Supplementary information for

Probing the role of oscillator strength and charge of exciton forming molecular J-aggregates in controlling nanoscale plasmon-exciton interaction

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1. Synthesis of HGNs

Hollow gold nanoprisms (HGN) were synthesized using sacrificial galvanic replacement method. A detailed description of the synthesis of the HGN is available in previous reports.[S1,S2] Six different HGNs were prepared by varying the amount of Ag nanoseed from 100µl to 2.5ml added to the growth solution and the HGNs have been designated as HGN I (2.5ml seed), HGN II (1.5ml seed), HGN III (1 ml seed), HGN IV (500µl seed), HGN V (250µl seed), HGN VI (100µl seed).
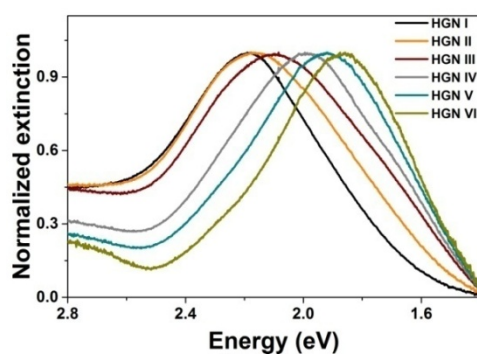
Figure S1. Normalized extinction spectra of six different HGNs synthesized in this work.

2. Transmission electron micrograph of HGNs
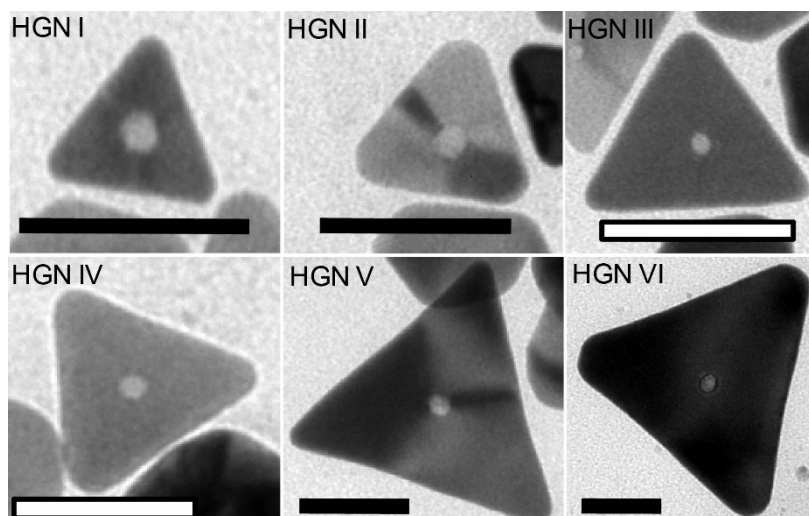
Figure S2. Transmission electron micrographs of six HGNs are shown. Scale bars correspond to 50 nm.

## 3. Preparation of HGN-Cyanine J-aggregate composite

An aqueous solution of 1mM TDBC was prepared and stored in dark at room temperature. Hybrid nanocomposites with TDBC dye were prepared by adding different amounts of dye solution to the as prepared HGN solution. No pretreatment of the HGN was required. The solutions were kept undisturbed for 24 hours. Excess (not attached to HGN surface) TDBC was removed by centrifuging at 7000 rpm for 15 min and the residue was redispersed in water. The details regarding the preparation of HGN-PIC nanocomposite can be found in our previous report.[S2]

4. Surface modification of HGNs with polystyrene sodium sulfonate (PSS)

5ml of HGNs solution was centrifuged once at 8000 rpm for 15min to remove excess CTAB and redispersed in 2.5ml of water. To this centrifuged solution, 2.5 ml of PSS stock solution (10mg/5ml) and 25µl 10mM NaCl solution were added under gentle stirring. The reaction was continued overnight and then the solution was centrifuged once again to remove excess PSS and the residue was redispersed in water for further studies.
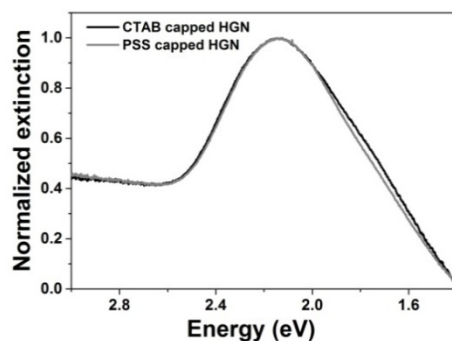
Figure S3. Normalized extinction spectra of CTAB capped HGNIII and PSS capped HGNIII.

Preparation of PSS capped HGN-TDBC/PIC composite

PSS capped HGN-TDBC/PIC composites were prepared by the same method as used for preparing the CTAB-capped HGN-TDBC/PIC composites.

5. Dark-field Scattering Microspectroscopy

Dark-field scattering microspectroscopy is a technique with which the Rayleigh scattering spectra can be acquired at the single particle level. Dark-field imaging of HGNs and J-aggregate

coated HGNs were done using an inverted optical microscope (Nikon Eclipse Ti2E). Light from a halogen lamp source is passed (via Kohler illumination) through a dry dark-field condenser (Nikon, numerical aperture or NA =0.80-0.95), which focuses it as a hollow cone of light onto the sample. The sample is prepared by drop-casting and drying a very dilute solution of HGNs or HGN-J-aggregate composites. Only the light scattered by individual particles are collected by an objective (having smaller NA (0.70) than the condenser). The light collected is focused on to the entrance slit plane of a spectrometer (Kymera 193i-A, Andor Technology) and finally imaged by a sCMOS detector (AndorZyla) that is attached to the exit port of the spectrometer. The particles appear as bright spots on a dark background. After recording the image, the slit width is adjusted to select a single nanostructure of interest to acquire its scattering spectrum. Each of the scattering spectra is corrected by subtracting from the background noise and normalizing with respect to the detector response and lamp profile.

6. EDX image of HGN-TDBC composite

Following are the EDX images obtained for HGN-TDBC sample
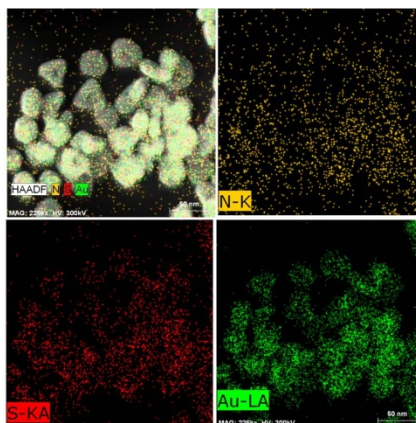
Figure S4. EDX images of HGN-TDBC composite showing that the S atoms are located exactly at the sites of HGNs.

7. Quantification of adsorbed dye molecules on the surface of HGN

The net concentration of the dye in the HGN-J-aggregate composite solution is known as we added a measured volume of the dye solution having known concentration to a measured

volume of HGN solution. After centrifugation, the supernatant was collected. For HGN-PIC composite, the supernatant is diluted with water and the absorbance of the diluted solution is recorded. The concentration is determined using the known molar extinction coefficient of PIC in water. It is preferable that the concentration of the solution is<4.78µM.[S3] From the estimated concentration of the diluted supernatant solution we calculate the concentration of the supernatant simply by using $V_1S_1=V_2S_2$. In case of HGN-TDBC system, the concentration of TDBC in the supernatant cannot be directly calculated as its molar extinction coefficient in water is not available in the literature. The collected supernatant was subjected to lyophillization to get a solid residue which was dissolved in methanol (spectroscopic grade) since the molar extinction coefficient of TDBC in methanol is known. From the absorption spectrum of this methanolic solution, the actual concentration of TDBC in the supernatant solution was determined. Now, the number (and hence the concentration) of the dye molecules adsorbed on the HGN surface is calculated by subtracting the number of the supernatant from the total number of the dye in the HGN-dye composite solution. From this number the number of dye molecules adsorbed on the surface of one HGN particle was calculated by dividing by the number of the HGN in the solution.

## 8. Dye-concentration dependent extinction spectra of HGN-PIC and HGN-TDBC composites
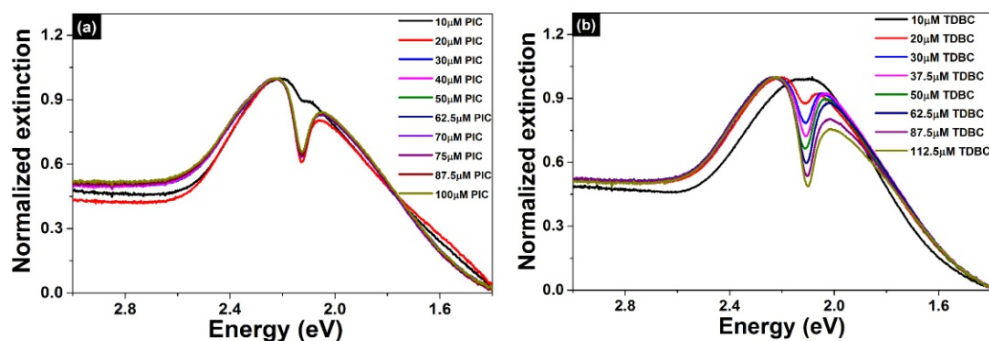
Figure S5. Normalized extinction spectra of CTAB-capped HGNIII-PIC and CTAB-capped HGNIII-TDBC composites as a function of concentration of PIC and TDBC

Table S1. Rabi splitting energy values of CTAB-capped HGNIII-PIC and CTAB-capped HGNIII-TDBC composites at different concentration of the respective dyes

Concentration of PIC (μM)	Energy of splitting (meV)	Concentration of TDBC (μM)	Energy of splitting (meV)
10	117	10	No splitting
20	165	20	140
30	176	30	174
40	180	37.5	194
50	177	50	204
62.5	170	62.5	212
70	183	75	213
75	175	87.5	213
87.5	176	100	213
100	176	112.5	212

9. Variation of dip minima of CTAB-capped HGN-PIC and CTAB-capped HGN-TDBC composites with concentration of dye
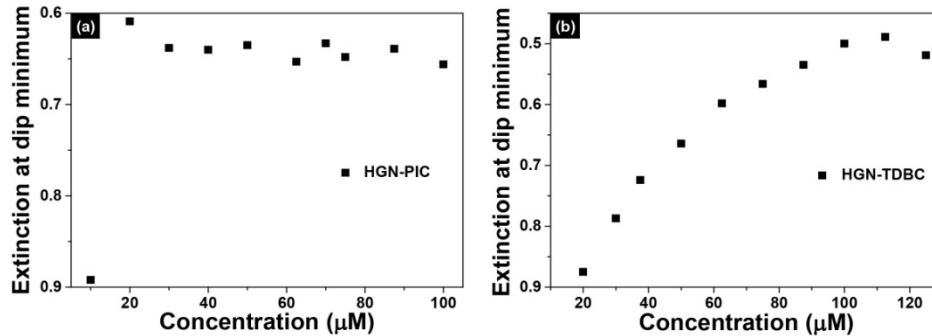
Figure S6. Plot of plexcitonic dip minima of CTAB capped (a)HGNIII-PIC and (b)HGNIII-TDBC composites as a function of concentration of PIC and TDBC respectively.

10. Calculation of oscillator strength of excitonic system

Oscillator strength (f) of an exciton is expressed as[S4]

$$f = \frac{8\pi^2 m\nu |\mu^2|}{e^2 3h} \quad \text{...(1)}$$

where m is the mass of electron, e is the charge of the electron, μ is the transition dipole moment, h is the Planck's constant, ν is the frequency of the J-aggregate at the absorbance maximum.

Transition dipole moment of an exciton is expressed as[S4]

$$\mu = \sqrt{\left(\frac{3}{4\pi^3} h\sigma_J \varepsilon_0 \gamma_0 \lambda\right)} \quad \text{..(2)}$$

where h is the Planck's constant, σ_J is the absorption cross-section of the exciton (J-aggregate) and is given by [S4]

$$\sigma_J = \frac{2.3\ DN_d}{n_m l} \quad \text{...(3)}$$

where D is the absorbance of the J-band maximum, N_d is the delocalization length i.e., the number of molecules over which the exciton is delocalized forming the J band, n_m is the

concentration of monomers and l is the light path length (1 cm) in the absorption measurement. ε_0 is the vacuum permittivity, 8.85×10^{-12} $C^2N^{-1}m^{-2}$, γ_0 is the FWHM of the J-band in s^{-1}, λ is the resonance wavelength. For PIC J-aggregate it is 575 nm and for TDBC J-aggregate it is 587 nm.

Calculation of N_d for J-aggregate

Absorption spectra of PIC J-aggregate at different monomeric concentration ranging from 10μM and 15 μM were measured in 5M NaCl. FWHM of the J-aggregate and the monomer at all those concentrations were extracted by deconvoluting the absorption spectra of PICin 5M NaCl. The contribution from H-aggregate (the shoulder at ~465nm i.e., 2.67 eV) has not been taken into consideration.

N_d (or aggregation number) is calculated using the method reported by Knapp[S5]

N_d= [(FWHM of monomer / FWHM of J-aggregate)^2]………………………………………..(4)

and the average values of the aggregation numbers at those two concentrations have been calculated to be 347. For TDBC J-aggregate, N_d is taken to be 15, as reported in literature.[S6] For TDBC J-aggregates, FWHM were extracted from the absorption spectra of the dye in 5M NaCl.

The absorbance values at J-band maxima for PIC and TDBC J-aggregates can be obtained from their respective absorption spectra. The absorption cross section (σ_J) of the exciton can be calculated using equation (3). Taking these σ_J values, transition dipole moment (μ) of excitonic system at different concentration were calculated using equation (2) and finally the values of oscillator strength were calculated using equation (1). The values of oscillator strength have been estimated to be 2.94 and 0.51 for J-aggregates of PIC and TDBC, respectively.

11. References

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