Coupled Molecular Emitters in Superstructures Interact with Plasmonic Nanoparticles

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Using hyperspectral measurements, J-aggregate nanorods of porphyrin molecules embedded in plasmonic Au nanoparticles arrays are studied. Measurements of J-aggregate nanorods that cross onto a plasmonic array exhibit a shift in their absorption peak, and display weak coupling properties only for the embedded part. Furthermore, a significant thickness-dependent redshift in the plasmonic resonance for the J-aggregate clusters is observed. Such redshift is also dependent on the ratio of J-aggregate in the plasmonic dipole interaction area, reaching values of up to 120 meV for ~40% coverage. In addition, for large clusters of J-aggregates, the plasmonic spectrum shows coupling behavior between the systems indicated by a small Rabi splitting. The findings are validated by a quasi-static model based on the change of the dielectric environment around the embedded nanoparticles. Using the model, the fraction of embedding J-aggregates in the plasmonic interaction area is correlated with the change in plasmonic resonance peak. These results offer insight into the coupled nature of molecular emitters in supramolecular structures and their interaction with plasmonic nanoparticles and can lead to new types of sensitive optical detectors based on these interactions.

1. Introduction

Localized surface plasmon resonances (LSPRs) are confined free electron oscillations, which arise in small metal nanoparticles (NPs) under an external electric field. These have been studied extensively for several decades,[1–3] due to their ability to focus light below the diffraction limit,[1,4,5] as well as their use in optoelectronic,[6] sensors,[7,8] and light-harvesting systems.[9] LSPR can be tailored to specific wavelengths by an appropriate material, NP’s shape and size, and the dielectric environment. In this context, the dielectric function of the surrounding environment or the substrate can modify the LSPR of the NP. For example, the presence of a thin indium tin oxide (ITO) coating on the substrate, often used as an adhesion layer for metal deposition on glass, can redshift the resonance of the plasmonic particle.[10]

Of special interest is the interaction of plasmons with excitons.[11–16] In the weak boundary of such interactions, the plasmonic peak is often redshifted due to changes in the dielectric environment.

One of the promising systems to explore these phenomena are porphyrins molecules in their J-aggregate form.[17–28] Compounds that exhibit J-aggregates are composed of supramolecular structures of dye molecules that possess optical and electrical properties distinct from their base monomer. J-aggregates of porphyrins can form single layers or distinct structures such as spheres or rods.[29] Specifically, the J-aggregate of the 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (TPPS-4) can form rod-like shapes under acidic conditions.[29] At this form, a sharp peak dominates the extinction spectrum for these rods at 2.53 eV in the J-band. This peak is shifted from the single porphyrin Soret band peak at 2.88 eV and is originated from the Frenkel exciton transition and the porphyrin Q-band transition, which is redshifted to 1.72 eV. The narrower peak shapes in the J-aggregate spectrum in this form can be explained by the coherent coupling of the individual porphyrin monomer units.[30–32]

J-aggregate coupled to plasmonic systems have been studied in previous works and have been shown to exhibit strong coupling properties.[33] The strong coupling was observed for both the J and tric properties distinct from their base monomer. J-aggregates –J-aggregate coupled to plasmonic systems have been studied in previous works and have been shown to exhibit strong coupling properties.[33] The strong coupling was observed for both the J and tric properties distinct from their base monomer. J-aggregates –
averaging over a large area in the plasmonic array, and therefore localized interactions have been ignored.

In this study, we synthesize and characterize porphyrin J-aggregate nanorods (PJJaNRs), which are embedded in plasmonic AuNP arrays with variable sizes. These well-defined nanorods are formed under acidic conditions and exhibit a large aspect ratio.\(^{29}\) Deposition of the PJJaNRs on top of the plasmonic arrays results in parts of the rods interacting with the NP and portions outside the array’s area. This arrangement enables the study of distance-dependent interactions PJJaNRs with the plasmonic arrays. Moreover, stacked deposition of the rods allows us to investigate the system’s thickness-dependent characteristics. Localized spectra were achieved using a hyperspectral measurement system, which allowed us to analyze the system’s spatial-dependent properties. To explain our observations, we develop an analytic theoretical model that explains the red shifting of the plasmonic spectrum.

2. Sample Structure and Measurement System

2.1. Sample Structure

NP plasmonic arrays were fabricated using the electron-beam lithography technique on an ITO-coated glass substrate (thickness of 200–300 Å). Each sample contained a series of 20 × 20 μm plasmonic NP arrays in the shape of nanodisks with a thickness \(h = 35\) nm, and each array was fabricated with a different diameter \(D = 50–190\) nm and pitch \(P\) (distance between the centers of two adjacent disks in the array), see Figure 1A.

The synthesis of porphyrin tubes on the Au NP was performed via two steps. The first was the self-assembly deposition of a thin polypeptide (PP) film on the Au surface, which anchors the tubes. In the second step, the Au nanostructure coated by the peptide film was placed in a beaker with 2 mL deionized water. To that 40 μL of TPPS (Dojindo laboratories), 0.5 mM solution was added. After gentle steering, 20 μL of 1 M HCL was added and gently steered. The sample was kept at RT overnight and then washed with deionized water and dried in an \(\text{N}_2\) stream. Atomic force microscopy (AFM) measurements show that the resulting rod’s thickness is in the range of 300–400 nm and height of 16–20 nm, with a length of \(\approx 1–20\) μm (Figure 1B,C).

2.2. Measurement System

Figure 2A shows a schematic drawing of the hyperspectral microscope optical path and sample structure. The system uses a BX51 Olympus microscope body with a 100× magnification objective. Spectrum was measured using a mounted commercial optical head from ASI and equipped with a halogen lamp light source. The light collected by the microscope objective is passed through an interferometer before imaging onto a CCD detector. By recording a series of images at different steps on the interferometer path, each pixel on the CCD maps an interferogram of the imaging area. A hyperspectral image (i.e., an image where each pixel composed of a spectral measurement of that area) was formed by using Fast Fourier transform to generate the spectrum for each pixel from the recorded interferogram.

![Figure 1](image1.png)

Figure 1. A representative sample of a plasmonic array and PJJaNR. A) Environmental scanning electron microscope (ESEM) micrograph of NP plasmonic array of NP on ITO-coated glass. In red, the diameter D and pitch P of the array is marked. B) AFM scan of PJJaNR deposited on ITO-coated glass is a marked cross-section of the rod in red. C) Measured cross-section of representative PJJaNR (from the red line marked in B).
The hyperspectral information was processed via Spectral Python (SPy) to create a false-color image and spectral data. K-means clustering spectral analysis was used to sort the different pixels in the hyperspectral data to different spectral areas. K-means is an iterative data sorting method that requires no prior training. The user defines for the algorithm, the number of initial clusters (K), usually two more than the expected number of different detected areas after sorting, and the maximum number of iterations to perform. Figure 2B shows a schematic description of the algorithm sorting process (for a more detailed description see Supporting information).

3. Results and Discussion

After the deposition of PJaNR on samples, they were examined using an optical microscope. Optical images of samples indicated a uniform dispersion of PJaNR across the sample, with a few hair clusters or stacks on the samples, Figure 3A. The majority of the plasmonic arrays contained at least one deposited rod, and some contained clusters of several rods with increased thickness. AFM scans of samples showed that PJaNR has a rolled-up sheet-like shape (Figure 3B), indicating the possible formation of the J-aggregate from a “rolled” layer.[29] The absorbance spectrum of the PJaNR as shown in Figure 2C shows two strong peaks at ~2.45 eV (J band) and ~1.72 eV (Q band); the shaded area shows the measurement range for the ITO samples.

AFM measurements of PJaNR deposited on the NP array show that the nanorods are embedded and encase the NP arrays completely. ESEM images confirm that the PJaNR is deposited between or covering the NP (see Figure S3, Supporting Information).

The absorbance spectra measured for the NP arrays before PJaNR deposition are shown in Figure 4A,B. The measured spectra are similar to previously reported results for Au nanodisk arrays.[4] After PJaNR deposition, the absorbance of the NP arrays was remeasured using the hyperspectral microscope. Using K-means spectral analysis, we calculated the mean absorbance spectra from sections of the NP arrays containing only a single PJaNR (Figure 4C,D).

Figure 2. Hyperspectral measurements of J-aggregate on Au NP array. A) schematic of Hyperspectral system and sample. A halogen light source is focused on the sample using a condenser with NA = 0.9 in transmission mode and a 100× objective. Hyperspectral optical head records interferometer measurement of the image for each CCD pixel, which is converted to spectrum via Fourier transform. The sample substrate is ITO-coated glass. Au NP arrays (R = 25–95 nm) are deposited via an electron beam deposition method on the substrate, PJaNRs are then deposited on the array. B) Schematic process of K-means algorithm used to sort hyperspectral data. C) The absorbance spectrum of a PJaNR cluster on ITO glass substrate. The spectrum shows two major peaks at ~2.45 eV (J band) and ~1.72 eV (Q band); the shaded area shows the measurement range for the ITO samples.
Figure 3. PJaNR deposited on ITO-coated glass substrate. A) Optical microscopy image of PJaNR (white rods) and clusters on ITO coated glass and Au NP array (square). B) AFM scan of PJaNR cluster showing a “rolled up” structure for the rods.

Figure 4. Absorbance spectrums were measured for the Au NP array before and after PJaNR deposition process. The results were taken from the mean spectrums calculated by K-means method. A,B) The results for NP arrays with pitch = 2*D for A and pitch = 3*D for B before PJaNR deposition. C,D) The same arrays after the PJaNR deposition. The K-means method was used to calculate the spectra only from areas with a single PJaNR on the array, to remove the effects resulting from clusters of PJaNR. The spectrum for a single PJaNR was added to the graph (black dotted line) and a vertical dotted red line marks the energy of the Q-band Peak. The arrays with deposited PJaNR show small energy split around the Q-band energy (~0.07–0.1 eV) indicating weak coupling of the systems.
A small energy split is observed in the peaks of the absorbance spectra, especially for the NP arrays with resonances close in energy to the Q-band (≈1.72 eV). This split is seen both for the 2 * D and 3 * D pitch arrays. The energy of the split is about ≈0.07–0.1 eV, which is smaller than the full width at half maximum (FWHM) for the plasmonic NP peak (≈0.2 eV) and similar in size to that of the PJaNRs FWHM (≈0.9 eV). The small energy splitting observed in the spectrum and absence of a transparency indicates weak coupling behavior between the single PJaNRs and the Au NP arrays.

**Figure 5A** shows a hyperspectral map of the system in which half of the rod is embedded in the NP array (D = 150 nm) and the other half lies on the substrate. The K-means spectral analysis shows different spectral areas for the embedded and unembedded length of the PJaNR. Figure 4B shows the mean spectra for the PJaNR on and off the area as well as the unmodified Au array. The mean spectrum exhibits the PJaNR peak at ≈1.72 eV and the array plasmonic peak at a small redshifted detuning compared to the PJaNR at ≈1.71 eV. The embedded part PJaNR has two peaks at ≈1.645 and ≈1.745 eV, which corresponds to the shifted location of the Au NP and PJaNR, respectively. The shifted location of the peaks is consistent with the small coupling effect between the exciton of the J-aggregate and the plasmon of the array (splitting ≈0.1 eV) observed for other NP arrays with single PJaNR. The coupling effect does not seem to extend beyond the area of the array.

In some of our sample’s clusters of 2–4 stacked PjaNR were deposited on the Au plasmonic array. These clusters enable us to measure the effect of increased thickness of the PJaNR on the strength of the PJaNR-Au NP coupling. **Figure 6A** shows an AFM measurement of a cluster of PjaNR on a D = 170 nm NP array; the cluster seems to be two combined PjaNR. Since the PjaNR were embedded in the NP of the array, the thickness measurements of the PjaNR using the AFM was inaccurate. Figure 6B shows the results of hyperspectral data after K-means clustering (12 seeds, 200 iterations); the inset shows a false-color image of a PjaNR deposited on the NP array. In the center of the image, a single hair (red arrow in Figure 6B) and crossing it underneath a second shorter one (yellow arrow Figure 6B) match the structure seen in the AFM scan.

The spectrum for the plasmonic array taken from areas with no PJaNR exhibits a strong resonance at ≈1.64 eV with an FWHM of ≈0.12 eV, which matches the reference spectrum measured before deposition, the LSPR is detuned from the PJaNR Q band peak by 0.08 eV. The results of the K-means cluster analysis showed seven distinct spectral clusters in the measurement (Figure 6B). Two clusters (yellow and pink) show areas with no PJaNR, the spectral difference between the two clusters is likely due to small amounts of adsorbed single porphyrins. The area with deposited PJaNR shows five spectral clusters (Figure 5B). Cluster 1 is a combined spectrum of embedded and unembedded NP around the PJaNR. Clusters 2–5 are embedded NP under different thicknesses of PJaNR. Figure 6C shows the mean spectrum of each cluster form areas with deposited PJaNR. The spectrum displays two spectral peaks, a stationary one at ≈1.75 eV and a moving peak at lower energy ≈1.6–1.525 eV. The peak at ≈1.75 eV matches the higher energy J band absorption peak of the PJaNR (as shown in Figure 2B). The second peak belongs to the Au array plasmonic resonance and undergoes red shifting with increased PJaNR thickness.

The shifting in peak location is only observed for the Au NP resonance peak, while the PJaNR absorption peak is unmodified, these strengths the conclusion from the previous sample indicating weak coupling occurring between the J band transition and the LSPR of the Au NP array, as shifting of both peak locations would occur for strong coupling. A shift in the plasmonic resonance could be a result of the change in the dielectric environment around the NP due to the PJaNR.

A model to explain the plasmonic peak shifting using the quasi-static model for the dipole approximation of an NP in a dielectric medium was constructed. The polarizability of an oblate spheroid in the quasi-static limit can be calculated using Mie-Gans formula:

\[
\alpha(\omega) = \frac{\epsilon_m(\omega) - \epsilon_e(\omega)}{\epsilon_e(\omega) + \frac{L[\epsilon_m(\omega) - \epsilon_e(\omega)]}{4}}
\]  

(1)
where $V$ is the spheroids volume, $\varepsilon_m$ and $\varepsilon_e$ is the complex dielectric function of the NP material and the environment, $\omega$ is the wave frequency, and $L$ is the geometric factor that is dependent on the radius $r$ and thickness $h$ of the NP.

$$L(r, h) = \frac{r^2 h}{2} \int_0^\infty dq \frac{\sqrt{r^2 + q^2}}{(r^2 + q)^2(h^2 + q)}$$

We used the Lorentz-Drude dielectric to describe the dielectric function of Au for the NP. As we used large NP in our work, the dipole approximation needs to be corrected for dynamic depolarization and radiation damping by the modified longwave approximation:

$$\alpha_{MLWA}(\omega) = \frac{\alpha(\omega)}{1 - \frac{\omega^2}{4\varepsilon_\infty^2}\alpha(\omega) - \frac{\omega^2}{6\varepsilon_\infty\alpha(\omega)}}$$

The extinction spectrum can then be calculated from

$$C_{\text{abs}} = k \cdot \text{Im}(\alpha_{MLWA}(\omega))$$
$$C_{\text{scattering}} = \frac{k^4 |\alpha_{MLWA}(\omega)|^2}{6\varepsilon_\infty}$$
$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{scattering}}$$

The effect of the PJaNR on the spectrum can be calculated by a change to the dielectric function of the environment $\varepsilon_e$ around the Au NP and an added absorption of the PJaNR itself. The change in the dielectric environment can be written as a change in the dielectric function $\varepsilon_e$

$$\varepsilon_e = 0.5 \cdot \varepsilon_s + 0.5 \cdot \frac{(1 - f) \cdot \varepsilon_\text{air} + f \cdot \varepsilon_{\text{PJaNR}}}{f}$$

where $f$ is the ratio between PJaNR and air above the NP and $\varepsilon_s$, $\varepsilon_\text{air}$, and $\varepsilon_{\text{PJaNR}}$ is the dielectric constant of the substrate, air, and PJaNR, respectively. The total interaction area of the NP with the environment is limited by the near field area of the NP. Similarly, an expression for the substrate dielectric function can be written as
\begin{equation}
\varepsilon_s = \frac{f_{ITO} \cdot \varepsilon_{ITO} + (1 - f_{ITO}) \cdot \varepsilon_{glass}}{2}
\end{equation}

where \(\varepsilon_{ITO}\) and \(\varepsilon_{glass}\) is the dielectric function of the ITO and glass substrates and \(f_{ITO}\) is a parameter representing the thickness of the ITO coating. In order to account for variation in the size of the deposited NP, we added two fitting parameters to the radius \(r = r + \delta_r\) and pitch \(4r + \delta_p\) of the NP. The initial model fitting is performed on an unmodified NP array to fit initial values for \(\delta_r\), \(\delta_p\), and \(f_{ITO}\). The fitting parameters for the Au NP array \(D = 170\) nm are \(\delta_r = -2.18\) nm, \(\delta_p = -58.3\) nm, and \(f_{ITO} = 0.64\). Using these parameters, we manage to fit the data for the areas embedded with PJaNR (Figure 6D). The model shows a good match to the measured results. The redshift in the plasmonic peak increases with increasing \(f\) parameters, representing the ratio of PJaNR to air in the NP interaction area (Figure 6D inset). The model shows that for a plasmonic redshift of \(\approx 0.12\) eV only \(\approx 38.4\)% of the volume around the plasmonic NP is occupied by the PJaNR. In our calculation, we simplified the problem by keeping the interaction strength between the molecule and plasmonic NP equal for all interacting PJaNR, whereas interaction strength decreases with distance.

The second cluster sample measured (\(R = 155\) nm) had a smaller detuning value (0.03 eV), which should increase the coupling strength. Figure 7A shows an AFM measurement of the cluster of PJaNR on the array while the cluster exhibits four combined PJaNR. Figure 7B shows the results of hyperspectral measurement after K-means clustering (12 seeds, 200 iterations). Figure 7B - inset shows a false-color image of a PJaNR deposited on the NP array; the image shows a deposited cluster of four rods on the Au array. The K-means clustering shows four spectral areas. The mean of the spectral clusters is presented in Figure 7C and shows increasing red shifting of the plasmonic resonance peak towered the point of the 4 nanorod crossing. The plasmonic resonance peak is shifted by \(\approx 120\) meV at the intersection of the four PjaNR in the sample. Using the developed model, we performed fitting to find \(f\) for each cluster; initial fitting parameters were calculated using the reference plasmonic peak location (\(\delta_r = 2.2\) nm, \(\delta_p = 59.14\) nm, and \(f_{ITO} = 0.639\)) and are a good match for those calculated for the \(D = 170\) nm
array. Our model shows good fitting to the peak of the experimental data (Figure 6D) but does not show the peak broadening of the plasmonic peak. The ratio of embedding PJaNR (f) increases to ≈40% for the area with 4 crossing nanorods. This indicates that even for a large cluster the ratio of PJaNR to air remains under 50%, these can be explained by limited coverage by the PJaNR due to their limited thickness even when stacked.

4. Conclusions

In this work, we studied the interaction of PJaNR with Au NP arrays. Porphyrin J-aggregates nanorod enables us to locally place the coupled excitonic system on plasmonic NP. The interaction between plasmon-exciton systems depends strongly on the distance between them. Furthermore, due to the coupled nature of the porphyrin in the J-aggregate structure, the interaction has a broader range than that of noncoupled porphyrin layers.

Using hyperspectral measurement techniques enabled us to study the effect of the interaction between the systems locally around the PJaNR. Whereas other methods for spectral measurements, such as UV–vis is often averaged over a large measurement area, we were able to use the hyperspectral system to study the change in absorbance at different areas of the structures with good spatial resolution. In combination with the K-means cluster method, hyperspectral measurements have shown great potential as a tool to study coupled systems of plasmonic NP and single or clustered J-aggregate supermolecules or other systems having localized spectral shifts.

When PJaNR is partially embedded on the Au NP plasmonic array, only the embedded section showed weak coupling behavior, while the unembedded section is unmodified. This points to the limited coherent coupling distance in the J-aggregates supermolecule. PJaNR clusters on Au NP arrays had a variable redshift of the plasmonic peak (0.02–0.12 eV) dependent on the PJaNR coverage. By fitting the results to a quasi-static model, we showed the dependence of the plasmonic redshift on the ratio of PJaNR to air in the plasmonic interaction volume. It is shown that for large clusters, PJaNR reaches up to ≈40% coverage. Using this model, it is possible to calibrate the required PJaNR coverage to shift the plasmonic peak to the desired energy, this is a useful computational tool for optical device design.

The PJaNR showed an ability to modify the plasmonic peak of the Au array while maintaining its spectral peak constant. This modification is spatially limited to the close vicinity of the PJaNR and the array. These properties can be used to create devices with a variable spectral shift in small areas, which can be used for variable absorption/emission for optical nanodevices.

5. Experimental Section

Materials and Substrate Preparation: All solvents used in this work were purchased from Sigma-Aldrich (USA) in regent quality. Class-coated ITO substrates were purchased from Sigma-Aldrich (USA). The substrates were cut into four 10 × 10 mm² pieces using a diamond scribe. Samples were cleaned by sonication for 10 min in three individual solvents: Aceton, Hexane, and IPA. Between each solvent sonication, samples were washed by IPA and dried by N₂ stream. Next, the samples were treated by O₂:Ar (1:1 ratio) plasma in 40 W for 5 min. Finally, the samples were sealed in an N₂ backfilled container for further use.

E-Beam NP Fabrication: Before processing, cleaned ITO-coated glass samples were activated by O₂ plasma treatment 10 W for 5 min. Samples were then spine coated with an A4 PMMA layer (2000 RPM). E-Beam lithography was performed using a RAITH150-2 system, and developed in a cleanroom. Next, samples were coated with 35 nm of Au by physical vapor deposition in an electron beam evaporator system. Lift-off was then performed by immersion of samples in Aceton for 24 h.

Measurement Systems: ESEM scans were performed using a Quanta 200 FEG Environmental SEM. AFM measurements were performed using a Nanospec measurement system. The Hyperspectral system used is an ASI developed in a cleanroom. Next, samples were coated with 35 nm of Au by physical vapor deposition in an electron beam evaporator system. Lift-off was then performed by immersion of samples in Aceton for 24 h.

K-Means Spectral Analysis: Hyperspectral data were analyzed using Python 3.7. The analysis and K-means spectral sorting were performed using Spectral Python 0.21.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

coupling, hyperspectral imaging, J-aggregates, nanoparticles, plasmonics

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