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**Electronic Supporting Information for:**

# Self Assembly of plasmonic core-satellite nano-assemblies mediated by hyperbranched polymer linkers

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## Synthesis of the hyperbranched polymer

HBPs were prepared by polymerising polyethylene glycol monomethylether methacrylate (PEGMA) (monomer), with ethylene glycol dimethacrylate (EGDMA) (branching agent) which was initiated by azobisisobutyronitrile (AIBN), in the presence of dimethyl (prop-2-ynyl propanoate)yl butyl trithiocarbonate as the RAFT, where dioxane was used as a solvent. The reaction mixture was degassed with argon and the polymerization was carried out at 75 ºC for 24 h. A ratio of [M]/[RAFT]/[EGDMA]/[AIBN] = 20/1/1/0.1 was employed. The polymerization reached 96% conversion, as determined by Raman spectroscopy where the consumption of the double bonds during the reaction was monitored. The polymer was then precipitated in n-hexane and its aqueous solution dialyzed for 5 days against water. The dialyzed samples were freeze dried for 2 days. They were further dried over magnesium sulphate and finally overnight in oven to remove the last traces of water. The samples were analyzed by $^1$H NMR and GPC-MALLS. The $M_n$ of the branch was calculated by the ratio of methylene groups of p(PEGMA) to that of methylene group adjacent to the terminal alkyne end group i.e., the ratio of peak integrals at 4.0 ppm ($CH_2CH_2O$) to 4.6 ppm ($CH_2CCH$) from $^1$H NMR. Thus, calculating the number of branches from the ratio of GPC-MALLS $M_n$ and $M_n$ of the branch from NMR, detailed calculation by Thurecht and co-workers.[1,2]

**Preparation of hybrid gold nano-assemblies for different HBP coverage.** 50 µL of the aqueous polymer solution of various concentrations in the range of 0-1.5 µM, was added with stirring to 3 mL of 0.11 nM citrate stabilized gold NPs with average diameters of 48 nm. The mixture was further stirred for at least 3 minutes. The colloid was left standing overnight to allow formation of gold NPs coated with the linker polymer, referred to as the “intermediate hybrids”, having net polymer concentrations of 0-20 nM. By varying the amount of polymer added, a series of “intermediate hybrids” were prepared that constituted gold NPs with varying degrees of polymer coverage from 0-100%. The further steps were carried on as described in the experimental section in the main text.

**Effect of linker HBP coverage on the formation of core-satellite nano-assemblies.** We have recently reported that the linker HBP concentration, hence the HBP coverage, plays an essential role in the formation of dimers and higher order (i.e., number of NPs per assembly) nano-assemblies for equimolar ratios of NPs.[3] Hence, a series of HBP coverage with an excess of satellite to core NPs (mole ratio of 30) was investigated, to understand its importance in the core-satellite assembly formation. Core gold NPs (~48 nm) were coated with HBP to give surface coverage of 0% - 100%, forming the "intermediate hybrids". The polymer coverage was calculated based on the surface area of core NPs, the hydrodynamic size of the HBP linker and their relative concentrations (detailed calculation has been provided below). The unbound polymer was removed by centrifugation and then the NPs were re-suspended to give concentrations of ~100 nM, after which a 30 mole excess of citrate stabilized satellite gold NPs (~15 nm) were added. After allowing 3-4 hours for the self-assembly process to reach equilibrium, the resulting nano-assemblies were centrifuged to remove unattached satellites.

## <u>Calculation for HBP coverage</u>

**Average number of HBP macromolecules required for a theoretical coverage of 100% for 48 nm diameter core NPs.**

$$= \frac{surface\ area\ of\ core\ at\ distance\ of\ radius\ of\ HBP}{area\ covered\ by\ 1\ HBP} * packing\ factor$$

$$= \frac{10032.79}{56.76} * .634$$

$$= 112$$

$$\textbf{No. of HBP macromolecules per NP} = \frac{net\ HBP\ conecentration\ (nM)}{net\ gold\ NP\ concentration\ (nM)}$$

$$HBP\ stoichiometry\ for\ 100\%\ coverage = \frac{No.\ of\ HBP\ macromolecules\ per\ NP}{No.\ of\ HBP\ macromolecules\ per\ NP\ for\ 100\%\ coverage}$$

$$= \frac{No.\ of\ HBP\ macromolecules\ per\ NP}{112}$$

| **Net HBP concentration (nM)** | **Number of HBP macromolecules per NP** | **HBP stoichiometry** |
|---|---|---|
| 4.979 | 45.27 | 0.4 |
| 9.7889 | 88.99 | 0.8 |
| 14.597 | 132.70 | 1.2 |
| 19.57 | 177.97 | 1.6 |

The 0% HBP coverage representing citrate stabilized core gold NPs served as a reference. The formation of nano-assemblies was followed by monitoring the qualitative color change (pinkish to purplish or bluish) and quantitative red-shift in SPR of the colloid. A higher SPR shift demonstrates higher aggregation and is a result of an increase in satellites per core NP, in addition to, the reduction in core-satellite inter-particle distance.[4, 5] Figure S1 shows that with increasing coverage of the HBP, a secondary peak at 635 nm was observed to increase in intensity relative to the primary peak at 535 nm. The secondary SPR peak confirms aggregation of the NPs into assemblies and the increase in relative SPR intensities indicates that a higher degree of aggregation occurs with increasing polymer coverage.

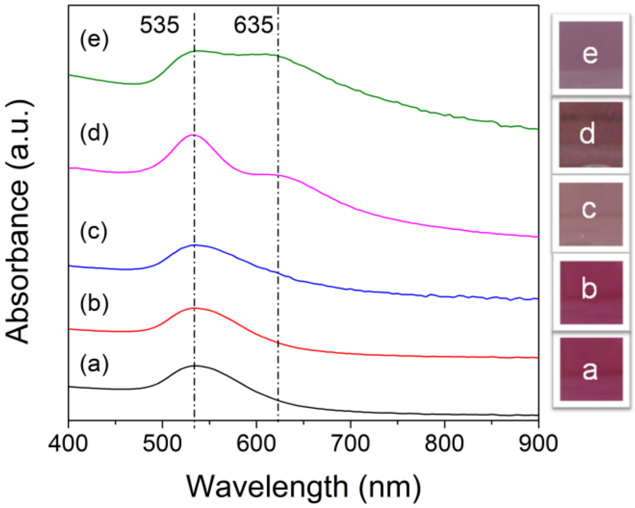

**Figure S1**. Visible spectra of core-satellite nano-assemblies prepared using HBP stoichiometries relative to 100% coverage of (a) 0, (b) 0.4, (c) 0.8, (d) 1.2 and (e) 1.6 with satellite-core mole ratio of 30. The colloid color is shown in the inset. The spectra are offset by 0.25 a.u.

SERS provides useful information with respect to the formation of nano-assemblies and has been extensively utilized by researchers as a means to characterize the extent of aggregation and nano-assembly formation. It has been well documented in literature that higher Raman signal intensity is obtained with formation of higher order assemblies.[6] The HBPs occupying the hot-spots provided us with a better understanding of the nano-assemblies and hot-spot density. A typical SERS spectrum of HBP within nano-assemblies is shown in Figure S3. The peak at 1380 $cm^{-1}$

was assigned to δ($CH_3$) from the p(PEGMA), while the peaks at 1022 cm$^{-1}$ and 800 cm$^{-1}$ were assigned to the υ(C=S) and υ(C−S) modes respectively which can be attributed to the trithiocarbonate end groups. Although the concentration of the HBP on the core NP is low (~10$^{-9}$ M) and is not sufficient to provide a good SERS at single gold NP surfaces, prominent signature peaks are observed with the formed nano-assemblies. As shown in Figure S2, we observed that the SERS intensity at 1380 cm$^{-1}$ increases with the increase in HBP coverage. This therefore confirms, in addition to the relative SPR intensities, that higher HBP coverage results in the formation of higher order assemblies with increased satellite density, thus providing higher SERS activity.

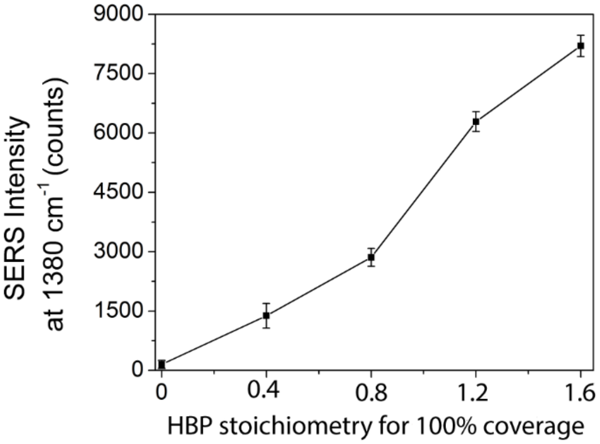

**Figure S2**. Plot of SERS intensity at 1380 cm$^{-1}$ due to linker HBP with respect to HBP coverage of intermediate hybrids of core NPs.

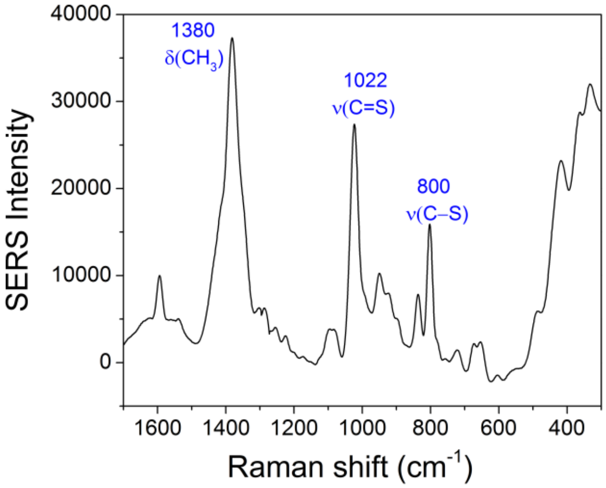

**Figure S3**. SERS spectrum of HBP linker in core-satellite assemblies.

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