Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Plasmonic multi-shell nanomatryushka particles as highly tunable SERS tags with built-in reporters

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Experiment section

All materials were used as received without any further purification. Chloroauric chloride ($HAuCl_4 \cdot 4H_2O$), 4-Methylbenzenethiol (4-MBT, 99%) and ascorbic acid were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Sodium borohydride ($NaBH_4$, 98%) was obtained from J&K Chemical Ltd (Shanghai, China). 1, 4-Benzenedithiol (BDT, 98%) was received from TCI (Tokyo, Japan). Cetyltrimethylammonium chloride (CTAC, 97%) were purchased from Aladdin (China). Nanopure water (>18.0 MΩ) was used for all experiments.

SERS spectra were characterized on a 785nm confocal Raman microscope through a 10× objective (N.A. =0.3) with 16 mW power and 5 s integration time. TEM images were collected from a JEM-2100F Transmission Electron Microscopy (JEOL, Japan) operated at 200 kV. UV-Vis spectra were collected on a UV1900 UV-Vis spectrophotometer (Aucybest, China)

Synthesis of Au cores. Au cores were synthesized using a seed-mediated process. Typically, seed solution was firstly prepared by vigorous mixing of 5 mL of aqueous CTAC solution (0.2 M), 4.5 mL water and 515 µL of $HAuCl_4$ (4.86 mM) with 450 µL of $NaBH_4$ solution (0.02 M). The seed solution was allowed to stay at 30° C for 1 hour in a hot bath and further diluted by 10 times. Then 10 mL of CTAC solution (0.1 M) was mixed with 515 µL of $HAuCl_4$ (4.86 mM) and 75 µL of ascorbic acid (0.04 M). 100 µL of diluted seed solution was added into the solution under sonication and kept undisturbed under darkness for two days to obtain highly uniform spherical nanoparticles. The size of the Au cores obtained at this stage was about 22 nm. The concentration of Au cores were 1 nM according to the 450 nm absorbance in the UV-Vis spectrum.

Synthesis of nanomatryoshka particles with single gold shell. The obtained CTAC-capped Au cores (10 mL) were mixed with 400 µL of Raman reporter (2 mM) under vigorous sonication for 20 minutes. These modified cores were then washed for three times by centrifuge at 10000 rpm for 10 minutes to remove excess reagent, and further dispersed in 5 mL aqueous CTAC solution (0.1 M).

The Au NMs with single gold shell was prepared by adding 120 µL of Raman reporter modified core solution into the mixed growth solution of 2 mL CTAC solution (0.1 M), 100 µL of ascorbic acid (0.04 M), and 100 µL of $HAuCl_4$ (4.86 mM) under vigorous sonication. Finally, the gold particles were stored undisturbed under darkness for 120 days.

Synthesis of nanomatryoshka particles with double gold shells. The obtained Au NMs with single gold shell (6 mL) were mixed with 400 μL of Raman reporter (2 mM) under vigorous sonication for 20 minutes. The samples were then washed for three times by centrifuge at 10000 rpm for 10 minutes to remove excess reagent, and further dispersed in 3 mL aqueous CTAC solution (0.1 M).

The Au NMs with double gold shell was prepared by adding 1 mL of Raman dye modified Au NMs with single gold shell into the growth solution of 10 mL CTAC solution (0.1 M), 1100 μL of ascorbic acid (0.04 M), and 550 μL of $HAuCl_4$ (4.86 mM) under vigorous sonication. Finally, the gold particles were stored undisturbed under darkness for 120 days.

Synthesis of nanomatryoshka particles with triple gold shells. The obtained Au NMs with single gold shell (6 mL) were mixed with 400 μL of Raman reporter (2 mM) under vigorous sonication for 20 minutes. The samples were then washed for three times by centrifuge at 10000 rpm for 10 minutes to remove excess reagent, and further dispersed in 3 mL aqueous CTAC solution (0.1 M).

The Au NMs with triple gold shell was prepared by adding 1 mL of Raman dye modified Au NMs with double gold shell into the growth solution of 10 mL CTAC solution (0.1 M), 1100 μL of ascorbic acid (0.04 M), and 550 μL of $HAuCl_4$ (4.86 mM) under vigorous sonication. Finally, the gold particles were stored undisturbed under darkness for 120 days.

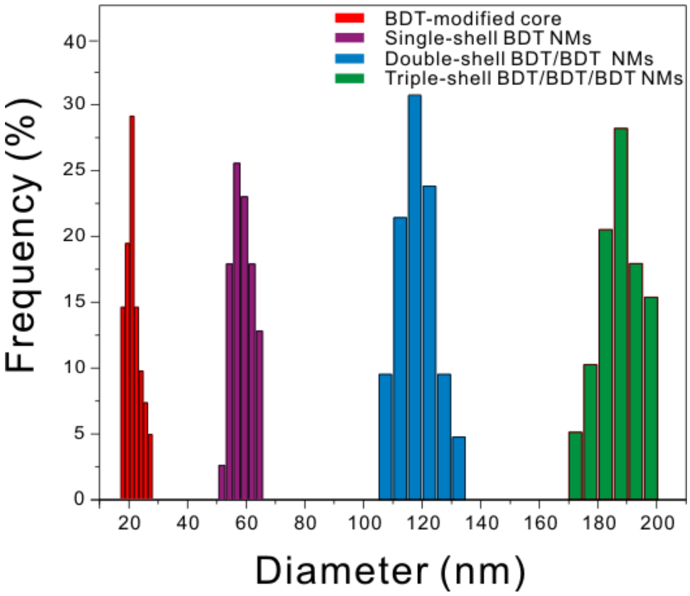

Figure S1. Size distribution of BDT-modified cores (red), single-shell BDT NMs (purple), double-shell BDT/BDT NMs (blue) and triple-shell BDT/BDT/BDT NMs (green).

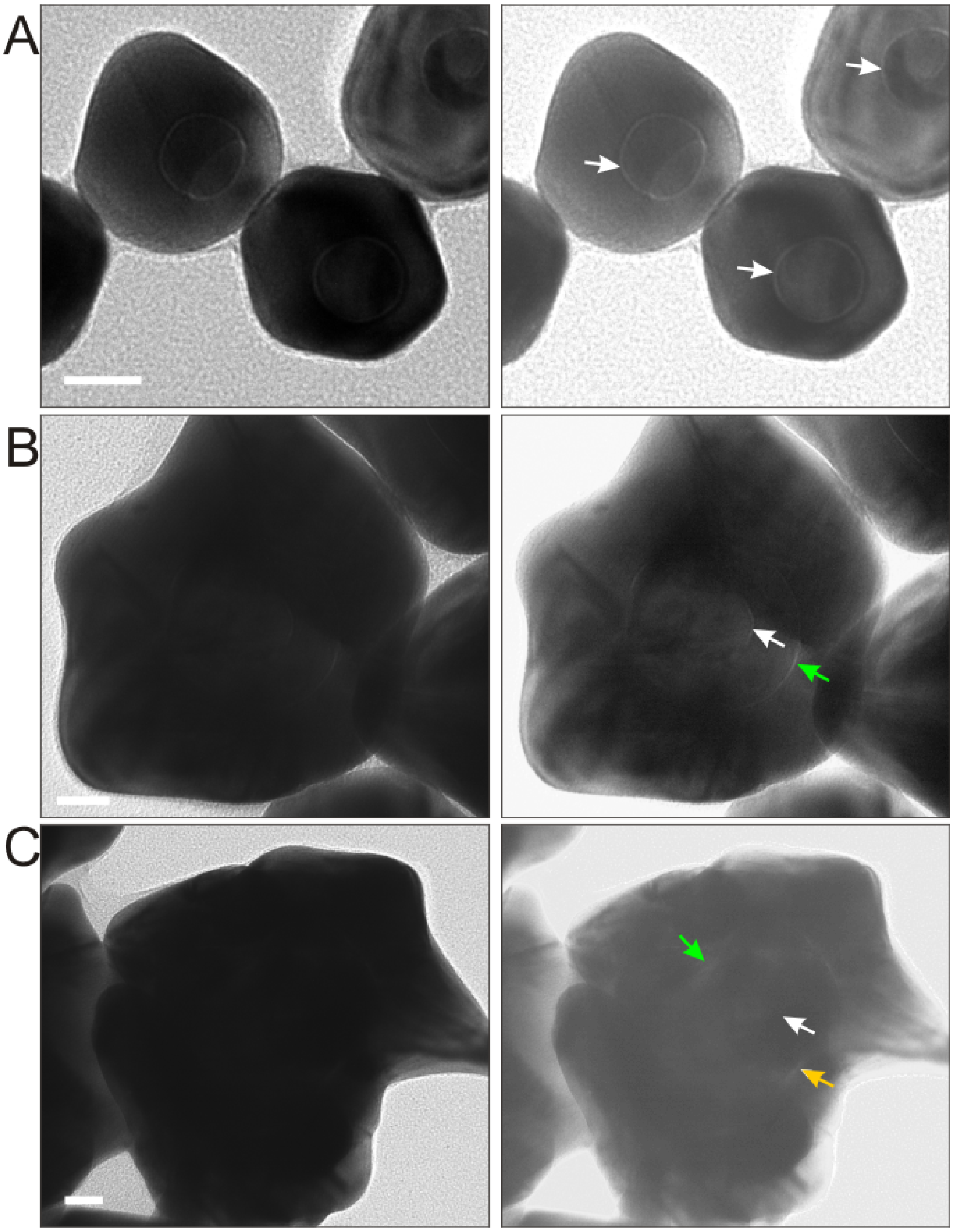

Figure S2. The original HRTEM images (left column) and images with brightness and contrast adjustment (right column) of (A) BDT single-shell NMs, (B) BDT/BDT double-shell NMs and (C) BDT/BDT/BDT triple-shell NMs. The first, second and third gap layer are indicated by white, green and yellow arrows respectively. All scale bars are 20 nm.

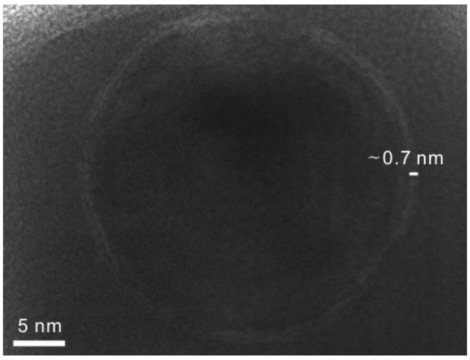

Figure S3. HRTEM images of single-shell BDT NMs revealing the uniform gap with a majority of ~0.7 nm.

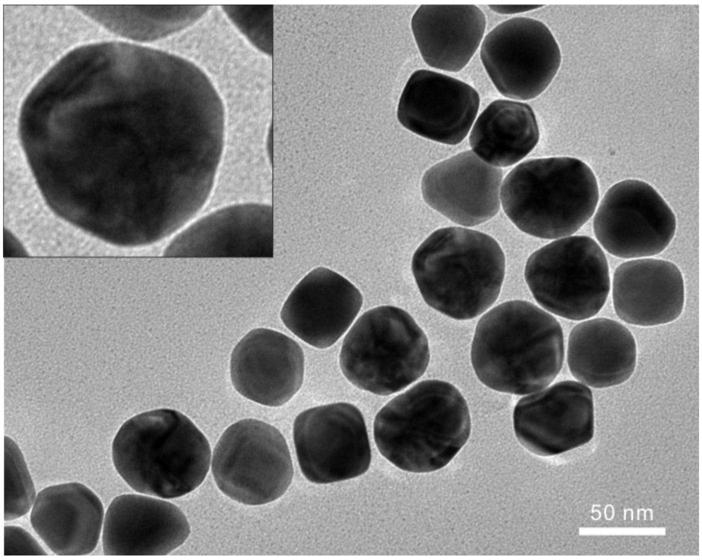

Figure S4. TEM images of gold single-shell NMs without built-in Raman molecules, i.e. only CTAC-stabilized gold nanoparticles serving as seeds for shell formation. No gap structure was observed.

Table S1. Data set for calculating the SERS intensity ratio from the four samples in Figure 1.

Sample	BDT-modified Core	Single-shell NM	Double-shell NM	Triple-shell NM
As-synthesized concentration (nM)	1	0.1	0.015	0.002
Concentrated solutions for SERS measurements (nM)	48	0.2	0.02	0.02
SERS intensity (counts at 1555 cm^{-1})	186	1846	4060	3816

$I_{Triple\text{-}shell\ NM} = (0.02/0.02\times3816/4060) \times I_{Double\text{-}shell\ NM} = 0.94\times I_{Double\text{-}shell\ NM}$

$I_{Double\text{-}shell\ NM} = (0.2/0.02\times4060/1846) \times I_{Single\text{-}shell\ NM} = 22 \times I_{Single\text{-}shell\ NM}$

$I_{Single\text{-}shell\ NM} = (48/0.2\times1846/186) \times I_{BDT\text{-}modified\ Core} = 2.38 \times10^3 \times I_{BDT\text{-}modified\ Core}$

Note: SERS spectra of the four samples were collected with different particle concentrations, and then normalized to the same concentration in Figure 3.

Table S2. Data set for calculating the SERS intensity ratio from the BDT/BDT and BDT/MBT double-shell NMs samples in Figure 4.

Sample	BDT/BDT-NM	BDT/MBT-NM
As-synthesized concentration (nM)	0.015	0.015
Concentrated solutions for SERS measurements (nM)	0.02	0.02
SERS intensity (counts at 1555 cm^{-1})	4060	227

$I_{second\ BDT\ layer}$ =(4060-227)/227 × $I_{first\ BDT\ layer}$ = 16.9 × $I_{first\ BDT\ laye}$

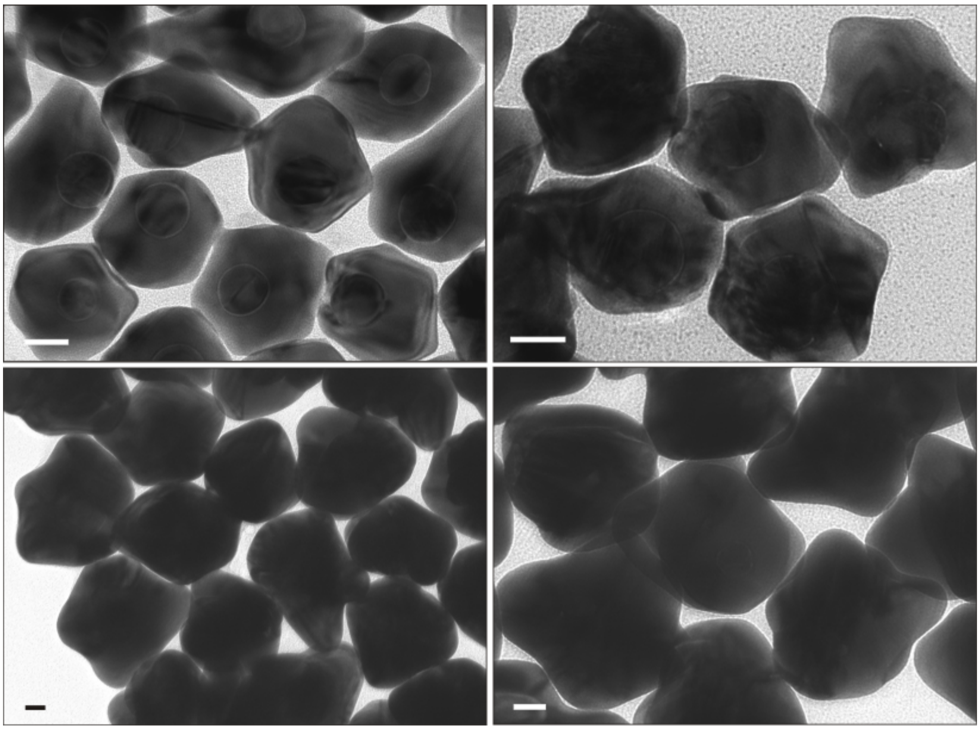

Figure S5. Many-particle TEM images in Figure 4: (a) single-shell BDT NMs, (b) single-shell MBT NMs, (c) double-shell BDT/BDT NMs and (d) double-shell BDT/MBT NMs. All scale bars are 20 nm.

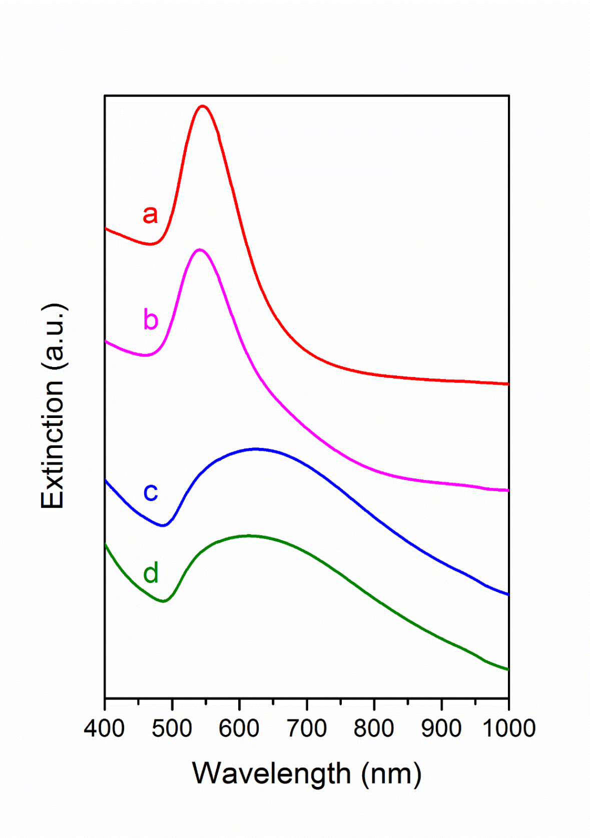

Figure S6. UV-Vis spectra of: (a) single-shell BDT NMs, (b) single-shell MBT NMs, (c) double-shell BDT/BDT NMs and (d) double-shell BDT/MBT NMs.

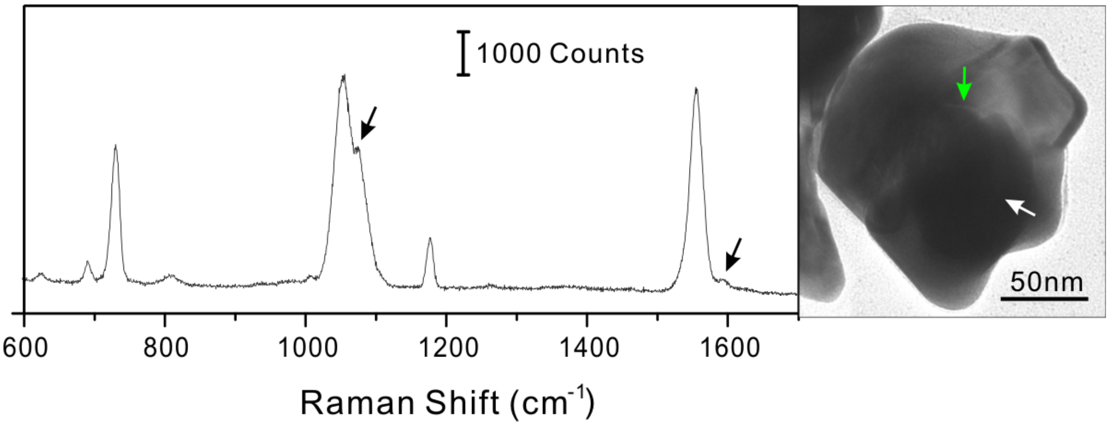

Figure S7. Raman spectrum and TEM images of double-shell MBT/BDT NMs. In left panel, the arrows indicate two weak characteristics peaks of MBT. In right panel, the first and second gaps are shown by white and green arrows, respectively.

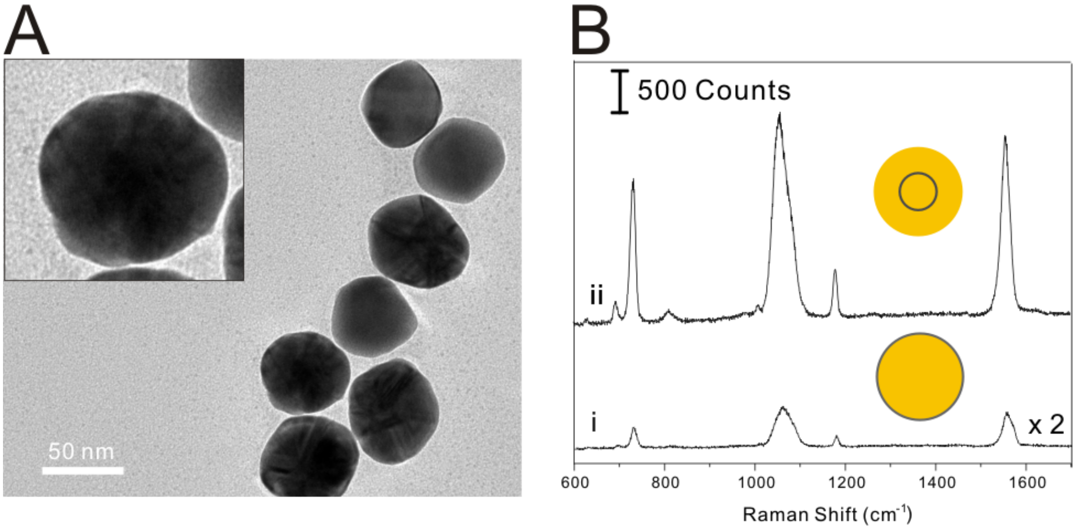

Figure S8. (A) TEM images of BDT-modified Au core with the size of 57.3±2.9 nm. (B) The Raman spectrum of (i) BDT-modified Au core with the size of 57.3±2.9 nm. (ii) single-shell BDT NMs with the size of 58.9 ± 3.1 nm.

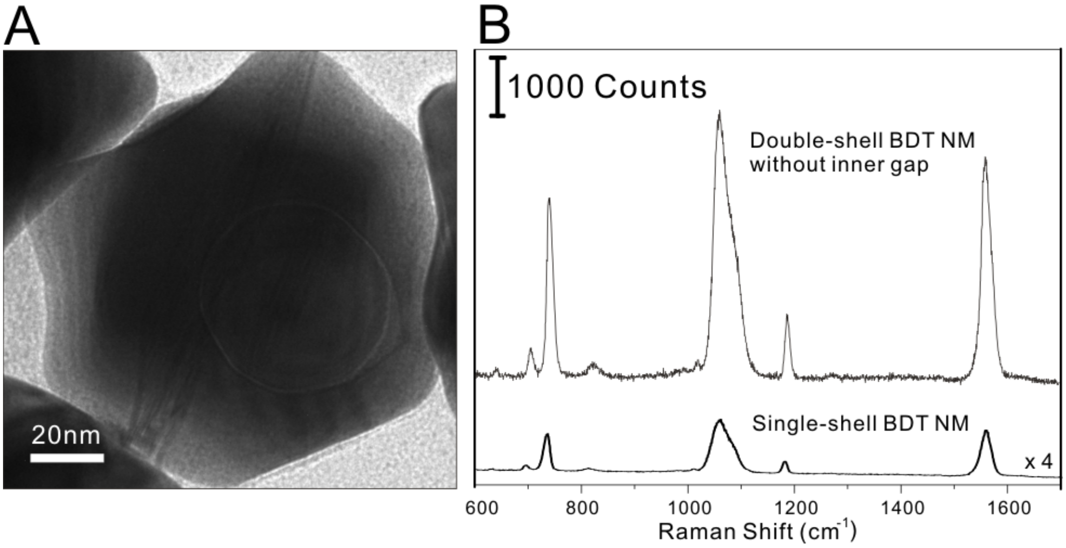

Figure S9. (A) TEM images of double-shell BDT NMs without inner gap layer. (B) The SERS spectrum of double-shell BDT NMs without inner gap layer and single-shell BDT NMs.