Reviewer: 1

Recommendation: Publish in ACS Nano after minor revisions noted.

Comments:
Hamans et al. report super resolution imaging of the different coupling behaviour of single emitters with a localized plasmon resonance or lattice resonances. Both LSPR and SPR are supported by the nanoparticle array built by the authors, and the emitter is placed in two different locations so the effect of each resonance can be more clearly distinguished. The combination of numerical simulations with the impressive optical imaging technique illustrates the different behaviour of each resonance with the emitter. The work is well described and organized and the results are sound. I would recommend the acceptance of this work if the authors provide the following information:

- There are 2 resonances sustained by their array (LSPR and SPR) and there are two possible locations of the emitter (S1 and S2), yet the authors only present the results of the optimal coupling for each case (LSPR in S1, fig 3 and SPR S2 fig 4). I would like to see also what happens to the other two possible results (LSPR in S2 and SPR in S1). In the case of the LSPR, it would illustrate how the emitter is influenced by the proximity of a metal antenna out of resonance, and what are the typical values of the Purcell factor and D. For the case of the SPR it looks like there is also near field excited at the base of the nanoantenna which could be interesting to analyze in the S1 configuration.

AUTHOR REPLY
This is a very interesting point and it was also raised by reviewer #2. In fact, we had already performed these measurements, but we did not include them in the manuscript, as their results were rather unsurprising. The requested experiments and the corresponding simulations are now placed in sections 6 and 7 of the Supporting Information.

For sample S1, in which the emitters are placed at the bottom of the nanoparticles, when filtering the emission at 575±20 nm, corresponding to the SLR, we observe very similar patterns as when filtering the emission at 650±20 nm, corresponding to the LSPR. This can be easily seen by comparing the maps in Figure 3 with the ones now given in Figure S7 and reported here below.

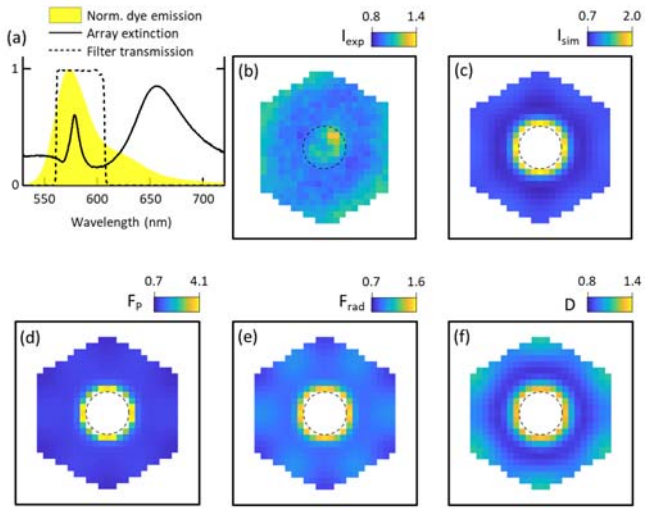

Figure S7. Enhanced emission of single molecules preferentially coupled to the LSPR, while filtering at the wavelength of the SLR. (a) Normalized dye emission (yellow), array extinction (solid line), and emission filter transmission (dashed line). (b) Two-dimensional histogram of the experimentally observed emission enhancement I_{exp}. Simulated (c) emission enhancement I_{sim}, (d) Purcell factor F_P, (e) enhancement in power radiated to the far-field F_{rad}, and (f) directivity enhancement D. Figures (b-f) have 20 x 20 nm^2 bins. The dashed lines denote the base of the nanostructure.

This similarity is expected as the SLR has significant field enhancement also at the bottom of the particles, as shown in Figure 1f.

For sample S2, in which the emitters are placed 250 nm above the substrate, when filtering the emission at 650±20 nm, corresponding to the LSPR, on the contrary, we observe a very different pattern than when filtering at 575±20 nm. This difference can be seen by comparing the maps in Figure 4 with the ones now given in Figure S8 and reported here below.

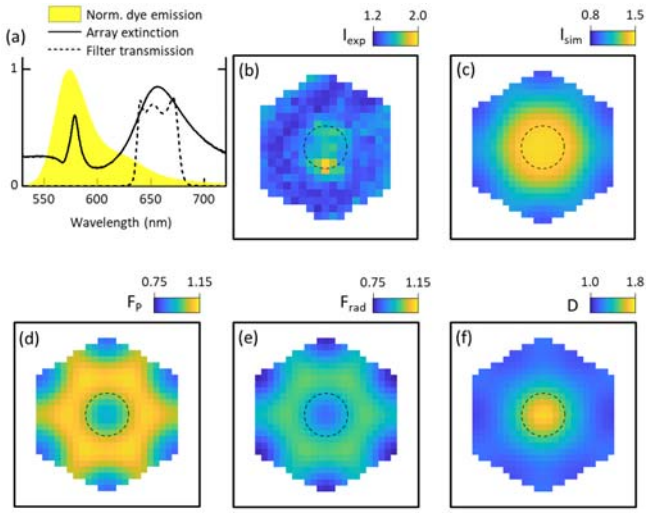

Figure S8. Enhanced emission of single molecules preferentially coupled to the SLR, while filtering at the wavelength of the LSPR. (a) Normalized dye emission (yellow), array extinction (solid line), and emission filter transmission (dashed line). (b) Two-dimensional histogram of the experimentally observed emission enhancement I_{exp}. Simulated (c) emission enhancement I_{sim}, (d) Purcell factor F_P, (e) enhancement in power radiated to the far-field F_{rad}, and (f) directivity enhancement D. Figure (b) has 25 x 25 nm^2 bins and Figures (c-f) have 20 x 20 nm^2 bins. The dashed lines denote the base of the nanostructure.

In this case, the directivity enhancement observed right above the particles is simply due to their high reflectivity: light emitted by the molecules is reflected by the aluminum particles and collected in the objective.

Besides updating the Supporting Information with the above mentioned results, in the new version of the manuscript, we refer to these control experiments and simulations and their interpretation as follows:

> *"We also perform a control measurement on sample S1 with an emission filter that targets the SLR wavelength and we simulate the emission enhancement at the same wavelength (see Figure S7). Interestingly, we obtain a similar emission enhancement map as in Figure 3b, due to the similar spatial profile of the near-fields at the bottom of the nanoparticles for both the SLR and LSPR (see Figures 1d and 1f)."*

and

> *"For sample S2 we also perform control measurements and simulations, now at the LSPR wavelength (see Figure S8). Interestingly, the extended nature of the SLR is now lost, as the enhancement remains limited to molecules in the middle of the unit cell. While both F_P and F_{rad} remain largely unchanged due to the large emitter-nanostructure separation, the directivity enhancement D shows values up to ~ 1.8 for molecules placed right above a nanostructure. Such directivity enhancement is due to light emitted towards the underlying nanoparticle and reflected back into the objective. A similar directivity enhancement is in fact expected for the case of emitters placed above individual aluminum particles (see also SI section 8)."*

- I found a bit confusing the directivity enhancement D described in page 10. This magnitude comes from the simulation of the fraction of power reaching the objective, however experimentally the

NA of the objective is 1.4, that implies a large light cone angle. Is this the same cone angle defined for the simulation?

AUTHOR REPLY
The NA of 1.4 is indeed also used in the calculation of the directivity. This was mentioned in the text as follows:

> "*The simulated enhancement in emission intensity I_{sim} is obtained by performing a near-field to far-field transformation on the field monitored in the direction of the objective, in which we neglect all waves propagating at angles that fall outside the numerical aperture of the objective of our microscope (NA = 1.4).*"

As the directivity D is calculated from the far-field intensity I_{sim} (which is calculated with NA = 1.4) and the enhancement in total power radiated to the far-field F_{rad}, the calculation automatically includes the NA of 1.4. To further clarify this in the text, we added the following sentence after the description of how we calculate the directivity:

> *"Since the directivity enhancement D is calculated from I_{sim}, the resulting values for D are also defined with an NA of 1.4."*

- The normalized emission of the dye shown in fig c, in which conditions was it measured? is it in solution or it is measured on the array?

AUTHOR REPLY
The emission spectrum was measured in solution and taken from the website of the dye manufacturer. We added appropriate referencing in the text and in the caption of Figure 1c (see reference 33 in the new version of the manuscript). Given the extremely low dye concentrations used in the present work (300 nM), the emission spectrum in solution is a good approximation of the one expected in our polymer matrix (see for example Shundo et al., Macromolecules 2012, 45, 329–335).

Reviewer: 2

Recommendation: Reject, but encourage resubmission if the specific points reviewer makes are addressed.

Comments:
In this paper, the authors used a super-resolution microscope to explore the enhanced emission of single emitters by LSPRs and SLRs. They claimed that their results demonstrated that different from LSPRs the enhanced emission of single emitters by SLRs mostly originates from an enhanced directivity. This work can be very interesting and insightful. But, after thoroughly reading this paper, I find that there are some important problems in this paper. In addition, the authors drew their conclusion from just 2 positions of 2 samples, so their results are not systemic and comprehensive. Therefore, this manuscript is premature to be published in ACS Nano and needs significant revisions and more comprehensive results. Detail comments are listed below:

(1) The authors claimed that the narrow peaks at 580 nm were derived from SLRs, but the coupled dipole approximation (CDA) and many previous studies indicate dipolar lattice modes have a longer wavelength than LSPRs of individual nanoparticles (see Chem. Rev. 2018, 118, 12, 5912-5951 and PHYSICAL REVIEW B 90, 075404 (2014) as references). Therefore, it is highly possible that the narrow peaks at 580 nm in extinction spectra are not from dipolar lattice modes. While, it has been demonstrated recently that Al nanoparticle arrays can support quadrupolar lattice modes, which can have a shorter wavelength than LSPRs (Proc. Natl. Acad. Sci. USA 113, 14201-14206 (2016)). But, in this scenario, the 655 nm resonances should be dipolar lattice modes not LSPRs. Therefore, the authors should thoroughly study what are the actual origins of those extinction peaks. To do so, I suggest the authors study different plasmonic particle arrays with at least 3-5 sets of lattice parameters.

AUTHOR REPLY
We believe that this comment originates from our unclear wording when introducing the different resonances in our sample. The reviewer is fully correct in pointing out that dipolar lattice modes have a longer wavelengths than LSPRs of individual nanoparticles. However, we have not assigned a dipolar character to the lattice modes in the manuscript. A full and detailed description of the localized and extended modes in a very similar sample was given by us in Phys. Rev. Lett. 113, 247401 (2014). In this PRL article we showed with calculations of the superpolarizability tensor and with finite element simulations that the SLR does not have a dipolar character but it has an enhanced magnetic and magnetoelectric response due to the tapering and height of the nanoparticles (pyramidal shape). Similarly, the localized resonances have two opposed electric dipoles at different heights from the base of the nanoparticles due to retardation of the scattered fields with respect to the incident field. In that manuscript we also showed that, compared to the 580 nm resonance, the 655 nm resonance has a character more localized to the individual nanoparticles. For this reason, we find the term localized resonance appropriate, although the dispersion of this resonance is not fully flat, as we showed later in Phys. Rev. B 94, 125406 (2016), indicating the hybridized character of the resonance.

The coupled dipole approximation (CDA) suggested by the reviewer and discussed in Chem. Rev. 118, 5912 (2018) and Phys. Rev. B 90, 075404 (2014) is therefore a too simple approximation and cannot be applied to our sample. The reviewer suggests to thoroughly study what are the actual origins of the extinction peaks by measuring different plasmonic particle arrays with at least 3-5 sets of lattice parameters. However, we find that our previous works and the mentioned references already describe the origins of the resonances in great detail. Moreover, the scope of our paper is to demonstrate how super-resolution techniques can be applied to map the interaction between single emitters and extended or localized resonances in nanoparticle arrays. In this respect, a detailed analysis of the origins of these extinction peaks lies beyond our objectives and would add little to the already extensive literature on nanoparticle arrays.

Nevertheless, to remove any uncertainty and properly address the reviewer's remarks, we have added references to Phys. Rev. Lett 113, 247401 (2014), PNAS 113, 14201-14206 (2016), and PRB 94, 125406 (2016) in the revised manuscript to direct the interested readers to a detailed description of

the resonances. Also, to avoid confusion between the array LSPR at 655 nm and the localized surface plasmon resonance of a single particle we have changed

> *"We design a plasmonic particle array in which the LSPR and SLR are spectrally separated, yet both overlapping with the emission of a fluorescent molecule."*

into

> *"We design a plasmonic particle array which supports two spectrally separated lattice resonances, both overlapping with the emission of a fluorescent molecule."*

and added the following sentence

> *"Note that this LSPR is still a hybrid plasmonic-photonic mode, as its dispersion is not fully flat,[34] and therefore does not correspond to the localized surface plasmon resonance of the individual nanoparticles, which is expected to be much broader.[35]"*

For clarity, we have also changed the structure of the section "Sample design": the FDTD simulations that demonstrate the distinctive characteristics of the resonances are now discussed earlier. In this section we also added the following sentence, in which we refer to the appropriate literature:

> *"A detailed description of the origin of these lattice resonances and their electromagnetic properties was already provided in previous work.[34-37]"*

(2) The authors should add super-resolution mappings of the enhanced emission at 580 nm for the sample S1 and at 655 nm for the sample S2 as control experiments.

AUTHOR REPLY
Please see our reply to the first comment of reviewer #1.

Moreover, the authors should also provide more results from multiple nanoparticles in nanoparticle arrays instead of just one nanoparticle to verify their conclusions and rule out potential experimental errors.

AUTHOR REPLY
We think this comment may be due to a misunderstanding. During a typical super-resolution experiment we image with a field-of-view of ~70 × 70 μm (cropped from the total 133 μm x 133 μm field-of-view of the camera), which contains ~28,000 aluminum nanoparticles. At the beginning of each experiment we determine the x,y position of each nanoparticle with a precision of ~7 nm, by collecting a transmission image and fitting all local maxima with a 2D Gaussian. In a typical fluorescence experiment, we collect 10,000 frames (100 ms integration time) and detect an average of 200 fluorescent events per frame. During the fluorescence experiments, for all the molecules detected in our field-of-view we determine their position with sub-diffraction resolution and these positions are subsequently redefined relative to the nearest aluminum nanoparticle. In this way, all fitted positions are then collapsed into a single unit cell.

To clarify this further in the text we changed

> *"At the beginning of each experiment, we first take a transmitted white light image of the array. From this image we localize all nanostructures by fitting the local maxima to a two-dimensional Gaussian."*

to

"At the beginning of each experiment, we first take a transmitted white light image of the array. From this image we localize all nanostructures in the field-of-view of 133 µm by 133 µm by fitting all local maxima in the image to a two-dimensional Gaussian."

We also changed

"After localizing all molecules, we redefine their positions relative to their nearest nanostructure, so that all positions fall into a single unit cell, as indicated by the yellow hexagon in Figure 2a."

to

"Since we detect molecules over a large field-of-view, we can average over thousands of nanostructures by redefining the positions of all molecules relative to their nearest nanostructure. This procedure results in all molecule positions falling in a single unit cell, as indicated by the yellow hexagon in Figure 2a."

Lastly, we also added further explanation in section 4.4 of the Supporting Information.

(3) I also suggest the authors obtain super-resolution mappings of the enhanced emission by LSPRs of single nanoparticles, which are not in the nanoparticle array.

AUTHOR REPLY

We agree that this would be very interesting experimentally, but unfortunately it is unfeasible in the current timeframe. As we mentioned in the previous comment, in order to get statistics, we average the emission of molecules coupled to thousands of particles in our field of view. In order to suppress any lattice contribution, we would have to measure on an array of particles that are randomly distributed rather than evenly spaced. Given that these samples are prepared with substrate conformal imprint lithography (SCIL), the preparation of an entirely new sample geometry would take a lot of time (and resources) and falls outside the scope of the present paper.

To address the reviewer's comment, however, we have simulated the interaction between single dipoles and individual particles. We have placed the results and their interpretations in section 8 of the Supporting Information. We also refer to them in the main text as follows:

"To further investigate the collective nature of the lattice resonances and their influence on single molecule emission, we compare our experiments and simulations on extended arrays to simulations on a single nanostructure. As can be seen in Figures S9 and S10, simulations of dipoles coupled to a single particle can describe most behavior observed in sample S1, both at the SLR and the LSPR wavelength. This result can be understood from the fact that emission enhancement in this sample mostly happens when the dipole is very close to the surface of a nanostructure, where it is not influenced by other nanostructures far away. The emission enhancement we experimentally observe on sample S2, however, is described poorly by simulations on a single particle, see Figures S11 and S12. The emission enhancement at the unit cell corners observed in Figure 4b is not reproduced with a single particle, confirming that this is indeed the result of constructive interference between the scattering from multiple particles. Further discussion on the comparison between the results on the extended array and those on a single particle can be found in section 8 of the Supporting Information."

(4) The authors claimed in Figure 2b that the recorded white spots were single emitters, but they didn't have any discussion about how they confirmed it. Therefore, more discussion or experiments should be added to confirm whether the enhanced emission is from single emitters.

AUTHOR REPLY
Given the very low number of fluorescent events per frame (see also our reply to comment (2)), the expected number of emitters that are placed in the same diffraction-limited area is smaller than 1%. We have written an additional section in the Supporting Information outlining this calculation and we refer to it in the text as follows.

> *"By keeping the number of fluorescent events per frame low, we can assume that the observed diffraction-limited spots are single molecules, see section 3 of the Supporting Information."*

(5) The authors should add a scale bar to the zoom-in image in Figure 2a.

AUTHOR REPLY
The image in Figure 2a is actually just a schematic drawing used to illustrate what we intend for "unit cell". For this reason, we think that adding a scale bar would be inappropriate, as it may suggest that it is an experimentally obtained image. We have clarified this by adding the underlined word to the figure caption:

> *"The zoom-in <u>drawing</u> schematically illustrates the hexagonal unit cell of the array (yellow hexagon)."*

Reviewer: 3

Recommendation: Publish in ACS Nano after minor revisions noted.

Comments:
This manuscript describes an imaginative way of studying the effect of coupling the photoemission of single molecules dispersed in a polymer slab to either the localized plasmonic mode or the extended hybrid (photonic/plasmonic) mode of a predesigned metallic array. In order to do so the polymeric slab must be precisely located at a predetermined height above the metallic array, for the case of the extended mode, or partially embed the metallic array, for the case of the localized mode. By mapping the metallic array with a fluorescence microscope while filtering the signal to select the spectral range of the emission that matches one resonance or the other, it is possible to identify the position of isolated dipole emitters (single molecules) randomly distributed in the slab and know the origin of the changes observed in their luminescence. Hence this work provides an interesting approach to discriminate between the effects, on the photoemission of surrounding species, of the optical resonances that typically arise in metallic arrays. However, and this is my only minor criticism, claiming that these results could "bring plasmonics closer to real applications by merging the benefits of nanophotonics with the need of large resonant structures in devices" seems to me an overstatement. In fact, it might not even be extrapolated to the analysis of other single emitters unless they can be properly caged, dispersed and couple to a metallic array. In summary, although the results are interesting and new, and I am favorably inclined towards publication of this work, I feel it should be presented in a way in which not too high expectations are set. The manuscript needs some rephrasing in order to better put the achievements described in the right context.

AUTHOR REPLY
In order to address the reviewer's comment we have changed the following text in the abstract:

> *"Our results can guide the design of plasmonic particle arrays and thereby bring plasmonics closer to real applications by merging the benefits of nanophotonics with the need of large resonant structures in devices."*

into

> *"Our results can guide the rational design of future optical devices based on plasmonic particle arrays."*

Furthermore, as also suggested by the editor, we have removed claims of novelty where necessary: "*unique*" in the abstract and "*paves the way*" in the conclusion.