Plasmonic Enhancement of Adenosine Nucleotide Photoluminescence by Laser Induced Periodic Silver Metasurface with Silver Nanoprisms

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The effect of strong plasmonics enhancement of the PL (fluorescence + phosphorescence) of the 5’-deoxyadenosine-monophosphate (dAMP) has been revealed at room temperatures.
Plasmonic metasurfaces was based on the Ag laser induced periodic surface structures (LIPSS) with arranged periodic sub-micron and nanosized features on the surface and Ag triangular nanoprisms (Fig.1). The micron and submicron LIPSSs and nanoscale features on the surface of the Ag substrate have been fabricated under femtosecond laser irradiation.
The plasmon enhancement of dAMP PL (Fig.2) has been studied in four types of Ag metasurfaces: Ag smooth substrate; Ag LIPSS; Ag smooth substrate/Ag nanoprisms; Ag LIPSS/Ag nanoprisms. Quartz plate was used as reference substrate.

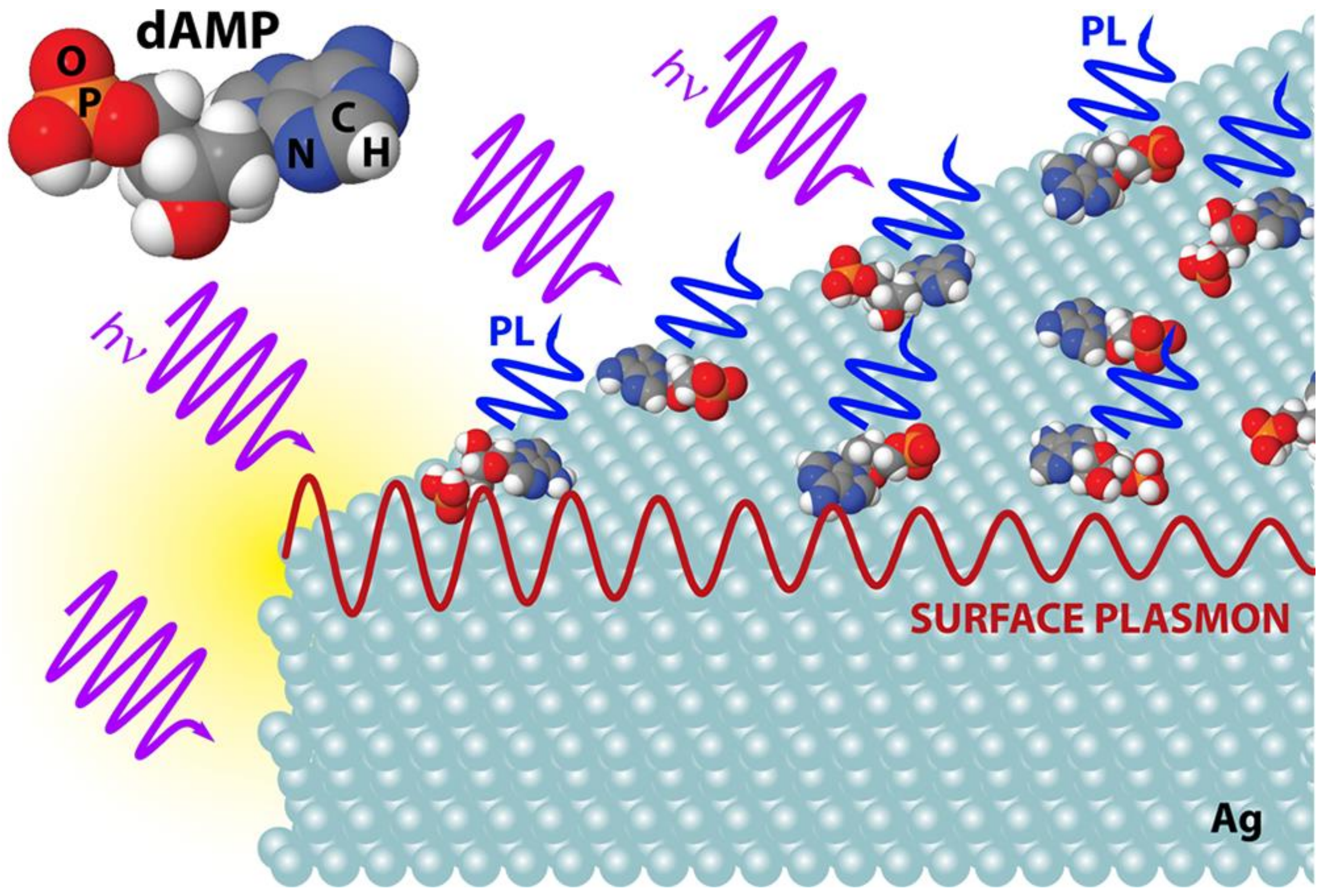

Fig. 1. Scheme representing the effect of plasmonic enhancement in the PL of dAMP molecules on a Ag metasurface.

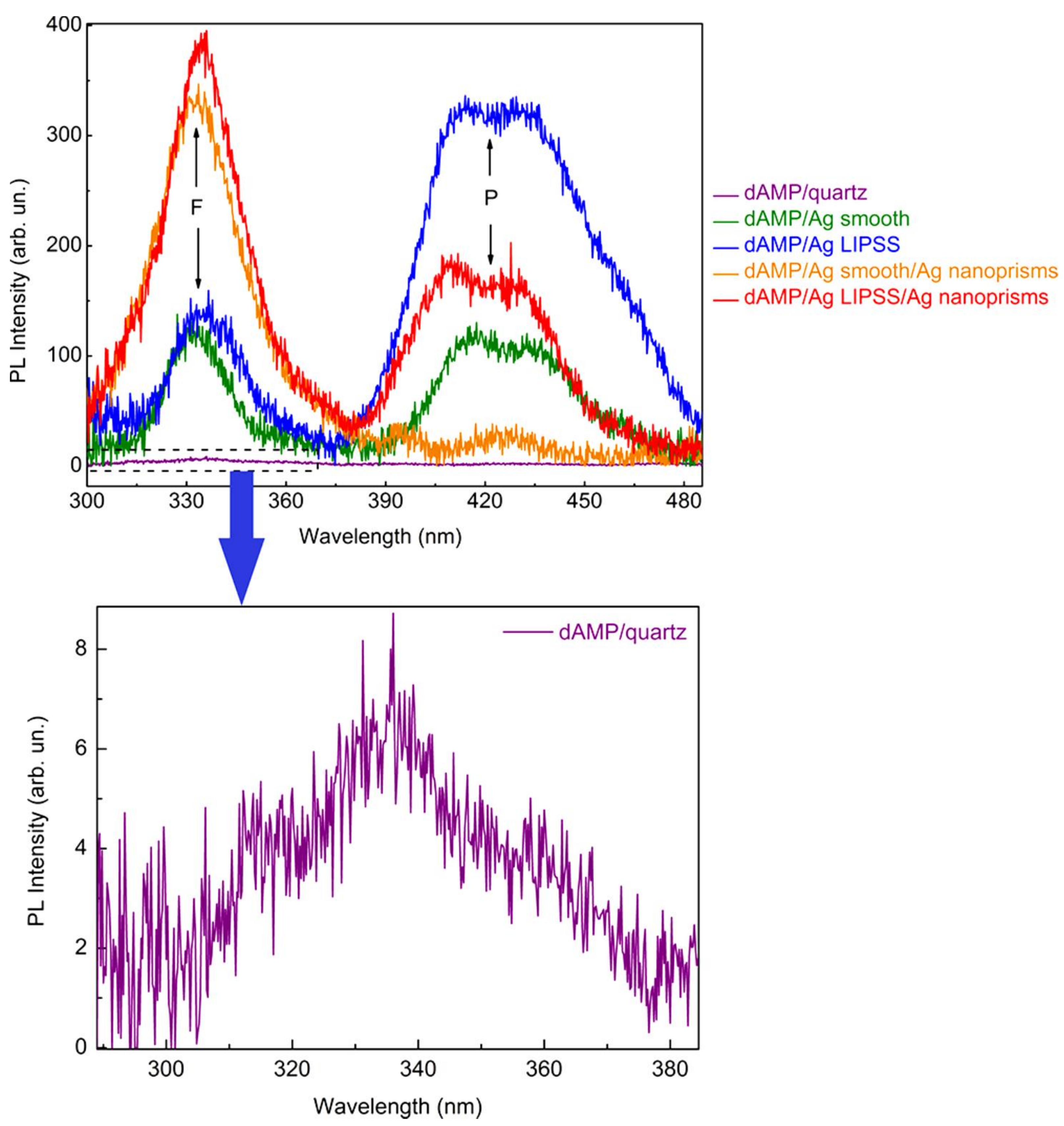

Fig. 2 PL spectra of dAMP molecules deposited on different substrates: quartz plate (purple line), Ag smooth substrate (green line), Ag LIPSS (blue line), plasmonic cavity metasurfaces Ag smooth substrate/Ag nanoprisms (orange line), and Ag LIPSS/Ag nanoprisms (red line) measured at room temperature. The intrinsic fluorescence spectrum of dAMP on quartz in a dashed rectangle in the top figure is zoomed in the bottom one, because of it weak intensity.

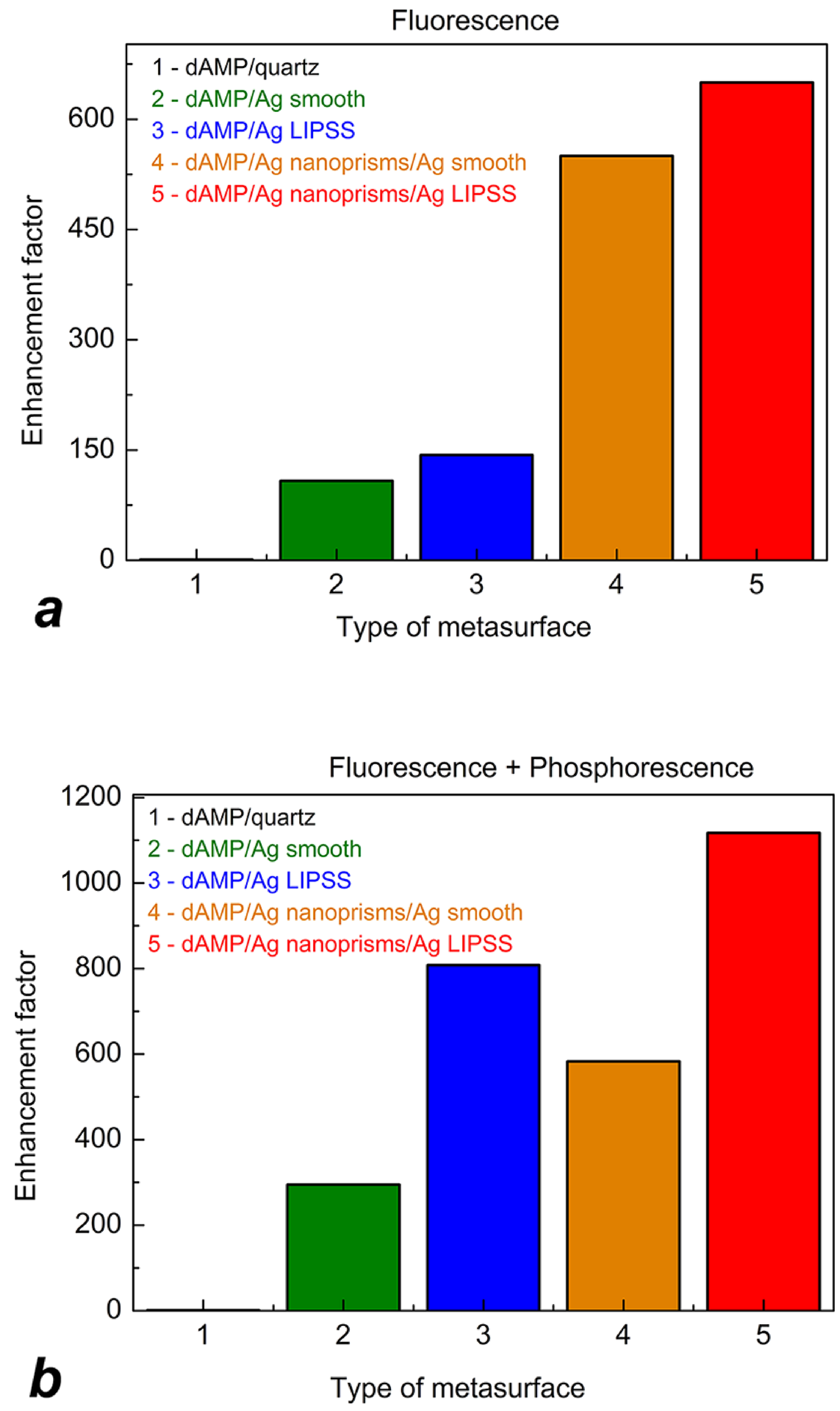

Fig. 3. Enhancement factors of the (a) fluorescence and (b) total PL (fluorescence + phosphorescence) of dAMP molecules deposited on different substrates.

Results

The quantitative comparative study of the enhancement factor of PL of dAMP deposited on our metasurfaces gives the PL enhancement factors ranging from 295 to 1120 depending on the metasurface type (Fig.3). The higher dAMP PL enhancement has been observed for the metasurfaces containing Ag nanoprisms, which are plasmonic cavity nanosystems with strong near-field coupling of the LSP modes of Ag nanoprisms and the propagating SPP modes of Ag surfaces (smooth or laser-structured). The highest 1120-fold enhancement has been achieved by the Ag LIPSS/Ag nanoprism metasurface.
This might be a result of the synergetic action of the generation of hot spots near the sharp edges of LIPSSs and nanoprisms, together with excitation of the collective gap mode of the plasmonic cavity. Another interesting effect has been observed; namely, the phosphorescence intensity is substantially higher for dAMP on the LIPSS than on the smooth surface, while the fluorescence intensities differ slightly for these Ag surfaces. Such an effect has been interpreted as a result of the larger overlap of the phosphorescence spectrum with the SPP spectral region, which provides the higher plasmonic enhancement for the phosphorescence than the fluorescence.

Conclusions

Thus, we have shown that the plasmonic cavity metasurfaces consisting of metal LIPSS and non-spherical metal nanoparticles with sharp edges are perspective for highly sensitive detection of the biomolecules at room temperatures without using any dye labels. Such ability arises from the synergetic action of the strong plasmonic near-field coupling in the cavity and high concentration of the hot spots.

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