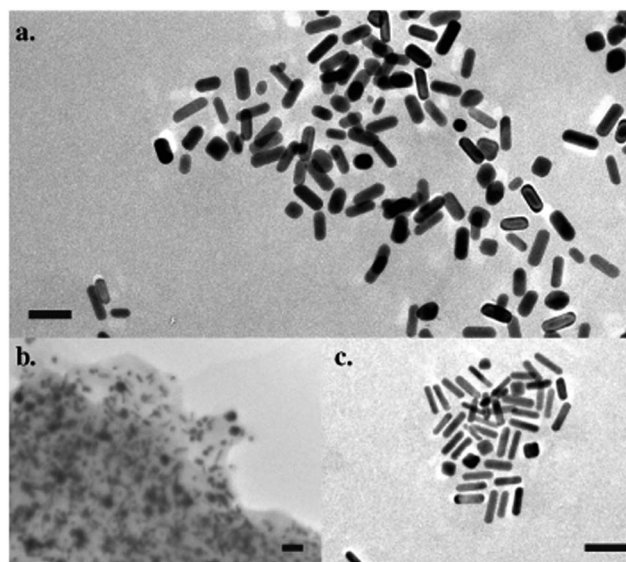


Fig. 4 TEM images of (a) **2** in the presence of **3b** and CB[7], (b) **2** in the presence of **3a** and CB[8], and (c) **2** in the presence of **3b**, CB[8] and **4**. Scale bars = 50 nm.



seen that in the presence of CB[7], 93% of AuNRs show no end-to-end alignment. The remaining 7% of AuNRs are found only as dimers. This is consistent with previously reported observations for AuNR end-to-end alignment in the absence of the required stimulus.¹⁵ A low proportion of aligned AuNRs is also observed in the presence of **4** with similar percentages of AuNRs aligned as in the CB[7] control. A clear difference can be observed by TEM when the larger macrocyclic host CB[8] is used, which leads to an almost 8-fold increase in AuNRs aligned end-to-end (Fig. 3). Table S1† gives a breakdown of AuNRs that are aligned end-to-end, showing that the large majority of aligned AuNRs are dimers, likely due to the short drying times. However, unlike the very small number of aligned AuNRs observed in the CB[7] controls, larger numbers of aligned AuNRs are observed with CB[8], with nearly one-fifth of all aligned AuNRs resulting in trimers and over 10% of the remaining aligned AuNRs being found in chains of four nanorods or more. The number of AuNRs per chain is likely to be dependant upon the concentration of **3b** in solution as well as the time between mixing all of the components and imaging, which has previously been shown to be of great importance.⁴ This observation is additionally supported by the decreasing proportions of dimers, trimers, tetramers *etc.* observed. Further investigations into the factors that control the degree of aggregation and ultimately chain length are currently underway in our group.

We have shown, for the first time, that a three component system is capable of aligning AuNRs through supramolecular host-guest interactions leading to control over AuNR end-to-end assembly. Viologen end-functionalised AuNRs were prepared that were capable of selectively binding to a CB[8] macrocyclic host molecule. These end-functionalised AuNRs could participate in 1 : 1 : 1 ternary complexation with synthesised telechelic linker molecules bearing second guest moieties, in the presence of CB[8]. When the linker length was long and flexible aggregation and precipitation of AuNRs were readily observed, but with no control over the AuNR conformation. On the other hand, when the linker length was shortened thereby imparting a more rigid connection between neighbouring gold nanorods, the end-to-end assembly of AuNRs was achieved. In the presence of a small macrocyclic homologue, CB[7], or after the addition of a competitive guest for CB[8], no alignment was observed, clearly demonstrating that ternary complex formation is critical to the alignment of AuNRs in this system. Thus, the end-to-end assembly relies upon both having a relatively short and rigid linker as well as the specific, yet tuneable supramolecular 1 : 1 : 1 ternary complexation between the three components.

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