Supramolecular Gold Nanoparticle-Polymer Composites formed in Water with Cucurbit[8]uril

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Experimental

Materials and general methods. ^{1}H NMR (400 MHz) spectra were recorded using a Bruker Avance QNP 400. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ with the internal reference set to δ 7.26 ppm or MeOD with the internal reference set to δ 3.31 ppm. ^{13}C NMR (125 MHz) spectra were recorded using a Bruker Avance Cryobrobe ATM TCI DRX 500 or a Bruker Avance 500 BB-ATM. Chemical shifts are recorded in ppm (δ) in $CDCl_3$ and MeOD with the internal reference set to δ 77.16 ppm and δ 49.00 ppm, respectively. ATR FT-IR spectroscopy was performed using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. High-resolution mass spectra was recorded on a Bruker BioASpex II 4.7e FT-ICR mass spectrometer liquid chromatography-mass spectrometry Waters ZQ. UV-visible studies were performed on a Varian Cary 4000 UV-vis spectrophotometer. Gel permeation chromatography (GPC) was carried out in dimethylformamide (DMF) 0.1 M LiBr. DMF GPC was performed on two Jordi 5 μm DVB-Glucose columns connected in series with a SPD-M20A prominence diode

array detector and refractive index detector (both Shimadzu) calibrated in relation to poly(methyl methacrylate) standards. Samples were filtered over 0.45 μm nylon filters before injection using a 0.75 mL / min flow rate. All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. CB[8] was prepared as documented previously.[1] Transmission electron microscopy (TEM) characterisation was carried out by a JEOL 2000FX TEM under an accelerating voltage of 200 kV. Samples were prepared by applying one drop of the as-synthesised gold nanoparticles onto a Holey® carbon coated copper TEM grid (400 mesh). Centrifuge experiments were conducted using an eppendorf Minispin® centrifuge at 12,100g for 2 h at room temperature. Ultracentrifugation experiments were conducted on a Beckman Coulter Optima TLX Ultracentrifuge using a TLA 120.2 rotor at 90,000 RPM for 5 min (290,000g) using polycarbonate tubes at 20 ^{o}C.

Synthesis of 5 nm AuNPs

Synthesis of DDAB-stabilised AuNPs. AuNPs were synthesised *via* a seeded-growth method according to a modified literature procedure.[2] DDAB stock solution was first prepared by dissolving didecyldimethylammonium bromide DDAB (925 mg, 2.28 mmol) in toluene (20 mL). $HAuCl_4$ (50 mg, 0.13 mmol) and dodecylamine DDA (450 mg, 2.42 mmol) were added to 12.5 mL of the stock solution and sonicated until dissolved. The gold was then reduced by dropwise addition of TBAB (125 mg, 0.49 mmol) in 5 mL of DBAB stock solution under vigorous stirring, producing the (4 nm) seed solution, which was aged for 24 h. A growth solution was then prepared by adding 7 mL of the aged seed to a previously prepared solution containing toluene (50 mL) with $HAuCl_4$ (200 mg, 0.51 mmol), DDAB (1 g, 2.46 mmol) and DDA (1.85 g, 7.19 mmol). Finally, hydrazine (131 μL, 4.22 mmol) in 20 mL of the DDAB stock solution was added dropwise under vigourous stirring. Thus preparing a deep red solution of AuNPs (5 nm).

In order to successfully functionalise the synthesised AuNPs it was necessary to remove excess capping ligands *via* a washing procedure. MeOH was added to the toluene AuNP solution in a 1:1

(v/v) ratio. After 2 h precipitation of NPs is sufficient enough to allow removal of supernant. The precipitate is re-dissolved in 1 volume of MeOH and allowed to stand until all NPs have re-precipitated the supernant was removed and the process repeated once more. The resulting precipitate was easily dispersed in toluene (half original amount of toluene used) to give a deep red solution of AuNPs. To ensure solubility of AuNPs after functionalisation it was necessary to add MeOH to the toluene prior to functionalisation. The thiols EG_3 **1** and MV^{2+} **2**, in varying quantities of MV (a = 8%, b= 16% and c=32%), were immobilised onto the AuNP surface in an toluene/methanol solvent mixture for 48 hours and the MV^{2+}-AuNP **3a-c** were then isolated from any excess ligands with hexane. After removing the organic solvent *in vacuo*, the functionalised AuNPs **3a-c** were readily dispersed into water.

Synthesis of Tri(ethylene glycol)-1-butanethiol (1)

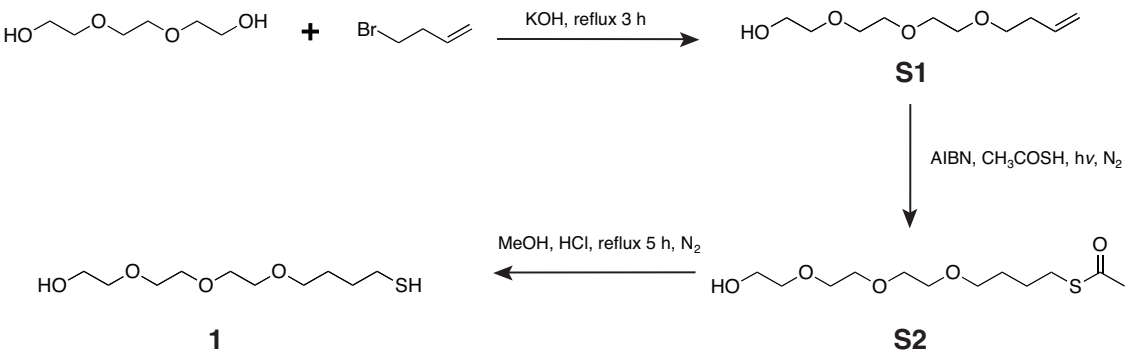

Figure S1: Synthesis of Tri(ethylene glycol)-1-butanethiol **(1)**.

*Synthesis of Tri(ethylene glycol)-1-butene (***S1)**. Potassium hydroxide (1.61 g, 28.7 mmol) was added to triethylene glycol (4.63 mL, 33.9 mmol) and the mixture was stirred until it formed a homogeneous solution. The solution was then cooled to -20 ^{o}C and 4-bromo-1-butene (2.5 mL, 24.6 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min and then at 60 ^{o}C for 3 h. After cooling, the mixture was partitioned between DCM/H_2O (1:1). The aqueous layer was collected, washed with DCM (2 x 75 mL) and then dried with magnesium sulfate ($MgSO_4$). The product **S1** was then isolated by column chromatography (ethyl

acetate/ethanol/H_2O, 25:2:1) as a colorless liquid (256 mg, 5.1 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.27 (m, 1H), 5.00 (m, 2H), 3.60 (m, 12H), 3.46 (m, 2H), 2.40 (s, 1H), 2.38 (m, 2H) ppm.

*Synthesis of Tri(ethylene glycol)-1-butanethioacetate (***S2)**. Tri(ethylene glycol)-1-butene **S1** (150 mg, 0.73 mmol), Azabis-(iso-butyronitrile) (AIBN) (0.0225 g, 0.14 mmol) and thioacetic acid (0.198 g, 2.6 mmol) were dissolved in toluene (3 mL). The solution was irradiated with a UV lamp at 365 nm for 5 h with gentle stirring. The mixture was then dissolved in DCM (50 mL) and washed with 1 M $NaHCO_3$ (50 mL). The organic layer was collected and washed with 1 M NH_4Cl (3 x 50 mL). The product **S2** was isolated by column chromatography (ethyl acetate/ethanol/H_2O, 25:2:1) to give a colorless oil (128 mg, 62.5 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.60 (m, 13H), 3.46 (m, 2H), 2.85 (m, 2H), 2.30 (s, 3H), 1.6 (m, 4H) ppm.

*Synthesis of Tri(ethylene glycol)-1-butanethiol (***1)**. Tri(ethylene glycol)-1-butanethioacetate **S2** (140 mg, 0.50 mmol) was dissolved in methanol (1.5 mL) was added to 1.25 M HCl in methanol (1.5 mL). The mixture was refluxed for 5 h. The solvent was removed under reduced pressure to give the title product **1** (109 mg, 91.5 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.60 (m, 12H), 3.46 (m, 2H), 2.52 (s, 2H), 2.18 (s, 4H), 1.66 (t, 4H), 1.33 (s, 1H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ = 72.5, 70.8, 70.8, 70.6, 70.6, 70.5, 70.3, 70.2, 70.1, 69.0, 61.8, 38.7, 30.7, 28.4, 28.3, 25.8, 25.8, 24.5 ppm. Mass Spec = 261.17 $[M^+ + Na^+]^{2+}$.

Synthesis of 1-methyl- 4,4'-bipyridinium-dodecanethiol (2)

*Synthesis of 1-Methyl-4,4'-bipyridinium iodide (***S3)**. 4,4'-Bipyridine (10.0 g, 64.0 mmol) was dissolved in dichloromethane DCM (150 mL). Methyl iodide (5 mL, 81.0 mmol) in DCM (50 mL) was then added drop-wise under stirring. The resulting mixture was refluxed for 1 h. Crude product was collected by suction filtration. The product **S3** was purified by recrystallisation from methanol

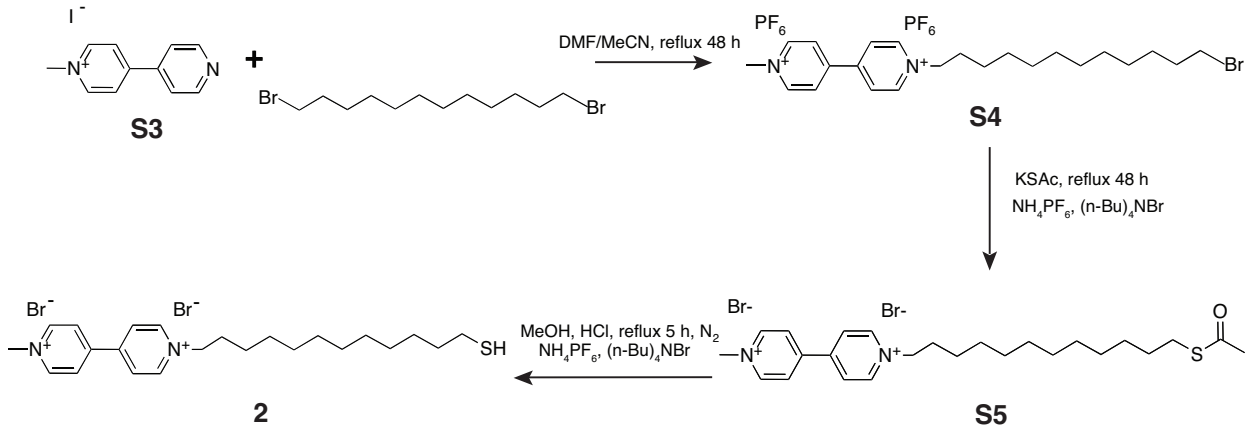

Figure S2: Synthesis of 1-methyl-4,4'-bipyridinium-dodecanethiol **(2)**.

and washed with ether to give 4.49 g of yellow crystals (24 %). ^{1}H NMR (500 MHz, D_2O) δ = 8.8 (d, 2H), 8.7 (d, 2H), 8.3 (d, 2H), 7.9 (d, 2H), 4.4 (s, 3H) ppm.

*Synthesis of 12-Bromo-1-(methyl-4,4'-bipyridinium)-dodecane (***S4)**. 1-Methyl-4,4'-bipyridinium iodide **S3** (1.0 g, 33.5 mmol) and 1,12-dibromododecane (2.17 g, 6.60 mmol) were dissolved in a mixture of DMF (6 mL) and acetonitrile (30 mL). The resultant mixture was refluxed for 48 h to afford an orange solid **S4** (460 mg, 12 %) which was collected by vacuum filtration. ^{1}H NMR (500 MHz, DMSO) δ = 9.32 (d, 2H), 9.22 (d, 2H), 8.75 (dd, 4H),4.70 (t, 2H), 4.43 (s, 3H), 3.52 (t, 2H), 1.32 (m, 20H) ppm.

*Synthesis of 1-methyl-4,4'-bipyridinium-dodecanethioacetate (***S5)**. 12-Bromo-1-(methyl-4,4'-bipyridinium)-dodecane **S4** (1 g, 1.6 mmol) was dissolved in a mixture of H_2O (100 mL) and ethanol (40 mL). Potassium thioacetic acid (0.456 g, 4 mmol) was then added and the mixture was refluxed for 48 h under nitrogen. The crude product was obtained by the addition of NH_4PF_6 (1.04 g, 6.4 mmol) and collected as a white powder. The powder was then re-dissolved in acetonitrile and treated with 4 eq. tetrabutylammonium bromide (2.13 g, 6.4 mmol) to yield the title product **S5** (0.61 g, 66 %). ^{1}H NMR (500 MHz, DMSO) δ = 9.0 (dd, 4H), 8.44 (dd, 4H), 4.13 (t, 2H), 4.4 (s, 3H), 2.75 (t, 2H), 2.25 (s, 3H), 1.99 (m, 2H), 1.45 (m, 3H), 1.20 (m, 12H) ppm.

Synthesis of 1-methyl-4,4'-bipyridinium-dodecanethiol bisbromide **(2)**. 1-Methyl-4,4'-bipyridinium-dodecanethioacetate **S5** (130 mg, 0.188 mmol) was dissolved in methanol (1.5 mL). To this was added 1.25 M HCl in methanol (1.5 mL) and the mixture was refluxed for 5 h. The solvent was removed on the rotary evaporator and the crude product resuspended in H_2O (50 mL) before the addition of NH_4PF_6 (1.04 g, 6.4 mmol). The isolated white powder was then re-dissolved in acetonitrile and treated with 4 eq. tetrabutylammonium bromide (2.13 g, 6.4 mmol) to yield the title product **2** (0.97 g, 97 %). ^{1}H NMR (500 MHz, D_2O) δ = 8.97 (d, 4H), 8.91 (d, 4H), 8.39 (dd, 4H), 4.57, (t, 2H), 4.36 (s, 3H), 2.38 (t, 2H), 1.93 (t, 2H), 1.43 (m, 2H), 1.16 (m, 16H) ppm. ^{13}C NMR (125 MHz, D_2O) δ = 149.9, 149.7, 146.2, 145.3, 126.8, 126.5, 62.1, 48.2, 32.9, 30.4, 28.4, 28.4, 28.3, 28.2, 28.0, 27.8, 27.3, 25.0, 23.7 ppm. Mass Spec = 371.34 $[M^+ - 2Br^- - 1H]^+$.

Synthesis of Poly(2-hydroxyethyl acrylamide)-co-(naphtholtriazole acrylamide) (5)

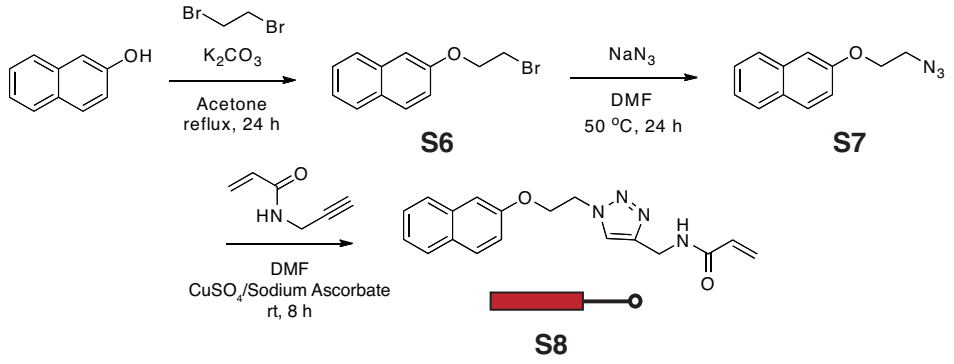

Figure S3: Synthetic scheme for the preparation of 2-naphthol functional monomer **(S8)**.

Synthesis of 2-(2-bromoethoxy)naphthalene **(S6)**. A solution of 2-naphthol (10.00 g, 69.4 mmol) in acetone (100 mL) was added to a flask containing 1,2-dibromoethane (65.20 g, 346.8 mmol) and stirred at reflux for 72 h. The reaction mixture was extracted into dichloromethane (2 x 400 mL)

from 1M HCl (400 mL). The combined organic extracts were washed with water (400 mL) and brine (400 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure yielding a brownish oil. The oil was dissolved in ethyl acetate (10 mL) and petroleum ether (40:60) was added to precipitate out the product, which was filtered and dried under vacuum to afford a white crystalline solid (11.67 g, 67 %). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.73 - 7.65 (3H, m, Np-*H*), 7.38 (1H, m, Np-*H*), 7.29 (1H, m, Np-*H*), 7.12-7.07 (2H, m, Np-*H*), 4.33 (2H, t, Np-O-CH_2-CH_2-Br), 3.66 (2H, t, Np-O-CH_2-CH_2-Br) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 156.5, 134.8, 130.1, 129.7, 128.1, 127.2, 126.9, 124.4, 119.2, 107.6, 68.3, 29.5 ppm. FT-IR (ATR) ν = 3055, 2946, 2862, 1628, 1591, 1456, 1424, 1381, 1353, 1256, 1216, 1178, 1073, 1013, 955 cm^{-1}.

*Synthesis of 2-(2-azidoethoxy)naphthalene***(S7)**. The naphthalene **S6** (5.00 g, 19.9 mmol) and sodium azide (1.42 g, 21.9 mmol) were dissolved in DMF (100 mL) and stirred at 50 ^{o}C for 24 h. The reaction mixture was then diluted with water (300 mL) and extracting with diethyl ether (3 x 100 mL). The combined organic extracts were washed with water (3 x 100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford a white crystalline solid (4.12 g, 97 %). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.85-7.80 (3H, m, Np-*H*), 7.45-7.48 (1H, m, Np-*H*), 7.34-7.37 (1H, m, Np-*H*), 7.17-7.19 (2H, m, Np-*H*), 4.28 -4.30 (2H, t, Np-O-CH_2-CH_2-N_3), 3.71-3.73 (2H, t, Np-O-CH_2-CH_2-N_3) ppm. ^{13}C-NMR ($CDCl_3$, 125 MHz) δ = 156.0, 134.3, 129.6, 128.7, 127.6, 126.8, 126.6, 123.9, 118.5, 107.1, 66.9, 49.6 ppm. FT-IR (ATR) ν = 3050, 2940, 2102, 1628, 1599, 1509, 1456, 1381, 1354, 1256, 1215, 1178, 1059, 1012, 963 cm^{-1}.

Synthesis of N-((1-(2-(naphthalen-2-yloxy)ethyl)-1H-1,2,3-triazol-4-yl)methyl)acrylamide (NpTAM) **(S8)**. The azide **S7** (5.00 g, 23.4 mmol), N-(prop-2-yn-1-yl)acrylamide (2.56 g, 23.4 mmol), and sodium ascorbate (0.46 g, 2.3 mmol) were combined in dry, degassed DMF (50 mL). $CuSO_4 \bullet 5H_2O$ (0.58 g, 2.3 mmol) was dissolved in dry, degassed DMF (10 mL) and added under N_2 to the re-

action vessel. The mixture was allowed to stir for 8 h. Saturated potassium iodide (100 mL) was then added and the mixture extracted with ethyl acetate (3 x 75 mL). The organic fractions were then combined and washed with saturated potassium iodide (3 x 75 mL). The organic layer was collected, dried over magnesium sulfate and the solvent was removed under reduced pressure to afford the title compound **S8** as a white solid (7.33 g, 97 %). ^{1}H-NMR (DMSO-d6, 400 MHz) δ = 8.62 (1H, t, -CO-N*H*-), 8.09 (1H, s, triazole-*H*), 7.82-7.71 (3H, m, Np-*H*), 7.48 (1H, m, Np-*H*), 7.38 (1H, m, Np-*H*), 7.24-7.16 (2H, m, Np-*H*), 6.31 (1H, m, acrylamide-*H*), 6.17 (1H, m, acrylamide-*H*), 5.61 (1H, m, acrylamide-*H*), 4.83 (2H, t, Np-O-CH_2-CH_2-triazole), 4.55 (2H, t, Np-O-CH_2-CH_2-triazole), 4.41 (2H, d, -CONH-CH_2-triazole) ppm. ^{13}C-NMR (DMSO-d6, 125 MHz) δ = 164.84, 156.07, 145.52, 134.50, 131.89, 129.78, 129.004, 127.88, 127.10, 126.84, 125.78, 124.18, 123.87, 118.84, 107.55, 66.60, 49.27, 34.51 ppm. FT-IR (ATR) ν = 3279 (s), 1650 (s), 1628, 1536 (s), 1465, 1392, 1255, 1234, 1217 (s), 1044 (s), 990, 951, and 835 (s) cm^{-1}. MS (M+/z): Calculated = 323.15, Found = 323.1534.

General synthesis of Np-functional polymer (5)

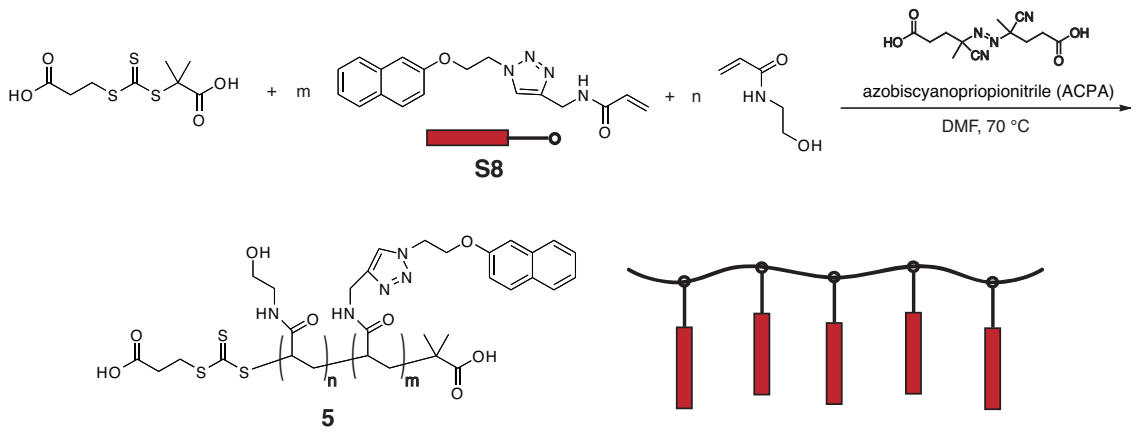

Figure S4: Synthetic scheme for preparation of Np functional polymer **(5)**.

Synthesis of Poly(2-hydroxyethyl acrylamide)-co-(naphtholtriazole acrylamide) **(5)**. NpAM **S8** (0.175 g, 0.54 mmol, M/CTA = 5), diacid (3.64 mg, 13.6 μmol), HEAm **6** (0.25 g, 2.17 mmol,

M/CTA = 160) and ACVA (0.4 mg, 1.4 μmol) were dissolved in DMF (1.5 mL) in a Schlenk tube and the solution was degassed by bubbling nitrogen for 30 min (overall M/CTA = 200, 20% Np loading). The Schlenk tube was then sealed and heated in an oil bath set to 70 ^{o}C for 12 h. Aliquots were removed periodically to analyze conversion. The reaction was quenched in liquid nitrogen and the polymer isolated by precipitation from cold diethyl ether, then filtering and the resulting solid dried under vacuum to afford the title compound **5** as a light yellow amorphous solid (0.40 g, 94 %). ^{1}H-NMR Spectroscopy (DMSO-d6, 500 MHz) δ = 8.36-7.86 (1H, br, triazole-*H*), 7.85-6.93 (7H, br, Np-*H*), 5.14-4.13 (6H, br, Np-O-CH_2-CH_2-triazole-CH_2- from NpTAM), 3.71-2.72 (15.6 H, br, HO-CH_2-CH_2- from comonomer), 2.28-0.80 (14.7H, br, polymer backbone). Overall P(HEAm$_{3.9}$-r-NpTAM$_1$) ppm. FT-IR (ATR) ν = 3280 (s, br), 2932 (s), 1640 (s), 1600, 1549 (s), 1511, 1439, 1256, 1216 (s), and 1056 (s) cm^{-1}. GPC (DMF): M$_n$ (PDI) = 24.6 kDa (1.31).

UV/visible Spectra of MV^{2+}-AuNP (3a)

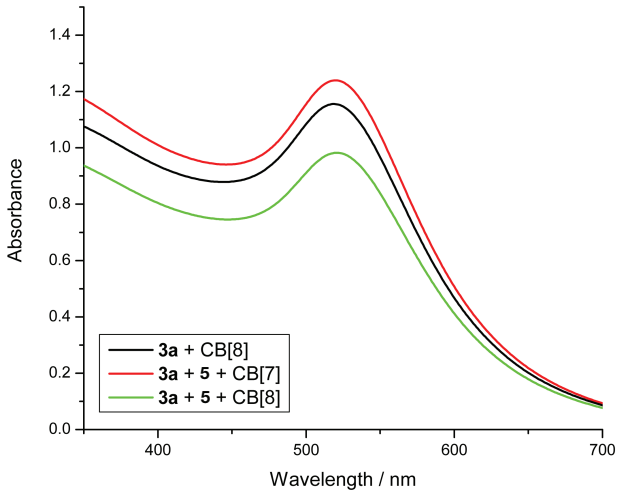

Figure S5: UV/vis spectra in water of MV^{2+}-AuNP **3a** in the presence of CB[8] (black), CB[7] + **5** (red) and CB[8] + **5** (green).

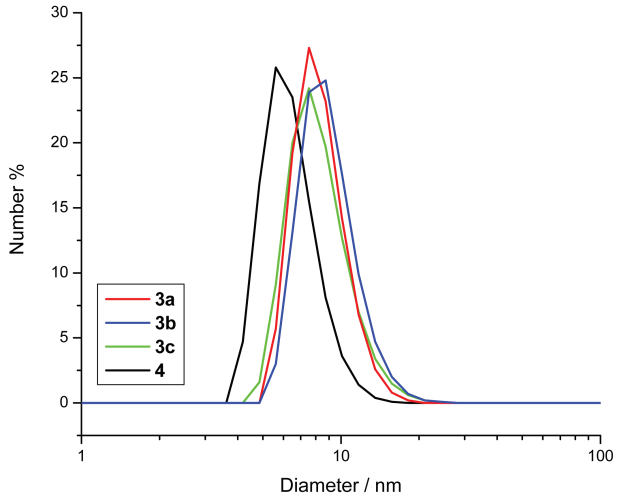

Figure S6: Dynamic light scattering (DLS) results showing the hydrodynamic diameter difference between MV^{2+}-AuNPs **(3a-c)** and EG_3-AuNP **4**.

DLS of AuNPs

Centrifugation Experiments

MV^{2+}-AuNP **3a-c** or EG_3-AuNP **4** (1 mL) was mixed with CB[n] (1 mL, 45 μmol) followed by 20 equivalents of polymer **5** (dialysed from DMF to water). After 24 h a portion of this mixture was transferred to the centrifuge and ultracentrifuge tubes and were photographed immediately upon centrifugation completion.

References

(1) Kim, J.; Jung, I. S.; Kim, S. Y.; Lee, E.; Kang, J. K.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2000**, *122*, 540–541.

(2) Jana, N. R.; Peng, X. *J, Am. Chem. Soc.* **2003**, *125*, 14280–14281.