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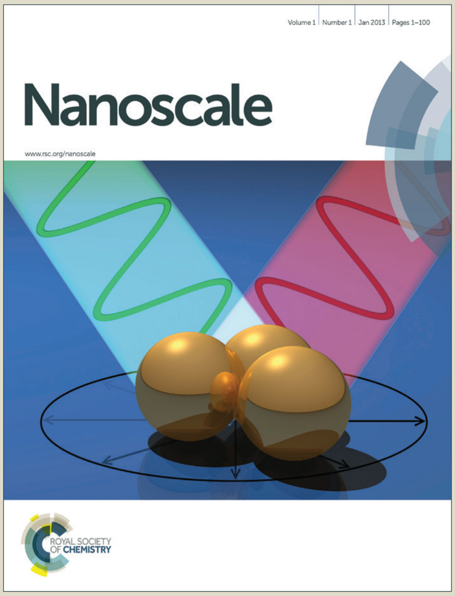

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Catalytic polymeric nanocomposites *via* cucurbit[*n*]uril host-guest interactions†

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Polymeric nanocomposites were prepared by using cucurbit[7]uril as a 'supramolecular anchor', as well as stabilising ligand to immobilise catalytic transition-metal nanoparticles on the surface of methyl viologen-bearing polymeric colloids. This facile and spontaneous supramolecular approach allows for control over size, morphology and composition of the nanocomposites. The small metallic nanoparticles impart the nanocomposites with great potential in catalysis.

Transition-metal nanoparticles (TMNPs) have attracted much attention for catalysis on account of their heterogeneous nature imparting both easy removal from reaction mixtures and recyclability.[1–3] Moreover, their unique large surface-to-volume ratio endows metallic nanoparticles with high catalytic activity.[4,5] Unfortunately, most TMNPs are unstable and tend to aggregate, suppressing their catalytic efficiency greatly.[6,7] Over the past few decades, various materials have been employed to stabilise metallic nanoparticles (NPs), such as polymeric nanofibers,[4] meso-porous silica,[8] micelles and graphene derivatives.[9,10] Such structures are mainly based on the conjugation between metallic NPs and the functional moieties in the supporting matrix, for example, thiols,[11] pyridine,[9] phenylenediamine,[10] and carbonyl groups in macrocyclic molecules.[12]

Cucurbit[*n*]urils (CB[*n*], n = 5-8, 10) belong to a family of macrocyclic host molecules.[13] They have cavities of various sizes and are able to encapsulate guest molecules through two identical carbonyl-fringed portals.[14] The binding constant (K_{eq}) for CB[*n*]-based host/guest complexation can reach up to 10^{17} M^{-1}.[13] CB[*n*] has been employed as a supramolecular linker in the preparation of supramolecular hydrogels,[15–17] micelles,[18] microcapsules,[19] core-shell polymeric colloids[20] and a number of materials.[21,22] In addition, CB[*n*] shows high affinities towards metallic NPs through their carbonyl portals.[23,24] The resulting structures have been confirmed by the enhanced signal from Raman spectroscopy.[25] A broad range of research has taken place in fields of nanoparticle assembly and nano-sensing.[25,26] Recently, Kim *et al.* reported the decoration of catalytical NPs onto CB[6]-based polymeric nanocapsules.[27] However, in this study, the polymer nanocapsules are made of $(allyloxy)_{12}$cucurbit[6]uril through a thiol-ene photopolymerisation. The synthesis of $(allyloxy)_{12}$cucurbit[6]uril suffers from low reaction yield and a laborious separation process. Therefore, the material might be limited by cost as well as high scale production.

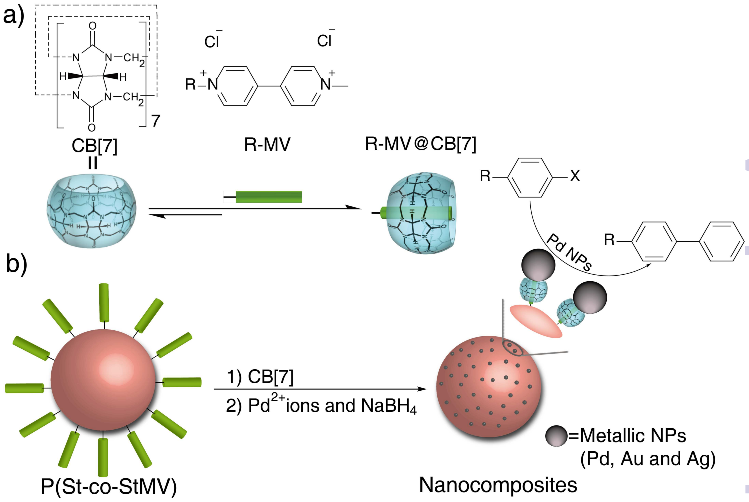

Fig. 1 a) Complexation between viologen derivative and CB[7]; b) schematic formation of polymeric nanocomposites by an *in situ* reduction of metallic ions in an aqueous suspension of the poly(styrene-*co*-styrene methyl-viologen) [P(St-*co*-StMV)]/CB[7].

Herein, we report a facile route to prepare polymeric nanocomposites with metallic NPs immobilised on the surface of methyl viologen (MV) bearing polymeric colloids, as shown in Fig. 1b. The essence of this approach lies in the complexation between CB[7] and MV guest moieties on the

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surface of the polymeric colloids and the strong portal affinity of CB[7] towards metallic NPs. Hence CB[7] is acting both as a stabilising ligand as well as a supramolecular anchor. Moreover, such an approach can be applied to immobilise a wide variety of transition-metal nanoparticles, such as silver, gold and palladium, which have been applied in a variety of catalytic applications. This represents the first report where bare metallic NPs are stabilised on colloids *via* host-guest chemistry.

The MV-bearing polymeric colloids of poly(styrene-*co*-styrene methyl viologen) [P(St-*co*-StMV)] were prepared using a soap-free emulsion polymerisation (SFEP) of styrene and StMV.[28] On account of the hydrophilic StMV moieties, the as-formed colloids could be readily dispersed in aqueous solution. Moreover, the size of the colloids could also be controlled by changing the feed ratio of the StMV monomer. Polymeric colloids were prepared with an average diameter of 42 ± 2 nm, confirmed by TEM (Fig. 2a), and a narrow size distribution (polydispersity of 0.005) confirmed by dynamic light scattering (DLS) analysis (ESI, Fig. S1-2). Based on the binding studies between perylene bis(diimide) (PDI) and MV@CB[8], the concentration of accessible MV moieties in the P(St-*co*-StMV) dispersion was calculated as 3.0 mM (ESI, Fig. S5-6).

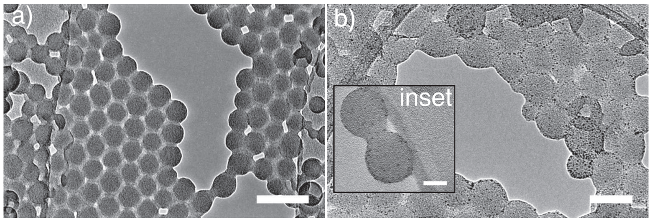


Fig. 2 TEM images of a) P(St-*co*-StMV) colloids (scale bar: 100 nm), b) Pd@P(St-*co*-StMV) (**A**) nanocomposites (scale bar: 50 nm) and inset (scale bar: 20 nm). Average size of Pd NPs: 2.4±0.4 nm.

The fabrication of nanocomposites was carried out by reducing the metallic ions *in situ* in an aqueous mixture of P(St-*co*-StMV) and CB[7]. CB[7] was first fed into the P(St-*co*-StMV) suspension at a 1:1 molar ratio with respect to quantified StMV, achieving a host-guest complexation with MV moieties. The UV spectra (ESI, Fig. S7) show a blue shift upon addition of Pd ions from 237 to 232 nm. This could indicate the preliminary interactions between Pd ions and CB[7], possibly through the carbonyl portals. As shown in the TEM images of the Pd@P(St-*co*-StMV) (**A**) nanocomposites (Fig. 2b), the Pd NPs are immobilised onto the surface of P(St-*co*-StMV) colloids. The average size of the Pd NPs is approximately 2.5 nm with a narrow size distribution. Additional attempts on the different feed ratio of CB[7] were studied, the results indicates excess of free CB[7] has little impact on the formation of Pd nanocomposites (ESI, Fig. S8). Under reducing conditions, Pd NP forms and immediately binds with the carbonyl portals of CB[7]. The hypothesis was further investigated in corresponding control experiments. In the absence of CB[7], aggregation of Pd NPs up to 10 nm in diameter was observed (ESI, Fig. S9a). It is probably due to a lack of stabilisation as metallic NPs cluster to avoid high surface area. This is in agreement with further visual observation, whereas the dispersion of Pd@P(St-*co*-StMV) (**A**) remains well-dispersed for months (Fig. 3a), the corresponding dispersion in the absence of CB[7] results in a precipitate after 12 hours, as shown in Fig. 3b.

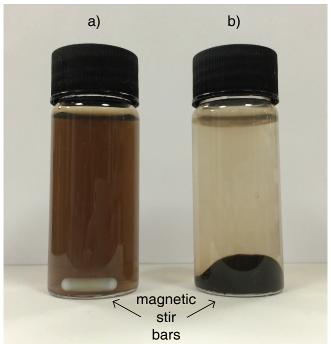


Fig. 3 Images of a) Pd@P(St-*co*-StMV) (**A**) dispersion prepared with CB[7]; b) Pd@P(St-*co*-StMV) dispersion prepared without CB[7].

When the reduction of Pd ions was carried out *ex situ* and subsequently added to the mixture of CB[7] and P(St-*co*-StMV), aggregation was observed and Pd clusters were not immobilised onto the surface of the colloids, as shown in Fig. S9b (See ESI). Conversely, when the reduction of Na_2PdCl_4 was carried out in the CB[7] solution followed by addition into the P(St-*co*-StMV) dispersion, Pd NPs formed flocculates through portal interactions of CB[7] (ESI, Fig. S9c). The gaps (approx. 1 nm) in the Pd aggregates indicated the presence of CB[7], in agreement with literature.[23,29] These aggregated structures resemble work on honeycomb-like palladium nanostructures,[12] in which CB[7] was employed as a capping agent to stabilise Pd nanoclusters and applied in catalysis. However, in this work by Geckeler *et al.* Pd NPs formed large aggregates bridged *via* CB[7], consequently reducing the total active surface area of Pd NPs that could substantially decrease its catalytic performance. In our case, the CB[7] was first bound strongly onto the polymeric colloids *via* MV@CB[7] host-guest complexation, leaving only one side of the carbonyl portals available to stabilise the Pd NPs as shown in Fig. 1b. Therefore, aggregate formation through CB[7] bridging was avoided. Polymeric colloids are critical in immobilising these Pd NPs and preventing them from aggregating. This is a versatile approach to fabricate polymeric nanocomposites with other transition metals. Using a similar protocol, gold and silver nanocomposites were prepared as described in the supporting information (ESI, Fig. S11-12). TEM images of the resultant Au@P(St-*co*-StMV) and Ag@P(St-*co*-StMV) also show immobilised metallic NPs through conjugation with CB[7].

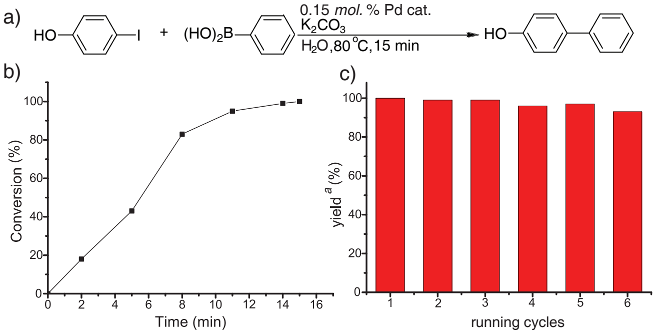
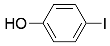
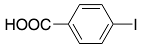
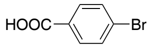
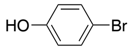
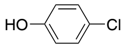
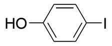
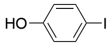


Fig. 4 a) Typical Suzuki reaction between 4-iodophenol (1 mmol) and phenylboronic acid (1.5 mmol); reaction condition: aqueous dispersion 20 ml containing Pd@P(St-*co*-StMV) (**A**) catalyst (0.15 mol%), K_2CO_3 (3 mmol) and 80 °C. b) Kinetics plot of conversion against reaction time. c) Recycle test of the Pd@P(St-*co*-StMV) (**A**) catalyst for the reaction between 4-iodophenol and phenylboronic acid; [a]yields determined by HPLC analyses.

In light of the extensive use of metallic NPs in catalysis, we chose the Pd@P(St-*co*-StMV) (**A**) nanocomposites with a focus on the Suzuki coupling reaction. This is one of the most successful methods for generating asymmetric biaryls on an industrial scale. Many intermediates for pharmaceuticals or fine chemicals are obtained through this carbon-carbon coupling reaction.[30] The model reaction between 4-iodophenol and benzyl boronic acid was tested initially. Water was chosen as the reaction media for its low cost and 'green' nature. With a low loading of 0.15 mol% Pd catalyst, the reaction reached completion after 15 min, as shown in the plot in Fig. 4b and a yield as high as 99% was achieved in comparison of the control experiment of commercial catalyst Pd/C as shown in table 1. The products were collected by simple organic extraction followed by reloading of the starting materials. The Pd@P(St-*co*-StMV) (**A**) nanocomposites were fully recyclable, as shown in Fig. 4c. Yields higher than 90% could still be detected after six cycles. Slight surface deformation of the supporting colloids was observed after a few cycles (ESI, Fig. S13), which may be due to swelling from the organic extractions, could possibly lead to the slight decrease in yield as observed in Fig. 4c. Additional studies were investigated on the the effect of excess CB[7] in catalysis. Previously prepared Pd@P(St-*co*-StMV) (**B**) with 10:1 molar ratio of CB[7]/MV shows similar catalysis ability (Table 1).

It is known for Suzuki coupling that more economical aryl chlorides and aryl bromides are less reactive than aryl iodides, and there are few reactions conducted in water.[4] Some Suzuki coupling reactions catalysed by other palladium nanoparticles generally do not work with aryl chlorides.[11] We therefore attempted Suzuki coupling on a number of different aryl halides with Pd@P(St-*co*-StMV) (**A**) as the catalyst. Various asymmetric biaryl derivatives were synthesized with high yields (Table 1).

Table 1 Suzuki coupling of aryl halides and $PhB(OH)_2$.

Entry [a]	Substrate	Catalyst	Time (h)	Yield [b]
1		A	0.25	99%
2		A	0.25	100%
3		A	4	95%
4		A	4	95%
5		A	6	88%
6		Pd/C [c]	0.25	72%
7		B [d]	0.25	98%

[a]Reactions 1-5 were carried out in water using 1.0 equiv. of aryl halide, 1.5 eq. of phenylboronic acid and 3.0 eq. of K_2CO_3 in the presence of Pd@P(St-*co*-StMV) (**A**) (0.15 mol%) at 80 °C. [b]Yields determined by HPLC analyses. [c]A control reaction using 0.15 mol% of Pd/C (10 wt%). [d]A control reaction using 0.15mol% of Pd@P(St-*co*-StMV) (**B**).

Apart from palladium, gold and silver NPs are also extensively applied in catalysis. For example, Lambert *et al.* reported using small gold entities (1.5 nm) in the selective oxidation of styrene.[31] On account of the versatility of the CB[7]-based supramolecular approach, we have shown extended work in fabricating gold and silver nanocomposites with catalytic NPs range of 2 nm.[16] Thus, these nanocomposites are expected to show great potential in other catalysis systems.

In conclusion, our CB[7]-based supramolecular strategy provides a facile and efficient platform to fabricate nanocomposites of various transition metals under mild conditions. By taking advantage of the dual role (host/guest complexation and portal conjugation) of CB[7], metallic NPs were successfully synthesised with diameters of 2 nm and immobilised onto the polymeric colloids. In addition, the polymeric nanocomposites were confirmed as high-performance catalysts, in light of the Suzuki coupling with Pd@P(St-*co*-StMV). This fabrication strategy based on cucurbit[*n*]uril host-guest chemistry may potentially produce nanostructures not only with prescribed morphology but also designed chemical properties that would be useful for diverse applications, such as catalysis and sensing.

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