The tuneable complexation of gold nanoparticles†

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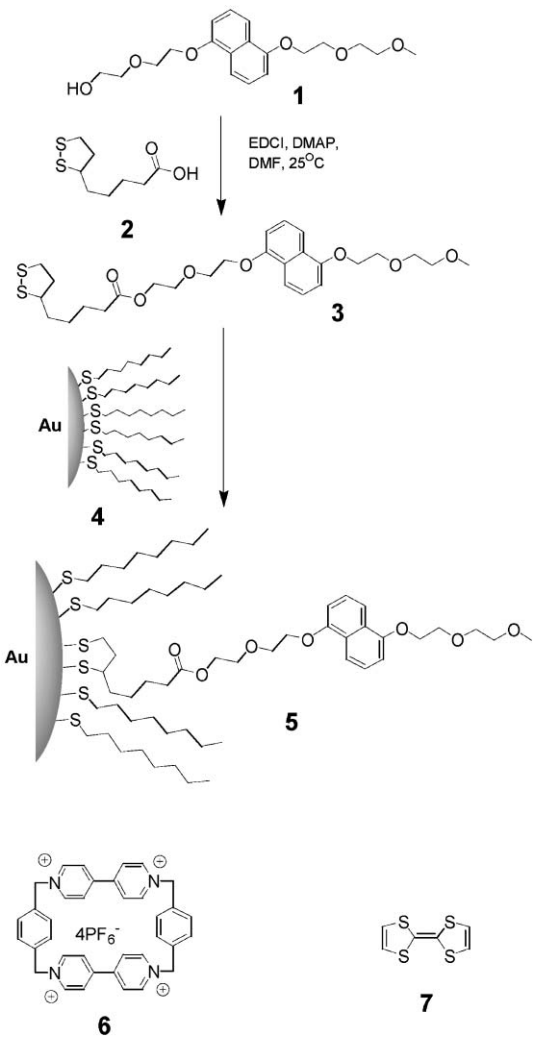
Mixed monolayer protected gold nanoparticles have been fabricated incorporating 1,5-dialkyloxynaphthalene moieties that are capable of forming complexes with the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene); electrochemical reduction of the cyclophane or the addition of tetrathiafulvalene results in disassembly of the complexes.

The development of convenient routes to fabricate monolayer protected clusters (MPCs)[1] and their subsequent ability to have their structure further tailored using place-exchange reactions to create mixed monolayer protected clusters (MMPCs)[2] have ensured these nanosystems have a wide range of applications.[3] In particular, the ability to conveniently functionalise nanoparticles with solubilising and recognition groups has undoubtedly been largely responsible for their present level of interest.

The majority of the efforts towards nanoparticle functionalisation have been directed towards covalent strategies. Non-covalent modification, on the other hand, offers a highly versatile and modular approach, allowing "plug and play" creation of multiple particles from a single precursor.[4] This process proceeds in a reversible, thermodynamic fashion, providing potentially recyclable materials. A particularly attractive method of functionalizing the periphery of these nano-scaffolds has proved to be through the formation of pseudorotaxane architectures, as these systems can be reversibly assembled in a range of environments.[5] Pseudorotaxanes created from the electron deficient cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and 1,5-dialkoxynaphthalene units have arguably become one of the most important building blocks for the synthesis of functional supramolecular systems with near-binary recognition properties.[6] In particular, as the electrochemical reduction of the cyclophane unit results in the expulsion of the naphthalene unit from its cavity, systems of this type could be incorporated into the periphery of a nanoparticle as a means of reversibly modifying their structure and function. Here, we report the synthesis of 1,5-dialkyloxynaphthalene functionalised MMPCs and their subsequent reversible complexation with $CBPQT^{4+}$.[7]

Scheme 1 outlines the synthesis of MMPC **5** (see also ESI). Compound **3** was synthesized in good yield by an EDCI/DMAP catalysed esterification of **1** and thioctic acid **2**. Compound **3** successfully underwent place-exchange reactions with 2 nm core octanethiol protected gold cluster **4**,[8] to afford the MMPC **5**. ^{1}H NMR spectroscopy confirmed the success of the place-exchange reaction by the appearance of broad resonances in the aromatic region corresponding to the naphthalene moieties, and similarly broad signals for methylene protons of the ethylene glycol groups. Comparison of the integrals of the signals for the CH_3O– group of **3** *versus* the terminal CH_3 group of the octanethiol groups provides an estimated ratio of surface coverage of 1 : 15, respectively. The addition of the naphthalene moiety greatly enhanced the solubility of the nanoparticle, by extending solubility to polar solvents (*e.g.* DMSO, acetone), where the parent nanoparticle **4** has poor solubility.



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis of **3** and **5**. See DOI: 10.1039/b608543a

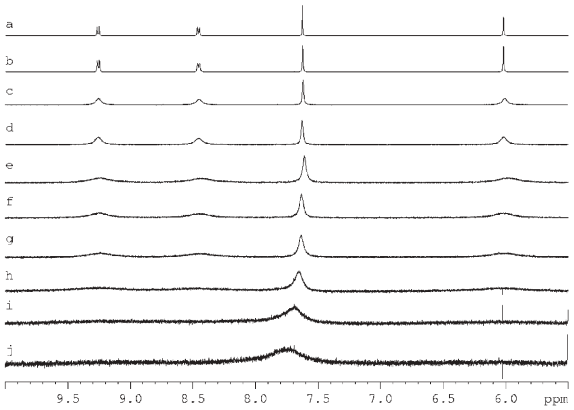

Fig. 1 Partial ^{1}H NMR spectra of **6** (a) ($\sim$4.5 $\times$ 10^{-3} M) and upon the addition of aliquots of **5** ((b)–(j)). Total amount of **5** added = 20 mg. Recorded in CD_3COCD_3 at 298 K.

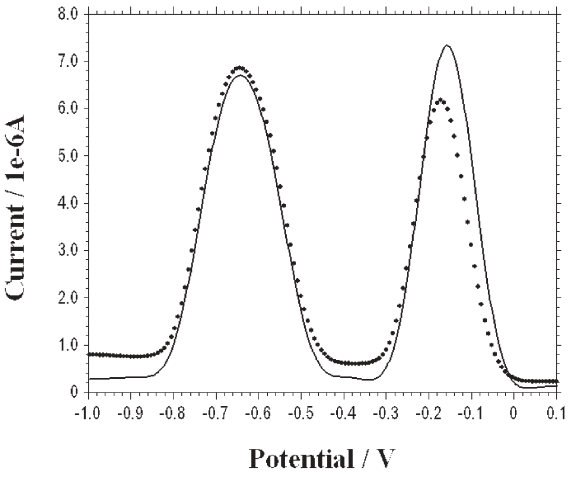

Fig. 2 Square wave voltammogram of **6** (—) ($\sim$3.2 $\times$ 10^{-4} M) and upon the addition of **5** (…) (20 mg).

The good solubility of **5** in polar solvents was vitally important for the investigation of the molecular recognition properties with the tetracationic cyclophane $CBPQT^{4+}$ (**6**). ^{1}H NMR spectroscopy was used to investigate the effect the addition of **5** has to a solution of **6** in acetone-d_6 (Fig. 1). A significant broadening of the $CBPQT^{4+}$ proton resonances was observed upon the addition of aliquots of MMPC **5**, which is indicative of the cyclophane being associated to the large nanoparticle architecture.[5] The addition of an excess of nanoparticles eventually led to the resonances becoming so broad that they became indistinguishable from the base line. When aliquots of **6** were added to a solution of **5**, the gradual disappearance of the signals corresponding to the naphthalene protons occurred. In both experiments, negligible changes in the signals corresponding to the protons of the terminal methyl groups of the octyl moieties occurred, arguing against non-specific recognition.

We next turned our attention to whether complex formation could be controlled using an external stimulus. It has previously been shown that $CBPQT^{4+}$-based complexes can be disassembled by reducing the cyclophane to its diradical dicationic state.[6] To investigate if this process can be applied to the present system, we have recorded the square wave voltammograms of compound **6** upon the addition of excess **5**.[9] Square wave voltammetry indicated that the first reduction wave of **6** was shifted by $\sim$20–30 mV upon addition of **5**, presumably due to donor–acceptor interactions resulting from complex formation between the naphthalene and cyclophane moieties, stabilizing the diradical dication state of the cyclophane (Fig. 2).[6] The reduction potential of the second reduction wave is largely unaffected, indicating the naphthalene unit disassembles when the cyclophane is first reduced.

Finally, we have explored the addition of tetrathiafulvalene **7** to disrupt the initial complexes formed between **5** and **6**,[10] as it is well established that this heterocycle is an effective guest for $CBPQT^{4+}$-based cyclophanes.[11] The addition of cyclophane **6** to a solution of **5** in acetone resulted in the formation of a broad shoulder (400–600 nm) in the UV-vis spectrum, which is presumably due to complex formation between 1,5-dialkyloxynaphthalene moieties of **5** and **6** (Fig. 3). The further addition of one equivalent (compared to **6**) of **7** immediately resulted in the appearance of a new absorption centered around 856 nm, characteristic of tetrathiafulvalene–$CBPQT^{4+}$ pseudorotaxanes. Thus, the UV-vis data are consistent with the TTF unit disrupting complex formation between **5** and **6**.

To further prove the ability of **7** to disrupt complex formation, we have investigated the change in the ^{1}H NMR spectra of an admixture of **5** and **6** upon the addition of **7** (Fig. 4). Immediately upon the addition of **7** to the NMR tube, the signals corresponding to the cyclophane became less broad, indicating that the cyclophane units are no longer complexed to the periphery of the nanoparticle. Furthermore, the TTF and cyclophane resonances are shifted (compared to the spectra of **6** and **7**), providing further evidence for the formation of tetrathiafulvalene–$CBPQT^{4+}$ pseudorotaxanes, and thus disruption of the initial complexes formed between **5** and **6**.

In conclusion, we have established that complexation between $CBPQT^{4+}$ and 1,5-dialkoxynaphthalene units can be extended to the solid–liquid interface formed between a MMPC and an organic solvent. Furthermore, we have shown that the resulting complexes can be disrupted by either the electrochemical reduction of the cyclophane or the addition of TTF. Further work in our laboratory will develop water soluble analogues of the systems

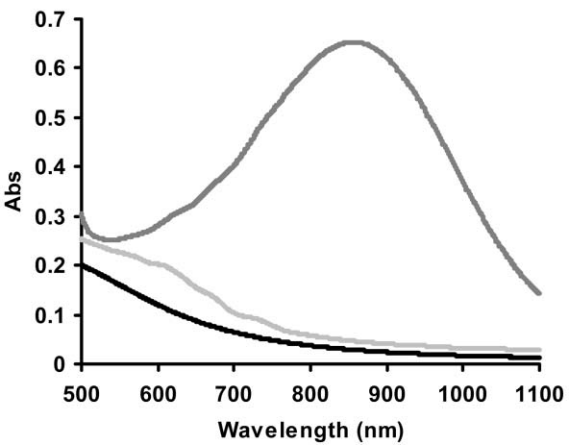

Fig. 3 UV-vis spectra of **5** (black) (18 mg in 10 mL) in acetone and in the presence of **6** ($\sim$3 $\times$ 10^{-4} M) (light grey) and then **7** ($\sim$3 $\times$ 10^{-4} M) (dark grey).

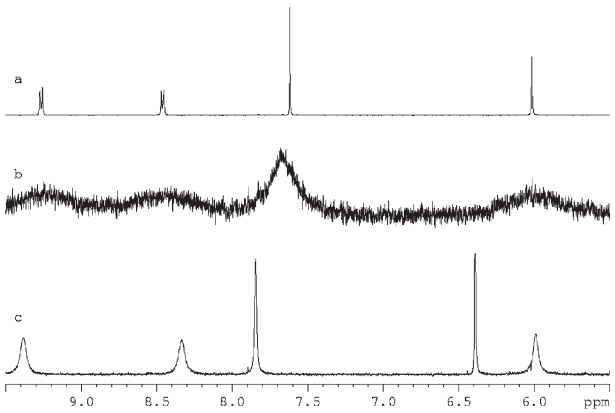

Fig. 4 Partial ^{1}H NMR spectra of: (a) **6** ($\sim 4.5 \times 10^{-3}$ M), (b) and upon the addition of **5** (10 mg), (c) upon the addition of one equivalent of **7** (compared to **6**). Recorded in CD_3COCD_3 at 298 K.

described here in endeavors to extend this methodology to biologically relevant systems. Our work in this area will be reported in due course.

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