Supplementary information for the manuscript "*The single molecule probe: nanoscale vectorial mapping of photonic mode density in a metal nanocavity*"

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In the pLDOS calculations described in the manuscript, we can determine the contribution of each of the modes in the cavity to the total pLDOS by applying the formalism described in ref. 33 (Barnes, W. L. *Journal of Modern Optics* **1998**, 45 (4), 661-699). In the following figure, the emitted power as a function of molecular position *x* (with respect to the center of the cavity), and in-plane wave vector k_p (normalized with repect to free-space wave vector k_0) is given for both dipole orientations for an $i = 3$ cavity ($d = 670$nm). Figure (a) depicts the emitted power for a dipole with an orientation parallel to the cavity interfaces, figure (b) the same information for a perpendicular oriented dipole. We observe clear, distinct cavity modes for values $k_p/k_0 < 1.49$ (= n_{PMMA}) and a surface plasmon polariton (SPP) mode for $k_p/k_0 = 1.66$. The cavity modes can be assigned as TE and TM modes depending on their mode profile (figure (c)). For the parallel oriented dipole, we see that the emission is dominated by coupling to the TE, and slightly weaker the TM, cavity modes, with a noticeable coupling to the SPP mode only for very short distances from the metal interface. Contrarily, for the perpendicular oriented dipole, excitation of the SPP mode is dominant over distances up to 150nm from the metal cavity interface. In addition, closer to the cavity center, emission into TM_0 and, very weakly, TM_1 modes occurs. For the perpendicular oriented dipole, TE modes are forbidden. As expected, the dipole-mode coupling strength is proportional to $|\boldsymbol{u}\cdot\boldsymbol{E}(x)|^2$, where, as in the main text, $\boldsymbol{u}$ is the dipole transition moment.

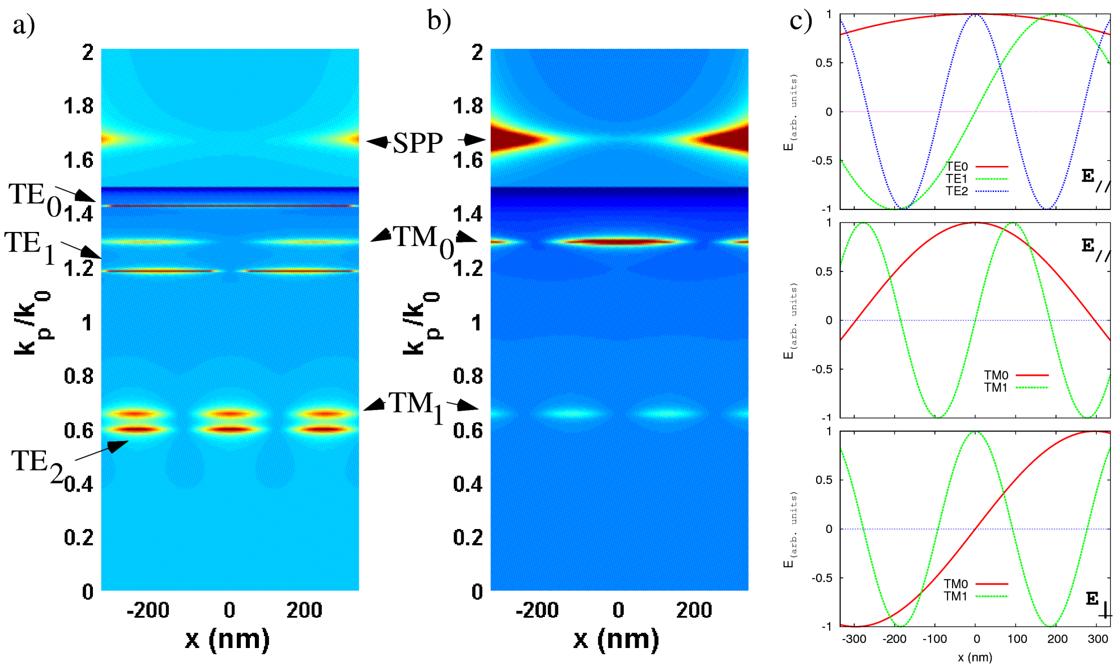

Figure: (a) Emitted power as a function of both molecule position and in-plane wave vector (relative to free-space wave vector) for a dipole parallel to the cavity interface. (b) Same information for perpendicular orientation. (c) Cavity modes profiles. The modes effectives indices are $n_{eff}(TE_0)=1.42$, $n_{eff}(TE_1)=1.18$, $n_{eff}(TE_2)=0.59$ for TE polarization and $n_{eff}(TM_0)=1.29$, $n_{eff}(TM_1)=0.65$ for TM polarization, and $n_{eff}(SPP)=1.66$.