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

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S.1 Synthesis and characterization of PSt-co-StMV

![Chemical structure](image)

Figure S1: Synthesis of PSt-co-StMV *via* soap-free emulsion polymerization (SFEP).

![Hydrodynamic distribution](image)

Figure S2: Hydrodynamic distribution of a) PSt-co-StMV and b) PSt-co-StMV/CB[7] in water.
Figure S3 shows the FTIR spectrum of the PSt-co-StMV corona. The characteristic absorption at 1600, 1493, 1452, 757, and 697 cm\(^{-1}\) are attributed to the PS segment, and the absorption between 3780-2820 cm\(^{-1}\) represents the C-H stretch next to nitrogen group.

![Figure S3: FTIR spectrum of PSt-co-StMV.](image)

Figure S4: TEM images of a) PSt-co-StMV\(_{70\text{nm}}\) (scale bar: 50 nm) and b) PSt-co-StMV\(_{90\text{nm}}\) (scale bar: 100 nm).

![Figure S4: TEM images.](image)

Figure S5: Changes in the UV/vis spectra of perylene diimide (PDI) and CB[8] complexes at different concentrations.

![Figure S5: UV/vis spectra.](image)
**Figure S6**: The calibration curve for PDI and CB[8] complexes at 537 nm.

**S.2 UV studies of the complexation between CB[7] and Na$_2$PdCl$_4$ into CB[7] solution**

**Figure S7**: UV/vis spectra of Na$_2$PdCl$_4$ (1.2 mM) in water (red line) and Na$_2$PdCl$_4$ (1.2 mM) in CB[7] (1 mM) solution (black line). A blue shift of 5 nm was observed for the Pd/CB[7] solution (red line) at 232 nm compared to the aqueous Pd solution alone (black line), indicating the complexation between the CB[7] and Pd ions.
S.3 Pd nanocomposites with different feed amount of CB[7]

![TEM images](image1.jpg)

**Figure S8:** TEM images of a) Pd@PSt-\textit{co}-StMv with 1:2 molar ratio of CB[7]/MV (scale bar: 50 nm) b) Pd@P(St-\textit{co}-StMv) (B) with 10:1 molar ratio of CB[7]/MV (scale bar: 50 nm) and c-d) Size distribution of Pd NPs 5.6±1.8 nm and 2.3±0.4 nm respectively. This indicates when the feeding amount of CB[7] is limited compared to the available MV moieties in the solution, the resulted Pd NPs show a wide size distribution. In addition the excess of free CB[7] has little impact on the formation of Pd nanocomposites and the size of Pd NPs.

S.4 Pd nanocomposite control experiments

![TEM images](image2.jpg)

**Figure S9:** TEM images of a) the formed aggregates when CB[7] is absent during the preparation of the palladium nanocomposite (scale bar is 50 nm); b) the formed aggregates when Pd ions are first reduced and subsequently added to the mixture of CB[7] and PSt-\textit{co}-StMv\textsubscript{70nm} (scale bar is 100 nm); c) the formed aggregates when Pd ions are reduced in the CB[7] solution followed by addition of the PSt-\textit{co}-StMv\textsubscript{70nm}, the gap between metallic NPs indicates the CB[7] bridging (the scale bar is 100 nm).
S.5 Pd nanocomposites with different size

Figure S10: TEM images of a) Pd@PSt-co-StMV\textsubscript{70 nm} dispersion and b) Pd@PSt-co-StMV\textsubscript{90 nm} dispersion (scale bar: 50 nm).

S.6 Gold nanocomposites

Figure S11: TEM images of a) Au@PSt-co-StMV (scale bar: 50 nm) and b) the formed aggregates when CB[7] is absent during the preparation of the gold nanocomposite (scale bar: 500 nm).

S.7 Silver nanocomposites

Figure S12: TEM images of a) Ag@PSt-co-StMV (scale bar: 50 nm) and b) the formed aggregates when CB[7] is absent during the preparation of the Silver nanocomposite (scale bar: 100 nm).
S.8 TEM image of Pd@PSt-co-StMV after reaction

![ TEM image of Pd@PSt-co-StMV after reaction ](image)

**Figure S13:** TEM images of the Pd nanocomposite after the Suzuki coupling reaction (scale bar: 20 nm).

S.9 Support Information

S.9.1 Materials and general methods

All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. CB[7] and CB[8] were prepared as documented previously.\(^1,2\)

\(^1\)H NMR (400 MHz) spectra were recorded using a Bruker Avance QNP 400. ATR FT-IR spectroscopy was performed using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. UV-\(\text{vis}\) studies were performed on a Varian Cary 4000 UV-\(\text{vis}\) spectrophotometer. Transmission electron microscopy (TEM) characterisation was carried out on a FEI Philips Tecnai 20 TEM under an accelerating voltage of 80 kV. Samples were prepared by applying one drop of the as-synthesised microspheres onto a Holey R carbon coated copper TEM grid (400 mesh) drying overnight. Dynamic light scattering (DLS) and zeta potential (ZP) measurements were performed on Malvern Zetasizer NS90 instrument.

S.9.2 Synthesis of StMV monomer

StMV was synthesized by a one-step electrophilic substitution. Typically, 1-methyl-4,4’-bipyridinium iodide (6.02 g, 20 mmol) was placed in a 500 mL flask with addition of acetonitrile (260 mL). The mixture was heated to 80 °C until all 1-methyl-4,4’-bipyridinium iodide dissolved. Then 4-choloromyethylstyrene (10 mL, 60 mmol) was added into the system and heated with stirring at 60 °C for 24 hours. After cooling to room temperature, the orange crude product was filtered, washed with acetonitrile and dried under reduced pressure to give a yellow-orange powder (5.4 g, 60%). \(^1\)H NMR (500 MHz, D\(_2\)O), 9.09 (d, 2H), 9.0 (d, 2H), 8.46 (q, 4H), 7.56 (d, 2H), 7.45 (d, 2H), 6.77 (dd, 4H), 5.85 (t, 4H), 5.37 (d, 2H), 4.46 (s, 1H).

S.9.3 Synthesis of PSt-co-StMV

Polymeric microspheres of PSt-co-StMV were synthesized by soap free emulsion polymerisation (SFEP) technique. To a 250 mL flask, 1-methyl-1’-(4-vinylbenzyl)-[4,4’-bipyridine]-1,1’-diium chloride iodide\(^3\) (StMV) (0.92 g, 2.0 mmol) was first dissolved in water (100.0-mL) to form a homogeneous solution.
Subsequently, styrene (St) (5.21 g, 50.0 mmol) was added dropwise. Nitrogen was purged into the mixture for 1 h before elevating the temperature, and the nitrogen blanket was maintained throughout the polymerization. After stabilizing at 80 °C, polymerization was initiated by addition of 2,2’-azobis(2-methylpropionamide) dihydrochloride (AIBA) (0.27 g, 1.00 mmol). After 24 h polymerization, the product of the PS-co-PStMV nanospheres was purified by dialysis and dispersed in 100 mL water.

**S.9.4 Quantification of MV groups on the PSt-co-StMV colloids**

CB[8] can bind with perylene bis(diimide) (PDI) and another guest such as MV inside its cavity, leading to strong ternary complexes of CB[8]/PDI/MV.\(^4\)

To determine the density of accessible MV on the PSt-co-StMV colloids, 10.0 mL PDI/CB[8] solution (PDI:CB[8] = 1:1, 20 µM) and 10.0 µL PSt-co-StMV dispersion were added into 9.99 mL H\(_2\)O, stirred at room temperature for 5 min. The resulted dispersion was then filtered against dialysis tube (MWCO 12400). The concentration of PDI/CB[8] in the filtrate was obtained from fitting the UV-vis result to the calibration curve (Figure S6). The concentration of accessible MV group in the PSt-co-StMV dispersion was calculated as 3.0 mM (obtained from the concentration difference between the original PDI solution and the filtrate). The density of accessible MV on the PSt-co-StMV colloids is 0.26 MV molecules per nm\(^2\) calculated by the equation below:

\[
d_{MV} = \frac{n_{MV} \times N_A}{4\pi r^3 \times N} = \frac{m_p}{\frac{4}{3}\pi r^3 \times \rho}
\]

\(d_{MV}\): the density of MV on the PSt-co-StMV colloids; \(n_{MV}\): moles of accessible MV groups on PSt-co-StMV colloids; \(N_A\): Avogadro constant; \(r\): average radius of PSt-co-StMV colloids from TEM images; \(N\): number of PSt-co-StMV colloids; \(m_p\): weight of PSt-co-StMV colloids; \(\rho\): density of PSt-co-StMV colloids. Assuming that MV-NP corona is ideal sphere, and \(\rho = 1 \text{ g/cm}^3\).

**S.9.5 Synthesis of palladium nanocomposites**

The procedure was carried out in a stepwise fashion. Firstly, CB[7] (22 mg, \(1 \times 10^{-2}\) mmol) was dissolved into 18 mL of H\(_2\)O. After sonicating for 10 minutes, 1 mL of PSt-co-StMV nanoparticles dispersion was added to mixture with sonication for an additional 5 minutes. 700 µL of PdCl\(_2\) solution (30 mM) was taken and added into the mixture with vigorous stirring. After 10 minutes, it was treated by reduction with NaBH\(_4\) (3.78 mg, 0.1 mmol) dissolved in 1 mL of water.

**S.9.6 Control experiments of palladium nanocomposites**

1 mL of PSt-co-StMV nanoparticles dispersion was diluted into 18 mL water with sonication of 5 minutes. 700 µL of Na\(_2\)PdCl\(_4\) solution (30 mM) was taken and added into the mixture with vigorous stirring. After 10 minutes, it was treated by reduction with NaBH\(_4\) (3.78 mg, 0.1 mmol) dissolved in 1 mL of water. The mixture was sampled and observed by TEM.
S.9.7 General protocol used for Suzuki couplings

Aryl halide (1 mmol), phenylboronic acid (1.5 mmol), and base (3 equiv) were added to 20 mL of deionized water in a Schlenk tube. The solution was purged by nitrogen and stirred at 80 °C. Pd nanocomposites (0.15 mol%) was then added to the stirred solution, and the reaction mixture was stirred for 0.25–4 h. After the reaction mixture had cooled to room temperature, the organic product was extracted with diethyl ether (3 × 50 mL). The organic fractions were washed with deionized water and then dried with MgSO₄. After filtration, the solvent was removed under reduced pressure to give the final product. A sample was analysed by HPLC.

References


