Alignment of Gold Nanorods *via* Cucurbit[8]uril ternary complex formation

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Materials and general methods

^{1}H NMR (500 MHz) spectra were recorded using a Bruker Avance BB-ATM 500. 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 were 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. 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) characterization was carried out by a JEOL 2000FX TEM under an accelerating voltage of 200 kV. Samples were prepared by

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applying one drop of the as-prepared mixtures onto a Holey® carbon coated copper TEM grid (400 mesh).

General Synthetic Procedures

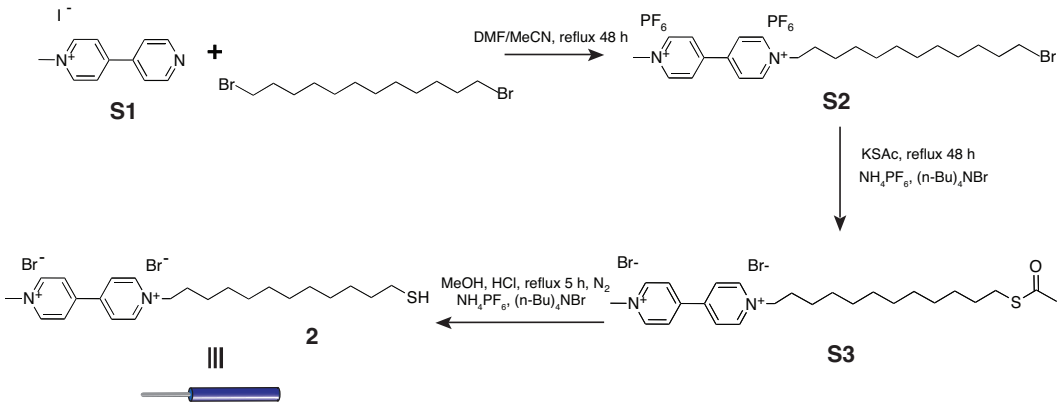

Figure S 1: Schematic representation for the synthesis of 1-methyl-4,4'-bipyridinium-dodecanethiol **(1)**.

*Synthesis of 1-Methyl-4,4'-bipyridinium iodide (***S1***)*. 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 **S1** was purified by recrystallization from methanol 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 (***S2***)*. 1-Methyl-4,4'-bipyridinium iodide **S1** (1.0 g, 33.5 mmol) and 1,12-dibromododecane (2.17 g, 6.60 mmol) were dissolved in a mixture of dimethylformamide (DMF) (6 mL) and acetonitrile (30 mL). The resultant mixture was refluxed for 48 h to afford an orange solid **S2** (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 (***S3)**. 12-Bromo-1-(methyl-4,4'-bipyridinium)-dodecane **S2** (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 (TBAB) (2.13 g, 6.4 mmol) to yield the title product **S3** (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 **(1)**. 1-Methyl-4,4'-bipyridinium-dodecanethioacetate **S3** (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 **1** (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. m/z = 371.34 $[M^+ - 2Br^- - 1H]^+$.

General synthesis of gold nanorods (AuNRs). Gold Nanorods (AuNRs) with an aspect ratio of 4 (40 nm x 10 nm) were prepared by a previously published seed-growth method as follows.[2] A 0.1 M cetyltrimethylammonium bromide (CTAB) stock solution was made by dissolving 4.05 g of CTAB in H_2O (111 mL) by heating. To prepare the seed solution; 250 μL of a $HAuCl_4$ solution (0.01 M) was added to 10 mL of the CTAB stock solution and stirred vigorously whilst being maintained at 24°C. To this solution was added 600 μL of freshly prepared, ice cold, $NaBH_4$ (0.01 M) rapidly. Vigorous stirring was maintained for 30 sec and then the solution was left at

24°C for 30 min. To prepare the growth solution; 2.5 mL of a $HAuCl_4$ (0.01 M) solution was added to 100 mL of the CTAB stock solution and mixed by swirling. To this mixture was added 600 μL of a $AgNO_3$ solution (0.01 M) and mixed by swirling. Ascorbic Acid was then added (300 μL, 0.1 M) and the mixture swirled. The colour of the solution changed from yellow to colourless. Finally 360 μL of the freshly prepared seed solution was added and the whole mixture swirled before incubating at 27°C for 22 hrs. Freshly prepared AuNRs were purified by centrifugation at 12,100 g and re-dispersion in 1 mM CTAB solution three times.

Synthesis of MV^{2+}-AuNRs (**2**). End-functional AuNRs were prepared by mixing **1** with freshly prepared AuNRs. AuNRs were first concentrated by centrifugation of 10 mL of the as synthesized AuNR solution and re-dispersing in 3 mL of H_2O. To a 10 mL solution of **1** (0.77 mg, $1.6x10^{-4}$mM) in H_2O was added 0.5 mL of the concentrated AuNRs. The mixture was left to incubate over 12 hrs and the resultant solution purified by three centrifuge wash cycles at 12,100 g to give **2**.

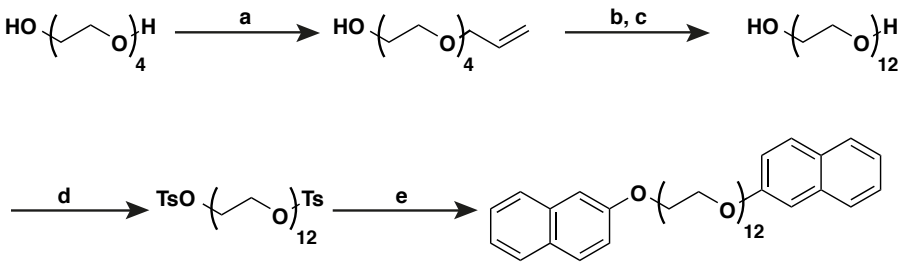

Figure S2: Schematic representation for the synthesis of **3a**. Conditions: **a)** allyl bromide, *t*BuOK, THF, rt, 24 hr; **b)** tetraethylene glycol di(*p*-toluenesulphonate), KOH, TBAB, toluene, 100 ^{o}C, 2 hr; **c)** 10% Pd/C, *cat.* TsOH·H_2O, MeOH/H_2O (25:1), reflux, N_2, 24 hr; **d)** TsCl, KI, Ag_2O, DCM, 0 ^{o}C→rt, 24 hr; **e)** 2-naphthol, K_2CO_3, DMF, reflux, N_2, 2 d. EG = ethylene glycol repeat unit.

*Synthesis of tetraethylene glycol mono(allyl ether) (***EG-All***).* To an anhydrous tetrahydrofuran (THF) solution of potassium tert-butoxide (6.1 g, 54.6 mmol), tetraethylene glycol (20 g, 0.1 mol) was added at room temperature. The resulting mixture was stirred for 0.5 hrs, after which allyl bromide (4.8 mL, 55.6 mmol) in THF was added over 1 hr. After being stirred at room temperature for 24 hrs, the reaction mixture was filtered though a celite plug, and the solvent was evaporated. The residue was then purified by flash column chromatography with EtOAc as the eluent, to yield **EG-All** as a colourless oil (7.7 g, 32%); ^{1}H NMR (500 MHz, $CDCl_3$): 3.52-3.67 (m, 16 H), 4.02 (d, J = 6 Hz, 2H), 5.18 (dd, J = 17, 2 Hz, 1H), 5.28 (dd, J = 17, 2 Hz, 1H), 5.85 (ddt, J = 17, 10, 6 Hz, 1 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): 61.6, 69.2, 70.3, 70.5, 70.5, 72.2, 72.3, 117.1, 134.3.

*Synthesis of dodeca(ethylene glycol) bis(allyl ether) (***12EG-All***).* Freshly powdered KOH (5.9 g, 0.11 mol) was added to a stirred suspension of monoallylated tetraethylene glycol (24.8 g, 0.1 mol), tetraethylene glycol di(*p*-toluenesulphonate) (25.2 g, 50.2 mmol) and TBAB (3.3 g, 10.1 mmol) in toluene (80 mL). The resulting reaction mixture was heated at 100 ^{o}C for 2 hrs and after this time the reaction was allowed to cool to room temperature, whereupon DCM was added to the reaction mixture. The resulting suspension was filtered and the solid was washed with DCM. The filtrate was then concentrated under reduced pressure, and the crude product was further purified by flash column chromatography with EtOAc as the eluent, to yield **12EG-All** as a viscous oil (5.6

g, 37%); ^{1}H NMR (500 MHz, $CDCl_3$): 3.23-3.66 (m, 48 H), 4.02 (d, J = 6 Hz, 4 H), 5.18 (dd, J = 17, 2 Hz, 2 H), 5.28 (dd, J = 17, 2 Hz, 2 H), 5.85 (ddt, J = 17, 10, 6 Hz, 2 H); ^{13}C NMR (125.7 MHz, $CDCl_3$): 69.7, 70.50, 70.66, 72.12, 117.0, 134.6; *m/z* (ESI) 649.17 (M^++ Na^+, 18%)

*Synthesis of dodeca(ethylene glycol) (***12EG***).* To a stirred solution of dodeca(ethylene glycol) bis(allyl ether) (13.4 g, 21.3 mmol) in MeOH-water (100:4 mL) was added tosic acid monohydrate (0.2 g, 1.1 mmol) and 10% Pd/C (10 g). The resulting reaction mixture was refluxed under an atmosphere of N_2 for 24 hrs, and, on cooling, filtered through a cotton plug. The filtrate was then concentrated under reduced pressure to afford **12EG** as a colourless oil (11.3 g, 97%); ^{1}H NMR (500 MHz, $CDCl_3$): 3.5-3.65 (46 H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$): 62.15, 69.08, 69.64, 70.75, 71.0, 71.15, 72.85.

*Synthesis of dodeca(ethylene glycol) bis(*p-*toluenesulphonate) (***12EG-OTs***).* Tosyl chloride (TsCl) (11.5 g, 60.4 mmol) was added to a mixture of dodecaethylene glycol (8.9 g, 15.1 mmol), Ag_2O (10.5 g, 45.3 mmol), and KI (10.0 g, 60.4 mmol) in dry DCM at 0 ^{o}C. The mixture was stirred for 30 min and then warmed to room temperature, stirring was then continued for another 24 hrs at room temperature. After washing with brine, the organic phase was dried over $MgSO_4$. Upon filtering and removing the solvent under reduced pressure, purification by flash column chromatography with DCM-methanol (35:1) afforded **12EG-OTs** as a colourless oil (4.0 g, 31%); ^{1}H NMR (500 MHz, $CDCl_3$): 2.32 (6 H, s), 3.5-3.65 (44 H, m), 4.12 (4 H, m), 7.24 (4 H, d, J = 8 Hz), 7.68 (4 H, d, J = 8 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$): 22.05, 62.15, 69.08, 69.64, 70.75, 71.0, 71.15, 72.85, 120.0, 128.23, 130.22, 133.45, 145.18.

*Synthesis of dodeca(ethylene glycol) bis(2-naphthol) (***3a***).* K_2CO_3 (2.59 g, 18.72 mmol) was added to dry DMF and sonicated for 40 min. 2-Naphthol (2.02 g, 14.04 mmol) was then added, the solution degassed with N_2, and then the mixture was heated to 80 ^{o}C. **12EG-OTs** was dissolved in dry DMF (25 mL) and added to the mixture via syringe over 1 hr, after which the orange-coloured

reaction mixture was heated at 100 °C. After 40 hrs, the mixture was allowed to cool to room temperature, and the dark orange mixture was filtered and the solvent removed under reduced pressure. The resulting dark brown oil was dissolved in DCM and washed with 10% aqueous NaOH solution (4 x 80 mL), and the organic extracts were combined and washed with KBr brine (2 x 100 mL). The resultant green solution was dried over $MgSO_4$, and the solvent removed under reduced pressure to yield a crude brown oil, which was further purified twice by flash chromatography using $CHCl_3$-methanol (70:1) as the eluent to yield **3a** as a light brown oil (410 mg, 11%); ν_{max}/cm^{-1} 2868.85 (s), 1628.58, 1600.11, 1510.56, 1454.27, 1390.08, 1349.43, 1258.33, 1217.21, 1183.47, 1101 (vs), 969.55, 947.13, 839.29, 813.41, 749.25, 721.36; ^{1}H NMR (500 MHz, $CDCl_3$): 3.5-3.7 (40 H, m), 3.82 (4 H, m), 4.17 (4 H, m), 7.05-7.1 (4 H, m), 7.25 (2 H, t, *J* 12 Hz), 7.35 (2 H, t, *J* 12 Hz), 7.65 (6 H, m); ^{13}C NMR (125.7 MHz, $CDCl_3$): 62.2, 67.9, 70.1, 71, 71.3, 72.9, 107.2, 119.5, 124.1, 126.8, 127.2, 128.1, 129.5, 129.8, 135, 157.2; *m/z* (+ESI) 821.4094 ($M^+ + Na^+$). Found: C, 64.83; H, 7.73. $C_{44}H_{62}O_{13}$ requires C, 66.15; H, 7.52.

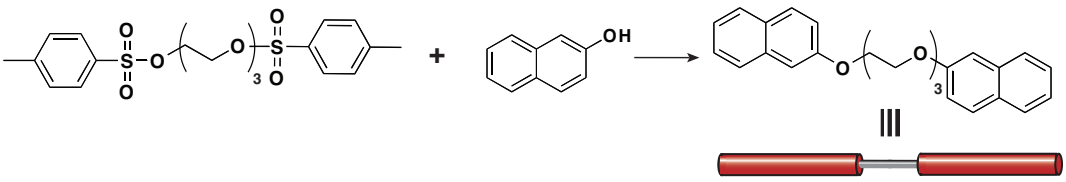

Figure S3: Synthesis of tri(ethylene glycol) bis(2-naphthol) (**3b**)

Synthesis of **3b**: 2-Naphthol (2.8 g, 19.2 mmol), triethylene glycol di(*p*-toluenesulphonate) (4.8 g, 8.7 mmol), and anhydrous K_2CO_3 (2.9 g, 2.1 mmol) were refluxed in dry MeCN (250 mL) under N_2 for 48 hrs. The crude mixture was filtered, and the light brown solid was dried under reduced pressure, and redissolved in DCM. The solution was washed with brine, and the organic phase dried over $MgSO_4$. Upon filtration, the crude green liquid was dried under reduced pressure, and recrystallized from a DCM-hexane mixture affording light brown crystals (1.9 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): 3.74 (4 H, s), 3.87 (4 H, t, *J* = 4 Hz), 4.18 (4 H, t, *J* = 4 Hz), 7.06-7.11 (4 H,

m), 7.25 (2 H, t, J = 12 Hz), 7.35 (2 H, t, J = 12 Hz), 7.61-7.69 ppm (6 H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$): 67.9, 70.2, 71.4, 107.1, 119.4, 124, 126.4, 126.7, 127.2, 129.8 ppm; IR (FTIR): $\bar{\nu}$ = 2899.95 (s), 1625.51, 1597.99, 1511.75, 1469.24, 1449.74, 1379.97, 1253.83, 1214.60, 1131.33, 1051.06, 966.61, 930.45, 878.14, 814.63, 740.72; Elemental analysis calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51; found: C, 77.63; H, 6.54. *m/z* (+ESI) 425.17 $(M + Na)^+$.

MV^{2+}-AuNRs UV-Vis Spectrum

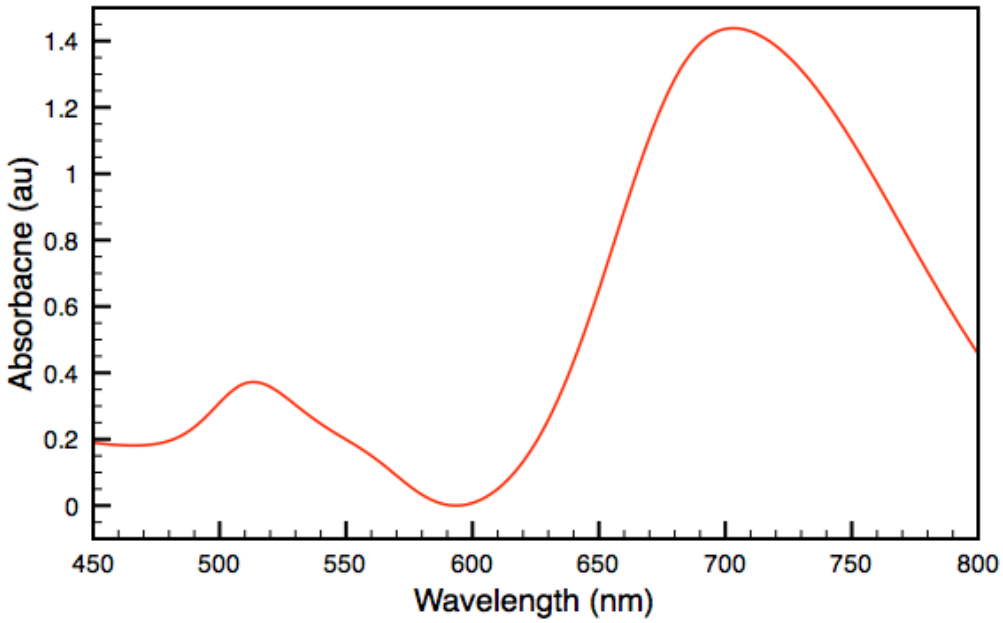

Figure S4: UV-Vis spectrum of MV^{2+}-AuNRs

Representative TEM images

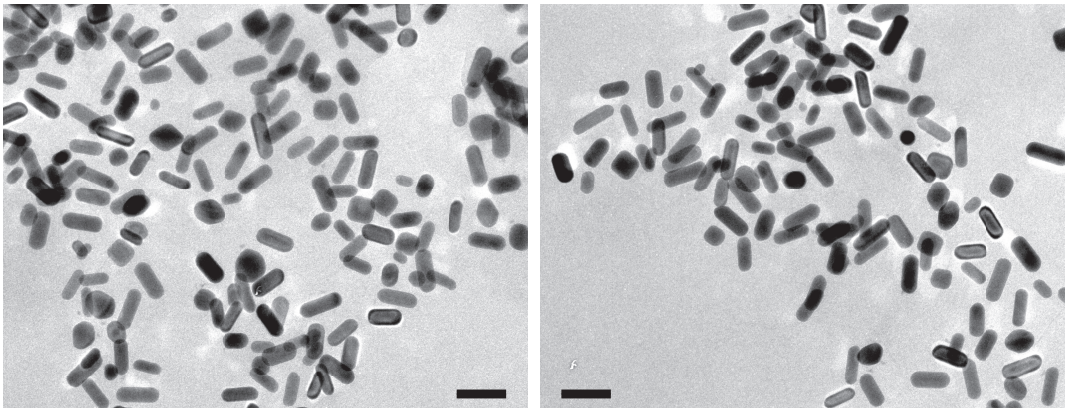

Figure S5: Representative TEM images, of the control experiment, MV^{2+}-AuNRs (**2**) and Np-Dimer (**3b**) in the presence of CB[7]. No alignment is observed due to CB[7] having a smaller annulus incapable of ternary complex formation. Scale bars = 50 nm.

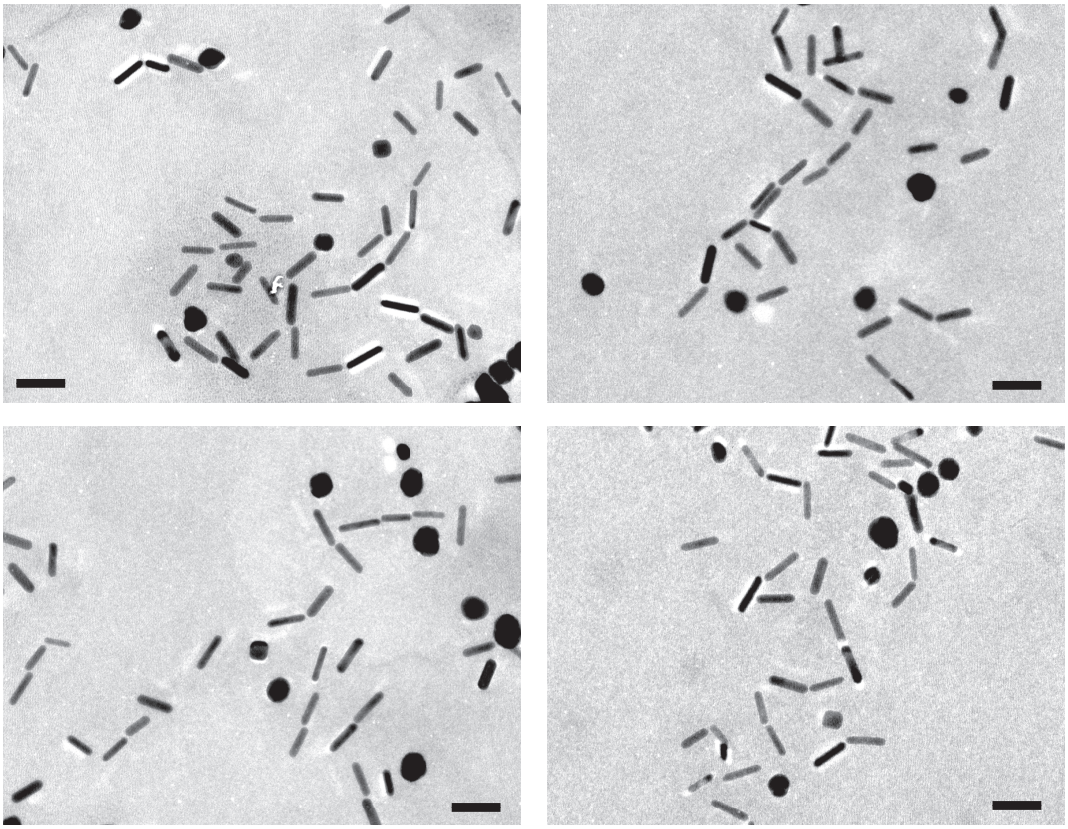

Figure S6: Representative TEM images of MV^{2+}-AuNRs (**2**) and Np-Dimer (**3b**) in the presence of CB[8]. Alignment of AuNRs is observed due to the formation of CB[8] ternary complexes. Scale bars = 50 nm.

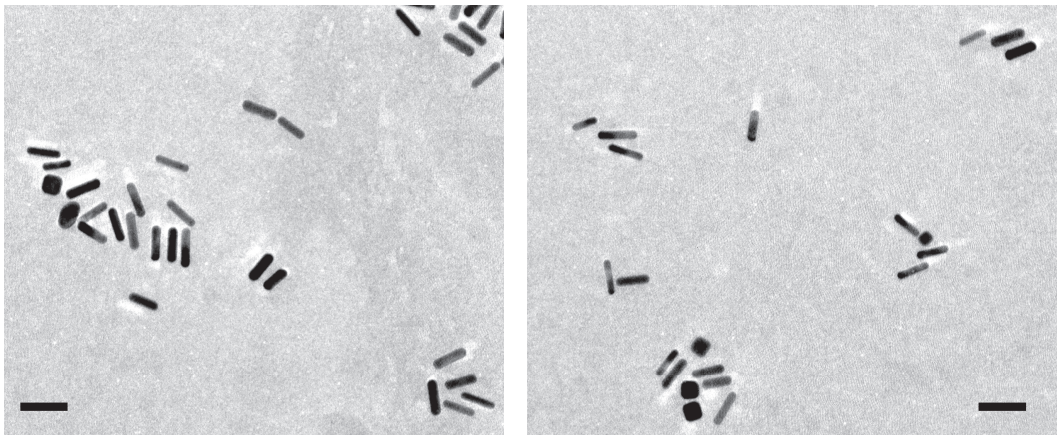

Figure S7: Representative TEM images of, the control experiment, MV^{2+}-AuNRs (**2**), Np-Dimer (**3b**) with CB[8] in the presence of **4**. **4** occupies the CB[8] cavity hindering the formation of a ternary complex. Scale bars = 50 nm.

Table S1: Analysis of TEM images of **2** with **3b** in the presence of different CB analogues and in the presence of an external stimulus.

Sample	Aligned #	Dimers % (#)	Trimers % (#)	Tetramers % (#)	≥Pentamers % (#)
CB[8] [a]	741	69.24 (520)	17.98 (135)	9.05 (68)	3.73 (18)
CB[7] [b]	60	100 (60)	~	~	~
CB[8] + 4 [c]	37	91.89 (34)	8.11 (3)	~	~

[a] Data obtained by counting 1418 individual AuNRs. [b] Data obtained by counting 947 individual AuNRs. [c] Data obtained by counting 384 individual AuNRs.

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) Nie,; Fava, D.; Rubinstein, M.; Kumacheva, E. *J. Am. Chem. Soc.* **2008**, *130*, 3683–3689.