Supplementary information for

"Exploring the coherent interaction in a hybrid system of hollow gold nanoprism and cyanine dye J-aggregates: Role of plasmon-hybridization mediated local electric field enhancement"

Kamalika Das,[a] Bidhan Hazra[a] and Manabendra Chandra [a*]

Department of Chemistry

Indian Institute of Technology, Kanpur, Uttar Pradesh-208016, India

*Corresponding author, Email: mchandra@iitk.ac.in

Table of Contents

1. Synthesis of Hollow gold nanoprisms:

Synthesis of hollow gold nanoprisms (HGN) was carried out in two steps using a protocol described in previous reports.[S1,S2] First step is the formation of silver nano-seeds of 4-5 nm diameter. In the second step HGNs are produced *via* sacrificial galvanic replacement method. Stepwise details are given below

Step I: Preparation of silver nanoseed. An aqueous solution of 0.5 mL of 0.01 M $AgNO_3$ was added drop wise into 20 mL of Milli-Q (18 MΩ-cm) water, kept under constant stirring. To this solution, 0.2ml of 0.025 M trisodium citrate (TSC) was gradually added. Next 60 µL of 0.01 M ice cold fresh stock of $NaBH_4$ was added drop by drop with stirring and the stirring was stopped within 10 sec. The color of the solution gradually became transparent yellow. The solution was kept undisturbed in dark for 4 hour before using it as the seed for the growth process.

Step II: Growth of HGNs. 2 ml of 0.01 M $AgNO_3$solution was added drop wise to a 45mL ~0.03 M aqueous solution of CTAB under stirring condition. Next, 300 µL of 10^{-2} M $HAuCl_4$ solution was added drop by drop. The color of the solution turned yellow-brown. This was followed by drop-wise addition of 320 µL of 0.1 M ascorbic acid, making the solution colorless. To this colorless solution, another 300 µL of 10^{-2} M $HAuCl_4$ and 320 µL of 10^{-1} M of ascorbic acid (AA) were added in a quick succession. Immediately after this second addition, different amount of seed solutions were added to the growth solution. Volumes of seed solution added varied from 100 µl to 4 ml and the HGNs are designated as HGN I (4 ml seed), HGN II (3 ml seed), HGN III (2.5 ml seed), HGN IV (2 ml seed), HGN V (1.5 ml seed), HGN VI (1 ml seed), HGN VII (500 µl seed), HGN VIII (250 µl seed), HGN IX (100 µl seed).

2. Normalized absorption spectra of the HGNs

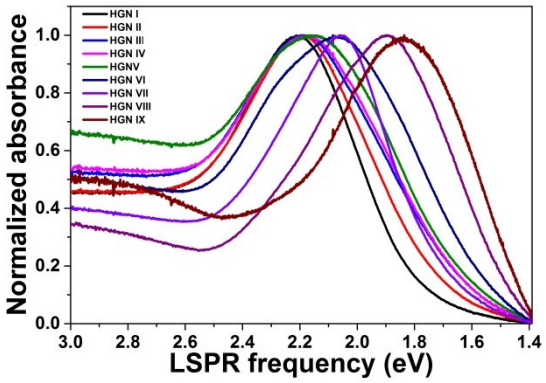

Figure S1. Normalized absorption spectra of the HGNs

3. Transmission electron micrograph of HGN-V

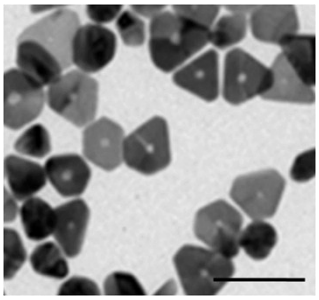

Figure S2. Transmission electron micrograph of HGN-V is shown. Scale bar corresponds to 100 nm.

4. Preparation of sample for Surface enhanced Raman scattering (SERS) measurements

A 400 µl aliquot of 21.4 µM pseudoisocyanine (PIC) iodide dye was added to 1.6 ml of as prepared HGN III (2.5ml seed) and mixed well. This solution was kept undisturbed in dark for 72 hrs. No aggregation of the HGNs was caused by addition of PIC as evident from the fact that we did not observe any shift in the LSPR spectra upon the addition of the dye. After aging for 72 hours, the HGN-PIC mixture was centrifuged twice at 8000 rpm to remove excess PIC dye molecules which were not bound to the surface of the HGN and the sediment was redispersed in water. The final sample was prepared by drop-casting a couple of microliters of an extremely diluted portion of the HGN-dye composite solution onto a cover-glass and drying under nitrogen. A He-Ne laser (632.8, 18 mW, AIRIX Corp.) was employed for the Raman excitation.

5. Concentration dependent absorption spectra of PIC

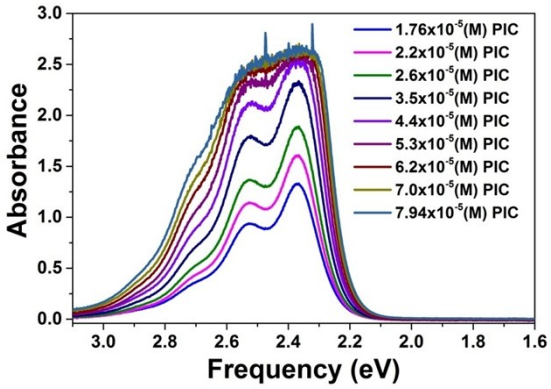

Figure S3. Absorption spectra of aqueous solutions of different concentrations of PIC dye ranging from 1.76×10^{-5} M to 7.94×10^{-5} M. The absence of any J-band peak in all these spectra confirms that no J-aggregates are formed at these concentrations.

References

S1. D. Senapati, T. Senapati, P. S. Wate, R. Kanchanapally, Z. Fan, A. K. Singh and P. C. Ray, *Chem. Commun*., 2012, **48**, 6034-6036.

S1. B. Hazra, K. Das, S. Das Chakraborty, M. S. Verma, M. M. Devi, N. K. Katiyar, K. Biswas, D. Senapati and M. Chandra, *J. Phys. Chem. C,* 2016, **120**, 25548-25556.